Energy & Environment Division

Annual Report 1978

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Energy Analysis

Introduction

Energy futures for America will employ an ever widening range of sources of energy and of specific technologies to extract and convert base energy resources into end use energy products. The choices available to the Department of Energy for defining the direction of both the nation's near term and long term energy supply future are rapidly expanding. However, the availability of these choices brings with it the responsibility for the consequences of the path chosen. A growing awareness of the complexity, endurance and interconnectivity of the environmental, socioeconomic and human health impacts of many energy development choices has presented DOE with a requirement to unravel and identify the broad range of impacts of a variety of specific processes and technologies, of individual energy delivery pathways, and of total energy supply packages.

It is this set of strongly interconnected impacts to which the Energy Analysis Program directs its attention, aided by a diverse set of diagnostic techniques, computer models and massive banks of data. In general, energy analyses address a range of impact areas including regional and local economics impacts, water availability and quality questions, air quality, land use changes, siting of facilities, local and regional ecological impacts and human health impacts. Further, these areas are addressed from two perspectives, or levels of study. The first perspective includes assessments of regional and subregional impacts of alternate future energy supply systems and energy growth patterns. For these integrated regional assessments the Energy Analysis group addresses each impact area for the western region (California, Hawaii and Nevada) and addresses one impact area, socioeconomics, at a national scale.

The second perspective embraces the impacts of a specific energy technology, such as coal, geothermal energy or natural gas, and the economics, environmental and institutional constraints on their use. Alternatively, this type of study will address a particular energy end use sector (e.g., agriculture, or heavy industry) and will address the impacts of, and constraints on the use of alternate energy supplies to satisfy the demands of this sector.

The major integrated subprograms arise from national energy policy (contemplated or enacted) and from major energy technology R and D programs pursued by DOE. In conjunction with the other national laboratories, Lawrence Berkeley Laboratory (LBL) has participated in an assessment of the national energy plan. This study, conducted at a national level, produced an overview of the various costs and benefits created by the realization of the national energy plan. LBL's

contribution to this study was an assessment of the direct and secondary impacts accruing to each sector of the economy as a result of the investment, direct employment and direct material demands of this plan. A subsequent study, the Regional Issue Identification and Assessment (RIIA), was undertaken to identify the key issues and actors associated with the use of a specified mix of energy supply technologies to supply future energy needs. While LBL conducted an assessment of the national level economic impact of this mix, the primary focus of the RIIA program was at the regional and subregional level. This multifaceted program involves the identification of major energy development issues and of the various regional perspectives on those issues, the quantification of the impacts of the energy supply plan which will influence the outcome of each issue, and the identification of mitigation strategies for major impact areas.

Supporting these detailed environmental, socio-economic and human health assessments, LBL has undertaken the preparation of a detailed regional and state energy and environmental data book. This effort represents a coordinated national program involving the national laboratories to develop consistent, comparable data bases for all regions.

Complementing these continual scenario related programs are studies which address the energy issues and impacts of a single sector of human economic activity, or which address the impacts of a particular energy technology. Energy and water use in agriculture are very closely connected. The 1976-1977 drought forced both substantial water conservation by California's agriculture and an increased shift to the use of ground water for irrigation. The resulting impacts on energy use were complex. Some water conservation measures require increases in energy use; however, some water conservation measures also conserve energy. An increased use of ground water, and a general lowering of the ground water table result in more energy being used for water pumping. LBL initiated a detailed study of the use of water and energy in agriculture and of the relationship between these two vital resources.

A number of energy technology and energy fuel specific studies have been conducted. Changing national and regional priorities for the use of natural gas raised the need for a detailed analysis of California trends in the use of this fuel. The impact and success of federal and state initiatives will depend upon these current trends and the probable effect of selected future actions on the use pattern. The study to address these questions

was undertaken jointly by LBL and Lawrence Livermore Laboratory.

An extensive assessment of decentralized solar technologies has been conducted by several of the national laboratories. LBL characterized and evaluated four renewable resource energy technologies which have been included in the solar program: municipal solid waste, cogeneration, marine biomass system and total solar systems. Additionally LBL is conducting a series of community level assessments through outside contracts. These studies are designed to identify and evaluate impacts which will accrue uniquely at the community or subcommunity level from

the deployment of decentralized solar technologies. Still another study has addressed investment potential and alternatives for on-site solar technologies.

Finally, a series of conservation studies has been undertaken. These studies have evaluated the potential energy savings of alternate conservation measures, the capabilities of several conservation oriented energy supply technologies, and the motivations and decision making processes associated with energy conservation. The findings of all of these assessments are intended primarily to aid DOE and other agencies' decision makers in formulating policy and energy technology R&D programs.

Regional Studies Program

Direct and Indirect Economic Impacts of a National Energy Plan Scenario*

J. Sathaye and H. Ruderman

INTRODUCTION

This study assessed the direct and indirect economic impacts associated with future energy supplies as characterized by a scenario based on the National Energy Plan (NEP). Direct impacts refer to the capital costs and manpower skills required to construct and operate energy and energy related transportation facilities to the year 2000. Indirect impacts refer to the secondary employment and value added (income) stimulated by construction of new energy facilities.

Historically, capital and manpower requirements have been increasing rapidly in most sectors of the energy industry, especially since 1971. Capital expenditures in energy-producing industries more than doubled during the six-year period from 1971 to 1977, growing from \$21 to \$47 billion.¹ Employment in some selected energy industries such as coal mining, oil and gas extraction, and electric utilities also increased rapidly from 1970 to 1975.² As the domestic energy industry begins to develop new fuel supplies such as offshore oil or nuclear power, the capital costs may increase faster than their historical growth rate. On the other hand, a slowdown in the rate of growth due to conservation and other measures could slow the rate of increase in capital costs and manpower requirements.

To examine the future economic impacts of energy supply to the nation, it is essential to define the types and quantities of fuels that would be available to meet the anticipated demand. A scenario interpreting the energy supply and demand elements of the National Energy Plan was formulated by the Department of Energy (Fig. 1).

Fig. 1: Energy supply scenario (XBL 792-339).

A modified version of the Energy Supply Planning Model (ESPM)³ was used to convert the NEP scenario into the number of facilities needed to supply energy up to the year 2000. (The model requires specification for nine

Fig. 2: Analytical methodology (XBL 792-336).

years beyond the last date for which results are computed). From construction and operation data for each type of facility, the model then estimates direct impacts for 150 categories of occupational skills and materials (Fig. 2).

Construction and operation data were based on 1974 equipment designs. Data on costs, working capital, and escalation and interest rates were expressed in constant 1977 dollars. Cumulative five-year effects were estimated, and annual effects were estimated based on the assumption of linear distribution in each five-year interval. Annual effects reported should therefore be interpreted with caution.

Indirect effects from 24 categories of construction manpower, materials, and equipment were calculated by disaggregating them in proportion to the appropriate final demand vector from a 368-sector national input-output table for 1972. Estimates of the output, value added, and employment generated in the 368 sectors by this increase in final demand were then converted to 1977 dollars (for output and value added) by use of GNP inflator of 1.40.⁴

FINDINGS

Capital

Annual investment in the energy industries increases from \$50 billion in 1975 to \$65 billion in 1985, then declines to \$56 billion in 1990. This represents 32 percent in 1975 and 17 percent in 1990 of the projected overall national investment in equipment and private construction in all sectors.⁵ Cumulative five-year energy

investment increases from \$262 billion during 1976-80 to \$304 billion during 1986-90. Twenty-five percent of the investment in the first period and 22 percent in the second, will be for coal facilities. Investment in nuclear power plants will remain stable in the range of 20 to 22 percent of total energy investment through 1990, while investment in solar space heating increases four-fold, from 8 percent in 1975 to 30 percent in 1990 (active solar-heating units in new construction are assumed.) It appears that the aggregated capital requirements for energy development will not impose any additional burden on the availability of capital.

In addition to construction capital, energy facilities require substantial expenditures for operation and maintenance. These expenditures, excluding fuel cost, grow steadily from \$74 billion in 1975 to \$109 billion in 1990; coal facilities account for 5 percent in 1975 and 10 percent in 1990.

Manpower

Manpower requirements for energy industries follow the same temporal pattern exhibited by capital costs: the five-year cumulative requirements increase steadily through 1990. The portion engaged in coal-related activities declines from 23 percent in 1976-80 to 16 percent in 1986-90; annual requirements for coal-related manpower, 20 percent in 1976, peak at 25 percent in 1980, then decline to ten percent by 1990.

A surprisingly large fraction of energy-engaged manpower will be involved in construction of solar space heaters: from 15 percent in 1975 to 48 percent in 1990. In part, this projected increase results from the assumption implicit in the ESPM that all solar heating needs will be filled by active solar units in new construction. Both capital investment and manpower needs may therefore be somewhat overstated, since alternatives (such as passive solar heating) are less capital and labor intensive.

This large fraction of manpower for solar heating also affects the estimates of types of skills needed for energy construction in general. More civil engineers than mechanical or electrical engineers are projected to be required in 1980, but by 1985 mechanical engineers, who are more heavily involved in construction of solar units, rank ahead of all other engineering skills. Manual skills are affected even more strongly: between 1980 and 1985 the requirements for pipefitters, carpenters, teamsters, and laborers for energy-related construction increase 100 percent. Demand for carpenters engaged in constructing energy facilities, for example, increases from about 22,000 in 1980 to about 52,000 in 1985, an annual growth rate of 19 percent; in the same period the total demand for manual labor increases 8.2 percent per year. The maximum growth rate of such demand in the past has been about 7 percent. Despite this high growth rate, energy-engaged carpenters will represent only about 2 percent of all American carpenters in 1980, and 5 percent in 1985. The effect of this growth rate on carpenter

availability will depend on the demand for them from the rest of the economy.

The energy sector accounted for about 6 percent of national construction manpower in 1975, and will account for 9 percent in 1990. The coal sector will account for about 2 percent in 1985 and 1 percent in 1990. In contrast to this decline in coal-related construction, operation and maintenance manpower for coal facilities will increase from 25 percent of such manpower for all energy facilities in 1975 to 33 percent in 1990. Nuclear plants require a large part of the construction manpower, but only about 1 percent of operating manpower in any year.

Indirect Effects

Indirect or secondary effects of constructing energy facilities result from payment of wages to workers and payments to suppliers of materials and equipment. The recipients use these payments to purchase goods and services from all sectors, with resulting stimulation of employment and income (value added) in those sectors.

Indirect effects show the same trends as do the direct effects. For total energy facilities alone they peak between 1981 and 1985 and then decline. The indirect effect of all energy construction will produce income of about \$32 billion per year and employment for

about 1.4 million persons per year, roughly 1.5 percent of the 1977 GNP and employment respectively. Coal facilities will generate about 29 percent of these increases in the 1976-80 period and about 22 percent in the 1986-90 period.

Expenditures on materials and equipment will produce secondary effects mainly in the primary metals, metal products, and machinery sectors, plus a substantial effect on professional and business services. Labor expenditures will affect mainly the commercial sectors. One of the largest impacts will be on the primary metals industry, in which employment for about 90,000 persons will be generated during 1986-90, about 7.5 percent of total 1990 employment in that industry.

Table 1 summarizes the 5-year cumulative investment in construction of energy facilities and the resulting direct and indirect employment. The ratio of indirect to direct employment decreases over the 15-year period, primarily because of the increase in labor-intensive solar heating construction. Direct employment is due to primary labor expenditures alone, while indirect employment is due to expenditures for both labor and materials.

The secondary effects shown may be somewhat overestimated, because they are marginal effects, which increase more slowly than their average

Table 1. Employment impacts

	1976-80	1981-85	1986-90
<hr/>			
Capital Investment (10 ⁹ \$)			
Manpower	52	63	76
Materials	30	37	46
Equipment	43	44	42
Other	137	145	140
Total	262	289	304
<hr/>			
Employment (thousand man-years)			
Direct Construction	1,751	2,077	2,488
Direct Operation	6,511	7,568	8,977
Indirect ^a	6,208	7,089	7,910
Total	14,470	16,734	19,376
<hr/>			
Indirect Employment per 10 ⁶ \$ of Total Capital Investment			
In Materials and Equipment	41.6	41.7	41.6
In Manpower	47.8	47.8	47.8
<hr/>			
Employment per 10 ⁶ \$ of Total Capital Investment			
Direct	6.7	7.2	8.2
Indirect	23.7	24.5	26.0
Indirect/Direct	3.54	3.40	3.17

^aIndirect employment includes the portion of direct operating required to satisfy the incremental construction requirements. It is not strictly correct to add the direct and indirect figures.

primary values. Construction workers, for example, have above-average incomes and thus (probably) a lower marginal tendency to consume. In addition, the employment coefficients have not been corrected for the trend toward increases of a few percent per year in labor productivity. For these reasons the estimated indirect effects may be 10 to 30 percent too high in 1990.

It should be noted that these results do not necessarily represent net increases in employment and income for the economy as a whole. They would represent net increases if there would otherwise be unemployment in the skill categories required, but in a situation of full employment they would indicate rather the extent of competition by the energy sector for workers.

CONCLUSIONS

In conclusion it should be noted that over the fifteen years, the energy supply scenario calls for a definite shift towards increased expenditure on labor and materials as opposed to equipment, leading to an increase in direct labor intensiveness. Among the manpower skills, requirements for carpenters, pipefitters, teamsters and laborers increase at twice their historical rate of growth after 1980. Whether this will result in a shortage of such skilled manpower will depend on their demand in the rest of the economy.

Indirect impacts amount to roughly three times the direct impacts. Again the overall impacts are small, although as much as ten percent of the employment in sectors such as metal products would be devoted to producing goods for energy facility construction.

In comparing the direct and indirect employment impacts, it should be noted that a dollar spent on personal consumption leads to 15 percent more employment than would a dollar spent on materials and equipment. Consequently construction of energy facilities that are more labor-intensive would lead to more indirect employment.

The study has not identified any absolute economic constraints on implementing the NEP over the period 1975 to 1990. Partly this is because the capital and manpower requirements called for by the NEP represent a small fraction of the total demand placed on these resources by the rest of the economy. If the economy in some future year is at full employment, then these manpower requirements may not be met, or they might be met by transferring workers from other sectors. On the other hand, if the economy were at a high level of unemployment, such energy development could provide employment to significant numbers of skilled workers. Furthermore, there has been considerable occupational mobility in the past so that a shortage in a given skill category can be remedied in the few months or years needed for retraining. Generally speaking, capital investment in a project is based on the expected return and the perceived risk. If the energy facilities called for by the NEP have returns commensurate with the risks involved, there should be minimal difficulty raising the necessary capital.

FOOTNOTE AND REFERENCES

*Condensed from Lawrence Berkeley Laboratory Report, LBL-8454.

1. U.S. Dept. of Energy, Energy Information Administration, "Annual Report to Congress, Vol. II, 1977," DOE/EIA-0036/2, April 1978, p. 50-51.
2. U.S. Dept. of Commerce, Bureau of the Census, "Statistical Abstract of the U.S. 1977," 98th Edition Sept. 77, Wash. DC, pp. 402-404.
3. Bechtel Corporation, San Francisco, California, The Energy Supply Planning Model, Volumes I and II, NSF-C867, August 1975.
4. U.S. Dept. of Commerce, "Survey of Current Business," February 1978, p. S-2.
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A Regional Energy — Environment Data Book*

H. Ruderman

The staff of the Energy Analysis Program has compiled and published a databook containing energy, environmental and institutional data for the states of California, Hawaii and Nevada. The purpose of the databook is to provide in a single publication information of use to people who make decisions about energy in the region. Its development was sponsored by the DOE Division of Regional Assessments as an element of their regional studies effort.

Similar databooks covering the rest of the country have been published by five other national

laboratories. The laboratories have made an effort to keep the structure, content, and coverage of the databooks consistent by using nationwide sources of data where available. These data were supplemented by data from regional sources. Most of the detailed data are presented for 1975, the latest year for which they are published. The institutional and legal data are current to 1977. Because of space limitations, most tabular data are presented on the state or air or water basin level of detail. Whenever possible maps were used to show more geographic detail.

Fig. 1: Production of electricity by source, 1977. Source: U.S. Department of Energy, Inventory of Power Plants in the United States, DOE/RA-0001, December 1977. (XBL 791-7892)

The databook is organized into four chapters. The first presents data on the energy conditions in the region, the second presents data on the environmental conditions in the region, and the third presents information on the institutional conditions in the region. A fourth chapter provides the references, appendices, an index, a glossary, and energy and metric conversion factors. An overview to each chapter provides a regional perspective on the energy, environmental, or institutional situation. The overviews are followed by a discussion of the quality and availability of data for the region. A summary matrix at the end of each chapter attempts to indicate the additional data available but not used in the databook. A typical page from the databook is shown in Fig. 1.

The publication of the databook is part of the Regional Characterization Program in the Office of Technology Impacts under the Assistant Secretary for Environment in the Department of Energy (DOE). Work was started on the databook in March, 1978, a draft was sent to DOE for review in July, and the final version was published in October as LBL-7821. During FY-79 a set of Regional Characterization Reports will be prepared which will include the results of statistical analyses of the regional data as well as more recent energy and environmental data.

FOOTNOTE

*Condensed from Lawrence Berkeley Laboratory Report, LBL-7821.

Regional Issues Identification and Assessment

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INTRODUCTION

Significant changes in the pattern of the nation's production and consumption of energy are likely to occur during the remainder of this century. The resulting impacts to the environment and the implication for social concerns such as public health and safety, employment or economic growth, vary in effect

and importance from region to region and from site to site within regions. The Division of Regional Assessments within the Office of the Assistant Secretary for Environment is responsible for assessing the environmental, health and safety, social, economic and institutional issues and impacts which may occur as a result of Department of Energy (DOE) RD&D efforts and activities associated with the

development and deployment of various energy technologies.

The Department of Energy has developed a set of six national energy scenarios. These future scenarios provide detailed data on the anticipated demand and supply of various forms of energy for each region of the country. The Regional Issues Identification and Assessment (RIIA) project will identify and quantify the potential environmental, social, economic and institutional conflicts which may evolve if the various future energy scenarios developed by DOE were to be implemented. The six national laboratories participating in the project will analyze the scenario impacts for their geographic region of interest. The region studied by LBL includes the states of California, Nevada and Hawaii.

The scenario provided by DOE was regionalized to provide the detailed energy demand information by individual sector for each economic area in the country. The coal mines, refineries and other energy supply facilities were sited by economic area, whereas the power plants were sited by county. The siting of energy facilities was conducted at Oak Ridge National Laboratory based on regional information from the other five laboratories.

ACCOMPLISHMENTS DURING 1978

The first scenario provided by DOE specifies detailed energy demand and supply information for 1985 and 1990. By 1990 the scenario calls for 108 quadrillion (Q) Btu's of national energy consumption, a growth rate equivalent to 2.9 percent/year from the 1975 figure of 71 quadrillion. The largest growth forecast is for the nuclear sector at 12 percent per year, whereas coal supply is forecast to increase at 4.5 percent per year.

A summary of the growth rates within the western region for individual energy sources for this particular scenario, titled the Series C scenario, is shown on Table 1. Table 2 summarizes annual primary energy use within each state for each five year period through 1990. In addition to summaries of primary energy use, the scenario details electrical energy generation by state and county and by the type of fuel used to generate the electricity. Table 3 shows this electrical energy summary for the state of California.

The projections shown in Tables 1 to 3 do not represent a prediction of the future. Rather, they represent what would occur if a specific set of actions, policies and decisions were enacted and if there were no external "surprises" over the life span of the scenario. Thus the analysis of a scenario determines the potential impacts of a set of plausible policy options, and not the impacts of a particular set of development actions (as would be done by an Environmental Impact Statement).

Using the scenario as a starting point, LBL is approaching the regional assessment in a multi-step analytical process. These steps are:

1. Identify regional issues.
2. Make a quantitative estimate of the direct environmental impact of the scenario in each area of environmental quality.
3. Analyze impacts with respect to identified issues and define conflicts arising from implementation of the Scenario.

Analysis of the issues has begun with a detailed assessment of the physical implications of the scenario. New energy related activity

Table 1. Growth rates for selected energy types annual change in percent 1975 to 1990

	California	Nevada	Hawaii
Gasoline	1.6	3.2	1.8
Residual Fuel	-1.2	-4.3	-2.0
Distillate	2.6	4.8	4.4
Jet Fuel	1.0	1.5	0.8
Total Oil	1.2	2.7	0.6
Natural Gas	~ 0	3.6	8.0*
Coal	3.2	1.0	7.3*
Nuclear	11.2	-	-
Geothermal	7.8	-	-
Total Primary Energy	1.2	2.4	1.6
Electricity Sales	1.6	4.5	-1.1
Population Growth	1.4	3.2	2.0

*1980 to 1990

Table 2. Regional primary energy use summary (10 12 BTU)

<u>California</u>	<u>1975</u>	<u>1980</u>	<u>1985</u>	<u>1990</u>
Gasoline	1276.9	1385.1	1493.3	1625.1
Residual Fuel	714.1	681.1	648.1	595.2
Distillate	263.9	395.3	346.8	392.7
Jet Fuel	324.7	351.6	378.5	379.9
Other Oil	53.3	97.5	141.8	167.3
Natural Gas	1928.8	1848.3	1767.9	1919.2
Coal	54.3	66.5	78.6	88.2
Hydro	407.0	429.3	451.7	457.6
Nuclear	61.0	175.7	290.4	329.3
Geothermal Solar	61.0	111.1	161.2	196.7
TOTAL	5145.1	5451.7	5758.3	6151.1
<u>Nevada</u>				
Gasoline	51.4	61.0	70.6	82.8
Residual Fuel	9.1	6.6	4.1	4.8
Distillate	14.9	20.3	25.6	30.7
Jet Fuel	27.6	29.3	31.0	34.4
Other Oil	2.0	3.3	4.5	6.0
Natural Gas	63.4	80.6	97.7	108.7
Coal	100.4	106.7	113.0	115.8
Hydro	.2	.2	.2	.2
TOTAL	269.2	308.0	346.8	383.3
<u>Hawaii</u>				
Gasoline	35.9	39.1	42.2	46.7
Residual Fuel	67.4	59.3	51.1	50.1
Distillate	15.4	21.3	27.3	29.6
Jet Fuel	78.5	84.3	90.0	88.2
Other Oil	3.5	4.0	4.4	5.2
Natural Gas	0.0	15.9	31.7	32.9
Coal	0.0	.9	1.7	2.0
TOTAL	200.8	224.7	248.6	254.8
REGIONAL TOTAL	5615.1	5677.2	6353.7	6789.2

has been sited to county and water-body level. Ambient (1975-1977) environmental quality has been mapped and areas where new or expanded energy activity could pose a significant environmental concern have been noted. This portion of the analysis has been divided into eight topical areas, each of which is being analyzed separately. These areas are: local and regional air quality, water resource availability (water quantity), water quality, regional and local socioeconomic impacts, land use and solid waste, ecological impacts, institutional impacts, and public health implications. For each of these specific regional impact areas the direct physical implications of the scenario (e.g., acres of land required for various activities, acre feet of water consumed, tons of air emissions, etc.) have been calculated.

In addition to its regional responsibility, each laboratory has been designated to estimate one or more types of impacts nationwide. For example, LBL, as the lead laboratory in analyzing economic impacts, is estimating the impacts on capital investment, employment and secondary income for the scenario. Similarly, Argonne National Laboratory is conducting the air and water quality analysis. These lead laboratory analyses are being made available to each national laboratory for use in its regional impact assessment.

PLANNED ACTIVITIES FOR 1979

The lead laboratory analyses completed this year for each topical area will be evaluated in detail for the region of interest to LBL.

Based on this evaluation, alternate mitigation strategies will be identified. These strategies

will be incorporated in future energy demand forecasts and supply plans formulated at DOE.

Table 3. Electricity generation 1975, 1977 and Series C projections for 1985 and 1990 for California

Technology	Technology	1975 Capacity MW	1975 Generation Gwh	1977 Capacity MW	1977 Generation Gwh	1985 Capacity MW	1985 Generation Gwh	1990 Capacity MW	1990 Generation Gwh	Capacity Change, MW 1977-1990
1	Gas Turbine	1349	a	1555 ^b	a	2246	1055	2245	1056	+ 690
2	Oil Turbine									
3	Nuclear	1368	6100	1311 ^f	8100	5781	29037	5781	32932	+ 4470 ^f
4	Combined Cycle	0	0	544	a	1408	6252	1408	9771	+ 864 ^g
5	Coal Steam	0	0	0	0	0	0	0	0	0
6	Gas Steam	285	27300	497	35600	2578	13249	3614	14708	+ 3117
7	Oil Steam	21662	48300	22280	77300	18961	48716	18587	42805	- 3693
8	Hydroelectric	8950	40700	8950 ^c	14200	9862	45173	9862	45761	+ 912
9	Solar	0	0	0	0	20	69	210	749	+ 210
10	Geothermal	544	6100	675 ^d	3600	2300	16120	2700	18919	+ 2025
11	Pumped Storage	200	0	970 ^c	0	3095	2361	3655	2782	+ 2685
12	Other	0	0	0	0	0	0	0	0	0
TOTALS		34358	128500	36782	138800	46251	162032	48062	169483	+11280

a. fuel included in oil and gas steam

b. includes 162 MW Oakland on line and 45 MW Contra Costa on line 1978.

c. generation capacity - dry year capacity 1,500 MW less in 1977.

d. includes geothermal #12 of 119 on line in 1978.

e. includes 5 units at Castaic.

f. Diablo Canyon 2,270 MW completed 1979 and 2,200 MW at San Onofre complete in 1981-83.

g. Coolwater 472 MW in San Bernardino on line in 1978 and Grayson in Pasadena 121 MW in 1979.

Ecological Impacts of Future Energy Development in California, Nevada, and Hawaii*

J. Holdren,[†] P. Deibler,[†] and P. Gleick[†]

INTRODUCTION

Within the structure of the DOE (OTI/DRA) Regional Issue Identification and Assessment program (RIIA),¹ Lawrence Berkeley Laboratory has established a separate group within the Energy Resources Group (ERG) at UC Berkeley to conduct the ecological effects investigation. The efforts of this group have been directed toward identifying and assessing the ecological implications of the increases in electricity generating capacity within California, Hawaii, and Nevada projected by the Department of Energy's MID-MID scenario (the scenario being used for all RIIA assessments).

Because time constraints limit the depth of this assessment, this study will identify only the most critical issues. That is, those most likely to involve ecological impacts severe enough to call into question the viability of the scenario if they are neither avoided nor mitigated. For each such issue, an attempt will be made to characterize the state of relevant data and analysis--what factors are relevant, whether these have been studied systematically, where the information exists (if it does), and what further research is needed to produce necessary information that does not yet exist. In addition, relevant institutional factors that affect or are affected by the ecological impacts will be discussed.

The results from the Ecological Group will be incorporated into a final RIIA report to the Department of Energy, along with the contributions of the working groups on land use, water quality and availability, air quality, health, solid waste, and western long-range transport of sulfur oxides. Our final report will include a completed matrix for qualitative ecological impacts. The matrix format which was developed by the Department of Energy is intended to permit a rapid 'snapshot' overview of each topical assessment.

ACCOMPLISHMENTS DURING 1978

Our approach to assessing the impacts is composed of three stages. The first stage is an examination of each energy technology represented in the scenario to identify problem areas of greatest potential ecological impact. The second stage consists of reviewing the literature concerning the critical problem areas that have been identified. The final stage is the relating of information on critical areas of impact to the specific fuel mixes that the scenario provides for California, Hawaii, and Nevada. In what follows, the term 'problem area' is used to refer generally to identified ecological issues of widely varying types. Care is taken to describe how these problem areas differ.

The crucial step in the above process is the first stage since at this point the decision is made as to which of the identified problem areas will receive concentrated attention. Accordingly, a brief explanation of this winnowing process is included here to aid in tracing the thoughts that connect the scenario to the chosen problem areas. Impact analysis facilitates a disaggregation of the overall ecological effects question into component parts without accidental omissions of pertinent considerations.

Impact analysis commences with a look at the energy supply options represented by the RIIA scenario and with a detailing of the stages of each supply option and of the phases of operation within each stage. This process was undertaken for all nine supply options (with pumped storage included under hydroelectric generation) represented by the scenario. For each of the supply options there are nine stages beginning with exploration and finishing with end use. For the purpose of this study we omitted the marketing and end use stages because our interest extends only through the conversion (electricity producing) stage. Each of the nine stages is composed of five phases beginning with research and development and ending with the management of long-lived wastes.

The next part of the impact analysis involves the use of a framework for tracing all the effects from the source (the particular supply option), and determining the costs imposed by the effects. The framework has been modified for our use to include only the portions pertaining directly to environmental and ecological effects. However, this modification does not exclude damage to those economic goods and services such as crops which are direct ingredients of human well-being.

This framework consists of a six step progression: source, impact, pathway, stress, response, and cost. Impacts include pre-emption or consumption of resources, material effluents, radiation, heat, noise, and direct physical damage or transformation. Pathways are the media through which the inputs reach the environment. The stresses can be characterized as the environmental effects of the inputs. The stresses are reduced resource availability, altered chemical concentrations, altered temperature, loss of habitat, etc. The responses are the ecological result of the environmental changes wrought by the stresses. Responses are economic goods and services lost or forgone, and damage to environmental goods and services such as agriculture and forestry. Finally, the cost criteria for evaluating ecological severity include magnitudes of inputs, stresses, and responses, temporal and spatial distributions of harm, scaling, resistance to remedy, irreversibility, and the quality of evidence of harm.

Utilizing the above framework, the Ecological Group has identified four problem areas for detailed study. The first two areas are hydroelectric and geothermal generating capacity. These two areas are specific sources of impacts whose ecological responses may potentially incur major costs in light of the large additions of such generating capacity in the scenario for California. Issues including seismic activity associated with hydroelectric facilities and wine grape damage from air emissions at the Geysers geothermal site cause geothermal hydroelectric power to be important areas for examination.

The third problem area is crop sensitivity to sulfur dioxide. Sulfur dioxide effects are damage-mechanisms and are an ecological response to impacts imposed by fossil fuel combustion and tapping of geothermal sources for electricity. This problem area is especially important because of the economic role of agriculture in the region under study. Our final problem area of major importance is endangered species. Endangered species are targets of ecological stresses imposed by the impacts created in a number of stages of each supply option. Loss of habitat, for instance, is a stress that is a component part of almost all energy activities and is one with possible irreversible consequences.

In addition, we are including in our study a grouping of problem areas under the label of "uncertainties." At this point two problem areas, acid rain and estuarine degradation are pinpointed for analysis. Acid rain is a response to environmental stresses created by fossil fuel combustion. Estuaries are ecosystems that have suffered from the effects of a variety of energy activities, ranging from decreased flow due to upstream hydroelectric plants to chronic oil pollution. Estuarine degradation and acid rain are both problems of increasing concern in this region.

Analysis of impacts is an objective process within the bounds of our knowledge of the ecological consequences of energy activities. The final stage of choosing problem areas may be subjective to some degree because of the difficulties inherent in comparing and assessing the costs, most of which are not quantifiable. This apples-and-oranges comparability problem is immensely important, but we do not attempt to grapple with it in our study. However, our final report will provide additional justification for our choice of ecological problem areas.

The Ecological Group's progress to date can be summarized with reference to the four questions posed in the second paragraph of this essay. The relevant factors for consideration in each problem area are synonymous with the end product of the impact analysis. In comparing ecological effects from the various stages of each supply option, one is comparing the relevant factors of the problem areas.

Thus there is a smooth flow from the impact analysis to the detailed assessment of each problem area. For instance, a potential ecological effect of increased geothermal electricity production is subsidence impacting on irrigation in Imperial County. The generalized effect of subsidence is distilled from the impact analysis, while its specific character in Imperial County results from the relating of our general knowledge to the particular scenario. We have completed the connecting of general relevant factors to the scenario for the problem areas of hydroelectric, geothermal, endangered species, and crop sensitivity to sulfur dioxide. Work remains to be done on this stage for acid rain and estuarine degradation.

The problem areas of interest to us have been studied systematically to widely varying degrees. For instance, the ecological effects of the hydroelectric supply option have been extensively documented over a period of decades on an international basis. Work on geothermal effects, while considerable, is not as extensive. Literature on the other four problem areas is much scantier and has evolved more recently.

Our identification of sources of information for each problem area has progressed almost to completion for geothermal and hydroelectric ecological effects. The existence of information on endangered species and sulfur dioxide effects on crops has been assessed on a preliminary basis with an initial search through the literature. This phase of work has not yet begun for the problem areas of estuarine degradation and acid rain.

Finally, our group has tentatively identified research needed to produce necessary information on hydroelectric effects. One area of needed research, for instance, is the ability of different animal species to adapt to a loss of habitat resulting from the filling of a reservoir in a river canyon. Far too little is known about species displacement due to habitat losses caused by energy activities in general. This final phase of identifying areas for research has not yet begun for the other five problem areas being considered.

FOOTNOTE AND REFERENCES

[†]UC Berkeley, Energy Resource Group

1. See previous paper ("Regional Issue Identification and Assessment") for more detail on the RIIA program.
2. A more thorough presentation of impact analysis can be found in John P. Holdren, "Environmental impacts of alternative energy technologies for California," in P. Craig, M. Christensen, M. Levine, O. Mukamel, and M. Simmons, Eds., "Distributive Energy Systems in California's Future," LBL-6831-revised, vol. II (Lawrence Berkeley Laboratory of the University of California, Berkeley, March, 1978).

Recent Trends in California Natural Gas Consumption

R. Sextro, I. Borg,[†] C. Anderson,[†] and B. Rubin[†]

INTRODUCTION

Since 1973, total natural gas consumption in California has declined with annual decrements as high as 10 percent. The biggest changes in gas use have been by industrial customers and for electrical generation. In addition there have also been significant changes in residential and commercial use on a per customer basis.

This study has attempted to detail the recent gas consumption trends by end-use sector and to examine possible explanations for the declining consumption. It has proceeded in two phases. The first produced an overview of trends during 1975, 1976 and 1977, and presented several factors thought to influence gas consumption. The second phase extended the data collection to 1973 and 1974, and tracked more recent monthly gas consumption through part of 1978. Additional issues were explored, including the effect of recent changes in gas rate structures. The major factors thought to have influenced changes in gas consumption in California are discussed in the article "Analysis of Recent Changes in California Natural Gas Demand" in this same volume.

NATURAL GAS SALES AND DISTRIBUTION

Three major gas utilities service most of California, as indicated in Fig. 1. About 93 percent of the gas used in California is regulated by the Public Utilities Commission (PUC); 4 percent is used in the production of oil and gas in the state, and 3 percent is sold directly by California producers to industrial customers. With gas production from California fields declining, all but about 10 percent of the gas supplied to the three major utilities has been from out-of-state sources (see Table 1).

While both California and U.S. gas consumption has dropped in recent years, the end-use patterns

Fig. 1. Gas utility service areas in California.
(XBL 789-2284)

Fig. 2. Comparison of natural gas consumption trends.
(XBL 792-455)

Table 1. Source of natural gas purchased by California utilities (109 ft 3).

	1972	1973	1974	1975	1976	1977
<u>SoCal</u>						
California Source ^a	74	53	38	22	24	22
Out of State						
El Paso Natural Gas Co.	636	610	597	586	567	553
Transwestern Pipeline Co.	271	274	240	213	190	187
Pacific Interstate Transm. Co.	-	-	-	-	1	10
PG&E	42	2	-	-	-	-
<u>PG&E</u>						
California Source ^a	238	233	147	139	141	131
Out of State						
El Paso Natural Gas Co.	409	378	384	357	320	296
Pacific Gas Transm. Co. (Canada)	368	374	346	365	376	373
<u>SDG&E</u>						
Other Utilities (Southern California Gas Company)	94	86	80	71	62	61

^aState and federal.

differ, as indicated in Fig. 2. Nationwide, industrial gas use predominates, while in California residential gas consumption is the largest single end-use. Proportionately more gas was used for electrical generation in California than nationwide until 1973, when electric utilities in the state began using greater quantities of fuel oil. Table 2 summarizes recent oil and gas usage by electrical utilities. Gas sales trends for industrial customers formerly classed as firm and interruptible are shown in Fig. 3. In 1976, a new classification system for gas service based upon end-use priorities was instituted replacing the old price-volume interruptible and firm gas contracts for industrial users. The utilities have maintained the accounting distinction through 1977, enabling comparisons to be made with gas sales prior to 1976. As seen in Fig. 3, firm gas sales have remained nearly constant over the 5 year

period (note log scale), while total interruptible sales for PG&E have declined by as much as 10 percent over the 5 year period.

The trends for residential and commercial gas consumption are shown on a per customer basis in Fig. 4. There are similar patterns among the three utilities for both these end use categories. During this same 5 year period, the number of customers increased an average of about 10 percent for these end uses in each service area. There is a net overall decrease in gas consumption by these end uses.

The data for residential and commercial end-use categories are corrected for extremes in weather, by monthly comparison to average heating-degree days for a given month. This is done in order to facilitate a more meaningful comparison of the different years. Residential

Table 2. Fuel oil and natural gas used by electric utilities in California.

	1975		1976		1977 (Preliminary)	
	Gas, 10 ⁹ ft ³	Oil, 10 ⁶ bbl	Gas, 10 ⁹ ft ³	Oil, 10 ⁶ bbl	Gas, 10 ⁹ ft ³	Oil, 10 ⁶ bbl
Pacific Gas & Electric (PG&E)	157	11.4	197	26.9	217.4	35.2
Southern California Edison (SCE)	71	41.3	63	45.0	91.1	57.8
Los Angeles Department of Water & Power (LADWP)	20	13.0	12	12	20.7	16.6
San Diego Gas & Electric (SDG&E)	<u>14</u>	<u>9.4</u>	<u>12</u>	<u>10.8</u>	<u>15.9</u>	<u>12.6</u>
Total	262	75.1	284	94.7	345.1	122.2

Fig. 3. Recent trends in industrial gas consumption (not temperature adjusted). (XBL 792-450)

Fig. 4. Recent trends in residential and commercial gas use (temperature adjusted). (XBL 792-451)

California Residential Gas Use Monthly Sales/Customer (Temperature Adjusted)

Fig. 5. Comparison of average monthly gas sales. (XBL 792-452)

gas use is predominated by space heating, and will therefore be sensitive to weather conditions. However, the heating-degree day concept relies upon the daily mean temperature, and does not take into account different meteorological conditions such as solar insolation or rapid changes in weather patterns that might also influence actual gas use.

It is useful to compare annual gas consumption data on a monthly basis. Figure 5 shows monthly residential gas consumption for three years (1975-1977) in each utility service area. The 1977 monthly consumption (temperature-corrected) is lower than 1975 or 1976 in almost all cases, with as much as a 20 percent decrease for both PG&E and SDG&E in the late spring and early summer of 1977 over the comparable months in 1976.

DISCUSSION

While a more detailed discussion of possible explanations for the general declining trend in gas consumption is offered in the companion report, several features of the data are discussed here.

The second sequential year of drought began in 1977, and with it came an awareness that water conservation was an essential element of public policy. This had a direct impact on gas consumption in that reduced hot water usage resulted in a decrease in residential gas consumption. This effect would be most pronounced in the summer months when water heating becomes a significant factor in residential gas use as space heating demand declines. Our estimate is that at most a 3 percent effect on annual gas consumption can be attributed to reduced water use.

Other factors relating to the drought include a general increase in the awareness of conservation, which in turn affects other uses of energy. At the same time, fuel shortages in parts of the east coast and midwest during

the winter of 1977 heightened public awareness. In order to make available to eastern users some gas destined for California, the California Public Utilities Commission moved to restrict some non-essential uses of gas, such as heating of swimming pools and decorative lighting, and called for the lowering of household thermostats. We estimate that this latter factor could result in an overall savings of about 16 percent in per residential customer use for a 30F change in thermostat setting.

Thus it appears that behavioral changes might account for some of the savings in gas consumption noted in the residential and commercial sectors. Added stimulus for these changes might have resulted from the general conservation awareness fostered in part by the conservation campaigns of the utilities, public officials and regulatory agencies.

FOOTNOTES

*Condensed from Lawrence Livermore Laboratory Report UCRL-52498.

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Analysis of Recent Changes in California Natural Gas Demand*

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INTRODUCTION

A number of possible factors is offered as an explanation for the recent observed decline in natural gas use in California. As noted in the earlier companion report, conservation campaigns initiated due to the California drought in 1976 and 1977 and to fuel shortages in other parts of the U.S. undoubtedly played a role in the recent decline of gas use. Other events have also had an effect, such as changes in building codes, rate structure alterations, increasing prices, and industrial fuel switching.

It should be noted that these are presented as plausible explanatory factors, without attempting to designate which, if any, is the most important. A number of changes have occurred simultaneously. It is not likely that any single set of cause-and-effect relations could be extracted from such complex circumstances.

CONTRIBUTING FACTORS

Different end-use categories are affected to different degrees by the same factors. The price of gas as discussed below has probably impacted industrial uses to a greater extent than residential customers. On the other hand, residential and commercial users appear to have responded well to calls for voluntary

conservation, especially in 1977. In the longer term, price increases will undoubtedly affect residential gas as well as induce greater conservation efforts in other end-use sectors.

Prices and Rate Structure Changes

Over the time period used in this analysis, the California economy has shown continued growth, hence reduced gas usage is not due to a decline in general economic activity. However, there has been a substantial change in gas rate structures, which has resulted in large price increases for non-residential gas users. Prior to 1975, rates for California gas utilities were in declining blocks, so that the larger users paid less per unit of gas than the smaller customers. In 1975, the California Public Utilities Commission (CPUC) began to flatten the rates. The Miller-Warren Energy Lifeline Act was enacted in 1975, and its provisions became effective in 1976. This act placed a ceiling on unit gas prices for gas consumption up to a certain volume by residential customers. These monthly volume limits are dependent upon the time of the year, and the differences in average climatic conditions, and are summarized in Table 1. This lifeline allowance has basically become the first gas block in an inverted rate structure for gas. The prevailing rate structure (as of September

Table 1. Residential lifeline gas allowance (therms/month).

Heating Degrees-Days*	Summer (May through Oct.)		Winter (Nov. through April)		Typical Services Areas
	Single Family	Multi-Family**	Single Family	Multi-Family**	
2500	26	21	81	54	Most of southern Calif.
2500 to 4500	26	21	106	69	Most of northern Calif.; southern Central Valley; San Luis Obispo
4500 to 7000	26	21	141	90	Eureka area; southern Calif. mountain resorts
7000	26	26	166	110	North Lake Tahoe

*65°F reference point.

**Master-meter.

1978) is shown in Fig. 1. Residential gas use falling within the lifeline allowance shows a declining unit price up to the lifeline limit, since the monthly customer charge is also included in these changes. Above the lifeline amount, unit prices rise (very steeply for PG&E and SDG&E), showing the effect of inverted rates. For commercial customers using up to 31,000 therms per month, the unit prices are higher than for residential use (and decline somewhat for higher volumes as the effect of customer charges are spread over a larger quantity of

gas). Finally, industrial gas rates generally are higher than those for commercial gas use, with the exception of PG&E's G-50 and G-52 rate schedules.

The lifeline rates have, in effect, insulated a portion of the typical residential gas consumer's bill from rising gas prices. Until September 1978, no major changes in lifeline rates had occurred for any of the three gas utilities, while overall system prices had increased by 40%. However, depending upon the utility involved,

Fig. 1. Utility gas rates as of Sept. 11, 1978. Charges include customer service charge. (XBL 792-454)

few residential customers have monthly gas use less than the lifeline allowance, hence price increases for gas volumes above the lifeline amount will be reflected in customer bills. The wide variation among the utilities in the number of customers whose use is within the monthly lifeline allowance (2-4% for PG&E, 27-31% for SCG and 43-65% for SDG&E, with the range reflecting seasonal differences) indicates that the lifeline allowance is not adequately corrected for variations in average climatic conditions.

A second major problem in the implementation of the lifeline act is that few customers know of its existence, or how it has been applied. Neither the utilities nor the CPUC have embarked on major public awareness campaigns regarding lifeline rates. Most residential customers are not aware that unit gas prices rise significantly for volumes above the lifeline allowance, or that lowest unit prices are achieved by maintaining monthly use below the lifeline allowance. At this point, it appears that price increases have not been a major factor in residential gas use. Prices have played a more significant role in the industrial sector. Most industrial customers have had alternate fuel capability for several years, since the former interruptible service classification generally required back-up fuels. The new end-use priority system is generally based upon the availability and feasibility of stand-by fuels. As unit gas prices began to rise, and early fears of large curtailments in the industrial sector developed due to gas supply shortages, many industrial customers began to prepare for fuel switching. Some industrial customers, (e.g., cement plants) switched to coal, and away from gas entirely. Others acquired or rented larger oil storage capacities for back-up fuels.

Toward the end of 1977, the price of residual fuel oils began to fall as a result of developing West Coast surpluses. Figure 2 shows oil and gas prices for the past three years. Many industrial users with dual fuel capability were able to take advantage of the prevailing low oil prices this past summer. This, in part, was the impetus for the establishment of PG&E's G-52 rate schedule, which set gas prices more competitive with prevailing prices for No. 6 fuel oil.

Recent changes in entitlements and a temporary authorization to export excess residual oil to Japan will likely result in rising spot prices for oil. However it may take some time before the market stabilizes and gas and oil prices equilibrate.

Curtailments

Curtailments have not been a significant factor in the past few years for most industrial users. The electric utilities, with the lowest priority for gas service, have had the largest curtailments in recent years; however, this loss of gas service has been supplanted by the use of oil as fuel for electric generation. The recent trends are shown in Table 2. It is important to note that in California curtailments have meant switching to back-up or alternative fuels rather than involuntary cessation of industrial activity.

During the past year, with relatively mild weather and generally reduced gas consumption due to conservation and fuel switching, there have been no curtailments of industrial customers, and very little curtailment of gas service to electric utilities. In fact, gas use as fuel for electric generation this past year has reversed the declining trend of previous

Fig. 2. Comparison of spot fuel oil prices and industrial gas prices (G-50, 52 rate schedules). (XBL 792-453)

Table 2. Gas deliveries and curtailments (10⁹ ft³).

Gas Utility	Year	Industrial				Electric Utility Curtailment Volume	Total Curtailment Volume
		Gas Use	Curtailment Volume	% of Use	% of Total Curtailment		
PG&E	1975	315.4	10.3	3	14	65.6	75.9
	1976	283.7	6.2	2	3	240.8	247.0
	1977	253.0	3.2	1	1	305.8	309.0
SoCal	1975	232.8	37.3	16	12	267.2	304.5
	1976	222.2	36.8	17	11	294.0	330.7
	1977	219.9	10.4	5	2	454.7	465.1
SDG&E	1975	8.76	0.23	3	< 1	59.9	60.1
	1976	8.01	0.35	4	1	65.2	65.6
	1977	7.93	0.53	7	1	76.3	76.8

years. While the present surpluses are due, in part, to variables such as weather and market prices that are subject to change, gas demand continues to be winter-peaked. Hence constant year-round gas deliveries from suppliers may lead to load management problems that will require greater in-state storage volumes, reduced interstate deliveries during the summer, or continued use of gas by low-priority consumers.

Factors in Residential Gas Consumption

The companion report describes recent trends in residential consumption of gas and offers some observations on possible explanations. Since comparisons are made using data corrected for changes in weather severity, the temperature correction methodology was investigated. It appears that the degree-day concept does not adequately correct for extreme weather conditions (either much milder or much more severe than the average). It also does not account for differences in weather conditions (cloudy, sunny, etc) which can affect gas consumption (solar gain, wind effects on conductive losses, etc.).

It does appear that real reductions in gas consumption per residential user have occurred, and that changes in building codes and insulation levels have had an effect. Figure 3 documents statewide changes in insulation levels in single-family and multifamily housing due to both new construction standards and retrofit of existing structures. Using these figures and assuming that 90% of the retrofit insulation activity is in single-family housing (consistent with historical activity), the overall effect from 1975 to 1977 represents about a three percent reduction in average gas consumption per residential user.

CONCLUSIONS

Price changes brought about, in part, by rate structure alterations in the last 2 to 3 years

TRENDS IN CALIFORNIA RESIDENTIAL INSULATION

Fig. 3. Single family and multi-family housing stocks. (XBL 792-449)

have had an impact on the rate of gas consumption, and will undoubtedly play a similar role in the future. At the same time, external events such as the extended California drought, recent winter time natural gas shortages in the Eastern U. S., and a short-term West Coast oil surplus have each had an effect on consumption rates. The conservation consciousness which was spurred-on by the drought has probably resulted in many permanent hardware changes

and in voluntary changes in living patterns which may be less permanent, but which have significantly affected gas consumption in the last 2-3 years.

While reductions in natural gas consumption are consistent with national energy policy, several secondary effects will have to be dealt with. Among these are problems in correcting for variations in weather; methods to manage

summertime gas surpluses and winter time peak demands; and rate structure designs that are consistent with alternative fuel prices.

FOOTNOTES

*Condensed from Lawrence Livermore Laboratory Report UCRL-52631.

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Energy & Water Use in Irrigated Agriculture During Drought Conditions*

R. L. Ritschard and K. Tsao

INTRODUCTION

Approximately 9 million acres harvested in California during 1977 were irrigated. Electrical energy is an essential input to this form of agriculture since over 90 percent of the irrigation pumping units in the state are electrical. A higher than normal demand from the agricultural sector for electric power can result from pumping ground water in areas where the surface water supply has fallen below normal as a result of drought conditions.

The authors undertook a study for the Department of Energy (DOE) to define the relationship between water and energy for irrigated agriculture. The objectives of the study were to:

- (1) determine water and energy use for agricultural irrigation during the 1977 season,
- (2) describe the response of agriculture to the drought conditions of 1977,
- (3) identify the present and potential water and energy conservation strategies applicable to California.

The analysis of electricity and water requirements for irrigated agriculture was begun as part of a two-phase project conducted by Lawrence Berkeley Laboratory in cooperation with the San Francisco Operations Office of the DOE.¹ The purposes of that overall study were to assess the impacts of the drought on California electricity supply and demand, to evaluate remedial measures, and to develop a methodology for such assessments.

ENERGY DEMAND FOR IRRIGATION WATER

The methodology used to determine electricity requirements to pump irrigation water focused on the hydrologic basins of the Central Valley. The method employed several factors to calculate the final energy demand for pumping. The factors

included: unit energy use to obtain ground and surface water, average water use by individual crop, type of irrigation, and estimated crop acreage planted in 1977. The total energy requirements for pumping in the Central Valley were estimated to be 5.91 billion Kwh, which was slightly higher than the total yearly electrical sales to agriculture reported by PG&E.

Growers used several energy and water use strategies in response to the drought conditions of 1976 and 1977. The strategies included an increased use of ground water, increased irrigation efficiencies, and shifts in cropping patterns. Drought-related losses to irrigated agriculture were minimized as a result of these modifications.

Fig. 1. Comparison of energy demands for different irrigation methods. (XBL 771-11032)

Table 1. Strategies of agricultural electricity conservation.

Strategy	Time of Implementation	Electricity Savings	Implementation Criteria
<u>Maintaining and Augmenting Surface Water Supply:</u>			
Phreatophytic control	now	Through water savings	Ecological alteration
Ditch and canal lining and covering	now or a few months	~10% water savings	Loss of percolation
Use of reclaimed water	4-8 years	5-10% water saving energy cost in processing	Dependent on basin hydrology & topography
<u>Power Use Efficiency:</u>			
Well maintenance	now	some	Best for new wells, also reactivated wells
Well efficiency	4-7 years	2-10%	
Pump maintenance	now	15-35% probably 15%	Especially for pumps older than 5 years
Pump & motor efficiencies	5 years	2-5%	Big pumps are more efficient
Cogeneration on distribution canals	now	some	Need sufficient drop to generate electricity
<u>Irrigation Efficiency:</u>			
Cutback irrigation	now	Through water savings	Greatly improves water use efficiency of surface irrigation & leaching uniformity
Tailwater reuse	now	See Fig. 1	Benefit depends on basin hydrology, water costs & topography
Sprinkler systems	now	See Fig. 1	Benefit depends on well depth; can increase plant diseases; inefficient in desert areas
Drip	A few months	See Fig. 1	Not for use in extreme soil types; most profitable for high value crops
Gated pipe	months	Through water savings, very small energy cost	Prevents erosion on steep slopes; increases areal distribution from single water source
Irrigation management	now	25%	Limited trained personnel, tailored to site, increased yield offsets fee
Reduced application	now	Through 10% water savings	Allow program depletion of available soil moisture

Ground water pumping increased by over 20 percent during 1977 to compensate for surface deficiencies. There were an estimated 7500 new wells drilled and many dormant wells were reactivated. Use of ground water, however, caused increased pumping costs, a drop in water tables, and overdrafted ground water reservoirs. The overdraft in 1977 was estimated to be 10 million acre-feet as compared to just over 2 million acre-feet in 1975. About 80 percent of the overdraft occurred in the Central Valley.

Farmers increased irrigation efficiencies in several ways. "Cutback irrigation" which diminishes runoff and reduces soil percolation in furrow systems was practiced to a great extent in 1976 and 1977. There were changes in irrigation methods towards such systems as sprinklers and drip systems, both of which improved efficiency. Although a net decrease in water use may have occurred from the use of sprinkler and drip irrigation methods, the implementation of such systems may lead to an increased energy use especially if ground water is used (Fig. 1).

A second efficiency measure practiced during this period was the reduction of water application through "deficit irrigation," which is simply the application of less water than usual. The application of less water reduces both surface evaporation and more importantly evapo-transpiration which accounts for the greatest loss of water by a crop. Associated with this strategy is the concept of "minimized leaching" or using less water to leach the salts from the root profile. Leaching was reduced drastically during the drought. The leaching requirements are dependent upon the salt sensitivity of the crop, soil salinity, soil drainage, and quality of the irrigation water. All of these parameters are very site-specific. Minimized leaching during the summer when surface water supplies were reduced was accomplished by postponement of leaching until the off season or next growing period.

Various changes in cropping patterns were identified during the 1976 and 1977 seasons. Some of these changes may have been related to reduced quantities of available water in addition to other economic factors. Specific examples of cropping pattern changes related to the drought included: reduction in double cropping, substitution of low water demand crops, e.g., oats, safflower, tomatoes, for high water demand crops, e.g., rice, and the increased planting of salt tolerant crops such as cotton.

Some future problems may have been created, however, by obtaining the needed water supplies for 1976-77. These problems include the effects of extensive water pumping on ground water reservoirs and ground subsidence. In addition, reduced water application by less frequent irrigation and changes in irrigation methods may affect the total salt balance picture for future years.

CONSERVATION POTENTIAL

Since the overall purpose of this study was to determine if the information on water and energy savings developed during the drought of 1976 and 1977 would carry over into future years, the present and potential conservation strategies applicable to California were identified and presented. Among the general approaches are: maintaining and augmenting surface water supply, increasing pump and well efficiencies, and improving irrigation efficiencies. Table 1 outlines the various strategies within each general category according to the time of implementation, potential electrical savings, and the implementation criteria.

In the agricultural sector, conserving water and energy are complexly inter-related. The treatment of conservation in this paper emphasizes strategies that could be implemented in the near term. Specific actions suggested for facilitating conservation include: expanded irrigation management system, efficient water delivery at the irrigation district level, improvements in pumping efficiencies and irrigation system design, and support of a statewide water and energy conservation study. Specifically, the individual growers are encouraged to continue their efforts to use resources during periods of normal rainfall as they were under drought conditions.

FOOTNOTES AND REFERENCES

*Condensed from Lawrence Berkeley Laboratory Report, LBL-7866, Energy and Water Use in Irrigated Agriculture During Drought Conditions, R. L. Ritschard and K. Tsao, 1978.

1. P. Benenson, et al., "Effects of the drought on California electricity supply and demand," LBL-6356, June 1977.

Technology Assessment of Solar Energy

Characterization of Solid Waste Conversion and Cogeneration Systems

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INTRODUCTION

The Characterization of Solid Waste Conversion and Cogeneration Systems was conducted under the Technology Assessment of Solar Energy Systems (TASE), directed by the Department of Energy, Division of Technology Assessments within the Office of Technology Impacts. The overall purpose of the TASE program is to evaluate the potential environmental and public health impacts and implications of a large scale and wide spread use of decentralized solar energy technologies. The program is being jointly conducted by several of the national laboratories including LBL. Phase I of the program was conducted during FY 1978 and emphasized the characterization of a number of specific solar energy and other renewable energy conservation technologies. This report describes two of the technologies assigned to LBL for phase I characterization: Municipal Solid Waste (MSW) energy recovery, and cogeneration. Four specific processes were evaluated during the course of this study:

1. Pyrolysis of MSW to either pyrolytic oil or gas,
2. Production of Refuse Derived Fuel (RDF) from MSW,
3. Direct combustion of MSW, and
4. Three cogeneration schemes.

The rationale for inclusion of these technologies in the TASE program was two-fold. First, solid waste material and waste heat in various industrial processes represent a significant renewable energy resource. Second, the growing scarcity of available land fill sites and rising costs of MSW disposal are creating solid waste management crises in many municipalities. Combined with the rising costs of conventional energy sources, this makes MSW energy recovery attractive both as an energy source and as a means of solid waste volume reduction.

For each of the four technologies listed above specific typical applications were defined. Capital and operating requirements for material, capital and labor were defined for each application. Environmental residuals created by the operation of each system were identified and the rate of their generation was calculated. Finally, constraints to the expanded use of each technology were identified and discussed. This paper briefly outlines the system designs included in each technology application.

TECHNOLOGY CHARACTERIZATION

Municipal Solid Waste

Three MSW energy recovery systems were selected for analysis, one typical of each of the three major groups of MSW conversion systems which have been tested in the United States. They are: pyrolysis systems, refuse derived fuel (RDF) systems, and direct combustion systems.

Pyrolysis Systems

Pyrolysis is a process in which organic material is decomposed at elevated temperatures in either a low oxygen or an oxygen-free environment. Unlike incineration with air, which is a highly exothermic reaction, pyrolysis is endothermic and requires the application of heat, either through the addition of fuels or through partial oxidation of the pyrolysis reaction. Again, unlike incineration, which produces primarily carbon dioxide and water, pyrolysis produces a complex mixture of combustible gases, oils and solid char residues. The mix of gas and oil produced is variable and is dependent primarily upon reaction temperature.

Pyrolysis offers several significant advantages over MSW energy recovery systems. First, either gas, liquid fuels, or electricity may be produced. Second, pyrolysis has a small atmosphere waste stream for emissions control.

The major drawbacks of pyrolysis are that the technology is still in a developmental stage and has not been demonstrated in a large plant, and that both the capital and operating costs of pyrolysis tend to be higher than other systems.

The Union Carbide PUROX system was the pyrolysis system selected for characterization in the study, based on a number of environmental and operational advantages over other pyrolysis systems. This system is a high temperature (3000°F) slagging pyrolysis process which produces a low to medium Btu gas rated 300 to 320 Btu/scf. The PUROX process provides for ferrous metal and aluminum recovery, using a vertical shaft pyrolysis furnace whose reaction is driven by pure oxygen. Inert slag passing from the bottom of the furnace is quenched and sold as a glass aggregate for construction.

The PUROX system has several specific advantages in addition to the general pyrolysis advantages. These include minimal air emissions, production

of a sellable solid waste stream (slag), and the generation of only one significant waste flow--the aqueous waste stream. Major waterborne residuals from this system include Hg, Zn, Pb, Ni, Cd solubles and sludge.

Refuse Derived Fuel

RDF is a mechanically processed interim product of MSW. It is characteristically uniform in size and consistency, is easy to handle and store, and is used as a supplementary boiler feedstock with traditional fuels (e.g., coal). Several individual processes to produce RDF have been developed and include:

- 1) wet processing (hydropulping) followed by component separation and dewatering of the fuel fraction.
- 2) dry processing (shredding) followed by chemical processing to produce what is called ECO-Fuel II. And
- 3) dry processing (shredding) followed by air classification.

The technology description presented in our report focusses on the finely shredded air-classified fuel, since the major part of the industry experience relates to this technology. The product is combustible with a reasonably high heat of combustion and is being utilized as a supplementary fuel in the utility boilers at several locations. In this system, the refuse is first shredded in a hammermill to 8-13 cm (3-5 in.) particles, and is then air classified. This separates the combustible light fraction (about 80 percent of the input refuse) from the heavy non-combustible fraction. The heavy fraction from the air classifier goes to a magnetic separator which removes the ferrous metals.

The light fraction is sent to a secondary shredder (fine shredder) where it is reduced to final size of 2.5 cm (1-2 in.) particles. This RDF typically comprises 10-20 percent of a boiler feedstock. Pollutant sources at the processing plant include dust from the shredders and air classification systems, sound from equipment operation, odors, water-borne contaminants from wash of storage areas, and residue destined for landfill.

Direct Combustion of MSW

Direct combustion systems generally involve no front end systems but rather load MSW directly into incinerators. They may be differentiated from RDF systems by this absence of pre-processing of received refuse. Heat resulting from the MSW combustion is partially recaptured through boiler tubes. There are two general types of direct combustion systems currently being used in the U. S.: refractory wall incinerators and waterwall incinerators. Steam is the basic energy produce of both systems and can either be used directly or can be converted to electricity in a steam turbine. Waterwall incinerators have the advantages of higher burning temperatures

(1700°F to 1800°F) and lower requirements for excess air. The major pollutant flow from these systems are the stack emissions and the solid char residue. Stack gas includes NO_x, CO, HCl, NH₃, particulates and SO₂. The scrubber waste flow is high in dissolved solids; the quench water waste has a pH of approximately 9.9, is also high in suspended solids, and is about 90°C at the outlet.

Cogeneration System

Three separate cogeneration systems were evaluated during this study. As the name implies, cogeneration is a method of simultaneously producing process heat and electricity by matching the heat rejected from a primary process to the heat required by a secondary process. The method has attracted attention because it provides a method to utilize fuel efficiently.

Fluidized bed combustion is a non-conventional method of incineration which is compatible with cogeneration processes. The method employs the rapid flow of air up through a grid plate upon which rests the bed of material to be burned. The air flow is sufficient to introduce turbulent flow to the bed and results in complete combustion of fuel even in quantities as low as 2% of bed volume. If most of the bed material is limestone, SO₂ is efficiently removed as a dry solid. By locating heat exchanger tubes directly within the turbulent bed, high rates of heat transfer can be achieved at relatively low temperatures.

The second cogeneration system characterized during this study involves a methane powered diesel system. Since the report describes a cogeneration process in which methane generated by a biomass conversion process is converted to electricity, heat and pumping power. A reciprocating diesel is combined with a topping cycle waste heat boiler which generates 12.6 Mw of steam at 27.4 x 10⁶ Btu/hr. While the system has a calculated efficiency of 37%, it suffers from high NO_x emissions.

The last cogeneration system characterized found application in enhanced oil recovery operations. Because oil well recovery factors are usually one third or less of the oil in place, it has become economically practical to heat subterranean oil by high pressure steam prior to extraction. In this system, inexpensive first tier oil is gasified and used to drive a combustion turbine. The turbine generates very high pressure steam which is used to recover second tier oil which is roughly twice as valuable as the fuel used to operate the turbine. In addition, the turbine produces 260 MWe of electricity.

SUMMARY

A complete description of each of the technology applications introduced in this paper is contained within the project report. These descriptions include detailed process and schematic flow information, capital and operating cost data,

Table 1. Systems output comparison (tons/day/10¹² Btu steam per year).*

No.	Parameter	Systems							
		LG	GP	PX	DC	RDF	FB	DI	E0
1	Steam (tons)	4.32x10 ⁵	5.97x10 ⁵	0	4.72x10 ⁵	3.34x10 ⁵	2.1x10 ⁵	2.1x10 ⁵	144
2	Electricity (kW-hr)						1.31x10 ⁸	1.76x10 ⁸	2.20x10 ⁸
3	Fuel Oil	0	4.03x10 ⁴	0	0	0	--	--	--
4	Fuel Gas	0	1.97x10 ⁴	0.65x10 ⁴	0	0	--	--	--
5	Ferrous Metal	1.26x10 ³	1.61x10 ³	8.45x10 ³	1.18x10 ⁴	9.73x10 ³	--	--	--
6	Non-Ferrous Metal	--	1.58x10 ⁴	1.05x10 ³	--	1.39x10 ³	--	--	--
7	Glass	3.06x10 ⁴	1.06x10 ⁵	2.96x10 ⁴	8.65x10 ³	1.11x10 ⁴	--	--	--
8	Waste H ₂ O	4.68x10 ⁴	1.32x10 ⁴	4.3x10 ⁴	1.08x10 ⁵	--	--	--	--
9	Char	1.44x10 ³	35.05	0	1.73x10 ⁴	4.75x10 ⁴	3.5x10 ³	950	2.28
10	Stack Effluent	585	1.06x10 ⁵	1.17	1.63x10 ⁶	4.17x10 ⁴	412	3.15x10 ³	101
11	Water Effluent	4.68x10 ⁹		5.6x10 ⁴	335.17	2.78x10 ⁴	--	--	--

LG = Languard pyrolysis
 GP = Garrett flash pyrolysis
 PX = Union Carbide Purox process
 DC = Direct combustion
 RDF = Refuse-derived fuels

FB = Fluidized-bed cogeneration
 DI = Diesel cogeneration
 E0 = Enhanced oil recovery (cogeneration)
 *blank indicates no available data

and quantitative information for the rates of residual generation.

It was found that while land requirements are minimal for all systems, the recommended RDF system is the most efficient in terms of energy recovery per Btu input and is also the least expensive to build. The report points out that while the fluidized bed system has the highest overall efficiency, the PUROX system uses the least energy and is the only system which does not require process water. Table 1 compares the major systems studied for selected inputs and outputs.

Clearly the potential of MSW makes it worth further study. In this country alone the yearly collection is estimated at 1.25×10^8 tons with an average energy content of 4500 Btu/lb. This provides a total potential resource of 1.125×10^{15} Btu/yr. It would appear sufficient to guarantee MSW a place in our energy future.

FOOTNOTE

*Condensed from Lawrence Berkeley Laboratory Report, LBL-883.

Community Level Studies of Decentralized Solar Energy Technologies

R. Ritschard, K. Haven, and J. Kooser

INTRODUCTION

The Technology Assessment of Solar Energy (TASE) program which commenced in mid-FY 1978 is being conducted cooperatively by six of the Department of Energy national laboratories. The focus of the TASE Program is to provide impact analysis of various solar technologies at the national level. Since local or community impacts (e.g., land use, transportation modes, institutions, labor needs, etc.) may be more important than state, regional or national impacts with regard to solar technologies, a series of community level studies were initiated within the Energy Analysis Program.

The overall objective of the community level studies is to investigate the impacts of various solar-based energy systems on the community environment and its physical and social structure. Furthermore, the studies will identify issues and constraints to local and regional deployment of decentralized solar energy technologies. In order to fulfill this objective the project is divided into three major areas: community impact analysis, threshold impact study and solar city end-state analysis.

ACCOMPLISHMENTS DURING 1978

The major accomplishment during 1978 was the organization, design and commencement of the individual community level studies. The study design for each of the specific areas, for the most part, has been developed by outside investigators. During the latter part of 1978 (September) contracts were awarded to several groups and work commenced. The overall integrated organization, however, has been coordinated by the Energy Analysis Program. In addition, national scenarios based on the Domestic Policy Review Committee's figures were adapted to the community level for use by the individual tasks. A final accomplishment has been the

characterization of various solar technologies for deployment at the community level. The technologies, which are consistent with other TASE activities, include: photovoltaics, wind, solar flat plate collectors, compound parabolic collectors, and wood combustion.

PLANNED ACTIVITIES FOR 1979

The specific tasks within each major impact analysis area are given below:

Community Impact Analysis

The objective of this task is to assess the physical, environmental and institutional impacts of solar energy utilization on spatially constrained communities. The approach is to identify impacts through analysis of technology siting and the physical layout. The results of the community impact analysis will be a matrix of impact indicators for various levels of solar penetration and for various community spatial configurations.

The impact analysis is divided into several subtasks which include: identification and characterization of various prototypical land use sectors; determination of energy and use requirements for each land use prototype; identification of the requirements of the various decentralized solar technologies; and an estimation of the feasibility and first-order impacts of implementing solar technologies on site and at the neighborhood scale.

Specifically, the task is taking prototypical land use patterns (varying in configuration, density and type) in the form of aerial photographs from several U. S. cities and determining whether there is a surplus or deficit of area available for solar collectors. Coefficients have been developed to determine the area requirements of solar collectors given different solar con-

tributions. A template is then used to determine whether sufficient area exists on rooftops, in yards or on vacant land. This template also indicates whether shading by vegetation or buildings will be a problem.

Another aspect of the community impact analysis is an exploration of urban morphologies to investigate the ability of future urban forms to "absorb" solar energy systems. This approach will help identify the interaction between urban function and form.

Threshold Impact Study

The threshold impact study is intended to examine in a hypothetical situation the ability of communities to absorb social and institutional changes incurred by adaptation to an energy system heavily based on decentralized solar energy technologies. The approach is to identify, for a particular level of solar penetration to the year 2025, community and institutional impediments and their rate of change over time. A series of scenarios representing a range of U. S. cities and the rates and compositions of solar diffusion were derived to identify the basic impediments or threshold indicators.

Two workshops held with representatives of various shareholder groups will be used to refine the original list of impediments, suggest new ones and propose how new attitudes could remove these impediments. The first workshop will be held in California and will identify impacts based on community scenarios. The second workshop will be conducted in Washington, D.C. and will be based on the impacts of the individual solar technologies. For policy purposes, an impediment or threshold is defined as a delay or identifiable resistance by as much as three to five years under current operating procedures.

Six shareholder groups have been identified by the study team: financial; regulatory and planning; environmental; construction, maintenance, distribution; energy supply; and energy demand. The results of the threshold analysis will be a summary of institutional relationships which determine if various community forms may reach a state of non-adaptability in which

they are unable to assimilate further increments of solar energy.

Solar City End-State Analysis

The objective of the end-state analysis is to depict for a prototypical city the possible end-state communities under varying solar growth assumptions to the year 2025. The approach of this study is to present a visualization of the consequences of available choices of community environmental design.

A hypothetical city is assumed to undergo changes with time coincident with absorption of solar energy technologies into its community structure. A city will be analyzed in its end-state after a period of growth (to the year 2025) based on a business-as-usual scenario, which continues present energy supply patterns. Similarly, the same city will be examined in its end-state after a period of growth representing a high solar scenario that substitutes solar technologies up to about 35 percent of the community's energy needs. In a third case, a hypothetical city built "de novo," but maximizing solar energy sources and processing the same characteristics as the other cities in the year 2025 in terms of population, goods and services produced, and energy demand, will be examined in its end-state.

As a part of the "de novo" city analysis, a computer model will be developed that describes the thermal characteristics of different building designs given different climatic conditions. The basic concept is to start with passive design and fill energy needs with "low level" solar technologies first. The next step is to assemble these building designs together to develop the "de novo" solar city.

The results of the end-state analysis will be the presentation of the physical, environmental and socioeconomic characteristics of the emergent cities according to the various growth patterns. These results will address the debate over the desirability of solar energy by providing information that considers the relative attractiveness of the end-state to which such decisions today might lead us in terms of future life style and community structure.

Marine Biomass System: Anaerobic Digestion and Production of Methane*

K. Haven, R. Ritschard, and M. Henriquez

INTRODUCTION

The objectives of this project were to investigate the feasibility of converting marine biomass into energy products, to define a state-of-the-art system design for this energy conversion technology, and to estimate the life cycle

residuals which would be generated by the operation of the system. The project was undertaken as a part of Phase I of the DOE Division of Technology Assessment (DTA/OTI) program Technology Assessment of Solar Energy (TASE). It is the purpose of this program to assess the impacts and implications to the environment and to

public health and safety resulting from widespread implementation of decentralized solar and selected renewable resource technologies. The analytical efforts undertaken in 1978 for Phase I of the TASE program have been directed toward characterizing various solar technologies and applications for subsequent use in assessing the impacts of a widespread excursion into the use of solar technologies (Phase II).

This project characterized one technology (Marine Biomass) through two specific applications (an oceanic kelp farm system, and a natural coastal kelp bed system). Detailed system designs were prepared; the material, capital and labor required to construct and maintain the systems were calculated; and environmental residuals generated by the system operation were estimated. Some of the results and system design information of this project are summarized below.

KELP PRODUCTION

Several aquatic micro-algae have been considered for use in the conversion of incident solar radiation into a useful energy product. However, marine micro-algae make inefficient use of the oceanic water column, require extensive systems to maintain optimal growth (bloom) conditions, and do not result in production yields (kg/acre) of harvestable biomass as large as those attainable from some macro-algae. Of particular interest is the California giant kelp (*Macrosystis pyrifera*). Typically, this kelp attains annual growth rates in natural coastal beds of approximately 8 dry ash-free (DAF) tons/acre-year.¹ However, this growth rate can be significantly enhanced through the addition of appropriate nutrients. Klaus² reported enhanced growth rates of as high as 49 DAF tons/acre year for some experimental beds. Such enhanced yields could make giant kelp an attractive energy crop.

Two systems were considered in this study for enhancing kelp growth rates: an oceanic farm concept, and a nutrient enriched natural coastal bed. The major features of each system are described below.

Ocean Farm System

The oceanic farm system design was based on studies by Wilcox³ and Dynatech.⁴ No oceanic farm has been tested, and the design must be considered conceptual at this time. The oceanic farm employs an artificial substrate to support kelp plants and is located in deep ocean waters. Open ocean siting allows the development of large area farms (hundreds of square miles) and thus sufficiently large masses of annual kelp production to make a significant contribution to the national natural gas supply. Growth rates of kelp plants attached to the artificial substrate will be enhanced by pumping nutrient rich waters up into the kelp growth zone to increase surface water nutrient availability. Nutrient rich waters will be obtained from below the photic zone (500 m-800 m depth).

The major components of the oceanic farm system are the artificial substrate, a series of deep water pipes and pumps, and an anchoring system. Wilcox³ proposed the use of a modular concept for the oceanic farm using a series of quarter acre modules (QAM). Each QAM would act as an independent mini-farm. Others (e.g., Dynatech) have proposed the use of a single large horizontal grid for the farm substrate. The QAM system was adopted as the system of choice for this study because of its flexible and feasible system designs. A small (11.56 sq. mi) farm was designed and farm yield was estimated to be 4.83×10^6 wet tons/yr (50 DAF tons/acre-yr).

While this system provides the advantages of high yields per acre and can be designed for a large farm size to produce large total yield, it also has several major problems. First, the ability of a large (100 sq. mi) rigid structure to maintain long term structural integrity in an oceanic environment has not been demonstrated. Second, the ability of the mooring/anchoring system to hold the farm on station in several thousand feet of water has not been demonstrated. Third, the system costs far too much to be profitable. The small (1.50 sq. mi) ocean farm system will cost \$1.6 billion to construct and locate. Total annual production costs will be as high as \$25 to \$30 million BTU.

Natural Kelp Bed System

The selected natural kelp bed system uses a small (2 sq. miles) coastal kelp bed. Enhanced growth rates were obtained by using a municipal sewer outfall as a nutrient feed. A numerical model of kelp growth for this system was developed and yields of 12-16 DAF tons/acre-year were achieved. At this yield, 300 tons per day (wet) per square mile of kelp bed are harvested for delivery to a processing plant.

The principal advantage of this system is low capital cost. By using a natural kelp bed there is no cost associated with the production system. The principal disadvantages are the reduced yield, small bed size, and potential problems with trace element uptake from the sewage outfall by the kelp.

Processing System

An anaerobic digestion system was designed to convert kelp into methane. Preprocessing steps were designed to reduce water content and to free the volatile solids from the kelp structure. These steps included coarse and fine grinding, a heat and calcium chloride pretreatment, and pressing to remove juices. The remaining cake represented approximately 20 percent of the original mass but included 60 percent of the volatile solids. Gases produced by the anaerobic digestion process were 60 percent CO₂ and 40 percent CH₄. This gas was scrubbed to produce 96 + percent pure methane. Through this process 4.35×10^5 Btu of methane were produced per ton of incoming kelp with a conversion efficiency of approximately

Fig. 1. Kelp to methane processing plant schematic.
(XBL 792-337)

65 per cent. Waste flows were not reprocessed to maximize final methane production. Rather, waste flows were used as feedstock for a fluidized bed boiler which provided all process heat and electricity required by the conversion process. Figure 1 shows a schematic of this processing system. Figure 2 shows the unitized material and energy flows through the processing plant. The plant structure is identical for the oceanic system and the natural bed system since modular design allows for plant capacity to be expanded as required to match the anticipated kelp harvest rate.

Residuals for each system were identified and, where possible, quantified. Major residual flows were found to exist as aqueous waste from the processing plant, atmospheric emissions from the ocean farm pump motors and generators, and, to a lesser extent the waste sludge from the fluidized bed boiler and stack emissions from the conversion plant.

CONCLUSIONS

- Neither the ocean farm nor the natural bed system is economically attractive so long as methane is the sole product of the system. Energy costs for the system described in this report are from \$10 to \$30 per million Btu of generated gas. It is probable that this cost could be reduced to the \$5 to \$8 per million Btu range for a site-optimized natural bed system.

Fig. 2. Materials and energy flow. Kelp to methane system.
(XBL 792-335)

- The production of side products (algin and/or feedstocks) appears to be feasible as part of the methane production process and is economically essential in order to produce a commercially viable system.
- Enhanced growth of kelp through the application of treated sewage outfall appears to be feasible and economically attractive. Additional research is required in the area of nutrient dispersion and availability, kelp uptake of heavy metals, and non-nutrient growth limiters for the kelp.
- The environmental impact of the ocean farm system is primarily associated with the deep ocean water pumping system which releases significant quantities of air pollutants and alters surface water characteristics of the entire area of the farm. The major conversion plant residual flow is the waste water flow (160 gal/tons of wet incoming kelp). The pollutant constituents of this flow are not well known but should include a significant presence of heavy metals and BOD.

FOOTNOTES AND REFERENCES

*Condensed from Lawrence Berkeley Laboratory Report, LBL-8460.

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Design and Characterization of Two Decentralized Total Solar Energy Supply Systems*

M. Henriquez, A. Ghirardi, and K. Haven

INTRODUCTION

The development of thermal and photovoltaic solar energy conversion systems was carried out as part of the Technology Assessment of Solar Energy Systems (TASE), which was conducted by the Division of Technology Assessments (Office of Technology Impacts) of the Office of the Assistant Secretary for Environment (ASEV/OTI/DTA) of the Department of Energy.

Work undertaken during this project resulted in the design and characterization of decentralized commercial and industrial scale systems. However, this study differs from conventional TASE assessments because it was not intended to characterize an entire technology, but rather to define two plausible decentralized solar energy supply systems and to identify environmental residuals associated with the development and operation of these two specific systems.

Unlike most existing or proposed solar conversion systems, the designs developed and characterized under this project were conceived to provide 100% of the support activities: space heating, cooling, electrical and process heat requirements. Furthermore, constraints placed on potential engineering approaches dictated that all discrete

components for both systems must represent an existing technology which has been proven to the extent that reliable operating data allow a realistic appraisal of long term performance. Additionally, it was required that all of these components be readily available to the consumer market at rated efficiencies within the next five years.

SYSTEM DESIGN

Accomplishments

- Thermal Collector for Industrial Support

The thermal portion of this study stipulated the use of flat plate collectors to support 100% of a typical modern brewery's space, water, process heat and power requirements. During the preliminary phase of this study, some fifty existing industries with installed solar conversion systems were examined with respect to the employed technology, site, and process requirements. Additionally, some 200 non-industrial solar demonstration projects were similarly evaluated. Next, a number of varying quantitative design approaches were analyzed and finally, the techniques of mathematical systems analysis were employed to set specifications, develop and

optimize a unique system within the limits of project completion.

The system eventually developed had the following features:

- 1) It satisfied a total load of 1.4 MW electricity, 10,000 lbs/hr process steam at 200°F and 20 psia, and 655 tons of adsorption refrigeration.
- 2) It contained a concentrating flat plate collector array consisting of conventional collectors assisted by mylar planar reflectors. These reflectors assumed a mild concavity when suspended on the reverse slope of adjacent collector support trusses. Due to the specular reflectance of mylar and the specific mounting orientation, it was shown that concentration factors of 2:1 can be achieved.
- 3) It contained a mixture of dyphenal and dyphenal oxide (Dow A) for the collector working fluid, and Toluene for the power generation cycle working fluid.
- 4) A wall mounted Thermic Diode array was used to provide both winter heating and summer air conditioning. Because these solid state liquid devices contain their own thermal storage, they were operated on a separate loop, thus eliminating the possibility of transient process variables degrading environmental quality.
- 5) While not specifically called for by the load demand profile and not included in the basic plant energy supply system, a seasonal storage system was developed. This involved multiple excavated tank units operated by a third level computer control hierarchy. Because the surface of these structures could be optimized for retention of heat generated by incident solar flux, it is possible to maintain high working fluid temperatures over long periods of time.
- 6) Conventional storage of latent and sensible heat was provided with a 6×10^8 Btu capacity.
- 7) Modular design allows easy expansion of the energy supply system to support future expansion of plant capacity.

Figure 1 shows a detailed schematic of the major components of this energy supply system and depicts the plant energy balance using the described collector arrays.

● Photovoltaic Collector for Commercial Application

The photovoltaic system detailed in this report supports the energy requirements of an elementary school and is based on a 3 ft by 8 ft module of silicon cells. Each cell has two covers which are separated by an air gap. The silicon semiconductor is located on an aluminum base under the second cover and is arranged so that a stream of coolant is allowed to flow

Fig. 1. Industrial total solar energy distribution. (XBL 792-334)

between the rear of the base and the thermal insulation which separates the base from the back cover of the assembly. It should be noted that cell electrical output decreases as cell temperature increases and that silicon semiconductors are liable to heat damage above 60°C. Therefore, maximum electrical output is not achieved by sacrificing thermal output, but rather by increasing thermal transfer in order to maintain the cells at a lower temperature.

As a result, photovoltaic systems can be designed in a cogeneration mode which provides both space heating and electricity. It was shown that the combined system would have an output of 191 kwh/m² for electricity and 755 kwh/m² for heat. Required collector area for these selected loads was calculated as 45,899 ft², which involved mounting the cells on the uppermost six feet of south facing exterior wall and on the entire school roof surface.

The hot water load was activated at 360 gal/day delivered at 50°C. The water is heated in two stages using separate underground tanks of 1.5m³ and .5m³ capacity respectively. Hot air from the collectors is used to heat the contents of the first tank to between 20°C and 35°C. The hot effluent is directed to the second tank where its temperature is further raised to 50°C by means of a 10kw resistive heating element.

It was calculated that on clear winter days a minimum interior temperature of 17°C could be maintained by solar cell exhaust circulation alone, while on cloudy days supplemental 180kw resistive space heaters may be required to compensate for the reduced incident thermal radiation.

Storage is provided by lead acid batteries which, in comparison to alternative systems, were found to be an expensive storage system

but did have the advantages of simplicity, familiarity, and availability. The batteries were rated at 1300 amp-hours and were sufficient for two days capacity.

Fig. 2. Electrical system schematic.
(XBL 792-338)

Finally a subsystem was developed to interface the various loads and power requirements of the system with existing utility grids. As a result, a power conditioning system was specified which performs the following functions:

- 1) Regulation; voltage regulator stabilizes photovoltaic output to levels consistent with safe battery charging.

Table 1. Summary of energy flows.

DESTINATION	MWY/YR
Incident on collector	7357
Reflected	1886
Transmitted to structure	1498
Converted to electricity	736
Converted to heat	3237
Electricity generated	736
Stored in the battery	589
Used by the load	288
Heat generated	3237
Lost from electric modules	1295
Lost from combined modules	1752
Transmitted to the load	190
Used by the load	82

- 2) Inversion; the inverter receives D.C. voltage from the battery and converts it to 60 Hz A.C. for use by load. It can also charge the battery from A.C. supplied by the grid.

- 3) Interface; controls the switching of load input power between the grid and the solar array.

A systems schematic is presented in Fig. 2 while an energy summary for this system is presented in Table 1.

FOOTNOTE

*Condensed from Lawrence Berkeley Laboratory Report, LBL-8459.

Solar Ownership and Marketing

Utility Investment in On-Site Solar: Risk and Return Analysis for Capitalization and Financing*

E. Kahn

INTRODUCTION

This project is designed to analyze one generic strategy aimed at accelerating the adoption of solar heating by residential consumers. This strategy involves utility financing of the capital investment costs of solar heating. Local utility companies are currently involved in a variety of programs to promote energy conservation. The finance of residential insulation is a close analog to the finance of solar heating.

Despite the potential benefit of such financial activities by utilities, there is concern that

these programs would have a harmful effect on competition among home heating suppliers, contractors and lenders in a utility service area. Therefore recent national legislation has provided for regulation of this activity. Developing such regulation will require information about the economic impacts of utility financing of solar heating. This study aims to establish some of the necessary data for the development of efficient regulation.

The research activity is divided into three areas: risk and return analysis for utility finance, analysis of the lender market structure

for solar finance, and analysis of the vendor market structure for home heating. The focus of this activity is oriented to California conditions. The basic issues have been raised in hearings held jointly by the State Public Utilities Commission and the Energy Resources Conservation and Development Commission. Furthermore the California legislature is requiring that policy guidelines be developed for utility participation in the marketing, manufacture and financing of solar energy equipment.

LBL began its work in June, 1978. The first area of investigation was financial analysis of utility investment in on-site solar systems. Starting in 1979 emphasis will expand to include analysis of lender and vendor market structure.

ACCOMPLISHMENTS DURING 1978

Research during 1978 was concentrated on the application of modern finance theory to the analysis of utility involvement in the finance of on-site solar. If such programs are ultimately found to be beneficial on balance, the fundamental problem facing regulation is the determination of an interest rate to be charged for the loans. Underlying the whole strategy of utility solar finance is the intuition that low cost capital ought to be available for this purpose because of the utility's access to the capital market. Yet there has been virtually no analysis to support such propositions or to help determine what "low cost capital" might mean in practice.

To approach these problems through modern financial theory, extensive use was made of the Capital Asset Pricing Model (CAPM). CAPM is a quantitative theory of asset valuation which provides a means of trading off investment risk against expected return. In order to be attractive, riskier investments require higher returns than safer investments. The basic task of financial analysis is to construct a definition of investment risk. Within the framework of CAPM, risk is defined by the covariance of an asset's earning stream with the average return of the capital market portfolio. This measures the "volatility" of returns; the extent of their correlation with macro-economic fluctuations. This definition assumes that diversification of investment risk is fundamental to the pricing and valuation of assets in the capital market.

CAPM also provides an apparatus for estimating appropriate minimal rates of return for individual projects. This minimal rate of return, called a "hurdle-rate", sets the lower bound on acceptance of projects for profit-maximizing firms. The hurdle rate is expressed as follows:

$$\text{Hurdle Rate} = \text{Risk-free Rate} + \text{Risk Premium of Return,}$$

where the Risk Premium is measured by the volatility of a project's return multiplied by the market price of risk. Thus,

$$\text{Risk Premium} = \text{Volatility} \times \text{Market Price of Risk}$$

$$= \frac{\text{Cov}(R_p, R_m)}{\text{Var}(R_m)} \left[E(R_m) - R_f \right],$$

where R_p = rate of return on project p

R_m = rate of return of market portfolio

R_f = risk-free rate of return

and E , Cov , and Var are the expectation operator, covariance operator and variance operator respectively.

Although CAPM is a formally complete approach to risk quantification, its application is not straight-forward for projects that are so new that there are insufficient statistics to calculate the co-variance term in the volatility coefficient. For on-site solar projects this is the case. Therefore volatility must be estimated by a method of risk enumeration and impact assessment. The following paragraphs introduce the major risks of utility investment and how they impact the returns on solar.

Solar investment presents utilities with a default risk in addition to the other risks facing conventional utility investment. A reasonable proxy for the default risk is the uncollectible rate on utility bills. Regression analysis shows, however, that this risk is negligible. Compared to that of finance companies for example, the default risk for utility investment is insignificant.

Conventional utility investments are becoming increasingly risky compared to historical risks faced by this industry. These increased risks are due to the uncertain demand in the future, the long lead times required to construct new centralized power plants, and the exposure of these big projects to cost over-runs in excess of inflation. The changing risk structure is reflected in higher requirements for return on utility equity.

Solar investment avoids most of this risk. There is relatively little elasticity of demand for hot water and space heat, so uncertainty is removed. The lead time for on site solar is short, and the potential for cost overruns is correspondingly limited. Solar investments are vulnerable to decreases in future energy prices. Since the likelihood of this appears small, there is little risk from this factor. Finally, solar investment is a long term commitment of capital and as such bears an interest rate risk. To develop an estimate of the interest rate risk, the return on corporate bonds was selected as a reasonable proxy for long run investment. Regression analysis shows that an index of such bonds does exhibit limited volatility in the sense of CAPM.

A preliminary estimate of the appropriate hurdle rate for utility investment in on site solar was developed using estimates of long term values for the risk-free rate of return, the volatility of the investment, and the market

Table 1. Internal rate of return as a function of region, system, lifetime, and taxation.

ASSUMPTIONS: Solar Hot Water Heater Capital Cost = \$1500
 Annual Maintenance Expenses = \$60/yr
 Energy Price Escalation Rate = 5.1% (real dollars)/yr
 Inflation Rate = 5%/yr

Regional Performance and Value (Energy Displaced and 1978 cost per unit)

San Diego: 4800 kwh, 4.8¢/kwh
 Northern California: 2800 kwh, 4.0¢/kwh

Internal Rate of Return

	Lifetime		
	10 yrs	15 yrs	20 yrs
Case 1.			
No Federal Tax			
San Diego	14.5%	20.0%	22.3%
Northern California	0	6.0%	10.0%
Case 2.			
48% Federal Tax			
San Diego	8.8%	13.3%	15.3%
Northern California	0	3.8%	6.8%
Case 3.			
55% State Tax Credit			
33% Personal Income Tax			
San Diego	25.5%	29.5%	30.8%
Northern California	3.5%	11.5%	15.0%

Note: California grants a 55% state income tax credit for solar. This benefit, however, also shows up as a reduced deduction for federal tax purposes. The cost of the reduced deduction is the dollar magnitude of the state solar tax credit times the marginal federal tax rate. These joint impacts can be expressed as a reduction to an "effective" state tax credit by the formula:

Effective Tax Credit = Nominal Credit - Marginal IRS Rate x Nominal Credit

price of risk. These estimates yield a hurdle rate of about 8.5%. Regulatory policy must be set for solar finance programs by estimating expected returns for on site solar investment. Table 1 develops some rate of return calculations for the case in which solar displaces electric water heating.

If the regulators choose to subsidize solar investment, then rates of return less than 8.5% would be acceptable. If the regulators allow utilities to own on site solar devices and the rate of return is more than 8.5%, then the solar investment would be subsidizing other customers unless there were a revenue adjustment. Finally, if the utility were to act simply as a financial intermediary, then the consumer would make the the decision to invest based on his expected return. This latter case would involve California state solar tax credits. Cases 1, 2 and 3 in Table 1 correspond to these choices. That is, cases 1 and 2 represent

the extremes of the influence utility capital structure would have on solar rates of return. Case 3 represents the financing option.

PLANNED ACTIVITIES FOR 1979

In 1979 there will be further investigation into appropriate measures of utility investment risk. In addition various regulatory actions will be examined to determine the sensitivity of interest rates for solar finance.

The vendor and lender markets will also be analyzed to determine if in fact there is a role for utility investment in solar that would not be anti-competitive.

FOOTNOTE

* Condensed from Lawrence Berkeley Laboratory Report, LBL-7876.

Distributed Energy Systems

Distributed Energy Systems in California's Future

P. Craig and M. D. Levine

INTRODUCTION

The Distributed Energy Systems project has as its overall objective the exploration of a broad spectrum of issues relating to the possible implementation of energy systems relying on renewable resources and energy conservation. This objective encompasses research that will shed light on the five major themes of the project:

1. Technical and economic aspects of the renewable energy supply systems and of the renewable energy resource base of the state.
2. Technical and economic aspects of energy use systems (current and future systems).
3. Public policy issues affecting the possible implementation of energy conservation measures and the use of renewable energy resources; assessment of costs, benefits, and distribution of costs and benefits of:
 - measures to increase the symmetry between decisions to expand supply and to reduce demand
 - measures to encourage the use of renewable energy resources.
4. Issues affecting the likelihood and impacts (favorable and unfavorable) of a transition to an energy conserving/renewable energy system in California, including:
 - energy decision making at all relevant levels of society (consumer, energy industry, state and local government, other important sectors that influence energy decisions)
 - changes in the economic, institutional, social and/or political environment of California that are consistent with (or occasioned by) increased use of renewable energy resources and energy conservation.
5. The implications to the United States energy system and policies of the assessment of these California issues.

BRIEF HISTORY OF THE PROJECT

The Distributed Energy Systems study was initiated in August, 1977. The first phase of the work led to the release of a preliminary report, "Distributed Energy Systems in California's Future," in April 1978. The main focus of

Volume 1 of the preliminary report was the exploration of outcomes for the year 2025 based on centralized and distributed energy systems, primarily in terms of technical feasibility. A draft summary description of the results of the second phase of the DES project will be available in early January, 1979. The second volume of the preliminary report consisted of a series of issue papers examining particular aspects of distributed energy systems outcomes and certain aspects of the initiation of pathways to such outcomes. The results of these issue papers were summarized in Chapter 7 of Volume 1; no attempt was made at this time to integrate the results of the separate issue papers into the assessment of the 2025 outcome of the first volume.

Some of the major observations in the first interim report about the renewable energy supply/demand balance in 2025 are:

- By paying close attention to conservation, it appears technically feasible to provide almost all of the energy needs of California from indigenous renewable energy resources in 2025, while supporting an increasing affluent population.
- Liquid fuels are a major energy supply problem from any outcome that relies primarily on renewable fuels (or does not have access to conventional sources of oil) and uses liquid fuels in the transportation sector.
- Energy supply from renewable sources to meet industrial and urban needs may pose difficult land use issues.

Several observations regarding the comparison of renewable and conventional energy supply/demand balances in the long term in California were also made in the first interim report:

- The environmental impacts of the energy systems of the 2025 renewable energy "outcome" are expected to be markedly smaller than the impacts of virtually all of the conventional energy systems. This does not mean, however, that the impacts of the renewable systems will not cause some significant problems, particularly regarding aesthetic and land use issues.
- The transition process of any energy scenario in California--be it renewable or conventional--is likely to be fraught with a high degree of organizational and institutional problems and conflicts. However, the different pathways imply

different types and kinds of stresses on institutions.

- Issues of stability of energy supply and reliability of service (and at what cost) are likely to become increasingly important and problematical in any energy future. In a "renewable" future, new attitudes about reliability of energy supply may be required.
- The cultural context--beliefs, behaviors, and attitudes of people--will play a significant role in shaping development of energy systems.

Work since the initial phase (since April, 1978) has emphasized key issues raised in the preliminary report. Major effort was devoted to analyzing critical economic issues, especially those likely to be important in the near term. A computer model was developed to permit the comparison of investment in expanding sources of supply with investment in energy conservation measures. An extensive data base relating to the costs of demand reduction and alternative supply options was assembled. An integrating summary of the research findings of the second phase of the project is nearing completion. The summary indicates ways in which a renewable energy "outcome" in 2025 can be made more plausible by introducing larger quantities of fossil fuels, particularly to meet long term demands for liquid fuels. It also provides an analysis of the economics of energy conservation and renewable energy sources in California. The summary notes that in the near and intermediate term dramatic increases in energy conservation can be accomplished at no increase in net cost to the energy consumer, and assesses the uncertainties in the long term economic potential of renewable energy systems. The summary also addresses several important institutional and political issues related to the transition to a renewable energy future in California. The importance of consumer decision making in effecting energy conservation in the near term is stressed, as is the key factor of investment decision making in the California energy industry. Selected policies for future analysis in these two areas are identified.

In addition to this integrating summary, the project is preparing for release to DOE in January, 1979, technical reports on the following subjects:

- reliability of wind power from dispersed sites
- reliability planning in distributed electric energy systems
- the potential of the California biomass resource base as an energy source
- the economics of scale of biomass energy conservation

- a comparative analysis of the energy efficiency of California and other U. S. industry
- decision making in the California energy industry
- analysis of energy planning at the substate level: Davis, California case study
- environmental assessment of renewable and conventional energy systems
- evaluation of the physical constraints on residential solar energy use
- optimal investment strategies for energy conservation
- economic tradeoffs among conventional space heating systems, active solar systems, and energy conservation in California
- economic implications of alternative energy futures for California

PLANNED ACTIVITIES FOR 1979

As currently planned, the distributed energy systems study will continue its dual emphasis on selected key technical issues related to a transition to a renewable energy future in California, and on an integrated analysis of the results of the technical analyses. The proposed technical analyses for 1979 and 1980 include:

- assessment of passive solar opportunities in California
- quantitative analyses of consumer decision-making as regards energy conserving and energy consuming products
- assessment of the determinants of peak electricity demand
- commercialization studies for industrial solar process heat and biomass collection and conversion systems
- issues of integrating wind and hydroelectric energy systems
- scale economies of photovoltaic systems
- continued analysis of economic and employment impacts of alternative energy futures
- continued analysis of energy industry decision making
- continued analysis of substate energy planning

The project also plans to engage its research staff in several conferences that will permit public review of the work effort in progress.

The integration tasks will focus on near and mid-term policy and institutional issues in a transition to energy conservation and renewable energy sources in California. Increasing atten-

tion will be devoted to national energy policy implications of the analysis of California energy futures.

Consumer Decision Making on Energy Consuming and Energy Conserving Products

J. Corfee and M. D. Levine

INTRODUCTION

Analysis to date has underscored the critical role of the consumer decision making process in achieving significant increases in energy conservation in the United States. An example of the importance of consumer decision making is provided in Fig. 1, which shows two sets of energy demand forecasts for residential refrigeration. The top projection (solid line) is based on the assumption of no change in consumer decision making in their purchases of refrigerators in California. The bottom set of projections is based on the assumption that life cycle costing is used. Under this assumption increased initial costs of more energy efficient refrigerators are balanced against the increased energy use of less efficient refrigerators. The dotted line assumes no increase in the real cost of electricity while the dashed line assumes a 2.8 percent annual increase in electricity cost. The difference between the upper projection (decision making as usual) and the bottom set of projections (life cycle costing decision making) represents a dramatic saving in energy demand, and is equivalent to reducing the need for three one thousand megawatt power plants in California over the time frame of the projections.

Large savings in energy use can be shown for many other energy consuming activities if life cycle costing were the major decision criteria of the consumer. For example, space heating demand would decline over time throughout the nation for several decades if the full range of cost effective energy conservation measures were implemented in houses (both new and retrofit).

The dramatic energy savings that are possible at no net increase in cost to the consumer raise important issues about how government policy might be used to encourage the use of life cycle costing. The long term objective of this project is to analyze these policy issues. For the next year, the project will emphasize the first step in analyzing these policy issues: understanding and quantitatively characterizing the factors that have in the past most significantly influenced consumer decision making in purchase of energy consuming and energy conserving products.

Fig. 1. Projected electricity consumption by refrigerators in California. Two different decision making algorithms. (XBL 792-333)

Perfect information, rational consumers, profit maximizing producers, and perfectly competitive product markets do not exist. In the case of energy related products, information about energy efficiency is not always available or understandable to consumers, nor have producers marketed products that are optimized for energy performance. Although the concept of life cycle costing provides a basis for consumers to make energy and cost efficient choices in the market place, available data suggest that few consumers either use or understand how to use life cycle costing criteria. There is legislation at both the federal and state levels requiring energy labeling of many appliances, but the degree to which this will be

effective in inducing consumers to purchase more energy efficient appliances is not yet clear. Very little analysis has yet been undertaken on such subjects as how consumers value future energy bills associated with products currently purchased, what policies will be effective in increasing the flow of information about energy efficiencies of products to consumers, and what public policies might provide suitable incentives to manufacturers to build more energy efficient products. We hope that by evaluating in a systematic way the available data relevant to the consumer decision making process, we will be able to provide some answers to these types of questions.

THE MODEL

The task of modeling consumer decisions is not an easy one as there are many intangible psychological and behavioral variables to be considered. Consumers have many different sets of criteria for market choices. Some consumers may be interested in minimizing initial cost, others may seek distinctive styles or brands, and still others may wish to obtain as cost effective and energy efficient a refrigerator as possible. Obviously, psychological/sociological factors are governing the distinctly different decisions that consumers make. In our attempt to model consumer decisions, we must first locate tangible, quantifiable variables that will act as indicators of these different types of consumer behavioral patterns.

The first step is to consider a variety of casual (or indicator) factors that describe the consumer decision making process. For example, we wish to know how the likelihood of making energy efficient decisions changes with income level, or with the socio-economic status of the decision maker. We also wish to know if there is a level of fuel costs at which certain classes of consumers begin to take notice of the energy costs of appliance, space heating systems for houses, and other consumer durables. We wish to know how responsive consumers are to manufacturers advertising, and the degree to which their decisions depend on the state of the economy. These questions deal with a few of the many possible factors that have a major influence on energy decisions.

We have chosen to perform an econometric study of energy consuming product market shares and energy conservation behavior of consumers. By using econometrics as the methodology, it will be possible to determine the statistical relationships of the hypothesized behavioral indicators of actual energy decisions. Initially, econometric analysis will be performed using times series data with product market shares represented as a function of product first cost, product energy intensiveness, fuel costs and cost escalation, consumer discount rates, manufacturing marketing effort, specific product attributes (color, size, etc.), and average disposable income. The specific brand/model market share then will be cast as the dependent variable with the detailed brand/model characteristics of the product used as the independent

variables. Thus, we have $MS_i = f(LCC_i, ME_i, \vec{X}_i, Y_i)$ where

MS_i = market share of i product type/model

LCC_i = the life cycle cost of i product type/model*

ME_i = marketing effort of the manufacturer for product i

$\vec{X}_i$ = a vector of product attributes

Y_i = the average disposable income

In addition to the standard econometric analysis, we are conducting qualitative analyses of the data. Included in this part of the study is a consideration of factors that can not easily be quantified, or for which we lack data, but which may significantly influence energy decisions. An example of this type of relationship is the rapid rise in American mobility and the resulting shorter payback periods for energy conservation investments. This qualitative analysis will prove to be particularly useful in the study of energy conservation behavior of consumers.

DATA NEEDS

Many of the past consumer models have lacked consistent data. In the last three or four years, California utilities have performed saturation surveys and recently have begun to monitor conservation behavior in their districts. We have obtained the data from these surveys. In addition, industry and trade association statistics will be used extensively, providing the most consistent time series data set available at this time. In addition, the Department of Energy is sponsoring a nationwide survey of households designed to monitor energy related product purchases and conservation behavior in the residential sector. The survey was sent into the field October 30, 1978 and resulting data should be made available late in the summer of 1979. Checking the survey results with utility billing and weather data should increase the accuracy of the resulting data.

DOE has also conducted special tabulations of conservation behavior in the residential sector. These data have special significance as a measure of consumer's responses to the unprecedented rise in fuel costs. The 1975 Washington Center for Metropolitan Studies study of the American energy consumer for the Ford Foundation Energy Policy Project gathered survey data which provided quantitative information about the relation between levels of energy usage and socio-economic characteristics

*Note that implicit in LCC are fuel cost and consumer discount rate assumptions. The former will be an averaged annual rate varied by region. Consumer discount rates are estimated by using regressions to determine the tradeoff between first cost and operating costs of each product.

of individual households. Many of these data sources will be directly useful to our proposed modeling effort.

USES AND LIMITATIONS OF THE APPROACH

Perhaps the most valuable output from the consumer decision making model will be an improved market penetration algorithm for new products. It is common knowledge that energy efficient products are now offered in the market place, but the rate at which they are purchased and utilized remains an unknown. The availability of new data sources on market/consumer activity is the key to sophisticated development of the algorithm. Once the data have been obtained

and analyzed, we intend to use the information as input to one or more energy demand projection models.

We expect to encounter problems in obtaining a consistent set of data for the analysis. Fortunately, past studies have delineated specific data problems from which we can learn.

Econometric methods present additional limitations when analyzing a subject matter that includes qualitative or intangible relationships. As mentioned previously, we intend to supplement the econometric analysis by performing a qualitative review of factors that might be expected to influence consumer decision making.

Energy Conservation: Policy Issues and End-Use Scenarios of Savings Potential*

Project Overview

*P. Benenson, R. Codina, B. Cornwall, D. Dornfeld, B. Greene,
J. Elliott, W. Kempton, C. Langlois, H. Nelson, J. Nides,
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The focus of this work¹ was determined in consultation with the Director and staff of the Conservation and Advanced Energy Systems Policy Office, Department of Energy, following their review of our interim report. At that point we agreed on several guidelines for our subsequent work:

1. Take a holistic view of energy conservation policies by describing the overall system in which they are implemented;
2. Provide analytical tools and sufficiently disaggregated data bases that can be adapted to answer a variety of questions by the users;
3. Identify and discuss some of the important issues behind successful energy conservation policy;
4. Develop an energy conservation policy in depth.

In addition to these guidelines, we selected five specific subjects to investigate:

1. Residential and Commercial Buildings: an examination of court cases against new energy efficient building codes and suggestions for avoiding future litigation.

2. Recreational Travel: information strategies to effect a modal shift to public transit for the recreational trip.
3. Industrial Decision Making: a methodology to identify potential barriers to energy conservation by analyzing how a conservation measure's attributes interact with the characteristics of an industrial subsector.
4. Recycling: an analysis of the energy, economic, and environmental tradeoffs between landfill and combined programs of resource recovery and energy generation from waste.
5. End Use Energy Conservation Data Base: completion of energy conservation scenarios by calculating the energy conservation potential of specific measures applicable to particular end uses.

Our current work results from the application of the overall guidelines to the above subjects. For example, we have described the system in which each policy or issue is set by the use of flowcharts and accompanying text. In some cases, the flowchart describes a physical activity (constructing buildings or recycling waste materials). In other cases, it describes a decision-making process (industrial investment or transportation modal choice). The following

five articles summarize the major findings of each of these investigations.

FOOTNOTES AND REFERENCES

*Condensed from Lawrence Berkeley Laboratory Report of the same title in six parts, LBL-7896.

1. Contained in "Construction of Energy Conservation scenarios: Interim Report of Work in Progress," LBL Report 7834, June 1978.

Energy Efficient Buildings: The Causes of Litigation Against Energy Efficient Building Codes

W. Kempton, B. Cornwall, and H. Nelson

INTRODUCTION

Unlike traditional building codes which have been imposed to regularize construction practices, some new energy efficient codes attempt to mandate change. These new codes require as much conservation as is cost effective for the home occupant. Compared with traditional codes, such new codes are usually more rigorous, increase costs, and are more disruptive to the building industry. This paper discusses three industry suits against building codes. Two suits claimed that supposedly cost-effective codes were too rigorous (the California Residential Building Code and the Farmers Home Administration standards). The third suit claimed that the code (the California nonresidential code) was overly prescriptive. The specific objections made in the litigation against these three codes are listed, and the industry conditions and beliefs behind the objections stated in court are discussed. Other cases attempting to strengthen building codes, such as Polrized Corporation's current suit against ASHRAE 90-75, are not examined in this paper.

FINDINGS

Three objections against rigorous codes are based on anticipated higher costs of building under the new codes: (1) appraisals would not be raised enough to compensate for higher construction costs, especially in the FmHA program; (2) low-income buyers would be priced out of the market, and (3) capital shortages in the loan market and higher costs would reduce availability of loans. Builders also claimed that the computed payback periods were too long. They felt that the additional costs of conservation measures should pay back to the first buyer, rather than paying back over the life of the building. They also argued that materials, such as glass fiber insulation, are unavailable, and that industries such as electric resistance heating will collapse.

One source of difficulty in adapting to new standards is the diffuse nature of the industry. There are many small independent builders who are not in close contact with professional associations. New information may not reach them and adjustment to new requirements will be difficult. But for the same

reasons, change would be very slow without building codes. Builders will experience hardships in the transition to new mandated practices, and may be inefficient until they have rethought old practices and adjusted to the new ones. For example, the proposed California code requires two inch by six inch framing in many parts of the state to accommodate R-19 insulation. While builders could minimize cost increases by changing from two-by-four studs on 16 inch centers to two-by-six on 24 inch centers, they may instead minimize changes in layouts by installing two-by-sixes on 16 inch centers. Such failures to optimize quickly will increase costs considerably in the transition period.

Two general beliefs not stated in court are behind many of the explicit court allegations. The first unstated belief is that the market, not the government, should determine what is built. The second is that the buying public does not want more efficient buildings.

Implementors of new building codes can increase their acceptability by: (1) working with lending institutions prior to implementation, (2) making cost calculations understandable to the public, and (3) insuring that the codes are truly performance-based. Occupants of efficient buildings have lower utility bills and thus more money available for mortgage payments or rent. Also, their bills undergo smaller seasonal fluctuations. If lenders had good information about these advantages, they might permit more favorable loan terms for such buildings. Next, if the cost calculations on which the codes are based are correct and widely understood by the public, special interests would be more reluctant to impede them. Finally, codes must be based on performance, allowing alternatives to prescriptions of materials and techniques. But many local building inspection departments are unable to evaluate innovative conservation or solar techniques. Thus, to be true performance codes, code implementation must provide for staff and facilities to approve innovative plans without inordinate delay.

Two issues underlie many policy questions about energy conservation building codes. One is whether market forces will make the necessary adjustments without codes. Many factors suggest that they will not. These include: (1) market

decisions are based on currently low energy prices; (2) homebuyers are not always rational economic actors with respect to energy consumption (for example, prestige or comfort often supersede economic considerations; (3) builders overestimate the costs of change, perpetuating current practices, and (4) given current energy prices and public awareness, the seller of a higher-priced efficient home is at a competitive disadvantage. The second underlying issue is whether or not governments should use building codes to accomplish long-range planning. Building codes which maximize cost effectiveness for the occupant depart from past codes and attempt to effect a change in building practices. The failure of market forces, the longevity of housing stock and the large amount of energy involved argue for such mandated change. But if such mandated change is perceived as unfair, then many of the objections that have arisen in the past are likely to be made again. Initiators of such codes should be prepared for these objections.

A DESCRIPTION OF THE BUILDING PROCESS

In conjunction with this work, a flow chart was developed that provides an overview of the building process and that can be used to assess the impact of proposed policies. The chart is composed of two major elements: a

base chart and a transparent overlay chart. The base chart diagrammatically portrays the current building process from inception through construction, occupation and eventual demolition. Included are the links, the actors, resources, policies, decisions, information and regulations of the process with an emphasis on how information about energy efficient buildings is currently incorporated.

The base chart is divided both horizontally and vertically. The vertical divisions represent the major sequential activities in the building process: (a) programming, (b) development planning/design, (c) construction, (d) completion/delivery, (e) occupancy/maintenance, and (h) destruction and replacement. The horizontal divisions both above and below represent the inputs flowing to these stages of the building process: Policies/regulations/standards, actors and motivations lead to the provision of either the resources or the information necessary for the completion of any stage in the building process. The diagram expands only some areas, emphasizing points where a change could encourage energy conservation. Once such a point is identified, the policy designer can trace the consequences of this change back through the actors providing the information or resource, the policies and standards affected.

Energy Efficient Recreational Travel

B. Cornwall and C. Sullam

INTRODUCTION

Energy consumed for recreational travel is an important component of total transportation energy consumption. Most of this recreational travel takes place in the automobile, which not only consumes energy, but also pollutes, makes noise, and causes other environmental stress which may diminish the recreational experience for the very travelers who use it. Accordingly, how to bring about a modal shift to a more efficient means of transportation for recreational trips is an appropriate policy issue. An examination of the traveler's decision-making process indicates that information is a weak link in the modal choice decision. Moreover, the information is biased toward the private auto. In this report, we focus on an information policy designed to bring about a modal shift toward public transit for the weekend recreation trip.

We begin by summarizing the policy and placing it in the context of the issues it addresses. Following that, we develop in detail an information policy to link use of national parks with transit for the weekend trip. This policy derives from an examination of the importance of the recreational and weekend trips in terms of trip numbers, purposes, modes, and energy

consumption. We then describe verbally and graphically the traveler's decision-making process. Several potential problems and policy targets are revealed, of which the information link is one. Finally, we present a broad spectrum of information policy suggestions that would strengthen this link.

FINDINGS

The information policy we developed emphasizes the joint roles of the National Park Service (NPS) and the Department of Energy (DOE). Although the policy could be implemented by various agencies including DOE, the policy is couched primarily in terms of NPS's role because of recent legislation, described below, that authorizes them to address transportation and energy conservation issues. DOE's potential role is discussed after the structure of the policy is described.

In the past, the purpose of the NPS was to preserve natural resources rather than to bring people into park areas. The agency had neither the authority nor the funding to address problems of access to the parks. Very recently, however, Congress passed legislation (P.L. 95-344) authorizing the NPS to formulate transportation plans and implement transportation programs.

The purpose of the act is to support modes other than the automobile for access to and within national parks and thus preserve the parks and conserve energy. Included in the legislation's mandate is the need to establish information programs to notify the public of alternative travel modes.

In the spirit of the recent legislation, we suggest three components for the NPS to develop in its initial information dissemination program.

1. An inquiry and response system to centralize the multiple sources of recreational and transit information. This system could include the following features:
 - a mail service, consisting of a pre-printed card with blanks for name, address, recreation area, travel constraints and requirements and special information.
 - a telephone service, consisting of a toll-free telephone number, preferably an acronym such as FUNTRIP.
 - a walk-in service at each park (e.g., a visitors' center), which emphasizes transit for on-site travel.
2. Brochures and pamphlets to convey information in an effective manner which should include:
 - clear, specific and up-to-date transit facts, such as routes and schedules.
 - detailed information about the site so recreationists do not feel compelled to maximize their flexibility by travelling in an auto.
3. Media campaigns to tap into the many and varied information conduits that exist today. Strategies should include:
 - a speakers bureau to orient specific market segments to recreational transit.
 - maps and displays in the telephone book, an information source widely used for trip planning.
 - site condition reports, such as ski or surf bulletins, which mention transit opportunities.

DOE could strengthen this program in several ways. First, it could supplement NPS funding and analysis of park transportation. Data on energy consumption and energy conservation potential could be gathered and analyzed. Second, it could coordinate the information system; operation of the toll-free telephone number could build upon the experience of DOE's

Solar Division with a toll-free public information number for solar energy. Third, it could develop public relations material on recreational travel. Fourth, it could initiate a demonstration project for recreational transit to determine energy savings. And finally, it could support research and development on energy-efficient public transportation systems.

DECISION MAKING FOR THE RECREATIONAL EXPERIENCE

The design of the policy described above is based in part upon an analysis of decision-making for a recreation trip. We developed a flow chart to describe this experience, which is represented as a system--a set of components and their interrelationships. Decision makers can use the flow chart to aid in determining which components of the system could be altered to achieve a greater balance between the automobile and other modes for recreational travel.

The system depicted in the flowchart divides the recreational experience into five phases. During the PLANNING phase, the recreationist makes most of the major decisions of the trip: where and when to go, what mode to use, who will go, what to do, etc. During the TRAVEL TO phase, travel time is often an important variable in the selection of mode and route. However, travel time can become a less critical variable if the trip itself is enjoyable. ON SITE experiences are the portion of the trip most often associated with "recreation." TRAVEL FROM, the fourth major phase, resembles the "travel to" phase in terms of origin and destination; however, the route and time spent in transit may vary considerably. RECOLLECTION, the final phase, generally forms the basis for planning and making decisions for the next recreational experience.

We use the flowchart to identify which aspects of the recreational system need to be addressed to alter the modal distribution, increase the use of public conveyances, and conserve energy in recreational travel. Our analysis reveals that the modal decision occurs after two other decisions, "Where to Go" and "When to Go." These first two decisions may determine the modal choice for the recreational trip and possibly eliminate transit as an option.

As a result of this analysis, we suggest the following objectives and strategies for public policy on recreational travel:

1. Create and/or strengthen the links between transit information and that of other recreational sources.
2. Design a centralized system of recreation/transit information, and
3. Stress the recreational potential of transit trips when developing information systems.

Policy Barriers and Investment Decisions in Industry

J. Nides, R. Barnes, D. Dornfeld, P. Benenson, and J. Elliott

INTRODUCTION

The industrial sector provides policy-makers with substantial opportunity for effecting energy conservation. Each year decisions are made regarding investments in conservation measures that could substantially reduce energy consumption. Many of these decision outcomes could be influenced by applying the appropriate government action (e.g., financial incentives, regulatory restrictions, or information provision). Government intervention should be confined, however, to situations where it is both necessary and likely to be effective. To this end we have developed a methodology to aid policy-makers in the recognition of such situations and facilitate understanding of the barriers that block conservation efforts.

The methodology employs two flow charts and a matrix. The flow-charts detail the principal participants, information flows, and criteria and constraints which underlie the investment decision-making process. The matrix expands upon the set of criteria and constraints given in the flowcharts and analyzes how characteristics of the particular sector and attributes of the measure in question interact to form barriers to conservation efforts.

FINDINGS

Industrial decision-makers consider a number of factors before deciding whether or not to invest in a conservation measure. Each factor or attribute can increase the likelihood of a measure's adoption or pose a barrier to it. We have identified seven primary attributes:

Attributes

- cost effectiveness,
- relative cost,
- unreliability (expected unscheduled downtime),
- disruption to install,
- technical sophistication needed to install the measure,
- environmental impact,
- change in dependency of the firm on outside fuel supplies.

During a preliminary examination, it may appear that a particular attribute increases the desirability of a given conservation measure. For a particular industrial subsector, there may exist, however, other factors (economic, regulatory, or technical) which can alter the attribute's impact on the investment decision. We refer to these other factors as subsector characteristics and have identified nine:

Characteristics

- market growth,
- capital intensity,
- energy intensity,
- access to credit,
- rate of return on investment,
- regulatory restrictions,
- age of plant,
- availability of fuels, and
- technical complexity.

We have, therefore, broken down the investment decision into a three stage analysis to include considerations of the effects and interactions of attributes and characteristics. First, decision-makers consider the influences of the conservation measure attributes on the desirability of implementing the measure. Second, they estimate the impacts of the industrial subsector characteristics on each attribute. Finally, they re-evaluate the influences of attributes in light of the impact of characteristics.

To incorporate this three stage analysis into our methodology, we developed a matrix which arrays columns of attributes against rows of characteristics for the selected conservation measure. First, each attribute is qualitatively rated. Second, the effects of each characteristic on the evaluation of each attribute are determined and are entered in every cell of the matrix (i.e., the interface of an attribute and a characteristic). Finally, attribute columns can be examined for ratings which might alter the favorable impact of an attribute on the investment decision. By inspecting the matrix, one can determine:

1. Which conservation measures have no apparent barriers in a given subsector and therefore require no government action.
2. Which conservation measures have so many apparent barriers in a given subsector that only massive government intervention appears as a solution for achieving implementation.
3. Which conservation measures are reasonable targets for government policy after further investigation of the barriers revealed by the methodology.

Policy-makers may then refer to the flow charts to ascertain which participants in the decision-making process are most likely to be concerned with the particular barriers which have been identified. By knowing the nature

of barriers and the identity of participants concerned with them, policy-makers can more easily select the most effective policy to influence the outcome of the investment decision. The final choice of an effective policy is not uniquely determined by this analysis; rather, the set of choices is substantially reduced.

To test the methodology, we selected four conservation measures--Improved Housekeeping, New Plant Construction, Waste Heat Recovery, and Process Change/Major Renovation--and three industrial subsectors in California--steel, chemicals, and petroleum. The conservation measure attributes describing Improved Housekeeping and New Plant Construction were arrayed against subsector characteristics for the steel and chemical subsectors; attributes associated with Waste Heat Recovery and Process Change were arrayed against the chemical sector characteristics.

We found none of the conservation measures to be completely free of potential barriers requiring government action. Nor did we find measures that had so many barriers that only massive government intervention could achieve implementation. They were all likely targets. Potential barriers indicating the need for more quantitative work to decide if governmental action should be taken were identified in individual matrix cells (i.e., in the attribute/characteristic interfaces).

Our report traces, with the aid of flow charts, the process of investment decisions. The flow charts and text portray large corporations as the model for industrial organization because such firms account for the bulk of industrial energy use. An abbreviated discussion is provided for small firms. The decision areas important for the installation of conservation measures differ if the equipment is to be retrofitted or included in the design of new facilities; consequently, two flow charts were formulated.

Categories of major factors in the decision process are listed on each chart: information, actors, criteria and constraints, and motivations. The horizontal headings of each chart (Concept Introduction or Conceptualization and Design), Analysis and Decision, and Implementation) represent the three broad stages of the decision process. The specific factors which are important at each stage (who the actors are, which particular criteria and constraints they apply, what their motivations are, and what kind of information they receive) change as the decision process advances. The pertinent factors can be located by examining the interfaces of factor categories and decision stages. In addition, the charts reveal the points in the decision-making process at which policies can be applied; given a particular obstacle to conservation, the charts suggest the most likely points and the general types of policy to achieve successful implementation.

Tradeoffs of Municipal Solid Waste Processing Alternatives

R. Codina and C. Langlois

INTRODUCTION

Solid waste generation in the United States is expected to increase from the 1975 level of 3.4 pounds per person per day to five pounds per person per day in 1990. Many strategies have been proposed to cope with the anticipated increase. The objectives of this report are to assess the performance and advantages of several processing and disposal techniques, and to examine the issue of large scale recycling of waste material.

Five general methods of solid waste disposal and processing are discussed: close-in landfill, remote landfill, refuse derived solid fuel (RDSF), pyrolysis and incineration. Landfilling is the most prevalent disposal technique in use. The method is inexpensive, requires small capital outlays, and is relatively energy efficient. But close-in landfill sites are nearing capacity and additional close-in sites are either unavailable or extremely expensive.

Landfills can also be an environmental hazard through water contamination, odor, occupation of land, and production of explosive methane

gas. Moreover, landfilling represents the disposal of energy-rich materials and recyclable resources. Remote landfill is costly since operating costs for landfill increase dramatically with distance from the area served. Increasing attention has therefore been given to the possibilities offered by the recycling of source-separated materials.

The importance of such issues is exemplified by the number of states implementing waste disposal policies. For example, California has implemented over 130 recycling programs in different communities, while six major cities which cumulatively comprise the bulk of the state's population are considering the creation of large-scale resource recovery facilities.

The major issue at this time concerning municipal solid waste disposal is whether to continue landfill operations as the primary method, or to use some combination of source separation, resource recovery and energy generation with landfill. The constraints surrounding this issue are capital and labor costs, technical feasibility, environmental impacts (especially air pollution), marketability of the derived

energy and recycled resources, and public cooperation.

DESCRIPTION OF THE RESOURCE RECOVERY PROCESS

The recovery of energy from municipal solid waste (MSW) through source separation programs and resource recovery facilities occurs at the back end of a long process. Virgin materials are transformed into consumable products, distributed, used, and ultimately disposed of as solid waste. The large diagram which accompanies our main report presents an overview of this process and emphasizes other points in the resource stream where energy recovery from materials reclamation can occur.

Structurally, the diagrams consist of the following components: (1) the main activities and associated actors and resources; (2) existing government policies related to these activities; and (3) the motivational concerns of the main actors.

The main activities, resources, and actors comprise the underlying skeleton of the whole schematic. The six main activities are: mining and harvesting, manufacturing, converting, distributing, consuming and disposing. Resources are processed at each of these six stages and their identities change as a result. From different points along these resource paths, scrap materials can be removed and recycled into the main resource flow.

FINDINGS

It is not possible to determine on a generic level which of the three techniques--RDSF, pyrolysis and incineration--is more economically advantageous. Only site specific analysis can determine the best choice of techniques. Three variables (design options, financing arrangements and marketing arrangements) differ too greatly from site to site to allow generalization of their effects on the choice of process.

Recycling of glass, aluminum and ferrous metals is compatible with energy generation

whether done mechanically at the recovery plant or by the public prior to MSW collection. This holds because these materials must be removed prior to energy production. Of these recyclables, ferrous metals are most efficiently recovered through mechanical means. At present, glass and aluminum appear to be best recovered through public recycling and source separation programs, although this situation is subject to state-of-the-art developments, in recovery equipment, local market conditions and the costs of local collection. Newsprint can be either recycled or converted to energy, but the former appears more energy efficient.

An effective source separation program, in a high participation scenario, can reduce the MSW by 15%. It is important to consider this potential in planning resource recovery options since any reduction in the MSW stream will have a bearing on the size of the facility that will be necessary. The location of waste processing facilities is the most important factor in assessing the pros and cons of any particular process. MSW processing plants are of obvious interest in densely populated areas where pollution problems (in particular air pollution) are most severe. Preference for one process rather than another does not necessarily reflect data derived from market forces alone. California, for example, has imposed stringent regulations on air pollution--hence preference in this state is given to pyrolysis despite economic disadvantages (both capital and operating costs), since air pollution from this system is negligible. Also under consideration in California are low-cost package incinerators but use of these is contingent upon federal and state evaluation of their air quality impact.

The separate collection of recyclable materials is generally compatible with garbage reprocessing centers. The degree of compatibility, however, is dependent on several factors, including the types of materials collected by each system, the market value of the recycled products, the cost of collection and the efficiency of the mechanical recovery equipment.

End Use Energy Conservation Data Base and Scenarios

D. Dornfeld, B. Greene, P. Benenson, and R. Barnes

INTRODUCTION

The end use energy conservation scenarios discussed below show the combined effect on energy consumption of implementing a number of conservation measures. The scenarios serve two overall purposes. First, they contrast nonconservation cases based on assumptions of growth rate and appliance saturation with conservation cases based on similar assumptions. Second, they provide detailed data and

documentation for the savings potential of each conservation measure, the stock affected, and the calculation of total energy savings. Included are conservation measures of both a behavioral nature (e.g., night thermostat setback) and a technological nature (e.g., better hot water heater insulation). Several water conservation measures and the associated energy savings were also incorporated to demonstrate how water conservation could be factored into a comprehensive energy conservation program.

The scenarios include assumptions about economic, demographic, behavioral and technological variables, such as population, growth and decay of energy using stocks, appliance saturation, and conservation implementation levels. Some assumptions are imbedded in projections used as input to the scenarios. These assumptions cannot be changed directly and are so noted in the main report. Other assumptions form the basis of calculations made and can be changed to construct alternative scenarios. These also are indicated.

Assumptions can be changed to reflect different conditions, such as attitudes regarding family size, durability estimates of energy using stocks, or lifestyle changes that affect the purchase or use of a given appliance or transportation mode. The implementation level of a conservation measure also can be changed to reflect a variety of responses to a given policy. In addition, conservation measures can be combined and new ones added. Quantitative estimates of energy consumption and conservation potential in the major residential and commercial end-uses, transportation modes, and industrial subsectors have been made.

SCENARIO FINDINGS

Computer software was developed to construct scenarios that calculate the cumulative effect of various conservation measures. The basic approach for the conservation scenario construction is to quantify base year unit energy consumption by end use, travel mode or industrial subsector; reduce unit consumption by the estimated conservation potential in the appropriate year; adjust for saturation; and extrapolate to account for growth and decay of the appropriate energy using stock. The projections were made for 1980, 1985, 1990, 1995, 2000 and 2020.

The behavioral and technological measures that are incorporated in the scenarios were selected on the basis of their potential for effecting large energy savings in the major end uses within each sector. The measures included in the scenario are as follows:

1. Industrial Sector--housekeeping (leak-plugging, equipment maintenance, insulation); process improvements; waste heat recovery; new, more efficient facilities; in-plant recycling.
2. Commercial Sector--building and appliance efficiency standards for water heaters, spaceheaters, and air conditioners in new and old buildings; low-flow devices to reduce water consumption, and solar water heaters with efficient backups; and reduced task lighting in new buildings and delamping in old buildings.
3. Residential Sector--solar water heating systems with efficient electrical backup heaters designed for loads reduced by water conservation; building and appliance

efficiency standards for space heating and air conditioning; and replacement of frost-free refrigerators and freezers by non-frost-free units.

4. Transportation Sector--reduced travel speed; smaller and lighter weight automobiles with improved engines; continuously variable transmissions and streamlining of trucks with emphasis on diesel engines; airplanes with high by-pass engines on narrow bodies and improved passenger load factors; and streamlined, lighter passenger and freight trains with improved passenger load factors and reduced empty freight car back hauling.

The scenario results show a more gradual growth of energy consumption in the conservation case compared to the base case, with a widening gap between the two cases over time in the total amount of energy consumed. By extrapolating the growth variables, a gap results between the two cases by the year 2020 of approximately 6.3 quads, which is 115% of 1975 energy consumption. Total energy consumption increases from 5.5 quads in 1975 to a 2020 estimate of 13.2 quads with conservation and 19.5 quads without conservation. The largest savings occur in the industrial and transportation sectors (2.7 and 2.4 quads respectively) and the smallest savings in the commercial sector (0.6 quads) and the residential sector (0.7 quads). The sectors with the largest savings are the ones with largest consumption.

No analysis of the growth rates of the variables that partially determine the magnitude of energy consumption in each sector (e.g., per capita value of industrial shipments, travel demand, rate of increase in commercial floor space or number of residential housing units) has been made to determine the most likely rates. Varying the growth rate for one such variable will change the amount of energy consumption and energy savings. A change in the rate of growth could be attributable, for example, to a change in population, fuel availability, attitudes or values. These in turn may result in changing preferences for the type or density of housing, demand for goods and services, and derived demand for intermediate and primary industrial production.

The data upon which the results are based are presented in tabular form in the main report and its appendices. For each sector the tables for a base and conservation scenario are included. The resulting scenarios indicate the energy consumption by end use, fuel type, transportation mode, industrial subsector and utility service areas that can be aggregated into two climate zones (northern and southern California) permitting application to many other areas of the United States. The scenarios are not intended to provide point estimates of energy consumption in a particular year, but rather to contrast two conditional consumption scenarios and evaluate the potential savings due to energy conservation.

Inventory of Energy Conservation Potential in California*

C. Blumstein, K. Hudson, P. Kuhn, and C. York

INTRODUCTION

The purpose of this project is to assist the California Energy Commission (CEC) in establishing a system for organizing and analyzing information on energy conservation opportunities. This information is needed by the CEC to plan its conservation programs efficiently and to forecast the effect of all conservation activities, including CEC programs, on future energy requirements. To demonstrate the inventory system, we are preparing inventories of energy conservation potential in selected portions of the manufacturing sector of the California economy. Drawing on existing literature as well as primary data collection, these inventories will provide estimates of energy conservation potential as well as information on the technical aspects, economic costs, and environmental considerations of individual energy conservation measures. While a complete inventory covering the manufacturing sector, let alone the entire state's economy, is beyond the resources of this project, the limited inventories will be useful in a) providing a model for the inventory system and b) increasing the scope and coherence of the CEC's information on energy conservation potential.

The approach we are using to estimate energy conservation potential in California's manufacturing sector emphasizes the detailed technical and economic aspects of energy conservation measures and the equipment or processes to which they might be applied. Our primary objective is to provide as realistic and accurate a picture as is possible of the technical and economic feasibility of conservation measures and the savings they might provide. The results of our project should prove useful in econometric studies of conservation potential or in modelling future energy use, but such analysis lies outside the present scope of our project.

ACCOMPLISHMENTS DURING 1978

To date we have developed a plan for an inventory system and demonstrated it by compiling inventories of energy conservation potential for boilers and steam supply equipment in manufacturing plants and for the cement industry.^{1,2}

The plan for the inventory system includes topics for the initial work, to be done at LBL, and a format for presenting the information, both of which have been selected in close cooperation with the CEC to maximize the usefulness of the project's output. The topics chosen for inventories to be done at LBL are 1) boilers and steam supply equipment in manufacturing plants, 2) cement plants, 3) pulp and paper mills, 4) fruit and vegetable canneries, 5) sugar refineries, and 6) glass factories. The inventory system has a three-part structure with increasing levels of detail provided in each part. The format begins with a summary report, followed by more in-depth reports on individual conservation

measures, and ends with an indexed collection of references. This structure allows individual parts of the system to be easily updated to reflect new information. Within each of the reports, the format allows quick access to the various kinds of information the user might require, including the conclusions and estimates of conservation potential, background information on the energy-using equipment or system that is the topic of the report, explanations of the technical aspects and costs of the conservation measures, environmental considerations, and calculations.

The two inventories that have been completed demonstrate two approaches for analyzing energy conservation potential. The first considers a class of equipment e.g., boilers and steam supply equipment to which the same group of energy conservation measures could be applied. This approach discounts the fact that the equipment is employed in "systems" for the production of quite different goods and services. A boiler, for example, can be tuned to save fuel regardless of whether it provides steam to melt tallow or to make tomato paste. The second approach considers a system for the production of a homogeneous good, e.g., the cement industry, that incorporates many types of equipment. A set of energy conservation measures for the associated equipment may then be evaluated in the context of their interaction within the system.

The two approaches are necessary to achieve the project's goal of providing information on the full range of energy conservation potentials in California. The equipment-oriented approach yields the most detailed information on possible increases in the efficiency of specific energy-using devices, the costs of the improvements, and other pertinent considerations. The system-oriented approach, on the other hand, can consider the effects of substitutions among devices, choice of feedstocks, cogeneration, and other measures that cannot be covered by the equipment-oriented approach.

In a more practical sense, the two approaches are made necessary by the limitations of available information. Information on the energy-using characteristics of some industries is too sketchy to permit proper treatment of the industry with the system-oriented approach; for these industries conservation potential for part of their energy use can be analyzed by the equipment-oriented approach. The opposite case is even more prevalent. Data on stocks of many types of equipment in California, including electric motors and pumps, is presently so inadequate that no estimate of energy conservation potential can be produced by the equipment-oriented approach. By considering the equipment as part of systems, however, conservation measures for the equipment can be evaluated in the context of the applications of that equipment in a

particular system. A part of the conservation potential in electric motors, for example, would be captured in a study of the chemical industry, a major user of electric motors for pumps and fan drives.

The following summaries of the case studies will highlight only the estimates of energy conservation potential and other important conclusions. More complete information can be found in Refs. 1 and 2.

Boilers and Steam Supply Systems

This equipment is used to convert fuel energy into the thermal and mechanical energy content of steam and to distribute steam to a variety of equipment for end use. About 40% of the fuel purchased by the manufacturing sector for heat and power (i.e., excluding 'waste' fuels and feedstocks) is consumed in this equipment. In 1976 most of this fuel was natural gas. We have estimated that between five and ten percent of this fuel could be saved by more efficient tuning of burner controls and by recovering heat from stack gas and from the blowdown water expelled from boilers to prevent build-up of impurities in the water used to generate steam. At 1976 rates of consumption, these savings would amount to between 8 and 16 billion cubic feet of natural gas and 180 to 360 thousand barrels of oil per year. Additional savings could be achieved by measures including insulation of steam lines, maintenance of steam traps, and returning more condensate to the boilers to recover heat. However, available data do not permit an estimate of these savings.

Cement Plants

This industry is one of the largest in state industrial energy consumers. In 1976 the twelve cement plants in the state accounted for nearly 9% (44 trillion BTU) of the fuel and 3% (1 billion

kWh) of the electricity purchased by all manufacturers. Energy costs now account for up to half the total costs of production in the plants. This situation, coupled with the current storage of production capacity, has induced a number of the companies to plan replacements or expansions of their plants with more efficient equipment. If the installations occur as scheduled, we estimate that the industry's average fuel consumption rate per ton of cement will decline to 4.4 million BTU/ton in 1982. In 1976 it was 5.3 million BTU/ton. Although the new equipment will have slightly higher electricity requirements, installations of cogeneration equipment that are being considered could effect a modest overall reduction in the industry's average electricity consumption rate from 124 kWh/ton of cement in 1976 to 115 kWh/ton in 1982.

PLANNED ACTIVITIES FOR 1979

By June of 1979, we expect to complete inventories of energy conservation potential in California paper and pulp mills, fruit and vegetable canneries, sugar refineries, and glass factories. These inventories, together with the two completed in 1978, will be assembled into a final report.

FOOTNOTES AND REFERENCES

*Work supported by the California Energy Commission Contract No. 400-088(7/8) .

1. P. Kuhn, K. Hudson, C. Blumstein, C. York, "Preliminary Report on an Inventory of Energy Conservation Potential in California: The Cement Industry," in preparation.
2. P. Kuhn, K. Hudson, C. Blumstein, C. York, "Preliminary Report on an Industry of Energy Conservation Potential in California: Boilers and Steam Supply Systems," in preparation.

Solar Energy

Measurement of Circumsolar Radiation*

D. Evans, D. Grether, A. Hunt, and M. Wahlig

INTRODUCTION

Circumsolar radiation refers to light that, to an observer on the ground, appears to originate from the region around the sun. Aerosol particles cause this radiation by scattering light through small angles. The aerosol particles may be composed of ice crystals or water droplets in thin clouds, dust or sea salt particles, or photochemical pollutants. The amount and character of circumsolar radiation vary widely with geographic location, climate, season, time of day, and observed wavelength.

Focusing solar energy systems, such as parabolic troughs or the Central Receiver, typically collect the direct beam solar radiation (that coming directly from the sun) plus some fraction (usually small) of the circumsolar radiation. The exact fraction collected depends upon many factors, but primarily upon the angular size (field of view) of the receiver, the surface or cavity that absorbs the sunlight. A somewhat larger receiver will collect more of the circumsolar radiation but will experience somewhat larger radiation losses. Knowledge of circumsolar radiation can be a factor in optimizing a receiver design, or in choosing between competing designs for a particular application.

The pyrheliometer, the instrument normally used to estimate the direct beam radiation, has a 5° - 6° field of view as compared to the $1/2^{\circ}$ subtended by the sun. The pyrheliometer thus measures a substantial fraction of the circumsolar radiation as well as the direct beam radiation. For most focusing systems, the pyrheliometer will overestimate the amount of radiation that will be collected. Knowledge of the circumsolar radiation at a given location can thus be used to correct the pyrheliometer measurement.

Four instrument systems have been constructed at LBL to measure the circumsolar radiation. The basic instrument is a telescope that scans through a 6° arc of the sky with the sun at the center of the arc. The output is a digitization of the brightness of the sun and circumsolar region every 1.5 minutes of arc. Additional details of the instrument are given in previous annual reports.

ACCOMPLISHMENTS DURING 1978

Operation of Telescopes

Three of the instruments continued to be operated at 1) the Solar Thermal Test Facility at Sandia Laboratories, Albuquerque, NM, 2) Barstow, California, near the future site of the 10 MWe Central-Receiver pilot plant,

and 3) Georgia Institute of Technology, the site of a 400 KW Central-Receiver test facility. The fourth telescope was located at Argonne National Laboratory until November, at which time it was returned to LBL for general maintenance and the installation of an automated sunphotometer (see below).

Routine Processing of Data

A major task of the project is to process the large quantities of data (240 data points/minute/15 hours each day/telescope) to a form suitable for analysis. This processing is done in two steps. In the first step, the information from the original magnetic tapes (one/telescope/week) is transferred to a mass storage system on the LBL computer. The second step is to reduce the data to a more compact form and to apply various correction and calibration factors. This "reduced data base" is then used in the analyses. During this year the data from June 1977 thru June 1978 was transferred to mass storage and a preliminary version of the reduced data base created. There is now a two year period of record for three of the telescopes, and about a year and one-half for the fourth.

Data Analysis

The data analysis proceeded along the lines discussed in last year's report: the analysis of instantaneous values of the circumsolar radiation, and the calculation of the average effect of circumsolar radiation on the performance of concentrating solar energy systems.

The objective of the analysis of instantaneous values is to develop correlations between circumsolar levels and other, more readily measured, solar or meteorological parameters. The circumsolar radiation could then be estimated for locations other than those covered by the limited number of telescopes. Figure 1 is presented as an example of this work. Figure 1(a) plots values of the circumsolar radiation (intensity of light from the edge of the sun out to $\sim 30^{\circ}$) versus the reading of a pyrheliometer (see above) for a month's worth of data. There are three distinct regions: 1) a dense concentration of points at high pyrheliometer and low circumsolar value corresponding to clear sky conditions in the middle portion of the day, 2) a tail of roughly constant circumsolar values but rapidly decreasing pyrheliometer values corresponding to clear sky conditions towards sunrise or sunset when atmospheric absorption dominates and 3) a "crescent" of decreasing pyrheliometer values accompanied by initially increasing and then decreasing circumsolar levels, corresponding to periods when atmospheric scattering dominates.

Fig. 1(a) Pyrliometer readings versus the corresponding radiation level for each of 1299 measurements made during November 1977 at Barstow, CA. "NI 12" refers to 159 measurements (not shown) with very low pyrliometer values. The smooth curve gives the results of a simple atmospheric scattering model.

(b) A subset of the above measurement when the effective air mass (m^*) was less than 1.2.

The rather sharp outer limit of the crescent suggests some physical constraint.

Figure 1 illustrates two approaches to placing the above observations on a more quantitative basis. The smooth curve in Fig. 1(a), which describes reasonably well the outer limit of the crescent, is from a simple atmospheric scattering model that essentially conserves energy. Progression from the upper end to the lower end of the curve corresponds to an increasing load of scattering centers (aerosols) in the atmosphere.

A second approach has been to correlate the pyrliometer and circumsolar values with the amount of atmosphere between the sun and the telescope. The usual characterization of this quantity is the "air mass" (m), defined as the amount of atmosphere relative to local vertical. We have found a seasonal dependence of the correlation between pyrliometer value, circumsolar level and air mass which is largely eliminated by using an "effective" air mass (m^*), defined as the amount of atmosphere relative to that at solar noon. Figure 1(b) is for those measurements with $m^* \leq 1.2$. This selection tends to isolate the outermost points of the crescent. For moderate pyrliometer readings (100-900 W/m^2) Fig. 1b can be used to limit possible circumsolar values to a fairly narrow range. Selection on other ranges of m^* tend to isolate other regions of Fig. 1(a), although the resulting distributions are progressively smeared out with increasing m^* .

Figure 2 is presented as an example of the average effect of the circumsolar radiation on concentrating solar energy systems. The data are for the period May 1976 thru December 1977 at Albuquerque. Assume that the maximum energy available to an arbitrary concentrating system is the direct solar radiation plus the circumsolar radiation. One may then ask how much of this maximum is "lost" (falls outside the field of view) of a system with a particular operating threshold (the solar plant is in operation whenever the solar radiation exceeds this threshold) and a particular aperture radius (half the angular field-of-view) of the receiver. Figure 2 is for a threshold of 50 watts/ m^2 . Consider a highly concentrating system with an aperture radius of $.38^\circ$. The loss would range from about 2% to 5%, depending on the particular month.

Fig. 2. The energy lost because of circumsolar radiation in a concentrating solar energy system depends on the effective aperture. The values are for a system with an operating threshold of 50 W/m^2 incident solar radiation.

This loss could, in principal, be recovered by using a larger receiver. However, this receiver would have higher reradiation losses and other disadvantages. An optimum design will include considerations of the circumsolar radiation as well as these other effects.

Other Activities

The Solar Energy Research Institute (SERI) is examining in detail the effect of circumsolar radiation on specific types of concentrating collectors. LBL has been involved in preparing the data in a form that can be readily used by SERI.

A collaborative effort with a DOE-funded engineering firm (Watt Engineering, Limited) is just underway to examine correlations of average values of circumsolar radiation with meteorological or climatological variables such as cloud cover. This work is expected to complement the correlation studies of instantaneous values discussed above.

As an ancillary use of the data, a quasi minute-by-minute pyreheliometer data base was constructed for cloud transit studies at Sandia Laboratories, Livermore. The telescopes have a ten minute cycle, each cycle consisting of a scan and pyrreheliometer measurement thru each of a clear filter, eight colored filters, and an opaque filter. To construct the data base, the colored filter values were scaled to an approximate clear value. A smoothing technique was used to reduce some artificial fluctuations; the resulting time resolution is about 2-3 minutes.

A Sunphotometer, on loan from NOAA, was modified for automatic operation on one of the telescopes. The Sunphotometer is a simple, hand-held instrument used to measure the attenuation of direct solar radiation at discrete wavelengths.

The measurement is then used to calculate the "turbidity," a quantity related to the atmospheric aerosol content. A network of these instruments has been in operation for the EPA for many years to monitor air quality. The thrust of the present effort is to make simultaneous circumsolar/turbidity measurements in order to determine the extent to which the existing turbidity data base might provide estimates of circumsolar levels. To this end, the Sunphotometer has been enclosed in a temperature controlled and environmentally sealed box, and the mechanical components placed under control of the telescope electronics. The output of the instrument will be recorded on the telescope's magnetic tape.

PLANNED ACTIVITIES FOR 1979

The measurement program will continue. Plans are to move the telescope that is currently at LBL to SERI. Longer range plans are to take measurements in as yet unsampled areas, such as the Great Plains, eastern Oregon or Washington, and Florida.

The various analyses, including the work with SERI and Watt Engineering, will continue with the overall goal of further understanding the relationship of circumsolar radiation to other solar/meteorological variables, and to the performance of solar energy systems.

FOOTNOTE

*This work has been supported by the Department of Energy through Conservation and Solar Applications (Solar Heating and Cooling - Research and Development Branch), and through Solar, Geothermal, Electric, and Storage Systems (Central Solar Technology-Solar Thermal Branch, and Distributed Solar Technology-Photovoltaics Branch).

A Small Particle Heat Exchanger*

A. J. Hunt

INTRODUCTION

The purpose of this work is to develop a new type of solar thermal receiver that is placed at the focus of a central tower or a parabolic dish concentrator system. The principle of operation differs from other advanced receiver designs under development, in that the solar to thermal conversion is accomplished by a dispersion of very small particles suspended in a gas to absorb the radiant energy from concentrated sunlight. The very large ratio of surface area to volume exhibited by small particles makes them ideally suited for this application.

An open cycle Brayton heat engine utilizing a Small Particle Heat Exchange Receiver (SPHER)

would operate by compressing ambient air and injecting a very small mass of fine particles into the gas stream. The air-particle mixture then enters a transparent heating chamber where the solar flux is concentrated. The particles absorb the radiation and, because of their very large surface area, quickly release the heat to the surrounding gas. The air-particle mixture continues to heat until the particles vaporize. The heated gas then passes through the expansion turbine to provide power for the compressor and load before going to a recuperator and being exhausted.

A dispersion of particles distributed throughout a volume of gas is a very efficient absorber of sunlight if the particle size and optical constants are chosen properly. If the characteristic

absorption length for light passing through the material comprising the particles is greater than the particle diameter, the entire volume of the particle is active as the absorber. For this and other reasons, sub-micron particles are used.

The choice of the composition of the particles is determined by the desired optical and physical properties. Various forms of graphite and carbon are ideal choices because of their optical characteristics and the fact that the method of production affects their combustion rate. They have the additional advantage that the combustion product is carbon dioxide. The amount of CO₂ generated is less than one-one hundredth of that produced by a conventional plant of the same power.

The major advantage of SPHER over conventional receiver designs such as the honeycomb heat exchanger, or a cavity lined with refractory pipes, are its simplicity, efficiency, light weight and lower chamber temperatures for the same output gas temperatures. The concept has the additional advantage that it is easy to incorporate conventional fuel injectors into the system, thus enabling the plant to operate in a hybrid mode during periods of cloudiness or in the evening.

The idea for the small particle heat exchanger receiver was originated in 1976 and some basic calculations were performed at that time. The bulk of the work reported here was undertaken in 1978 as part of a project under sponsorship of LBL to investigate the feasibility of the concept.

ACCOMPLISHMENTS DURING 1978

The basic goal of the limited effort in 1978 was to critically evaluate the major optical, physical and chemical considerations involved in designing, building and operating a solar receiver utilizing a dispersion of fine particles in a gas. To this end, a theoretical analysis of the optical characteristics of small particles was undertaken to determine optimum particle size, density and optical properties. The thermodynamic properties of the particles were investigated to determine whether the heat fluxes and equilibrium temperatures would be suitable for solar thermal applications. Particle production techniques and gas reaction processes were surveyed to ensure compatibility with design requirements. In addition, particle confinement schemes and system considerations as well as safety and environmental factors were studied. A small laboratory apparatus was constructed that successfully demonstrated the concept. The work mentioned above validated the basic concept and helped to identify specific areas for research and development.

Principles of Operation

Light passing through a medium containing small particles may be scattered or absorbed. If the particles are sufficiently small and are composed of material that is intrinsically

absorbing, the extinction (the combined effect of scattering and absorption) of a beam of light passing through the medium will be dominated by absorption. The mass of particles per unit volume of gas necessary to produce a given amount of absorption for a set receiver area is constant for very small particles and begins to rise roughly linearly with size for larger particles.¹ The amount of light scattered back out of the receiver is also a function of particle size, with the smallest particle offering the least losses. Thus from an optical point of view very small particles (less than 0.1 micrometer diameter) are best suited to this application.

Energy Balance

Once the particles have absorbed the incoming radiation they begin to heat up. If the particles are small, the thermal inertia (heat capacity) of the particles is very small. This condition may be used to simplify the particle temperature analysis by considering only the in and out going fluxes. The equilibrium temperature calculated on this basis will be reached in an extremely short time compared to the residence time in the heating chamber. The condition for temperature equilibrium of a particle in a gas is given by,

$$P_A - P_E - P_C = 0$$

where P_A is the power absorbed by the particle and is a function of the integral of the product of the wavelength dependent absorption of the particle and the solar and infrared flux densities. P_E is the power emitted by the particle and is a function of size and the integral of product of the emissivity of the particle and the Planck black body function at the temperature, T_p , of the particle. P_C is the power lost by collisions and is a function of size and temperature of the particles, and the density, specific heat, and temperature, T_g , of the gas. An iterative technique is used to solve for the equilibrium temperature of the particle.

The results of the calculation are given in Table 1. They are dependent on the particle radius only through the dependence of the absorption efficiency on size. The calculations are based on a combination of graphite optical constants of Phillipp² in the infrared and Arakawa et al.³ in the near infrared and visible. The incoming solar flux was assumed to be 1 kW/m² and has a concentration of 2000, typical of advanced concept solar power plants. For conditions of interest, the particle temperature never rises over 0.1°K above the gas temperature. The table also indicates that below 1500°K the heat loss process is dominated by conduction. The low ratio of emission to conduction for $T < 1500^\circ$ also means that infrared reradiation from the particles is suppressed. The temperature difference $T_p - T_g$ is roughly inversely proportional to the gas pressure. The ratio of P_E/P_C is independent of pressure.

The last temperature entry in Table 1 indicates that for the assumed conditions the maximum attainable temperature is 2375°K. The maximum

Table 1. Temperature differences between particles and gas and the ratio for power loss by emission and conduction for various temperatures at a pressure of 6 atm.*

$T_p(^{\circ}\text{K})$	$T_p - T_g(^{\circ}\text{K})$	P_E/P_C
600	0.09	0.0004
1000	0.069	0.007
1500	0.052	0.079
2000	0.029	2.1
2375	~ 0	(all emission)

*The results of this table are based on values of absorption efficiency for particles of 0.025μ radius and the conditions given in the text.

temperature will depend on the particle size and will increase for smaller particles. This extremely high temperature capability may be relevant to solar high temperature process heat applications.

Particle Production

Small particles for heat exchanger applications may be produced in several ways. Dispersion of premanufactured powders is extremely difficult due to the tendency of small particles to agglomerate because of large surface forces. The best approach is to produce the particles, entrain them in a gas system, and conduct them to an injection port, thus minimizing the chances for agglomeration.

The choice of the operating parameters of the heating chamber and the gas turbine determine the desired characteristics of the particles. The most important physical characteristic of the carbon particles for the present application is the oxidation rate at a given temperature in air. Very little experimental data on this topic is available for small particles. However, measurements on bulk material show large differences in the reaction rate at a given temperature for different allotropic forms of carbon. Based on published bulk reaction rates at 1000°C , the calculated time for complete combustion of particles with a diameter of 0.1μ varies from approximately 20 microseconds for baked carbon to about 0.5 seconds for vitreous carbon. Thus the choice of particle composition offers a control of the lifetime of the particle in the chamber. An experimental program is clearly necessary to determine the best particle production technique to match to a given application.

Window Design

The window of the heat exchanger allows the solar flux to enter the chamber, confines the pressurized gas-particle mixture, and prevents substantial losses of heat by infrared radiation. The best candidates are pyrex and quartz.

These materials pass nearly the entire solar spectrum and are also opaque to infrared radiation with wavelengths greater than 4 micrometers.

The pressure requirements on the window are modest, on the order of two to six atmospheres for the open cycle Brayton engine. The optimum window-cavity design to confine these pressures depends on a number of factors, including the window temperature, temperature cycling, and aperture size. Pyrex has excellent strength qualities and is cheaper than quartz but does not have the high temperature capabilities of quartz. Figure 1 illustrates a receiver in which the outer window is made of pyrex and forms the pressure chamber. It is a cylindrical section facing inward to ensure the window remains in compression (the direction to provide the maximum strength for glass). The inner window is a thin sheet of quartz and acts as a heat shield. Particles are introduced only into the space behind the shield by putting the injectors below the top of the shield. Since no heating occurs in the cavity between the windows, the compressed air stream serves to cool the windows.

Fig. 1. Conceptual design for a small particle heat exchanger. (XBL 787-2593)

Power Plant Considerations

The Small Particle Heat Exchanger may be used to heat gas for use in either an open or a closed Brayton cycle. The open cycle operates by drawing in ambient air, using it as the working fluid, and discharging it again to the atmosphere. This once-through process avoids the need for the large cooling towers that are usually associated with electric power plants. The closed cycle recirculates the work-

ing fluid, and therefore requires active cooling facilities to cool the gas before recompressing.

An important question in the analysis of solar-electric production is determining the optimum size for the collector-receiver module. The optimum size for a solar-hybrid power plant utilizing small particles depends strongly on window design and has not yet been determined. However, to calculate some of the operating characteristics of a plant incorporating SPHER, the module size will be assumed to be 10 MWe. The results are based on an assumed pressure ratio of six and 80% recuperation of the exhaust heat. For a gas temperature of 980C° the plant efficiency would be about 40%. The volume of gas passing through the plant would be about 250,000 cubic meters per hour. At this flow rate the amount of carbon needed is only about 10 Kg/hr. This modest requirement for carbon can easily be met by a number of processes. The amount of CO₂ produced from this carbon is of the order of that generated by a single automobile. Thus, the environmental impact of this aspect of the plant is minimal.

PLANNED ACTIVITIES FOR 1979

The activities in the year will concentrate on deepening and broadening the examination of all major aspects of the Small Particle Heat Exchanger. The goal is to anticipate and answer fundamental and engineering questions involved in building and testing an experimental unit of moderate size at a national solar test facility. To this end there will be both an experimental and theoretical program to demon-

strate and predict the operation of the critical components of the system.

The experimental effort will be divided into two parts: A demonstration program will investigate methods of producing, controlling and heating small particles; and a more basic, parallel program will characterize the small particles and try to relate their optical and physical properties to their composition and production process.

Another effort will be to investigate the particle confinement considerations such as window materials, cooling, sealing, and chamber design. The theoretical effort will concentrate on producing modest computer programs to predict the steady state behavior of each process in a small particle heat exchanger.

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*This work has been supported by funds from the Director's Office, Lawrence Berkeley Laboratory, Berkeley, CA.

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Passive Systems Analysis and Design*

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INTRODUCTION

The objective of this project is to explore the application of passive solar design concepts to the non-residential building sector. Thermal models which describe the unique heat transfer characteristics of passive solar heating and cooling systems are being developed. The models will be incorporated into the public domain building energy analysis computer programs BLAST and DOE-1. The computer codes will be utilized in systems studies and in the design of commercial buildings on a case study basis. It is anticipated that these coordinated design/analysis efforts will lead to engineering field test buildings which employ a broad range of passive design features.

BACKGROUND

The thermal analysis portions of the LBL efforts began in early FY 1978; they resulted

from a perceived need to provide passive solar system analysis capabilities to the building design and engineering communities. Special emphasis was placed on commercial buildings where little attention had previously been given to passive design concepts. This work is a joint undertaking of the Solar Group at LBL and the WX-4 Group at Los Alamos Scientific Laboratory,¹ who have had responsibility for the development of the active solar simulation capabilities in DOE-1. The project is being coordinated with the conservation group at LBL which has had primary responsibility for the past and future development of the conventional building analysis capabilities of DOE-1. Some of the passive solar analysis and design projects are also related to work being done in the Windows and Lighting program at LBL. Currently, the relationship includes joint funding of one subcontract and development of a joint solar/conservation competitive solicitation.

The work also draws upon other DOE contractors including Consultants Computation Bureau and the Energy Engineering Group. The former was involved in the original development of DOE-1 and is investigating possible methodological limitations of existing analysis techniques when applied to passive solar systems. The latter contractor is expected to provide detailed data on the performance of mass storage wall thermocirculation systems which can be used in validating algorithms currently being developed at LBL.

During the latter portion of FY 1978, the LBL efforts were expanded to include design-oriented tasks. The minimal attention that has been given in the past to commercial building applications of passive solar concepts dictates that basic design concept generation and evaluations be performed. The intent, therefore, is to coordinate the thermal analysis and design tasks in order to explore the potentials for passive solar in these new areas of application.

The passive program at LBL began in November of 1977. Progress to the beginning of 1978 was limited to task definition and scheduling and to the initiation of research on thermal analysis of thermocirculation systems.

ACCOMPLISHMENTS DURING 1978

Algorithm Validation

Algorithms describing the thermal performance characteristics of thermocirculation systems for both laminar and turbulent flow were developed during 1978. These algorithms are based on a detailed thermal analysis of natural and forced convection of air between parallel plates at constant temperatures.^{2,3} Efforts to incorporate these algorithms in BLAST were initiated during the final weeks of the year.

Both analytic and experimental studies of natural convection airflow patterns within room geometries and between the thermal zones in a building were initiated. The analysis work has led to a computer program which will describe the steady state circulation under arbitrary boundary conditions on surface temperatures and forced air inputs. The small-scale experimental test will attempt to obtain qualitative data on the exchange of heat between rooms. The experiment was designed and construction completed near the end of 1978.

Near the end of the year, attempts to validate BLAST for direct gain systems were also completed. The predictions of the interior temperatures of small test rooms located at LASL were successfully compared to the measured temperatures. These validation efforts included examination of the relationship between thermal performance and the distribution of the thermal mass within the cell. This has aided in identifying the alterations that must be made to BLAST in order to provide general capabilities for analyzing direct gain systems.

Design Tasks

The design tasks were defined and initiated during the last quarter of 1978. These efforts include both conceptual designs for prototype passive solar systems and actual physical designs for DOE facilities which have been proposed for construction during 1979.

Initial efforts have been made to define ways in which natural convective thermocirculation systems might be applied to commercial buildings. These systems can produce sizable volumetric flow rates. Possible applications include: (1) preheating and delivery of ventilation air to occupied spaces during heating periods; (2) fresh air ventilation driven by opening the top of the convection channel to the environment and drawing air out of the occupied space, with make-up air provided through openings in the building envelope; and (3) space cooling by coupling the space to a pre-cooled thermal storage system such as a rockbed--thermocirculation would be used to vent the occupied space and make-up air would be supplied through the storage system. Preliminary work has begun on architectural integration of thermocirculation systems into commercial buildings.

Two DOE facilities have been identified for case study examination of passive applications. The Heavy Ion Institute at Oak Ridge National Laboratory will be an underground structure with an exposed south facade with either direct solar gain or mass storage wall elements. At the request of the Pittsburgh Energy Technology Center, LBL has performed an initial schematic design for the Energy and Conservation Building, resulting in a design that is a variation on an earlier non-passive concept.

Finally, the Passive Solar Group (PSG) was involved in a program to define and document a full range of performance indices for passive building evaluation. LBL has produced a concept paper⁶ which identifies a procedure for quantifying the conventional energy savings which result from including passive design concepts in a structure. This work has been performed in cooperation with the National Bureau of Standards.

PLANNED ACTIVITIES FOR 1979

Future thermal analysis efforts will focus on completion of the tasks which modify BLAST to provide analysis capabilities for direct systems, Trombe walls, and other thermocirculation systems. New modeling tasks are also being undertaken; they include:

- rockbed thermal storage systems
- roof pond systems
- salt gradient stabilized solar ponds

When completed, these models will also be added to BLAST and DOE-1. In addition, the natural convective zone coupling studies will continue. A comparative analytic evaluation of various existing and proposed passive domestic hot

water heating systems is to be completed during 1979. A promising candidate design concept will be selected, fabricated, and tested in 1980.

In cooperation with the Radiative and Passive Cooling Project in the Solar Group at LBL, a design and analysis project for a passive cooling system will be undertaken. This will be done in conjunction with a local designer/builder and will provide an engineering field test for a passive system.

The thermocirculation concepts will be further developed and entire building systems will be specified and analyzed. The systems that demonstrate significant potential will be documented in a commercial building concept manual and case study demonstrations will be sought. The LBL involvement in the case studies will continue through the design development stage and the post-occupancy evaluations of the passive structures.

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Nitinol Engine Development*

R. Banks, R. Kopa, M. H. Mohamed, and M. Wahlig

INTRODUCTION

Low grade heat, in the form of thermal energy at temperatures below the boiling point of water, is a widespread energy resource that could make a significant contribution to world wide energy needs if an economical technology can be developed for converting it to useful work. The Nitinol Engine Development project is investigating the feasibility of using the thermally-activated shape-change phenomenon in certain intermetallic Shape Memory Alloys, particularly the nickel-titanium compound "55-Nitinol",¹ as the basis for thermal-to-mechanical energy conversion at temperatures available from such sources as industrial waste heat, low-temperature geothermal brines, solar-heated water, or the moderate temperature differences that exist in the ocean thermal gradient. An important advantage in using a solid rather than a fluid working medium in such applications is the possibility of eliminating the heat exchangers required by closed-cycle fluid systems, which often constitute major cost and maintenance items in conventional low-temperature energy conversion technologies.

A prototype Nitinol heat engine has been in operation at the Lawrence Berkeley Laboratory since August 1973. Since that time, several

iterations of engine design have led to an improved understanding of the important practical considerations in applying this material to energy conversion in continuously cycling heat engines. These studies, as well as experimental and theoretical investigation of the material's thermodynamic and metallurgical properties, have confirmed the potential for developing useful and practical machines for the recovery of thermal energy from low-grade or waste heat.

ACCOMPLISHMENTS DURING 1978

The work of the past year has been primarily focused on detailed study of the cyclic behavior of individual Nitinol elements through a variety of theoretical and experimental approaches. Early in 1978 an instrumented cycle-simulator was constructed which enabled evaluation of the effects of repetitive stress-strain-temperature cycles under controlled conditions. A parallel study of material properties has investigated the relationship between maximum work output per unit mass of Mitinol, maximum thermodynamic conversion efficiency, and fatigue lifetime, in order to identify an ideal cycle capable of achieving an optimum combination of these parameters. As a part of the materials study, a high-resolution laser-beam dilatometer was developed by means of which very small changes

in length of a Nitinol element (on the order of 100 μm) may be observed as a function of stress and temperature.

Cycle Simulator

The fabrication of the electronically controlled Cycle Simulator, which is shown in Fig. 1, was completed in March 1978. After calibration and integration with the data acquisition system, the planned experimental program was started in June 1978.

The Cycle Simulator was designed to operate fully automatically and be capable of continuous operation for millions of cycles, faithfully repeating any specific type of thermodynamic cycle selected during the research program. Test parameters that can be varied include stress levels, stress rates, percent of elongation, temperature levels, heating and cooling rates and cycling speeds.

The isothermal engine cycle was selected as the first type of thermodynamic cycle to be investigated. Although thermodynamically inferior, this cycle was investigated because most known solid state heat engines operate on the principle of an approximately isothermal cycle.

Several Nitinol wire elements obtained from different sources and with different mechanical and heat-treatment histories were subjected to tests extending over thousands of repeated cycles. The rate of wire straining, and the periods of heating and cooling (which additively determine the cycling speed), were adjusted so that the resulting cycling speeds of these tests were in the range of 5-20 cycles per minute.

This corresponds to typical operating speeds of various prototype Nitinol heat engines.

The heat input to the wire element was determined by three independent methods. The resulting stress-strain work diagram produced by the Nitinol wire was continuously monitored on an oscilloscope and, with all other pertinent test parameters, periodically recorded on a video tape.

After an initial "training" period of the wire elements (approx. 1000 thermal cycles with low strain), the strain was adjusted to the highest level which still permitted the continuation of the cycling without noticeable cumulative irreversible elongation of the wire element. The temperature of the cold bath was maintained at 2°C or at 18°C, and the temperature of the hot bath was varied until the optimum energy conversion efficiency was attained. The cycle was then repeated automatically until the failure of the wire or a noticeable deterioration of performance occurred.

It was found that at cycling speeds of 5-20 per minute a strain of approximately 1.5% was the limit beyond which a progressive irreversible elongation would occur and cause eventual failure of the wire element. The resulting efficiency of the conversion of heat to mechanical work at this strain level and $\Delta T = 80^\circ\text{C}$ was on the order of 0.5% for a simple isothermal cycle and about 1.0% for the constant stress-isothermal cycle.

However, significantly higher efficiencies were observed for isothermal cycles in which the rates of wire straining, heating and cooling were substantially reduced. Preliminary tests showed that, for presently available Nitinol

Fig. 1. Cycle simulator experimental system. (CBB 786-7380)

elements, an absolute efficiency of about 2% (equivalent to about 10% of the Carnot efficiency) was obtained in a constant stress-isothermal cycle at substantially reduced rates of straining, heating and cooling. Further investigation and corroboration of these results will be pursued.

The second type of cycle investigated was the adiabatic cycle. It is theoretically the most efficient thermodynamic cycle; however, it is also more complex and not so easily realized in a practical solid state heat engine design. Furthermore, in the adiabatic cycle the strain rates must be fast (full strain in less than 300 ms) in order to prevent excessive heat losses from the wire element during the straining period. Understanding these effects is of key importance in identifying methods of attaining higher efficiencies, and is the object of the current investigation.

Materials Studies

We have been studying, both theoretically and experimentally, the parameters that govern conversion efficiency, work output per unit mass, and fatigue lifetime of Nitinol wire elements. An expression relating the thermal conversion efficiency of Nitinol to a set of materials properties with reference to an ideal cycle consisting of two isotherms and two isochores has been derived:

$$\eta_{\text{thermal}} =$$

$$\frac{\sigma_y^{\text{htp}}(1 - e^{-N\epsilon}) \cdot \epsilon}{\Delta H + \bar{C}_p [(A_f^0 - A_s^0) + (A_s^0 - M_f^0) + (dA_f/d\sigma) \sigma_y^{\text{htp}} (1 - e^{-N\epsilon})]}$$

where:

- σ_y^{htp} = the yield strength of the high-temperature phase;
- ϵ = strain within the recoverable range ($\leq 8.0\%$ elongation);
- N = the number of crystallographically equivalent martensite variants;
- H = the latent heat of the transformation;
- $\bar{C}_p$ = the average specific heat of the material over the temperature range across the cycle;
- A_s^0, A_f^0 = the temperature at which reversion of martensite to the high-temperature phase starts and finishes, respectively, upon heating in the absence of an external stress.
- M_f^0 = The temperature at which the transformation to martensite finishes upon cooling, in the absence of external stress;
- dA_f/d = the rate of increase in the A_f temperature with an external stress.

The above properties have been measured for the particular Nitinol alloy under current investigation. From these measurements and the above expression, the maximum possible efficiency was calculated to be 9.0% for a $\Delta T = 690^\circ\text{C}$ (the calculated work output is 4.3 J/gm), which amounts to 45% of the corresponding Carnot

efficiency. This 9% efficiency, however, requires 8% recoverable elongation and a stress amounting to 0.85 of the yield strength of the high temperature phase. At such a high stress level, an early fatigue failure might be expected. If the maximum stress on the material during the course of an engine cycle is reduced to 0.5 of the yield strength of the high temperature phase, a working lifetime of many millions of cycles could be anticipated, but conversion efficiency will be correspondingly reduced to a value on the order of 2.0% (13% of the Carnot limitation for these temperatures).

Our attention is now focused on the possibility of increasing the yield strength by various methods. In particular, one procedure currently being investigated holds promise (on the basis of electron microscope observations) for higher conversion efficiencies. It entails confining the thermal cycling to within the transformation temperature range. Other efficiency-limiting factors, such as the magnitude of the thermal hysteresis associated with the transformation, are also under investigation.

In the course of cycle studies performed with the laser-beam dilatometer, a method for increasing the practical efficiencies of the solid state engine cycle by means of partial heat recovery (a regenerative cycle) has been investigated. Because of the thermal hysteresis exhibited in the Nitinol cycle, there is a temperature range during both the heating and cooling processes in which negligible shape change (and therefore transformation) occurs. Heat absorbed or rejected by the material during these parts of the cycle is therefore almost exclusively sensible or specific heat, and may be stored conveniently during the cooling path (rather than rejected to the heat sink) and reabsorbed by the element on the heating path. Preliminary tests simulating such a cycle indicate that in principle cycle efficiencies in excess of 3% (absolute) may be achieved, or $\geq 40\%$ of the corresponding Carnot efficiency.

PLANNED ACTIVITIES FOR 1979

The Cycle Simulator studies are planned to continue principally in two important areas:

- 1) Studies aimed towards fundamental understanding of the effect of strain rates and of heating and cooling rates on the mechanism of the lattice transformation process, and subsequent investigation of methods leading to effective increase in those rates without adverse effect on the cycle conversion efficiency;
- 2) Investigation and testing of other SME materials, and of the effect of alloying on their thermodynamic performance characteristics.

The ultimate objective of the planned research is the demonstration of the practicality of an adiabatic engine cycle which could be incorporated in the design of a solid state heat engine. Since the theoretical efficiency of the adiabatic engine cycle approaches that of the Carnot cycle, it should, even given the non-ideal

behavior of SME materials, yield a substantially higher conversion efficiency than has thus far been attained in isothermal cycles.

In the materials program we will focus our attention on improving materials properties that lead to better efficiencies, while maintaining a reasonable fatigue life. In particular we plan to investigate:

1) the functional dependence of the yield strength of the high temperature phase on thermal cycling and previous heat treatments;

2) the temperature dependence of the stress required to induce martensite transformation. This relationship, and the variation of the yield strength with temperature, will determine the ranges of stresses and temperatures through which the undesirable irreversible plastic deformation during an engine cycle is minimized;

3) the dependence of fatigue life on stress, strain, and the temperature at which the strain is induced in relation to the transformation temperatures;

4) the effect of prior heat treatments on the transformation temperatures and magnitude of the thermal hysteresis;

5) the effect of cold memory on the efficiency and the relationship between this memory and the microstructure.

Further investigation of the regenerative cycle and of "incomplete" thermal cycles, during which the material is not fully transformed either on heating or cooling, is planned as part of the continuation of the dilatometric studies. The effect of these, and other cycles on the long-range working lifetime of the material will be investigated by means of a high-cycle fatigue test stand to be constructed early in 1979.

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Radiative and Passive Cooling*

M. Martin, P. Berdahl and M. Wahlig

INTRODUCTION

The major objective of this project is to determine the feasibility of using radiative and passive cooling systems in various parts of the country. This effort includes a determination of atmospheric infrared emission characteristics to identify geographical regions

in which selective and non-selective radiators might be effective. This will be accomplished by use of atmospheric radiation models and by an experimental program of sky radiation measurements. A computer analysis of radiative cooling will model the entire system, including the atmospheric characteristics, the blackbody or selective radiating surface, and the building

load. If the performance and economics of radiative cooling systems appear favorable, studies of infrared absorptance and emittance of candidate materials for radiating surfaces and windscreens will be carried out. Finally, convective and evaporative cooling systems will be integrated into the study so that all aspects of passive cooling will be included.

The computer simulation of the performance of passive cooling systems, a major component of this project, is to be performed in conjunction with LBL's Passive Solar Analysis Group. This group has the corresponding responsibility to perform computer simulations of passive heating systems.

In order to accurately predict the net heat exchange between the sky and a surface of known infrared characteristics, it is necessary to have a knowledge of the intensity of infrared radiation produced by the atmosphere. A knowledge of the intensity as a function of both zenith angle and wavelength is required. When this project began (March, 1977), a major effort was directed toward developing a computer model to predict this atmospheric radiation, based on the meteorological state of the atmosphere. This program is based on the public domain computer model LOWTRAN 3B¹. Also during 1977 basic design of a filter spectrometer for measurement of atmospheric infrared radiance was completed.

ACCOMPLISHMENTS DURING 1978

A major activity in 1978 was the construction and siting of three infrared radiometer system for measurements of infrared atmospheric radiance. Since the first instrument was sited in August (Tucson), data collection has been a major activity.

Description of the Spectral Radiometer System

The spectrometer design incorporates a Barnes Corporation model 12-880 radiometer equipped with an eight-position filter wheel, germanium lens, and pyroelectric detector. Of the eight filter positions, one is an open hole and one is a closed hole used to determine the instrument's zero offset. The remaining 6 filter positions contain infrared interference filters with "halfpower" cuton and cutoff points given in microns (μm) by (8.3, 9.1), (9.4, 9.9), (10.0, 11.4), (14.0, 15.8), and (16.6, 21.6). In addition to a stepping mechanism which allows the filter wheel to be positioned automatically, the instrument contains a rotating mirror assembly which allows the instrument's 2° field of view to be directed into the vertical direction or into a 70°C black body cavity. The entire instrument is under microprocessor control and is accessible to Lawrence Berkeley Laboratory through a MODEM telephone link. The accumulating data is transmitted over this link at intervals of one to three days.

Several measurements are made to supplement the basic radiometer data. Total infrared radiation is monitored with an Eppley pyrgeometer. Temperature and dewpoint are measured using standard techniques. The presence or absence of rain is also monitored.

Three radiometers are located in the field at the end of 1978. Systems were installed at Tucson, Arizona in August 1978; at San Antonio, Texas in September 1978; and at Gaithersburg, Maryland in November 1978.

Samples of the Sky Radiance Data

Figures 1-3 show samples of the radiometer data, superimposed on calculated spectra for similar meteorological conditions (identical air temperature and dewpoint). The measured radiances are assumed to be constant within each filter passband, or to be a segment of a black body curve, whichever is more appropriate. The calculated spectra (smooth curves) are obtained from a modification of the computer program LOWTRAN 3B¹, described in more detail in last year's Annual Report.² Except as constrained by surface air temperature and humidity, the atmospheric constituents were assigned typical midlatitude summer values. The general agreement between the calculated and measured values of spectral sky radiance confirms that both the computer program and the radiometer produce reliable information.

Fig. 1. Spectral radiance, both computed and measured, for clear sky conditions at Tucson, Arizona. The 10.7 micron filter is absent. Radiance in the 9.9 to 13.7 micron band is deduced from measurements through the 8.1 to 13.7 micron filter, after adjusting for the filters at 8.7 and 9.6 microns. (XBL 792-322)

Fig. 2. Spectral radiance, computed and measured for clear sky conditions at San Antonio, Texas. Radiance in the 11.4 to 13.7 micron band is deduced from measurements through the 8.1 to 13.7 filter, after adjusting for the filters at 8.7, 9.6, and 10.7 microns. (XBL 792-323)

Fig. 3. Spectral radiance, computed and measured under conditions virtually identical to those of Fig. 2, but with a cloud in the field of view. In the computed spectrum, the cloud is regarded as a black body at an elevation of 4 km. (XBL 792-324)

PLANNED ACTIVITIES FOR 1979

During 1979 we plan to undertake a more accurate comparison between the theoretical computer model and the experimental data. This comparison will use radiosonde data (temperature and humidity profiles) as input to the computer program, and will also take into account the detailed spectral characteristics of the infrared bandpass filters.

The field radiometers will be recalled for maintenance and will be modified to make radiance measurements at several zenith angles. The instruments will then be relocated in the field for the summer of 1979, to obtain further data during periods of high air conditioning load.

Substantial effort will be invested in the development of computer codes which can be used to simulate the performance of passive cooling systems for existing and future conceptual designs. Computer simulations of buildings with passive cooling features must be validated against the measured performance of full-scale buildings in order to achieve an adequate level

of confidence in their predictions. Accordingly, one or more buildings will be instrumented for this purpose during 1979.

An experimental test facility will be constructed at LBL for the purpose of measuring radiative cooling rates that can be achieved by a variety of radiating surfaces and infrared-transparent glazings. Both black body radiators and selective surfaces will be studied.

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Development of Solar-Driven Ammonia-Water Absorption Air Conditioners and Heat-Pumps*

K. Dao, R. Wolgast and M. Wahlig

INTRODUCTION

The objective of this project is the development of absorption refrigeration systems for solar heating and cooling applications. Two absorption cycles are under investigation: the basic single-effect cycle operating with low heat source temperatures compatible with flat plate collectors, and advanced multi-stage cycles operating with high heat source temperatures compatible with concentrating collectors for higher COP (coefficient of performance).

In the first phase of this project, the basic single-effect ammonia-water absorption cycle was tested experimentally to obtain answers to key technical questions concerning the use of such a cycle for solar cooling. The following constraints on the engineering and design of the test air conditioner were assumed:

- The condenser and the absorber must be air-cooled.
- The maximum heat source (hot water) temperature must be obtainable from flat plate collectors; that is below 230°F.
- The refrigerated medium (chilled water) produced must be below 50°F.

The test model was a modified ARKLA gas-fired $\text{NH}_3/\text{H}_2\text{O}$ absorption chiller.

The first phase of this project has been concluded and has experimentally demonstrated¹ that the single-effect ammonia-water absorption can indeed be used for solar cooling, using an air-cooled condenser-absorber and flat plate collectors.

The second phase of the project has continued from early 1977 to the present with the main objective being to explore the commercial potential of the $\text{NH}_3/\text{H}_2\text{O}$ single-effect absorption air conditioner. It is assumed that the following constraints must be met for a commercial unit:

- Total prime heat exchanger area: 120 ft² maximum.
- Cooling capacity: 3 tons minimum.
- Coefficient of performance: 0.65 minimum.
- Hot water temperature: 230°F maximum.
- Chilled water temperature: 45°F maximum.
- Cooling air temperature: 95°F minimum.
- Total parasitic electric power: 700 watts maximum.

A completely new 3 ton single-effect unit was engineered and designed to perform within the performance criteria stated above. The key components of this new unit are tube-in-tube heat exchangers for high effectiveness and low cost. Incorporated in this unit are

techniques for recuperation of mechanical energy from the high pressure subcooled weak solution and recuperation of heat content from the ammonia vapor produced in the generator.

The commercialization program for this type of single-effect $\text{NH}_3/\text{H}_2\text{O}$ absorption chiller has started with the award of a subcontract to Phillips Engineering Co. for the design review of this new unit.

The success of the single-effect unit will not obviate the need for development of more advanced chillers with higher COP's compatible with high temperature collectors (above 230°F). Accordingly, this project is investigating advanced absorption cycles whose COP increases with temperature, maintaining a relatively constant fraction of the Carnot COP over a wide range of operating temperatures.

ACCOMPLISHMENTS DURING 1978

The fabrication of the new single-effect $\text{NH}_3/\text{H}_2\text{O}$ absorption air conditioner was mostly completed by July 1978. Its installation for testing is underway.

Figure 1 shows the major part of this chiller at the point where it was about to be connected to its condenser-absorber unit (shown in Fig. 2). The main improvements incorporated in this new unit as compared to the conventional single-effect cycle are:

- The use of a combined preheater-rectifier for the high-pressure vapor and the weak solution flow paths, instead of using separate components for these functions of heat recuperation and vapor rectification. A small 1/8 in. tube is used to collect the condensate at the middle of the vapor tube of the preheater. Since the concentration of this condensate is fairly high, it is expanded in the precooler to subcool the liquid ammonia exiting the condenser.
- The use of a newly designed pair of piston pumps. One pump uses the pressure drop of the weak solution (otherwise wasted) as the driving force to circulate about 70% of the strong solution from the absorber outlet to the generator inlet via the preheater. The remaining strong solution will be circulated by the other paired pump, which is driven by a small flow of high pressure ammonia vapor extracted from the condenser inlet. These pumps replace the usual electrically driven circulation pump.

Brief descriptions of the major components of the unit are:

1. Generator: Triaxial tube-in-tube counter-flow heat exchanger (inner coil in Fig. 1).

Hot water flows in the outermost annular channel and also inside the innermost tube. Boiling $\text{NH}_3/\text{H}_2\text{O}$ solution flows in the middle annular channel. Outside diameters of triaxial tubes: outermost, 1.875 in.; Middle, 1.375 in.; Innermost, 0.75 in. total length: 56 ft in a 30 in. diameter coil.

2. Preheater: Triaxial tube-in-tube counter-flow heat exchanger (outer coil in Fig. 1). The weak solution leaving the generator flows in the outermost annular channel. The strong solution flows in the middle annular channel on its way to the generator. The ammonia vapor produced in the generator flows in the innermost tube as it heads towards the condenser. Outside diameters of triaxial tube preheater: outermost, 1.375 in.; middle, 1.0 in.; innermost, 0.625 in. Total length: 96 ft coiled in a 38 in. diameter coil.

3. Condenser-Absorber: Finned-tube crossflow heater exchanger (Fig. 2); 8 fins per inch, 0.625 in. OD tube, 3 rows (2 rows for the absorber, 1 row for the condenser); Frontal area: 39 x 41 in.²
4. Fan Motor: 3/4 HP, 6900 cfm.
5. Evaporator: Double coils in the annular spaces of 3 cylindrical shells. Tube OD: 0.5 in., shell diameters: 10 in., 9 in., 8 in.; height: 38 in. Total tube length: 190 ft. A vapor extraction chamber and orifice were installed between the two coils to reduce the pressure drop across the evaporator.
6. Pair of circulation pumps: Cyclinder bore: 2.5 in.; stroke: 2 in. Each pump is a tandem piston pump. The use of 2 pistons per pump assures the continuity of the delivery of the strong solution. Specially designed valves are used for the intake, exhaust, suction and delivery.

Fig. 1. Main assembly of the single-effect $\text{NH}_3/\text{H}_2\text{O}$ absorption air conditioner. The outermost 10-turn coil is the preheater and the inner coil with larger tubing is the generator. Surrounded by the generator coil are the evaporator (short, largest-diameter tank), the precooler (thin, tallest cylinder) and the two solution storage tanks. The solution pumps are located above the evaporator, slightly toward the back of the unit. (CBB 786-7686)

Fig. 2. Condenser-absorber unit, before connection to the air-conditioner. The first row of tubes on the left is the condenser, and the two remaining rows are the absorber. (CBB 782-2501)

The expected performance of the new chiller is summarized in the following table:

Capacity (tons)	2	3	4	5
COP	0.72	0.70	0.68	0.64
T _{hot water} (°F)	192	216	239	263
T _{cond-absorber} (°F)	104	108	114	119
T _{evaporator} (°F)	43	41	38	34

Cooling air is 95°F; chilled water produced is 45°F

Electrical power: Fan ≈ 550 W
Water pumps ≈ 150 W

Installation of this new chiller was begun in the test setup at LBL following the dismantling and removal of the previously tested chiller. Ductwork for the new condenser-absorber was installed. An SCR-controlled electric water heater was designed for use as the heat source of the new unit. This pressurized water heater has the capacity of 120,000 Btu/hr at 320°F maximum; its output temperature can be maintained constant within ±2°F. Its fabrication was underway by the end of 1978.

The instrumentation of the test setup includes 32 thermocouples, 3 absolute and 5 differential pressure gages, and 2 turbine-type flow meters.

The initial fabrication of the pair of circulation pumps was completed, and extensive testing of the pumps continued throughout the remainder of the year. Several modifications were tried to eliminate or reduce vibrations and banging during operation at high pressure. Very smooth operation of the pumps has not yet been achieved, and additional modifications are planned.

Computer models for the components of the new chiller have been completed and debugged. The mathematical model for each component includes detailed heat transfer, pressure drop, mass and energy relationships, and takes into account specific properties of the materials used. Given the inlet conditions, the model calculates the outlet conditions for that component. The main program that connects the component subprograms is not yet completed. This computer program will be capable of optimizing the principal dimensions of any single-effect absorption chiller that is similar in design to the new LBL chiller.

The preliminary analyses and conceptual designs of two advanced absorption systems were completed and reported in Refs. 3 (Cycle 1R) and 4 (Cycle 2R). These new advanced absorption cycles are particularly compatible with solar collectors that operate in the range of 160°-350°F. The practical COP of these systems can be about 60% of the Carnot limit; i.e., given the heat source temperature T_s , the heat sink temperature T_0 , and the refrigerated fluid temperature T_E , the system COP equals $0.6[(T_s - T_0)/T_E]$.

PLANNED ACTIVITIES FOR 1979

The installation, testing, and evaluation of the new single-effect absorption air conditioner will be completed during 1979. Reports on the testing of the chiller and of the pumps will be printed and distributed near the end of 1979.

The design, fabrication and testing of a multi-stage (8-stage) pump will be carried out. This pump will be a key component of the advanced absorption refrigeration system (Cycle 2R chiller), the design of which will also take place during 1979.

The multi-stage pump consists essentially of one double-effect piston driver linked to a group of 8 piston pumps arranged in two rows of 4 pumps each. Each pump is also double-acting with 4 check valves connected to a common intake and a common discharge pipe. For a 3-ton chiller, the piston diameters are on the order of 1.5 in. for the driver and 1.25 in. for the pumps.

Properties of refrigerant-absorbent pairs other than H_2O/NH_3 , such as $R22/E181$, will be explored for possible use with advanced cycles. Since the concept of advance cycles, particularly cycle 1R, is completely different from that of the conventional single-effect cycles, the criteria of choosing working fluids are also different. The criteria will give less weight to pumping work and heat transfer rates in recuperators because the pumping and heat exchange rates will be smaller in the advanced cycles. Of more importance will be material compatibility and high temperature potential because the construction of advanced systems will require more complicated configuration and because the COP will increase with temperature. Working fluids are desirable that will be compatible with easily brazed materials, such as copper and copper alloys.

Analysis of the advanced cycle 1R will continue throughout 1979 in search of a good system configuration for a test model that can be fabricated in 1980.

FOOTNOTE AND REFERENCES

*This work has been supported by the Solar Heating and Cooling Research and Development Branch, Office of Conservation and Solar Applications, U. S. Department of Energy.

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Appropriate Energy Technology*

C. W. Case, H. R. Clark, and F. B. Lucarelli

INTRODUCTION

The Appropriate Energy Technology Program was commissioned by the U. S. Department of Energy (DOE) and established by the San Francisco Operations Office (SAN) during the summer of 1977. It began with a preliminary or pilot program (Phase I) in Federal Region IX, the Pacific Southwest, which includes Arizona, California, Hawaii, Nevada, American Samoa, Guam, the Trust Territories of the Pacific, and the Commonwealth of the Northern Marianas. Like the national program to follow in 1978, the pilot was designed to encourage the ingenuity and resourcefulness of individuals, small businesses, state and local agencies, local nonprofit groups, and Indian tribes.

DOE set aside \$500,000, exclusive of operating costs, for this initial effort and expected the grants to average \$10,000 with the ceiling placed at \$50,000. Because of the general quality of the submissions, DOE added \$850,000 to the award money (\$1,350,000 total), and the 108 grants averaged \$12,500, with a range stretching from \$328 for a beeswax melter to about \$49,000 for a hydroelectric project. The grants were awarded for development of a broad variety of small scale energy innovations and demonstration projects from wind-bouys to coffee dryers to greenhouses to geothermal residential hot water heating. All were chosen using guidelines that defined as eligible those projects which made best use of available renewable energy resources, used locally available materials, emphasized decentralized technologies, increased energy self-reliance at the community level, and/or were labor intensive and environmentally sound.

The three-step procedure for allocating the grants included the prescreening step, which ascertained whether each application was complete and whether it required special handling (e.g., referral to another agency for funding), the technical/economic review step, and the peer review step by committees set up by the governor's office of each state. These committees, aided by the technical and economic advice from the second review, made awards with final approval by DOE/SAN. In 1977 LBL prescreened all 1116 proposals received.

ACCOMPLISHMENTS DURING 1978

For the pilot program, LBL did the technical/economic reviews of all proposals from Arizona, Nevada, Guam, and the Trust Territories of

the Pacific. Those from Hawaii were reviewed by the University of Hawaii, and most of the applications from California were reviewed by the California Office of Appropriate Technology (OAT). However, LBL reviewed about twenty of the more technically demanding proposals, which OAT could not handle.

Since the beginning of the Program, LBL has performed various program management functions such as establishing the procedures used during review processes as well as compiling and analyzing data. These functions will expand to include assistance to all other Federal Regions as Phase II gets under way. The Laboratory has been involved with DOE in the commercialization strategies for some of the more advanced projects and is presently monitoring the performances of the thirty projects funded in Arizona and Nevada. A single trip to Guam and the Trust Territories, where seven projects are dispersed among the islands, served the purposes of monitoring, advising, stimulating local interest, and setting up the machinery for self-monitoring and possibly technical and peer self-reviewing. LBL has also established an Appropriate Energy Technology Library, designed to serve people involved in this program as well as other interested Laboratory employees.

Pilot Program--Phase I--Awards

The 108 grants made in the pilot phase of the Appropriate Energy Technology Program totalled approximately \$1,350,000, as mentioned above. Categorizing these projects cannot do justice to their individuality or variety. Generally, however, forty-two were solar-related with six concentrating on storage solutions and eleven on hot water. Four deal with waste heat recovery, twelve with energy conservation, eleven with wind projects, and one with geothermal. Of eleven biomass projects four are wood and seven are recycle. There are three hydroelectric, four aquaculture, five integrated systems and fourteen educational programs and workshops.

The number of awards distributed to each state or territory were:

Arizona	19
California	58
Hawaii	13
Nevada	11
Trust Territories and Guam	7
	108

PLANNED ACTIVITIES FOR 1979

The other federal regions are now instituting Appropriate Energy Technology Programs with each region devising its own timetable. In Region IX the Phase II program began with DOE accepting applications from November 1978 to 15 January 1979. DOE has set aside \$530,000 for the awards in Region IX, and will make these awards during the summer.

LBL expects to support Phase II with the same kind of assistance that was necessary in Phase I, and to provide technical backup for any federal region that so requests, and

to conduct policy analysis/program evaluation studies for the grants program as a whole. The Laboratory will also assess the energy savings which might accrue from successful completion and commercialization of the projects and consider improvements for administering and implementing future programs.

FOOTNOTE

*This work has been supported by the Buildings and Community Systems Division, Office of Conservation and Solar Applications, U. S. Department of Energy.

Support Activities for DOE Solar Heating and Cooling Research and Development Program*

*M. Wahlig, M. Martin, R. Kammerud, W. Place,
E. Wali, and B. Boyce*

INTRODUCTION

This project consists of technical support activities for the Solar Heating and Cooling Research and Development Branch of the DOE Office of Solar Applications. Areas in which LBL provides program support are controls for solar heating and cooling systems, passive cooling, active solar cooling, and passive solar analysis and design. These activities include the following: (a) peer review of unsolicited proposals; (b) preparation and evaluation of Program Research and Development Announcement (PRDA) and Request for Proposal (RFP) solicitations; (c) technical monitoring of projects performed both by other DOE contractors and by LBL subcontractors; (d) program planning, reviews and summaries; and (e) inter-laboratory coordination of support activities. Program responsibilities of the Laboratory have increased due to implementation of a program decentralization plan approved in the fall of 1978. Under this plan LBL and SAN (San Francisco Operations Office of DOE) work together to manage the national R&D program in these assigned areas, with SAN providing the project management and LBL the technical support. DOE headquarters transfers block funds to the DOE/SAN office to support the outside research and development contracts being performed under these program elements. Most of the staff members of the Solar Energy Group have participated to some extent in this effort during 1978.

ACCOMPLISHMENTS DURING 1978

Review of Unsolicited Proposals

LBL solar energy group members participated in formal review sessions for unsolicited solar energy proposals in the areas of active cooling, passive systems, and active systems. In addition,

approximately eleven controls and passive cooling proposals were reviewed individually, as received. Input was provided to headquarters for the preparation of guidelines for reviewing unsolicited proposals.

Preparation and Evaluation of Program Solicitations

No new solicitations were released during 1978 in the program areas where LBL has responsibility. Recommendations were drawn up outlining desirable solicitations for the passive cooling and controls program elements for 1979. Work proceeded on the preparation of several solicitations in the active cooling area, to be released during 1979; these are concerned with advanced components and systems, marketing studies, and field testing. In the passive area, work started on the development of a solicitation for marketable products.

In response to a related DOE request for technical assistance, three LBL staff members participated in a review of proposals submitted in response to a Program Opportunity Notice (PON) issued by the Commercial Demonstration Branch.

Technical Monitoring of Projects

Project monitoring consists of the continuous technical evaluation of projects being performed by other contractors, including site visits, review of progress reports, and organization of contractor meetings as appropriate. Site visits were made to all contractors performing passive cooling or solar controls work under LBL jurisdiction, and individual project review meetings were held with three contractors during the summer. A controls contractor meeting was held at the end of February to review early

results of the 12 newly initiated projects and two continuing projects.

During the final quarter of 1978 LBL took on the additional task of program responsibility for the active solar cooling program element. Personnel were added to handle contract monitoring tasks for this expanded program, and transfer was initiated of the back files on the active cooling projects from Brookhaven National Laboratory to LBL. Status reviews of the active cooling contracts were held during September and December.

In addition, two contracts have been issued by LBL; one contractor is preparing a passive solar design workbook. The second contractor is performing a review and evaluation of information, data and materials properties of relevance to passive solar applications. This contractor is surveying both the open and classified DOD and NASA literature. These contracts are likewise being monitored by LBL staff members.

Program Planning, Reviews and Summaries

Several program summaries were prepared for DOE regarding the status of controls and passive cooling projects, and presentations were made at the annual contractors' meeting to review progress in these projects for which invited papers were not submitted. Assistance was provided in writing the annual DOE "Solar Heating and Cooling Research and Development Summaries" publication.

Overview presentations of the Controls Program and of the Passive Cooling Program were given during the Cooling Workshop held in early 1979. LBL participated actively in planning and conducting the Solar Controls Workshop held in Hyannis, Massachusetts in May 1978.

Program planning activities by LBL included participation in a meeting to update and review the National Program Plan for Research and Development in Solar Heating and Cooling, as well as involvement in planning for specific program elements. The latter includes assistance in developing the National Program Plan for Passive and Hybrid Solar Heating and Cooling, Retrofit Program Plan, Joint U. S.-Saudi Arabian Passive Cooling and Active Cooling Plans, and the Systems Plan. In addition, LBL had the major responsibilities for writing the Commercialization Plan for Passive Solar Heating as well as the Solar Controls Plan.

Interlaboratory Coordination

LBL has participated in the two 1978 meetings of the Support Laboratories Coordinating Committee, which meets regularly to discuss the state of implementation of the R&D program, and to insure that the various laboratories are acting harmoniously in performing their many tasks. A coordinated effort took place with NBS, LASL and PRC to develop performance evaluation factors and data acquisition requirements for passive solar systems. Coordinated activities between LBL and SERI included joint work on the national passive solar program plan, preliminary work on meshing the Controls Plan and the Systems Plan, and shared responsibilities for technical monitoring of active cooling projects.

PLANNED ACTIVITIES FOR 1979

Activities in all the above areas will continue throughout 1979. Unsolicited proposals will be reviewed and evaluated as they are received. The Solar Controls plan is scheduled for completion and implementation early in the year. Solicitations are anticipated for the Passive Solar Technology, Controls, and Active Cooling program elements. Monitoring of outside contracts is expanding rapidly in the active solar cooling area, whereas the first set of contracts for Passive Cooling and Solar Controls will have been completed by early 1979. Several follow-on and unsolicited proposals are likely to be approved for funding during 1979. A Controls Workshop and a Cooling Workshop are scheduled for Fall 1979 and topical workshops on Rankine cycle fluids and absorption cycle fluids are planned for mid-1979. Additional meetings of the Support Laboratories Coordinating Committee will be held during the year. Finally, it is certain that numerous LBL staff members will be called upon to assist in the review and evaluation of proposals submitted to DOE solar energy PRDA, RFP and PON solicitations issued during 1979.

FOOTNOTE

*This work has been supported by the Solar Heating and Cooling Research and Development Branch, Office of Conservation and Solar Applications, U. S. Department of Energy.

Experimental Test Facility for Evaluation of Solar Control Strategies*

M. L. Warren and M. Wahlig

INTRODUCTION

An experimental test facility for solar heating and cooling has been constructed to evaluate the operation and performance of an LBL-developed solar controller that has promising commercial potential. The LBL controller was designed to be intermediate in performance between a simple differential thermostat and an on-line microprocessor. A schematic of the solar controller is shown in Fig. 1. Electrical signals from up to eight solid state temperature sensors are standardized. By use of a pin matrix board, PPM, pairs of temperature sensors can be selected for comparison. The logic signal outputs from the comparators are used to drive Programmable Read-Only Memory (PROM) chips which in turn drive relay outputs. The controller operates the solar system according to a preprogrammed algorithm that translates operating state conditions (fluid temperatures, switch positions, comparator outputs) into a set of operating instructions (open or close valves, turn pumps on or off). The operating algorithm can be changed by reprogramming or exchanging this plug-in integrated circuit component.

The experimental solar heating and cooling system serves to test the relative performance of different controllers and alternative control algorithms for a variety of input meteorological conditions and output load demands. The measure of performance is the amount (and cost) of the auxiliary back-up energy saved by different

control strategies. The experimental evaluation of the cost effectiveness of controllers and control strategies is expected to be the primary output of this project. The development of the LBL controller and the experimental facility have been described in detail elsewhere.^{1,2}

ACCOMPLISHMENTS IN 1978

The major activities during 1978 involved improvements to the experimental test facility. The facility has a simulator for the solar heat input (the pseudo-collector) and a simulator for the building load. Instrumentation has been added to the facility for data acquisition and analysis. Heat balance tests using solar collector and simulator heat input have been carried out. In addition, storage heat loss experiments have been conducted without heat input or load. The TRNSYS computer program was employed to predict system performance and the results were compared with experimental measurements. Recent work is described in Refs. 3 and 4.

Instrumentation

A major development in 1978 was the implementation of the system for data acquisition and experiment control. An HP-9825A microcomputer arrived in November 1977 and has been interfaced with the 100 channel DORIC data-logger, with the multiprogrammer, and with the solar controller. Additional memory for a total of 24 kbytes was installed in August 1978. The

Fig. 1. Schematic of the LBL-developed Solar Controller. The inputs from 8 sensors are standardized and compared. The comparator outputs and other digital data drive the Programmable Read Only Memory (PROM) that generates relay output signals to control the solar energy system. (XBL 785-886)

microcomputer will perform four major functions in future experiments: 1) data acquisition and on-line data reduction; 2) building load and response simulation; 3) solar collector response simulation; and 4) controller status monitoring and microcomputer override. A schematic of the instrumentation and data acquisition system is shown in Fig. 2. The temperature sensors used to generate input signals for the solar controller and about 30 copper-constantan thermocouples used to monitor solar system performance, are wired into the DORIC data acquisition system, and are available to the microcomputer for on-line data analysis and experiment control. The microcomputer incorporates building and collector response models and generates control signals through the multiprogrammer to control the load simulator and the pseudo-collector. Meteorological and insolation data from standard DOE weather tapes for various geographic regions are used to drive the load and collector model equations. Thus, the experimental facility can be operated under diverse simulated weather and load conditions to test solar control strategies. The microcomputer is also interfaced to the main LBL computer system for off-line data analysis and storage.

Heat Input and Load Output Simulators

To make meaningful comparisons between alternate control algorithms, the heat input and the load conditions must be reproducible. Therefore, it was decided that the solar energy input to the system and the building output load should be supplied by simulation devices that permit repeated runs under

the same external conditions. The heat input simulator, the pseudo-collector, is a boiler with a controlled mixing valve that allows precise adjustment of the input-output temperature difference, ΔT . A resistance proportional to ΔT is generated and used to control the pseudo-collector. In future experiments the microcomputer will generate collector temperature increase information using solar insolation data, weather data, measured system parameters, and a collector response model. An output resistance of about 2 ohm/°C, proportional to the temperature increase, generated by the multiprogrammer D/A converter, controls the pseudo-collector. Another voltage output signal generated by the multiprogrammer D/A converter is used to simulate the output of the solar collector temperature sensor and is based on the collector model calculation. The main controller for the solar heating and cooling system cannot distinguish whether the system is operated from solar collector panels or from the pseudo-boiler.

An automated air flow load channel has been designed and fabricated to simulate the building return air flow across the heating or cooling coil in the furnace ductwork of a residential system. The load simulator provides a controlled and reproducible residential building load isolated from the inappropriate laboratory environment in which the solar system is actually located. Both heating and cooling loads can be simulated. The temperature within the ductwork is carefully controlled by an electric resistance heater and an air conditioner. The microcomputer gives on/off control to the air conditioner if the inlet air temperature is too high, and gives proportional control to the duct heater

CONTROL TEST FACILITY INSTRUMENTATION

Fig. 2. Schematic of the instrumentation and data acquisition system. All experimental measurements are available to the microcomputer for online data analysis and experiment control through the DORIC data-logger. (XBL 794-1149)

if the air temperature is too low. The microcomputer also models the building heat loss in response to weather conditions, and monitors the rate at which energy is being delivered to the load by the heating or cooling coil. This information enables the microcomputer to determine when the building load has been satisfied, thus serving as the building demand thermostat for the solar system controller.

Heat Balance Tests

The energy flows from the collector loop and from storage should exactly balance the energy flows to the load, to storage and to ambient air. The heat input and load output, as well as all heat flows within the system, are carefully monitored. Precision flow rate and temperature measurements are recorded over time intervals of typically 5 to 15 minutes and used to calculate these heat quantities.

The heat balance error is defined as the unaccounted energy flow divided by the incoming energy flow:

$$\text{Heat balance} = \frac{\text{Heat In} - \text{Heat to Load} - \text{Heat Loss} - \text{Storage}}{\text{Heat In}}$$

where $\Delta\text{Storage}$ is the net heat delivered to storage.

$$\% \text{ Error} = 100 \times \frac{\text{Heat Balance}}{\text{Heat in} - \Delta S}$$

where $\Delta S = \Delta\text{Storage}$ if $\Delta\text{Storage} < 0$; and
 $\Delta S = 0$ if $\Delta\text{Storage} \geq 0$.

The heat balance error depends critically on the accuracy of the fluid flow and the temperature measurements. The digital flow rate measurement is accurate to within 1%. The calibrated temperature sensors are accurate to $\pm 0.1^\circ\text{C}$. The copper-constantan thermocouples were found to be accurate to within $\pm 0.5^\circ\text{C}$. Wiring the thermocouples in pairs produced temperature difference measurements accurate to about $\pm 0.2^\circ\text{C}$. The heat balance error for the initial day-long experimental runs varied from 1% to 12% with the average about 7%.

For assessment of the reduction in auxiliary energy consumption associated with various control strategies, a measurement of the energy balance to an accuracy of $\leq 5\%$ appears to be necessary. Error analysis indicates that this can be achieved if the temperature difference measurements can be made to within 0.1°C . Better measurements of the temperature distribution within the storage tank, plus use of amplifiers for the thermocouple difference signals have significantly reduced temperature measurement errors. Heat balance experiments are underway to determine how successful these improvements have been. A more recent experimental run shown in Table 1 indicates a heat balance error of 3.7%, which is within our goal of 5% heat balance accuracy.

Computer Modeling

The TRNSYS program was used to calculate system performance for comparison with experimental measurements. Simple controllers were

Table 1. Heat balance experiments

	PREVIOUS RUN	RECENT RUN
HEAT IN	210.7	205.5
HEAT TO LOAD	754.4	923.7
HEAT LOSS	55.7	61.0
STORAGE	-542.2	-744.1
HEAT BALANCE	-57.1	-35.1
% ERROR	-7.6	-3.7

Notes: Heat is given in units of megajoules (10^6J).

studied with the computer model. As reported last year, many studies of on/off controllers and proportional controllers ran into numerical convergence problems, apparently caused by the static equations used to describe components in TRNSYS. This problem is now being addressed by researchers at Drexel University and at the present time we have no plans to pursue this computer modeling of control algorithms.

PLANNED ACTIVITIES FOR 1979

In 1979 work will continue to refine measurement precision and to complete microcomputer control of data acquisition and experimental operation. The LBL solar system controller evaluation studies will begin with a series of twenty-four hour runs to shake down data acquisition and on-line data reduction procedures using simulated collector heat input and building load output based on simple models. The simulation models will then be refined. A series of seven day runs will then compare system performance of different control algorithms using the LBL developed controller.

The experimental program will expand to include proportional flow modes. Modifications to the controller and to certain actuators should allow testing of proportional flow algorithms, and thus their comparison with on/off strategies. This experimental performance testing of alternative control strategies will continue throughout 1979.

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PG&E/LBL Solar Data Network*

D. Anson

INTRODUCTION

Lawrence Berkeley Laboratory (LBL) and Pacific Gas and Electric Company (PG&E) have been cooperating in the implementation of a solar radiation data collection network in northern California. This discussion will briefly summarize the project history, characteristics of the network itself, details about data collection, instrumentation problems, and near-term accomplishments and goals.

The project objective is to provide a high quality solar radiation data base for well-located sites in northern California. This is to be accomplished through the establishment of a solar data network using accurate instruments and data analysis techniques, and will be followed by prompt data dissemination. This project is the northern California complement to the extensive solar data networks in the Los Angeles and San Diego areas of southern California.

The solar radiation measured by this project will likely provide the only data of suitable quality for solar applications available to designers, architects and engineers in much of this region. Once in full operation, the network will provide a valuable user-oriented resource.

PROJECT HISTORY

The PG&E/LBL network originated in July 1974 as part of a larger, National Science Foundation supported solar heating and cooling project at LBL. The following year the program was transferred to ERDA, which made a policy decision not to support local solar data collection networks. However, by this time instruments had been purchased and arrangements made to implement the project. Work on the network continued at a low and discontinuous level until February 1978 when it became possible for a part-time LBL staff member to take on overall responsibility for the effort. As a result, the network is now operational, albeit with some remaining problems to be worked out.

The motivation for persevering in this effort is that there is no other comparable array of stations producing high quality solar radiation

data for northern California. The DOE supported National Weather Service Network has only two stations in California, at Fresno and Los Angeles. Neither of these locations can be considered representative of the Bay Area, the northern coast, or the interior regions to the north of Fresno.

Network Description

The organizational relationship between PG&E and LBL is such that PG&E is primarily responsible for three tasks: routine maintenance, changing the magnetic tapes used for data collection, and raw data conversion. LBL is responsible for overall technical integrity (annual calibration, non-routine maintenance), data reduction, analysis and reporting. The current status of individual stations in the network varies considerably--from those with almost a year and a half of data (e.g., Berkeley) to the Eureka station which was established during July 1978.

Each station in the network consists of one thermopile-type pyranometer (Fig. 1) and a specially modified PG&E supplied tape recorder.

Fig. 1. A thermopile-type pyranometer used to measure solar radiation at each of the six network stations. (CBB 791-376)

The pyranometer measures the total radiation (direct sunlight plus diffuse skylight) incident upon a horizontal surface. The solar instrument used is a model 8-48 pyranometer (The Eppley Laboratory, Inc.). The network consists of six locations throughout PG&E's northern California service area: Berkeley, Red Bluff, Salinas, Santa Rosa, Auburn, and Eureka. These locations complement individual solar stations currently operated in northern California by other organizations. A contact person at each network station is responsible for routine servicing and for tape changes. A seventh instrument is maintained as a traveling calibration standard and is itself calibrated twice yearly by the NOAA Solar Radiation Facility in Boulder, Colorado.

The recorder is a modified Westinghouse WR-1C used in standard utility magnetic tape recording systems. The pyranometer is interfaced to the recorder with LBL-developed electronics that produce pulses on the tape at a rate that is proportional to the intensity of the incident solar radiation.

Maintenance

Unrealistic variations in the recorded data provide the primary diagnostic tools for revealing station malfunctions. The Santa Rosa station, for example, produced results for three months with all zeros. Investigation revealed a two-fold problem: one, the data pulse circuitry was not operating; and two, the inside of the instrument was saturated with moisture. The moisture inside the pyranometer dome was apparently the result of allowing the desiccant to become saturated. Thus, even if the circuitry had operated properly, the data would have been in error (too low) due to the condensation on the inside of the dome. The sensor surface was damaged by the condensate and returned to the manufacturer for resurfacing and recalibration. This incident occurred soon after network start-up and points out the necessity for preventive maintenance and rapid processing of the data. These problems with recorder malfunction and instrument moisture saturation are not expected to reoccur with the present more careful, weekly routine of checking each pyranometer.

ACCOMPLISHMENTS DURING 1978

The accomplishments during this past year are grouped into administrative, hardware, and data processing. Administrative tasks included: establishing a list of contact people and responsible personnel at the various station locations, setting up a calibration schedule, assembling a draft service manual for use by the network coordinator, compiling a draft maintenance manual to assist on-site trouble shooting, developing contacts with persons coordinating solar networks in other states, and visiting each of the six stations for inspection and recorder check-out.

Hardware activities were primarily related to the detection of breakdown, repair and recalibration of two pyranometers, and verification of recorder gain and zero-offset adjustments. Also, a digital voltmeter and frequency counter were acquired for pyranometer and recorder

servicing. Documentation and test methods were developed for use by other personnel if necessary. A spare pyranometer was purchased as a back-up to reduce data record gaps when instruments are inoperative or disconnected. Also, the annual calibration program was begun at the LBL station.

Each of the six solar data stations require routine and responsible attention. Adequate service procedures are the most important factor in both the short and long term success of producing high quality solar data.

The data processing is partially developed and has been used to detect hardware malfunctions in two pyranometers. More complete data analysis and data presentation methods are in progress.

Data turn-around times have been excessively long during 1978. This has been largely the result of procedural changes at PG&E's data processing center. The raw solar data reduction is not yet a routine task and is an area that needs much improvement.

Figure 2 shows a sample trace of recorded solar radiation data from the LBL pyranometer. The information available from curves such as this include hourly, daily and monthly totals of radiation on a horizontal surface, and the amount and frequency of cloudiness. In practice, the solar quantity normally used is the radiation on a tilted surface (e.g., roof-mounted solar panels or a south-facing window). Standard methods are available to estimate such quantities from the basic pyranometer measurement on a horizontal surface.

Fig. 2. Solar radiation measured at Berkeley, California on a day with morning cloudiness and scattered clouds in the early and late afternoon.
(XBL 791-241)

PLANNED ACTIVITIES FOR 1979

The primary activities during this year will be 1) continued, routine operation of the network, 2) improvement of the data turn-around time from PG&E, 3) development of a more complete data analysis system, and 4) the presentation of the data in forms useful to designers, engineers, architects, and others interested in the utilization of solar energy in northern California.

Should sufficient support be available, it is planned to upgrade the instrument systems. The first priority would be the replacement of the pyranometers with a type that is now known to be more reliable and accurate. Another priority item is the replacement of the tape recorders with microprocessors that periodically report the data on cassettes or over phone lines. Systems

of this type are now in operation for several other LBL projects.

FOOTNOTE

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The Role of the Proton Pump . . .Bacteriorhodopsin*

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INTRODUCTION

The Nobel Prize in Chemistry was awarded this year to Dr. Peter Mitchell for having developed the chemiosmotic theory, a conceptual framework for relating the development of proton gradients and electrical potentials across membranes, expressed as the protonmotive force (PMF) as $PMF = \Delta\psi + 60mV \Delta pH$ to other energy-linked cellular processes.¹ An ideal experimental system for studying the relationship of ion gradients to each other is found in the halobacteria which live in concentrated salt solution and hence divert much of their energy to salt pumping. These bacteria derive their energy either from respiration of substances scavenged from their environment or

from sunlight (Fig. 1). Unlike photosynthetic membranes which contain complex structures of oxidation and reduction catalysts, the halobacteria achieve conversion of light into electrical energy by means of a photocycle operated by a single, relatively simple protein, bacteriorhodopsin, which establishes a proton gradient across the membranes which this protein spans.²

Bacteriorhodopsin molecules contain a single chromophore, retinal, and occur in clusters of trimeric units that form large purple "patches" which can be isolated in pure form. Because of its purity and crystalline arrangement, the purple membrane can be more readily studied by physical

Fig. 1. Overall scheme of energy conversion by *Halobacterium halobium*. Direct conversion of sunlight into electrical current (proton movement) occurs within the "purple patches," crystalline arrays of the protein bacteriorhodopsin. Proton gradients are collapsed by being coupled to salt pumping and chemical energy synthesis in the form of adenosine triphosphate (ATP) by other catalysts in the cell envelope membrane. (BBC 7810-13460)

methods than can complex photosynthetic membranes containing more randomly dispersed components.

The small molecular size (about 26,000 Daltons) of bacteriorhodopsin has made it possible for a large team of Moscow scientists to determine its amino acid sequence. Thus molecular studies of the mechanisms of action of the protein are now facilitated.

There are compelling advantages for using chemical modification to study bacteriorhodopsin. The protein is stable to drastic alterations in the ionic strength of its environment and has proven to retain activity after extensive reaction with several chemical reagents. Certain reactive amino acids like cysteine and histidine are not found, thus minimizing cross reaction of the reagents with different amino acids. Also the retinal chromophore can be removed from the protein in a reversible manner, thus allowing the binding site environment to be probed.

Bacteriorhodopsin is probably the simplest and most stable naturally occurring light energy converter presently known. The program in the Membrane Bioenergetics Group is directed toward the elucidation of the proton conductance of this protein. Our research includes: electrical studies using planar membranes and spin probes, chemical modification studies of specific amino acid residues to obtain molecular information about the groups essential for proton conduction and light absorption, and computer assisted structural studies. A tentative hypothesis for the mechanism of proton conduction has been advanced and is now being tested and perfected.⁵ The coupling of proton currents to salt pumping is also being investigated.

ACCOMPLISHMENTS DURING 1978

Chemical Modification Studies

To elucidate the mechanism of light driven proton movements which form an electrochemical gradient, it is important to know which amino acids in bacteriorhodopsin are involved in the proton movement. Our working hypothesis is that light-induced conformational changes and/or isomerization of the retinal chromophore causes movement of the proton attached to the Schiff base nitrogen of the chromophore and that this is the primary step in the proton pump. This proton movement probably occurs over a small distance relative to the transmembrane dimension which protons must finally traverse (which may be estimated to be overall about 45 Å based on the dimensions of molecules).⁸ There is considerable interest in how the protein is organized to effect the remaining charge separation. One goal of our current research is to elucidate the amino acid arrangement along this proton "channel". Last year we used the tryptophan reactive reagent, N-bromosuccinimide, to demonstrate that one or two tryptophan residues were located in close proximity to the chromophore; however all four of the tryptophans in the molecule appear to be involved in photocycling activity since progressive loss of all tryptophan absorbance by N-bromosuccinimide coincided with progressive loss of activity.⁹

During the past year we have shown that at least one of the eleven tyrosines in the molecule was directly involved in the light dependent proton movement across the protein.⁵ Iodination was used to alter tyrosine residues which were accessible to this reagent. In analogy with the downward pK_a shift of iodinated tyrosine molecules in water, the kinetics of photocycling of iodinated bacteriorhodopsin were observed to undergo a downward shift in their pH dependence relative to the control protein. Of particular interest is the observation that the decay of the 412 nm intermediate became significantly prolonged during iodination (Fig. 2). Since it has been established previously that the 412 nm decay is due to re-protonation of the Schiff linkage of the chromophore, we have inferred that tyrosine is a source of the protons which are donated to the chromophore. These studies indicate that aromatic hydrophobic amino acids play an important role in maintaining a proper environment in the vicinity of the chromophore and elsewhere in the molecule to afford proton conductance.

Fig. 2. Effect of iodination on the pH dependence of the decay of the 412 nm photocycle transient of bacteriorhodopsin measured by the flash photolysis technique. (XBL 782-210)

Studies of the Proton Channel within Bacteriorhodopsin

We have assumed that the chromophore retinal fulfills the function of pumping protons in a light driven reaction and that the protons subsequently are conducted along a proton "channel" to reach the bulk aqueous phases. Another approach towards understanding the nature of this proton "channel" is to remove the chromophore and study the residual protein for proton conductivity.

The chromophore can be removed by a bleaching process whereby the retinal is displaced from the protein by illuminating bacteriorhodopsin in the presence of a large excess of hydroxylamine.¹⁰ It has been shown that this process is reversible, i.e. the light driven proton pump can be recovered upon addition of retinal to the bleached protein.

Using the above procedure bleached bacteriorhodopsin was prepared and added to lipid vesicles which were loaded with potassium and then suspended in sodium ion medium.¹¹ It is expected that negligible proton leakage will occur from these potassium-loaded vesicles since no permeability mechanism is presumed available for movement of ions other than protons. However, upon adding the potassium-specific ionophore valinomycin to the vesicles, a diffusion potential was established and resulted in electroneutral exchange of H^+ for K^+ ions. The addition of retinal to the bleached bacteriorhodopsin led to a substantial decrease in the proton movement. Thus the experiment suggests qualitatively that protons may be able to move through the bleached bacteriorhodopsin molecule in the dark. To obtain a measure of the capability of bacteriorhodopsin to promote proton fluxes, vesicles containing native bacteriorhodopsin were illuminated in the presence of valinomycin. The light-induced and the passive proton fluxes were comparable to one another.

Photoelectrical Studies

It has been shown that a photovoltaic cell can be constructed from bacteriorhodopsin incorporated into Millipore filter membranes.^{6,7} The filter membrane serves as a support for biological lipids which comprise the permeability barrier of the membrane. Bacteriorhodopsin was incorporated into the filter membranes by a multi-step absorption and fusion process. The current-voltage characteristics of the photocell were studied at high light intensity. A maximum open circuit voltage of 300 millivolts and a maximum short circuit current of 0.9 milliamp were obtained. Relative to the incident light intensity the power output of the cell was determined to be 0.07%. Under continuous high intensity illumination the activity of the cell declined, and no photovoltage could be observed after ninety minutes. One goal of future research is to improve the stability and efficiency of the photocell.

Conductance Studies

Planar membranes are a useful tool for discriminating between channel conductance mechanisms. Channels which are open intermittently can lead to discrete conductance jumps across lipid bilayer membranes provided that the opening and closing process is long enough to be observed. Using planar membranes painted across a small teflon orifice, we have attempted to obtain discrete conductance jumps when bleached bacteriorhodopsin was incorporated into the membranes. We incorporated bleached bacteriorhodopsin into such lipid bilayers by means of the calcium absorption and fusion technique which was developed earlier

for the Millipore filter system.⁶ Discrete conductances are indeed observed. Alterations in the concentrations of sodium, potassium or calcium did not significantly alter the conductance magnitude.

The principal conclusion to be drawn from these experiments is that bleached bacteriorhodopsin is not an open channel for protons or other ions when an electrical potential is applied across the membrane bearing the protein. However, at infrequent intervals an occasional bacteriorhodopsin molecule seems to open up to protons. We have attempted to define the mechanism whereby this channel opening occurs by varying the composition of the planar membranes and the aqueous phase so as to induce changes in the conductance jump frequency. Thus far the parameters we have found which affect the jump frequency are the concentration of bleached bacteriorhodopsin and the temperature. Another finding of interest was that such current fluctuations in the bleached molecule were only exhibited by ions having a similar hydrated radius as K^+ and Rb^+ , suggesting an effective "pore" radius of about 3-4 Å.

Surface Charge Effects in Illuminated Purple Membrane Sheets

Recently developed spin probe techniques for measuring surface potentials¹² were used to measure changes in electrical potentials at surfaces of purple membrane sheets under illumination. No change was observed in native purple patches suspended in distilled water, but when beauvericin and valinomycin, a mixture of two ionophoric compounds, i.e. compounds which conduct ions across membranes, was added to the sheets substantial changes in the spectra of the probe were observed suggesting that the electrical potential had decreased during illumination. The changes with the spin probe were observed under the same experimental conditions where a slowdown in the decay of the 412 nm photocycle intermediate and an increase in light induced proton release from purple membranes are observed¹³. This effect, however, may not be caused by the ionophoric properties of the antibiotics but by their tendency to disrupt the purple membrane as hydrophobic perturbants.

Computer Modeling

Knowledge of most of the amino acid sequence of bacteriorhodopsin from the work in Moscow⁴ has made it feasible to attempt construction of a molecular model of the protein. The electron density map with seven Angstrom resolution suggests that the molecule consists of nearly cylindrical array of seven helical coils with their axes oriented almost perpendicular to the plane of the membrane. Studies with digestive enzymes have shown that the amino terminus of the sequence faces the extracellular space while the carboxyl terminus lies within the cytoplasm. These factors imply that the seven helices are connected by six nonhelical regions at the membrane interfacial region.

The overall symmetry of the protein suggests that the helical regions are of nearly equal lengths. To identify the amino acids directly involved in the bend portions several criteria should be satisfied: polar or charged groups will be stabilized at the polar aqueous interface, and certain amino acids, particularly proline residues, interrupt alpha-helical structure. In addition it is known that bacteriorhodopsin is an intrinsic membrane protein so the majority of residues in the helical regions should be hydrophobic to promote their hydrophobic interaction with the hydrocarbon chains of lipids. Because the amino acid sequence contains eleven proline residues, it appears that there must be nonhelical regions of the protein imbedded within the protein as well as within the interfacial region. Moreover, the charged amino acids are distributed in a manner that is inconsistent with their exclusive location at the polar interface of the membrane. This suggests that some ionic bridges are located within the interior of the protein and that ionic bridges may be responsible for the protein interactions which stabilize the crystalline array.

Using the above criteria a preliminary model of bacteriorhodopsin has been constructed (Fig. 3). A space filling model constructed from plastic CPK atoms was used to estimate bond angles within the peptide backbone. These angles were fed into a computer which has been programmed for molecular model building at the NASA Ames Research Center.¹⁴ At present only the graphic capabilities of the Ames program are being utilized to examine some of the probable conformations of the protein. In the future we

Fig. 3. Photograph of the three dimensional spacefilling model of bacteriorhodopsin assembled from the amino acid sequence of Ovchinnikov *et al.*⁴ The model shows the distribution of aromatic tryptophan and tyrosine residues in the vicinity of the retinylidene lysine chromophore (marked with two light parallel strips of tape). The view is of the interior of the bacteriorhodopsin molecule and shows four of the seven helices.
(BBC 7810-13516)

intend to carry out energy calculations for the more probable conformations so as to eliminate some of them from consideration. A particular goal of these studies is to understand protein conformational changes that can result from the possible photo-isomerizations and rotations of the chromophore. A further goal is to identify which amino acids are directly involved in protein conduction.

Photodesalination Studies with Cell Envelopes of Halobacterium Halobium

Ion movements across cell envelope vesicles of *H. halobium* are being assayed with a newly developed spin probe method. The method uses spin labeled amines (see Fig. 4) or carboxylic acids to monitor transmembrane pH gradients.¹⁵ The basic assumption is that pH gradients are achieved rapidly due to the limited buffering capacity within the vesicles. Subsequent proton movement across the membranes in response to this gradient must be balanced by the movement of other ions (Fig. 1). The secondary ion movements result from an exchange mechanism whereby a cation moves in one direction while a proton moves in the opposite direction. The pH gradient is coupled to the development of a Na^+ gradient which can be observed with the spin probes. As shown in Fig. 4, a rapid initial H^+ extrusion is followed by a reversal of the proton movement when sodium ions are present within the cell envelopes. The interpretation of this experiment is that there is a proton-sodium exchange mechanism in the membranes which allows protons to move into the vesicles and sodium ions to move out, and that this mechanism is only triggered after a threshold value of the initial proton gradient has been achieved.¹⁶ As depicted in Fig. 1, the extrusion of sodium ions is compensated for by potassium ion uptake (and chloride ion efflux, depending on the concentration of potassium ions added).

PLANNED ACTIVITIES FOR 1979

Chemical and electrical studies will be continued with the objective of detailing the mechanism of H^+ conduction and the importance of localized electrical changes in improving the photovoltaic effect of bacteriorhodopsin. Photodesalination studies will also be continued.

Chemical Studies

The special role of one of the eleven tyrosines of bacteriorhodopsin in light dependent proton conductance will be studied further using tyrosine-specific reagents. Proton conductance by bleached preparations will also be studied. Lactoperoxidase, an enzymic method for iodination, should only label surface exposed to tyrosines. This procedure inhibits photocycle activity, and we shall explore its significance for light dependent proton conduction and conduction of protons in bleached preparations in the dark.

Modification of amino groups of lysine have previously shown that loss of 80% of these groups does not inhibit H^+ conduction per se unless they are cross-linked together within the molecule.

Fig. 4. Light-induced proton release from *H. halobium* cell envelopes loaded with sodium ions, assayed with the spin-labeled amine, Tempamine. The probe distributes across the membrane in direct proportion to the proton concentrations. Quenching of the signal outside the vesicles with ferricyanide allows the intra-vesicle signal to be observed. In the first trace of the line height with time, a delay in proton extrusion is observed as sodium ion movement allows protons to reenter the vesicles. On subsequent illumination rapid efflux of protons is observed since no sodium is left within the vesicles. (XBL 791-3011)

One of the amino groups in the interior has not yet been probed. Also the amino group where retinal binds can be probed. We intend to use imidoesters to attack in bleached molecules the amino groups at the retinal binding site. These studies together with spin label analogs of retinal will be used to explore the environment of the chromophore which is optimal for proton conduction.

We will subject the purple membrane fragments to the action of proteolytic enzymes. It has been shown that the protein can be fragmented when heated with papain and other proteolytic enzymes. These studies will help to determine which portions of the molecule are essential for proton conduction energized by light and for

conductance of protons through other regions of the molecule. Computer assisted modeling of the protein structure will aid the interpretation of these experiments.

Electrical Studies

The analysis of light dependent surface charge changes will be pursued by the use of a unique charged spin-labeled amphipathic molecule.¹² These studies will enable us to obtain, in purple membranes and in the native envelope vesicles of the membrane, information on a number of interesting questions, including how localized regions of charge control proton conduction; how salts affect surface charge; how localized surface charges changes on each membrane surface affect

the development of the membrane potential; and how, together with pH gradient, electrical forces provide the proton motive force for salt transport.

Construction of an improved photovoltaic device will be continued. We intend to use several membranes, including Teflon, and plan to change the manner of membrane formation to increase efficiency and reduce susceptibility to photo-degradation. Intermolecular chemical cross-linking studies will be pursued to determine if molecules after being chemically crosslinked in the purple membrane exhibit improved stability against photodestruction.

West German researchers have shown that at low light intensities the number of protons released per photon increases. This cooperativity may depend on the aggregated state of bacteriorhodopsin. Using newly developed techniques of saturation transfer EPR which gives information on the rotational mobility of spin labeled proteins, we will try to correlate the state of aggregation of bacteriorhodopsin with this cooperative effect.

Photodesalination Studies

We will employ the recently developed spin label Tempamine assay to further characterize the requirements for light dependent proton transients across envelopes of *H. halobium* coupled to sodium transport. We shall also develop an artificial liposome system containing the Tempamine probe, to test those fractions isolated from natural membranes with suspected sodium antiporter activity. Sodium specific and other specific artificial ion carriers will be employed as controls. These studies will enable us to develop some simple models of a photodesalination system. We hope to develop a planar membrane photodesalination device which can operate on a continuous flow basis.

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*This work has been supported by the Division of Basic Energy Science, Office of Energy Research, U.S. Department of Energy.

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Chemical Storage of Thermal Energy*

A. S. Foss and S. Lynn

INTRODUCTION

Economical energy storage is essential if solar power plants are ever to supply a significant fraction of the needs of a power grid. The purpose of this study is to develop flow-sheets for technically feasible and efficient processes for the use of the sulfur oxide system,

in energy storage. The forward reaction for this system is endothermic and can be used to absorb energy. The reverse reaction is exothermic and releases the energy that has been stored.

Funding for this work was initiated in November, 1975. During calendar year 1977 the major effort in the project was in flowsheet development. The major factors affecting system efficiency were identified and the primary factors causing energy losses were made the subject of further study.

ACCOMPLISHMENTS DURING 1978

Chemical Storage

This year has seen the completion of the computer simulation of the storage process as shown in Fig. 1. Liquid sulfur trioxide from storage is pumped to 40 atm, vaporized and heated by the reactor effluent in the recuperator HE-1. The reactor tubes are mounted in a solar receiver. The interior tube walls are coated with a suitable catalyst such as iron oxide.

Upon exiting the reactor, the gas exchanges heat with the reactor feed and then heats the reboiler of the distillation column. The gas is further cooled to condense SO_2 and unreacted SO_3 , and is then stored. The SO_2 - SO_3 liquid is distilled; SO_3 is recycled to the solar reactor and the SO_2 is stored as a liquid until needed.

Heat for the vaporization of SO_3 is obtained from extraction steam from the parallel steam-cycle power plant. Part of the cooling of the reactor effluent, on the other hand, is used to preheat boiler feed water for the power plant. This integration is intended to maximize the energy efficiency of the system.

Energy is recovered from storage by recombining the SO_2 and O_2 . Liquid SO_2 is vaporized, added to the O_2 stream, and heated to a temperature high enough to activate the catalyst, about 400°C . As reaction proceeds the temperature rises until the equilibrium composition is reached. The hot gas stream then passes through heat exchangers, forming superheated steam for the power plant. Three reactor

stages are needed to convert about 97% of the SO_2 and O_2 back to SO_3 . The SO_3 vapor then exchanges heat with the feed gas, and is condensed in the SO_2 vaporizer.

High-Temperature Reactor

Figure 2 shows typical temperature and composition profiles for a single tube of the solar-heated reactor. In this example about 75% of the energy flux through the tube wall is absorbed by the endothermic reaction and the remainder increases the sensible heat of the gas stream. The bulk temperature of the gas stream closely approaches the tube wall temperature at the outlet end, whereas the outlet bulk SO_3 conversion is significantly less than the conversion at the wall, which is assumed to be at equilibrium. Mass transfer is thus shown to be the limiting factor for this case.

Energy Efficiency

The overall second-law efficiency of the process is simply the sum of the net electrical outputs from operation of the daytime power plant and of storage divided by the sum of the thermal inputs to the power plant and the storage reactor:

$$E_{OA} = \frac{P_{\text{Day}} \cdot \theta_{\text{Day}} + P_{\text{Sto}} \cdot \theta_{\text{sto}}}{(Q_{\text{PR}} + Q_{\text{SR}}) \theta_{\text{Day}}}$$

where

P_{Day} = Net power produced by daytime power plant (MW_e)

P_{Sto} = Net power produced from storage (MW_e)

θ_{Day} = Duration of daytime operation (HR)

θ_{Sto} = Duration of storage discharge operation (HR)

Q_{PR} = Rate of thermal input to power plant receiver (MW_t)

Q_{SR} = Rate of thermal input to storage receiver (MW_t)

Low- and intermediate-temperature heat is exchanged between the power plant and the storage system. The power plant efficiency is defined arbitrarily as

$$E_{PP} = \frac{P_{\text{Day}} \cdot \theta_{\text{Day}}}{(Q_{\text{PP}} + Q_{\text{BFW}} - Q_{\text{VAP}}) \theta_{\text{Day}}}$$

Where

Q_{BFW} = Rate of heat transfer to boiler feed water (MW_t)

Q_{VAP} = Rate of heat transfer to SO_3 vaporizer (MW_t)

(a)

DAYTIME OPERATION SCHEME (CHARGE MODE)

MAIN STREAM DATA - SULFUR (S) SYSTEM								MAIN STREAM DATA - WATER (W) SYSTEM							
Stream	S-1	S-2	S-3	S-4	S-5	S-6	S-7	Stream	W-1	W-2	W-3	W-4	W-5	W-6	W-7
Flow (kmole/sec)	1.94	5.76	6.72	1.06	5.66	1.84	3.82	Flow (kg/sec)	287	426	426	374	374	287	66
Composition* (mole%)								Temperature (°C)	140	243	538	316	538	349	427
SO ₂	1.0	1.0	28.7	8.2	32.1	99.0	1.0	Pressure (bar)	4	208	167	37	33	8	15
SO ₃	99.0	99.0	56.8	1.2	67.9	1.0	99.0	State (W-water; S-steam)	W	W	S	S	S	S	S
Temperature (°C)	90	700	800	40	108	55	104								
Pressure (bar)	10	40	40	40	40	10	10								
State (L-liquid; G-gas)	L	G	G	G	L	L	L								

*Oxygen content makes the balance.

XBL 774-8394

(b)

NIGHT TIME OPERATION SCHEME (DISCHARGE MODE)

MAIN STREAM DATA - SULFUR (S) SYSTEM										MAIN STREAM DATA - WATER (W) SYSTEM						
Stream	S-1	S-2	S-3	S-4	S-5	S-6	S-7	S-8	S-9	Stream	W-1	W-2	W-3	W-4	W-5	W-6
Flow (kmole/sec)	0.96	0.53	1.50	0.80	0.26	1.06	1.00	0.007	0.993	Flow (kg/sec)	24	29	29	26	26	24
Composition* (mole%)										Temperature (°C)	140	243	538	316	538	349
SO ₂	99	8.2	66	11	11	11	1.3	1	1.4	Pressure (bar)	4	208	167	37	33	8
SO ₃	1	1.2	1	83	83	83	98	9	98.6	State (W-water; S-steam)	W	W	S	S	S	S
Temperature (°C)	55	40	500	600	600	350	400	40	90							
Pressure (bar)	10	40	10	10	10	10	10	10	10							
State (L-liquid; G-gas)	L	G	G	G	G	G	G	G	L							

*Oxygen content makes the balance.

Fig. 1. Flowsheet for chemical storage of thermal energy.
(XBL 774-8393)

Fig. 2. Temperature and composition profiles in solar reactor. (XBL 7811-13306)

The thermal storage efficiency is defined as the ratio of usable heat delivered by the storage system to the heat input to the storage system

$$E_{TS} = \frac{\sum Q_{Sto} \cdot \theta_{Sto}}{(\dot{Q}_{SR} + \dot{Q}_{VAP} - \dot{Q}_{BFW}) \theta_{Day}}$$

where

$\sum Q_{Sto}$ = Sum of rates of heat transfer to power plant system from storage discharge (MW_t)

Sensitivity Analysis

Figure 3 shows the effect on E_{QA} , E_{pp} , and E_{TS} of the maximum allowable tube-wall temperature, $T_{W \max}$. As this temperature is increased a larger fraction of the SO_3 can be converted to SO_2 and O_2 . As a result, a larger fraction of the heat absorbed by the gas stream results in chemical reaction and a smaller fraction increases the sensible heat of the gas. The ratio Q_{PR}/Q_{SR} drops with increasing $T_{W \max}$ because a smaller stream of SO_3 is needed to absorb the heat in the solar reactor and hence there is less heat to transfer to boiler feed water. E_{QA} increases slightly and E_{TS} increases substantially because there is relatively less low-temperature heat to dissipate to the environment per unit of chemical heat stored.

The maximum tube-wall temperature is only one of the system parameters being studied. The sensitivity of the system behavior has also been determined for variations in the solar reactor pressure, the temperature rise in the reactor, and the temperature at which heat can be rejected to the environment.

Sensible-Heat Storage

For purposes of comparison with chemical-heat storage, a sensible-heat storage system

Fig. 3. Effect of maximum allowable tube wall temperature on system performance. (XBL 7811-13307)

was designed for use with a steam cycle power plant. The system utilizes a checker-work of magnesia brick. A heat-transfer medium such as helium or nitrogen is circulated through the solar receiver to bring heat to the power plant superheater, reheater, and boiler. The storage system is placed between the receiver and the power plant heat exchangers. It cycles between the temperatures of about 816° and 327°C. In this way the energy stored loses little effective thermodynamic potential since it is at all times hotter than the highest temperature in the steam cycle. The behavior of this system has been simulated by computer; the flowsheet is being compared in cost and energy efficiency to the chemical storage system. The use of pre-stressed cast iron vessels to contain the magnesia bricks appears to offer attractive cost advantages.

PLANNED ACTIVITIES FOR 1979

As was also recognized by Carl Hiller of Sandia Laboratories, a typical chemical energy storage system can be utilized in an unusual thermodynamic cycle.¹ In such systems the endothermic reaction yields an increase in the number of molecules. The hot gas from the reactor can thus be expanded through a gas turbine with a high yield of work. After the gas stream is cooled it can be recompressed. Interstage cooling causes condensation, thus reducing the work required to reach storage pressure. Discharge of storage can also be

effected with a gas turbine. The gas is preheated before entering the first-stage reactor, where it attains a temperature approaching that in the dissociation reactor. It is then expanded through the gas turbine and is thereby cooled. Passage through the second- and third-stage reactors provides the heat required to preheat the first-stage reactor feed. A flow-sheet for this energy system is being simulated by computer to allow evaluation of the system's potential. This will be the primary activity on chemical storage systems in 1979.

Support for Commercial Solar Demonstration Program*

S. Peters, F. Salter, T. Webster

INTRODUCTION

The Solar Applications Group at LBL provides technical consulting and management services to support the DOE San Francisco Operation Office's (DOE/SAN) overall management of commercial-building solar demonstration projects and hotel/motel hot water solar projects located throughout the Northwestern States and Hawaii. These projects are part of the National Solar Heating and Cooling Demonstration Program,¹ whose primary objective is to stimulate a solar industry and to promote the use of solar energy as a means of reducing demand on conventional fuel supplies.

The group is currently involved in support for projects in this program as follows:

<u>Projects</u>	<u>Program solicitation</u>	
1	NSF-1	Cycle I
15	DSE-76-2	Cycle II ²
17	PON 4200	Cycle III ³
3	PON 1450	Hotel/Motel ⁴

A detailed description of activities of this group is contained in the E&E Division Annual Report for 1977.

ACCOMPLISHMENTS DURING 1978

During 1978 activities continued on Cycle II and Hotel/Motel projects and work commenced on seventeen additional Cycle III projects. As of the end of the year, construction was complete and operation initiated on six Cycle II projects and one Hotel/Motel project. One Cycle II and four Hotel/Motel projects were cancelled primarily due to project participant funding problems. All other projects were either near completion or still being designed or bid. Two of the Cycle III projects are currently under construction with the remainder in the design stage. In addition to other activities, LBL was requested to assist with field checkout of the IBM monitoring instrumentation system of those projects where the system

FOOTNOTES AND REFERENCES

*This work has been supported by the Energy Storage Division, Office of Energy Technology, U.S. Department of Energy.

1. J. Dayan, et al, "A New Power Cycle that Combines Power Generation with Energy Storage," 13th Annual IECEC. San Diego, CA Vol. I, 285-291 (1978).

installation was completed. As of year's end, instrumentation installation and checkout is complete on only two of the Cycle II projects.

During startup and initial operation of most of the completed systems, a number of difficulties were encountered. The most frequent problem was with controls, i.e., sensor failures, erroneous wiring, and incorrect logic. Other problems encountered were storage tank over-pressurization, damaged or poorly installed piping insulation, corrosion failure, snow and ice accumulation on collectors (resulting in some damage to collector and flashing strips and shading of the array), and excessive leakage in one air system. All of these problems have been or are currently being resolved by the contractors.

PLANNED ACTIVITIES FOR 1979

During the remainder of FY 1979, activities of this group will continue at current level of effort (3 men). However, LBL has been directed by DOE to curtail activities in this area; involvement in currently assigned projects is to be reduced to the level of one man. It is expected that all LBL activity in this program will cease after FY 1980.

FOOTNOTE AND REFERENCES

*This work has been supported by the Solar Heating and Cooling Demonstration Branch, Office of Conservation and Solar Applications, U.S. Department of Energy.

1. National Program for Solar Heating and Cooling of Buildings, ERDA 76-6, November 1976.
2. Commercial Integrated Projects for Use in Demonstrations of Solar Heating and Cooling, PON DSE 76-2, ERDA, 1976.
3. Commercial Integrated Projects for Use in Demonstrations of Solar Heating and Cooling, PON EG-78-N-01-4200, DOE, 1978.
4. Hot Water Initiative for Hotel/Motel Installations, PON EG-77-N-03-1450, ERDA, 1976.

LBL Solar Demonstration Project (Building 90)*

T. Webster

INTRODUCTION

The building 90 solar demonstration project is one of eleven projects selected to be part of the FY 1977 Department of Energy (DOE) Facilities Solar Demonstration Program, a pilot program for the Solar Federal Buildings Program recently authorized by the National Energy Act. The objectives of this pilot program are to establish procedures and techniques for assessing and implementing solar systems for federal facilities, and to assist in energy reduction within DOE facilities.

The following criteria were used to select projects for this initial program:

- Buildings should be suitable for retrofitting; i.e., possess orientation, location, and configuration amenable to solar.
- Solar space and hot-water heating should be emphasized.
- Buildings should be typical government buildings.
- Design and construction should not cost more than \$200,000.

The LBL project is funded by the DOE division of Solar Energy through the Construction, Planning, and Support Division. LBL Plant Engineering is responsible for design and construction of the project with assistance provided by the LBL Solar Group. A detailed description of the building and preliminary and final design considerations is contained in the 1977 Energy & Environment Division Annual Report.

ACCOMPLISHMENTS DURING 1978

In order to facilitate completion of the system design the collectors were pre-bid in early 1978. A life cycle costing procedure was used to evaluate and select the collector. A Sunworks, single-glazed, black chrome collector was selected. This collector has the advantage of utilizing factory supplied, pre-sized balancing orifices in the manifolds which will allow 17 collectors in each row to be internally manifolded together. This arrangement results in significant piping savings of about \$1/sq.ft. of collector (SF_C). After the collectors were selected the support structure was redesigned and other system details completed. Prefabricated collector supports were ruled out since they were not feasible for this application. Two pumps were included for the collector loop to provide redundancy in the event of a pump

failure. Figure 1 is a schematic of the final design.

Bids for the system installation were received in July. These bids ranged from a high of \$137,000 ($\$110/SF_C$) to a low of \$79,000 ($\$63/SF_C$). An alternate bid for one row of on-site constructed collectors was eliminated due to high cost, \$12/ SF_C more than for the commercial collector rows. This indicates that there is no advantage in using on-site constructed collectors in this type of project. However, the extra cost for the on-site constructed collectors, as shown by the bids for this one row probably is not a realistic indication of what an entire array of these collectors would cost.

A contract was awarded to the low bidder and construction of the system commenced in August. By year's end only one major problem had occurred: the collector support structure roof penetrations did not seal well resulting in substantial leakage during a storm (occurring two months before the rainy season). The leaks were traced to an incompatibility between the roofing mastic and the elastomeric roof jacks. The roofing contractor was unaware of this problem until it occurred here and the roofing materials manufacturer is researching the problem. The problem has been temporarily corrected, but further work is anticipated.

By year's end the system installation was about 50% complete. Design of the monitoring instrumentation system was completed and instruments were ordered from IBM (the DOE instrumentation contractor). Further work on modeling system performance with the DOE-1 computer program indicates that initial estimate of annual solar performance of 33% may have been high and actual performance may be closer to 23%.

PLANNED ACTIVITIES FOR 1979

System installation should be complete in early 1979. The instrumentation system and peripheral items such as walkways and observation platform and stairs should be complete by Spring 1979. Further analysis with the DOE-2 computer program will be made to obtain a better estimate of annual system performance.

FOOTNOTE:

*This work has been supported by the Solar Heating and Cooling Demonstration Branch, Office of Conservation and Solar Applications, U.S. Department of Energy.

Fig. 1. Bldg. 90 solar retrofit piping and control schematic.
Engineering Drawing 4B90-P043-B

Energy Efficient Buildings

Building Envelopes Program

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INTRODUCTION

Residential and commercial buildings account for one-third of the U.S. total energy use; of this, roughly 60% goes for space heating and air air conditioning.¹ This energy is lost through the skin, or envelope, of the building, by both conduction and air infiltration. Conductive losses (about 2/3 to 3/4 of the 60%) occur through the windows, walls and roof of the structure, while air infiltration (about 1/4 to 1/3 of the 60%) occurs through cracks in the walls, around doors, windows, fireplaces, or any other opening in the building envelope. To understand the nature of these heat losses, it is necessary to systematically study not only individual components, but the energy performance of the building as a whole.

The Building Envelopes Program was established in April 1977 as part of LBL's broad-based study of energy conservation in buildings. The primary objective of the program is to provide information for a fundamental understanding of the thermal operation of a residential building. Such an understanding, in turn, will lead to the recommendation of energy-conserving construction guidelines and standards for new buildings.

Three projects are currently underway: the first studies the mechanisms of air infiltration in buildings, the second examines heat transfer through exterior walls, and the third project determines efficiencies of fireplaces and their related accessories. Common to all three of those projects is the development of portable instrumentation for making these measurements in a wide range of houses and climates.

During the initial period of program activity, techniques were developed for measuring and modeling air infiltration in houses and heat losses in walls. Concurrent with this work was the preparation of an annotated bibliography on air infiltration in buildings.^{2,3} By the end of 1977, a house had been rented in Walnut Creek, California, and to the bewilderment of the neighbors, the experiments began.

The Research House, located twenty miles to the east of LBL, was selected because of its typical wood frame construction and location in a region which had a larger climatic variation than the Bay Area. The plan of the building is shown in Fig. 1. Built in 1964, it is a one-story, three bedroom structure, with a central forced-air gas heating and air conditioning system having air supply ducts in the crawl space, and the return duct in the attic.

Fig. 1. Plan of Research House. (XBL 788-1537)

While the Research House is used primarily for experiments, it has also proved valuable as a working classroom for high school and college instructors, as well as numerous foreign visitors. With the completion of the experiments, the house will be super-retrofitted and then monitored for reduced energy consumption. The results of the Research House experiments will be published in a form useful to homeowners who are planning to undertake conservation retrofit measures.

AIR INFILTRATION STUDIES

Air infiltration is the uncontrolled leakage of air into a building. It is the result of pressure differences between the interior and exterior of the building which are caused by the wind and by indoor-outdoor temperature differences.

Good indoor air quality in houses requires at least one half air changes per hour (ach); some sources even recommend 1 ach. The yearly heat loss associated with 1 ach in a typical house in a climate as severe as Chicago is about 13,000 kWh_t/yr (450 Therms/yr), costing about \$100/yr. Electric heating (instead of fossil fuel) would more than double this extra fuel bill.

Two strategies are possible to save energy and dollars caused by air infiltration. The first is to tighten the envelope (through caulking, weather-stripping, etc.) to reduce the infiltration rate to 0.5 - 1 ach at typical weather conditions. This strategy is most suitable for existing housing, where air infiltration rates may be well in excess of 1 ach. In new construction, the envelope can be made tight enough to reduce the infiltration rate to about 1/4 ach, as presently done in Sweden. To overcome the health hazards associated with such low rates, mechanical ventilation coupled with heat exchangers can provide for sufficient fresh air without excessive heat loss. Both indoor air quality standards and residential heat recovery devices are part of the Energy Efficient Buildings Program. Those projects are described elsewhere in this report. Our Envelopes group is concerned with measuring, modeling and reducing air infiltration rates. Research in this area is divided into three sections: 1) develop instrumentation for the accurate measurement of air infiltration rates. 2) correlate air infiltration data and air leakage data taken when the structure is deliberately pressurized, and 3) test and evaluate the effective measures for reducing air infiltration. After developing experimental procedures at the Research House, a survey of several houses was carried out to determine the applicability of the tests to other houses.

Accomplishments During 1978

An automated controlled flow tracer gas technique for measuring air infiltration was first tested in the Research House in February, 1978.⁴ Infiltration rates of up to two air changes per hour were measured using nitrous oxide (N₂O) as the tracer gas. In May, an intercomparison of tracer gases was conducted by Honeywell, Princeton University, and LBL.⁵ Simultaneous measurements of air infiltration rates were taken at the Research House, using methane, sulfur hexafluoride, nitrous oxide, and ethane. The close agreement among the various methods facilitated the design of multi-chamber experiments, in which the coupling of air flows between house, attic, and crawlspace are measured with three different tracer gases.

A weather tower mounted on the roof of the house records local wind speed and direction and outdoor air temperature. These data show little correlation to the air infiltration rates as measured in the house. The lack of correlation is not surprising since the weather data is measured ten meters above the ground and the house is heavily shielded by trees and fences. An array of surface pressure taps has been mounted on the exterior surfaces of the house, in an attempt to understand more closely the

micro-climate effects. A micro-processor samples sixteen taps in sequence, averaging pressures for one minute at each tap. These data show that small pressure fluctuations on all sides of the house ranging from -1 to +1 Pascals (about $\pm 10^{-5}$ atmospheres) are an important mechanism driving air infiltration. We have developed a model which predicts air infiltration based on these surface pressures and on the air leakage curve of the structure (Fig. 2).

Air leakage is measured by a simple and inexpensive technique in which the entire house is pressurized by a high-capacity blower, temporarily sealed into an exterior doorway. By adjusting the flow rate through the fan, a standard pressure difference between the interior and exterior of the building shell is determined; we are taking measurements in a range of -75 to +75 Pascals. Knowing the flow rate through the fan into the house, mass flow continuity gives the air flow through the cracks and openings of the building's exterior surfaces. We use smoke sticks during the test to locate leaks. Qualitatively, houses with air leakage rates show low air infiltration rates, but specifying the relationship is more difficult. The uniform pressures established by the fan blower are not directly analogous to the non-uniform surface pressures which drive natural infiltration. Determining the relationship between air leakage and air infiltration is important for energy conservation, as it allows a simple technique to measure the large heat loss due to air infiltration. In addition, the blower technique could assess the maximum permitted air leakage in new buildings if such a construction quality standard is established.

Fig. 2. Pressurization curves for Research House. Solid line is with heating ducts open, dashed line is with ducts sealed. (XBL 7810-6630)

Using our model of air leakage and surface pressures, we look at the low pressure region of the air leakage curve and find the air flow for typical values of the measured surface pressures (Fig. 3). We are extending the tests to several additional houses, with different shielding patterns, and in different climates.

Fig. 3. Infiltration rates as a function of average surface pressures on the house. The solid line is the prediction of the simple infiltration model; the dashed line, the fit of the data.
(XBL 7810-6629)

Planned Activities for 1979

The work in 1979, in addition to continuing this year's investigations, will take several new directions. Wind tunnels will allow us to study the shielding effects of trees and adjacent buildings on surface pressures, furthering our understanding of the effects of wind on air infiltration rates.

A major effort will be in the continued collaboration with the International Energy Agency (IEA) in coordinating pressurization and infiltration research in the member countries.

One of the first projects will be the establishment of an international data base for air infiltration at the Infiltration Data Management Center in Great Britain.

An important goal will be disseminating our results to a wide audience. We hope to develop more suitable infiltration algorithms for computer modeling of building energy use. We are developing techniques for measuring construction quality in new houses, and will examine the possibilities for establishing guidelines to assist architects and builders in producing tighter building construction.

Also, we will provide the Ventilation Group with updated instrumentation to measure air infiltration for their air quality studies, and will collaborate with them on a project to study the effectiveness of air-to-air heat exchangers at the Research House.

THERMAL PERFORMANCE OF WALLS

The thermal performance characteristics of actual building walls are largely unknown. Even though they may be well designed, variation in construction methods and aging of materials can result in a substantial variation in wall thermal performance. Where measurements have been made in actual buildings, the thermal resistance of the walls is often 20% to 30% less than what would be expected from laboratory measurements and standard calculations. Recommendations for building and planning for energy conservation should be based on what actually happens in buildings rather than on largely unverified inferences from laboratory measurements and computer models.

Accomplishments During 1978

As in the infiltration work, an initial effort was the compiling of a comprehensive annotated bibliography on performance measurements of building walls.⁷ The first experiments were of two types: one measured the air leakage through the wall using a tracer gas technique, the other measured wall thermal resistance using an array of thermometers and heat flux sensors mounted on both sides of the wall. Working in the northeast corner of the house in order to avoid direct sunlight on the wall, thermal resistances were measured both through the studs and through the adjacent insulated cavity. The measured average thermal resistance across the cavity was 40% less than what was expected on the basis of standard calculations using handbook methods, possibly due to the aging of the 15-year-old fiberglass insulation.⁸ We will pursue this further in 1979. Experience from these preliminary experiments showed that our technique is not very practical and is highly dependent on a constant outdoor temperature. A different approach was then developed using a new device, the Envelope Thermal Testing Unit (ETTU).⁹

ETTU is designed to make in-situ measurements of dynamic and steady-state heat transfer in walls. The device consists of surface heaters

applied on both sides of the wall to be tested. The analysis will determine experimentally the "admittances" of the tested walls. The admittances are frequency-dependent and govern the transient heat conduction through the wall as expressed by the following matrix equation:

$$\begin{pmatrix} \phi_1 \\ \phi_2 \end{pmatrix} = \begin{pmatrix} Y_1 & -Y_m \\ -Y_m & Y_2 \end{pmatrix} \times \begin{pmatrix} T_1 \\ T_2 \end{pmatrix}$$

where ϕ_1, ϕ_2 are the Fourier-Transforms of the heat flux into both surfaces (1 and 2) of the wall;

T_1, T_2 are the Fourier-Transforms of the temperature at both sides of the wall;

Y_1, Y_2 are the admittances into the two surfaces

Y_m is the mutual admittance coupling the two surfaces.

The frequency-dependent admittances define uniquely the thermal response of a wall. To determine them experimentally, we drive both wall surfaces with time-varying heat fluxes with a uniform frequency spectrum (white noise). The surface temperature response is Fourier-analyzed by an on-line microprocessor, yielding all admittances. A prototype ETTU is presently under construction (Fig. 4).

The Envelopes group was a major contributor to a collaborative effort with ORNL, NBS, and DOE in developing a National Program Plan for Building Thermal Envelope Systems and Insulating Materials.¹⁰ The National Plan is part of the Federal Government's effort to further research and technology transfer in the area of building envelopes.

Planned Activity for 1979

The main focus of the walls program will be in the continued development and use of ETTU in the Research House and in the survey houses. ETTU results will be compared to those from non-portable laboratory measurement apparatus for wall performance evaluation.

FIREPLACE TESTING

Like any combustion heater, a fireplace is an appliance that converts the chemical energy in a fuel into useful heat delivered to the dwelling. Unlike other heaters, however, a fireplace delivers fuel energy to the room primarily through radiation from luminous gases and incandescent embers, with little gain from convection.

The higher heating value (HHV) of wood is typically 5.56 kWh/kg (8,600 Btu/lb).¹¹ A typical good-sized fire consumes hourly 5 to 6 kg of wood releasing heat at a rate of about

30 kW (appr. 100,000 Btu/hr). Most of this heat is lost up the chimney. The gross efficiency of a fireplace is defined as:

$$\epsilon_{\text{gross}} = \frac{(\text{heat delivered to dwelling})}{(\text{HHV of fuel})}$$

The best fireplaces have gross efficiencies of only 20%.

The operation of an open fireplace sucks warm room air up the chimney, causing additional outside air to infiltrate the dwelling, above and beyond the normal infiltration caused by wind and temperature differences. The amount of heat necessary to warm the additional infiltrated air should be subtracted from the heat delivered to the dwelling by the fireplace. This leads to the definition of net efficiency:

$$\epsilon_{\text{net}} = \frac{(\text{heat delivered to dwelling}) - (\text{heat to warm additional infiltrated air})}{(\text{HHV of fuel})}$$

Figure 5 illustrates typical values of fuel energy paths when an open fireplace is operated on a cold day. After subtracting the air leakage debit from the radiant heat gain, it can be seen that in particularly unfavorable circumstances the net efficiency of a fireplace can actually become negative!

We used gas burners rather than wood logs for our initial testing since it is difficult to control the rate of fuel consumption in a wood fire. Four 15 cm diameter gas burners are arrayed in a row about 0.7 m long, to produce a luminous flame with power ranging up to 47 kW (160,500 Btu/hr), measured by a separate gas meter on the domestic gas supply. These burners yield a luminous flame which looks much like the flame of a wood fire.

To determine the useful amount of heat that reaches the dwelling, we heat the house electrically and determine how much less electric power is needed when the fire is burning than when it is not. During the test, the house temperature is maintained at about 25°C (77°F) by thermostatically controlled radiant heaters placed above the fireplace and by small electric heaters with fans (approximately 1.5 kW per room) distributed throughout the dwelling. They are run for several hours before and after igniting the fire, in order for the house to reach thermal equilibrium. The electric power consumption of the heaters is measured by four watt-hour meters as well as by the house meter which also registers any other useful electric power, such as the heat generated by lights and refrigerator. This technique, called electric co-heating, measures the trade-off between electric heating decrease and the heat supplied from any heating appliance. We use this method to measure the combined effect of the radiant heat gain from the fire and the heat loss from additional air infiltration caused by the chimney draft.

Fig. 4. Interior and exterior views of ETTU, and cross section of wall sandwiched between ETTU units.
(XBL 7812-13357)

Fig. 5. Fireplace Energy Balance, Typical Net Efficiency: -10% to +15%. (XBL 7812-13355)

We measure independently both the heat loss through the chimney and the heat lost by fire-induced extra air infiltration. To do this, the house air temperature is monitored with 20 solid-state temperature sensors distributed throughout the inside and outside of the house. The temperature of the gas in the chimney is monitored with an array of 5 thermocouples in parallel. The volumetric air flow rates into the house from outside and up the chimney must be measured separately. Both flow rates are measured by the tracer gas technique: ethane and nitrous oxide are introduced at known flow rates into the house air and the chimney base, respectively. Their concentrations are separately sampled with commercially available infrared analyzers. The ethane is injected at four locations throughout the house and mixed with the air by operating the fan in the furnace continuously. The resulting ethane concentration is sampled in the return air duct. The exhaust gas flow up the chimney is found by injecting nitrous oxide at a location about one meter above the flame and measuring its concentration about 0.3 meters below the chimney exit. In both cases, the air flow rate is the quotient of tracer gas injection rate divided by tracer gas concentration.

The results of a typical six-hour run for testing fireplace efficiency are shown in Fig. 7a and 7b. The run is divided in three

Fig. 6. Measurement Apparatus for the Fireplace Experiment. (XBL 7812-13356)

Fig. 7a. Electric Heating and Air Infiltration for Regular Fireplace Operation. (XBL 7812-13358)

* Air infiltration in kW evaluated using temperature difference from Fig. 7b.

Fig. 7b. Indoor and Outdoor Temperatures for Regular Fireplace Operation. (XBL 7812-13358)

periods: before, during, and after fireplace operation. The electricity consumption needed to maintain a constant temperature is plotted in the form of 40 minute averages. The graph shows an average 781 watt decrease while the fireplace was operating at 46,450 watt. The net efficiency is thus:

$$e_{\text{net}} = \frac{781\text{W}}{46,450\text{W}} = 1.7\%$$

The air infiltration in the three periods is plotted in units of heat loss rate in the same figure, and shows a doubling during fireplace operation. The resulting increase in heat load, indicated by the shaded area in Fig. 7a, is 1,025 watt. Without this loss, the gross fireplace efficiency would be:

$$e_{\text{gross}} = \frac{1,025 + 781}{46,450} = 3.9\%$$

Had the damper been shut before and after fireplace operation, the air infiltration debit would be even larger, and the net efficiency correspondingly smaller. With the damper closed, but everything else unchanged, the air infiltration rate would be about 0.6 ach, causing a 1,427 watt extra infiltration debit and a 0.8% net efficiency. More severe weather, colder than the relatively mild night in this run, would further reduce the efficiency to a few percent below zero because of the higher heating load debit associated with the air exchange rate, even if that rate remained unaffected by the colder weather. Results from recent runs with wood as a fuel suggest, however, that the extra radiation from the embers raises the net efficiency by several percentage points. Our future work will clarify this and other disputed issues in a quantitative fashion.

Planned Activities for 1979

Our testing procedure is designed to allow measurement of the effectiveness of most fireplace accessories and operating strategies. We are planning to test a number of commercially available and laboratory-built accessories in 1979. We are also planning to simplify the test equipment to make it transportable. At that time we will test fireplaces in other houses, possibly in different climates. With the same equipment and the same electric co-heating strategy, the efficiency of any heating system can be measured, such as that of the furnace and the air conditioner installed in the house. Such measurements have already been carried out with satisfactory results elsewhere.¹³

They will be extended to other houses and systems as a part of our program.

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Ventilation Program

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INTRODUCTION

The Ventilation Program is a major component of Lawrence Berkeley Laboratory's (LBL) Energy Efficient Buildings Program (EEB). Funded by the Department of Energy (DOE), Office of Buildings and Community Systems (BCS), the Ventilation Program is part of a coordinated effort to respond to the need for conserving the nation's energy while maintaining the health and comfort of occupants of the built environment. The overall objective of the Ventilation Program is to conduct in-depth research and development on existing and proposed ventilation requirements and mechanical ventilation systems in order to provide recommendations for the establishment of energy-efficient ventilation standards and ventilation designs for residential, institutional, and commercial buildings. LBL is also providing both technical and management support to DOE headquarters for other related ventilation projects.

LBL Ventilation Program activities for 1978 can be categorized as follows:

- 1) field monitoring of indoor air quality;
- 2) laboratory studies of building materials emissions;
- 3) demonstration and assessment of mechanical ventilation systems utilizing air-to-air heat exchangers;
- 4) additional subcontract activities consisting of:
 - assessment of ventilation requirements for odor control in buildings;
 - reassessment of hospital ventilation standards;
 - field survey of current practices in enforcement of ventilation regulations;
 - study of automatic variable ventilation control systems based on air quality detection in institutional and commercial buildings.
- 5) development of a ventilation data base.

Residential, institutional, and commercial buildings together account for approximately one-third of the energy consumed annually in the United States, as shown in Fig. 1. More than half of this energy is used to maintain human comfort conditions through the heating,

cooling, and ventilating of buildings. Significant savings in the energy used to heat and cool buildings can be realized in at least two ways: 1) by changing the thermal properties of the structure; and 2) by reducing the natural and mechanical ventilation rates. The ventilation program is concerned primarily with the latter method.

Air changes in buildings take place through the random introduction of outdoor air by infiltration or its regulated introduction by natural

RESIDENTIAL ENERGY CONSUMPTION DATA (1976)

TOTAL 18.95 Quads

COMMERCIAL ENERGY CONSUMPTION DATA (1976)

TOTAL 10.3 Quads

Fig. 1. Primary energy consumed in the U. S. by residential and commercial buildings. Numbers in parentheses are in units of quads or 10¹⁵ Btu. Source: Department of Energy, Office of Conservation, Buildings and Community Systems, Five Year Program Plan. (XBL 785-903)

ventilation or mechanical ventilation. In the United States, the latter mechanism is essentially limited to non-residential buildings. Ventilation, in general, is required for the following reasons:

- Establishment of a satisfactory balance between the metabolic gases (oxygen and carbon dioxide) in the occupied environment.
- Dilution of human and nonhuman odors to a level below an unacceptable olfactory threshold.
- Removal of contaminants produced in the ventilated space by heating, cooking, construction materials, etc.
- Removal of excess heat and moisture from internal sources.

Ventilation requirements are currently set by state and local governments and are found to vary from one jurisdiction to another. Most of the existing building codes, wherein ventilation requirements are found, are based on rather vague health and safety considerations and in general ignore energy conservation.

Through Public Law 94-385, Congress has mandated that building energy performance standards (BEPS) for new construction be promulgated by 1980 for adoption by state and local government jurisdictions having authority to regulate building construction through building codes

and other mechanisms. The Department of Housing and Urban Development (HUD), and the Department of Energy (DOE) are working together to develop these standards. The Ventilation Program is performing research necessary for understanding ventilation requirements as part of the effort to develop building energy performance standards.

Since the heating or cooling of outside air as it is introduced into a building requires a significant amount of energy, a large fraction of the potential energy savings in buildings can be accounted for by minimizing the use of fresh ventilation air. Table 1 illustrates the magnitude of these possible savings. An energy savings of one million barrels of oil per day (2 quads* per year) would result if ventilation requirements were relaxed and infiltration reduced so as to achieve a savings of 12.5% in the energy used to condition indoor air. The potential national impact, an annual savings of nearly \$5 billion, is significant. In 1976, the United States imported 7.3 million barrels of oil per day at a cost of approximately \$30 billion.¹ One way to achieve this potential energy savings of a million barrels of oil per day would be to "tighten" about two-thirds of existing residential buildings to reduce infiltration by a factor of about two, and to decrease the outside air requirements of about two-thirds of non-residential buildings by a factor of two.

*One quad equals 10^{15} BTU.

Table 1. Potential energy savings[†] with energy efficient ventilation systems and lowered infiltration.

Total U.S. energy consumption	75 x 10^{15} BTU/yr
Total U.S. energy consumption for buildings	29 x 10^{15} BTU/yr
50% of building energy used to condition air (includes mechanical ventilation systems)	14.5 x 10^{15} BTU/yr
Assume ventilation requirements can be relaxed and infiltration lowered to give a 15% savings in energy used to condition air	
Potential energy savings	2.2 x 10^{15} BTU/yr
2.5% of national energy budget (7.5% of building energy budget)	1.0 x 10^6 barrels of oil/day
At present prices of \$12/barrel	Savings of \$12 million/day
At estimated 1985 prices of \$25/barrel	Savings of \$25 million/day

[†]1976 energy use estimates from Energy Research and Development Administration, Office of Conservation, "Buildings and Community Systems, Five Year Program Plan."¹

The introduction of energy-saving measures in buildings, however, may adversely affect indoor air quality. But there is a little agreement on the levels of fresh air required for the health and comfort of building occupants. The U.S., unlike some European countries, has no mandatory air quality standards developed specifically for the indoor environment. Low air change rates may contribute to:

- The growth of mold on walls due to high internal humidity;
- the feeling of stuffiness arising from "stale" or polluted air; and
- the buildup of chemical contaminants emitted from building materials and other indoor sources.

Previous research at LBL on the impact of combustion-generated indoor air pollution concluded that it is essential to consider the impact of reduced ventilation on indoor air quality.^{2,3} This research has shown, among other things, that typical gas stoves operating under current design conditions produce unacceptably high concentrations of noxious pollutants. An effort will be made to establish a scientific basis for ventilation standards and to provide data and recommendations for the establishment of energy-efficient ventilation standards in different classes of buildings.

It is anticipated that all of the projects in this program will produce data on energy conservation and indoor air quality that will be of important practical use not only to scientists and engineers, but also to building contractors, architects and related building trades people, as well as to the public at large. One of the principal means that will be used to disseminate this information is the LBL ventilation data base. The main objective of the data base project is to collect research data and other pertinent information on building ventilation and to convert it into a form which allows users easy access through a computerized data management system.

FIELD MONITORING OF INDOOR AIR QUALITY

(Berk, Brown, Ko, Koonce, Loo, Pepper, Turiel, Young)

In order to establish criteria for setting energy-efficient ventilation standards, the Ventilation Program staff is involved in a comprehensive assessment of indoor air quality in different types of buildings under a variety of ventilation conditions. Table 2 lists several indoor contaminants, identified as potential health hazards, and their sources. LBL is assessing a significant number of the pollutants shown.

The Ventilation Program staff is conducting field monitoring of indoor air quality at hospitals and educational facilities before and after energy conserving retrofits are implemented. In addition, prototype energy efficient residential

Table 2. Indoor air pollution in buildings.

Sources	Pollutant Types
<u>Outdoor</u>	
Ambient Air	SO ₂ , NO, NO ₂ , O ₃ , Hydrocarbons, CO, Particulates
Motor Vehicles	CO, Pb
<u>Indoor</u>	
Building Construction Materials	
Concrete	Radon
Particleboard	Formaldehyde
Insulation	Formaldehyde
Adhesives	Organics
Paint	Mercury, Organics
Building Contents	
Heating and cooking combustion appliances	CO, SO ₂ , NO, NO ₂ , Particulates
Furnishings	Organics, Odors
Water service; natural gas	Radon
Human Occupants	
Metabolic activity	CO ₂ , NH ₃ , Organics, Odors
Human Activities	
Tobacco smoke	CO, NO ₂ , HCN, Organics, Odors
Aerosol spray devices	Fluorocarbons, Vinyl Chloride
Cleaning and cooking products	Hydrocarbons, Odors, NH ₃
Hobbies and crafts	Organics

homes and other buildings are being studied as possible models for energy conservation. The LBL Ventilation Program staff and subcontractors are measuring:

- temperatures and relative humidity
- odors
- toxic chemicals (gases and particulates)
- microbial burden

EEB Mobile Laboratory

The Energy Efficient Buildings (EEB) Mobile Laboratory⁴ is a facility designed for field studies of ventilation requirements and energy utilization in buildings. The EEB Mobile Laboratory was equipped in early 1978 with the instrumentation listed in Table 3, in order to monitor the contaminants shown in the same table. The EEB Mobile Laboratory was designed to assist field monitoring efforts, and to facilitate R&D studies of ventilation requirements and energy utilization in residential, institutional, and commercial buildings.

The laboratory contains sampling, calibration, and monitoring systems which provide an index of the overall air quality in a building.

Table 3. Instrumentation for Lawrence Berkeley Laboratory ventilation requirements system

Parameter	Principle of Operation	Manufacturer/Model
Field		
Continuous Monitoring Instruments:		
Infiltration		
N ₂ O or C ₂ H ₆ (Tracer gas)	IR	LBL
Indoor Temperature and Moisture		
Dry-Bulb Temperature	Thermistor	Yellow Springs 701
Relative Humidity	Lithium Chloride Hygrometer	Yellow Springs 91 HC
Outdoor Meteorology		
Dry-Bulb Temperature	Thermistor	Meteorology Research 915-2
Relative Humidity	Lithium Chloride Hygrometer	MRI 915-2
Wind Speed	Generator	MRI 1074-2
Wind Direction	Potentiometer	MRI 1074-2
Solar Radiation	Spectral Pyranometer	Eppley PSP
Metric Rain Gauge	Tipping Bucket	MRI 382
Gases		
SO ₂	UV Fluorescence	Thermo Electron 43
NO, NO _x	Chemiluminescence	Thermo Electron 14D
O ₃	UV Absorption	Dasibi 1003-AH
CO	NDIR	Mine Safety Appliances-Lira 202S
CO ₂	NDIR	M.S.A. Lira 303
Radon	Alpha Dosimetry	LBL
Particulate Matter		
Size Distribution	Optical Scattering	Royco Particle Counter 225
Radon Progeny	Under Development	LBL
Sample Collectors		
Gases		
Formaldehyde	Chemical Reaction/Absorption (Gas Bubbler)	LBL
Total Aldehydes		
Selected Organic Compounds	Adsorption (Tenax GC Adsorption Tubes) for GC Analysis	LBL
Particulate Matter		
Aerosols (Respirable/Non-respirable)	Virtual Impaction/Filtration	LBL
Bacterial Content	Inertial Impaction	Modified Anderson Sampler
Data Acquisition System		
Microprocessor		Intel System 80/20-4
Multiplexer A/D Converter		Burr Brown Micromux Receiver MM6016 AA Remote MM6401
Floppy Disk Drive		ICOM FD3712-56/20-19
Modem		Vadic VA-317S

Air change rates are measured using a tracer gas system⁵ (developed at LBL) in which nitrous oxide is injected and monitored continuously under controlled conditions at the sampling sites. This and the other continuously monitored parameters are recorded on a microprocessor-controlled floppy disk. The recorded information is transmitted back to LBL by telephone or by sending the floppy disks back to LBL where they may be read into the LBL computer system.

The EEB Mobile Laboratory, shown in Exhibit 1, is positioned outside the building to be studied. Air from four locations within the structure is drawn through teflon sampling lines into the trailer for analysis. By sequentially sampling the lines (one of which is used to monitor outdoor ambient air), the air quality can be monitored in several rooms.

For some pollutants, grab sampling techniques are used. The size distribution of the particulate matter in the sampled air is measured by means of an optical scattering instrument and automatic dichotomous air samplers; the latter are also used to collect particulate matter for chemical analysis. The dichotomous air samplers,⁶ developed at LBL, separate the aerosols into respirable and non-respirable fractions (below and above 2.5 micron size, respectively) using a flow-controlled virtual impaction system, which deposits the particulate matter on teflon filters. The particulates collected on the filters are analyzed at LBL using beta-ray attenuation to measure mass concentration, and x-ray fluorescence to determine chemical composition for 27 elements. Some of the contaminants must be collected with gas bubblers and other sampling techniques requiring subsequent laboratory analysis.

Exhibit 1. The EEB Mobile Laboratory.

These contaminants include radon, formaldehyde, total aldehydes, other selected organic compounds (shown in Table 4), and microbial content.

Field Monitoring

During 1978, four sites were included in the field monitoring program. Indoor air quality was monitored at Carondelet High School, an air-conditioned high school in Concord, California; at occupied and unoccupied Minimum Energy Dwellings (MED) in Mission Viejo, California; the Naval Regional Medical Center in Long Beach, California; and the Iowa State University Energy Research House in Ames, Iowa. Preliminary results from Carondelet indicate that the fresh air ventilation rate could be substantially reduced without compromising the health or comfort of the occupants. Data from the other three sites are currently being analyzed. At the MED houses and at the Iowa State University house, the indoor air quality is of considerable interest because these residential buildings were constructed to have low air infiltration. In the case of the Long Beach hospital, the air quality is being measured before and after energy-saving retrofits are implemented.

Carondelet High School is a two story air-conditioned building with about 40 classrooms and 700 occupants. The heating, ventilation and air conditioning (HVAC) system is a combination air-water type with room induction units. There is one air-supply fan for the air distribution system.

The fresh air entering the roof was measured, reduced, and regulated to save energy. Three of the four sides of the air intake unit intake dampers were sealed and an air-flow measuring device and flow controller were installed in the remaining side. The air quality in two classrooms, in a corridor, and outdoors was monitored under three ventilation rates. The first rate (20,000 cfm) was the normal operating mode, with roof dampers in the full open position. The second and third rates (3700 cfm and 2300 cfm, respectively) restricted total fresh air in the school. The decision to restrict the fresh air to 2300 cfm was not made until it had been established that the indoor air quality at 3700 cfm was still very good. In a typical classroom with twenty students, these ventilation rates correspond to 18 cfm, 3.3 cfm and 2.1 cfm fresh air per person. Data were collected for the three fresh air ventilation rates indicated. Carbon dioxide was the only pollutant detected in significant concentrations inside the school. This is not surprising, since there were no obvious indoor sources of pollution other than the occupants themselves. The school borders on a main thoroughfare; during rush hour periods when increased levels of nitrogen oxides and ozone were present outdoors, smaller but measurable concentrations were observed indoors. Indoor concentrations of these pollutants actually decreased as the "fresh" air ventilation rates were reduced.

Figure 2 shows the CO₂ buildup and decline during a typical day at the restricted fresh air ventilation rate of 3700 cfm for the entire school. Concentrations in the two classrooms and outdoors are shown. Although CO₂ concentrations inside the classroom increased as ventilation rates were lowered, at no time did they exceed 2000 ppm, and only occasionally did they exceed 1500 ppm. This should be compared to the National Institute for Occupational Safety and Health (NIOSH) recommended ten-hour maximum of 10,000 ppm;⁷ the American Conference of Governmental Industrial Hygienists (ACGIH) recommended 8-hour maximum of 5000 ppm;⁸ and the Occupational Safety and Health Administration (OSHA) recommended 8-hour maximum of 5000 ppm.⁹ These concentrations refer to a time weighted average concentration for up to 8 and 10 hour workshifts in a 40

Fig. 2. CO₂ concentrations at Carondelet High School in Rooms 10 and 11 and outside. Total air flow is 3700 cfm. May 31, 1978. (XBL 791-250A)

Table 4. Tentative list of indoor organic air contaminants to be sampled by either Tenax GC sampling tubes for gas chromatographic analysis or gas bubblers for wet chemistry analysis.

Compounds	Health Effects	Possible Sources and/or Uses
C _n Alkanes N = 5 ~ 16	Narcotic at high concentrations; moderately irritating	Gasoline, mineral spirits, solvents, etc.
C _n Alkenes N = 5 ~ 16	Similar to that of alkanes	Similar to that of alkanes
Benzene	Respiratory irritation; recognized carcinogen	Plastic and rubber solvents; from cigarette smoking; used in paints and varnishes, including putty, filler, stains and finishes
1,1,1-Trichloroethane	Subject of OSHA carcinogenesis inquiry	Aerosol propellant, pesticide, cleaning solvents
Trichloroethylene	Animal carcinogen; subject of OSHA carcinogenesis inquiry	Oil and wax solvents, cleaning compounds, vapour degreasing products, dry cleaning operations; also used as an anaesthetic
Toluene	Narcotic; may cause anemia	Solvents; by-product of organic compounds used in several household products
Ethyl Benzene	Highly irritating to eyes, etc.	Solvents; used in Styrene related products
Xylene	Narcotic; irritating; high concentrations may cause injury to heart, liver, kidney, and nervous system	Used as solvent for resins, enamels, etc.; also used in non-lead automobile fuels and in manufacture of pesticides, dyes, pharmaceuticals
Styrene	Narcotic; can cause headache, fatigue, stupor, depression, incoordination and possible eye injury	Widely used in manufacture of plastics, synthetic rubber and resins
Chloro Benzenes	Strong narcotic; possible lung, liver, and kidney damage	Used in production of paint, varnish, pesticides, and various organic solvents
Polychlorinated Biphenyls (PCB's)	Suspected carcinogens	Used in various electrical components; may appear in waste oil supplies and in plastic and paper products in which PCB's are used as plasticizers
Formaldehyde and other Aldehydes	Eye and respiratory irritation; may have more serious long term health effects	Out-gassing from building materials -- particle board, plywood and urea-formaldehyde insulation foam; also generated by cooking and smoking

hour work week. Studies have shown that workers may be repeatedly exposed to these concentrations day after day without adverse health effects.⁷

To assess the potential reaction of the students to the changes in ventilation rates, a questionnaire on the quality of the indoor environment was designed and distributed to the occupants of two classrooms. Exhibit 2 is a sample questionnaire. The students' subjective judgment of odor level at various ventilation rates was of particular interest since odor control is probably the basis for current ventilation requirements in most schools. The questionnaires were filled out every other day at the same time and the results from one classroom are shown in Fig. 3. The subjective rating ranged from 1 to 9 with lower numbers cor-

responding to the first adjective in parenthesis. For example, for odor intensity the high numbers would indicate strong odor perception, whereas low numbers would indicate little or no odor perception. As can be seen in the figure, odor intensity essentially remained constant at all of the ventilation rates shown. There was a significant correlation between temperature and air movement. Subjective evaluation of both variables changed substantially over time.

During 1978, Carondelet was also one of the two sites included in the biological field monitoring project. This work is being performed by the Naval Biosciences Laboratory (NBL), under subcontract to LBL. The purpose of the project is to generate scientific and technical information pertaining to the sampling, assay, and data analysis of airborne bacteria in several of the facilities in which field monitoring is being carried out. Utilizing the data gathered, efforts will be made to determine whether the implementation of ventilation-related conservation retrofits gives rise to unacceptably high levels of airborne microbes. The analysis of the data is based primarily upon the magnitude of the changes in the number and size of the microorganisms present before and after ventilation rates have been reduced.

The bacterial content of the air is measured by modified Andersen samplers¹⁰ fabricated and operated by NBL. These devices collect airborne particles on 6 size-selecting plates of Agar nutrient media. Living microbes on or in such particles will, within two days, grow to such an extent that a visible spot (colony) will appear on the surface of the medium, and the colonies can be counted.

Date _____ Room No. _____

Male _____ Female _____

No odor _____ Strong odor _____

Pleasant odor _____ Unpleasant odor _____

Cold _____ Hot _____

Drafty _____ Stuffy _____

Humid _____ Dry _____

Quiet _____ Noisy _____

Exhibit 2. Quality of indoor environment questionnaire submitted to student occupants of Carondelet High School.

Fig. 3. Six indoor air quality parameters plotted as a function of day of month and ventilation rate. Data taken from questionnaire. The subjective rating ranged from 1 to 9 with lower numbers corresponding to the first adjective in parentheses. (XBL 791-251A)

One of the three sampling points at the field site is also equipped with an optical particle size analyzer such that the total number of airborne particles in selected size ranges (e.g., 0.8 to 2, 2-4, 4-7, 7-10, and greater than 10 μm in diameter) can be recorded. NBL will attempt to establish whether the data are correlated with Andersen sampler data in order to determine if an instrument of this type would be suitable for general microbial burden monitoring.

The raw data appear in the form of numbers of colonies per stage. They may be transformed to percent of the total sample per stage, and the cumulative percentage distribution plotted on a log-probit grid, shown in Fig. 4, from which the number median diameter (NMD) can also be obtained. Data are presented in the form of numbers of colony-forming particles (CFP)* per cubic meter of air. As the study proceeds, these values will be correlated with ventilation rates and other factors such as temperature and relative humidity.

A summary of microbial data from Carondelet High School is shown in Table 5. There is an increase in the number of CFP/ m^3 and in the NMD of the particles with occupant density. This is consistent with theory since CFP originating from human activity (i.e., mostly skin shedding) tend to be larger than those from other sources.

*An airborne particle may contain many or no viable bacteria. The presence of a colony after the sample medium is incubated indicates the collected particle had at least one viable cell; how many more cells may have been present cannot be ascertained. Hence they can only be referred to as "colony forming particles" rather than bacterial numbers.

SAMPLE 138B, 1000-1020, 5-18-78, CLASSROOM #1,
CARONDELET HIGH SCHOOL

Fig. 4. Example of treatment of typical sample for analysis of particle size. Numbers of colonies found on each stage are totaled, and the percentage of the total number is determined for each stage. The cumulative percentages are plotted on a probit scale vs. log of size. The 50 percentile size is the Number Median Diameter (NMD), in this instance 3.5 μm . The log scale is chosen because the data most often conform to a straight-line relationship on a log-normal basis.

Table 5. Summary of data on airborne/colony forming particles collected at Carondelet High School (Based on 114 samples).

Fresh Air* Exchange Rate (cfm)	Room 1 (CFP/ m^3)		Room 2 (CFP/ m^3)	
	Occupied	Unoccupied ⁺	Occupied	Unoccupied ⁺
18	160(5.4)	54(4.3)	107(5.4)	27(2.4)
2.7	115(6.6)	47(3.5)	75(5.8)	37(2.8)

⁺ = 0700 sample; ventilation turned on at 0630.

() = The Number Median Diameter (NMD) in μm (10^{-6}m).

* = Fresh air per person for average of 20 students.

However, only the rise in NMD appears to be statistically significant.

It is not known why the number of airborne bacteria is consistently higher in Room 1 than in Room 2. Surprisingly, an increase in the amount of fresh air almost always produced an increase in the number of viable airborne molecules. This result was unexpected and tends to indicate that there might be a significant source of bacteria in the outside air.

The change in number of CFP/m³ as a function of time of day is shown in Fig. 5. It can be seen that the respirable burden (particles 5 μ m in diameter or less) was greatest at 7:00 a.m. and declined during the day. The total number of microbes increased markedly between 7:00 and 10:00 a.m. One possible explanation is that there were two populations of airborne bacteria in the school: one (large-size CFP's) arising and the other (respirable CFP's) decreasing during the day. No firm conclusion about the variations of airborne bacteria with time and ventilation rates can be made with these limited data. The results at Carondelet do show, however, that decreasing the ventilation rate did not increase the microbial burden in the classrooms.

Results of the field monitoring project at Carondelet High School indicate no significant change as a result of decreased ventilation in any of the parameters measured, with the exception of carbon dioxide. While CO₂ levels

"RESPIRABLE BURDEN" (PARTICLES 5 μ m IN DIAMETER OR LESS) AT CARONDELET HIGH SCHOOL (●) AND TOTAL NUMBERS (▲).

Fig. 5. Respirable and total number of colony-forming particles are shown as a function of time of day.

increased, concentrations were still far below levels considered to be a health hazard. In fact, the air quality improved in the school for some parameters (nitrogen dioxide and ozone) when the ventilation rate was reduced. Results of the survey of subjective impressions of indoor air quality showed no deterioration of student comfort caused by decreased ventilation rates.

Since the amount of outside air entering the school could be decreased without any adverse affect on the health, safety, or comfort of the occupants, substantial energy savings could be achieved by lowering the fresh air ventilation rates at Carondelet.

Total energy use for this high school in Concord, CA, including gas and electricity (used for space conditioning, lighting and hot water) costs about \$40,000 per year. If the ventilation rate were changed from 20,000 cfm to 2,300 cfm, it is estimated that savings would amount to \$3500 to \$4000 per year or 9% of total annual energy costs for the building.

Educational facilities in the U.S. consume approximately 1.8×10^{15} Btu per year (1.8 quads), which amounts to 2.4% of total U.S. energy use. Space heating and cooling requirements consume about 2/3 of the energy budget of an average school. A significant portion of the energy is used to heat or cool incoming outside air. If we assume that one third of the heating, ventilation, and air conditioning (HVAC) system energy is used to condition outside air, then the total energy used to condition outside air in schools is approximately 0.4×10^{15} Btu or 0.4 quads. Decreasing ventilation requirements by a factor of two in schools results in a nation wide savings of 0.2×10^{15} Btu, or more than 10% of the total energy used in educational buildings. Thus, there are large potential energy savings to be realized by reducing the amount of outside ventilation air.

Analyses of the data from the Naval Regional Medical Center and the energy-efficient residential buildings are currently in progress.

Planned Activities for 1979

The following sites will be included in the field monitoring study of indoor air quality during 1979:

- Fairmoore Elementary School, Columbus, Ohio
- Energy Efficient House, Carroll County, Maryland
- LBL Research House, Walnut Creek, California
- Minimum Energy Dwelling II (Production Model) and Conventional House, Mission Viejo, California
- Naval Regional Medical Center (post retrofit), Long Beach, California
- Veterans Administration Hospital, Omaha, Nebraska (pre- and post-retrofit)
- School (to be determined), New York City.

STUDIES OF BUILDING MATERIALS EMISSIONS

As buildings are "tightened up" to reduce air infiltration, thus reducing energy requirements, there is an increased risk that contaminants emitted from building materials and generated by indoor activities (such as smoking and cooking) may remain inside buildings in concentrations hazardous to the health of the occupants. The Ventilation Program staff has begun to identify contaminant emissions from building materials to determine the contaminant source strengths and to recommend and verify means for the energy efficient controls of these emissions. The studies have focused on two major categories of potentially hazardous substances:

- radon, a naturally occurring radioactive trace element found in most rock and soil, and
- organic vapors originating from indoor and outdoor sources

RADON

(Berk, Boegel, Nazaroff, Stitt, Zapalac)

The Ventilation Program staff is currently active in two areas of radon measurement: development of passive monitors for integrated measurements, and development of a chamber and Lucas cells¹² for laboratory measurements of radon emanations from building materials.

Radon and its decay daughters have always been present as part of the natural radiation burden; however, since radon emanates from indoor sources, reduced ventilation will lead to higher indoor concentrations and the attendant increased radiation exposure to lung tissue.¹¹ The possible increased risk of disease, especially lung cancer, must be considered when adopting building energy conservation standards. The risk should be assessed in the context of the naturally occurring exposure to radon daughters and the possible health impact of this exposure to the general population. Measures such as air-to-air heat exchangers (see below) and ventilated crawl spaces are available to limit increases in indoor radon daughter concentrations indoors while still achieving energy conservation in buildings.

Radon-222 is an inert, radioactive, naturally occurring gas which is part of the uranium-238 decay chain. Any substance that contains radium-226, the precursor of radon, is a potential emanation source. Since Ra-226 is a trace element in most rock and soil, indoor radon sources include concrete, brick, and other building materials. Ra-226 has a half-life of 1602 years and its presence in building materials results in a continuous source of radon for the life of the building. Other potentially significant sources of radon in buildings include the soil beneath the foundation and the tap water, especially if the water is taken from wells or underground springs in areas where significant amounts of radium are present.

The alpha decay of Ra-226 produces a chemically inert, recoiling radon-222 atom which has a 3.8 day half life. If the atom ends its recoil in an interstitial space of the solid source material, it may migrate to the surface and enter the air. Radon has four short-lived daughters, each with a half-life of less than 30 minutes. Figure 6 shows the decay chain for radium-226. The subsequent production of Pb-210, with a 22-year half-life, effectively ends the sequence as far as biological effects are concerned.

The four radioactive daughters of radon are not inert. Most attach themselves by chemical or physical means to airborne particulates, generally less than a micron in size. These particulates, when inhaled, may be retained in the lung bronchi, where subsequent decay to Pb-210 results in a radiation dose to the lung. The primary hazard is due to the alpha emission of polonium-213 and polonium-214. Since alpha particles have a very short range (a few tens of microns) in tissue, essentially all of the energy is deposited near the surface of the lung.

Radon emanation rates vary widely from one substance to another. Indoor levels are strongly affected by the manner in which materials are incorporated into a building, and by other aspects of the building's design, particularly the infiltration and ventilation rates.

Fig. 6. Decay chain, radium-226 to lead-210 (α , β energies in MeV). (XBL 7212-4903B)

Passive Monitors for Integrated Measurements

Two dozen passive monitors¹³ for integrated measurements of radon levels were fabricated in 1978. The LBL passive monitor, shown schematically in Fig. 7, is cylindrical in shape, approximately 8 inches in diameter and 12 inches high. The sensitive volume is defined by a metal funnel and perforated steel screen. A rubber stopper with a brass electrode is placed in the neck of the funnel. A lithium fluoride, thermoluminescent dosimeter (TLD) chip is held in place above the end of the electrode by a molded plastic holder. Three 300 V dry cells provide -900 V to the electrode with the funnel and screen as reference.

Radon gas is driven by diffusion to a concentration in the sensitive volume equal to that in the surrounding air. Radon atoms which decay via alpha emission form positively charged Po-218 ions. The electric field in the sensitive volume attracts these Po-218 ions towards the electrode, where they are deposited on the TLD chip. Since the Po-218 collection efficiency of the instrument is humidity dependent, the 3" desiccant bed is needed to provide a constant, low humidity environment in the sensitive volume. Subsequent alpha decays of Po-218 and other short-lived radon daughters are recorded by the chip. After a one or two week sampling period, the chip is sent back to LBL for readout.

When a thermoluminescent material is exposed to ionizing radiation, electron hole pairs are generated, some of which enter metastable states above the ground state. These metastable states have potential energy wells deeper than room

Fig. 7. Schematic drawing of Passive Radon Monitor.
(XBL 791-252)

temperature thermal energy, so the electron hole pairs do not recombine until additional thermal energy is supplied. A photon is emitted when the atom returns to its ground state. The procedure for determining alpha exposure is to heat the chips in a prescribed manner and measure the light emitted using a photomultiplier (PM) tube. The PM tube current is proportional to the integrated radon concentration during exposure.

Radon Emanations from Building Materials

In addition to the studies using passive radon monitors, laboratory studies are being conducted to measure the rates at which radon emanates from various building materials. Air-tight chambers are being fabricated into which building materials will be placed. By measuring the radon buildup in the chambers, radon emanation rates can be determined. Materials to be studied in 1979 include concrete of varying composition and origin, brick, and gypsum board.

The airtight chambers are aluminum, 15 inches on a side, and have shelves for the placement of slabs of the material being studied. A tedlar bag approximately two liters in volume is attached to the chamber to allow daily air samples to be withdrawn without reducing the pressure inside the chamber. The air samples are transferred into Lucas cells fabricated at LBL. These cells are 2-inch diameter copper flasks of 100 cc. volume, coated on the inside with zinc sulfide phosphor and having a quartz window adhered to one end to allow light transmission. These flasks are vacuum pumped and then filled with the chamber air containing radon. After allowing a few hours for radioactive equilibrium to occur between the radon gas and its daughters, the cells are placed on a photomultiplier tube counting system to count alpha particles produced in the flasks. From these counting rates, the radon concentration can be calculated.

ORGANIC CONTAMINANTS

(Lin, Anaclerio, Anthon, Fanning, Wiebe)

The Ventilation Program staff began its study of organic vapors in the indoor environment in 1978. Two approaches are being used: field monitoring of the air in various indoor environments, and laboratory analyses of emissions from building materials.

The results of LBL studies and other work¹⁴⁻¹⁶ indicate that air in various indoor environments is contaminated with a range of organic vapors that originate from indoor and outdoor sources. Inside buildings, organic vapors, e.g., formaldehyde can be emitted from common building materials such as urea-formaldehyde foam insulation, plywood, and particle board.¹⁶ Adhesives, used in forest products and other furnishings, are also sources of such emissions. Indoor activities (such as cooking, cleaning and smoking) can also generate organic contaminants.

Many of these volatile organic contaminants are known to have serious health effects. Because of their chemical complexity and extremely low concentrations, the hazardous organics found in the air are very difficult to measure quantitatively. Instruments for continuous monitoring are not currently available for measuring most organic contaminants in ambient air. It is therefore necessary to use appropriate adsorbing materials to concentrate these organics in the field for laboratory analysis. To date, little work has been done on sampling and analysis of organics in non-occupational indoor environments. Thus, major efforts are required to develop capabilities in analyzing airborne trace organics for indoor air quality studies.

Analytical Techniques

A chemistry laboratory has been equipped with high resolution analytical instruments for the studies at LBL. The facility includes:

- 1) a Varian 3711 Gas Chromatograph (GC) with a Flame Ionization Detector (FID) and Electron Capture Detector (ECD)
- 2) a Varian Cary 219 UV/Visible Spectrophotometer
- 3) a Finnigan 4023 GC/MS (with INCOS data system)

Based on an extensive literature search, a list of indoor organic contaminants, shown in Table 4, has been developed for study. Compound selection was based on possible indoor source strengths as well as the seriousness of the health risks posed by exposure.

The Ventilation Program staff has adopted gas chromatographic techniques for the separation of most of the selected volatile organics shown in Table 4. Polymer resins (e.g., Tenax GC, XAD2) will be used as adsorbents to collect ambient organic vapors in the field. The adsorbed sample

will be either extracted with suitable solvents or thermally desorbed at high temperatures. Splitting the column effluent into ECD and FID fractions allows simultaneous detection of halogenated and non-halogenated compounds. To identify the compounds on the chromatogram, internal standards will be added to the adsorbent and relative retention times will be studied. Frequently, gas chromatographic techniques will be used in conjunction with mass spectrometric techniques (GC/MS) to confirm the identity of the isolated compounds.

The Ventilation Program staff has developed and fabricated a grab sampling control system for taking accurate air samples. These samples are taken over periods of eight hours in the daytime and sixteen hours in the nighttime. The grab sampling control system, shown in Fig. 8, is currently used in conjunction with four gas bubbler systems for sampling formaldehyde and total aldehydes. In the field, indoor and outdoor air are sampled with a 0.05% MBTH solution for collection of total aldehydes. Simultaneously, distilled water is used to collect samples in order to compare the MBTH, pararosaniline and chromotropic acid analytical methods and to determine the formaldehyde concentration of the total aldehydes.

The sampling procedure developed at LBL is a modified version of the standard methods recommended by various government agencies. The precision and accuracy of the LBL method is an improvement over traditional techniques. At sampling points, air is drawn through a sintered coarse glass frit (70 to 100 μ pore size) for effective aldehyde collection. The air sample is then passed successively through a cool demister, a pair of filters, and plastic tubing to a control system located in the EEB Mobile Laboratory. From there the air travels through a flow regulator, a fine needle valve, a rotameter, a vacuum regulator, pressure gauges, and a diaphragm pump system.

Fig. 8. Formaldehyde/aliphatic aldehydes grab sampling system. (XBL 791-257A)

The control system developed during our tests of sampling systems provides a constant and accurate air flow for sampling (better than $\pm 3\%$ versus $\pm 20\%$ using a critical orifice as recommended by government agencies). This has been achieved by utilizing a flow controller to maintain a constant pressure difference across the needle valve opening. Since a constant vacuum regulator is added downstream adjacent to the needle valve, the immediate upstream and downstream pressures of the valve are kept constant at all times. At a given temperature (the EEB Mobile Laboratory is maintained at a constant temperature), the air flow is a function of the pressure difference. Thus, the system samples air at a constant mass flow rate regardless of possible pressure changes of the bubbler and/or filter (caused by clogging, or by non-uniformity among frits, etc).

The Ventilation Program staff also has been comparing various wet chemical analytical techniques for measuring formaldehyde and total aldehydes in air. It has been determined that although they are applicable to analyses of ambient air, both the pararosaniline and chromotropic acid methods are not as sensitive as reported in the literature and are less sensitive than the MBTH method. The pararosaniline method uses toxic reagents which requires special handling. It takes considerable time (up to two hours) to develop color for spectrophotometric measurement if the concentration of HCHO is very low. The chromotropic acid method is also difficult to work with because concentrated H_2SO_4 is required for this technique. There had been difficulty in generating a standard calibration curve (concentration of formaldehyde vs. photometric absorption) for the chromotropic acid method due to improper reagent ratios in the method described by the National Institute of Occupational Safety and Health (NIOSH);¹⁹ this difficulty has since been resolved at LBL. Chromotropic acid (reagent grade) obtained from commercial sources need repurification to obtain proper sensitivity with this technique. Moreover, several serious interferences have been reported²⁰ in the chromotropic acid method. Although the chromotropic acid methods is recommended by NIOSH and various professional associations, and is therefore used widely, the method does not seem to be a good technique for measuring formaldehyde in ambient air. Although the MBTH method is sensitive and straightforward, the technique is reactive to all aliphatic aldehydes. Alternative methods such as the ion chromatographic technique and solid absorbent collection with gas chromatographic analysis are currently being studied at LBL.

Field Monitoring of Indoor Organic Contaminants

As part of the ventilation field monitoring project, total aliphatic aldehydes have been measured (as formaldehyde) at the occupied and unoccupied Minimum Energy Dwellings (MED) in Mission Viejo, California; at the Naval Regional Medical Center in Long Beach; and at the Iowa State University Energy Research House in Ames, Iowa, in 1978. Preliminary results indicate that the average concentration

of aldehydes in the occupied MED house with an air exchange rate of 0.2 air changes per hour is about 65 ppb compared to 21 ppb in the unoccupied MED house and 8 ppb in outdoor air as shown in Fig. 9. The unoccupied Energy Research House in Ames has a ventilation rate of about 0.3 air changes per hour and has an average aldehyde concentration of 74 ppb compared to an average of 8 ppb outdoors shown in Fig. 10.

Fig. 9. Indoor/outdoor aldehyde concentrations. Minimum Energy Dwellings, Mission Viejo, California, September 1978.

(XBL 796-1749)

Fig. 10. Indoor/outdoor formaldehyde/aldehyde concentrations. Iowa State University Energy Research House, December 1978.

(XBL 795-1488A)

From the data, it is clear that the built environment contributes to aldehyde concentrations. When combined with contributions from the occupants' activities, the indoor concentration of aldehydes sometimes exceeds recommended formaldehyde standards¹⁸ for indoor air (100 ppb). In a well-ventilated hospital, on the other hand, no significant differences in aldehyde concentrations between indoor and outdoor air was found (see Fig. 11).

Outdoor air and indoor air collected from an LBL office trailer have also been analyzed for formaldehyde and total aldehyde concentrations. Each sample was analyzed by MBTH, pararosaniline and chromotropic acid methods. The preliminary results show that the concentrations of total aliphatic aldehydes in a 3-month old trailer (insulated with fiberglass, not urea-formaldehyde foam which is commonly used in trailers and is known to emit high amounts of formaldehyde) range from 23 to 89 ppb. Outdoor aldehyde concentrations of 1.0 to 70 ppb were substantially lower than the parallel indoor measurements. The ratio of formaldehyde (determined by both pararosaniline and chromotropic acid methods) to total aliphatic aldehydes (using the MBTH method) is 78% on average. Plywood constructed with urea-formaldehyde resin is a possible source of indoor aldehydes in the trailer.

Fig. 11. Indoor/outdoor aldehyde concentration. Naval Regional Medical Center, Long Beach, California, October 1978. (XBL 796-1747)

Planned Activities for 1979

In 1979 radon studies will continue with field monitoring of radon using the passive monitors and lab analyses of radon emissions from concrete, brick, and gypsum board. The Ventilation Program staff will continue to study various measurement techniques to develop reliable methods for determining the concentrations

of formaldehyde and total aldehydes in air. Besides spectrophotometric methods, the ion chromatographic and gas chromatographic techniques will be investigated for effective quantitative analysis. This work will encompass experiments with various GC columns and solid adsorbents. Grab sampling and analytical techniques for other organic vapors will be developed. In the field, samples will be collected at residential and commercial buildings in several geographical locations in the U. S. for the analysis of formaldehyde, total aldehydes, as well as other hazardous ambient organics. In addition, an environmental chamber will be fabricated in the laboratory for the study of hazardous organics emitted from common building materials such as adhesives, sealants, paints, and wood products.

MECHANICAL VENTILATION SYSTEMS USING AIR-TO-AIR HEAT EXCHANGERS

(Roseme)

The Ventilation Program staff began a study on the use of air-to-air heat exchangers and mechanical ventilation systems for residences in October of 1978. The project consists of four parts:

- Analysis and experimental evaluation of air-to-air heat exchangers;
- Testing of a mechanical ventilation system utilizing an air-to-air heat exchanger in the EEB Walnut Creek test house;
- A cost-benefit analysis of these systems operating in different climate zones of the United States;
- Installation and testing of a number of systems in occupied homes.

About 15% of the total energy consumed in the U.S. is used for space heating and cooling in residential structures. Two major modes of heat loss or gain in a residential structure are the conduction of heat through the walls, ceilings and floors, and the natural infiltration of outside air into the structure. After a house has been reasonably well insulated, the natural infiltration of outside air into the building usually becomes the single largest mode of heat gain or loss. Houses in the United States have infiltration rates ranging from one to two air changes per hour. Homes have been built, however, in Sweden, Canada and the United States with measured air infiltration rates on the order of 0.25 air changes per hour.

Fig. 12. Residential heat exchanger system.

Fig. 13. Principle of operation of heat exchanger.

Many homes in the U. S. and Europe have conserved energy by reducing infiltration; however, problems associated with this reduction in ventilation have been recognized. These problems include excessive humidity levels, increased intensity of odors from human activities, and increased levels of chemical contaminants, such as formaldehyde and radon from the outgassing of building materials.

One method of alleviating these problems is to introduce a mechanical ventilation system into a nearly air-tight structure and thereby ventilate in a controlled manner when it becomes necessary. A heat exchanger or heat recovery device installed directly in the mechanical ventilation system (see Fig. 12) can save a substantial amount of energy by pre-heating or pre-cooling the incoming outdoor air. An air-to-air heat exchanger is a device that brings the incoming and exhaust air streams into close proximity so that heat can be exchanged between these streams as shown in Fig. 13.

The ramifications of a reduction in infiltration rate can be understood by examining the impact on a hypothetical house in the Chicago area during the months of December, January and February. The average temperature for these months is 26.7°F.²¹ Assume a 1500 square foot house with temperature held at 68°F, unregulated humidity and a natural infiltration rate of 1.0 ach (air changes per hour). This represents a 19.27 MBTU uncontrolled ventilation load on the heating system for the three months. If the natural infiltration were reduced from 1.0 to 0.25 ach, the ventilation load would be reduced to 4.82 MBTU, a reduction of 75%. The problem, however, is that while infiltration has been significantly reduced and energy savings achieved, air quality has probably deteriorated. In several energy conservation houses, there have been reports of very high internal humidity levels, causing mold to grow on the walls. In Sweden, where low natural infiltration rates are mandated by law, there have been significant problems with the outgassing of formaldehyde from

particleboard used in construction. Installation of a mechanical ventilation system with a heat exchanger in a nearly air-tight structure, however, would provide sufficient ventilation (thus assuring good air quality).

A mechanical ventilation system is a combination of electric fans and duct work designed to provide controlled ventilation air whenever necessary. This is in direct contrast to uncontrolled natural ventilation. The inclusion of a heat exchanger between the incoming and outgoing air streams can save over half of the heat that otherwise would have been lost in the exhaust air.

If the homeowner in Chicago were to install a mechanical ventilation system utilizing an air-to-air heat exchanger with a 60% temperature efficiency and operate it so that it provides 1 ach for 12 hours per day, the total ventilation load (including two 1/6 HP fans) would be 9.6 MBTU. This would represent a 50% reduction in the ventilation load. If the ventilation load for the house in Chicago were half of the total heating load for the house, then the installation of a mechanical system with a heat exchanger would reduce overall heating load requirements by 25%. This reduction over the 3 month period would save the Chicago homeowner \$31.11 in natural gas costs (at \$2.26/MBTU and 70% furnace efficiency), or \$127 in electricity costs (at 4.5 ¢/Kwh). Additional savings could be realized at all other times when heating/cooling is required.

A theoretical analysis of commercially-available air-to-air heat exchangers in various modes of operation is being performed by the Mechanical Engineering Department at the University of California in Berkeley, under sub-contract to LBL. In addition, LBL is building a facility for testing commercially-available residential model air-to-air heat exchangers.

Planned Activities for 1979

A prototype mechanical ventilation system utilizing an air-to-air heat exchanger is to be installed in the EEB Walnut Creek test house. Efficiency measurements and indoor air quality tests will be performed.

A request for proposals (RFP) will be issued in the spring of 1979, for a study to install and evaluate residential mechanical ventilation systems with heat recovery devices in several residential houses in a region of the United States that has extreme summer and winter weather conditions. Energy savings, indoor air quality and different modes of operation are to be tested.

The heat exchanger performance data generated by this project will be combined with appropriate climatological and economic parameters, in order to develop an economic model evaluating life-cycle costs of heat exchanger utilization in single family dwellings. Results will be assessed against baseline data from "typical" single family dwellings in the same environment.

Returns on investment and payback periods will be estimated for various commercial heat exchangers operating in different environments.

SUBCONTRACT ACTIVITIES

(Turiel)

In addition to activities conducted by the Naval Biosciences Laboratory (previously discussed) and the University of Minnesota (see Hospitals Program), the Ventilation Program's technical management group has been directing three other major subcontracts:

- Assessment of ventilation requirements for odor control;
- Review of ventilation regulations and enforcement practices; and
- Development of automatic variable ventilation control systems.

Odor Control

The John Pierce Foundation of Connecticut, in collaboration with The Research Corporation of New England (TRC), is in the process of conducting a review of existing regulations for odor control in buildings and their underlying data base. It appears that the minimum ventilation rates established by various state and local governments for institutional and commercial buildings are based on research performed by C. P. Yaglou over forty years ago.^{22,23} He determined that for sedentary adults under "normal" conditions, approximately five cubic feet per minute per occupant of outside air is the minimum amount required for odor control in buildings. It is important to note that these studies were conducted under laboratory conditions and not in actual buildings. There have been few research studies^{24,25} measuring odors at locations where odor levels are relatively low. Most studies have been concerned with severe industrial-type odor problems.

Work on the odors project has been divided into two phases. Phase I, begun in 1978 by the John Pierce Foundation, consists of a literature survey of:

- 1) Existing and proposed ventilation requirements for odor control in buildings;
- 2) Odor measurement techniques, both analytical and subjective; and
- 3) Air treatment systems for odor control in institutional and commercial buildings.

In a second, related task, John Pierce has begun conducting a critical review of the existing data base in order to make specific research recommendations designed to fill the gaps in this data base.

Planned Activities for 1979

Phase II of the odors subcontract research is scheduled to take place in 1979 and 1980. It will combine both laboratory and field based investigations of ventilation requirements for odor control in buildings. Both subjective questionnaires and psychophysical²⁶ testing techniques will be used in the laboratory and field experiments.

We are seeking data on the perceived odor intensity as a function of several variables. Included among these variables are total mechanical ventilation rate, percent recirculation, infiltration rate, filtration and masking techniques, environmental variables and room occupancy variables.

The environmental and room occupancy variables of interest include:

1. Room volume
2. Number of occupants
3. Activity in room
4. Personal hygiene of occupants
5. Temperature
6. Relative humidity
7. Air movement in room
8. Quality of outside air

The Phase II work, to be performed by both the John Pierce Foundation and TRC, is outlined below in sequential steps:

- Task 1: Select measurement techniques and adapt them for odor evaluation in buildings
- Task 2: Conduct a field study of odors and their sources in the following types of buildings:
- a. Educational facilities
 - b. Hospitals
- Task 3: Perform field-based perceptual and behavioral studies in the buildings identified above and accompany these by laboratory-type odor intensity and threshold measurements.
- Task 4: Perform air quality characterization (analytical) of odors on samples taken during Task 3.
- Task 5: Recommend ventilation requirements and modifications in the HVAC systems for odor control in institutional and commercial buildings.
- Task 6: On the basis of Phase I work, propose air treatment systems for odor control in institutional and commercial buildings and conduct cost-benefit analyses which include energy considerations.

The ultimate objective of the odors project is to determine the minimum ventilation air quantities needed for human health, comfort, and productivity. Ultimately, it is hoped that the state of current knowledge on odor intensity

and perception can be expanded sufficiently so that ventilation standards for odor control in institutional and commercial buildings may be recommended and eventually codified by the appropriate governmental entities.

Review of Ventilation Regulation and Enforcement Practices

Melvyn Green & Associates, Inc., conducted a field survey of current practices in the enforcement of ventilation regulations. Minimum ventilation rates are specified in the various building codes adopted by state and local governments. On a national level, there are three principal model codes (from which local codes are often derived): the Uniform Building Code (UBC), the Basic Code (BOCA), and the Standard Code (SBCC).

Building codes are enforced by both a review of plans submitted for obtaining a building permit and by on-site inspection. The building department is usually a local governmental agency, although sometimes it is under state jurisdiction. Plan checkers are often licensed engineers or architects, whereas inspectors typically have experience in the construction trades.

Interviews were conducted in four states--California, Maryland, Ohio, and North Carolina--in order to obtain a cross-section of environmental conditions, as well as principal types of building regulations.

From an analysis of responses to the questionnaires, the following conclusions emerged:

- 1) Most mechanical plan checking and inspection emphasize only safety rather than both health and safety criteria;
- 2) Many building inspectors and checkers do not have the authority to enforce technical regulations for energy conservation;
- 3) Increased checking for energy requirements, including ventilation, is causing delays and cost increases in construction.

Some of the recommendations proposed to alleviate these problems are:

- 1) More practical training needs to be made available to building department staff to improve building code implementation;
- 2) Public recognition of ventilation as a health issue should be promoted;
- 3) Instructions for the enforcement of ventilation regulations need to be developed.

Automatic Variable Ventilation Control Systems

At present, mechanical ventilation systems usually provide a fixed quantity of "fresh" air to a building space based upon the maximum number

of people expected to occupy that particular space. When the use of a building space is below its design maximum, the amount of outside air brought into the space can be reduced, thus reducing energy consumption through lower heating and cooling loads. One method of determining the necessary ventilation rate for a particular space is to utilize an air quality detector (e.g., CO, CO₂, O₂) sensitive to building occupancy and activity load. The output of the detector can, in turn, be used to control ventilation rates. Before the control system can be implemented, however, it is necessary to determine the relationship between the detected air quality parameter and the required ventilation rate in an occupied space. Efforts will soon be underway to estimate the cost-effectiveness of such variable ventilation control systems and to assess their marketability, both now and in the future. In response to an RFP, eight proposals for development of automatic variable ventilation control systems, based on air quality, are being reviewed. In general terms, the scope of work to be carried out in 1979 and 1980 is as follows:

- 1) Establishment of the relationships between building air quality, occupant/activity loads, ventilation rate, and ventilation health and comfort requirements.
- 2) Design, fabrication and test of a variable ventilation control system with air quality sensors in one or more demonstration buildings. (It is expected the initial demonstration sites will be in educational facilities.)
- 3) Determination of the cost-effectiveness of variable ventilation control systems with air quality sensors for specific building types and for specific mechanical ventilation systems within these building types.
- 4) Evaluation of the effectiveness of the demonstration phase of the program and provision of an estimate of the magnitude of the energy savings expected through national implementation of automatic variable ventilation control systems based on building air quality.
- 5) Assessment of: current and future markets for the proposed automatic variable ventilation control system based on occupancy sensors; types of buildings in which these systems can be used; type of mechanical ventilation systems appropriate for automatic controls; and market penetration potential in these various types of buildings. Assessments will include consideration of both new and existing buildings.

VENTILATION DATA BASE

(Langenborg, Hillis, Nyberg)

The Lawrence Berkeley Laboratory, in conjunction with the Department of Energy, is involved in the development of a computerized data base

focusing on building ventilation and indoor air quality research. Largely in response to the increasing importance of national energy conservation, considerable research effort is being directed toward the areas of building ventilation and indoor air quality. These fields are expanding so rapidly that normal information transfer channels, both within the scientific community and the general public, were considered inadequate. Information transfer to the public sector will be streamlined by the introduction of a computerized information system. The data base, focusing on ventilation and indoor air quality literature, will be directly accessible via telephone lines and a high-speed computer network link. Reports and data abstracts produced by the LBL Ventilation Program will be added to the system in order to facilitate availability to technical and non-technical personnel.

The ventilation data base, when fully operational, will consist of fourteen resource modules:

- 1) Available resources
- 2) Bibliography
- 3) News
- 4) Seminars, workshop, and conferences
- 5) Who's Who in ventilation
- 6) Ventilation--research and development projects
- 7) Ventilation--business and finance
- 8) Ventilation--standards and guidelines
- 9) Models
- 10) Analysis
- 11) User alert service
- 12) Hard copy output
- 13) Utility routines
- 14) Help

Two basic functions of these modules are to aid the user in bibliographic information retrieval (module 2) and to offer a variety of information dissemination services. Basic user access will be via an interactive session with the data base, where English language instructions will be given in the phases of data selection, processing and display. User support will be available through the utility routines, help, and user alert service modules.

Since the bibliographic module spans a diverse range of technical disciplines, assistance was needed in conducting the initial literature survey. To aid in this capacity, and also to take advantage of existing expertise, LBL engaged subcontractors to conduct selective literature searches in the ventilation/indoor air quality field. Implementation of the survey was accomplished through standard retrieval procedures, including computerized literature searches. The references obtained through searches were evaluated and pertinent citations were manually compiled. When an abstract was not available, the article itself was retrieved and an abstract written. Keyword descriptors, used in the indexing process, were next assigned to each citation. These descriptors reflect an article's content and form a controlled vocabulary of precise words relating to the ventilation field. The resulting bibliography consists of citations, abstracts and keywords

relating to relevant domestic and foreign literature, both published and unpublished.

The scope of the initial literature surveys completed by LBL and subcontractors was delegated as follows:

<u>Area</u>	<u>Organization</u>
Contamination control	LBL
Infiltration	LBL
Radon	LBL
Odor Control	John B. Pierce Foundation of Conn., Inc.
Air hygiene in buildings	Naval Biosciences Laboratory
Hospital energy conservation and ventilation requirements	University of Minnesota

In the area of contamination control, the literature survey is restricted to contaminant control theory and application in residential, commercial and public buildings. Areas of emphasis are toxic gas control, general odor control, and non-viable particulate control.

The survey of infiltration literature includes studies of single family structures as well as high and low-rise commercial buildings. Measurement techniques used include tracer gas, pressurization, and wind tunnel investigations. Influences due to wind, temperature, humidity, and terrain are examined.

The radon literature survey contains studies relating to the physical properties of radon and its daughters, instrumentation for their measurement, health effects, air concentration surveys, and regulatory measures.

Literature surveyed by the John Pierce Foundation is an extension of the LBL contamination control survey. It encompasses existing and proposed ventilation requirements for odor control in buildings; odor measurement techniques, both analytical and subjective; and air treatment systems for odor control in institutional and commercial buildings.

The Naval Biosciences Laboratory has surveyed the literature on sampling, transmissions, and control of airborne biological contaminants in enclosed spaces.

In the area of hospital energy conservation, emphasis is placed on the patient environment, with respect to heating, ventilating, and air conditioning parameters. Topics include 1) general air hygiene, hospital-acquired infections, 2) characterization of gaseous chemical contaminants detected in the hospitals, 3) hospital-specific contaminant control procedures, and 4) variables affecting patient comfort, such as temperature, humidity and odor level. Related subject areas

include airborne contaminants related to HVAC systems, energy recovery technology, and alternative hospital HVAC system configurations.

Data access algorithms currently being written require the management system to support a single controlled vocabulary able to index any bibliographic citation maintained in the data base.

A noteworthy feature of the data base is the organization of the controlled vocabulary (keywords) into a set of loose tree structures in which logical relationships will be reflected whenever possible. These tree structures will reflect conceptual groupings within a field of interest and will provide the user with the option of surveying the entire vocabulary through either an alphabetical listing or a logical listing, surveying a logical sub-section of the vocabulary, or interactively stepping through the vocabulary and selecting the appropriate keywords. The purpose of the organizational strategy is twofold:

- 1) It may expand the user's knowledge. A single keyword match made by the user may reveal other keywords of interest.
- 2) It will quickly indicate keyword coding strategies used in the data base so that the user will not be forced to "outguess" the original abstractors.

Keywords presented to the user differ primarily in how they will be utilized in search algorithms. They are classified as either self-explanatory keywords or keywords linked to an explanatory scope note. Self-explanatory keywords will be a simple string of characters. That exact literal string will be displayed to the user, confirmed, and routed to the pattern matching search routines. Keywords linked to a definitional scope note will be displayed to the user accompanied by their scope note. The additional information from the scope note should aid the user in determining the applicability of the keyword. The scope note itself, however, is ignored in pattern matching. After user confirmation, the keyword will be treated as a self-explanatory keyword by the search routines. Synonyms, plurals, and variants will be mapped into the controlled vocabulary. An illegal synonym and its valid vocabulary counterpart will be displayed to the user, at which point the controlled vocabulary keyword may either be accepted or rejected. Unknown words will be echoed as such.

Information dissemination services available through the data base will provide the user with current awareness information. The information available in modules 4 through 6, conveniently obtainable from a single source, may be of special interest to data base users. "Seminars, Workshops, and Conferences" (module 4) will provide a calendar of events relevant to ventilation. "Who's Who in Ventilation" (module 5) will enable the user to obtain an alphabetical listing of individuals interested in ventilation and indoor air quality research. If a more

specific listing is desired, search parameters such as name, affiliation, or main field of interest may be designated. A listing of "Ventilation Research and Development Projects" (module 6) is to include both foreign and domestic projects and will, in addition, flag DOE-sponsored projects.

Remote user access to the data base will be available by direct dial telephone lines to a PDP-11/70 computer housed at LBL or via a high-speed link to the ARPANET computer network.

The data base will be supported on the PDP11-70 by the UNIX operating system and the INGRES data base management system. The ventilation data base, rather than being developed using assembly language, relies heavily on existing support programs provided by UNIX and INGRES, thereby greatly reducing implementation time while adding flexibility and clarity to the data base programs. INGRES is used to execute low-level search and retrieval routines for the data base, and thus implicitly has established the internal data structures.

User interface routines are currently being implemented in the programming language "C" and in the system calls to UNIX. These programs will initiate a user-friendly dialogue and translate user commands into appropriate INGRES and/or UNIX directives. The intent is to minimize the "learning time" necessary to use the resources of the data base.

In short, the scope of the ventilation data base project in 1979 is to establish a prototype data base offering a variety of services in a user-friendly environment. Emphasis is being placed on developing rather complete data structures. Once the data base is opened to the public, major data elements will be monitored and expanded or reduced as indicated by actual user demand. Future development will offer improved human-dialog software and information categories that are continually tuned to user needs.

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DOE-1 Computer Program for Building Energy Analysis

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INTRODUCTION

For the past two years LBL has been developing a comprehensive computer program called DOE-1 for predicting energy use in buildings. This project is funded by the Department of Energy, Division of Buildings and Community Systems. It is a collaborative effort between LBL, Argonne National Laboratory (ANL), Los Alamos Scientific Laboratory (LASL) and Consultants Computation Bureau, with LBL as lead laboratory.

The DOE-1 program is a tool which architects and engineers can use to design new energy efficient buildings and to analyze existing buildings for cost-effective energy-saving modifications.

The structure of DOE-1 is shown in Fig. 1. The program has four main simulation sub-programs:

1. LOADS--Computes hourly heating and cooling loads for each space in the building. The program accounts for loads due to infiltration, heat conduction, solar gain through windows, and internal gains due to people, lights, appliances and other equipment.
2. SYSTEMS--Simulates the operation of the HVAC distribution systems which heat and cool each space in the building, and (in large buildings) distribute fresh conditioned air.
3. PLANT--Simulates the operation of the building's primary heating, cooling, and electrical plant, and calculates the hourly, monthly, and yearly energy requirements for the building.

4. ECONOMICS--Calculates the life-cycle cost of the building, including capital costs as well as maintenance and energy costs. This sub-program also does a cost-benefit analysis, allowing the user to rank different design options on the basis of cost and/or energy use.

DOE-1 differs from earlier programs in two major respects:

1. It executes faster in the computer. DOE-1 is approximately five times cheaper to run than its predecessors. This allows economical study of many alternative design options, leading to a design which is acceptable both from a cost and energy consumption point of view.
2. Where earlier programs read data cards filled with numbers punched in fixed format from forms filled in by the architect-engineer, DOE-1 reads a new "Building Design Language" (BDL) designed to increase speed, flexibility, and reliability of input. Special commands and keywords permit the user to specify building properties and parameters such as geometry, construction materials, schedules, HVAC systems, fuel costs, etc. Environmental data are provided via standard meteorological tapes of hourly weather conditions.

Figure 2 shows sample BDL data input for a simple one-zone building located in Chicago. Figure 3 is an example of program output showing hourly values of outside drybulb temperature, direct solar radiation intensity, building heating load and building cooling load for a building with one interior zone and four perimeter zones.

Fig. 1.

Organization chart of DOE-1.
(XBL 771-7415)

```

TITLE LINE-1 * EXAMPLE BUILDING 1, CHICAGO *  ..

$ PROGRAM CONTROL INSTRUCTIONS $

RUN-PERIOD      JAN 1 1974 THRU DEC 31 1974  ..

DIAGNOSTIC      WARNINGS  ..
ABORT           ERRORS    ..
LOADS-REPORT    SUMMARY=(LS-A,LS-C,LS-D)  ..
BUILDING-LOCATION  LATITUDE = 42.0 LONGITUDE = 88.0
                  ALTITUDE=610
                  TIME-ZONE=6.0  AZIMUTH=30.0  ..

$ COMPUTE RESPONSE FACTORS $

WS-1=MATERIAL    TH=.0583  COND=.0667  DENS=32.    S-H=.3  $WOOD SHINGLES$  ..
PW-3=MATERIAL    TH=.0417  COND=.0667  DENS=34.    S-H=.29 $PLYWOOD SHEATHS$ ..
IN-2=MATERIAL    TH=.2957  COND=.025   DENS=6.     S-H=.2  $FIBERGLASS INS$  ..
GP-1=MATERIAL    TH=.0417  COND=.0926  DENS=50.    S-H=.2  $GYPSUM BOARD$   ..
WA-1-2=LAYERS    MAT=(WS-1,PW-3,IN-2,GP-1) I-F-R=.68  ..

RG-1=MATERIAL    TH=.0417  COND=.834   DENS=55.    S-H=.4  $ROOF GRAVEL$    ..
BR-1=MATERIAL    TH=.0313  COND=.0939  DENS=70.    S-H=.35 $BUILT-UP ROOF$     ..
IN-7=MATERIAL    TH=.0833  COND=.03    DENS=16.    S-H=.2  $PREFORM INSUL$     ..
WD-1=MATERIAL    TH=.0625  COND=.0667  DENS=32.    S-H=.33 $WOOD SHEATHS$      ..
RB-1-1=LAYERS    MAT=(RG-1,BR-1,IN-7,WD-1) I-F-R=.76  ..

$ CONSTRUCTION TYPES $

WALL-1           =CONSTRUCTION  LAYERS=WA-1-2  ..
ROOF-1           =CONSTRUCTION  LAYERS=RB-1-1  ..
FLOOR-1          =CONSTRUCTION  U = 0.05      ..

$ GENERAL SPACE DEFINITIONS $

ROOM-1           =SPACE        AREA = 5000
                                VOLUME=40000  ..

FRONT-1          =EXTERIOR-WALL HEIGHT = 8      WIDTH = 100
                                AZIMUTH = 180
                                CONSTRUCTION = WALL-1  ..

RIGHT-1          =EXTERIOR-WALL HEIGHT = 8      WIDTH = 50
                                X=100
                                AZIMUTH = 90
                                CONSTRUCTION = WALL-1  ..

BACK-1           =EXTERIOR-WALL HEIGHT = 8      WIDTH = 100
                                X=100 Y=50
                                AZIMUTH = 0
                                CONSTRUCTION = WALL-1  ..

LEFT-1           =EXTERIOR-WALL HEIGHT = 8      WIDTH = 50
                                Y=50
                                AZIMUTH = 270
                                CONSTRUCTION = WALL-1  ..

TOP-1            =ROOF          HEIGHT=50       WIDTH=100
                                X=0 Y=0 Z=8
                                AZIMUTH=180
                                TILT = 0
                                GND-REFLECTANCE=0
                                CONSTRUCTION = ROOF-1  ..

BOTTOM-1         =UNDERGROUND-FLOOR AREA = 5000
                                CONSTRUCTION = FLOOR-1  ..

END  ..
COMPUTE LOADS  ..

```

Fig. 2.

Sample DOE-2 Building Design Language input for a heating/cooling loads calculation on a simplified, one-space building with four exterior walls, roof, and slab-on-grade. (Windows and schedules for lighting and occupancy have been omitted in order to fit the input onto one page.)

Fig. 3. Example of an output plot. In DOE-2 hourly values of any of several hundred different calculated variables can be printed or plotted over time intervals chosen by the user. This example shows hourly values of outside drybulb temperature ($^{\circ}\text{F}$), direct solar radiation intensity ($\text{Btu}/\text{ft}^2\text{-hr}$), heating load (Btu/hr) and cooling load (Btu/hr) for a building with one interior zone and four perimeter zones. Values are printed for January 16.

PROGRAM AVAILABILITY AND VERIFICATION

General public use of DOE-1 began in April 1978. At that time Cybernet, a national computer timeshare network, made the program commercially available. Use of the program on Cybernet grew from 14 computer runs in the month of April to 440 runs in October. Architects and engineers are using the program on Cybernet to model many different types of buildings, ranging from single and multifamily houses to large office buildings and hospitals.

In December, the National Energy Software Center (at ANL), which is responsible for distributing the program, made a DOE-1 program tape available to the public. This tape, which costs \$400, contains the entire DOE-1 source code in FORTRAN, a library of hourly weather data for 75 U.S. cities, and sample input and output.

During 1978, eight different DOE laboratories--including LBL and Lawrence Livermore Laboratory--began using DOE-1 to analyze their own proposed and existing buildings for energy conservation. Most of the analyses were done on the LBL computer from remote terminals at the different sites.

In 1978, DOE-1 was also installed on a computer at two other national laboratories, LASL and Brookhaven National Laboratory.

In 1978, DOE assigned LASL the responsibility of coordinating a three-year effort to check DOE-1 against real building performance. This effort includes (1) laboratory measurements of HVAC system components and comparison with DOE-1 simulations; (2) comparison of DOE-1 results with standard manual calculations; and (3) comparison of DOE-1 results with the actual energy consumption of six different commercial buildings. As part of this validation effort, the Energy Efficient Buildings Program the Schools Group at LBL has already compared DOE-1 predictions with monthly gas, oil, and electric consumption for nine schools in different climate zones of the United States. Generally good agreement ($\pm 10\%$) was observed. Still another validation project is being carried out by the International Energy Agency. The aim of this project, in which the LBL Building Energy Analysis Group is participating, is to compare the predictions of sixteen different North American and European energy analysis programs with detailed energy-use measurements on an office building in England. Comparison results are expected by mid-1979.

PLANNED ACTIVITIES FOR 1979

A new version of DOE-1 will be released in April, 1979. This version--called DOE-2--will have improvements resulting from feedback from field use of DOE-1 as well as several new features, including the ability to accurately model central plants with heat recovery. The DOE-2 user documentation will include a Users Guide (an introduction to the program), a Reference Manual (detailed descriptions of the Building Design Language commands and keywords), a Sample Run Book (showing input and output for several different building examples), and a Program Manual (containing flowcharts and a description of each subroutine in the program).

After DOE-2 is released, work will begin on:

1. Commercialization of DOE-2 via workshops, seminars, and exhibits.
2. Parametric sensitivity studies -- using DOE-2 to determine quantitatively the parameters to which building energy use is most sensitive. Figure 4 is an example of a DOE-1 parametric study to determine how heating and cooling loads depend on the amount of thermal mass in a building.
3. Design Manuals -- guides for architects and engineers in the design of energy-efficient buildings, with many sample runs.
4. A special version of DOE-2 with simplified interactive input for use by architects in the conceptual design phase.
5. General improvements to DOE-2 to make it easier to use.

In 1979, the ability to model passive solar components, such as Trombe walls, will be added to DOE-2. This work is being carried out in joint project by the Passive Solar Groups at LBL and LASL. In addition, window management and daylighting routines have been developed by the Windows and Lighting Group at LBL will be added to the program. Daylighting routines will allow the user to determine, for a given building location and geometry, how much energy can be saved by using natural daylight. The window management routines will calculate energy savings which result from regulating solar gain (using shades, for instance) and heat loss (using insulative shutters, for instance) in accordance with changes in environmental variables such as amount of incident solar radiation or outside air temperature.

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Fig. 4. DOE-1 parametric study showing how monthly heating and cooling loads depend on amount of thermal mass. As part of the International Energy Agency Thermal Characteristics of Buildings Project, a 13-story office building located in Wethersfield, England, was analyzed using DOE-1 for three different construction: light, medium, and heavy (corresponding respectively to 30, 70, and 130 pounds of building material per square foot of floor area). The program shows that increased thermal mass leads to slightly lower heating and cooling loads. (XBL 792-438)

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(All DOE-2 documentation is available from the National Technical Information Service (NTIS), U. S. Dept. of Commerce, 5285 Port Royal Road, Springfield, VA 22161.)

Schools Program

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INTRODUCTION

In 1975 this program was initiated by the American Association of School Administrators (AASA) and funded by the Federal Energy Administration (FEA). Educational institutions use approximately 20% of all energy consumed in institutional and commercial buildings. On a per pupil basis energy costs have increased by nearly 50% between 1973 and 1975 with continued increases thereafter. School districts have large fixed labor costs so even small savings in operating costs are very desirable.

In 1975 an energy audit and monitoring program was developed to study the energy consumption of schools in the United States. The American

Association of School Administrators, with funds from FEA, proposed a demonstration project involving ten schools representative of climatic regions of the United States; the school locations are shown in Fig. 1. Cost effective retrofit measures were selected for these schools with suggestions made for a demonstration project to implement and monitor the effectiveness of such measures.

An effective energy conservation program can be divided into four phases:

1. Conduct an energy audit and identify energy conservation opportunities with an attractive payback period.

Fig. 1. Demonstration sites.

Table 1. Schools energy conservation opportunity modifications.

	Reduce Outside Air	Night Set Back	Roof Insulation	Replace Burners	Lower Thermostat Setting	Close Exhaust Dampers	Weather Strip	Increase Boiler Eff.	Reduce Glass %	Summer Equip. Shut Down	Auto Boiler Control	Improve A/C Use	Improve Indoor Lighting	Reset Air Temperature
1. Warwick	☐	☐	☐											
2. Glen Rock	☐		☐	☐	☐	☐								
3. Langhorne	☐		☐				☐	☐						
4. Hindman	☐													
5. Columbus	☐						☐		☐					
6. Lubbock										☐				
7. Lincoln	☐	☐			☐					☐			☐	
8. Sioux Falls	☐						☐							
9. Stevens Point	☐										☐	☐	☐	
10. Kennewick	☐	☐	☐				☐	☐				☐		

2. Select and design modifications.
3. Install retrofit modifications and verify installation.
4. Monitor the energy use of the buildings after retrofit and compare with the energy use prior to the modifications.

Phases 1 and 2 of this project had been completed when LBL became involved in June 1977. The laboratory was given the responsibility of administering Phase 3, implementing Phase 4 and overall management. At least one instrumented school will have its indoor air quality monitored by the Energy Efficient Buildings Program Mobile Van.

OBJECTIVE

The objective of the LBL involvement in the Schools Program is to evaluate the energy savings resulting from building and HVAC modifications implemented at nine of the selected elementary schools. Under a policy decision that paybacks of less than 12 years were cost effective, the retrofit modifications implemented in each school were determined to be attractive. Examples of proposed and implemented retrofit modifications are shown in Table 1. Modifications chosen by AASA for each school were based on an energy audit and computer model prediction of payback within the 12 year guideline.

The results of the Schools Program will provide data useful to school districts that elect to apply for the \$900 million dollar federal matching funds available under the 1978 National Energy Act.

RETROFIT IMPLEMENTATION

During 1977 and 1978, LBL implemented Phase 3. This was accomplished through a contract with the American Association of School Administrators. LBL is responsible for ensuring that the engineering designs reflect and accurately implement the proposed modifications. All proposed retrofits were installed by December 1978.

INSTRUMENTATION AND DATA ANALYSIS

In addition, LBL implemented Phase 4 at nine schools. We commenced analyzing data to determine the actual energy savings attributable to the installed modifications. At three of the schools (Eastridge, in Lincoln, Nebraska; Fairmoor, in Columbus, Ohio, and Washington, in Kennewick, Washington) microprocessor-based energy monitoring systems designed, built and installed by LBL are used to collect, store and do preliminary analysis on the data. At each instrumented school, from 35 to 70 hourly average readings of temperature, flow, on/off switch monitoring and meteorological data are gathered. These data are periodically transmitted by telephone line to LBL where the monitored parameters

are analyzed in detail and the schools' energy consumption and energy savings are calculated. The data are analyzed with the objective of identifying energy savings attributable to each modification and to the school buildings as a whole.

At all nine schools, utility and oil meter readings are taken every two weeks and sent to LBL. The heating fuel energy use is adjusted for degree-days. Energy use after the retrofits were installed is compared with energy use before the retrofits were installed to determine overall savings. The savings attributable to each modification at each school are estimated using the DOE-1 computer simulation program.

Since most of the retrofit modifications were installed during the latter part of FY 78 and early FY 79, there was little data gathered on this program during the 1977/78 school year. Data were gathered from the one school which was instrumented during a portion of the 1977/78 school year and that data indicated little energy savings.

The heating system and building were reanalyzed and Phase II modifications were implemented to correct defects in the system which were not

identified during the initial study. These Phase II retrofits were designed to improve the operation of the system and increase occupant comforts. Initial data gathered during the 1978/79 school year indicate an additional energy savings has now been achieved. This energy savings will be studied to see if it is attributable to the Phase II retrofit modifications or to other factors.

Preliminary data from all schools indicate savings from 0 to 40% in heating fuel use and 0 to 39% in electricity use. In most cases this is based on only four months of data. Savings projected in the Saving Schoolhouse Energy Report ranged from 18% to 54% in heating fuel consumption and 0 to 43% in electricity use.

LBL's DOE-1 simulation program was used to check the original savings projection for each school. The data obtained from the instrumentation system is being used to study the actual effects of each modification and to compare these effects to simulated results.

A final report analyzing energy use and the cost effectiveness of retrofit modifications will be available in July 1979.

Hospitals Program

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INTRODUCTION

With funding from the Department of Energy's (DOE) Division of Buildings and Community Systems, work on the Hospitals Program began in August 1977. The Hospital Program is a component of Lawrence Berkeley Laboratory's (LBL) Energy Efficient Buildings (EEB) Program, and is closely coordinated with the Ventilation Program.

In the United States, hospitals account for approximately 12% of all energy used in institutional and commercial buildings (or 1.1×10^{15} Btu).¹ This is equivalent to an annual nationwide outlay of 2.7 billion dollars at 1978 prices. In large part, this substantial expenditure is a result of the usual practice of U.S. hospitals to follow standards of design and operation (based on state and federal requirements) that provide the best possible environment for patients and staff, without giving full consideration to energy conservation opportunities.

We have singled out hospitals for special study because of their relatively large energy use. Hospitals are considerably more energy-intensive than most other buildings, especially for space and water heating, and for cooling (see Fig. 1). Heating ventilation and air conditioning (HVAC)

systems use more than 50% of the energy consumed in hospitals, with lighting and water the next two largest areas of use (see Fig. 2). LBL's Hospitals Program staff is looking closely at energy conservation opportunities in the HVAC systems, as well as in other hospital areas (e.g., water use, lighting requirements).

Fig. 1. Energy use indices for educational, retail, office, and hospital buildings, 1970.¹ Energy use in primary units.
(XBL 7810-11637)

Fig. 2. Hospital energy use in 1975.¹ Energy use calculated in resource or primary units. To account for conversion losses, the primary energy for electricity has been calculated in terms of 10,383 Btu/KWhr (the average heat rate estimated by the Edison Electric Institute for 1975). In addition, 9% electrical transmission-distribution losses have been assumed. (XBL 792-439)

A large percentage of the hospital community today believes that hospital patients may be more susceptible than the healthy population to airborne infections, to the deleterious effects of high concentrations of odors and chemical contaminants, and to changes in temperature and relative humidity. For this reason, the hospital design standards currently in existence, as exemplified by the Hill-Burton standards of the U.S. Department of Health, Education and Welfare (HEW), are extremely conservative. The ultimate objective of the LBL Hospitals Program is to develop energy conservation strategies which do not compromise the health, safety, and comfort of patients and staff.

With passage of the National Energy Act (NEA) in late 1978, the cost-effective energy conservation measures being identified by the Hospitals Program take on even more importance. The NEA will make funds available (on a cost-sharing basis) to many hospitals for energy audits and for energy-conserving retrofits. LBL's Hospitals Program will play a major role in disseminating information to hospitals about these cost-effective energy-conserving retrofits.

OBJECTIVES

The goals of the Hospitals Program are:

- 1) Assessment of the effects of energy conservation measures on indoor air quality (including air chemical content, microbial burden, odors and comfort factors) in hospitals, before and after energy-conserving retrofits, and in new "energy-efficient design" hospitals.
- 2) Development of cost-effective energy conservation measures.
- 3) Rapid transfer of advanced energy conservation technology in practical format to users.

In order to achieve these goals, LBL undertook in 1978 a number of different tasks:

- 1) A review of current hospital, ventilation and thermal standards with recommendations for hospital energy conservation opportunities compatible with the health, safety, and comfort of the staff and patients (subcontract to the University of Minnesota);
- 2) A study of energy-efficient water use in hospitals (subcontract to Hittman Associates, Inc.);
- 3) A baseline study on indoor air quality at the Naval Regional Medical Center (NRMC) in Long Beach, California, performed by LBL using the EEB Mobile Laboratory (see "Ventilation Program") and the University of California Naval Biosciences Laboratory, as well as an energy study of the NRMC (subcontract to the Consultants Computation Bureau); and
- 4) The groundwork for establishment of LBL as a coordinating and information dissemination center for energy conservation practices in hospitals (performed by the Hospitals Program staff).

Under the sponsorship of DOE and HEW, it is expected that a uniform set of energy efficient hospital ventilation, thermal, and water use standards will eventually be adopted by federal, state and local governments and the hospital community as a whole.

VENTILATION STANDARDS: ASSESSMENT AND DEVELOPMENT

The University of Minnesota's School of Public Health, under a subcontract managed by LBL's Hospitals Program staff, examined current hospital ventilation standards to determine if they could be relaxed on the basis of criteria that do not compromise the health, safety, and comfort of patients and staff. As part of this project, the University of Minnesota School of Public Health convened, in February 1978, an International Working Conference on Hospital Ventilation Standards and Energy Conservation. The conference brought together an International Advisory Panel of six American and four European experts

in the field, as well as fifteen observers. In brief, the major findings of the conference² were:

- 1) Hospitals in general are over-ventilated, and some reduction in ventilation rates seems possible. However, care must be exercised so that specific micro-environments, such as the operating and delivery rooms, are adequately ventilated.
- 2) High ventilation rates have traditionally been assumed necessary in the hospital for control of airborne infections. However, current studies indicate that airborne infections are only a very minor part of the overall hospital infection problem and would not be measurably affected by some reduction of ventilation air. The conference also reported that poor hygienic practices permitting interperson transfer of pathogenic microbes are the principal determinants of hospital-acquired infections.
- 3) Humidity does not need to be controlled on the basis of human comfort. Other factors, such as the control of static electricity, should define humidity endpoints.
- 4) The control of chemical contaminants is probably the limiting constraint on ventilation requirements. At the present time, no information exists

to adequately characterize the airborne chemical load in the hospital setting.

- 5) Rather than setting basic ventilation rates to dilute odors below their olfactory thresholds, odors should be controlled at their point source. The conference also stressed that Yaglou's seminal work on the subject (see "Ventilation Program") needs updating in the context of today's technology and changed cultural environment.

The University of Minnesota issued a report, Hospital Ventilation Standards and Energy Conservation: A Summary of the Literature with Conclusions and Recommendations, FY'78 Final Report, which was published in September 1978.³ In this report there is a discussion of hospital ventilation and thermal standards, the role of air in hospital-acquired infections, chemical contamination of hospital air, and the effect of thermal factors and odors on the patient care environment. Much of the information comes from an extensive literature survey⁴ undertaken by the University of Minnesota in 1977. The final chapter of this report includes conclusions and recommendations developed from the literature review, as well as from the international conference.

In December 1978, the University of Minnesota distributed proposed modifications of ventilation and thermal standards in hospitals to various government agencies, organizations, and individuals concerned with both energy conservation and the quality of the patient care environment. Table 1 summarizes their recommendation in

Table 1. Differences between Hill-Burton 79-14500 standard and the University of Minnesota discussion standard for hospital ventilation and thermal conditions for selected areas.

Area	Outdoor Air Changes		Recirculation By Room Unit		Temperature	
	Hill-Burton Standard	Proposed Standard	Hill-Burton Standard	Proposed Standard	Hill-Burton Standard	Proposed Standard
PATIENT ROOM	2	1			75	68-78
PATIENT CORRIDOR	2	1			75	68-78
EXAMINATION ROOM	2	1			75	68-78
MEDICATION ROOM	2	1			72	68-78
PHARMACY	2	1			72	68-78
TREATMENT ROOM	2	1			75	68-78
X-RAY, FLUORO-SCOPY ROOM	2	1	No	Optional	75	68-78
X-RAY, TREATMENT ROOM	2	1			75	68-78
PHYSICAL THERAPY & HYDROTHERAPY	2	1			75	68-78
SOLID UTILITY	2	1			72	68-78
CLEAN UTILITY	2	1			72	68-78
AUTOPSY	2	1			72	68-78
WORKROOM	2	1	No	Optional	72	68-78
LABORATORY, GENERAL	2	1			72	68-78
LABORATORY, MEDIA TRANSFER	2	1			72	68-78
FOOD PREPARATION CENTERS	2	1			72	68-78
LAUNDRY, GENERAL	2	1	No	Optional	72	68-78
CENTRAL SUPPLY						
SOILED ROOM					72	68-78
CLEAN WORKROOM					72	68-78
TRAUMA ROOM					75	70-76
NURSERY SUITE					75	72-76
RECOVERY ROOM					75	72-76
INTENSIVE CARE					72-78	72-76

comparison with the existing Hill-Burton standards. In nearly all the hospital areas considered (operating, recovery, delivery rooms, etc., are excepted), it is proposed that minimum ventilation be reduced from two to one air change(s) per hour. In all areas except in the operating, trauma, delivery and recovery rooms, nursery suite and intensive care unit, it is recommended that design temperature shall be 68°F for heating and 78°F for cooling. By comparison, the Hill-Burton 79-114500 Standard specifies 72°F or 75°F for each space. Except for the six areas noted above, proposed design criteria suggest a minimum level of relative humidity of 30% during the heating season. For cooling, it is suggested that humidity levels be selected within the comfort envelope defined by the American Society of Heating, Refrigerating and Air Conditioning Engineers (ASHRAE) Standard 55-74, entitled Thermal Environmental Conditions for Human Occupancy,⁵ for minimum total HVAC system energy use. If implemented, this standard would replace a maximum humidity level of 60% in most of these areas under Hill-Burton 79-14500.

Planned Activities for 1979

The University of Minnesota intends to compile a set of recommended changes in hospital ventilation and thermal standards after written comments on its draft standards are received and analyzed. In April 1979 a meeting will be held under DOE and HEW auspices to discuss the acceptability of the composite standards. Technically-oriented members of the hospital professional community (for example, certain members of ASHRAE, American Hospital Association (AHA) and HEW) will be invited to this meeting. Following publication

of final recommended ventilation and thermal standards by the University of Minnesota in the Summer of 1979, LBL will seek adoption of the revised standards at all levels through coordination with representatives of HEW (Health Resources Administration, Hill-Burton staff, and Communicative Diseases Center) DOE, ASHRAE, Veterans Administration, Department of Defense, Bureau of Indian Affairs, the hospital operating group of the Public Health Service, AHA, the Joint Committee for the Accreditation of Hospitals and other appropriate groups. It is estimated that if the modifications in ventilation standards are implemented in 25% of the existing hospitals, then 15×10^{12} Btu, or 1.5% of the total hospital yearly energy budget can be saved with minimal cost.

The University of Minnesota, under subcontract to LBL, will conduct a study of chemicals in hospitals. This study will involve a survey of several Minnesota hospitals in order to catalog toxicity, carcinogenicity, flammability, and other characteristics of chemicals found in hospital environments. The University of Minnesota will recommend control measures for the chemicals catalogued in an effort to minimize the impact of these chemicals on indoor air quality.

ENERGY EFFICIENT WATER USE IN HOSPITALS

In order to identify water-related energy conservation measures which can be implemented by hospitals without adversely affecting the patient care environment, LBL awarded a contract in October 1978 to Hittman Associates,

Table 2. Benefit cost matrix for identified hospital water heating conservation opportunities.

Conservation Measure	Annual Energy Savings (Therms/Year)	Cost Savings (\$/Year)	Cost Savings (%)	Energy Savings (%)	Cost (\$)	Payback (Months)
Repair Leaks in Piping	1,095	281	2.1	2.0	Minimal	Immediate
Use of Cold and 140°F Water in Laundry	41,750	10,040	76.6	74.9	4,200	5.0
Use of Cold Water in Floor & Bathroom Cleaning	511	96	0.7	0.9	Minimal	Immediate
Use of Cold Water in Dishwater Pre-Rinse	9,772	1,837	14.0	17.5	Minimal	Immediate
Lowering Dishwasher Temperature to 100°F from 160°F	1,844	442	3.4	3.3	3,000	81.4
Reduce Water Flow Rate in X-Ray Film Processing	808	405	3.2	1.4	Minimal	Immediate
TOTAL:	55,780	13,101	100	100	7,200	6.6

Inc. to study energy efficient water use in hospitals. The scope of work for this study is:

- 1) Define water and water heating energy use in hospitals with respect to functional areas, e.g., diet kitchen, cafeteria, laundry, etc.
- 2) Review existing and proposed energy conservation measures for diet kitchen and laundry hot water.
- 3) Survey existing and proposed methods for energy efficient water use with emphasis on diet kitchen and laundry applications, and review standards and regulations.

Drawing upon the preliminary findings obtained by the Hittman study⁶, Table 2 illustrates potential energy and cost savings that could be achieved by more efficient use of water in a "typical" hospital with a 200-bed capacity. Conservation measures numbers 2 and 5 in Table 2 require replacement of existing equipment with equipment designed for operation at low temperatures. Costs shown are estimated differential costs above the costs of conventional equipment, assuming equipment would have to be replaced in time anyway.

The Hittman study should result in the development of a comprehensive guide on methods for reducing the quantity of energy expended on the heating of water in hospitals.

Planned Activities for 1979

In 1979, the Hittman study on "Energy Efficient Water Use in Hospitals" will be completed, and results of the study will be available for implementation. Following completion of the study, the LBL Hospitals Program staff intends to select an appropriate site (several negotiations are currently underway), and conduct programs to test the results of the study. First, hot water energy use in existing operation will be measured, and then the appropriate recommendations from the Hittman study will be implemented. To provide a real-world validation of the savings predicted by the Hittman study, the hot water energy use will again be measured, and the level of sanitation evaluated.

FIELD STUDIES DEMONSTRATING ENERGY CONSERVATION OPPORTUNITIES IN HOSPITALS

The previously described studies (University of Minnesota and Hittman) have identified energy conservation opportunities (ECOs) in the ventilation, thermal and water use systems in hospitals. The LBL Hospitals Program staff is conducting field studies demonstrating the application of these ECOs and assessing their impact on the hospital care environment.

Initial work is focusing on indoor air quality measurements before and after ventilation system retrofits. LBL, using the EEB Mobile Laboratory, performed a baseline study on indoor air quality

at the Naval Regional Medical Center (NRMC) in Long Beach, California, in September and October, 1978. Air quality parameters, including chemical and microbial contaminants, were monitored in several different patient care areas, including an examination room, a cast removal area, and a four-patient ward room. Some of the microbial sampling was done in a cast removal room to consider "worst case" conditions. Detailed analysis of the baseline air quality data is in progress. This baseline data, obtained while the HVAC system was operated under conditions consistent with present ventilation and thermal standards, will be compared with data gathered during 1979 following implementation of a series of energy conservation measures.

To understand and model the NRMC energy consumption, and to develop the most favorable set of ECOs, LBL subcontracted with Consultants Computation Bureau (CCB) to perform an energy analysis of the NRMC.⁷ The study consisted of the following elements:

- 1) Construction of a computer simulation of the hospital for use as an analytical tool in the course of the present study, and for possible future energy analyses of the hospital.
- 2) Analysis of the present modes and levels of energy conservation.
- 3) Identification, analysis and ranking of ECOs.

The computer model used in this study was the public domain DOE-1 model, which CCB ran on LBL computing facilities. The final computer simulation of the hospital matched actual energy consumption quite closely for the year chosen, 1975.

Table 3 illustrates the predicted savings that can be achieved through the utilization of a combination of economically-feasible ECOs, including: (1) temperature-controlled economizer on an assembly hall air conditioning system; (2) expanded thermostat throttling ranges; (3) night shutdown of selected fan systems; (4) elimination of air tempering in some systems, and control of hot and cold duct temperatures by zone of greatest demand in other systems; (5) and division of one large air handling system into two smaller systems, permitting night shutdown of the larger of the two systems. It has been calculated that the cost to implement these changes is approximately \$170,000, the life cycle cost savings (25 year life cycle) are \$4,000,000, the reduction in resource energy consumption for the chosen year is 31.8%, and the annual savings amount to \$164,000 for a payback period of one year.

The engineering design for a series of modifications to a portion of the heating, ventilating and air conditioning system at NRMC Long Beach has been completed. These changes will implement some of the more favorable ECOs as determined by the CCB study, and will permit implementation of the reduced ventilation levels proposed by the University of Minnesota study.

Table 3. Predicted energy savings (in 10^9 BTU/year) through the utilization of energy conservation opportunities (ECOs).

	<u>Boundary*</u>			<u>Resource⁺</u>	<u>BTU/Gross Sq. Ft.-Year</u>	
	<u>Fossil</u>	<u>Electric</u>	<u>Total</u>	<u>Total</u>	<u>Boundary*</u>	<u>Resource⁺</u>
1975 Base	73.875	46.194	120.070	212.472	252,248	446,370
Combined ECO's	41.685	34.663	76.348	145.684	160,395	306,059
% Reduction	43.6	25	36.4	31.4	36.4	31.4

*Boundary energy use is the actual consumption of fuel and electricity within the confines of the facility. The conversion 1 KWH = 3413 BTU is used.

⁺Resource energy uses imposes a factor of 3 on electrical energy use within the boundary to account for generation, transformation, and distribution losses.

Planned Activities For 1979

To determine if proposed energy conservation alterations are detrimental to air quality, mechanical alterations to selected areas of the Long Beach NRMC will be completed in late spring of 1979. These mechanical alterations are based in part on the recommended ventilation and thermal standards proposed by the University of Minnesota. These measures will be implemented on a double duct air handling system serving an outpatient area. These include changing the existing temperature-controlled economizer to enthalpy control; modifications to the duct temperature control systems to provide just enough heat to satisfy the coldest zone, and just enough cooling to satisfy the hottest zone; and closed-loop control of outside air, supply air, and return air quantities at selected values. Finally, humidity will be controlled only to maintain a minimum of 30% relative humidity in the space. To determine the effects of these alterations, BTU energy measuring systems will be installed on heating and cooling coils of the selected air handler. Each of these systems consists of a vortex-shedding flow meter, supply and return temperature sensors, and analog devices to integrate the product of flow and temperature difference to determine BTU energy consumption of the coil.

During 1979, the EEB Mobile Laboratory will return to the Long Beach NRMC to determine what effect the energy-saving alterations described above and the implementations of the University of Minnesota recommendations will have had on indoor air quality. The CCB-predicted savings will be validated and the University of Minnesota recommendations will be released on the basis of these results.

Studies similar to those being conducted at the Naval Regional Medical Center will be performed at a hospital in a more severe climate. Discussions are in progress with the Veterans Administration (VA); the VA Hospital in Omaha, Nebraska is the most probable site for these

studies. These studies, to be initiated in 1979 and completed by late 1980, will include an energy audit, modifications to the ventilation system, indoor air quality studies to determine the impact of the ventilation modifications, and demonstration projects for waste water heat recovery and gray water re-use.

DISSEMINATING INFORMATION AND COORDINATING RESEARCH

In addition to coordinating and performing research to gain information on hospital energy conservation, the Hospitals Program staff is assuming a central role in disseminating such information. Results of the University of Minnesota study, recommending relaxation of ventilation and thermal standards in most areas of a hospital, are crucially important for reducing energy use in hospitals. Consequently, the Hospital Program staff presented these findings at a recent meeting of the American Hospital Association and participated in informal meetings with several federal and state agencies to facilitate widespread acceptance of the revised standards by national and local code-making and code-enforcing agencies. The Hospitals Program staff participated in a series of meetings and presentations during 1978, both to effect inter-agency coordination of present and future demonstration projects, and to present results of current research to interested groups.

Planned Activities For 1979

The Hospitals Program staff plans a major effort to become a clearinghouse for energy conservation information relating to hospitals, including assessment of ventilation and thermal standards on energy consumption, and methods for reducing hot water energy use in hospitals. Consequently, during 1979, the Hospitals Program will disseminate the results of its research to federal and state agencies, professional societies, hospital associations, and individual hospitals through a series of meetings, presentations and symposia.

In 1979, an annotated bibliography of energy audit source materials will be prepared at Lawrence Berkeley Laboratory and published. This bibliography should help individual institutions and state energy agencies to implement the energy audit provisions of the 1978 U. S. National Energy Act.

Finally, also in 1979, the University of Minnesota will conduct a survey of hospital energy conservation activities of state and federal agencies with the aim of disseminating this information to interested parties.

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Energy Efficient Windows Program

S. Berman, J. Klems, M. Rubin, S. Selkowitz, and R. Verderber

In the latter quarter of 1976, we initiated a program to plan, manage, and conduct an Energy Efficient Windows Research Program at LBL. Funding was provided from the Technology and Consumer Products (TCP) Branch of the Department of Energy. This branch is charged with supporting research, development, and demonstration (RD&D) activities in energy conservation that will:

- accelerate the efforts of private industry
- complement the efforts of private industry
- foster the acceptance of energy saving technology
- maximize the effectiveness of energy use
- minimize adverse socio-economic and environmental impacts.

The Energy Efficient Windows Program at LBL is designed to further these TCP goals. The potential impact of this program on total national energy consumption is large. Approximately 20% of annual consumption is used for space conditioning of residential and commercial buildings, and about 25% of that figure is required to offset loads resulting from windows. Thus 5% of

national energy consumption, 3.5 quads annually, or 1.7 million barrels of oil per day equivalent are tied to the thermal performance of windows. Although the conservation potential is enormous, there are significant obstacles to achieving that potential. Recent studies of problems concerning diffusion of innovation into the industry suggest that in the area of energy conservation, the development of technically usable, energy conserving products and design practices will not necessarily be sufficient to guarantee their acceptance, their utilization, or their effective impact in reducing energy consumption. The Energy Efficient Windows Program has initiated efforts that not only will develop and commercialize innovative and effective window designs, materials and accessories, but will also ensure that they are recognized, accepted and utilized by design professionals and the public at large. The LBL role encompasses overall program planning and assessment of research priorities, technical management of research activities subcontracted to private sector firms, and an in-house LBL windows research program.

ACCOMPLISHMENTS DURING 1978

Program accomplishments have been divided into two major areas: (1) program planning,

management and support activities, and (2) materials, processes and prototype developments.

In its Program Planning and Management role, LBL plays a vital integrative and catalytic role. The process of formulating short and long term goals and building an RD&D program around them is complicated by the fragmented nature of the "window" industry. Although a small number of large firms manufacture glass, a vast number of small businesses, most of whom service local markets, sell aluminum and wood frame windows. Additional progress has been made in refining a model of the structure of the window industry. We have looked in detail at several subsectors of the window accessories market to understand the relationships between product manufacturers and the distribution and sales networks that provide building designers and owners/operators with

product selections. As an example, Fig. 1 is a schematic of the solar control film industry.

A further characteristic of the window industry is that significant product developments can be generated by small firms with minimal resources. We have endeavored to assist this process by developing a publication which will be circulated widely through the professional community (architects, engineers, manufacturers, inventors, suppliers, code officials, researchers, etc.) to report on latest developments, patents, new materials and products, legislation, publications, etc. Response to the concept has been positive and, after many delays which saw the initial issue grow from a planned six pages to thirty two pages, Windows for Energy Efficient Buildings went to press just prior to the end of 1978. Publication of future issues is planned on a quarterly basis. Extensive product files, patent

Lawrence Berkeley Lab
Energy Efficient Windows
Program

Data shown above has been collected from a wide variety of sources and should be used with caution.

Fig. 1. Solar control film industry profile. (XBL 792-509)

files, bibliographies and related information resources have been compiled in the process of generating material for this publication.

A Building Technology Laboratory has been set up in the College of Environmental Design of the University of California, Berkeley to support research and development activities, to provide independent tests and evaluations of materials and products submitted by subcontractors, and to permit evaluation of new products being introduced to the marketplace. A calibrated hot box facility (shown in Fig. 2) was completed in 1978 and is now in use to test the thermal performance of windows and associated energy conserving accessories. Infiltration tests on windows can now be made easily in our laboratory. A UC transmission spectrophotometer has been fitted with a variable incidence angle reflectance attachment so that long wave IR properties of thin film coatings can be determined. A solar calorimeter has been designed and will be built in 1979.

Fig. 2. A calibrated hot box facility.
(CBB 789-10901)

Testing Capabilities

1. Mobile
 - Simulate N, S, E, W exposures
 - Three climatic zones within 100 miles
2. Dynamic testing
 - 24 hour cycle
 - Sun, wind, temperature, humidity
3. Comparative testing
4. Test of management strategies
5. Simulated buildings
 - Uninsulated $\longleftrightarrow$ well insulated
 - Thermal mass — low to high
6. Data acquisition system

Fig. 3. Mobile window testing facility schematic. (XBL 792-511)

Laboratory testing capabilities described above are all steady state measurements of static materials and devices. A major philosophical thrust of our program is the use of managed window systems, windows whose thermal/optical properties are changed (manually or automatically) over time. To test the performance of such devices, a Mobile Window Testing Facility was conceived in 1977. This unique facility would allow tests of net window thermal performance (combined infiltration, conduction/convection, radiation effects) as a function of climate and window orientation over many daily test periods. The four side by side test cells can be configured to simulate a range of building insulation levels as well as a range of building thermal capacities. Results from this test facility should provide good comparative results on which to base assessments of window performance, and against which analytical models can be validated. The conceptual design of the trailer was refined in 1978, and a data acquisition system was designed and ordered. Final design and construction will be completed in 1979 (see Fig. 3 for a schematic of this facility).

A detailed analytical model of the net heat transfer through a window assembly composed of an array of glazing elements and optical coatings was completed in 1978. This model will be expanded and refined in the coming year. A computer model for calculating optical constants for a variety of multilayer optical films was completed. Coating spectral properties are calculated and resultant optical coefficients can be generated for the solar spectrum, the visible spectrum weighted by the eye's sensitivity, and the long wave IR spectrum as a function of black body temperature.

In order to determine the effectiveness of window management strategies, the performance of the window must be assessed in the context of the performance of the entire building. For these studies, we have utilized a modified version of Building Energy Analysis Program (DOE-1). The program has been modified to incorporate a variety of window management strategies such as moveable shades and shutters. The output format has been revised to provide detailed quantitative information on the hourly performance of windows and a more qualitative, graphic perspective of the net gains and losses of windows on an hour by hour basis over the year (see Fig. 4).

The development of a Windows Program Plan was initiated in 1978, to be completed in draft form by mid-1979. This plan would outline and coordinate all DOE supported energy conservation activities related to windows, and would interface with the recently developed Thermal Envelopes and Insulating Materials Program Plan. Significant efforts were made in 1978 and will continue into 1979 to better coordinate with the DOE Passive Solar program, to avoid unnecessary duplication of efforts, and to initiate joint R&D activities.

The optimal use of daylighting in buildings promises substantial electrical lighting energy

savings. A panel was convened at LBL in November to review the state of the art in daylighting design practice and to discuss expanded activities that DOE might undertake to speed widespread use of daylighting in buildings. Several related projects are discussed in the Energy Efficient Lighting Program article in this volume.

The development and commercialization of new materials, production processes, and window prototypes is being supported through a variety of subcontract and in-house research efforts. These include:

Heat Mirror Commercialization

A heat mirror is an optical coating, applied to a glass or plastic glazing material, which transmits the full solar spectrum but reflects long wave infrared radiation emitted by room temperature surfaces. By reducing the radiative component of thermal losses, the heat transfer coefficient of a single or double glazed window is approximately halved. Work completed under subcontract in 1978 revealed that the lack of corrosion and abrasion resistance was a serious weakness in many heat mirror films. Suntek Research Associates, Corte Madera, CA completed a project to survey polymer overcoats which would provide their heat mirror coating with enhanced resistance to corrosive and abrasive stresses without serious degradation in the heat mirror emittance. Although a number of promising coatings were identified and tested, additional development will be required before such films have acceptable lifetimes. This problem suggests that heat mirrors may find their first use in sealed airtight spaces of new windows, rather than as retrofits to single glazing, as originally envisioned. Another approach to improving the abrasion/corrosion resistance of heat mirror films is to deposit them on IR transparent substrates and then sandwich the optical film between the glass and the plastic substrate. As an offshoot of their work on selective reflectance coatings, Kinetic Coatings, Inc., Burlington, MA has deposited heat mirror films on IR transparent plastic substrates using an ion beam sputtering process, which produces very durable metal-dielectric coatings. Most of the problems associated with deposition on FEP-type substrates have been solved and coatings are now undergoing test and evaluation.

If heat mirrors are to be incorporated in new windows rather than as retrofits to existing windows, the coatings can be deposited directly on glass, rather than on thin transparent substrates. We have initiated a review of vacuum deposition as well as electrochemical processes for depositing heat mirror films directly on glass. We are also examining various window configurations incorporating multiple glass, plastic and coating layers. Note that the best of the heat mirror window systems (Fig. 5) has a U value approaching that of a well insulated wall.

In 1978, several solar control film manufacturers have begun to market low emissivity solar control films. These improve the insulating

Horizontal map of the 365 x 24 array for the total window contribution to the total building load in BTU per sq. ft. of window

Fig. 4. Net window gain (X) or loss (') on an hourly basis. For each hour of each day, an (X) indicates that the windows are providing net energy to the building; a (') indicates that the windows are losing energy.

FIG.	HEAT MIRROR EMMITTANCE	U VALUE	SOLAR TRANS. (NORMAL)
9a	SINGLE GLASS, PLASTIC RETROFIT (H.M. on polyester, on inside surface)		
	.20	.76	.77
9b	DOUBLE GLASS (H.M. on air gap surface, glass)		
	.20	.35	.70
9c	SINGLE GLASS, PLASTIC RETROFIT & AIR GAP (H.M. on air gap surface, polyester)		
	.20	.34	.73
9d	DOUBLE GLASS, MID AIR GAP PLASTIC FILM (single H.M. on polyester)		
	.20	.24	.64
9e	DOUBLE GLASS, DOUBLE MID GAP FILM (single H.M. coating, folded polyester)		
	.20	.16	.53
9f	DOUBLE GLASS, DOUBLE MID GAP FILM (single H.M. coating, folded FEP film)		
	.20	.15	.58

Note: All air gaps .5"; $T_{out} = 0^{\circ}F$, $T_{in} = -70^{\circ}F$

Fig. 5. Window configurations incorporating heat mirrors. Standard winter U value for single glass is 1.1 BTU/ft²-hr⁰F and .5 for double glazing. These designs show promise of reducing the U value of .12 BTU/hr-ft²0F while still maintaining approximately 50% solar transmission. (XBL 792-513)

properties of windows as well as providing sun control. Market acceptance of these films will be watched closely since transparent heat mirrors will have to overcome many of the same market uncertainties and barriers.

Selective Reflectance Coatings

Reflective and/or tinted glass is widely used in many commercial buildings to reduce solar impact and thus energy requirements for air conditioning. Glazing with very low shading coefficients may reduce the opportunities for using available daylight and thus increase electrical lighting energy requirements.

Since approximately one half of incident solar radiation is short wave infrared which contributes nothing to illumination, an optical coating with selective reflectance properties could ideally reduce cooling load by 50% without reducing available illumination. Such coatings are being developed under subcontract by Kinetic Coatings, Inc., using novel ion beam sputtering techniques which produce very durable, weather

resistant coatings. This will allow the coating to be applied to the outside of a window where it will function more effectively in a solar control mode. A wide range of selective reflectance coatings and protective layers have been produced and tested for both optical performance and weatherability (Fig. 6). In 1978 efforts focussed on scaling up the sputtering deposition system to provide desired coating uniformity over a larger sample size. Results to date show uniformity of +5% in optical properties over a 1.5 square foot substrate area, with indications that further system refinements will allow coating substrates of architectural size with equal or better uniformity. Uniformity requirements for highly transparent coatings such as the heat mirrors are even less severe than for solar control coatings.

Convection Suppression Window Prototypes

Double glazed windows frequently incorporate venetian blinds or similar devices between the glass panes for light and glare control and to provide privacy. They also reduce heat loss although the design of the devices has not been optimized for that purpose. It is possible to produce double glazed windows with heat transfer rates approaching those of insulated walls by the use of a mechanism in the air space which segments the airspace to suppress

Fig. 6. Normal spectral transmittance and reflectance of selective solar control film with increased visible transmittance; glass substrate (1/8") - Cu (78A) - SiO₂ (500A); weighted spectral averages, $T_{solar} = 42\%$, $T_{visible} = 60\%$. (XBL 792-512)

convective transport. The Mechanical Engineering Department at the State University of New York, Stonybrook, is investigating the design and performance of such mechanisms. Prototypes have been built and tested with a thermal resistance of R5 in an open mode and R10 in a closed mode. A heat transfer gage with an approximately twenty square foot cross section was built in 1978 to allow tests on actual architectural size windows. Interferometric studies are underway to examine detailed heat transfer in the air spaces created by the parallel slats. Initially, ideal air spaces with no leaks were examined. Later studies have revealed that the heat transfer rate is not seriously increased when the slat to glass clearance is increased to as much as 1/8 inch. This suggests that commercially manufactured devices may have the same good thermal performance measured in the prototypes (Fig. 7).

Innovative Windows RFP

Simple modifications to existing windows and window accessories can show significantly improved thermal performance and can reach the marketplace sooner than some of the more speculative materials and devices discussed above. This solicitation was designed to support

Fig. 7. Isotherms in the air space derived from interferometric measurements of cellularized air spaces. The steep temperature gradient adjacent to the "hot" plate indicates the presence of a well-defined boundary layer and a significant heat flow by natural convection. (XBL 792-510)

development and demonstration of near term, low risk, innovative windows and window systems. Two contract awards were made in 1978 from a large pool of applicants and several additional contracts are under negotiation. Stevens Institute of Technology, Hoboken, NJ, will test and evaluate the sun control capabilities of a new class of highly reflective venetian blinds which should have shading coefficients of less than 0.2. Analytical models of performance will be used in conjunction with physical measurements to develop a validated model of blind performance under a variety of temperature and sun conditions.

Insulating Shade Company, Branford, CT, has developed a multilayer, aluminized plastic roll up shade with a thermal resistance of 15 in its deployed mode (Fig. 8). The resultant energy savings from 200 shades in a college dormitory will be monitored with a data acquisition system designed and built at LBL. Patterns of shade use will be studied and attempts may be made to motivate occupants to use the insulating devices more effectively.

Fig. 8. Cross Section of the Multilayer Insulating Shade which will be the subject of an LBL/DOE supported demonstration. Energy consumption in a college dormitory will be monitored with 200 shades installed. Multiple air spaces and low emissivity coating sharply reduce heat transfer and provide R15 insulation with a double glazed window. (Reprinted by permission of Insulating Shade Company, Inc., Box 282, Branford, CT 06405. Copyright 1978).

PLANNED ACTIVITIES FOR 1979

Most existing projects will be continued in 1979 and future activities were summarized in each section. Once the Windows Program Plan is developed, it will begin to shape the direction of future R&D activities, beginning with the FY80 budget in late 1979.

At LBL, expansion and refinement of both computer modeling capabilities and testing capabilities will be continued. The final design and construction of the window test trailer will be the major new testing effort in 1979. A variety of prototype and commercial windows and accessories have been purchased for test and evaluation in 1979, in both the test trailer and the laboratory, and in private testing laboratories.

A joint project was initiated with the Passive Solar Program in late 1978. Hughes Aircraft, Culver City, CA, is under contract to review the aerospace, military and NASA literature for information relevant to a long list of energy conservation and passive solar interests.

Results of these advanced materials surveys and literature searches will be available in early 1979.

The status of heat mirror commercialization is now under review and new efforts are planned in 1979. Programs will be initiated with window manufacturers to assist in generating a demand for the basic coated glass or plastic materials. Further computer studies of the performance of different types of heat mirror products in different climatic zones will be undertaken.

An optical shutter is a device which changes from highly transparent to highly reflective, either automatically, or in response to a sensor or controller. Such a coating on windows would provide energy conserving performance in both winter and summer. A chemically based optical shutter was examined under subcontract in 1977. It proved to be too expensive to represent a cost effective window product. Our attention is now focussed on options for producing thin film, solid state optical shutters. Plans are underway to initiate a new competitive solicitation in 1979 for R&D leading to a demonstration of successful optical shutter mechanisms.

Energy Efficient Lighting Program

S. Berman, R. Clear, J. Klems, S. Selkowitz, and R. Verderber

The prime objective of the lighting program is to accelerate the introduction of energy efficient lighting products and concepts in the marketplace. Thus, the lighting program includes interaction with scientific, professional and trade organizations to reduce institutional barriers for the introduction of new products, to assist in creating a market demand, and to support research and development of new products and concepts. Commercialization of new products and concepts is effected by reducing "risks," both for investors engaged in the manufacture of the product, as well as for the consumer who will employ the product for the first time.

This commercialization effort requires the timely transmittal of reliable information to the salient professional organizations [Illuminating Engineering Society (IES), Institute of Electrical and Electronic Engineers (IEEE), and the Architectural Institute Association (AIA)], and the standards associations [American National Standards Institute (ANSI), and the Underwriter's Laboratory (UL)]. For the end users, the prime organizations are the trade associations such as the Building Owners Management Association (BOMA) and government purchasing groups (GSA). Primary sources of information are R&D results from the LBL subcontractors, the LBL Lighting Laboratory, and the demonstration projects managed by LBL. We have developed a mailing list of interested organizations which receive the LBL publications. The program

is also discussed via professional trade publications and invited presentations at relevant professional society meetings.

Our initial lighting projects were concerned with energy conservation in the industrial and commercial sector of the lighting market, where energy is used during the peak demand hours. The program's effort has been expanded to include residential applications in the latter quarter of 1978.

ACCOMPLISHMENTS DURING 1978

Daylighting Studies

The solid state ballast demonstration at the PG&E building in San Francisco includes a project to collect daylighting availability data in the San Francisco area for one year. The building has been instrumented to collect and record the amount of solar and visible radiation available at the roof and incident upon windows on four sides of the PG&E building. An array of thirteen pyranometers and photometers has been installed and feeds readings to a data acquisition system at fifteen minute intervals.

A daylighting conference was held at LBL in November in which many of the most prominent figures active in the field of daylighting gathered to discuss their past and present activities. Diverse professional disciplines

were represented including lighting designers, electrical engineers, mechanical engineers, architects, window manufacturers, educators, scientists, and utility and state agency representatives. The main purpose of the conference was to identify and review the major problems inhibiting the use of daylighting in existing structures, as well as in buildings presently being designed. Several important needs were identified: 1) the need for collecting credible daylight availability data; 2) the need for dissemination of simplified design methods; 3) the need for a means of quantifying daylighting/thermal balances and tradeoff in buildings; 4) the need for commercialization of reliable, cost effective, automatic switches and control systems, that could respond effectively to the various conditions of daylight; and 5) the need for development of an array of educational tools and resource packages to promote professional daylighting education.

High Frequency--Solid State Fluorescent Ballast

The first phase of the solid state fluorescent ballast program for two F40 T-12 fluorescent lamps was completed in 1978. Both IOTA Engineering and Stevens Luminoptics met the program objectives in developing a reliable operating ballast that was significantly more efficient than the present core-coil ballast, showing improvements in energy efficiency of 20 to 25%.

In the second phase of the program, both firms were requested to supply about 500 ballasts to refit two floors of the PG&E building in San Francisco. The purpose of this demonstration was to measure the performance of a large number of solid state ballasts installed in an actual building, in comparison with the performance of standard core-coil ballasts in the same building. In addition, if there were any secondary adverse characteristics due to interactive effects, the large scale ballast installation would reveal their identity.

After four months of data collection, the ballasts have shown reliable performance and savings of 20 to 25% savings of energy. We have found a slight reduction in the audible noise level, up to 30 kHz. In addition, the temperature of the exhaust air from each fixture is 30 to 40°C less for the solid state ballast, demonstrating a reduction in cooling load impact in the building. Further assessment is scheduled for both the conducted and radiated RFI, as well as the lamp life effects under solid state ballast operation.

A standard fluorescent lamp life test with lamps driven by solid state ballasts is in progress in the LBL Lighting Laboratory (see Figs. 1 and 2). After 3000 hours of operation no adverse effects have been measured. In addition, measurements in the LBL laboratory of the new low wattage fluorescent lamps driven by solid state ballasts have demonstrated a system efficacy of 90 lumens per watt. In comparison with a standard fluorescent lamp and ballast (65 lumens per watt), this represents an improved efficacy of over 37% (see Table 1).

Fig. 1. Lamp life test facility rack. Over 3000 hours of standard lamp life testing (3 hours on, 20 minutes off) have been accumulated on lamps driven by electronic ballasts to determine effects of high frequency exertion on phosphor and cathode life.

Fig. 2. Integrating cylinder for measuring total lamp lumen output. Total light flux is measured under controlled temperature conditions with the lamp driven by a standard reactor ballast.

Table 1. Ballast performance with different fluorescent T-12 rapid start lamps.

Ballast	Standard Core			Efficient Core*			IOTA-EXCEL 64P-9			STEVENS 803-017		
Lamp Type	1	2	3	1	2	3	1	2	3	1	2	3
Lamp Temperature (°C)	40°	40°	40°	40°	40°	40°	40°	40°	40°	40°	40°	40°
Input Power (watts)	93.5	81	81.5	84	73.1	73	74.5	67	67	77	70	69.9
Power Factor	89.5	0.94	0.93	0.98	0.98	0.97	0.91	0.89	0.89	0.93	0.90	0.90
Power to Lamp (watts)	71	58.3	57.4	71	58.4	57.3	60.6	54	53.6	65	60	58.3
Light Flux	6093	5350	5606	6080	5402	5645	5862	5466	5760	6400	5952	6272
Ballast Efficiency	0.759	0.720	0.704	0.845	0.800	0.785	0.813	0.806	0.800	0.844	0.858	0.830
Lamp Efficacy (l/w)	86	92	98	86	92	98	97	101	108	98	99	108
System Efficacy (l/watt)	65	66	69	72	74	77	79	82	86	83	85	90

Lamp and system efficacy are shown for combinations of standard and high efficiency ballasts driving standard and high efficiency fluorescent lamps. The electronic ballast coupled with an improved lamp shows 90 lumen per watt system efficacy compared with 65 lumens per watt for a standard ballast/lamp combination.

Lamp 1 - Standard T-12 RS F40

2 - Efficient Type I T-12 RS F-35 (Mfg. A)

3 - Efficient Type II T-12 RS F-35 (Mfg. B)

*Average of 3 Ballasts from different manufacturers.

**Lamps dimmed with ballast to appropriate light levels.

Efficient Fixtures

The lighting fixture has a pronounced affect upon the overall efficiency of lighting systems. A contract has been awarded to the Optical Coating Laboratory, Inc. (OCLI) to apply multilayer thin film coatings on reflectors and lenses that will improve the reflectivity and transmission, respectively, thereby increasing the useful light delivered by the fixture. Two types of high intensity discharge (HID) fixtures are being designed for outdoor and indoor applications. The outdoor fixture will employ a high pressure sodium lamp (HPS), and the indoor fixture will use a metal halide lamp. Fixtures with and without these coatings will be tested for efficiency in 1979.

Residential Screw-In Circline Fluorescent Lamp

A contract was awarded to the EXCEL Corp. to develop a solid state ballast for the operation of a circline fluorescent lamp. The system will be packaged with an Edison type base so that it can fit standard residential incandescent light bulb sockets.

The ballast circuit will be designed to be ultimately manufactured as an integrated circuit, thereby reducing the size, weight and cost of the ballast. The system will feature a light output equivalent to a 150 watt incandescent bulb (2200 lumens). In addition, the ballast will permit the fluorescent lamp to be dimmed to accommodate the lighting desires of the user. This development should yield an efficacy of over 40 lumens per watt, which compares well with the 17 lumens per watt incandescent lamp it will replace.

Switching and Controls

We have started two switching and control demonstrations to assess the energy savings for a variety of switching and control strategies. Honeywell Inc. will supply the lighting control system for the first demonstration which will utilize one floor of the San Francisco PG&E building. This system controls groups of lamps and can dim the lamps over a continuous range of light level. GE will supply the control system for the second demonstration in the World Trade Center in New York. The GE system

allows only on-off control but fixtures can be individually controlled. Results from the two systems should allow evaluation of most control strategies, e.g., daylighting, group vs single, continuous vs step dimming, etc.

Smith Hinchman and Grylls has received a subcontract to develop a computer program that predicts the energy savings that can be realized by the use of various types of lighting control strategies and maintenance practices. Each of the demonstration sites will provide data to verify the accuracy of the computer program.

With the use of controls it is anticipated energy savings of over 50% can be achieved. Few buildings today employ lighting control systems, and the objective of this portion of our program will be to provide evidence of the performance and cost effectiveness of several systems. Hence, a market can be stimulated to encourage the widespread commercialization of control systems that are available today, as well as novel systems still in the R&D stage.

PLANNED ACTIVITIES FOR 1979

All of the above projects will be continued into 1979. In addition, two new projects will be started:

1) HID solid state ballast

The use of solid state ballast to drive HID lamps will improve system efficacy about 15%. Furthermore, HID lamps operated at high frequency eliminate flicker and noise as well as allow for reduced size and weight, making these efficient lighting sources very attractive for indoor and outdoor applications.

2) Replacement for incandescent lamps

There are several technical approaches for the development of efficient light sources that could replace incandescent lamps in many applications. These include electrodeless fluorescent lamps and the coated (IR reflecting) incandescent lamp. A multiphase program is being planned to evaluate the proposed schemes and then to support one or more efforts leading to commercialization and ultimate market introduction.

Chemical Process Research and Development

Introduction

The Chemical Processes program is conducting research in chemical-processing techniques as applied to biomass conversion to fuel, coal conversion, oil-shale retorting, coal cleaning, and chemical storage of thermal energy.

The bioconversion studies are aimed at developing economical methods of producing energy from the cellulose found in agricultural and forest wastes. A fungus enzyme is used to convert cellulose to glucose, which is then converted to ethanol by fermentation. Ethanol is being considered as a possible alternative to, or diluent for gasoline. In addition to ethanol, acetone and a number of other chemicals now made from petroleum products could be produced from low-cost glucose.

In coal-related research, there are projects dealing with the removal of sulfur from coal and with catalytic liquefaction. Sulfur removal is essential because of the release of sulfur dioxide upon combustion which would occur otherwise. Different methods are being evaluated comparatively. Accompanying fundamental studies are exploring the structure, accessibility and reactivity of sulfur in coal. The goal of the liquefaction studies is effective catalysts which operate at low severity and preserve as much of the fuel value of coal as possible.

Another project concerns processing methods for condensate waters from coal conversion and shale retorting. Studies involve innovative approaches to ammonia stripping and novel solvents for extraction of phenolics and acids.

Coal Desulfurization

S. Ergun, E. A. Grens, E. E. Petersen, T. Vermeulen, C. Figueroa, J. A. Mesher, D. Mixon, M. C. Smith, and J. A. Wrathall

INTRODUCTION

Coal cleaning prior to combustion is one option to enable increased coal utilization. An unpublished LBL study has indicated that coal desulfurization if coupled with prior physical cleaning, can be accomplished at a considerably reduced cost compared to other cleaning methods. Consequently a program has been started to evaluate four or more oxydesulfurization processes for removing pyritic and organic sulfur from coal. This objective is to be reached through joint execution of research, planning, and analysis by several participating organizations, with certain experimental studies to be carried out within Lawrence Berkeley Laboratory.

LOW-TEMPERATURE STUDIES OF COAL DESULFURIZATION

(Petersen, Mesher, Smith, Wrathall)

Two existing methods based upon chemical leaching with sodium hydroxide or ferric sulfate were previously tested and found to be quite effective in removing inorganic sulfur but not effective for organic sulfur removal. Research has therefore concentrated on removal of organic sulfur, using dibenzothiophene, thianthrene, benzothiophene, and diphenylsulfide, with metallic sodium dispersions as the reagents.¹ At temperatures below 200°C and moderate pressures, the desulfurization goes essentially to completion at reaction times of 0.5 - 1.0 hr.

The metallic sodium dispersion has also been found effective in removing sulfur from solvent refined coal. A current solvent refined coal (SRC) process yields two liquid products and a solid residue: a light distillate containing approximately 0.2% sulfur, which remains almost unchanged when SRC sodium-treated; a fuel oil with 0.44% S, which is reduced to 0.06% by sodium-treatment; and a residue of high sulfur content (normally reacted with steam to produce hydrogen), which after sodium treatment could be burned directly in a power plant without further desulfurization.

Sodium sulfide and sodium polysulfides have been examined as chemical leachants to remove sulfur from pyrite, producing ferrous sulfide which could then be reacted with dilute acids to remove the inorganic sulfur as H₂S. They were found to be reactive at a low temperature (80°C or less), but with less than 50% conversion of pyrite. Experiments at higher temperatures and pressures are now under way.

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DESULFURIZATION UNDER ACID CONDITIONS

(Vermeulen, Mixon)

Studies have been started to determine the effect of acid concentration on water-based desulfurization conversion and selectivity. The acid of choice is sulfuric acid which is produced from pyrite in the coal, or hydrochloric acid derived by addition of sodium chloride to the acid. Use of an aqueous solution 20% in H_2SO_4 and 15% in $\text{Fe}_2(\text{SO}_4)_3$ would provide the possibility of minimal consumption of water and chemicals, and production of potentially marketable crystalline $\text{Fe}_2(\text{SO}_4)_3$ and concentrated H_2SO_4 . The solu-

bility behavior of this system has been explored, and found to provide sharp separations which indicate a likelihood of simple and economical operation.

PLANNED ACTIVITIES FOR 1979

A continuous coal desulfurization bench-scale unit will be constructed and installed at the University of California Richmond Field Station. The research already underway will be continued and modified as needed to accomplish the overall objective--namely, to identify optimum desulfurization conditions.

Selective Hydrogenation of Coal

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INTRODUCTION

Existing technology for coal liquefaction is based on thermal decomposition (pyrolysis) of the coal with subsequent hydrogenation of the initial pyrolysis products. Such nonselective thermal bond breaking yields a wide range of products, including light hydrocarbon gases, and is therefore not efficient in hydrogen utilization. This project seeks to establish a basis for conversion of coal to liquids by selective scission, below pyrolysis temperature, of bonds linking conjugated hydroaromatic groups in the coal, including aliphatic bridges and oxygen links (e.g., ether or carboxyl). The reactions are promoted by homogeneous catalysts that, being dissolved in the liquid reaction medium, have access to reaction loci on the extensive interior surface of the coal.

The investigation involves studies of the interaction of coals with inorganic and organic reaction media, of the effects of homogeneous catalysts in promoting reactions at moderate temperatures, and of the use of mixed organic-inorganic media to obtain increased yields of liquid products. The effect of these treatments on model compounds representative of certain aspects of coal structure is also examined. The study considers the interaction of the pore structure of coal with the progress of reactions, and the influence on reaction rates of transport phenomena in this structure.

The project was initiated in January 1974. During the first three years of the program, equipment and laboratory procedures were developed, and studies undertaken of the interaction of sub-bituminous and bituminous coal with several organic solvents and with zinc chloride melts, phosphoric acid, and sodium hydroxide. In 1977, emphasis turned toward use of mixed organic-

inorganic treatment media, and, subsequently, another research program centered in that area was incorporated into this project.

ACCOMPLISHMENTS DURING 1978

The project activities planned for 1978 included investigation of the effect of composition of organic solvent mixtures on the interaction of these solvents with coal. However, the major thrust of the work has been towards elucidation and extension of very promising preliminary results achieved the previous year by treatment of coal in mixed organic-inorganic media. Studies of this approach have been conducted using zinc chloride melts in combination with organic solvents soluble in the inorganic phase.

The investigation of sulfur removal from coal that was previously a part of this program has been largely consolidated in a separate desulfurization project (see Coal Desulfurization).

INTERACTION OF COAL WITH ORGANIC SOLVENTS

(Grens, Lindsay, Zieminski)

The influence of the composition of binary mixtures of organic solvents on the interaction of these solvents with sub-bituminous (Wyodak) coal below pyrolysis temperature was explored for mixtures of specific (nitrogen base) and nonspecific solvents. Previous studies had shown that the choice of a nonspecific solvent was not very significant in the interactions; thus only toluene and tetralin were used in combinations with a variety of active solvents including pyridine, piperidine, quinoline, ethylenediamine, and tetrahydroquinoline. In this work the coal was successively contacted with fresh solvent batches at controlled temperature until further dissolution was not significant.

Table 1. Extract yields for Roland Seam (Wyodak) coal in binary organic solvent mixtures at 250°C (4 hours)

Mol % Active Solvent in Toluene	0	10	50	90	100
Active Solvent	Extract Yield - Wt % DAF Basis*				
Pyridine	7.5	7.6	11.0	15.1	14.7
Piperidine		5.9	12.1	18.3	25.0
Quinoline		11.5	17.9	28.0	35.5
Ethylenediamine		13.1	36.2	36.7	34.6

*Corrected for incorporation of solvent.

Yields of dissolved material (corrected for solvent incorporation) and the elemental analysis and average molecular weight of this material were determined. The results obtained for mixtures of several active solvents with toluene at 250°C are presented in Table 1.

For all active solvents investigated, with the exception of ethylenediamine, the extent of coal dissolution is found to vary almost linearly, on a mole-fraction basis, between the solubilities in the pure solvents. This result appears to exclude any specific reaction or association effect of any of the active solvents studied. It indicates that local continuum properties of the solvent in contact with the coal, rather than specific (e.g. acid-base) interactions, determine the extent of dissolution. The case of ethylenediamine is quite different. The ultimate yield is obtained at relatively low (less than 50%) active-solvent fractions, and indicates highly specific interactions of ethylenediamine molecules with the coal; this behavior is accompanied by very low atomic H/C ratios in the extract material (~0.5, compared to ~1.0 for other extracts), but not by unreasonably high solvent incorporation.

Investigations of the rate of interaction of coal with pure organic solvents in the temperature range 200-300°C are also being undertaken. For this purpose extraction equipment with a 30s time resolution has been developed (heating, cooling, and sampling times of order: 10s). For extraction with tetralin solvent the rates are found to decrease relatively slowly over the first hour. For instance, with Illinois No. 6 coal at 250°C (excess tetralin) with an ultimate extract of 12% (DAF basis), only about 0.3% is extracted in the first 30 seconds. It takes about 9 minutes for 1/4 of the ultimate yield to be reached and about 25 minutes for 1/2 to be attained.

The investigation of interaction rates is now being extended to other pure solvents, and to mixed solvents, with the objective of determining any difference in rate behavior for specific and nonspecific interactions.

TREATMENT OF COAL WITH ORGANIC-INORGANIC LIQUID MIXTURES

(Grens, Vermeulen, Hershkwitz, Maienschein, Shinn)

The use of inorganic melts, such as zinc chloride, as media for coal hydrogenation has been under investigation by coal researchers for a number of years. Our own research has shown that the utilization of two-phase reaction media composed of inorganic melts mixed with organic solvents can give considerably greater conversions of coal to liquid products under relatively mild reaction conditions (250°C) than can inorganic melts or solvents by themselves. At the same time, use of the two-phase media helps to overcome important problems associated with processing in inorganic melts: that is, control of the extent of reaction of initial liquid products dissolving in the melt, and recovery of product liquids from the melt.

Our previous studies of this treatment of sub-bituminous coal (Wyodak) have been extended to the use of other organic solvent materials. However, no such solvent appreciably more effective at 250°C than tetralin has been found. New specialized contacting equipment allowing better control of reaction conditions and much improved recovery of products has been developed to supplant simple commercial autoclaves. This has permitted collection and analysis of gases formed during treatment. These gases are found to represent only a very small fraction of the coal carbon and to contain little light hydrocarbon material. For example, for 250°C treatment with tetralin at 35 bar H₂ pressure (50g with 50g coal and 300g ZnCl₂ melt), dry gas represented only 0.8% (DAF basis) of the coal, and was mainly CO₂ with only 0.1% (DAF coal basis) hydrocarbons.

Analysis of the products of these coal treatments has been expanded to include gel-permeation chromatographic determination of molecular weight distribution. This shows, typically, a range of molecular weights of 200 to 10,000 for pyridine solubles and 100 to 500 for cyclohexane solubles with strong contributions in the 200, 500, and 5,000 molecular weight regions.

The treatment temperatures used have been kept below coal pyrolysis temperature (~325°C), but even in the lower range there is a strong increase in conversion with temperature, measured in terms of toluene-solubles (asphaltenes). This behavior is shown in Table 2 for Wyodak coal treated with zinc chloride and tetralin at 35 bar H₂ pressure.

The effects of the addition of up to 25% of other inorganic salts to the zinc chloride melt were also examined. Potentially certain salts can reduce the melt viscosity (or lower its melting point), and thus reduce the need for water in the melt. When alkali salts (NaCl + KCl at 25%, NaI + KBr at 37%) were added to the melt, the catalytic activity of the ZnCl₂ was essentially destroyed. This may be because they can reduce the concentration

Table 2. Effect of temperature on coal conversion
(50g Wyodak Coal + 275g ZnCl₂ + 25g H₂O
@ 35 bar H₂ for 1 hour)

Organic Solvent	Temperature °C	Cumulative % Soluble (DAF)	
		Toluene	+ Pyridine*
None	250	6	28
	300	19	51
Tetralin-50g	250	35	73
	300	62	95

*Corrected for incorporation of solvent.

of zinc cation by increasing polychlorozinc anions. However, the addition of 9% CaCl₂ to the melt showed no such harmful effect. This is important because calcium is present in some coal minerals and will enter the melt by dissolution and ion exchange. Small additions of anhydrous HCl and up to 10% additions of ZnO also showed no appreciable effect.

For the high-oxygen-content sub-bituminous coal used in this work (19.8% DAF O), the decrease of oxygen in the coal treated with zinc chloride/tetralin and other mixtures is notable. As shown in Fig. 1, for several types of treatment this decrease is roughly proportional to the extent of conversion of the coal to pyridine-soluble material. These results strongly suggest that oxygen-containing linkages in the coal structure are selectively attacked under reaction conditions and are responsible for a considerable part of the coal decomposition. For the case where

Fig. 1. Oxygen removal from coal by various zinc chloride treatments at 250°C as a function of conversion to pyridine solubles.
(XBL 7811-3697)

80% of the oxygen is removed, this alone could account for decomposition to 400 MW fragments if four links were broken per fragment and if 30% of the oxygen was in ether links that were broken. This result certainly indicates that low-rank coals are attractive candidates for treatments at mild conditions and that catalytic attack on ether bridges is a promising decomposition approach.

The study of organic-inorganic treatment media is now being extended to examine the effects of phase ratios, contacting procedures, and the possible influence of the water content and acidity of the ZnCl₂ melt. Experiments to measure rates for the decomposition reactions and to further describe their mechanisms are under development.

COAL CONVERSION IN A ZINC CHLORIDE/METHANOL MELT

(Vermeulen, Joyce, Shinn)

Converting coal to soluble material requires cleavage of enough chemical bonds to split the coal into subunits of only moderately high molecular weight. To lower the scission temperature below the pyrolysis region requires mobile catalysts which can penetrate thoroughly into the coal. Zinc chloride "melt" has proved to be a highly effective medium of this type. About 10 wt-% of water is required in the melt, because pure ZnCl₂ fuses at 317°C. We have now found that replacing water in the melt by methanol leads to large increases in pyridine solubility of product from the treatment.

Experiments were performed in a 600-ml Parr autoclave charged with 275 gm of ZnCl₂, the desired amount of methanol, 50 gm of undried Wyodak coal, and at times additives, for a reaction period usually 60 min.

Two grams of dried melt-treated coal (MTC) were extracted to exhaustion sequentially with benzene and pyridine in an atmospheric Soxhlet apparatus. The extracts and residue were dried and weighed to determine solubility of the MTC. In addition, the incorporation ratio R of methanol retained by the MTC ($R = \text{grams incorporated organic material/gram coal-derived organic material}$) was determined by a carbon balance on the reaction, and was used to correct the solubilities of the MTC.

Figure 2 presents the effect of hydrogen pressure and temperature on pyridine solubility, for a 60 min reaction time with 50 gm of methanol. Figure 3 indicates the effect of methanol amount at various hydrogen pressures. At all hydrogen pressures, there is a maximum solubilizing effect near 50g methanol (0.75/1 molar ratio for MeOH/ZnCl₂). To within experimental error, solubility is linear with hydrogen pressure.

As shown in Fig. 4, solubilization proceeds linearly with time at 250°C (800 psig, 50g MeOH) with total solubility achieved near 75 minutes. At 275°C, reaction is considerably more rapid, with total conversion possible in 30 minutes or perhaps less.

Fig. 2. Effect of hydrogen pressure and reaction temperature on corrected total pyridine solubility of Wyodak coal treated with zinc chloride/methanol melt for 1 hr. (XBL 7812-13446)

Fig. 4. Effect of run time on corrected total pyridine solubility of Wyodak coal treated with zinc chloride/methanol melt at 250°C and 275°C. (XBL 7812-13448)

Solvent additives to the melt (Table 3) were found to divide into two categories, extractive and reactive. The extractive solvents (decane, perchloroethane, o-dichlorobenzene, and pyrrolidine) had negligible or negative effect on solubility. Reactive solvents (anthracene oil, indoline, cyclohexanol, and tetralin) all incorporated strongly, and the donor solvents, tetralin and indoline, increase the total pyridine solubility.

In several runs, after water quenching of the MTC, 15 ml of 6N HCl was added to the cold water wash. Acid washing produced total pyridine solubility from a 65%-soluble water-washed MTC. The effect of acid washing on benzene solubility was less marked, with a maximum increase of 10-15% at 25% water-wash benzene solubility (the highest value). In some runs, a preliminary benzene wash was necessary before the product could be wet by $ZnCl_2$. The amount of dissolved material from the wash was added to the benzene Soxhlet yield for total benzene solubility. Benzene washing produces higher benzene solubility, whereas HCl washing produces higher pyridine solubility.

In conclusion, replacing water with methanol as a liquefying agent for $ZnCl_2$ results in large increases in pyridine solubility of the treated coal. Scanning electron micrographs of methanol-melt-treated coal show that methanol addition causes massive physical change in the coal particles, compared with almost no change for aqueous-melt-treated coal. There are several possible explanations for these effects: improved contacting between the coal and the melt; higher activity of $ZnCl_2$ in methanolic media; methylation of cleaved bonds, resulting in reduced char formation; and extraction of the reaction products, leaving the coal more accessible.

Conversion of pyridine-soluble MTC to wholly liquid product will require further activation of the coal, to cut additional carbon-carbon

Fig. 3. Effect of methanol charge and hydrogen pressure on corrected total pyridine solubility of Wyodak coal treated with zinc chloride/methanol melt for 1 hr.; or 250°C, for a feed containing 273 of $ZnCl$ and 50g coal. (XBL 7812-13447)

Table 3. Effect of solvent additives to ZnCl₂-methanol melt.
237 g ZnCl₂; 50 g coal; T = 250°C; t = 60 min.

Solvent (g)	P _{H₂} (psig)	Corrected Solubility (% DAF)	R (g retained MeOH/ g coal organic)
n-Decane (50)	250	41.4	0.19
C ₂ Cl ₆ (50)	200	40.5	0.43
o-Cl ₂ -benzene (60)	200	33.5	0.16
Pyrrolidine (10.5)	500	65.6	0.13
Cyclohexanol (10)	200	68.7	0.39
Anthracene Oil (10)	250	73.7	0.77
Tetralin (10)	200	77.4	0.65
Indoline (10)	500	81.5	0.27
Methanol only	500	70.3	0.18

bonds and remove more of the heteroatoms (O, S, and N). One route toward this objective may be provided by adding suitable co-catalysts and co-reactants. Another route may be provided by introducing a reusable extraction solvent when peak conversion has been reached, using this solvent to carry the solubilized coal to a second-stage treatment. These alternatives will be pursued in future research. With a high degree of chemical reactivity around 250°C having now been demonstrated for Wyodak coal, we plan also to examine the comparative reactivities of several other coals, of sub-bituminous and bituminous rank.

HYDROGENATION OF MODEL AROMATICS AND COAL

(Vermeulen, Derencsenyi)

Metal carbonyls known to be active as hydrogenation catalysts are usually unstable above 200°C; however, previously reported experiments in this laboratory have shown that substitution of one carbonyl group by a more tightly bonding ligand such as tributyl phosphine raises the stability limit of iron, cobalt, or manganese carbonyl to about 300°C.

The selectivity of hydrogenation is of particular interest for making polynuclear aromatics or heterocyclics susceptible to hydrocracking, without requiring a large consumption of hydrogen. Anthracene, in particular, is readily converted to equilibrium proportions of 9, 10-dihydroanthracene. Experiments on anthracene and also on Wyodak coal have shown that manganese or cobalt carbonyl can be used in the presence of a zinc chloride melt at 250°C, and enhances the hydrogen input above that from zinc chloride alone.

The kinetics for the hydrogenation of anthracene, A, by tributyl phosphine tetra-carbonyl manganese, M, in the presence of hydrogen and carbon monoxide (each at 10 to 30 bar), have shown that the following mechanism applies:

At low hydrogen pressures step (5) is rate-determining. At higher pressures (above 20 bar of H₂) step (4) becomes limiting, with the supply of active catalyst being curtailed by reaction (2).

PORE STRUCTURE OF UNTREATED AND TREATED COALS

(Petersen, Harris)

Surface area, pore volume, pore-size distributions, and true density measurements on raw, extracted, and reacted Wyodak sub-bituminous coal reveal that areas and pore volumes increase with extraction. Surface areas appear to approach an asymptotic value characteristic of the solvent used. Coals are similar to molecular sieves in having repeating pore constrictions separating larger volumes. Extraction enlarges some of the constrictions so as to make part of the micropore structure accessible to solvent molecules. Apparently, however, the complete coal pore system does not become accessible to solvent molecules. Moreover, the average pore diameter decreases with extraction; this suggests that pore roughness increases with extraction.

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Processing of Condensate Waters from Solid-Fuel Conversion

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E. Pittman, and G. Burns

INTRODUCTION

Solid-fuel conversion processes--such as oil-shale retorting, coal liquefaction and coal gasification--produce highly contaminated condensate waters. These contain large amounts of ammonia, phenolic compounds, sulfides and reacted carbon dioxide, along with other organic acids and bases, thiocyanates, cyanides and inorganic salts.^{1,2,3} There are also significant amounts of polynuclear aromatic hydrocarbons (PAH) probably present on suspended particulates. Waters from oil-shale retorting are similar to those from coal conversion, with the additional features that there is usually a substantial amount (0.5-1.0%) of emulsified oil present, that there are substantial amounts of alkyl carboxylic acids, and that the concentration of phenol itself is usually much less.

The object of this project is to develop clean-up methods for these waters, which will allow recycle of the water within the process and will allow safe discharge of any effluent. Re-use of water to the maximum extent possible is highly desirable, and is essential in arid regions. For phenolics and ammonia, and possibly carboxylic acids, there is also incentive for recovery in an unchanged chemical form. Solvent extraction and stripping are the processing approaches being given principal attention in the early part of this project. Microflotation, ion exchange and adsorption are other techniques of interest.

The project was started in October 1977. During late 1977 samples of condensate water from various coal-conversion processes were collected, and analysis of them was begun. Calculations were made using previously reported analyses to assess the major contributions to the acid-base balance in these waters. Theoretical and experimental tests showed that vacuum steam stripping is an effective method for removing residual solvent from the effluent waters of solvent-extraction processes.

ACCOMPLISHMENTS DURING 1978

Gas chromatographic and titrimetric analyses were made of condensate waters obtained from the Synthane coal-gasification process (PETC), the Lurgi coal gasification process (METC), and the solvent-refined-coal (SRC) liquefaction process (Pittsburgh & Midway Coal Co., Ft. Lewis, WA).

Dihydric Phenols

Previous analyses have given little or no information on dihydric or polyhydric phenols, because of difficulty in elution of these compounds from common gas-chromatographic column materials. Since these substances are particularly difficult

to extract and yet must be reduced to very low levels, we have devoted considerable attention to them.

Chemical synthesis of methyl ethers, followed by gas-chromatographic analysis using a Tenax column, showed that substantial quantities of dihydric phenols (resorcinol, pyrocatechol, hydroquinone) are present in the process-condensate waters from coal conversion. Subsequently, liquid chromatography (HPLC) with a C-18 column and an aqueous carrier was used to produce quantitative analyses of the phenolics. For the SRC process-condensate water, concentrations were found to be

Phenol	6700 ppm
Cresols	2900 ppm
Resorcinol	2400 ppm
Hydroquinone	1600 ppm

Comparable levels of pyrocatechol are also present in these waters; however, there is still uncertainty in the absolute values.

Further explorations with pyrocatechol (o-dihydroxybenzene) showed that it is the probable cause of the severe darkening problem associated with these waters. Since this color change should be avoided, pyrocatechol should be reduced to very low concentrations. Waters containing resorcinol also discolor upon standing when exposed to air.

More recently, we have found that an OV-17 column allows analysis of dihydric phenols by gas chromatography, although the peak shapes are far from ideal.

Effect of pH on Extraction of Phenolics

Previous conceptual designs have postulated the use of solvent extraction with di-isopropyl ether (DIPE) for removal of phenolics, following common practice for condensate waters from coke-oven processing. Since the process condensates under consideration can have relatively high pH values (9-10), an appreciable fraction of any phenolic compound can exist in the ionized form (pK_a for phenol is about 9.8). The ionized form should be non-extracted, and the apparent equilibrium distribution coefficient (K_D = wt. fraction in DIPE/wt. fraction in water) should thereby be diminished at high pH. Experiments have confirmed this prediction:

	pH	K_D
	5.92	36.6
	8.68	35.7
	9.14	24.1
	9.93	19.5
	10.56	6.5

The behavior for resorcinol is even more striking. K_D is about 1.9 at pH = 6, and also decreases substantially at higher pH. These results indicate that extraction with DIPE will become more difficult at high pH values and will be relatively ineffective for dihydric phenols. Past reports of performance of DIPE extractors for coke-oven condensate waters confirm that removals of dihydric phenols are poor.⁴

Amine Extractants

We have recently completed a study of the use of amine solvents for removal and recovery of carboxylic acids from industrial water streams.^{5,6,7} Tertiary C₈-C₁₀ amines, such as Alamine 336 (General Mills, Inc.), with suitable diluents, were found to be efficient and selective solvents for carboxylic acids, and could thus be useful for recovery of the carboxylic acids present in oil-shale retort water. Furthermore, amines have also been shown to be good extractants for anions of strong mineral acids (Cl⁻, SO₄⁼, etc.), and for phenol.⁸ Because of the acid-base interaction, amines could be effective for dihydric phenolics, whereas conventional, physically interacting solvents exhibit much lower K_D for dihydric phenols than for phenol.

Separatory funnels were used to accomplish a simulated three-equilibrium-stage counter-current extraction of a water containing 1.3 wt. % phenol at pH = 6.2, using a solvent mixture of 50 volume % Alamine 336 in 2-ethylhexanol, at a ratio of 0.123 kg solvent/kg water. 97.5% of the phenol was extracted.

Vacuum Stripping

Vacuum steam stripping has been explored further as a means of removing residual dissolved solvent from water after an extraction process. From the standpoints of K_D for phenol extraction and cost of the vacuum stripping operation, methyl isobutyl ketone (MIBK) appears to be a much more attractive solvent than the DIPE used in conventional coke-oven technology. The cost of stripping is quite sensitive to the pressure used, with the optimum pressure typically being the vapor pressure of water at the feed temperature.⁹

PLANNED ACTIVITIES FOR 1979

Conceptual design studies will be made to establish the most critical processing questions requiring research, to examine the merits of different sequences of processing steps, and

to identify the principal criteria by which potential solvents for extraction steps should be judged. We will explore the incentive for processes which use two separation methods simultaneously (e.g., stripping and extraction) to remove both acidic and basic substances.¹⁰ Vapor-liquid equilibria and acid-base equilibria underlying the stripping of ammonia will be explored theoretically and experimentally. Carbon dioxide and hydrogen sulfide are other strippable components interacting with ammonia. Solvent extraction of phenolics and carboxylic acids will be explored further, with particular attention to the problems associated with dihydric phenols and to the use of amine solvents. It is likely that considerably more focus will be placed on retort waters from oil-shale processing and the unique problems associated with them.

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Production of Sugars and Ethanol from Corn Stover

C. R. Wilke, R. D. Yang, A. S. Sciamanna, and R. P. Freitas

Corn stover was studied as a representative raw material for the production of sugars and ethanol. As a basis for process evaluation, small scale laboratory experiments were conducted to determine typical sugar yields employing enzymatic hydrolysis of acid pretreated stover with cellulase enzyme obtained from *T. viride* (reseei) QM9414.

The hydrolysis process is identical in concept to that described by Wilke, Yang and von Stockar¹ except for the incorporation of the pretreatment with dilute sulfuric acid. Table 1 gives the base case design specification of the hydrolysis plant.

The ethanol fermentation process is similar to that described by Cysewski and Wilke² with the additional feature of employment of cell recycle. The design basis of the fermentation plant is shown in Table 2.

Table 1. Acid pretreatment and enzymatic hydrolysis of stover base design case specification

Feed (2mm Corn Stover)	1376 T/D
Carbohydrate Content	58%
Acid Pretreatment	0.09 M H ₂ SO ₄ , 7.5% Susp. 100°C, 5.5 hr
Acid Extracts (70% xylose)	181 T/D, Sugar/Acid=2.4
Solids	885 T/D
Enzymatic Hydrolysis	3.5 FPA 0.61 U/ML, 5% Susp. 45°C, 40 hr
Enzyme Recovery	58%
Enzyme Productivity	0.46 U/(Ml-day), Cell = 7 gm/l
Cellulose Conversion	40% to Glucose
Hydrolyzate (90% glucose)	240 T/D, Glucose/Enzyme = 21
Sugar Solution	2.6%

Fig. 1. Material balance flow diagram for integrated processing scheme. (XBL 783-4670)

Table 2. Continuous ethanol fermentation with cell recycle design basis

Sugar Concentration	11.2% 90% Fermentable
Solution Rate	0.7 hr ⁻¹
Temperature	35°C
Cell Yield Factor, $Y_{x/s}$	0.10
Ethanol Yield Factor $Y_{p/s}$	0.46
Cell Concentration in Fermentor	50 g. Dry wt/l

Following yeast removal the bottom stream from the ethanol distiller containing cellobiose, pentoses and residual glucose is concentrated and processed by anaerobic degradation for methane generation.

Figure 1 shows the process flows and mass balance for the complete process.

A cost analysis of the process gives an estimated capital cost for the hydrolysis section of \$29,500,000 and costs for glucose and xylose of 10¢ and 5.1¢ per pound, respectively, exclusive of cost of the corn stover.

The fixed capital costs for ethanol production including the anaerobic digestion facility are estimated at \$7,000,000.

Table 3 presents an overall cost analysis and product summary indicating that ethanol might be produced in a municipal facility for approximately \$1.60 per gallon exclusive of raw material cost. On a private economy basis, assuming a corn stover cost of \$30 per ton, the ethanol cost would be approximately 3.50/gallon.

Based on the foregoing analysis the production of ethanol from agricultural residues such as corn stover does not appear economically feasible with the process as developed thus far.

The processing scheme is admittedly inadequate and will be superseded as research continues. Xylose in the acid hydrolyzate, for example, is not considered for further conversion to either furfural or ethanol because the system for conversion are not yet conclusively established. Studies of the fermentation of xylose are in progress. Nevertheless, efficient conversion of xylose to ethanol would increase the overall ethanol yield by up to 70%. Other anticipated areas of process improvement include development of more effective enzyme systems, of more economic enzyme production and methods for enzyme recovery and re-use.

Table 3. Product summary and overall cost analysis. (Corn stover feed--1376 T/D)

	Tons/Day	Production* Costs	Assumed Market Value	By-Product Cost Credit Per Gallon Ethanol
Ethanol	103	179 ¢/Gal	-	-
Xylose	126	-	-	-
Other Sugars	55	-	-	-
Carbon Dioxide	132	-	-	-
Yeast Cake	21	-	10¢/lb (45¢/lb) ¹	13¢ (60¢)
Mycelium	11	-	10¢/lb	7¢

*Exclusive of corn stover cost

¹Used as a protein food supplement

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Process Development Studies for the Production of β -Glucosidase from *Aspergillus Phoenicis*

M. J. Howell and C. R. Wilke

As part of an ongoing program toward the development of optimal enzyme systems for cellulose hydrolysis the production of β -glucosidase from *Aspergillus phoenicis* and use of the enzyme as a supplement to *Trichoderma viride* cellulase have been studied. Following the earlier work of Sternberg, et al,¹ it was desired specifically to assess use of β -glucosidase in the general hydrolysis scheme under development in the Berkeley program.² The present report is concerned primarily with β -glucosidase production.

Growth of the organism and enzyme formation were studied for a range of conditions and substances under batch and continuous culture. Figure 1 illustrates typical batch growth on starch at 30°C without pH control, showing that two distinct periods of growth exist. The results support the hypothesis that the observed growth kinetics result from a biochemical differentiation of the filament which is independent of the substrate concentration. The optimum temperature for cell mass and β -glucosidase production was found to be 30°C. The optimum pH for β -glucosidase production is 5 and the highest specific cell growth rate was observed when the growth medium was controlled at pH 4.5. The highest levels of β -glucosidase were obtained when the pH of the growth medium was adjusted initially to pH 5 and not controlled during fermentation. The β -glucosidase activity was partly intracellular with about half the enzyme activity retained in the mycelia after 100 hours of growth. The most economical substrate was 0.75 g/l of Solka Floc, a spruce wood pulp, plus 0.25 g/l of *Trichoderma viride* cellulase. The addition of cellulase was required because *A. phoenicis* does not produce all the enzymes required to solubilize cellulose.

When freeze-dried *A. phoenicis* enzyme was added to the hydrolysis of acid treated corn stover by *T. viride* cellulase, the total sugar yield was increased by 4 g/l of hydrolyzate over the yield of 20 g/l obtained without β -glucosidase addition. In addition, the cellobiose, which previously accounted for about 10 percent of the sugar concentration, was converted to glucose, a more widely usable product.

Preliminary designs of several processes for the production of β -glucosidase were made. The most economical processes were continuous production schemes which included methods of increasing the rate of release of intracellular enzymes. Ball milling was the most cost effective method, but the use of an elevated temperature stage was economical enough to warrant further study. The production cost of β -

Fig. 1. Growth phases of *A. phoenicis* (XBL788-5695)

glucosidase was found to be too high to justify its addition to a process for enzymatically hydrolyzing cellulose at this time. Further optimization of the enzyme production process and the hydrolysis reaction is required.

Figure 2 shows a tentative continuous processing scheme for production of β -glucosidase, employing the design basis given in Table 1.

A preliminary cost estimate indicates that β -glucosidase might be produced at a cost of 3.63¢ per million units at a production rate of 1.15×10^5 million units per hour.

Figure 3 shows how the glucose yield may be increased by incorporation of supplementary β -glucosidase in hydrolysis of 5% suspension of -20 mesh corn stover at 45°C with *T. viride* cellulase of 3.5 filter paper activity.

For complete details of the studies described above the full report (LBL-7867) may be consulted.

Fig. 2. Process scheme for production of β -glucosidase by *A. phoenicis* grown on Solka Floc and *T. viride* enzyme. Numbers are flow rates in gal/min. (XBL788-5712)

Fig. 3. Hydrolysis of corn stover by *T. viride* cellulase with various concentrations of *A. phoenicis* β -glucosidase: concentrations of glucose and cellobiose. (XBL788-5709)

Table 1. Continuous fermentation with cell disruption design basis.

Solka floc concentration	5 g/l
Temperature	30 °C
Average Aeration rate	0.022 vvm
Dilution rate	
Growth Fermentors	0.219 hr ⁻¹
Production fermentor	0.017 hr ⁻¹
β -glucosidase activity	
Product stream after fermentors	175 units/ml
Product stream after pebble mill	450 units/ml

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Utilization of Immobilized β -Glucosidase in the Enzymatic Hydrolysis of Cellulose

S. H. Issacs and C. R. Wilke

The purpose of this study has been to assess the possibility of utilizing supplementary β -glucosidase in immobilized form to improve the enzymatic hydrolysis of cellulose by reducing cellobiose inhibition and increasing glucose yield.

β -glucosidase obtained from *Aspergillus phoenicis* was immobilized onto phenol formaldehyde resins using glutaraldehyde as a fixing agent following the procedures developed by Olson and Stanley.² The resin, obtained from Diamond Shamrock Chemical Company, was a specially sized spherical material, Duolite ES-762 Enzyme Syoport. The resin in packed form has a void fraction of 0.36 and an average diameter of 251 microns.

Kinetics of cellobiose hydrolysis and other properties necessary for engineering analysis of potential process applications were determined for the natural and immobilized forms of enzyme. The optimum pH was found to be approximately 4.0. Michaelis-Menten constants were 1.39×10^{-3} M and 1.56×10^{-3} M for the soluble and resin bound forms respectively. Figure 1 shows the temperature stability of the enzyme.

The crystalline nature of the support allowed ready use in a fixed-bed reactor. Experimental and theoretical studies were made to determine the influence on the rate of reaction at various operating conditions of film diffusion of substrate to resin surface.

Three experiments were performed where the batch hydrolysis of a cellulosic source was carried out with a recycle stream through an immobilized β -glucosidase column in order to continuously remove cellobiose. The apparatus is shown in Fig. 2. The first two experiments using pretreated corn stover as the substrate showed no increase in hydrolysis over that of a control system, presumably because the cellobiose production was too low for cellobiose inhibition to occur. The third experiment, using Solka Floc as the substrate, which produced as high as 8.8 grams per liter of cellobiose, showed only a slight increase in soluble sugar production over that of the control system. Since the current process indicates the use of corn stover or a similar substrate, it does not appear useful to include an immobilized enzyme reactor in this manner.

Since the fermentation part of the process cannot use cellobiose to produce ethanol, the use of the immobilized β -glucosidase reactor to convert the cellobiose to glucose may have economic significance by increasing the ethanol yield in this fashion. A computer program was produced in order to simulate a fixed-bed reactor with diffusion limitations and to determine the cost per pound of glucose for a given reactor design. After many trials covering various parameters the optimal design was found to be a 2 x 3 column arrangement (2 columns in parallel, each

Fig. 1. Results of temperature stability experiments for both soluble and resin-bound β -glucosidase. (XBL788-9908)

Fig. 2. Experimental apparatus for the batch hydrolysis of cellulose using a recycle through an immobilized enzyme plug-flow reactor. (XBL 788-9910)

bank having three columns in series), each column having a diameter of 1.2 meters and a length of 3.5 meters. The column would be regenerated with fresh enzyme every 65 days. A cost analysis of the current hydrolysis process² with the addition of the immobilized β -glucosidase reactors indicated that the incremental glucose could be produced for 9.45 cents per pound. Therefore, use of the immobilized enzyme system would result in a savings in the cost of ethanol only if glucose were to cost more than the preceding figure when produced by the primary hydrolysis process. Therefore, this method of utilization of β -glucosidase does not appear economically attractive at present.

Details of the experiments, theoretical analysis and design are presented in the full report (LBL-7857).

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Environmental Research

Microcosms as a Tool for Aquatic Ecosystem Environmental Impact Assessment

J. Harte and D. Levy

INTRODUCTION

In an ecological context, a laboratory microcosm is simply a collection of chemicals and organisms within well-defined spatial boundaries, usually under controlled physical conditions, in a volume convenient for laboratory study. The need for a method of determining the response of natural ecosystems to perturbations of human origin has, in part, led to recent interest in these laboratory ecosystems. Microcosms potentially have the following desirable properties: (1) their small size and common environment permits replication; (2) the chemical composition of the medium and the trophic structure can be easily manipulated, so that analogs of qualitatively different ecosystems can be created; (3) the lack of complicated spatial heterogeneity allows more complete definition of physical, chemical, and biological characteristics; (4) perturbations of different physical, chemical, or biological variables can be carried out with little effort and expense; and (5) causal relationships often are more easy to deduce than in natural systems, where uncontrolled environmental variability complicates interpretation.

These potential advantages are not necessarily compelling, however. First, they may not be realizable in practice. For example, replication may not be achievable, even under careful laboratory conditions. Second, the causal relations deduced in a microcosm may have so little to do with those that exist in natural ecosystems that they would satisfy little more than curiosity. In view of the abnormal surface-to-volume ratio of laboratory systems and other possible problems with microcosms, this is not an idle worry; maximizing their usefulness as assessment tools is an important task and the one to which our work in 1978 is primarily addressed.

Our long-term objective is to develop predictive indicators that can reveal the sensitivity of a system to disturbance prior to the imposition of the disturbance. These indicators could be used to help in choosing sites for energy facilities where the environment is sufficiently robust, or buffered, to absorb the impact of energy-related stresses. The attainment of this objective would be greatly facilitated if microcosms could be used to generate the data necessary for the development and testing of such indicators.

Ecosystem microcosms can be effective tools for environmental impact assessment only to the extent that standardized procedures for their design, initiation, and operation can be developed. These procedures must lead to

systems which behave, in a replicable way, like either specific or generic natural systems. Studies carried out over three years in our laboratory with freshwater lake microcosms, ranging in size from 2 to 700 liters, have been directed toward understanding and improving their effectiveness. The systems studied contained a diverse assemblage of biota, initially obtained from natural lakes.

Three general types of experiments were conducted over the past two years, and a fourth is now in progress. Table 1 summarizes the configurations and principal goals of these four sets of experiments.

Our main results from completed experiments can be summarized as follows:

- The behavior of the microcosms, like natural systems, is dynamic, exhibiting frequent and large changes in biotic and abiotic parameters. Even after 6 months the systems were non-static.
- With the exception of one two-year experiment, the pelagic biota do not become conditioned by being in the laboratory and maintain their diversity and complexity.
- The dynamic behavior of the microcosms often resembles that of natural systems. Typically, a spring-like bloom (limited in some cases by grazing pressure and in others by lack of nutrients) occurs shortly after initiation, with a subsequent decomposition. In some cases, it is followed by a late-summer-like bloom.
- Inclusion of hydraulic flow-through, a thermocline, and a benthic substrate does not necessarily increase realism and generally is not warranted in lake-like microcosms.
- Inclusion of macrofauna (fish, gastropods) in microcosms less than 10 m³ in size reduces rather than increases resemblances to natural systems.
- Biological control of side growth is not feasible.
- Periodic pouring of microcosms into clean containers eliminates side growth. The pouring and consequent mixing changes microcosm behavior.
- Microcosms not subject to surface-growth control exhibit significant size-dependent differences; those subjected to periodic pouring to prevent side growth exhibit less size-dependence. Another approach to the

Table 1. Configurations and principal goals of four sets of experiments.

Experiment	Primary Purpose	Initiation Method*	Length of Run	Size of Tanks
700-liter (1976)	i) to study the similarity between lake and microcosm dynamics ¹ ii) to study biotic control of surface growth ²	inoculation	3,6 months	700 liters
perturbation (1977)	i) to study the effects of coal-conversion effluent on pelagic communities ³ ii) to test a potential predictive stability indicator ³			
decomposition	i) to study the response of decomposition activity to a detrital addition to a microcosm ³	whole water sample	2,4 weeks	2,4 liters
standardization (1978-79)	i) to assess the efficacy and effects of surface-growth control strategies	inoculation	3,48 months	15,200 liters
	ii) to study the extent to which microcosms track a parent natural water body	whole water samples	3 months	4,15,50,200 liters
	iii) to determine the effects of tank size on tracking, replication, and dynamics			
	iv) to determine the effects of the initial zooplankton population on phytoplankton bloom behavior	gnotobiotic	6,8 weeks	2,4 liters

* In the "inoculation" method for initiation, a small inoculum of natural lake water or of already-established microcosm water is added to nutrient-enriched deionized water. The inorganic N and P levels are adjusted to match the desired trophic state. The "whole-water sample" initiation technique uses water from the parent lake of interest to fill or nearly fill the microcosm.

problem of excessive surface growth in microcosms is to confine the period of research to the first spring-like bloom. During the first 40-60 days in a microcosm initiated by inoculation (depending on nutrient levels), there is no significant surface growth. To the degree that the initial bloom determines subsequent behavior of a natural system, these spring-like blooms are potentially good occasions to perform impact assessments.

- The amount of mixing within the water column is important in determining microcosm behavior and can lead to size-dependent differences
- Good replicability can be achieved, if care in initiation is taken.
- Microcosms can be used to simulate specific trophic types of natural systems in order to

assess the effects of particular perturbations on a given system. Because they provide a diverse assemblage of interacting biota, upon which a perturbation can be tested, phenomena are observed that would be missed in single-organism studies.

Based on our laboratory experience we conclude that with the adoption of optimized design and operating procedures, microcosms can play an important role in environmental impact assessment and in the elucidation of certain fundamental ecological mechanisms. While not all types of environmental stresses can be analyzed with this approach, and not all ecological relationships of interest can be studied, microcosms can provide a unique and useful tool for research.

ACCOMPLISHMENTS DURING 1978

One important breakthrough this year was the elimination of the problem of algal side-

growth.⁴ This is crucial since probably the most serious drawback associated with microcosms is their large surface-to-volume ratio as compared to natural systems. This means that surface growth of phytoplankton and associated nutrient flows can often dominate activities in the microcosm water column. In addition to the distorting influence of this effect, sampling of the sides and bottom is very difficult to perform reliably. Thus if the most frequent and reliable measurements are in the water column, then much of the activity in the microcosm is missed during periods of heavy side growth and efforts to balance nutrient budgets will be futile.

After pursuing other, more complicated and less effective, approaches to control of algal side-growth, we found that frequent (weekly) pouring of the contents of the microcosm into a clean container effectively eliminates the growth of algae on the surfaces of the tank, without introducing non-replicating behavior. We are now investigating whether this technique tends to influence the extent to which the microcosms resemble natural lakes.

In our studies of decomposition processes, one unusual effect was uncovered. Most models of decomposition mechanisms postulate that saturation mechanisms in the kinetics of detritus uptake by decomposers and density-dependence in the decomposer populations are the major manifestations of non-linearity. In a repeated experiment we found, in possible contrast, that decomposition in the water column exhibits a greater-than-linear, or threshold-like, dependence on the amount of detritus added to the system. We used net total increases in inorganic nitrogen species, NH_4 and $\text{NO}_3 + \text{NO}_2$, as well as increases in phytoplankton nitrogen to quantify decomposition of the detrital additions.

At this point we have not unraveled the mechanism responsible for this effect, although several promising theoretical models have been developed and explored by us. The effect, if true for a wide range of natural bodies, could have practical environmental significance in terms of setting limits, based on natural thresholds, for detrital loading of water bodies.

We have reported earlier³ that many environmental impact assessments and tests of stability indicators based on nutrient recycling behavior could not be carried out adequately in microcosms which, because of side-growth or other problems, could only be utilized for up to 2 or 3 months. However, our decomposition experiments have suggested a way to overcome this time constraint. The approach is to use detrital additions to provide a realistic forcing mechanism to push the system rapidly through bloom stages of its phytoplankton and zooplankton. To elucidate this possibility, consider an aquatic ecosystem initially in a relatively quiescent state. At some later time, increased availability of both organic and inorganic nutrients, due to natural processes in the system, will stimulate phytoplankton and/or zooplankton blooms and subsequent decomposition activity.

In many cases, the size and duration of these blooms is one of the ecologically significant features of the ecosystem. If an aliquant of water is taken from the original quiescent ecosystem and a spike of rich detrital material is added to it, then the subsequent decomposition of the added organic material will provide a diverse spectrum of nutrients of many of the biota in the aliquants. From experience gained in our recent experiments with microcosm response to detrital spikes, we have learned that some of the qualitative seasonal changes in the population of natural systems can be compressed into a short period of time in a "speeded-up" laboratory system. Suitable tracking experiments could now be used to determine how realistically the blooms in the spiked aliquants provide a "preview" of the bloom behavior to be expected over a long period of time in the original ecosystem.

In 1978, progress was made in understanding the mechanism of heavy metal concentration by algae. The accumulation and binding of copper by Scenedesmus has been the subject of our investigations. Colonies of Scenedesmus quadricada, a stock culture strain, have been conditioned and selected to enhance copper reduction. The mechanism responsible was studied with the goal of applying the mechanism to heavy metal treatment of wastewater.

Preliminary studies have led to the conclusion that copper is tightly bound by some chemical substance, rather than sequestered within a cellular compartment. Specifically, our work has shown that sonic destruction of the cellular architecture does not release soluble copper and that homogenates of heat killed cells (which are little more than masses of algal biochemicals) bind copper very effectively. In either case the copper remains associated with a fraction of the algae that is insoluble in both water and various organic solvents.

Because copper forms insoluble salts with phosphates, which are prevalent in algae, it was necessary to eliminate the possibility that the copper was simply precipitated as a phosphate salt. A demonstration that more than 80% of the copper remains in the insoluble mass when the pH is adjusted to a degree sufficiently acidic (~ 1.0) to solubilize copper phosphates is evidence that no more than 20% of the copper bound by Scenedesmus could be in the form of phosphate. The assumption that the majority of the copper is bound to an organic molecule is supported by the results of colorimetric tests specific for inorganic, but not organic, copper; these tests reveal little or no copper unless the algal mass is combusted in such a way as to render all copper in the form of an inorganic salt. Thus, the copper is seen to be tightly associated with an insoluble organic complex.

Although no solvent system has been found for the copper complex, it has been possible to form soluble complexes with the detergent dodecyl sulfate. Dialysis of these soluble complexes reveal that they are withheld by

membranes that normally pass substances of less than 12,000 molecular weight; filtration through gel matrices of selective pore sizes confirm the estimates that the copper containing complexes are of at least 10,000 molecular weight.

The fact that copper binding appears to be unhampered, and probably aided, by the physiological destruction of the algae suggests that these algae (or extracts from the same) may be particularly useful in removing heavy metals from wastewaters containing other toxins that would render inert many physiologically-dependent processes. The utility of this approach will depend on a number of factors: the ion specificity of the binding complex; the genetic stability of efficient metal binding strains; the production (growth) rate of these strains; the possibility of metal recoveries, from the extracts, that would lead to partial cost-offsetting; and the effective operating ranges of the algae or extracts.

We have also been active in preparing reviews and assessments of the current state of knowledge of ecological impacts of energy activities. An Annual Review of Energy article⁵ summarized the limitations of ecology today to provide predictive insight into ecosystem degradation under stress. It concluded that in many instances the predictive capability needed to make sound siting decisions, or to make choices among alternative technologies, is lacking. An article published in Science⁶ laid a groundwork for assessing the likely impacts on aquatic ecosystems arising from the water consumption requirements of energy technologies, taking into account empirical statistical measures of runoff variability.

PLANNED ACTIVITIES FOR 1979

Now in preparation is a set of experiments to study tracking of a natural lake by our microcosms. It will involve microcosms of different sizes which are initiated by using whole water samples from lakes at various stages in their seasonal cycle. The microcosms will be subject to the two mixing strategies as well as to no treatment for surface growth. Comparison of the behavior of the various microcosm configurations with their natural parent system should provide some concrete data on precise similarities and dissimilarities of various microcosm configurations with a natural body of water. The period of time considered will have to be restricted to one during which the lake's watershed and benthos do not greatly influence its planktonic behavior, and surface growth in the microcosm is eliminated or does not greatly influence the microcosm's planktonic behavior. Microcosms initiated entirely with water from a lake which is about to begin spring bloom, and either run for short periods of time (1-2 months) with or without surface-growth treatment, or treated for surface-growth control and run through the summer season, are good candidates for such tracking studies.

Further exploration of the use of detrital additions to study ecosystem behavior and stabi-

lity will be carried out in 1979. In trying to assess the effects of a perturbing agent, the use of detrital additions to force a system through periods of bloom could be very useful. Detritus (preferably taken from the lake) will be added to aliquants taken from the lake under investigation. The perturbing agent will be added to half the systems. Effects of the perturbing agent on decomposition activity as well as on various species of phytoplankton and the zooplankton are expected to result in altered growth of certain species of biota. Comparison of significant blooms in the treatments and controls should provide a preview of gross differences to be expected over moderate periods between the perturbed and non-perturbed systems.

A related use of detrital additions to probe ecosystem response to toxic substances involves assessment of the effect of the substances on decomposition rates. Because of the enormous variety of constituent substances in effluents from such energy activities as coal gasification or oil shale conversion, it is clear that a complete characterization of the chemical state of effluent-receiving waters is often impractical. In order to achieve a useful simplification in this characterization, many researchers have sought to identify indicator organisms, whose demise provides a measure of the state of the water. Another approach is to look for an indicator process rather than an indicator organism. Theoretical studies and empirical analysis of the medium- and long-term effects of altered decomposition rates in an ecosystem suggest that decomposition might be such a process. We will subject microcosms to a variety of toxic substances and then, in response to detrital additions, measure their relative change in decomposition rates. This will allow us to determine the strength of the correlation between known toxicity effects and effects on decomposition rates.

An investigation is beginning of how initial zooplankton and nutrient levels affect phytoplankton succession patterns. This study will employ a gnotobiotic approach to initiation, in which known mixtures of phytoplankton and zooplankton taken from pure cultures will serve as the inoculum. The purpose of the study is both to understand better the important and interesting process of succession, and to assess the need for a realistic zooplankton population in microcosm studies of lake ecosystems.

Acid precipitation is believed to exert undesirable changes in lakes and streams in the Northeast U. S., but the mechanisms by which this damage takes place are uncertain. Evidence to date is consistent with the possibility that toxic metals are implicated via the following pathway: depressed pH in aquatic systems and in runoff waters flowing through watershed soils results in the solubilization of these metals which then directly exert toxic effects on aquatic biota. We will explore this possibility by using our microcosm facility to study the effects of pH manipulations in lake microcosms on metals concentrations. Water and sediment samples will be taken from

a range of lakes in California (for which good background data exists and which are located in areas that meteorological considerations suggest are potential sites for acid precipitation problems). The pH manipulations will be carried out with synthesized acidic water, designed to roughly mimic acid rain.

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PAREP: Populations at Risk to Environmental Pollution- Data Base Description and Prototype Analysis

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INTRODUCTION

A project to assess Populations at Risk to Air Pollution (PARAP) was initiated in 1976, under funding from the U. S. Environmental Protection Agency (EPA). In September 1978, under funding from the Department of Energy (DOE), the project was extended to consider other environmental hazards (including low level radiation) and was renamed Populations at Risk to Environmental Pollution (PAREP). The PARAP-PAREP project is a collaboration between the LBL Energy and Environment (E&E) Division, the LBL Computer Science and Applied Mathematics (CSAM) Department, and the School of Public Health, University of California, Berkeley.

Activity in the project has involved:

1. Creation of an integrated data base containing data on socioeconomic and demographic characteristics, air pollution levels for several important pollutants, and disease-specific mortality data for the entire U. S. for each county;
2. Conversion of the data base for installation in the SYSTEM 2000 Data Base Management System, at Lawrence Berkeley Laboratory (LBL) and in the EPA computer in Research Triangle Park, North Carolina;

3. Installation of the data base and other related data in LBL Socio-Economic Environmental Demographic Information System (SEEDIS);¹
4. Analysis of possible associations between disease-specific mortality, air pollutant levels, and socioeconomic and demographic indices;
5. With the use of SEEDIS, quick response to specific data requests from DOE headquarters and elsewhere.

DATA BASE DESCRIPTION

The completed data file to be installed in SYSTEM 2000 will contain approximately 3000 data items for each county in the United States. (The first number in parentheses indicates the approximate number of data items for each county).

1. Socioeconomic and demographic data:
 - (280) 1970 demographic data by sex(2), race(3), and age(23), from 1970 Census, both uncorrected and corrected;
 - (220) 1970 demographic data by sex(2), race(3), age(9), and marital status(4);

- (200) 1970 socioeconomic characteristics by sex(2), and race(3);
- 2. Air Quality data:
 - (500) 1974-76 air quality by pollutant(11);
- 3. Mortality data:
 - (700) 1950-1969 cancer mortality by sex(2), race(2), site(35);
 - (900) 1968-1972 mortality by sex(2), race(2), cause(54);
- 4. Miscellaneous data:
 - (30) geocodes, county centroids, and miscellaneous data.

standard published EPA reports, provide estimates by county or AQCR (Air Quality Control Region) by simply averaging the estimates from all monitoring stations within the county or AQCR. Such an analysis ignores the actual locations of the monitoring stations as well as the distribution of the population.

In the PAREP project, the county population centroid is calculated from the population distribution reported in the 1970 Census. The same analysis can easily be performed for cities, census tracts, or any other political division. For the pollutant in question, the distance is calculated from the population centroid to all active monitoring stations, whether or not in the county. A weighted average (actually, geometric mean) is calculated, in which each station i receives a weight $w(i)$ equal to

$$w(i) = \exp[-0.5(d_i/d_0)^2]$$

Here, d_i is the distance from the centroid to station i , and d_0 is a constant of the order of 20 kilometers. Various values of d_0 will be estimated and tested.

AIR QUALITY ESTIMATES

The estimation of county level air quality is an innovative aspect of the PAREP project. Most analyses of air quality data, including

LOCATIONS OF AIR QUALITY MONITORING STATIONS CALIFORNIA, ANY POLLUTANT, ANY YEAR (313 STATIONS TOTAL)

Fig. 1. Locations of California air quality monitoring stations. (XBL 775-8638)

In the completed PAREP data file, not only calculated values of air pollutant concentrations, but also the corresponding weights will be included. Thus estimates having large uncertainty (no stations nearby) can be appropriately weighted in statistical analyses.

PROTOTYPE ANALYSIS

The analysis of the data generated from the PAREP database is in the developmental stages. California, with 58 counties, served as the prototype to test a methodology that will be applied to the more than 3000 counties of the entire United States.²

Examples of maps produced by the LBL computer mapping system (CARTE) for California are shown for locations of air quality monitoring stations (Fig. 1), nitrogen dioxide levels (Fig. 2), and cancer mortality (Fig. 3). A complete set of California cancer mortality maps has been generated which reflects the mortality from cancer in terms of standard deviations from the mean rate for California as a whole. That is, the level of mortality is not plotted directly as a rate but rather in standardized units relative to the mean rate for the entire state. This method of expressing risk of death from cancer both reflects the magnitude of

the rate and adjusts for effects due to size of the county. For example, when no deaths occur in Alameda and Alpine counties, the cancer mortality rate is zero for both counties. Nevertheless, these two rates do not reflect the different risks of cancer since the population of Alameda county is 2000 times larger than that of Alpine county. This type of standardization, therefore, allows direct comparison of counties with widely different populations.

Multiple regression analysis has been applied to the 58 counties of California, with the logarithm of the cancer mortality rate as the dependent variable and ten variables (county population size, median family income, median educational level of the county, and the levels of seven air pollutants) as independent variables. The logarithm of the mortality rate tends to normalize the dependent variable and at the same time stabilize the variability. Both properties are necessary for the estimation of valid significance probabilities ("p-values"). Adjusting for the socioeconomic variables removes, to some extent, known influences on cancer mortality and allows one to assess more clearly the individual associations of cancer mortality rates with specific types of air pollution. A linear model relating mortality to a series of county level variables was chosen as a first

Fig. 2. Nitrogen dioxide levels in California.

AGE-ADJUSTED CANCER MORTALITY RATES - STANDARD DEVIATIONS FROM AVERAGE
 CALIFORNIA WHITE MALES, NCI DATA 1950-69
 CANCER, ALL TYPES (ICD 140-205)
 TOTAL NUMBER OF DEATHS (20 YEARS) = 216761
 AVERAGE MORTALITY RATE = 171.72 $\pm$ 0.37 (PER 100,000)

Fig. 3. Cancer mortality in California. (XBL 775-8640)

step in a process that will produce more sensitive analyses. Such factors as the precision of the air quality measurements are not incorporated into the present linear model and, clearly, non-linear models may be relevant to the relationship under consideration. These types of inadequacies will be dealt with by applying more sophisticated analytic methods.

The prototype analyses were not intended and cannot be interpreted as a test of any epidemiological hypothesis relating air pollution to cancer mortality. It is, rather, a preliminary example of the kinds of analyses which are readily undertaken using the PAREP database. Significant epidemiological investigations clearly await the completion of the database containing all U. S. counties.

FOOTNOTES AND REFERENCES

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1. In late 1978, two E&E Division Seminars were presented, which explained the capabilities and applications of SEEDIS (a) in general; (b) in connection with PAREP. Interested persons may contact Virginia Sventek, LBL Ext. 5216, or Deane Merrill, LBL Ext. 5063, for further information.
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Indoor Air Quality: Gas Stove Emissions

G. W. Traynor, D. W. Anthon, and C. D. Hollowell

INTRODUCTION

Air pollution research has recently begun to focus on the problem of indoor air quality. Several studies have shown that the concentrations of some pollutants in residential buildings frequently exceeds those levels commonly occurring in the outdoor environment.¹⁻⁶ Chemical and biological contaminants released into indoor environments are undesirable but often unavoidable byproducts of human activity. Typical indoor contaminants include gaseous and particulate pollutants from indoor combustion processes (e.g., cooking, heating, cigarette smoking), toxic chemicals and odors from cooking and cleaning activities, odors and viable microorganisms from humans, and odor-masking chemicals used in several activities. In addition, a wide assortment of substances known to be potentially hazardous (e.g., asbestos, radon, formaldehyde, vinyl chloride) are released from indoor construction materials and furnishings.

Reduced infiltration and ventilation rates in buildings, proposed as important energy conservation measures, can lead to elevated levels of indoor-generated air contaminants. When contaminant concentrations reach excessively high levels, they may impair the health, safety, and/or comfort of the occupants.

Many studies have attempted to correlate air quality with both morbidity and mortality rates. The conclusions of such epidemiological studies are in serious doubt since they relied on outdoor air quality data only. Since most people spend 80% of their time indoor, outside air is not totally representative of the air people normally breathe. Another problem is that most such studies have concentrated on only a few gaseous pollutants (principally CO, O₃, SO₂, NO_x) and have ignored other important pollutants, especially the respirable fraction of particulates. If any such study is to succeed, the indoor pollutants must be characterized and traced from the point of origin to the receptor (population group under study). Only then can the quality of the air that is actually inhaled by the sample population be indexed in a manner that is both scientifically valid and applicable to large populations. Currently, a major effort is underway to develop models to assess the total exposure of the human population to various harmful pollutants. In order to do this, indoor air quality must be characterized and modeled for a variety of indoor environments. Factors such as pollutant emission rates from indoor sources and air exchange rates of buildings are very important in such modeling efforts.

This project critically analyzes the role of indoor combustion appliances and their impact on indoor air quality in residential buildings. Gas stoves pose the greatest problem since they are usually vented directly into the kitchen, unlike most furnaces or water heaters which

are vented to the outdoors. Although range hoods could alleviate some of the problems if installed, they are rarely used due in large part to the high noise levels associated with them.

Most studies have assumed that indoor air pollution occurs as a direct result of outdoor sources. Such studies have been concerned mainly with SO₂, CO, O₃ or total suspended particulate matter. Surprisingly little work has been directed toward analyzing other potentially important indoor air pollutant species, such as NO, NO₂, nitrates, sulfates, metals, organics, and the respirable fraction of particulate matter. Although emission of CO from gas stoves and heating systems has been extensively investigated, other emissions from indoor combustion sources have not been thoroughly studied. It is known that combustion processes can yield a wide variety of different and potentially hazardous substances, including aldehydes, nitrogen-containing compounds⁷ (e.g., nitrogen oxides, hydrogen cyanide, ammonia) and respirable particulates. There is evidence that interactions between primary combustion products result in the production of secondary species. For example, it has been shown that gaseous nitrogen compounds can rapidly undergo catalytic oxidation or reduction to other important air pollution species such as nitrates, nitric acid, ammonium, and other organic nitrogen compounds of the amino and pyrimidine type.⁸

The significance of indoor air pollution--only recently recognized--is now expected to have a large impact on (1) the overall assessment of the effect of air pollution on human health, (2) the design of epidemiological studies that must consider indoor as well as outdoor air pollution, (3) energy conservation strategies for buildings that might restrict indoor-outdoor air exchange, and (4) the need for more stringent control of air pollution from indoor combustion sources.

The work reported here represents the accomplishments of the ongoing laboratory studies which systematically examine gaseous and particulate air pollutants in residential buildings. The measurement techniques used in the field and laboratory experiments have been previously described.³⁻⁴

GASEOUS EMISSIONS: NITROGEN DIOXIDE, CARBON MONOXIDE, ALDEHYDES AND HYDROGEN CYANIDE

Our early field studies have shown that levels of CO and NO₂ approach or exceed existing U. S. ambient outside air quality standards in some residential buildings with gas appliances.³ Nitrogen dioxide levels in kitchens of houses with gas stoves were observed to be as high as 0.5 ppm when one top burner was operated for less than 30 minutes and as high as 0.8 ppm when the oven operated for 20 minutes. Concentrations of NO₂ were observed to be as high

as 0.6 ppm for eight hours in the bedroom of a house with a forced-air gas-fired heating system operating under normal conditions. These NO₂ concentrations can be compared with the short-term U. S. and foreign NO₂ ambient outside air quality standards shown in Table 1 (approximately 0.2 ppm for 1 hour).⁹⁻¹²

Table 1. Recommended and promulgated short-term NO₂ air quality standards.⁹⁻¹²

County	Short-Term NO ₂ Air Quality Standard (0.1 ppm ≈ 190 µg/m ³)	Status
Canada (Ontario)	0.2 ppm/1 hr 0.2 ppm/24 hr	promulgated promulgated
Japan	0.04-0.06 ppm/24 hr	promulgated
U.S.A.	0.25-0.50 ppm/hr	recommended
West Germany	0.15 ppm/short-term exposure	promulgated
WHO/UNEP	0.10-0.17 ppm/hr	recommended

Studies using an experimental room with a volume of 950 ft³ (27 m³) have characterized the emissions from a new gas stove operating in the room with air exchange rates ranging from 0.25 to 10 air changes per hour (ach).¹³

These laboratory studies have shown that gas stoves generate extremely high emissions of such species as CO, NO, NO₂, and respirable aerosols (size <2.5 µm), and that the concentration of these species becomes significant when the air exchange rate is controlled to less than 1 ach. We have observed that the CO concentration exceeds the 1-hour ambient outside air quality standards only under "tight" conditions (0.25 ach), but the NO₂ concentration exceeds the recommended 1-hour standard, even with an air exchange rate as high as 2.5 ach. Table 2 gives the 1-hour average NO₂ concentrations in the experimental room. Particularly noteworthy is the observation that a kitchen ventilation rate of 50 cfm (the upper limit of the recommended ASHRAE Standard 62-73 ventilation rate for residential kitchens)¹⁴ results in a 1 hour average NO₂ concentration of 0.4 ppm, a value considerably higher than the promulgated foreign standards. Lower ventilation rates result in even higher NO₂ concentrations.

Aldehyde emissions were also found to be significant. Total aldehyde levels reached a half-hour average of 670 µg/m³ (0.56 ppm as formaldehyde) under "tight" conditions (0.25 ach) when using two burners for 16 minutes. Similar levels of aldehydes were observed when the oven was operated for 1 hour at 350°F; the peak half-hour concentration was 760 µg/m³ (0.62 ppm as formaldehyde). It is very likely that formaldehyde constitutes most, if not all, of the aldehydes produced by the gas stove. In view of the present concerns about formaldehyde and its adverse health effects, these high concentrations of aldehydes are particularly significant.

Table 2. Nitrogen dioxide concentrations in a test kitchen.

Air Exchange Rate in Kitchen	NO ₂ in Kitchen*
0.25 ach (No stove vent)	1.2 ppm
1.0 ach (With hood vent above stove)	0.80 ppm
2.5 ach (Stove hood vent with fan at 50 CFM)	0.40 ppm
7.0 ach (Stove hood vent with fan at 140 CFM)	0.10 ppm
Outside during test	0.03 ppm

* (1-hour average concentration in kitchen with a gas oven on for 1 hour at 350°F).

Typical ambient outside NO₂ : 0.02 ppm (clean)--0.30 ppm (heavy pollution)

Promulgated and recommended 1-hour NO₂ standards : 0.20-0.40 ppm

ASHRAE ventilation requirements for kitchens in single family residential houses : Recommended: 30-50 CFM (ASHRAE 62-73)
Minimum: 20 CFM (ASHRAE 90-75)

As a component of indoor air, formaldehyde has received considerable attention primarily because of formaldehyde outgassing from building materials such as particle-board and urea-formaldehyde foam insulation. It is apparent that it can also result from combustion processes. Formaldehyde has a pungent and characteristic odor which can be detected by most people at levels well below 1 ppm. The toxicity of formaldehyde is apparent when it comes in contact with the skin or mucous membrane; exposure to formaldehyde can cause burning of the eyes, weeping, and irritation of the upper respiratory passages. High concentrations (above a few ppm) may produce coughing, constriction in the chest, and a sense of pressure in the head. Several studies reported in the literature indicate that swelling of the mucous membrane begins in the range of 0.05 and 0.1 ppm, depending on the individual sensitivity and environmental conditions (temperature, humidity, etc.). Review of the disease effects of formaldehyde are given in a recent EPA report,¹⁵ work reported in Denmark,¹⁶ and recent studies carried out in Sweden.^{17,18} Various recommended and promulgated formaldehyde air quality standards are given in Table 3. European countries are moving

rapidly to establish formaldehyde standards. In July, 1978, the Netherlands established a standard of 0.1 ppm (120 $\mu\text{g}/\text{m}^3$) as the maximum permissible concentration.¹⁹ Denmark, Sweden, and West Germany are all considering establishing a standard at approximately the same value (0.1 ppm).

The aldehyde levels measured in our experiments greatly exceed these European standards, as well as the recommended ambient outdoor standards for this country. Even at higher air exchange rates, it appears that the stove will generate concentrations in excess of these standards. It is our assumption that formaldehyde constitutes most of the aldehydes emitted by the stove; studies to measure formaldehyde with a specific colorimetric test are now in progress to confirm this hypothesis.

Hydrogen cyanide (HCN) was detected but only at very low levels. When the oven was on for 1 hour at 350°F, under tight conditions (0.25 ach), hydrogen cyanide concentrations reached a half-hour average of 90 $\mu\text{g}/\text{m}^3$ (0.08 ppm). This is well below the OSHA standard of 10 ppm, measured as an 8-hour time weighted average.²³ The

Table 3. Recommended and promulgated formaldehyde air quality standards.

Country	HCHO standard (0.1 ppm 120 $\mu\text{g}/\text{m}^3$)	Status
<u>AMBIENT AIR</u>		
U.S.A.	0.1 ppm maximum	recommended ²⁰
<u>INDOOR AIR</u>		
Denmark	0.12 ppm maximum	recommended ¹⁶
The Netherlands	0.1 ppm maximum	promulgated ¹⁹
Sweden	0.1-0.7 ppm maximum	recommended ^{17,18}
West Germany	0.1 ppm maximum	recommended ²¹
<u>OCCUPATIONAL AIR</u>		
Denmark	1 ppm TLV*	promulgated ²²
U.S.A.	3 ppm TWA	promulgated ²³ (OSHA)
	2 ppm TLV*	promulgated ²⁴ (ACGIH)
	2 ppm/30 min	recommended ²⁵ (NIOSH)
West Germany	1 ppm TLV*	promulgated ²²

TWA = 8 hours time weighted average.

*TLV = Threshold limit value.

low concentrations observed indicate that, in spite of its well-known toxicity, hydrogen cyanide constitutes a relatively minor health hazard, at least, in comparison with other emitted compounds.

Measured emission rates for several gaseous species from gas stove ovens and top burners are shown in Tables 4 and 5. The values from this study are compared with results from other works. Total aldehydes were measured using the MBTH (3-methyl-2-benzothiazolone hydrazone) method.²⁹ Samples were collected by bubbling air through a solution of MBTH in an ice bath;

under these conditions, the collection efficiency is approximately 91%. After collection in the bubbler, an oxidizing solution consisting of ferric chloride and sulfamic acid was added to each sample. The intensity of the green color which formed is proportional to the concentration of aldehydes present.

Hydrogen cyanide was measured using an ion-selective electrode.³⁰ Samples were collected by bubbling air through a solution of sodium hydroxide in an ice bath. The hydroxide traps nearly 100% of the HCN by converting it to cyanide ion; in this form, it can be analyzed with an

Table 4. Gas stove oven emission rates ($\mu\text{g/Kcal}$).

Pollutant	Lawrence Berkeley Laboratory	The Research ²⁶ Corporation of New England (TRC)	British ²⁷ Gas Corporation	American ²⁸ Gas Association Standard
	Oven at 350 ⁰ F	Old Stove Oven (Steady State)	New Stove Oven (Steady State)	Oven (General)
CO	600-1300	530	1620	{ 85
NO	20-50	91.4	77.9	
NO ₂	30-60	73.1	50.4	
SO ₂	0.5-1.0			
HCN	1.8			
Aldehydes	16			
Kcal/hr	2000	2200	2200	

Table 5. Gas stove burners emission rates ($\mu\text{g/Kcal}$)*

Pollutant	Lawrence Berkeley Laboratory	British ²⁷ Gas Corporation	American ²⁸ Gas Association Standard
<u>Gaseous Emissions</u>			
CO	720	{ 136	645
NO	47		
NO ₂	78		
SO ₂	0.85		
HCN	0.7		
Aldehydes	21		
<u>Particulate Emissions</u> (Respirable Fraction)			
Carbon	0.9		
Sulfur (as SO ₄)	0.04 (0-0.08)		
Total Respirable Mass	1.5(1.0-2.6)		
Kcal/hr burner	2500		

* Operated with water-filled cooking pots.

ion-selective electrode. In this device, similar to a pH meter, the voltage between a special cyanide-sensitive electrode and reference electrode is measured. By comparison of this voltage with that arising from a solution of known cyanide content, the cyanide content of the solution (and hence that of the air sample) can be determined.

PARTICULATE EMISSIONS

In 1978, a major effort was undertaken to characterize particulate emissions from gas stoves. The particulates were characterized for both size and chemical composition. Chemical composition measurements were made by collecting size-segregated aerosols on various filter substrates for subsequent laboratory analysis. It was necessary to segregate the samples by size in order to examine the respirable fraction of particulate matter. Aerosols collected on teflon filters were analyzed for mass (gravimetrically) and an array of elements (S, Pb, Ca, Fe, etc.) using X-ray fluorescence techniques. Aerosols were also collected on quartz filters to measure total carbon using a combustion technique. Aerosol size measurements were performed by a commercial electrical mobility analyzer.

Particulates are deposited in different parts of the respiratory tract, depending on their size (see Fig. 1). Particulates which pose the greatest health hazard are those with diameters

Fig. 1. Fraction of particles deposited in the three respiratory tract compartments as a function of particle diameter.³¹ (XBL 771-7190)

less than 0.5 microns. The very fine particulates can travel as far as the alveoli where removal mechanisms are slower than in other parts of the respiratory system. Once in the alveoli region, the particulates exert a toxic effect on the individual through various biological mechanisms.³¹

Figure 2 summarizes the size characterization of gas stove particulate emissions. Figures 2A and 2B show the particulate size distribution in experiments with two burners operating for 15 minutes. These experiments were conducted in the experimental room described previously. In both cases (Figs. 2A and 2B) an initial combustion emission peak near 0.025 microns was observed, but within minutes, the majority of particulates increased in size to a mode between 0.05 and 0.5 microns. These are the same particulates that pose the greatest harm to human health. For comparison, Fig. 2C shows particulate size distribution at the peak of an air pollution episode in the San Francisco Bay Area. It can be seen that burners of a gas stove generate large numbers of very small particulates that approach or exceed fine particulate levels on a very smoggy day.

Particulates were analyzed for chemical composition to account for all the mass emitted in experiments under similar conditions. Carbon was observed to be a major component of the particulate emissions from the gas stove. Its emission rate was constant in all burner experiments. The total mass emission rate of respirable particulates varied, however. In some cases (see Fig. 2B), 90% of the total mass was measured to be carbon. In other cases (see Fig. 2A), the mass of emitted respirable particulates was found to be 2 or 3 times the mass of carbon emissions. Thus, while all experiments were conducted under the same conditions, the stove generated a variable fraction of particulate mass which has not yet been identified. Sulfate (measured as particulate sulfur) was found to account for less than 10% of the unidentified mass.

Future laboratory studies will investigate the possibility that various particulate nitrogen-containing compounds contribute to the total mass emissions. One hypothesis is that carbon particles act as catalysts with gas phase compounds for secondary particulate formation. This catalytic behavior may vary as a function of several variables including temperature, humidity, air exchange rate, and background air composition. Studies in progress are testing this hypothesis.

Although use of the gas oven contributes significantly to the production of gaseous species, its contribution to the production of particulate species is relatively negligible compared to the amount of particulates generated by the burners. Particulates generated by oven use must traverse a constricted path before entering the kitchen environment. The particulates most likely coagulate very quickly and deposit on the inner surfaces of the stove. The emission rate of oven particulates into the kitchen en-

Fig. 2. Volume density and distribution of particulate emissions less than 0.5 μm in diameter. Figures 2A and 2B illustrate gas stove particulate emissions for two experiments under similar conditions in which two top burners were operated with water-filled cooking pots. The size distribution at 7, 11 and 15 minutes after turning on the burners is shown. Figure 2A shows the case where carbon accounts for 35% of the total emitted mass. Figure 2B shows the case where carbon accounts for 90% of the total emitted mass. In both cases, the absolute amount of carbon emitted is the same. Figure 2C shows the peak volume concentration distribution for a San Francisco Bay Area air pollution episode.

(XBL 791-235A)

vironment is an order of magnitude less than that of the burners, which inject particulates directly into the kitchen. Particulate emission rates from the burners are reported in Table 5, along with corresponding gaseous emission rates.

CONCLUSIONS

The field and laboratory measurements carried out thus far indicate that combustion-generated indoor air pollution may have a significant impact on human health. This study has demonstrated that elevated levels of gaseous air pollutants (CO , NO , NO_2 and aldehydes) and respirable particulate carbon and sulfur compounds are present in indoor environments where gas appliances are used. Observed levels of CO , NO_2 and aldehydes approach or exceed promulgated and proposed ambient air quality standards. Observed levels of respirable particulate mass are comparable to those present on a very smoggy day. Such levels are unacceptable for the indoor environment and are likely to limit effective implementation of energy conservation measures in residential buildings, unless other methods for ventilating air are built into energy-efficient buildings.

Indoor pollution levels are strongly affected by human activities in a building; by the manner in which building materials are incorporated into the structure; and by other aspects of the building's design, particularly the infiltration or ventilation rate. LBL is studying two design features that may be introduced to limit increases in pollution levels:

- (1) Mechanical ventilation systems could be coupled with an air-to-air heat exchanger to transfer heat (and not contaminated air) from the exhaust to the fresh air stream in winter and vice versa in summer. Already in use in larger buildings, small heat exchangers (50-500 cfm) are now being marketed for homes in Europe and Japan. These could be used to maintain air exchange rates and control contaminant concentrations at acceptable levels, while reducing heat losses from air exchange.
- (2) indoor air could be circulated through contaminant control devices (e.g., electrostatic precipitators, particle filters, chemical adsorbents) thus substantially reducing the concentration of particulate and gaseous contaminants.

PLANNED ACTIVITIES FOR 1979

Laboratory investigations of particulate and gaseous emissions from gas stoves will continue. The primary emphasis will be to characterize further the composition of the particulates and to determine why the respirable mass emission rate varies so widely. Nitrogen-containing compounds will be the first to be investigated in this respect.

In 1979, LBL will return to the field to assess the actual impact of combustion appliances

in residential buildings. The problem of pollutant dispersion throughout a residential building is particularly important. For future epidemiological studies, it is important to know whether the observed elevated contaminant levels are restricted to the kitchen area or whether they cause elevated levels throughout the house, thus making the 8-hour sleeping period crucial in epidemiological considerations. A heat exchanger will be installed in an experimental house in order to observe its contaminant removal and energy conserving attributes. Other contaminant removal schemes will be investigated for energy efficiency and air pollution control.

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Boron Migration in Soils

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INTRODUCTION

Domestic energy resources such as geothermal, coal and oil shale contain boron in concentrations at the ppm levels. Table 1 lists boron levels in selected sources. The use of these resources for power production and heating purposes results in wastes containing boron which can be introduced to soil systems by the leaching action of rainwater or wash water, or from spills. The interest in boron in soils stems mainly from its effects on plants if taken up in excessive quantities.

Table 1. Boron levels in selected power plant coals and process ashes, oil shale and geothermal reservoir fluids.

Source	Concentration, ppm
Coal	13±2, 92±1, 98±32
Bottom slag (coal)	17±3, 120±12, 120
Economizer (coal)	19±2
Precipitator fly ash (coal)	33±3, 240±5, 230
Raw shale oil	60 to 98
Spent shale	54 to 110
Geothermal	1 to 650

Boron in the form of boric acid and its water soluble salts is essential to the normal growth of all higher green plants. It is unique among the micronutrients because of the narrow range of concentration that is beneficial to most plants. Plants vary widely both in their requirements and tolerance for this element; for example, citrus crops can tolerate levels up to 0.5 mg/L in irrigation waters.

The project has as its objective a study of the mobility and sorption of boron through soils. The goals are twofold: (1) to analyze soil samples for their boron content, and (2) to study the sorption of boron by soils from waters such as geothermal brines.

ACCOMPLISHMENTS DURING 1978

A survey of the available information on the transport and uptake of boron in soil systems began in 1978. The result of this survey will be a report covering the following major topics: (1) natural and energy-related sources of boron, (2) effects of boron on plants, (3) uptake by plants, (4) methods for studying boron in soil systems, (5) boron in soils, (6) recommendations for additional research.

Table 2. Background concentrations of boron in selected rocks, soils, plant ash and waters.

Sample	Concentration (ppm)
Granite Rock (Precambrian; Missouri)	<20-20
Shale Rock (Sauk sequence; Western United States)	<30-220
Cultivated Soil (Plow zone, corn field; Missouri, Glaciated prairie)	<20-50
Plant Ash (Soybean, Missouri, glaciated prairie)	150-300
Rain	0.01
Fresh Water Lakes	0.2-3
Streams	0.013-5

Table 2 gives the background natural concentrations of boron in selected rocks, soils, plant ash and waters.

PLANNED ACTIVITIES FOR 1979

In 1979 a report on the sorption and mobility of boron in soils will be completed. The contents of the report are based on published material and will mainly cover the six topics listed above.

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Environmental Aspects of Geothermal Energy Development

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INTRODUCTION

The objective of this project is to collect, maintain and evaluate environmental data pertaining to geothermal energy development. Two areas of continuing social and economic concern pertaining to geothermal energy development involve hydrogen sulfide emissions and land subsidence. Data have been collected from various monitoring organizations and entered into a database management system, thereby facilitating continuous updating capabilities and retrieval features for data analysis.

ACTIVITIES DURING 1978

One of the most frequently cited environmental hazards associated with geothermal energy is the emission of hydrogen sulfide. The presence of low concentrations is evidenced by its odor, the discoloration of some paints, and the tarnishing of brass fixtures and silver. In vapor-dominated geothermal fields such as the Geysers-Calistoga field in northern California and the Larderello field in Italy, H₂S is simply a component of the steam. In liquid-dominated systems such as the Wairakei and Broadlands fields in New Zealand and the Imperial Valley geothermal fields in southern California, the H₂S equilibrates between the steam and water fractions before separation, but substantially all passes to steam during separation.

Generalizations about the environmental impact of geothermal emissions are inappropriate since each geothermal installation produces a unique set of chemical effluents which specifically depend upon the geochemistry and exploitation history of the hydrothermal reservoir.

The plant design and abatement technology may additionally influence the chemical composition of the effluents. For this reason, a work plan was developed to log emissions data characterizing the development of geothermal areas.

The hydrogen sulfide problem at the Geysers-Calistoga Known Geothermal Resource Area (KGRA) is considered to be the major obstacle to the growth of geothermal energy utilization. Current emissions are causing an odor nuisance leading to violations of the state's emissions standard. As a result of H₂S emission violations, the Northern Sonoma County Air Pollution District has formally requested canceling H₂S variance permits, which would result in long-term shutdowns. Additionally, the Lake County Air Pollution Control District has asked the State Air Resources Board to require the shutdown of old power plants when new and cleaner ones begin operation.

Geothermal brines in the Imperial Valley contain a minimal amount of hydrogen sulfide in the range of 1 ppm-50 ppm. In the East Mesa field, H₂S concentrations average less than 2 ppm. At the Niland facility, H₂S concentrations up to 30 ppm have been reported in the brine, although at an air monitoring station approximately 1 kilometer away and downwind, the H₂S emission did not exceed 10 ppb. In the Heber geothermal field, only traces of H₂S and other noncondensable gases have been reported from well samplings. However, in the Cerro Prieto field in Mexico about 30 kilometers from Heber, H₂S concentrations have been reported in the fluids to be as high as 300-400 ppm resulting in emissions higher than at the Geysers.

The Wairakei geothermal field is one of several in the thermal belt of the North Island

Table 1. Geodetic networks in eight geothermal areas.*

	Vertical Net		Horizontal Net	
	Status	Agency	Status	Agency
Geysers, Calif.	E	USGS	E	USGS
Long Valley, Calif.	E	USGS	E	USGS
Coso Hot Springs, Calif.	E	USGS	P	USGS
Heber	E	I	E	USGS
Brawley	E	I	E	USGS
Buttes	E	I	E	USGS
Raft River, Idaho	E	USGS	E	USGS
Roosevelt Hot Springs, Utah	P	USGS	P	USGS

* = Areas in the Gulf Coast geopressured zone are not shown.

E = Established.

P = Partially established.

I = Interagency, which includes the following:

National Geodetic Service

Imperial County

U. S. Bureau of Reclamation

California Division of Highways

U. S. Geological Survey

Note: The Imperial County Survey at El Centro is the repository of the vertical net data.

Ref. Geothermal Subsidence Research Program Plan LBL-5983 (1977).

of New Zealand. Although the Broadlands field is located only 20 kilometers from Wairakei, H₂S concentrations have been reported to be 30 times those of Wairakei.

Another environmental consideration in the development of geothermal energy is the subsidence of land within the area resulting from the withdrawal of geothermal brines. The interest in subsidence stems from two major concerns: (1) possible damage to the production field pipelines and power plants, such as the pipe distortion experienced at Wairakei; (2) possible effects on communities located near the production fields. For example, subsidence of Venice, Italy is due in part to non-geothermal water pumping at Porto Marghera, located 7 km from Venice.

The published data on land subsidence traceable to man's withdrawal of geothermal fluids is not extensive; this is especially true for reports on geothermal subsidence in the United States. It is expected that additional data will be available from the surveying nets established to monitor ground movement at several geothermal areas in the United States. Eight geodetic networks monitoring subsidence are listed in Table 1. In New Zealand, the Wairakei geothermal field has been the most extensively studied with monitoring networks for land subsidence at the Broadlands and Kawerau geothermal areas.

Additionally, there is a significant amount of literature detailing subsidence effects from oil and gas removal and groundwater pumping for petroleum and agriculture. Selected data from non-geothermal literature are included to provide relevant background information on the theory, causes, effects and means of controlling subsidence due to man's removal of subsurface fluids.

ACCOMPLISHMENTS DURING 1978

Hydrogen Sulfide

An emissions reference database in BDMS, the Berkeley Data Base Management System, is online and available for use. The areas covered include monitoring methods, environmental effects, environmental standards, emission controls, and environmental chemistry. A numerical emissions database was developed to monitor H₂S emissions at geothermal sites over time, thereby establishing a reference for future studies of the area. Selected data on the operating conditions of the geothermal power plants and the environmental conditions have been obtained and are entered into the database. PG&E and SRI provided the data for the Geysers-Calistoga field; the Department of Scientific and Industrial Research in New Zealand provided the Wairakei and Broadlands field data; the Comision Federal de Electricidad provided the Cerro Prieto data.

Land Subsidence

In FY 1978, activities were mainly compiling and coding publications for addition to the subsidence database. Categories covered in the database include the following: environmental, modeling, economics and reservoir characteristics. The period covered by this database is mainly from 1970-1978. This starting date was selected because published literature on geothermal subsidence began to be generally available at that time as a result of the United Nations conference in Pisa, Italy in 1970. Besides geothermal subsidence, the database includes portions of the literature on subsidence due to groundwater overdraft, oil and gas withdrawal typifying the theory of soil compaction and land subsidence, monitoring methods, methods for abatement and control, and reservoir characteristics. A site-specific file was also developed to contain data on horizontal and vertical ground movement, reservoir properties and subsidence monitoring for selected geothermal sites.

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Visible Light and Ozone Damage to Mammalian Cells and Membranes

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INTRODUCTION

This project is primarily concerned with the effects of environmental and polluting factors on mammalian cellular structure and activity. Our previous report¹ showed how sensitive cellular organelles (with endogenous photosensitizers, such as mitochondria) are to damaging species of oxygen generated by visible light. We have considerably extended both our photodamage studies in whole cells (hepatocytes) and the use of model lipid membranes to characterize ozone-induced conductance increases.

It is our assumption that high levels of environmental ozone and the damaging species of oxygen generated by several cellular photosensitizers in the presence of visible light, will react with enzymes and lipids so as to alter both their activity and structure. Cellular metabolism is known to be critically sensitive to membrane permeability and enzymatic activity,

and we expect that a deeper understanding of these damage-induced changes will allow us to monitor and investigate effective protection at the physiological level.

HEPATOCYTE STUDIES

There have been several recent reports of the damaging effects of visible light exposure (>400 nm) on various microorganisms^{2,3} and cultured mammalian cells.⁴⁻⁶ We have reported that human diploid cells on exposure to visible light⁷ and oxygen >10%⁸ lost their capacity to proliferate, while ultrastructural studies showed the presence of numerous damaged mitochondria in the illuminated cells.⁹ WI-38 human fibroblasts show a gradual decline in growth rate with exposure to visible light, with younger cells⁷ being more susceptible to photokilling and with partial protection afforded by dl- α -tocopherol (Vitamin E). Visible light-absorbing chromophores and Vitamin E are largely associated with the inner mitochondrial membranes.

Our studies on the effect of visible light exposure to isolated mitochondria¹⁰ have indicated a flavin-photosensitized initiation and oxygen dependent process of damage to energy coupling, flavin dehydrogenases and quinones, but not to the hemoproteins of the inner membrane.

Further studies with isolated hepatocytes¹¹ have led us to a characterization of the pattern of intracellular damage. Exposure of rat hepatocytes to visible light (400-720 nm) of intensity 300 mW/cm² over a 12 hour period results in a selective pattern of subcellular damage. Virtually no release of lactate dehydrogenase or uptake of trypan blue was observed. Also the plasma membrane enzymes 5'-nucleotidase and β -Leucyl naphthylamidase were only slightly inactivated. The plasma membrane is therefore highly resistant to damage.

Under the same conditions, however, other intracellular enzymes were markedly inactivated. Mitochondrial damage was indicated by a decrease in latency of cytochrome c oxidase and destruction of various enzyme activities in the following order: succinate dehydrogenase > succinate oxidase > glutathione peroxidase > NADH-cytochrome c oxidase > cytochrome c oxidase (Fig. 1). This pattern of inactivation was identical to the one found upon light exposure to isolated mitochondria,¹⁰ suggesting that continued studies with the *in vitro* system are indeed warranted. Lysosomal damage was also extensive, as indicated by the loss of latency and activity in the enzymes cathepsin-c, acid phosphatase and N-acetyl- β -glucosaminidase. Some evidence of damage to microsomal membranes was indicated by a decline in glucose-6-phosphatase activity.

Fig. 1. Time course of activity of various enzymes present in Hepatocytes as a function of light exposure.
(XBL 7710-3920)

The most light-sensitive enzyme was found to be catalase, an enzyme associated with the peroxisomal fraction. Another peroxisomal enzyme, urate oxidase, was relatively less susceptible to light damage. In addition to inactivation of protein enzymes, destruction of membrane lipids was indicated by lipid peroxidation.

Attempts to prevent visible light damage show that the addition of succinate + KCN were maximally effective. EDTA was effective in preventing succinate dehydrogenase inactivation and lipid peroxidation. It is well known that succinate + KCN and EDTA both lead to extremely reducing conditions. The reducing conditions necessary for protection against visible light may result from the fact that reduced flavins cannot act as efficient photosensitizers since they absorb very little visible light. DL- α -tocopherol and butylated hydroxytoluene were very effective against lipid damage but only the latter antioxidant appreciably affected the pattern of enzyme (succinate dehydrogenase) inactivation. Rats fed with a Vitamin E-deficient diet showed a marked increase in lipid peroxidation compared to rats on a Vitamin E-supplemented diet.

Catalase studies *in vivo* and *in vitro* demonstrate that the inactivation of this enzyme is oxygen dependent and can be prevented by substrates (100 μ M methanol or ethanol), while antioxygenic substances in general (0.25 M sucrose, 1 mM Histidine and 10 μ g/ml superoxide dismutase) have little protective effect. Superoxide dismutase does, however, partially protect purified catalase.¹²

Our results suggest that the location of flavin and heme photo-receptors in intracellular organelles and their relative absorption may determine the degree to which enzymes are inactivated. In this respect the lysosomal results could have been anticipated since the degradation of macromolecular enzymes would lead to the release of free flavins which will then act as powerful photosensitizers, thereby amplifying the whole process of damage. The marked sensitivity of catalase and the loss of latency and inactivation of mitochondrial energy-linked enzymes suggest that crucial systems involved in the protection against oxidative damage are light sensitive. Their destruction may lead to the photo-killing of cells. A hypothetical scheme of the mechanisms involved in photodamage mediated through different oxygen active species is summarized in Fig. 2. While several of the steps are undoubtedly incorrect, many will be useful in implementing future experimental strategies.

OZONE STUDIES

Ozone damage to cell membranes as a primary event in ozone toxicity is an attractive hypothesis.¹³ Biochemical mechanisms of ozone injury have been discussed in a recent review.¹⁴

We have investigated the effect of ozone on the permeability characteristics of biological

Fig. 2. Effect of dl- α -tocopherol on the time, course and extent of ozone induced membrane conductance changes. (XBL 782-2887)

membranes by assaying the conductance of model membranes composed of various lipids incorporated into Millipore filters.¹⁵

The electrical assay of lipid impregnated Millipore filter membranes has been previously described.¹⁶ Ozone was generated by passing oxygen through an enclosed UV light source and was bubbled into the aqueous medium on one side of the filter membrane. The protection afforded by the antioxidant dl- α -tocopherol (Vitamin E) to the lipid membranes was also studied. Spin-label probes were used to show that the bulk of the lipid in the filter membrane is randomly oriented.¹⁵

The effect of ozone exposure time and Vitamin E molar concentration upon membrane conductance increases is shown in Fig. 3. Values of ~1% molar ratio of Vitamin E/egg yolk lecithin in the membrane forming solutions could prevent any change in membrane conductance by ozone. After the ozone treatment was stopped, the conductance decreased reaching a steady state which was ozone concentration dependent. Further rinsing of the membrane with fresh bathing solution lowered the membrane conductance by as much as 40% relative to the unrinsed control.

We have also studied the effect of different lipids in the changes in steady state membrane conductance. In general, both the initial conductance as well as the ozone induced conductance increases were greatest for lipid mixtures containing a high proportion of unsaturated fatty acid residues.

We have also shown that the conductance of ozone treated and untreated membranes decreased as the bathing solution pH increased. The observation that ozone induced conductance changes, expressed as differences relative to the controls, diminish with increasing pH is consistent with the report that ozone breakdown in water depends on the hydroxyl ion concentration.

To gain insight into the extent of ozone penetration through the membrane, and the possible release of reaction products from it, the effect of ozone exposure on a double membrane was studied. The conductance of the membrane immediately exposed to ozone increased dramatically whereas that of the second (screened) membrane showed no significant increases in the conductance. Hence, there is little or no release of permeability enhancing factors from the untreated side of the first membrane into the environment and the second membrane.

The reaction sites of ozone with lipids are thought to be the double bonds of the fatty acid chains. The failure to observe conductance changes when using saturated lipids suggests that the conductance changes indeed result from the interaction of ozone with unsaturated lipids. The fact that the membrane conductance decreases again after ozone treatment ceases (Fig. 3) implies that some of the reactions of ozone and lipids continue for an extended period of time and that unstable intermediates may be responsible for part of the increased conductance.

We should add that the lipid impregnated filter membrane system is simple, convenient and sensitive and should be developed as a valuable assessment technique for evaluating the comparative effects of various types of pollutants and protective agents to cell membranes.

PLANNED ACTIVITIES FOR 1979

Our studies with visible light and ozone damage to cells and membranes have shown how different these effects will be in cells. Visible light in the presence of oxygen damages intracellularly (where the flavins and hemes are located) with very little effect on the cellular membrane; ozone on the other hand will damage (increase the permeability of) the first membrane it comes into contact with, viz., the cellular membrane. Both will have profound effects on the metabolism of the damaged cells. Further studies will attempt to elucidate the different roles of cellular and intracellular membranes in the initiation and propagation of structural and functional damage to cells.

Fig. 3. Possible pathways of oxidative damage in mitochondria. (XBL 795-9730)

Biochemical and biophysical assays will continue to play a fundamental role in the characterization of such damage. In particular the value of several electron paramagnetic spin probes developed in our laboratory and others¹⁷⁻¹⁹ will be explored to monitor the early changes in membrane permeability, surface charge and fluidity. We have already demonstrated that one of the first indications of lipid peroxidation at the membrane surface level is an increase in the net negative potential of that surface (which is partially quenched by antioxidants). We will further investigate this observation and its consequences to the ionic transport characteristics of the membrane and its overall metabolism. Fluorescent probes

will be used to study the release of membrane bound hemes and spin traps will be applied for the identification of intracellular free-radical intermediates. Since catalase is the key enzyme in the H_2O_2 metabolism, the importance of its inactivation both *in vivo* and *in vitro* to the overall metabolic protective capacity of cells will be carefully characterized to identify its significance to the time sequence of damaging events. And finally, the fact that fluorescence has been shown to monitor certain intracellular types of damage will be used to follow the localization and the kinetics of generation and decay of damaging intermediates in cell systems (in collaboration with Dr. D. W. Deamer at U. C. Davis).

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Chemical Structure and Toxicity: Multifactorial Predictive Techniques*

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INTRODUCTION

The logistics of toxicity screening of the more than 100,000 commercial chemicals currently in use, while simultaneously screening the estimated one to three thousand new substances introduced annually, imposes an almost insurmountable burden on the regulatory agencies--particularly the Environmental Protection Agency, which is responsible for the implementation of the Toxic Substances Control Act. A number of short term *in vitro* tests are available for screening compounds for potential carcinogenicity.¹ Of these, the best known--the Ames test--is based on the measurement of mutation rates of selected (activated) mutant bacteria, on the assumption that active mutagens have a high probability of also being carcinogens, since both processes involve reaction with genetic materials (e.g., DNA or RNA) in the cell nucleus. While these tests have the virtue of brevity and low cost, they are subject to considerable uncertainty, and an erroneous negative result could prove catastrophic if

it involved chronic exposure of a large segment of the population. For this reason it was clearly desirable to explore such statistical approaches as are amenable to varied inputs, from animal and *in vitro* tests to a multiplicity of chemical, physical and structural characteristics of substances.² Four techniques were explored for their potential for large scale *a priori* predictive application:

- 1) Quantitative Structure-Activity Relationships (QSAR)
- 2) Factor Analysis (FA)
- 3) Pattern Recognition (PR)
- 4) Molecular Connectivity (MC)

An overview of these four techniques will be presented in the remainder of this paper.

QUANTITATIVE STRUCTURE-ACTIVITY RELATIONSHIPS (QSAR)

The concept of a relationship between chemical structure and biological activity is well over

a century old. As early as 1870 Crum Brown and Fraser³ postulated that the biological response (R) to a drug was a function of its structure (C),

$$R = f(C) \quad (1)$$

thus laying the conceptual groundwork for future structure-activity relationship (SAR) investigations. Later quantitative treatments derived from Hammett's work with substituted benzoic acids,⁴ from which he deduced the expression:

$$\log K\sigma = \log k\mu + \sigma\rho \quad (2)$$

Here $k\sigma$ and $k\mu$ refer to rate or equilibrium constants of substituted and unsubstituted species, respectively, and σ and ρ are constants characteristic of the substituents and their location on the ring.

Hansch *et al.*⁵ introduced the substituent constant π , where

$$\pi = \log P_X - \log P_H \quad (3)$$

P 's are the respective partition coefficients in an octanol-water system of substituted (P_X) and parent (P_H) structures. Using this π function, Hansch obtained linear regressions for substituent effects on the biological activities of benzoic acids (mosquito larvae); phenols (g-positive and g-negative bacteria); phenylethyl phosphate (houseflies); thyroxines (rodents); dimethylaminoethyl benzoates (guinea pigs); and carcinogens on mice.

More recent applications of the SAR method include refinements which take into account steric influences on biological activity.⁶ Thus the neurotoxicities of substituted DDT analogs fall on a smooth curve (Fig. 1) very similar to a potential energy diagram for a

diatomic molecule when $\log LD_{50}$ is plotted against the Taft steric substituent parameter, E_s , where

$$\log LD_{50} = \alpha + \beta E_s^X + \gamma [E_s^X]^2 \quad (4)$$

The concept of molecular size and fit has been used extensively by Metcalf and others⁷ in designing DDT-analogous insecticides. These workers postulate that the DDT-like molecule is more or less neurotoxic depending on its ability to conform to a flexible boundary at the macromolecular receptor site. Figure 2 depicts three such flexibly bounded sites for DDT and two analogs, one with a smaller (S) and a larger (L) substituent than chlorine (Cl), a second with a substituent (M) similar in size to Cl.

Quantitative structure-activity relationships (QSAR) have provided an eminently productive technique when applied to drug design, where the focus is on a specific pathogen, pathology or locus. "The ultimate goal...is...to design a compound with a prescribed biological profile."⁸ However, the case of an environmental toxicant or carcinogen is much more complex because one must proceed from a generalized, multifactorial problem presented by a chemical compound, often ubiquitous in the eco-system (e.g., organohalides) or in wide use (PVC wrap, PVC pipe, etc.),⁹ and impinging on a large and varied population of undetermined sensitivities and widely varying detoxification capacities. In short, instead of a "prescribed biological profile," the environmental pollutant is normally biologically multidentate, and its potential cumulative health effects hopelessly obscured by the high background noise of other toxicants in the environment. It is therefore no wonder that even extensive epidemiological studies will not lead to absolute "proof"---and that most toxicological findings first emerge from the workplace, where relatively healthy individuals are exposed to high concentrations of specific toxicants.¹⁰

FACTOR ANALYSIS

This is one of a number of statistical methods which can cope with large quantities of data encountered in dealing with interactions in chemical and biological systems. Originally employed largely in the social sciences,¹¹ FA is currently finding increasing favor with workers in chemical and biological fields.^{12,13} While a detailed description of FA is outside the scope of this report, the requirements of a simple 2-dimensional matrix will be summarized below.

In the case of a 2-dimensional data matrix, two mathematical requirements must be satisfied by the property measured: (1) each data point may be expressed as a linear sum of terms:

$$D = d_1 + d_2 + \dots + d_n \quad (5)$$

Fig. 1. Relationship between toxicity and E_s for 1,1,1-trichloro-p-methyl-p'-x-diphenylethanes. (XBL 7710-6923)

Fig. 2. Flexible boundaries at DDT-analog receptor sites. (XBL 7710-6924-25)

(2) D is also a sum of row and column product terms,

$$D = r_1 c_1 + r_2 c_2 + \dots + r_n c_n \quad (6)$$

where r_k and c_k represent mutually independent row and column factors. In matrix notation this reduces to

$$[D] = [R] \cdot [C] \quad (7)$$

where $[D]$ is the product of a row and a column related matrix. Figure 3 depicts the stepwise procedure involved in processing and correlating data.

1) First, an experimental data matrix is used to construct the correlation matrix.

2) Second, the correlation matrix is decomposed into a number of linear factors, or abstract

eigenvectors, capable of reproducing the data points within experimental error (reproduction).

3) The linear factors obtained in Step 2 above are subjected to mathematical rotation, so that significant physical parameters are related to the abstract factors.

4) Combination of sets of real factors (vectors) reproduce the data matrix within the required precision, providing a best solution.

5) By applying a "free floating" technique, missing data may be predicted.¹²

PATTERN RECOGNITION (PR)

Long familiar to engineers, biologists and psychologists as a useful branch of artificial intelligence, PR has recently been applied to complex chemical problems involving large

Fig. 3. Factor analysis. (XBL 779-6919)

quantities of data.¹⁴ The methods of PR fall into two classes--parametric and nonparametric, of which the latter will be briefly described below.

Each experimental data point in a collection is treated as an object in n-dimensional space with measurements represented by co-ordinates. Thus, the distance d_{ij} between any two points is a measure of their similarity:

$$d_{ij} = \left(\sum_{k=1}^m (x_{ik} - x_{jk})^2 \right)^{1/2} \quad (8)$$

as $d_{ij} \rightarrow 0$, similarity increases, and a similarity function S_{ij} may therefore be defined as follows:

$$S_{ij} = 1 - d_{ij}/D_{ij} \quad (9)$$

where D_{ij} is the maximum distance between x_i and x_j .

Classification and learning processes operate on the n-space in one of two learning modes: supervised or unsupervised. In the former mode some of the points are classified and function as a "training set" which can then be used to classify unknown points by use of a classification rule derived from the training set. No training set exists in the unsupervised

Fig. 4. Functional analysis of pattern recognition techniques. (XBL 7710-6920)

learning mode. Instead, possibly significant relationships between points are inferred where clustering occurs. Figure 4 is a diagram of the PR process.

Fig. 5. Acids ($\square$) and bases ($\circ$): Non-linear mapping from 6-space to 2-space. (XBL 7710-6917)

Since n may be of any dimension, computer techniques are used to reduce data to a manageable $n = 2$ or 3 . Here non-linear mapping is a useful tool for preserving interpoint distances in the ordered space. Figure 5 illustrates acid-base separation achieved in a data set abstracted from the periodic table, using 6 properties to describe each element ($n = 6$). None of these properties alone can achieve such separation.¹⁴

The value of pattern recognition in the screening of anti-cancer drugs was demonstrated by Kowalski and Bender.¹⁵ Similar techniques need to be applied to the complex toxicity problems posed by industrial pollutants (e.g., chlorinated industrial effluents).

MOLECULAR CONNECTIVITY

The organic chemist is a topologist of sorts, since the structural formula is a topographical graph containing structural bonding (connectivity) information. Also, chemists have long recognized that even minor substitution in a benzene ring can have profound effects on physical properties, reactivity and biotoxicity. It is therefore valid to question the feasibility of employing abstract mathematical structures to correlate various chemical properties and structure. In Kier's words, MC is a "non-empirical derivation of numerical values that encode within them sufficient information to relate to many physico-chemical and biological properties."¹⁶

Graph Theory

A graph consists of a set of points (vertices) connected by lines (edges), as illustrated in Fig. 6(a). The chemical graph is a topological matrix which, in its hydrogen-suppressed form, may be converted to a matrix array:

$$\delta_i = \sum_{j=1}^{n_1} T_{ij} \quad (10)$$

This topological matrix lends itself to mathematical operations from which numbers characteristic of the graph may be abstracted and a topological index developed.¹⁶

The MC method assumes that a valence-weighted graph, G_v , contains the information essential to a quantitative correlation of organic molecular structure with properties. It further postulates a relationship between the graph's connectivity characteristics and certain molecular properties. This relationship is expressed as a sum of terms, each linearly dependent on the graph characteristics:

$$C(\chi) = b_0 + \sum_{m,t} b_t(m) m_{\chi t} \quad (11)$$

$C(\chi)$ is the connectivity function, $b_t(m)$ depends on the molecular property, and $m_{\chi t}$ is the connectivity index, defined by subgraph type

Fig. 6. Graph representations of chemical structures. (XBL 7710-6918)

t and subgraph order m . Connectivity indices are obtained by summing over all distinct subgraphs:

$$m_{\chi t} = \sum_{j=1}^{n_m} m_{S_j} \quad (12)$$

Here n_m refers to the number of type t subgraphs of order m . The m_{S_j} terms are obtained for each subgraph as reciprocal square root functions of valency:

$$m_{S_j} = \prod_{j=1}^{m+1} (8i_j)^{-1/2} \quad (13)$$

The j refers to a particular set of edges. Figure 7 illustrates the steps in a calculation of the connectivity indices, 1_{χ} , for two isomeric branched heptanes. Higher order $m_{\chi t}$ terms are calculated similarly. Figure 8 depicts a subgraph evaluation and algorithm for dimethylcyclohexane. Connectedness values are determined from edge counts, E_s , where

$$E_s = 1/2 \sum_{i=1}^{n_1} \sum_{j=1}^{n_1} A_{ij} \quad (14)$$

and A is the adjacency matrix. More detailed calculations and definitions of terms may be found in Refs. 2 and 16.

Steps	2,2,3-Trimethylbutane	2,4-Dimethylpentane
Write structural formula		
Draw hydrogen-suppressed graph		
Show valence of each vertex		
Compute product of end point valences for each edge		
Compute each edge term: reciprocal square root product		
Sum all edge terms	2.943	3.126

Fig. 7. Procedure for calculating connectivity index ${}^1\chi$. (XBL 7710-6921)

Some General Observations on the MC Method

Kier and others have successfully correlated MC with physical¹⁷ and biological properties.¹⁸ The method has the advantage of simplicity and flexibility. It can be used to represent molecular structure at a number of levels of complexity, each level providing some information uniquely related to the structure (graph or subgraph), and through it to physical, chemical and biological characteristics.

The $C(\chi)$ function is in essence a weighted count of substructures, described in terms of adjacencies within each structure. ${}^1\chi$ is concerned with adjacent influences on a specific atom. These are modified in the higher order subgraph terms. Other aspects of the χ calculation include the atom product $\delta_i\delta_j$ and the use of reciprocal square roots of this product in the calculation of χ 's.

What is astonishing about the MC method is that, despite its relative crudeness and approximation--for instance 3-dimensional and directional features are missing in the original treatment--this elementary graphical approach has yielded some excellent correlations.

SUMMARY AND CONCLUSIONS

Four techniques for assessing the multi-factorial problems of chemical toxicity and carcinogenicity were investigated:

- 1) Quantitative Structure Activity Relationships (QSAR)
- 2) Factor Analysis (FA)
- 3) Pattern Recognition (PR)
- 4) Molecular Connectivity (MC)

While it is clear that none of the above provides an easy answer to our vexing environmental problems, it appears that the more recent areas of PR and MC both merit more intensive investigation as predictive tools. In particular, the relative simplicity of the MC approach and the prospect of expanding the non-empirical mathematical component, provide strong incentives for further development of this method.

Finally, the potential for developing a predictive method utilizing the best features of all four techniques, QSAR, FA, PR and MC, should not be overlooked.

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Example Graph		Topological Matrix
$\begin{pmatrix} 0 & 1 & 1 & 1 & 1 & 0 & 0 & 0 \\ 1 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\ 1 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\ 1 & 0 & 0 & 0 & 0 & 0 & 1 & 0 \\ 1 & 0 & 0 & 0 & 0 & 0 & 1 & 0 \\ 0 & 0 & 0 & 1 & 0 & 0 & 0 & 1 \\ 0 & 0 & 0 & 0 & 1 & 0 & 0 & 1 \\ 0 & 0 & 0 & 0 & 0 & 1 & 1 & 0 \end{pmatrix}$		
Vertex Number Sets	Subgraph Matrix	v_i^s	Subgraph	Type
1 2 4 6	$\begin{pmatrix} 0 & 1 & 1 & 0 \\ 1 & 0 & 0 & 0 \\ 1 & 0 & 0 & 1 \\ 0 & 0 & 1 & 0 \end{pmatrix}$	2 1 2 1 $E_s = 3$		Path
1 2 3 4 5	$\begin{pmatrix} 0 & 1 & 1 & 1 & 1 \\ 1 & 0 & 0 & 0 & 0 \\ 1 & 0 & 0 & 0 & 0 \\ 1 & 0 & 0 & 0 & 0 \\ 1 & 0 & 0 & 0 & 0 \end{pmatrix}$	4 1 1 1 1 $E_s = 4$		Cluster (star)
1 2 3 4 6	$\begin{pmatrix} 0 & 1 & 1 & 1 & 0 \\ 1 & 0 & 0 & 0 & 0 \\ 1 & 0 & 0 & 0 & 0 \\ 1 & 0 & 0 & 0 & 1 \\ 0 & 0 & 0 & 1 & 0 \end{pmatrix}$	3 1 1 2 1 $E_s = 4$		Path/Cluster
1 4 5 6 7 8	$\begin{pmatrix} 0 & 1 & 1 & 0 & 0 & 0 \\ 1 & 0 & 0 & 1 & 0 & 0 \\ 1 & 0 & 0 & 0 & 1 & 0 \\ 0 & 1 & 0 & 0 & 0 & 1 \\ 0 & 0 & 1 & 0 & 0 & 1 \\ 0 & 0 & 0 & 1 & 1 & 0 \end{pmatrix}$	2 2 2 2 2 2 $E_s = 6$		Circuit
		$(E_s = \text{subgraph edge count})$		

^aAdapted from Ref. 29.

Fig. 8. Subgraph evaluation and algorithm for dimethylcyclohexane.
(XBL 7711-10514)

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Patterns of Hydrocarbon Contamination in California Coastal Waters*

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INTRODUCTION

This paper provides a preliminary and partial answer to the question "By how much has the chemistry of the coastal waters of California changed as a result of the activities of man?" Answers to this question and to the companion question "What is the direction of change?" would clearly assist in the formulation of long term policies of management and protection. The California coastal zone receives the wastes of many millions of people, is the site of expanding economic activities, including tanker traffic of crude oil and refined petroleum products, possesses submarine petroleum reserves that are now being exploited, and also contains many areas of incomparable natural beauty and biological diversity. It has long been known that the waters of the California coastal zone are contaminated by organochlorine compounds of the DDT and PCB groups;¹ this paper examines the present distribution of petroleum and petroleum-related hydrocarbons, for which relatively few data have thus far been obtained.

Because methodologies for the sampling and measurement of organic pollutants, including petroleum compounds, in seawater are still in a state of rapid development,² recent monitoring programs of coastal water quality have relied heavily on biological indicators of local pollution levels, in particular mussels, *Mytilus* sp., and other bivalves. Data presented in this paper were obtained in two such California programs:

- 1) the California State Mussel Watch Program, which is examining levels of pollutants accumulated by the mussel *M. californianus* from seawater in the intertidal zone of a series of biological reserves along the California coast designated as "Areas of Special Biological Significance;"
- 2) a three year baseline program undertaken by the U. S. Bureau of Land Management prior to the initiation of offshore drilling for petroleum in southern California.

Two supplemental questions relevant to the interpretation and significance of the data are also addressed:

- 1) although it is well established that mussels accumulate a variety of pollutants from the ambient seawater system,³ how are the pollutant levels in the mussels related to those in both the "dissolved" and particulate phases of seawater?
- 2) Gas chromatographic profiles of weathered petroleum from almost any source invariably contain a "hump" consisting of an unresolved complex mixture (UCM).⁴

To varying degrees, the UCM is also present in chromatograms of extracts of mussels from both areas of wastewater discharge as well as areas which are relatively pristine. How can the UCM's containing petroleum compounds be distinguished from those consisting of, or containing, complex mixtures of other hydrocarbons and related compounds, both anthropogenic and biogenic? Also, how can the UCM's of petroleum from different sources be distinguished? This is clearly a desirable goal in the study of coastal pollution patterns.

EXPERIMENTAL

Mussels were obtained from thirty of the Areas of Special Biological Significance in July, 1977, when upwelling generally occurs along the California coast, and again in November. Collection sites were: 1) San Miguel Island, west; 2) San Miguel Island, east; 3) Santa Cruz Island; 4) Anacapa Island; 5) Santa Barbara Island; 6) Santa Catalina Island; 7) La Jolla; 8) Ocean-side; 9) Corona del Mar; 10) Royal Palms; 11) Point Mugu; 12) Goleta Point, reference station; 13) Pt. Conception; 14) Pt. Arguello; 15) Montana del Oro; 16) Salmon Creek; 17) J. P. Burns State Park; 18) Soberanes Pt.; 19) Carmel; 20) Pt. Pinos; 21) Ano Nuevo Island; 22) Fitzgerald; 23) Farallon Islands; 24) Berkeley Pier, a reference station (*M. edulis*); 25) Point Reyes; 26) Bodega Head; 27) Salt Point; 28) Pygmy

Forest; 29) Shelter Cove; 30) Humboldt Bay; 31) Trinidad Head; and 32) Klamath River. Collection sites in southern California are shown in Fig. 1.

Fig. 1. Collection sites of the California State Mussel Watch program in the Southern California Bight in 1977.

Analytical methods have been described elsewhere; approximately 40 mussels from each site were pooled to form a composite sample to reduce sampling variance.⁵ Seawater samples were obtained in situ from R. V. INVINCIBLE at Goleta Point (34°24.1'N, 119°50.5'W), 1260 and 1474 liters on 4-5 Sept., 1977; at Dutch Harbor, San Nicholas Island (33°13.0'N, 119°29.0'W), 1275 and 1333 l, on 10-11 Sept., 1977; and on a transect between Pt. Fermin and Pt. Vicente (33°43.3'N, 118°25.0'W to 33°40.5'N, 118°17.5'W), 1456 and 1314 l, on 15-16 Sept., 1977. Water was collected through a stainless steel and Teflon tube mounted off the bow of the vessel with a Jupiter Teflon impeller pump and passed through a precombusted quartz fiber filter (293 mm, 0.3 m) and two Teflon columns packed with high density polyurethane foam, mounted in parallel. Flow rates and sample volumes were monitored by turbine flowmeters. Additional sampling details and analytical methodologies are described elsewhere.⁶

RESULTS AND DISCUSSION

The distribution of the concentrations of the unresolved component (UCM's) in the saturate fraction in mussels along the California coast is shown in Fig. 2. Levels at the shore stations of the Southern California Bight (7-13) are elevated over those on the offshore islands (1-6; Fig. 1). Station 12, Goleta Point, is the site of a natural oil seep. Levels were low in sparsely inhabited areas and significantly higher in the vicinity of Monterey (20), in San Francisco Bay (24), and in Humboldt Bay (30). With the exception of Goleta Point, the distribution of the unresolved component parallels closely the human population density along the coastal zone. We explain this dis-

Fig. 2. Distribution of concentrations of the unresolved component in saturate fractions of *Mytilus* along the California coast. Concentrations in micrograms/gram of the dry weight. Station sites are listed in the text.

tribution by attributing it to the discharge in wastewaters of petroleum, refined petroleum products, other hydrocarbons and various synthetic chemicals.

Using mass chromatography, Seifert and Moldovan⁷ have been able to distinguish a number of components of the UCM of California crude oils, including hopanes, steranes and monoaromatic steranes. These compounds are present in crude oils in characteristic ratios and abundances. This method of finger-printing provides not only a technique for distinguishing among crude oils, but also for differentiating between petroleum-derived mixtures and complex mixtures from other sources. It has been used to distinguish among tar balls of different origins in the Mediterranean.⁸ Multiple ion monitoring, using a Finnigan 4023 quadrupole mass spectrometer, equipped with a 30 m, 0.25 mm I.D., SP-2100 (J&W Scientific) glass capillary column, of mussel extracts for characteristic ions of hopanes (m/e 191, steranes (m/e 217) and dimethyl monoaromatic steranes (m/e 253) revealed the presence of series of peaks within the UCM for these ions. Mass fragmentograms of m/e 253 of the mussel extracts from Goleta Point and Palos Verdes (Royal Palms, near a large wastewater outfall) and of the seawater particulate fraction from Goleta Point are shown in Fig. 3. These preliminary results indicate that the technique can be used to obtain qualitative differences among unresolved mixtures which can not be distinguished by gas chromatographic techniques alone; they also provide a direction for continuing research.

The development of large-volume *in situ* seawater sampling techniques^{2,6} has permitted a comparison of hydrocarbon levels in mussels with those in the "dissolved" and particulate fractions of seawater sampled in the vicinity of the mussel beds. Concentrations of the total unresolved component in the saturate fraction and of DDE, PCB, pristane and squalene

Fig. 3. Mass chromatograms, $m/e\ 253 \pm 0.5$, characteristic of dimethyl monoaromatic steranes, of extracts of *Mytilus* from Goleta Point and Palos Verdes Peninsula, and of seawater particulates from Goleta Point. Time in minutes. (XBL 7812-13645)

are presented in Table 1. The ratio of the resolved to the unresolved component in the mussels (0.06) is substantially lower than in either the particulates (0.17) or the "dissolved" component (0.71). Differences of equivalent magnitude were also observed among the chromatograms of the aromatic fractions of seawater and mussels from Palos Verdes, and in extracts from Goleta Point and San Nicholas Island. Among the partition coefficients (ratio of concentrations in mussels to those in water) presented in Table 1, there is a variation over two orders of magnitude. Reasons for this variation are presently unknown, but may include a high variance in the water sampling--samples of seawater were obtained, however, over a full tidal cycle of 25 hours to minimize this component of variance--differences in the micro-environment of the surfzone and offshore, levels of dissolved organic material, etc.

In spite of the observed variation, calling for additional studies to permit fuller interpretation of the data, the results presented in Fig. 2 indicate that mussels appear to provide a meaningful first order estimate of the magnitude of chemical change in the California coastal environment.

FOOTNOTES AND REFERENCES

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		Palos Verdes		Goleta Point		San Nicholas Island	
DDE	"dissolved" phase	0.18±.02	(6 x 10 ⁶)	0.073±.024	(3 x 10 ⁵)	0.044±.007	(4 x 10 ⁵)
	particulates	.082	(1 x 10 ⁷)	.072	(3 x 10 ⁵)	.008	(2 x 10 ⁶)
	mussels	1100		22		18	
PCB	"dissolved" phase	0.13±.03	(3 x 10 ⁶)	0.074±.011	(4 x 10 ⁵)	0.10±.04	(6 x 10 ⁴)
	particulates	.044	(1 x 10 ⁷)	.019	(1 x 10 ⁶)	.011	(5 x 10 ⁵)
	mussels	440		27		6	
Pristane	"dissolved" phase	0.061±.03	(7 x 10 ⁵)	0.036±.011	(2 x 10 ⁷)	0.20±.00	(6 x 10 ⁵)
	particulates	2.0	(2 x 10 ⁴)	5.2	(1 x 10 ⁵)	2.2	(6 x 10 ⁴)
	mussels	40		640		120	
Squalene	"dissolved" phase	0.74±.35	(7 x 10 ⁶)	0.25±.07	(7 x 10 ⁶)	0.35±.16	(4 x 10 ⁶)
	particulates	32	(2 x 10 ⁵)	4.9	(4 x 10 ⁵)	30	(4 x 10 ⁴)
	mussels	4900		1700		1300	
Total unresolved saturates	"dissolved" phase	4.1±1.3	(3 x 10 ⁷)	5.6±1.2	(7 x 10 ⁷)	12±2	(3 x 10 ⁵)
	particulates	83	(2 x 10 ⁶)	970	(4 x 10 ⁵)	13	(3 x 10 ⁵)
	mussels	140,000		390,000		3,900	

Atmospheric Aerosol Research

Optico-Thermal Analysis of the Carbonaceous Fraction of Aerosol Particles

R. L. Dod, et. al.

Analysis of the carbonaceous fraction of atmospheric particulate material is complicated by the diversity of forms in which it exists. Total carbon can be determined readily by combustion, but chemical information is generally obtained only by tedious separation and analysis by such techniques as solvent extraction, GC, or GC-MS.

Malissa¹ has reported a method of analysis for the carbonaceous component of atmospheric aerosol particulate material by evolved gas analysis during a temperature-programmed combustion in oxygen. We have extended this analysis by constructing an apparatus which simultaneously measures the optical transmission of the particulate matter collected on a filter. Since the optical absorptivity of this material has been shown to be due to a graphitic component,² this combination of analytical techniques may provide a direct determination of the light-absorbing fraction of the sample. This technique has also been shown to be applicable to analysis of other carbonaceous materials, such as coals and oil shales, in which there appears to be a correlation between optical absorptivity and the fraction of these fuels which is aromatic in chemical nature (Fig. 1).

The apparatus constructed for these analyses is shown schematically in Fig. 2. The combustion tube is supplied with $\sim 1\ell$ /min of oxygen which has been scrubbed of carbon-containing species. A flow of 177 ml/min is maintained through the combustion tube and CO_2 analyzer by a pump operating through a critical orifice. The excess oxygen passes out of the system through a hole in the upstream end of the combustion tube. After passing and/or reacting with the sample, the gas stream is passed through a furnace section filled with CuO maintained at 900°C to assure conversion of all carbon species to CO_2 . The CO_2 -laden oxygen is then passed through a MSA LIRA 202S infrared CO_2 analyzer with a range of 0-50 ppm CO_2 in oxygen. The sample on a prefired quartz fiber filter is positioned perpendicular to the furnace axis, allowing incident light from a 0.5 mW He-Ne laser to be intercepted. The forward scattered light is collected by a quartz light pipe and conducted to a photomultiplier detector system. The combustion furnace temperature is increased in a linear ramp from near room temperature to 600 - 800°C at a rate of $10^\circ\text{C}/\text{min}$. The signals from both the CO_2 analyzer and the photomultiplier are fed to a stripchart recorder to produce a composite thermogram.

Analysis of weighed samples of carbon and pure organic compounds as well as portions of filter samples analyzed by another combustion

a

b

Fig. 1. Combustion thermograms in solid fossil fuels. Organic functional type determined by NMR spectroscopy. Dashed line is optical transmission.
(XBL 791-168A)

technique³ shows the method to be quantitative for carbon within about 10%. Reproducibility is somewhat better, with duplicate samples from a single filter agreeing within 3-5% and being identical in qualitative nature.

Fig. 2. Schematic diagram of the programmed combustion apparatus.
(XBL 791-167)

Thermograms of ambient and source samples generally show three characteristic features: (1) a low-temperature CO₂ peak corresponding to volatilization and incomplete combustion of material which is not optically absorbing, (2) a CO₂ peak at 300-350°C corresponding to combustion (and pyrolysis) of material which also is not optically absorbing, and (3) a high-temperature CO₂ peak which includes the optically absorbing component of the sample. The three peaks are not usually well separated, but show varying degrees of overlap, as might be expected of a complex mixture of organic and elemental carbon species.

Source samples show a wider diversity in their thermograms, as might be expected for uniform combustion conditions with a single fuel. Some samples show the carbonaceous particulate material to be composed almost entirely of light-absorbing material, probably graphitic in character (Figs. 3b, 4a); others show a dominant volatile fraction (Fig. 4b). Some are closer to an ambient aerosol in nature (Fig. 3a). In addition, a single source may show a different character at different times. It would be reasonable for ambient particulate carbon to be a composite of the various types of source constituents.

Ambient samples collected in widely separated locations show a substantial degree of similarity with variations in the relative amounts of the three characteristic carbon types (Fig. 5). Some variation in combustion temperature for the high-temperature (absorbing) component is observed, as well as variation in the structure of the CO₂ peak from the low-temperature (volatile) fraction. Experiments with graphite ground to varying particle sizes show that the temperature at which the absorbing component burns can be a function of particle size, with smaller particles burning at a lower temperature.

Fig. 3. Example of combustion thermograms of particulate material emitted from mobile sources. Dashed line is optical transmission.
(XBL 791-155A)

a

b

Fig. 4. Example of combustion thermograms of particulate material emitted from stationary sources. Dashed line is optical transmission.

(XBL 791-156A)

a

c

b

d

Fig. 5. Typical combustion thermograms of ambient particulate material from different geographic areas. Dashed line is optical transmission.

(XBL 791-164A)

Other effects, such as surface functional groups and varying porosity, also undoubtedly affect the combustion temperature.

The 300-350°C peak in the thermogram is subject to much less variation in shape and position, although combustion of this material may be accompanied in some samples by a substantial amount of pyrolysis, as can be seen from the increase in the optical absorption of the sample (e.g., Fig. 5c). We have labeled this fraction the polymeric fraction since this behavior could be observed with a polymer such as polystyrene, although we have not characterized the material in any other way.

The low-temperature material is variable in amount and in structure in the CO₂ thermogram. In this region one would expect to find small organic molecular materials volatilizing and burning. This material is removed by solvent extraction with benzene and methanol-chloroform.

Fig. 6. Carbon combustion thermogram of glutaric acid (optical attenuation not measured). (XBL 791-165)

The predominant compounds identified in secondary organic aerosol are the C₄-C₆ organic di-acids.^{4,5} These materials have relatively low melting points and generally decompose at temperatures below 300°C. The thermograms of these acids all show sharp decomposition or volatilization at temperatures below 250°C (e.g., Fig. 6). Similar sharp low-temperature

combustion was seen for a variety of aliphatic and aromatic compounds ranging to C₁₉ (methyl stearate). Based on these observations, the low-temperature CO₂ peak probably represents a complex mixture of both primary and secondary organic compounds. If these compounds are found to volatilize and/or combust only in this temperature region, it should be possible to place a general upper limit on their relative amount in ambient carbonaceous aerosol. In general, no more than 20-30% of total carbon falls in the low-temperature CO₂ peak. Since this would include both primary and secondary organics, the relative mass of photochemically produced secondary aerosol is clearly much less than has been assumed.

Further development of this technique is currently under way with attempts to identify at least portions of the volatile and polymeric fractions. We also hope to quantitate the absorbing material, a measurement of substantial importance because the graphitic material in soot has been shown to be catalytically active in SO₂ oxidation⁶ and has potential for catalytic activity in other atmospheric reactions.

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Solvent-Extraction-Aided Morphology Study (SEAMS)

W. H. Benner, et al.

Electron microscopy (EM) is one of the many techniques used to characterize ambient particulate matter. Russell¹ used EM in combination with X-ray spectroscopy and reported that ambient particles were often predominantly carbonaceous and that if nonmineral sulfur were present in the sample, the sulfur would be associated with the carbonaceous particles. Chung et al.² sequentially exposed soot particles to SO₂ and H₂O, to vacuum, and to NH₃ in a small chamber in an electron microscope. They observed that the particles became coated with a reaction product that was vacuum stable and concluded that soot particles can serve as sites for SO₂ oxidation. This conclusion supports the SO₂ oxidation mechanism of Chang et al.³ Husar⁴ noted that liquid ambient aerosols can contain electron-dense nuclei. We have extended the use of EM to study the changes in morphology of ambient particulate matter that can be induced by solvent extraction and heat treatment.

The preliminary observations indicate the presence of a liquid-like material in submicron aerosol particles. This material can be removed by suitable solvent extraction or by heat treatment procedures to expose a core of agglomerates which are morphologically similar to carbon black.

EXPERIMENTAL

Ambient and source-enriched air samples were collected on a multiple-jet four-stage impactor.⁵ Samples from the first stage ($D_p = 0.14\text{--}0.4\text{ }\mu\text{m}$) and second stage ($D_p = 0.4\text{--}1.6\text{ }\mu\text{m}$) were examined by scanning electron microscopy (SEM) before and after treatment. Particulate samples from an urban atmosphere, an underground parking garage, a freeway tunnel, and a natural gas boiler (300,000 Btu/hr) were impacted onto copper or aluminum foils.

NATURAL GAS FIRED BOILER PARTICLES ON 1st STAGE OF AN IMPACTOR ($D_p = 0.14\text{--}0.4\text{ }\mu\text{m}$)

(a) Untreated

(b) Methanol extracted

NATURAL GAS FIRED BOILER PARTICLES ON 2nd STAGE OF AN IMPACTOR ($D_p = 0.4\text{--}1.6\text{ }\mu\text{m}$)

(a) Untreated

(b) Methanol extracted

Fig. 1. Comparison between indicated untreated and methanol extracted natural gas boiler particles. The white bar represents 10 μm . (XBL 7812-15912)

Spots of impacted particles were cut from the metal foil impaction surfaces and several spots were extracted separately in methanol or benzene. A few samples were subjected to heat treatment. Extraction was performed by suspending the particle-laden piece of foil in 100 ml of warm solvent for 2 hours. The heat-treated samples were heated from room temperature to 350°C in an oven temperature programmed to heat at 10°C/min. Several impaction spots were also analyzed by a thermal analysis technique which recorded the amount of CO₂ evolved versus temperature as the sample was heated in pure oxygen.⁶

RESULTS

Figures 1-5 show SEM pictures of four types of impacted particles. The impaction spots were typically black and consisted of particles formed from agglomerates of smaller particles. Some samples also contained a liquid-like material. This material was apparently more fluid at an earlier time, as evidenced by cracks in the bulk of the deposit, which are thought to have formed as a result of drying or exposure to vacuum (Fig. 1). For the samples examined, only second-stage ambient samples were totally inundated by this material. Ambient particles collected on the first stage possessed a coating of the material but were never completely immersed in the liquid-like deposit (Fig. 2). Particles other than ambient contained various amounts of this liquid-like deposit and the following samples (all second stage) are ranked according to the amount of liquid-like material (Figs. 1-5):

ambient > boiler > parking garage > freeway tunnel.

Solvent extraction of the impactor spots removed a major portion of the liquid-like material and exposed individual particles morphologically similar to carbon black (Figs. 1, 3-5). Visual comparison of methanol- and benzene-extracted samples showed that methanol removed more of the material than did benzene (Fig. 3). Thermal treatment of an impaction spot indicated that heat could cause morphological changes similar to those changes that occurred when a sample was extracted in methanol (Fig. 3). In addition

to causing morphological changes, heating to 350°C removed 70% of the carbon from ambient second-stage particles. Undoubtedly heating also caused some of the sublayer particles to oxidize, so it is not possible to know from this analysis what fraction of the pyrolyzed carbon came from the liquid-like deposit. It is known from other studies in our laboratory that only a small fraction of graphitic carbon (source of the black color)⁷ is removed when soot particles are heated to 350°C.

DISCUSSION

The composition of the liquid-like material associated with many of the samples is unknown. Solubility of the material in methanol and benzene suggested the material was partly hydrocarbonaceous. X-ray fluorescence analysis of boiler particles indicated that the composition of the material was dominated by elements of $Z < 14$, which suggests C, H, N, O as possible components. However, composition of the ambient material was more soluble in methanol and benzene than the boiler material. The evolution of carbon from a heated ambient sample, the morphological changes, and the knowledge that the evolved carbon probably did not come from the graphitic carbon suggest that this liquid-like material in the ambient sample was, in part, carbonaceous. Since the ambient sample was not analyzed by XRF, the presence of sulfur or nitrogen in the ambient sample cannot be ruled out. Ammonium sulfate, ammonium bisulfate, and ammonium nitrate melt or decompose below 280°C and pyrolysis of these compounds possibly could have been related to morphological changes in the ambient sample.

Ambient particles collected on filters sometimes look like liquid droplets, but a thick layer of a liquid-like deposit has not been observed in filter samples to our knowledge. One possible mechanism for the formation of this deposit involves the presence of liquid water, which is known to condense onto airborne particles, even at relative humidities less than 100%. When these wet particles are packed closely together as in the impaction spot, the water could have coalesced into a layer of material

AMBIENT PARTICLES ON 1st AND 2nd STAGE OF AN IMPACTOR

Fig. 2. Particles collected from the ambient air in Berkeley, CA on a moderately hazy day. The white Bar represents 10 μm . (XBB 7812-15914)

AMBIENT PARTICLES ON 2nd STAGE OF AN IMPACTOR
($D_p = 0.4 - 1.6 \mu m$)

Fig. 3. Morphological changes that occur when particles are exposed to various treatments. The particles were collected from the ambient air in Berkeley, CA on a moderately hazy day. The white bar represents $10 \mu m$. (XBB 7812-15910)

FREEWAY TUNNEL PARTICLES ON 2nd STAGE OF AN IMPACTOR
($D_p = 0.4 - 1.6 \mu m$)

Fig. 4. Comparison between untreated and methanol extracted freeway tunnel particles. The white bar represents $10 \mu m$. (XBB 7812-15913)

covering the nuclei of the original particles. Evaporation of this layer, which presumably would contain nonvolatile dissolved substances, would then leave a vacuum-stable deposit. These observations could also have been due to a sampling artifact since water could have condensed onto the particles when the particle-laden air expanded adiabatically as it exited the impactor jet.

CONCLUSIONS

Solvent extraction and heating of impacted samples of ambient and source particulate matter were found to cause dramatic morphological changes in the sample. Variable amounts of liquid-like material were found to be associated with ambient and source samples. The composition and origin of the material are not known, and

PARKING GARAGE PARTICLES ON 1st STAGE OF AN IMPACTOR
($D_p = 0.14 - 0.4 \mu m$)

(a) Untreated

(b) Methanol extracted

PARKING GARAGE PARTICLES ON 2nd STAGE OF AN IMPACTOR
($D_p = 0.4 - 1.6 \mu m$)

(a) Untreated

(b) Methanol extracted

Fig. 5. Comparison between untreated and methanol extracted parking garage particles. The white bar represents 10 μm . (XBB 7812-15911)

a characterization of the material will be pursued in future experimentation.

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Contributions to the Problem of Quantitative Infrared Spectroscopic Analysis of Sulfates and Nitrates in Airborne Particles: A Modified Sampling System

R. Kellner*, et al.

INTRODUCTION

Sulfates and nitrates are major components of the respirable fraction of airborne particles.¹ Previous studies by ESCA² on impactor and filter samples and by wet chemical techniques³ indicate that airborne particles do not often contain $(\text{NH}_4)_2\text{SO}_4$ and NH_4NO_3 in their well-defined stoichiometry. It is therefore important to determine quantitatively the various molecular forms of the sulfate and nitrate species. We believe that infrared (IR) spectroscopy is extremely well suited for this characterization because of its high structural selectivity, high sensitivity, and potential applicability to quantitative analysis.

Several attempts to use IR spectroscopy for a qualitative speciation have been published earlier⁵⁻⁹ but, except for the work of Cunningham et al. with a Lundgren impactor,⁹ no reliable quantitative IR-spectroscopic speciation for 1- to 10- μg samples (compatible with a size-selective sampling method) has yet been reported. The major problems preventing quantitative speciation are unreliable standard materials; the IR opacity of the materials used for the collection of airborne particles, which makes a transfer step of the particles necessary; and difficulties of sample preparation, such as particle-size and matrix effects. Our work shows that these problems can be overcome and that a quantitative IR-spectroscopic analysis of infrared active molecules or ions, especially sulfates, in microgram amounts of airborne particles is possible under the following conditions:

1. Composition of the sampling system - ring jet impactor (design by A. Berner¹⁰) with particle-size segregation: stage 1, 0.14-0.4 μm ; stage 2, 0.4-1.6 μm ; stage 3, 1.6-6.4 μm ; stage 4, 6.4-25 μm aerodynamic diameter.
2. Direct deposition of the aerosols on the pelleting material (no scraping).
3. Application of a vibrating mill to ensure homogenization of the samples and to eliminate particle-size effects.
4. Use of wet chemical techniques to standardize the IR method.

SAMPLING SYSTEM

The sampling system is a crucial point in this method of analysis. Berner's impactor was first used in chemical aerosol characterization by H. Malissal^{11,12} because of the many advantages it offers in sharp particle size separation, low wall losses (<5%), and compatibility with several methods used in integrated dust analysis.

In this method, the airborne particles are deposited on thin Cu or Al foils to allow a gravimetric mass determination. This sampling technique is not *a priori* IR compatible because the sample must be scraped from the foil and transferred to the pelleting material, which means a loss of sample material. In several cases samples even to stuck Mylar and could not be removed quantitatively. Therefore, the sampling system had to be modified to make it IR compatible while maintaining the advantages of the original design.

As shown in Fig. 1, two 3-mm KBr pellets in 13-mm sample holders were mounted on stages 1, 2, and 3 so that the pellet surface is located in the plane of the Cu surface. This technique allows direct depositions on the KBr pellet, as well as simultaneous collection on the Cu substrate for gravimetric and further chemical analysis.^{13,14} Other foil materials, such as Al or Mylar, have also been used. Since we were interested in the respirable part of the aerosols, stage 4 particles were not collected in this modified way.

Fig. 1. Berner's ring jet impactor equipped with Cu foils and KBr pellets on stages 1, 2, and 3. (CBB 791-1072)

SAMPLE PREPARATION

The two loaded KBr pellets on each stage were first weighed (W_1), then transferred to the capsule of a vibrating mill and ground for 3 min. In an earlier study,¹⁵ it was found that this grinding step is sufficient to prevent particle-size and matrix effects on IR absorbance measurements as described in the literature. Duyckaerts¹⁶ describes a dramatic effect of particle size on IR absorbance in the >1- μm particle diameter range. Grinding was also performed on stage

Fig. 2. IR spectrum of 4.75- μ g $(\text{NH}_4)_2\text{SO}_4$ in KBr. (XBL 791-8167)

Fig. 3. Working curve for an IR spectroscopic $(\text{NH}_4)_2\text{SO}_4$ determination. (XBL 792-430)

1 samples to disperse probable agglomerates of single particles or amorphous masses in ambient and source samples,¹⁷ and to provide a necessary dilution step to overcome the matrix effect by the soot content of the particles.¹⁵ The homogenized samples were pressed into pellet form and weighed again (W_2). The ratio W_2/W_1 and the weight per spot (determined by the total weight and the number of spots on the Cu foil) permitted the calculation of the sample weight in the KBr pellet.

STANDARDIZATION

$(\text{NH}_4)_2\text{SO}_4$ is generally considered to be the most abundant form of S(VI) compound in respirable airborne particles, although sampling artifacts (neutralization) may enhance the $(\text{NH}_4)_2\text{SO}_4$ concentration even during sampling by impaction (Fig. 2). A working curve for the IR-spectroscopic determination of $(\text{NH}_4)_2\text{SO}_4$ was established by weighing different amounts of that substance, preparing KBr pellets according to the procedure described above, and measuring the respective absorbance values by FTIR spectroscopy (Nicolet 7199 FTIR-TGS detector; velocity of moving mirror, 0.227 cm/sec; resolution, 2 cm^{-1} ; NDP, 8192; NTP, 16384; Happ-Genzel apodization; no smoothing). The actual amount of SO_4 in the aliquots of the samples analyzed was determined gravimetrically. An IR-spectroscopic nitrate determination of samples collected in Vienna on Cu foils has been developed¹⁵ and should be easily adaptable to modified sampling.

RESULTS

Figure 4 shows the IR spectra of samples with an obvious content of $(\text{NH}_4)_2\text{SO}_4$; and Table 1 shows the results of the quantitative evaluation of the $(\text{NH}_4)_2\text{SO}_4$ content of various samples,

assuming that the sharp line located at 1110 cm^{-1} is due exclusively to this species. In general, the IR spectra of the aerosols collected in this work show more complexity in the sulfate region than do the IR spectra of $(\text{NH}_4)_2\text{SO}_4$. This is considered to be evidence of different degrees of acidity.⁹ Based on the modified sampling technique described here, which allows a quantitative transfer of aerosol samples down to 1 μ g from the collection surface to the final sample pellet, further model analyses will be carried out to elucidate the contribution to the atmospheric particulate burden of sulfate species other than $(\text{NH}_4)_2\text{SO}_4$.

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Fig. 4. IR spectra of ambient samples collected on stages 1, 2, and 3 of Berner's impactor.
a. LBL, Berkeley, California, 25 September 1978, 10:15 am-4:15 pm; air volume 26.6 m³, heavily loaded air (100 µg part./m³ on stages 1-4).
b. Fremont, California, 2 November 1978, 10:20 am-2:25 pm; air volume 18 m³ (97 µg part./m³ on stages 1-4).
c. Los Angeles, California, 10 November 1978, 2 pm-5 pm; air volume 13.2 m², relatively light loading (55 µg part./ m³ on stages 1 to 4). (XBL 792-431)

Table 1. (NH₄)₂SO₄ determination on various aerosol samples.

Sample Site	Date	Stage	Particulate Loading (µg/m ³)	Weight g/m ³ (NH ₄) ₂ SO ₄	Weight % (NH ₄) ₂ SO ₄
Lawrence Berkeley Laboratory	9/25/78	1	22.5	2.6	11.7
		2	24.8	1.6	6.3
		3	20.3	0.9	4.4
Fremont	11/02/78	1	19.2	2.1	10.7
		2	39.9	2.5	6.3
		3	9.9	-	-
Los Angeles	11/10/78	1	8.7	(peak overlapping)	14.4
		2	12.5	4.0	32.1
		3	14.6	2.2	14.7
Tunnel	10/03/78	1	68	6.2	9.1

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Determination of Nitrogen in Atmospheric Aerosols by Proton Activation Analysis*

M. Clemenson, et al.

The x-ray fluorescence method, an important tool in the determination of heavy-element concentrations, is of little use for low-Z elements because of large x-ray absorptive effects and low fluorescence yields. Neutron activation analysis is also limited by low reaction cross sections and the unsuitability of the induced radioactivity for counting. Combustion analysis, of course, is a useful tool for the analysis of most of the important low-Z elements; however, it is not a very sensitive technique. It is also destructive of the sample and thus does not allow other analyses to be performed on the same sample. These difficulties have led us to develop a new method of determination of one of the low-Z elements, nitrogen, utilizing protons of sufficient energy to induce the $^{14}\text{N}(p,\alpha)^{11}\text{C}$ nuclear reaction. The radioactive decay of the 20.4-min ^{11}C is followed via its 0.511-MeV

annihilation radiation. The method offers a simple approach to the problem of nitrogen analysis in atmospheric aerosols and is applicable to the routine analysis of these particles for nitrogen.

Irradiations were performed at the Lawrence Berkeley Laboratory 88-inch cyclotron. The initial energy of the proton beam was 16.0 MeV. Aluminum foils were placed in front of the sample foils to degrade the beam from the initial energy to the desired energy for each irradiation. The range-energy tables of Williamson, Boujot, and Picard were used to calculate the required aluminum thickness.¹ The length of bombardment was 1 minute and the average beam intensity was 1 μA . The targets were irradiated at different energies by the stacked-foil technique. The

total charge received from the Faraday cup was measured by an integrating electrometer.

COUNTING

The irradiated samples were analyzed by detecting the 0.511-MeV positron annihilation radiation of ^{11}C using a high resolution Ge(Li) detector coupled to a computer-controlled 4096-channel analyzer with a magnetic tape unit. The Ge(Li) detector used for this work was manufactured by Ortec, Inc., and has an active volume of 60 cm³. The decay of the 0.511 MeV γ -ray photopeak of an activated melamine target is shown in Fig. 1. The decay is a single component with 20.4-min half-life corresponding to the decay of ^{11}C in the target. The decay curves were analyzed using the CLSQ computer code.²

Fig. 1. Decay curve of the 20-min ^{11}C annihilation radiation for a melamine target. (XBL 766-3053)

AEROSOL SAMPLE ANALYSES

Silver-membrane filters were used for the collection of the ambient aerosol. The aerosol loading was approximately 500 $\mu\text{g}/\text{cm}^2$ for a typical filter sample. Two filter samples were irradiated in a single stack at proton energies of 7.5 and 6.0 MeV. Following the "relative" method of activation analysis, we irradiated a melamine target, which was used as the nitrogen standard, in the same stack with the aerosol samples. The nitrogen standard was irradiated

Fig. 2. Decay of the 511-keV annihilation radiation intensity with time following proton irradiation of an atmospheric aerosol sample. Length of bombardment = 1 min, at a beam intensity of 1 μA . (XBL 772-333)

at a proton energy of 9.2 MeV. The decay of the 0.511-MeV annihilation peak was then followed for 3 or 4 hours. A typical decay curve for the integrated 0.511-MeV photopeak is shown in Fig. 2. There are four components present in the decay curve: (a) a 10.0-min component due to ^{13}N produced from the $^{16}\text{O}(\text{p}, \alpha)^{13}\text{N}$ and $^{13}\text{C}(\text{p}, \text{n})^{13}\text{N}$ nuclear reactions, (b) a 20.4-min

Table 1. Comparison of methods for nitrogen determination in atmospheric aerosols.^a

Sample	N found, g/cm^2	
	Proton activation	Combustion
AS-1	129	144
AS-2	110	130
AS-3	326	368
AS-4	68	52
AO-1	162	147
AO-2	210	207
AO-3	261	279
AO-4	134	143
AO-5	136	133
AA-1	4.0	3.5
AA-2	8.0	6.5
AA-3	15	13
AA-4	76	99
AA-5	16	18
AA-6	59	59
AA-7	36	37
AA-8	46	54

^aAS are the laboratory-prepared ammonium sulfate samples; AO, the laboratory prepared ammonium oxalate samples; and AA, the ambient aerosol samples.

component from the $^{14}\text{N}(p,\alpha)^{11}\text{C}$ reaction, (c) a 109.8-min component due to ^{18}F produced by the $^{18}\text{O}(p,n)^{18}\text{F}$ reaction, and (d) a 6.5-hr component due to activation of the silver filter itself to produce ^{107}Cd by the $^{107}\text{Ag}(p,n)^{107}\text{Cd}$ nuclear reaction. By far the dominant component in this decay curve is the 20.4-min component, ^{11}C , which results from activation of the nitrogen in the aerosol. The amount of nitrogen present was calculated by comparing the A_0 value for the ^{11}C component in the aerosol to the A_0 value for the ^{11}C component in the nitrogen standard. Several blank filters were also analyzed for nitrogen and found to contain approximately $0.5\text{ }\mu\text{g}/\text{cm}^2$; this is normally a very small known correction to the total nitrogen found.

Samples containing varying amounts of nitrogen were nondestructively analyzed using the proton activation method. The same samples were then analyzed for nitrogen using a destructive combustion method. The results of these analyses are summarized in Table 1. The samples can be divided into two groups. One group of samples was prepared in the laboratory by depositing either ammonium sulfate, $(\text{NH}_4)_2\text{SO}_4$, or ammonium oxalate, $(\text{NH}_4)_2\text{C}_2\text{O}_4$, on a silver membrane filter. These samples correspond to the first nine listed in Table 1. The second group of eight samples is composed of ambient aerosols collected

in the San Francisco Bay Area under widely varying atmospheric conditions.

The comparison of the nitrogen found by proton activation analysis and that found by the independent combustion method shows an average percent difference of 14% for the 17 samples analyzed. This difference is essentially the same whether one compares only the laboratory-prepared samples or the ambient samples. It should also be noted that the agreement between the two methods holds over a range which spans two orders of magnitude in nitrogen concentration.

FOOTNOTE AND REFERENCES

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A Size-Segregating Aerosol Sampler

A. D. A. Hansen, et al.

INTRODUCTION

A routine daily ambient aerosol sampling program was established in mid-1977 with stations at LBL, Fremont (some 40 miles south of Berkeley), and Anaheim (in the Los Angeles area). To further investigate the nature and chemical composition of the aerosol, it was decided to deploy size-segregating samplers at sites widely separated in terms of both location and environment. As part of this program 12 aerosol samplers were designed and constructed at LBL to the following requirements:

1. To collect two parallel samples on prefired quartz fiber and Millipore filters.
2. To require a minimum number of operations when changing filters.

3. To have the option of complete aerosol collection or size-segregated collection (exclusion of particles of diameter $\geq 1.5\text{ }\mu\text{m}$).

4. To give an airflow rate of 1 to $2.5\text{ m}^3/\text{cm}^2\text{-day}$ through each filter, necessary to obtain suitable deposition for 24-hour samples of ambient air with carbon loadings in the range $5\text{--}30\text{ }\mu\text{g}/\text{cm}^2$.

5. To be small, self contained, and lightweight.

The option of size segregation is achieved in this sampler by the use of a Nuclepore prefilter membrane to exclude large particles. The filtration properties of Nuclepore have been extensively studied.^{1,2} At moderate face velocities, the mechanisms of impaction and interception remove from the airstream most particles larger than

Table 1. Relationship of face velocity to flowrates.

Filter flowrates	1.0	1.5	2.0	$2.5\text{ m}^3/\text{cm}^2\text{-day}$
Filter face velocity	11.6	17.4	23.2	29.0 cm/sec
Prefilter face velocity	2.1	3.1	4.1	5.2 cm/sec

a certain cut point, whose size depends on the prefilter pore size and the airstream's face velocity. The LBL sampler uses a Nuclepore prefilter of 8- μ m pore size and face velocities in the range of 2 cm/sec to 5 cm/sec (see Table 1), resulting in the effective retention on the prefilter of particles of diameter greater than 1.5 μ m (Fig. 1). Optimum prefilter performance is achieved at these face velocities that are many times smaller than the face velocities desired for adequate deposition on the sample-collecting filters. A size-analyzing sampler has been constructed by Cahill et al.³ on the principles of sequential filtration, but it uses a prefilter of the same size as the sample-collecting filter. By employing a prefilter of much larger diameter than the sample-collecting filters, we satisfy the face velocity requirements as well as greatly increasing the lifetime of the prefilter against clogging.⁴ In addition to incorporating these significant design improvements, the sampling head is constructed in such a way that with only one moving part, it locates the sample-collecting filters on their backing frits and clamps them by the pump suction acting on a pressure plate. The filters cannot be accidentally dislodged or contaminated by touching while the pump is on and the head top is in place.

Fig. 1. Filtration efficiency of 8- μ m pore size Nuclepore prefilter as function of particle size. Measurements performed at prefilter face velocity of 4.0 cm/sec on monodisperse DOP particles produced by a vibrating-orifice aerosol generator. (XBL 792- 500)

The filters may be either loose or mounted in 2"x2" slide frames, which allows for insertion and removal without tweezers or clean-handling procedures. All these features are attractive for unattended use with filter changing performed by unskilled personnel.

A photograph and diagrams of the sampler are shown in Figs. 2, 3, and 4. In the full-collection mode, the top prefilter membrane

Fig. 2. Exploded diagram of the sampler. (XBL 792-8301)

Fig. 3. Sectional drawing of one side of the sampler head (not to scale). (XBL 792-8300)

is omitted. The weathershield, insect screens, and prefilter support frit prevent entry of rain, insects, etc., though all suspended particulates are collected by the filters. For size-segregated collection, the prefilter

Fig. 4. Photograph of sampler. (CBB 791-106)

is placed on top of the sample head, resulting in an effective cut-off for particles of diameter greater than $1.5 \mu\text{m}$ (Fig. 1). This ensures collection of the majority of anthropogenic particulates, with the exclusion of windblown dust, pollen, etc. Under normal operating conditions in relatively dust-free locations, each prefilter can be used for periods in excess of one week without appreciable clogging.

METHOD OF OPERATION

Air enters the sampler through the Nuclepore prefilter B, supported by its frit M (Fig. 3 and Table 2). Face flow velocities through the prefilter range from approximately 2.1 cm/sec to 5.2 cm/sec for the flowrates used (see Table 1). Particles of diameter larger than about $1.5 \mu\text{m}$ are effectively retained by the prefilter (Fig. 1). At the low flow rates involved, the pressure drop across the prefilter is normally extremely small, so the air in the upper chamber O is at essentially atmospheric pressure.

This prefiltered air then passes through the quartz and Millipore filters mounted on their frits P. The range of flowrates employed results in face velocities varying from 11.6 cm/sec to 28.9 cm/sec through these filters. Pump suction, applied via the rotameter and needle valve by connection X to the filter chamber T, results in a reduction of pressure downstream of the filter. Because of the reduced pressure within the flowmeters, flow calibration curves are supplied with each unit and must be used instead of the rotameter readings.

Full pump vacuum is applied through port Y to space S, which is sealed by o-rings V, Q, and U. Since the pressure in the upper chamber

Table 2. Parts list for Figures 2 and 3.

Figure 2:

- A - prefilter clamp ring
- B - Nuclepore prefilter
- C - upper chamber
- D - adapter ring
- E - frit tube
- F - outer o-ring
- G - frit tube lower o-ring
- H - frit tube hole in baseplate
- I - rotameter and needle valve for quartz filter station
- J - rotameter and needle valve for Millipore filter station
- K - main power switch

Figure 3:

- L - prefilter clamp ring
- M - prefilter support frit
- N - upper chamber body
- O - upper chamber space
- P - filter support frit
- Q - filter clamp o-ring
- R - adapter ring
- S - vacuum space
- T - frit tube
- U - frit tube lower o-ring
- V - outer o-ring
- W - baseplate
- X - filter suction connection via rotameter and needle valve
- Y - clamping vacuum connection

O is essentially atmospheric, this causes the upper chamber body N to be firmly clamped to the baseplate W.

The filters are clamped and sealed on the frits P and adapter rings R by means of the o-ring Q. Sufficient compressibility is available from this o-ring and the lower o-ring U to accommodate filters of slightly varying thickness.

The pump used is an oil-less rotary carbon vane type, driven by an AC induction motor. Exhaust air from the pump itself is filtered before discharge into the atmosphere, so no recirculation contamination is anticipated. A fan draws air through the box louvers to cool the motor.

A tubular bulb mounted above the air intake warms the incoming air and the prefilter sufficiently to prevent dew condensation on the Nuclepore at night. Excessive condensation can effectively plug the Nuclepore, resulting in the development of a destructively large vacuum in the upper chamber O. The upper chamber vacuum is monitored by a vacuum sensing switch in the main chassis, so that a pressure drop of more than about 2 PSI in the upper chamber causes the motor to be turned off and stay off until the main power switch is reset.

To date, eight units have been sent out. The returned samples appear to be of good quality, and routine analysis shows no evidence of contamination or sampler artifacts.

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Optical Characterization of Ambient and Source Particulates

A. D. A. Hansen, et al.

INTRODUCTION

Characterization of the ambient carbonaceous aerosol in terms of its primary and secondary components is essential if meaningful control strategies are to be devised. Primary carbonaceous particulate material is defined as that emitted directly from anthropogenic sources, usually combustion. It contains extractable organic matter and nonextractable material, including "graphitic" soot. Secondary carbonaceous particulate material is material originally emitted in a gaseous state that has been transformed into a particulate state by atmospheric processes. Examples of these processes are (1) the accretion by adsorption of vapors onto the surface of primary particles, and (2) gas-to-particle conversion reactions whose occurrence in the atmosphere has been postulated under highly photochemically active conditions. If primary particulate material is dominant in the ambient aerosol, then particulate air pollution abatement strategies should include particulate emission control. If secondary particulate material dominates, emphasis should be on the control of the gaseous precursors involved in these secondary reactions. Due to the complex nature of the ambient aerosol, it has been a difficult analytical problem to distinguish clearly the contributions from these two sources of particulate carbon.

The most striking feature of filter deposits collected in urban environments is their dark coloration, which we believe is due to the strongly absorbing primary "graphitic" soot component. We assume that secondary reactions cannot produce this material. The "graphitic" component of filter-collected particulates may be conveniently measured because of its large optical absorption and used as a tracer for primary carbonaceous particles. In this paper we report on the optical characterization of a statistically large number of ambient and source samples taken under a wide range of conditions.

Our central result is that primary material appears to compose a major fraction of the ambient carbonaceous aerosol studied in two California air basins under widely varying conditions. Furthermore, we have seen no evidence for the significant production of secondary carbonaceous particulate matter in correlation with the ozone concentration, a conventional indicator of photochemical activity.

EXPERIMENTAL DETAILS

Sample Collection

Ambient aerosol samples have been collected daily since 1 June 1977 at LBL, Berkeley, California; since 15 July 1977, at the Bay Area Air Pollution Control District monitoring station, Fremont, California; and since 19 August 1977, at the Southern California Air Quality Management District monitoring station, Anaheim, California. Samples were also taken from 23 March 1978 to 9 April 1978 at Argonne, Illinois. All these samples were taken in parallel on 47-mm diameter Millipore filter membranes (1.2- μ m nominal pore size, type RATF) and prefired quartz fiber filters (Pallflex type 2500 QAO). The monitored flow rates varied between 1.0 and 2.6 m³/cm²-day (i.e., 0.24 to 0.62 CFM for the total exposed filter area of 9.6 cm²), corresponding to face velocities of 11.6 to 30.1 cm/sec. The samples were not size segregated, but the filter holders faced vertically downward to avoid settling deposition of dust, etc. Three-day samples collected over each weekend are not included in the data presented. The samples spanned almost the entire range of weather and pollution conditions; to date, in excess of 900 filter pairs have been analyzed.

A number of representative sources have also been sampled. About 100 analyses have been made of the following particulate emissions: (1) exhaust collected in a freeway tunnel under conditions of moving traffic with few diesel

trucks; (2) automobile exhaust collected in an underground parking garage under start-stop driving conditions with no diesel trucks; (3) exhaust from a small 2-stroke engine; (4) exhaust from a small 4-stroke diesel engine; and (5) stack samples from a natural-gas-fired domestic water heater.

Optical Attenuation Measurement

Both source and ambient aerosol samples have a large and uniform optical absorption throughout the visible spectral region; the dark coloration of the exposed filters is due to the "graphitic" soot component.^{1,2} The attenuation measurements are made by a laser transmission method on samples collected on Millipore filter membranes. The quantity recorded is defined as

$$ATN = -100 \ln (I/I_0) \quad (1)$$

where I_0 is the intensity of light transmitted through a blank Millipore filter, and I is that through the loaded filter.

Carbon Analysis

The carbon loading on the quartz fiber filters is determined by a total combustion/ CO_2 evaluation method.³ The filters are prefired overnight at 800°C to remove all combustible carbon before sample collection. Periodic analysis of blanks typically yields about 0.5 $\mu\text{g C/cm}^2$ compared with loadings after exposure in the range 20-100 $\mu\text{g C/cm}^2$.

OPTICAL ATTENUATION CHARACTERIZATION

Theory

As shown in Refs. 1 and 2, the dark coloration of ambient and source samples can be ascribed to the "graphitic" component of the carbonaceous particulates. We assume that a quantitative relationship between the optical attenuation and the "graphitic" carbon component can be written as

$$[\text{GRAPH}] = (1/K) \times ATN \quad (2)$$

In addition to "graphitic" soot, primary particulate material also contains organic material, which is not strongly optically attenuating. The total amount of carbon is

$$[C] = [\text{GRAPH}] + [\text{ORG}] \quad (3)$$

A fundamental characterization of a particular sample is given by its attenuation per unit mass, i.e., its specific attenuation, σ , since this is a measure of the fraction of "graphitic" carbon to total carbon:

$$ATN/C = K \times [\text{GRAPH}]/[C] \quad (4)$$

Measurements of the specific attenuation of numbers of source samples give insights into the relative graphitic-to-total-carbon fraction of primary emissions and the source variabilities.

The ambient aerosol contains primary carbonaceous particulates from a large number of individual sources and also secondary material (as defined in the introduction). The total optical attenuation and total particulate carbon mass are then given by a summation over all components, i.e.,

$$ATN_T = \sum_i ATN_i \quad (5)$$

$$C_T = \sum_i C_i$$

and the specific attenuation of the ambient sample is

$$\sigma_T = (ATN_T/C_T) = \frac{\sum_i ATN_i}{\sum_i C_i} = \frac{\sum_i \sigma_i C_i}{\sum_i C_i}$$

In other words, the specific attenuation of an ambient sample is an average of the specific attenuations of all its components, weighted according to the mass of carbon they each contribute.

Secondary material will not contain a "graphitic" component and therefore should not appreciably increase the total optical attenuation; its value of σ is very small. However, it does increase the total mass of carbon, and will therefore reduce the graphitic-to-total-carbon fraction and dilute the specific attenuation of the ambient sample. This is seen in Eq. (6) as the addition of secondary contributors, is, where σ_{js} is zero but C_{js} is non-zero. The presence of large amounts of secondary carbonaceous particulate material in the ambient aerosol will have the effect of reducing the specific attenuation of ambient samples relative to that of source samples.

RESULTS

Results on Source Samples

We first present quantitative support for the assumption of Eq. 2 that the optical attenuation of a particulate sample collected on a filter (i.e., the degree of its dark coloration) is proportional to the total carbon loading. This occurs if the "graphitic" soot component, responsible for the coloration, constitutes a constant fraction of the total amount of particulate carbon. Figure 1 shows results from one series of samples taken from a small diesel engine under identical load and speed conditions. The correlation between optical attenuation and total carbon loading is extremely good ($r = 0.99$) even up to heavy loadings, giving a constant specific attenuation of $\sigma = 5.6$. In contrast, Fig. 2 shows the results for a number of freeway tunnel samples spanning a wide range of traffic conditions. Although a similar correlation obviously exists, it is clear that the specific attenuation of these samples shows a greater variability (ranging from $\sigma = 3.75$ to $\sigma = 12.5$). We suggest that this is due to a varying fraction of "graphitic"

Fig. 1. Optical attenuation versus carbon loading for samples of diesel exhaust particulates from an engine running at constant speed under constant load. Least-squares fit line shown. (XBL 788-9881)

Fig. 2. Optical attenuation versus carbon loading for samples of vehicle exhaust particulates obtained in the vent bore of a freeway tunnel. Least-squares fit line shown. (XBL 788-9882)

soot to total particulate carbon in the mix of exhaust, depending on the mix of vehicles and driving conditions. Similar results have been obtained for the other sources: in all cases, samples of different loadings taken under identical source conditions show good correlation, while samples of mixed composition show more variability.

Results on Ambient Samples

In view of the variability of specific attenuation shown by source samples, the uniformity of results obtained from ambient samples is remarkable. Figure 3 shows optical attenuation vs. carbon loading for the samples collected at Berkeley, Fremont, Anaheim, and Argonne. All of the graphs have the same scale of axes, enabling direct comparison and determination of the following very important results:

1. There is a strong correlation ($r > 0.85$) between optical attenuation and total suspended particulate carbon mass at every site.
2. The mean specific attenuation, i.e., the coefficient of this proportionality, is virtually identical at each site.

DISCUSSION

Specific Attenuation Results on Source and Ambient Samples

The diesel source results show that the method of optical attenuation can indeed be used as an accurate quantitative measure of total particulate carbon mass for samples from individual sources under constant operating conditions, i.e., a presumed constant fraction of "graphitic" soot to total particulate carbon. The freeway tunnel results show that the net value of σ_T for an aerosol derived from many sources can vary according to the mix of contributions (C_i) and characteristics (σ_i) of each source. The ambient air contains material from a large number of primary and secondary sources covering the entire spectrum of "graphitic" content (i.e., of σ); if the patterns of daily input remain approximately constant, the net composition of our 24-hour samples may also remain constant. This, we believe, is the basic explanation for the results obtained from the ambient sampling program. Result (1) shows that for a particular site it is possible to estimate the amount of total suspended particulate carbon with a root mean square error

Fig. 3. Optical attenuation versus particulate carbon loading for ambient samples collected at Berkeley, Fremont, Anaheim, and Argonne. Least squares fit line shown. Note same scale of axes on graphs. (XBL 788-9886)

of 25% by means of the very simple measurement of optical attenuation. Furthermore, this is true independent of season, meteorology, or conventional air pollution indicators. This remarkable result implies that the fraction of "graphitic" soot to total particulate carbon is approximately constant under all circumstances studied.

The specific attenuation distribution of samples collected during summer pollution episodes in Anaheim is virtually identical to that of samples collected in Berkeley on extremely clear winter days, or in Argonne in winter, although the loading of these samples varied widely (from $2.9 \mu\text{g}/\text{C}/\text{m}^3$ to $52.4 \mu\text{g}/\text{C}/\text{m}^3$). Because the specific attenuation σ reflects only the aerosol's fractional "graphitic" composition, this result implies that the fraction of "graphitic" soot to total carbon in all these locations is approximately equal and constant.

The range of values of specific attenuation measured on ambient samples is overlapped by the range measured on source samples. This implies that the "graphitic" fraction of the ambient aerosol is similar to that of a representative mixture of primary emissions.

SPECIFIC ATTENUATION 643 AMBIENT SAMPLES JUN 77 - JUN 78

(a) peak ozone < 75 ppb

(b) peak ozone > 75 ppb

Fig. 4. Distribution of values of specific attenuation of ambient particulate samples, subdivided according to peak hour ozone concentration. (XBL 788-10619)

Secondary Particulate Carbon

The category of secondary carbon includes particulates formed from precursor gases in gas-to-particle conversion reactions in the atmosphere. Most of the proposed reactions responsible for the formation of secondary organic particles involve ozone as a reactant. If ozone-related atmospheric reactions are a substantial contributor of secondary particulate carbonaceous material in the ambient aerosol, we would expect larger contributions of this material on days characterized by higher ozone concentrations. This secondary material cannot contain a "graphitic" component and so would have a low specific attenuation, thereby diluting the total ambient aerosol's attenuation. The specific attenuation of the ambient aerosol on days characterized by high ozone levels would be expected to be lower than on days with low ozone levels.

Figure 4 shows the distribution of specific attenuation of ambient samples from all sites taken together, subdivided according to peak hour ozone concentration. Clearly, there is little indication that high-ozone days are characterized by aerosols of strongly diluted attenuation. Furthermore, the maximum correlation coefficients of peak hour ozone concentration and specific attenuation at any individual site or all samples taken together are only $r = 0.24$ and $r = 0.11$ respectively. This places a rather low limit on the maximum importance of secondary carbonaceous particulates formed in ozone-related atmospheric reactions.

Figure 5 shows the average diurnal cycles of specific attenuation for samples collected at the same time of year in Berkeley (relatively clean conditions average particulate carbon

Fig. 5. Average diurnal cycle of specific attenuation and ozone concentration at Berkeley and Riverside.
(XBL 788-9884)

loading $5.7 \mu\text{g}/\text{m}^3$) and Riverside, California (severe air pollution conditions, $33.2 \mu\text{g}/\text{m}^3$ average particulate carbon loading). These cycles, averaged over many days, are essentially identical in form and magnitude in spite of very different atmospheric chemical conditions at the two sites, including an average peak 1-hr ozone concentration of 240 ppb in Riverside vs <30 ppb in Berkeley. Certainly there is no evidence for the dilution of the specific attenuation of the Riverside aerosol relative to the Berkeley aerosol that would be expected if high ozone levels were associated with significant production of secondary particulate carbon.

CONCLUSIONS

We have demonstrated that the optical attenuation technique is a valid semiquantitative method for detection of the "graphitic" soot component of ambient aerosols, and that this component is an approximately constant fraction

of the total suspended carbonaceous particulate loading under the atmospheric conditions so far encountered at widely differing sites. We find that this "graphitic" fraction of the ambient aerosol is comparable to that of representative source emissions. We also find a lack of evidence for the substantial production of carbonaceous particulates from gaseous precursors in atmospheres characterized by high ozone levels. The results obtained from our ambient sampling programs so far indicate that primary particulates constitute a major fraction of the ambient carbonaceous aerosol in the two California air basins we have studied, unless we can find secondary reaction mechanisms (1) that are not accompanied by ozone formation, (2) that are independent of location, season, or meteorology, and (3) whose contribution to the total ambient aerosol mass is linked to the primary particulate loading (in order to maintain a constant composition fraction).

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Optical Attenuation: A Measurement of the Absorbing Properties of Aerosol Particles

Hal Rosen, et al.

The optical attenuation technique (described in detail elsewhere in this report) appears to be a direct measure of the absorbing component of aerosol particles and is apparently insensitive to its scattering properties. This has been demonstrated by noting that most of the mass of the aerosol responsible for scattering can be removed by solvent extraction or heat treatment procedures without appreciably affecting the optical attenuation measurement. It has also been shown that addition of the order of one monolayer of nonabsorbing particles to the filter substrate does not give an appreciable optical attenuation.¹ From a theoretical point of view, these results are not obvious, since it is unclear why the backscattered radiation from nonabsorbing particles should not make a significant contribution to the optical attenuation measurement. This is especially true where the absorbing component represents only a very small fraction of the aerosol mass. In this paper we will present a simple theoretical model which accounts for all these observations and points out the critical role of the filter substrate as an almost perfect diffuse reflector in the technique. Similar considerations may also apply to the opal glass method used by Weiss et al.²

For this model calculation, we will assume that the particles and the filter media can be treated independently and consider the geometry (Fig. 1). A similar treatment, where the light beam is first incident on the particles, gives identical results. After the light beam passes through the filter medium, it is incident on the particles with an intensity, I_0 . The particles forward scatter a fraction of the incident light, backward scatter a fraction, and absorb a fraction. These components in the low loading limit are respectively given by $n_s \sigma_F I_0$, $n_s \sigma_B I_0$, and $n_A \sigma_A I_0$, where n_s is the number of scattering

aerosol particles per unit area, n_A is the number of absorbing aerosols per unit area, σ_F is the forward scattering cross section, σ_B is the backward scattering cross section, and σ_A is the absorption cross section.

Since the optical attenuation technique only measures the forward scattering light, it would seem as if the backscattered light would be lost to the system and would contribute to the attenuation. However, the filter, in our method, is almost a perfect reflector. Under these circumstances, the backscattered light will be reflected in the forward direction and will again be incident on the particles. This process will continue until almost all the backscattered radiation is collected by the optics and therefore does not contribute to the optical attenuation. This result can be put in mathematical form, where I is the light detected by the collection optics and R_F is the reflectivity of the substrate.

$$\begin{aligned} I &= I_0(1 - n_s \sigma_B - n_A \sigma_A) + I_0(1 - n_s \sigma_B - n_A \sigma_A) n_s \sigma_B R_F \\ &\quad + I_0(1 - n_s \sigma_B - n_A \sigma_A) n_s^2 \sigma_B^2 R_F^2 \\ &\quad + \dots I_0(1 - n_s \sigma_B - n_A \sigma_A) n_s^n \sigma_B^n R_F^n \\ &= I_0 \frac{(1 - n_s \sigma_B - n_A \sigma_A)}{(1 - n_s \sigma_B R_F)} \end{aligned} \quad (1)$$

Consider several limits. Where $R_F \approx 0$, which normally would be considered an ideal substrate, Eq. (1) reduces to

$$I = I_0(1 - n_s \sigma_B - n_A \sigma_A).$$

Fig. 1. Schematic of experimental arrangement illustrating the role of the filter media as a reflector of the backscattered radiation from the particles. (XBL 791-280)

Under these conditions the backscattered radiation will contribute significantly to the optical attenuation and make the technique unsuitable for exclusively measuring the absorbing properties of the aerosol. In our method, however, $R_F \approx 1$ and Eq. (1) becomes

$$I = I_0 \left(1 - \frac{n_A \sigma_A}{1 - n_S \sigma_B} \right).$$

Or the optical attenuation in the low loading limit is

$$ATN = 1 - I_0 = \frac{I_0 n_A \sigma_A}{1 - n_S \sigma_B}.$$

From this expression it is clear that a nonabsorbing aerosol will make no contribution to the optical attenuation; this is consistent with our experimental results. The magnitude of the optical attenuation is somewhat dependent on the scattering properties of the aerosol; however, in the low loading limit, this effect is small. For example, if the substrate has 50% coverage, and if the scattering cross section of the particles, σ_S , is twice the particle area, then $n_S \sigma_S \approx 1$. If σ_B is about 20% of σ_S (the maximum value measured by Charlson and his coworkers³), then

$$1 - n_S \sigma_B \approx 0.8;$$

so that even for this rather high loading, the error in the absorption measurement due to scattering of the aerosol is about 20%. This treatment is only approximate since it assumes that the scattering properties of the particles not affected by the filter substrate and neglects the penetration of the particles into the substrate. Future analysis will try to evaluate the significance of these effects.

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Identification of the Optically Absorbing Component in Urban Aerosols*

Hal Rosen, et al.

Aerosol particles may play a significant role in modifying the local and global climate, and therefore it is important to study the optical properties of these suspended particulates. The overall effect of aerosol particles in heating or cooling the earth's surface depends critically on the relative magnitude of their scattering and absorption coefficients.^{1,2} In the past the effects of aerosols were thought to be due almost entirely to their scattering properties, but more recently it has been realized that the absorptivity of these particles is large. Therefore much more attention has been given to the imaginary index of refraction in heat balance calculations as well as in visibility degradation.^{3,4} To model the effects of fossil fuel combustion on climate and visibility, it is important to establish the nature of these absorbing species. In this report we will describe the application of Raman spectroscopy and an optical attenuation technique to show that the high optical absorptivity of urban particulates and particles

produced directly from various combustion sources is due to "graphitic" carbon, one component of combustion-produced soot, which also contains a complex mixture of organics.

Raman spectroscopy is a highly selective method of analysis which, until recently, has not been applied to be the characterization of air pollution particulates.⁵⁻⁷ The technique can often be used to make unambiguous identifications since different chemical species have characteristic vibrational modes and therefore characteristic Raman spectra. The Raman spectroscopy apparatus uses a Coherent Radiation argon ion laser producing 1 W of power at 514 nm. The laser beam is focused by a 75-mm focal length cylindrical lens to a spot .06 mm x 2 mm on the sample surface via a small mirror, and the backscattered radiation is collected and imaged by an f/1 lens onto the slit of a 1-m Jarrell Ashe double monochromator equipped with two 1180-grooves/mm gratings blazed at 5000 Å. The output of the spectrometer is

detected by an FW130 photomultiplier cooled to -20°C and used in a photon-counting mode. The pulses, after appropriate shaping, are counted and displayed on a multichannel analyzer. A computer-controlled grating drive made by RKB, Inc., allows a given spectral region to be scanned many times and added to the memory of the multichannel analyzer, greatly improving the signal-to-noise ratio. In order to minimize heating effects, the highly absorbing samples used in these experiments are rotated at 1800 rpm by a motor, which increases the area illuminated by the laser beam by a large factor with almost no loss in signal level. The focal spot of the laser is located approximately 5 mm below the axis of rotation so that the effective illuminated area is an annulus of radius 5 mm and width 2 mm, resulting in the low power density of $\sim 1 \text{ W/cm}^2$.

The Raman spectra between 900 and 1950 cm^{-1} of ambient, automobile exhaust, and diesel exhaust particulates are compared with the spectra of activated carbon and polycrystalline graphite in Fig. 1. It is evident that the spectra of activated carbon, diesel exhaust, automobile exhaust, and the ambient sample are very similar, with the positions of the two Raman modes coincident to within $\pm 10 \text{ cm}^{-1}$, the estimated experimental error. The ambient sample was collected as part of the RAPS program in St. Louis, Missouri; however, the same Raman modes are also evident in every urban sample studied, including samples collected in Buffalo, New York, and Berkeley, Fremont, and Anaheim, California. Koenig et al.⁹ have studied the Raman spectrum of activated carbon as being due to phonons propagating within "graphitic" planes. The close correspondence of the spectra in Fig. 1 indicates the presence of physical structures similar to activated carbon in both source and ambient samples. These graphitic species are formed directly in combustion, and we shall use the term "graphitic" soot to describe them.

Urban and combustion source particulates collected on various filter media have a gray or black appearance. The "graphitic" species identified by Raman spectroscopy are the most likely candidates for explaining this coloration. To test this hypothesis, we have developed an optical attenuation technique to measure quantitatively the various properties of the absorbing species. The optical attenuation apparatus compares the transmission of a 633-nm He-Ne laser beam through a loaded filter relative to that of a blank filter (Fig. 2). The loaded filters are placed in the beam with the loaded side towards the laser: after multiple scattering through the filter substrate, the light is collected by an f/1 lens and focused on a photomultiplier tube. The data presented in this paper were obtained from particles collected on Millipore or quartz fiber substrates, but the optical attenuation measurements can be made with a wide variety of filter media. This technique is based on a principle similar to that of the opal glass method used by Weiss et al.,⁴ and measures the absorbing rather than the scattering properties of the aerosol (see "Optical attenuation; a measurement of the

Fig. 1. Raman spectra between 920 and 1950 cm^{-1} of: a) Ambient sample collected in 1975 as part of EPA's RAPS program. The sample was collected on a dichotomous sampler⁸ and was in the small size range fraction. b) Automobile exhaust collected from a number of cold starts of a poorly tuned automobile using lead-free gas and having no catalytic converter. c) Diesel exhaust. d) Activated carbon. e) Polycrystalline graphite. (XBL 767-3091)

Fig. 2. Schematic of optical attenuation apparatus.
(XBL 787-1361)

Fig. 3. Plot of the percent of the optical attenuation remaining after Soxhlet extraction in benzene and a methanol-chloroform mixture as a function of the carbon remaining after extraction for various ambient and source particulate samples.
(XBL 782-177)

Fig. 4. Plot of integrated Raman intensity of the 1600 cm^{-1} mode versus percent optical attenuation at 633 nm for ambient, acetylene soot, and tunnel samples.
(XBL 783-344)

absorbing properties of aerosol particles" in this report).

Using this apparatus we have studied the temperature stability and solubility of the absorbing species in ambient and source particulate samples. Our results show that these species have high temperature stability with

only minimal oxidation up to 400°C ¹⁰ and are essentially insoluble in a wide variety of solvents.^{4,10} (See Fig. 3.) We have also shown, using a spectrophotometer, that to within 20% over the visible spectral region, the optical attenuation has a $1/\lambda$ wavelength dependence characteristic of a constant imaginary index of refraction.^{4,10}

All these results strongly suggest that the absorbing species in urban and source particulate samples is "graphitic" soot. A direct substantiation of this hypothesis is provided by comparing the integrated intensity of the 1600 cm^{-1} Raman mode with the optical attenuation of the same filter sample. These measurements have been done on acetylene soot samples, which were essentially pure carbon with only trace amounts of metallic impurities; on highway tunnel samples; on ambient samples collected in Berkeley and Fremont in the San Francisco air basin; and in Anaheim in the Los Angeles air basin. The results shown in Fig. 4 indicate that within experimental error there is a direct correspondence between the optical attenuation and the Raman intensity or "graphitic" soot content for all samples studied, despite widely different chemical compositions (e.g., for a given optical attenuation, the Pb and Fe concentrations vary by more than a factor of 100). The only reasonable explanation is that the optical attenuation is due to the "graphitic" soot content of the collected particulates.

In summary, we have shown that the species responsible for the high optical absorptivity of particulate samples has high temperature stability in air, is insoluble in a variety of solvents, and absorbs uniformly throughout the visible region. We have also demonstrated that the amount of the absorbing species is directly proportional to the "graphitic" soot content as defined by Raman spectroscopy. All these results taken together indicate that the high optical absorptivity of both ambient samples collected in urban environments and various source particulate samples is due to the "graphitic" component of the aerosol. The effects of these species on physical and chemical processes^{11,12} in the atmosphere require further investigation.

FOOTNOTE AND REFERENCES

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Chemical Characterization of Source and Ambient Particulate Samples by Solvent Extraction

L. A. Gundel, et al.

INTRODUCTION

Since polar organic extracts of ambient particulates have been shown to be direct-acting mutagens,¹⁻⁶ it is important to understand the chemical and physical processes which lead to the association of oxidized organic compounds with ambient particulates. Considerable effort has been directed toward demonstrating that photochemical reactions can account for the formation of aerosol-phase polar organics from gas-phase reactive hydrocarbons,⁷ and that polar compounds in ambient particulates result from such photochemical processes.^{8,9} It has been postulated^{8,9} that concentrations of polar compounds as carbon correlate with indicators of photochemical activity such as ozone concentration; whereas concentrations of nonpolar compounds as carbon and elemental carbon do not correlate with ozone concentration. If substantial concentrations of polar compounds are associated with ambient particulates collected during nonphotochemical atmospheric conditions, alternative mechanisms for generation of polar aerosol particulates must exist.

In this project we are attempting to answer the following questions:

1. How does particulate matter, characterized by solvent extraction, collected under non-photochemical conditions (Berkeley, winter)

compare with particulate episodes? Of particular interest here is the ratio of polar to nonpolar carbon (secondary to primary) for each condition.

2. How do ambient particulates compare with particulate material collected from various combustion sources, when characterized by the same solvent extraction technique?

3. What processes may contribute to the transformation of combustion-generated particulates to account for the difference in polarity between carbonaceous compounds associated with combustion sources and ambient particulates?

4. Does solvent extraction with carbon determination of the extracts allow recovery of all the carbon removed during extraction? This may affect conclusions based on previous work.^{9,10}

ANALYTICAL STRATEGY AND EXPERIMENTAL DETAILS

The solvent extraction method was chosen to allow direct comparison with results available from studies of particulates collected in the Los Angeles basin.^{9,10} The analytical strategy previously applied to samples obtained in the Los Angeles basin^{9,10} is based on several assumptions. First, benzene extraction followed by extraction with the methanol chloroform mixture removes all organic material from the filter, leaving

"elemental" carbon. The next assumption is that cyclohexane removes only "primary" or source-related organics from the particulate sample. This assumption is based on early work⁸ which showed no correlation between cyclohexane-extractable carbon and ozone level for samples collected during a photochemical episode; whereas the difference between total extracted carbon and cyclohexane-extracted carbon showed a positive correlation with ozone level. The difference has been attributed to polar compounds originating in photochemical reactions, which are "secondary" transformations of less polar primary gaseous compounds. In a Los Angeles episode (July, 1975), primary, secondary, and elemental carbon fractions all correlated positively with ozone level.¹⁰ Another assumption of the primary/secondary/elemental carbon breakdown is that all carbon removed by solvent extraction is recovered in the extract. Our results prove that this is not the case.

Samples were collected on prefired (800°C) quartz filters using a high volume sampler at 40 SCFM. Sampling time for ambient samples was typically 24 hours. For sources the sampling time varied with the output of the source; for example, Caldecott Tunnel samples gave loadings of 40 $\mu\text{C cm}^{-2}$ in about 20 minutes. Filter samples were stored at -5°C in aluminum foil and plastic bags. The Soxhlet extraction procedure was identical in most respects to that used by B. R. Appel et al.¹⁰ Using spectro-quality solvents, one quarter of each filter was extracted in cyclohexane, while a different quarter was successively extracted in benzene for 6 hr followed by a methanol-chloroform (1:2 vv) mixture the next day. The three extracts were concentrated to 10 ml, and 1 ml of each was allowed to evaporate to dryness before carbon determination by combustion. Carbon was also measured for portions of the filter at all stages of extraction. This is an addition to the analytical strategy,¹⁰ which permits comparison of the carbon content of each extract with the carbon lost by the filter during extraction.

Comparison of Berkeley and New York City Particulates with Los Angeles Particulates

The application of this solvent extraction method to ambient particulates collected in Berkeley and New York City allows a comparison with ambient particulates collected during a photochemical smog episode in the Los Angeles basin¹⁰ and with combustion sources. We have adopted the formalism which was used by those workers to differentiate between source-related carbon ("primary") and particulate carbon formed by photochemical processes ("secondary"). In this formalism

1. total soluble C = benzene-soluble C + methanol-chloroform-soluble C = total organic C
2. "primary" C = cyclohexane-soluble C = nonpolar C,

3. "secondary" C = total soluble C - "primary" C = polar C,

4. "elemental" C = total C - total soluble C = graphitic C.

Figure 1 presents the results obtained by carbon measurements of the evaporated extracts and direct combustion of the extracted ambient filters. Similar data are also presented for typical particulate sources, representing vehicle traffic in a highway tunnel, traffic in a parking garage, diesel passenger buses, and a natural gas boiler.

Several observations can be made from the data shown in Fig. 1. The major finding is that particulate matter in Berkeley, collected during low ozone conditions, appears to contain appreciable amounts of "secondary" or polar carbon. The "primary", "secondary", and "elemental" breakdown is very similar to that reported to Los Angeles.¹⁰ Roughly half the

Fig. 1. Characterization of particulate matter by selective solvent extraction and carbon determination. Results expressed as percentage of total original carbon. As applied to any filter sample, the formalism is SEC = "secondary" = polar carbon; PRI = "primary" = nonpolar carbon; ELEM = "elemental" = insoluble carbon. (XBL 791-9)

total carbon in Berkeley particulate samples is recovered in successive solvent extraction with benzene and the methanol-chloroform mixture, with about one-seventh of the total carbon recoverable in cyclohexane. The ratio of "secondary" to "primary" to "elemental" (S:P:E) for the Los Angeles samples is 40:17:43; that ratio is 38:13:49 for Berkeley particulates, averaged for winter and summer. There is no significant difference between winter and summer Berkeley samples (see Fig. 2). However, there appears to be slightly less "primary" carbon, and slightly less recoverable soluble carbon (in Berkeley samples), compared with the Los Angeles samples. Winter particulates in New York show a pattern similar to that in Berkeley and Los Angeles, although they appear to contain less soluble carbon and more elemental carbon than either Los Angeles or Berkeley particulate.

Comparison of Source with Ambient Particulates

Use of the formalism which has been applied to photochemical episodes^{9,10} shows that vehicle combustion sources produce particulates which contain more "primary" than "secondary" material (Fig. 1). The primary component is significantly larger for vehicle sources than for Berkeley ambient samples (17-32% compared with 13%). The sources we measured contain 11-19% "secondary" C compared with average Berkeley ambient samples where "secondary" C is 38%. Highway tunnel traffic and traffic in parking garage produce similar particulates when characterized by solvent extraction, with S:P:E ratios of 16:32:52 and 18:23:58 respectively. Diesel buses produce a smaller fraction of recoverable soluble organic material than the tunnel or garage, as do samples collected from a natural gas boiler exhaust. Although our results may be affected by the difficulties associated with source sampling, they indicate that ambient samples contain more "secondary" or polar carbon than sources, and that vehicle traffic and ambient particulates may contain a similar fraction of total soluble carbon. We have demonstrated that ambient particulate carbon collected under nonphotochemical conditions is similar to the particulate carbon collected during a photochemical episode, but both differ from sources when characterized by solvent extraction.

Comparison of Carbon in Extracts to Carbon Lost by Filters During Extraction

The results presented so far have been based on measurement of the carbon content of the evaporated extracts. The amount of carbon recovered in the extracts can be compared with the amount lost by the filter samples during extraction, since the carbon content of the filters can be measured directly by combustion. This provides another method with which to characterize ambient and source particulates. The lower part of Fig. 1 contains these results. Again, a clear difference can be seen between ambient and source samples. Compared with ambient particulates, sources show much larger fractions of carbon lost by treatment of the filter with cyclohexane ("primary" carbon) whereas ambient particulate shows more loss of polar carbon

Fig. 2. Variation of "primary" (nonpolar) and "secondary" (polar) carbon during one year (1977-1978) for ambient particulates collected in Berkeley, California. a) Carbon measured by combustion of evaporated extracts; b) carbon measured by combustion of extracted filters. (XBL 791-11)

("secondary" carbon). Significantly less carbon remains on the filter after extraction ("elemental" carbon) than predicted by combustion of the evaporated extracts, for both source and ambient particulates. Amounts of carbon remaining after extraction with benzene and methanol-chloroform ("elemental" carbon), appear to be similar for ambient particulates and particulates collected from a highway tunnel and parking garage.

"Secondary": "primary": "elemental" ratios are different when determined by these two methods. For example, Berkeley particulate gives 38:25:40 by combustion of extracted filters. The major difference is that less carbon is recovered in the cyclohexane extracted than is lost by the filter during the extraction. Table 1 shows the ratio of carbon measured by evaporation of extracts to carbon lost by the extracted filters for Berkeley ambient samples and for several sources. For cyclohexane and benzene, evaporation of extracts recovers 60-70% of the carbon lost by the extracted filter. Methanol-chloroform extraction

yields more carbon than has been lost by the filter, and this is not due to blank problems. The nonpolar extracts appear to lose volatile carbon, as is expected for adsorbed low boiling hydrocarbons. Since losses in the actual evaporation of the 1-ml aliquot have been shown to be minimal,¹⁰ volatilization is probably occurring during the actual extraction, since the boiling points of both cyclohexane and benzene are higher than those of many aliphatic hydrocarbons likely to be present as adsorbed species. The most extreme case of this loss of volatile material occurs with diesel particulates where only 18% of the carbon lost by the filter during cyclohexane extraction is present in the evaporated extract. The gain of carbon in the extract during methanol-chloroform extraction may be due to reaction of methanol with reactive polar compounds such as carboxylic acids and alcohols, so that esters and ethers are formed which contain one more carbon atom per molecule than the parent compounds. The gain in carbon during methanol-chloroform extraction may not completely offset the loss during benzene extraction, so that the total recoverable extracted carbon is underestimated. "Elemental carbon," the difference between original and extracted carbon is therefore overestimated by this method; for ambient Berkeley samples, this overestimate is close to one-third of the carbon remaining on the filter.

Direct measurement of carbon removed by combustion of extracted filters appears to be more accurate than measurement of carbon in evaporated extracts. The latter measurement suffers from loss of volatile material and reaction of the sample with solvent, but these processes do not affect carbon remaining on the filter. Another possible problem with the extracts is contamination, causing addition of carbon from solvents, glassware, and transfer operations, although these errors have been included in the blank corrections.

Solubility of Heavy Elements and the Question of Particle Loss During Extraction

A possible problem with direct measurement of carbon on the filters is physical loss of particles during solvent extraction, as small fiber particles can sometimes be observed in the methanol-chloroform extracts.¹⁰ We have attempted to assess this problem by following the concentrations of selected heavy elements by XRF analysis of several sections of a tunnel filter extraction.

For this sample the average carbon fraction lost was 0.53; lead, 0.44; Br, 0.97. However, only small fractions of Cr, 0.06; Cu, 0.00; and Fe, 0.11, were removed. C, Pb, and Br appear to be removed by solubilization, but the low losses of Cr, Cu, and Fe indicate that particle loss during extraction is small, certainly 10%. These findings on the high solubility of lead and bromine are consistent with the results⁵ of other workers on the occurrences of lead in polar extracts of ambient particulates. We find that losses of Pb and Br in benzene alone are $\leq 5\%$ in this experi-

ment; losses of the other metals are even smaller. Our results are consistent with the dissolution of PbBrCl or $\text{PbBrCl} \cdot \text{NH}_4\text{Cl}$ ¹¹ in methanol accompanied by no more than 10% physical particle loss during extraction. Thus, solubility characterization of particulates by measurement of carbon loss from extracted filters is possible.

Adsorption of Volatile Organic Species onto Quartz Filters During Hi-Vol Sampling

With this understanding of the limits of the extraction and carbon measurement techniques, it is possible to use them to address a sampling problem. The high efficiency of quartz fiber filters for particle collection has long been established. Another concern is the extent to which organic vapors may be adsorbed onto the filter itself or onto atmospheric soot during collection, so that soluble carbon measurements do not reflect ambient particulate composition but may include sampling artifacts. To explore the filter gas pickup problem, we collected ambient particulates for 24 hours in Berkeley using two filters in series, with all other hi-vol operations as normal. The downstream filter showed carbon loading equivalent to 11% of the upstream, particle-loaded filter. The top filter showed a typical ambient S:P:E distribution, but benzene removed all the carbon from the lower filter, and roughly 70% was recovered in the extract. This result implies that hydrocarbons are being trapped on the clean filter to a small extent. The source could be ambient air or outgassing from the particulate material on the upper filter. The volatilization of the lower filter cyclohexane extract is very similar to the behavior of ambient cyclohexane extracts, suggesting that part of the cyclohexane-soluble carbon may be due to a sampling artifact.

Conversion of "Primary" to "Secondary" Carbon under Nonphotochemical Conditions

The results presented so far have shown that ambient particulates contain more polar ("secondary") and less nonpolar ("primary") carbon than source particulates. The ratio of "secondary" (S) to "primary" (P) carbon for ambient and source particulate is given in Table 1. For carbon measured in evaporated extracts, ambient samples given S/P close to 3.0, while vehicle combustion sources have S/P = 0.85. For carbon measured by combustion of extracted filters, S/P ratios follow the same pattern. Coupled with these source-ambient differences is the fact that S/P ratios for ambient particulates do not depend on the ozone concentration, implying that the highly polar character of organic compounds associated with particulates is not related to the presence of a photochemically reactive atmosphere. These observations lead us to suggest several possible explanations:

1. Oxidation of reactive hydrocarbons and other organic compounds in homogeneous or heterogeneous reactions, such as oxidation of adsorbed compounds while they are associated with soot, in mechanisms which appear to be unrelated to

Table 1. Ratio of carbon content of evaporated extracts to carbon content of extracted filters. Effects on secondary to primary (S/P) ratios.

	Cx	Bz	MC	Elem	S/P Extract	S/P Filter	Number of Samples
<u>Ambient Particulate</u>							
Los Angeles	^a	^a	^a	^a	2.3	-	12
Berkeley	0.52±.16	0.69±.15	1.10±.39	1.28±.24	3.0	1.6	16
New York	0.42±.14	0.65±.02	1.09±.23	1.16±.06	2.8	0.87	2
<u>Combustion Sources</u>							
Caldecott Tunnel	0.63±.14	0.74±.14	1.56±.46	1.25±.24	0.52	0.17	6
Parking garage	0.56±.14	0.67±.03	1.50±.20	1.24±.02	0.83	0.27	3
Diesel bus	0.18±.11	0.24±.07	2.68±.47	32± 2	0.67	0.07	2
^a Not available.							

the photochemical activity of the atmosphere as indicated by the ozone concentration.

2. Replacement of nonpolar compounds adsorbed on soot by polar compounds which are less volatile during dilution of combustion effluent into the atmosphere or during the residence time of combustion generated particles in the ambient air.

3. Addition of polar aerosol compounds into the atmosphere from natural sources, such as marine air or fog, in high enough concentration to dilute anthropogenic source particulates.

4. Direct emission of polar compounds such as plasticizers into the atmosphere, followed by adsorption onto soot.

5. Replacement of nonpolar compounds adsorbed on soot or on filter fibers by polar compounds (sampling artifact).¹²

6. Reaction of atmospheric oxidant gases with compounds adsorbed on soot or filter fibers during sampling (sampling artifact).¹³

We have initiated experiments to transform combustion particulates into their more polar ambient counterparts so that we can deduce some of the contributing processes. Preliminary results indicate that hi-vol sampling does not lead to substantial replacement of nonpolar by polar compounds, nor do ambient gases oxidize a large fraction of adsorbed nonpolar compounds during sampling. So far we have no data concerning the possibility of dilution effects or soot-catalyzed oxidation of reactive hydrocarbons.

SUMMARY

Particulates collected under nonphotochemical conditions (Berkeley and New York City) appear

very similar to particulates collected during a photochemical episode in the Los Angeles Basin when characterized by solvent extraction. There appears to be no substantial seasonal variation in S:P:E ratios for Berkeley samples. "Secondary" to "primary" (polar to nonpolar) ratios based on extracts are close to 3 for all ambient particulates but less than 1 for source particulates.

We suggest that the significant differences between ambient and source samples could be due to chemical and physical transformation processes which do not require a photochemically active atmosphere.

We have also found that a substantial amount (30-40%) of nonpolar carbonaceous material associated with source and ambient particulates is lost by evaporation during extraction with cyclohexane and benzene, implying that earlier measurements^{9,10} of total mass or carbon content of these extracts do not reflect the total amount of material extracted.

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Characterization of Particulate Amines

L. A. Gundel, et al.

INTRODUCTION

In addition to nitrate and ammonium species,¹ a large fraction of the nitrogen associated with ambient particulate matter occurs in two or more chemically reduced forms.² These reduced species, N_x , have been tentatively identified² as amine, amide, and possibly nitrile species by means of x-ray photoelectron spectroscopy (ESCA or XPS). For simplicity and in the absence of a more rigorous term, we shall refer to these reduced species as particulate amines or N_x . N_x species occur in combustion-generated and ambient particulates, and species with similar ESCA spectra and thermal behavior in vacuum can be produced by reaction of soot or graphite with NH_3 .³

Both ESCA and traditional analytical methods have helped characterize particulate nitrogen, but their results for NH_4^+ , N_x , and NO_3^- do not agree.⁴ Whereas ESCA samples are subject to volatility losses in high vacuum, especially for NO_3^- , wet methods may modify the chemical composition of the samples by reactions such as hydrolysis, so that the technique affects the results. To reconcile the existing information and to further characterize particulate amines,

we have used a new nondestructive nitrogen determination,⁵ proton activation analysis (PAA), in conjunction with ESCA for ambient particulate samples, before and after solvent extraction. ESCA has also been used for the characterization of evaporated solvent extracts.

CHEMICAL CHARACTERIZATION OF PARTICULATE NITROGEN

ESCA has proved to be a very useful tool in identifying the variety of nitrogen species associated with ambient particulates, and its use has been extensively reviewed.⁶⁻⁸ The following observations about ambient particulate nitrogen are based on ESCA measurements on silver filter samples from several locations (Los Angeles, St. Louis, and Berkeley); the experimental evidence has been presented earlier^{4,6-8} and will not be repeated here.

1. Besides the expected salts-ammonium sulfate $[(NH_4)_2SO_4]$ and ammonium nitrate (NH_4NO_3)-which are relatively stable in vacuum, a more volatile ammonium species, probably ammonium chloride (NH_4Cl) or adsorbed NH_3 , is often associated with ambient particulate matter.

2. Particulate amines (N_x) typically account for up to half of the total nitrogen as determined by ESCA.

3. Nitrate nitrogen is typically much less abundant than ammonium nitrogen. Nitrate species are more volatile in vacuum than NH_4NO_3 , indicating that adsorbed nitric acid may be present. Wet methods tend to find much more (3-5x) nitrate than ESCA.⁴ Besides the volatility of HNO_3 , artifact nitrate on glass fiber filters⁹ can account for some of this difference.

4. ESCA determination of total reduced nitrogen ($NH_4^+ + N_x$) agrees with determination of NH_4^+ by wet methods.⁴ Since N_x is often more abundant than NH_4^+ in ambient samples, there is a serious discrepancy which is consistent with the conversion of N_x to NH_4^+ during the analytical procedure¹⁰ to determine NH_4^+ .

5. Based on studies of winter aerosol samples from Berkeley, California,¹¹ ESCA inventories nitrogen as 25% nitrate, 25% ammonium, and 50% N_x . Indirect evidence obtained in another laboratory¹² supports the existence of N_x by showing that nitrate and ammonium cannot account for all nitrogen associated with ambient particu-

lates. The average nitrogen deficiency is 25%.¹² Amides have been found in ambient particulates by high resolution mass spectrometry.¹³

Solubility Behavior of Particulate Nitrogen

A series of ambient particulate samples collected on silver filters during autumn and winter in Berkeley, California, was washed with water and organic solvents, with PAA and ESCA analyses performed after each step. Static extraction with distilled deionized water at room temperature for two hours removed a large fraction of the original nitrogen, as shown in Table 1. Further sequential Soxhlet extraction with benzene followed by methanol and chloroform (1:2 v:v) removed only a small fraction of the remainder. Nitrogen remaining on the filter accounts for between 2 and 25% of the initial nitrogen. Water-washing of all winter 1977-78 samples (Table 2) changes the nitrogen-to-carbon ratio from 0.32 0.26 to 0.040 0.020. For comparison we find that untreated vehicle exhaust collected in a highway tunnel has nitrogen-to-carbon ratio lower than untreated ambient particulates (0.046 0.010). The ESCA results in Fig. 1 show the effect of water washing on one of the samples (Dec. 1977). The other

Table 1. Solubility behavior of ambient particulate nitrogen. PAA results ($\mu g/m^3$).

Air quality	Haze episode	Overcast	Moderate haze	Sunny
Date	5 Nov 76	9-12 Dec 77	30 Jan-1 Feb 78	19-23 Jan 78
Duration, hr	6	72	48	96
Total weight loading ^a	229 ^b	71	49	22
Total N	8.9 ^c	5.0	2.2	0.67
N after H ₂ O wash ^{d,e}	4.6 (0.52)	0.23 (0.05)	0.08 ^f (0.04)	0.17 (0.25)
N after H ₂ O, Bz, MC wash ^g	0.89 (0.10)	0.22 (0.04)	0.05 (0.02)	0.17 (0.25)
Total C ^h	40.9	8.28	9.31	5.93
C after H ₂ O wash ^{e,i}	na	4.26 (0.51)	3.97 ^f (0.43)	3.69 (0.62)
C after H ₂ O, Bz, MC wash	na	0.83 (0.10)	na	na

^aNet mass loading, except as noted.

^bTSP

^cDrop of 14% compared with measurement made about 6 months earlier.

^dStatic extraction - 2 hours with deionized H₂O at 20°C except as indicated.

^eNumbers in parentheses give the fraction of initial total nitrogen.

^fStatic extraction - 2 hours with deionized H₂O at 80°C.

^gBz = benzene, MC = methanol + chloroform (1:2 v:v)

^hTotal C by combustion (LBL). Prefired quartz hi-vol filters were used for collection.

ⁱNumbers in parentheses give the fraction of initial total carbon.

Fig. 1. ESCA spectra in the nitrogen region for ambient particulate material collected in December, 1977, in Berkeley, California. Binding energy for nitrogen species: NO_3^- , 407 eV; NH_4^+ , 402 eV; N_x , 400 eV. Top: Untreated particulate material. Middle: H_2O -washed ambient particulate on Ag. Bottom: Dried H_2O extract. (XBL 783405A)

samples exhibit similar behavior except that they contain less nitrate. The nitrate peak occurs at binding energy close to 407 eV, NH_4^+ close to 402 eV, and N_x close to 400 eV. The reduced nitrogen peaks have been resolved into contributions from NH_4^+ and N_x by comparison

with standards. The untreated particulate material contains roughly equivalent amounts of ammonium, particulate amine, and nitrate species, with total nitrogen equal to 5.0 g m^{-3} . After water washing, the remaining nitrogen is N_x . It can be seen from Table 1 that 4.8 g m^{-3} of the initial nitrogen has been removed by water extraction.

The chemical speciation of the evaporated extract may be expected to reflect the initial speciation; however, as seen from Figure 1, the extract contains much less N_x than NH_4^+ and shows a higher NO_3^- -to- NH_4^+ ratio. These findings suggest two interpretations. First, assuming that all nitrogen removed in water washing appears in the dried extract, N_x present in the untreated extract has been converted to NH_4^+ during the extraction procedure or during evaporation. Hydrolysis of amides would convert N_x to NH_4^+ , and we shall discuss this further. The second observation, that more nitrate appears in the extract than in the untreated sample, implies that nitrate present in the untreated sample is quite volatile, and that a substantial fraction of the original nitrate is lost in the ESCA spectrometer. From the dependence of the nitrate peak intensity on X-ray and vacuum exposure time (Fig. 2), we can estimate the original NO_3^- intensity. It is important to note that the nitrate associated with the ambient sample is more volatile in vacuum than expected for a salt such as NH_4NO_3 . The water extraction has changed the chemical composition of the sample, so that conclusions based on methods employing extraction may not accurately characterize the original particulate material.

N_x species can be hydrolyzed during H_2O extraction and thus converted to NH_4^+ . The expected reaction, illustrated for particulate amides, is

ESCA distinguishes amide (N_x) from NH_4^+ ; and, indeed, the ratio of N_x to NH_4^+ is smaller in the extract than in the ambient sample, as mentioned previously. Amine salts would appear in the extract as N_x . In Table 2 we present nitrogen speciation for the Berkeley sample from December, 1977, whose ESCA spectra were shown in Fig. 1. Total nitrogen loadings are derived from PAA and speciation from ESCA, with volatility corrections for NO_3^- in the untreated sample based on vacuum behavior of nitrate in ESCA. We have assumed that all nitrogen removed from the sample during water extraction is retained in the evaporation extract so that the concentrations of dissolved species can be expressed in $\mu\text{g m}^{-3}$. The fact that NO_3^- concentrations of for the untreated sample and the extract agree within $0.1 \mu\text{g m}^{-3}$ provides a self-consistency check. We note that more NH_4^+ appears in the extract than was present on the untreated sample; less N_x appears in the extract than was present on the untreated sample. The N_x deficiency in the extract ($1.0 \mu\text{g m}^{-3}$) matches the surplus in NH_4^+ ($0.9 \mu\text{g m}^{-3}$). These

Fig. 2. Dependence of the nitrate peak intensity on high vacuum and X-ray exposure time during ESCA. Top curve: Dried extract. Lower curve: Untreated ambient particulate sample (December, 1977; Berkeley, California). (XBL 787-1273)

results provide evidence which is consistent with amide hydrolysis.

Removal of N_x by dissolution in water without hydrolysis can occur when N_x species are soluble stoichiometric compounds such as amines. Our results indicate that about half the original N_x is removed by hydrolysis and the other half

by dissolution, as expected for a mixture of amine, amide, and nitrile functional groups. Some of the species may be present as stoichiometric compounds and others possibly occur as surface species.

SUMMARY

Our principal results can be summarized as follows:

1. A large fraction of N_x (85%) originally present in ambient particulate matter can be removed by water extraction (whereas NH_4^+ and NO_3^- are completely removed).
2. Compared with the untreated sample, the NH_4^+ concentration in the extract increases by approximately the same amount as the N_x concentration decreases. We attribute this behavior to the hydrolysis of amide groups.

Extraction of particulate material with water may chemically change the nitrogen species so that the chemical composition of the extract is not representative of the original sample. Therefore, analytical methods based on extraction may give erroneous results. The conversion of particulate amides to NH_4^+ during extraction may yield NH_4^+ concentrations which are too high.

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Table 2. Effect of water washing on December 1977 ambient particulates.^{a,b}

	Ambient	H ₂ O extract ^c	Extract-ambient	H ₂ O-washed ambient
NH_4^+ as N fraction	1.4 0.28	2.3 0.47	+0.9	0.0 ^d 0.0
N_x as N fraction	1.7 0.34	0.7 0.14	-1.0	0.2 1.0
NO_3^- as N fraction	1.9 ^e 0.38	1.8 0.39	-0.1	0.0 0.0
Total nitrogen ($\mu g\ m^{-3}$)	5.0	4.8	-0.2	0.2

^a9-12 December 1977 Berkeley particulate on Ag filters (Table 2). Total nitrogen in $\mu g\ m^{-3}$.

^bSpeciation is based on integrated areas under curves shown in Fig. 1. Total nitrogen is from PAA except for H₂O extract. H₂O extract total nitrogen is the difference between ambient total N before and after H₂O washing.

^cValues for N are based on the assumption that all N removed by H₂O appears in the evaporated extract.

^dESCA results in Fig. 1 may show a small amount of NH_4^+ .

^eThe volatility correction is calculated from results presented in Fig. 2.

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SO₂ Oxidation by Water Droplets Containing Combustion Nuclei

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INTRODUCTION

Particulate sulfate comprises a significant fraction of the total suspended particulate matter in urban air and is thought to play an important role in visibility reduction as well as being a health hazard. The relative importance of currently known reaction mechanisms for SO₂ oxidation in the ambient atmosphere has not been determined. Recently, increased attention has been directed to reaction pathways involving liquid water. One reaction pathway which shows promise is the soot-catalyzed aqueous oxidation of SO₂.

Evidence in our laboratory has shown that the oxidation of sulfurous acid (which can be produced by hydrolysis of SO₂) to SO₄²⁻ by an aqueous suspension of soot is fairly rapid.¹ Extrapolation of the sulfurous acid

oxidation results to the atmosphere indicates that this reaction pathway may be an important source of SO₄²⁻. In this paper, preliminary results are reported of a laboratory study in which water droplets having soot nuclei were exposed to SO₂ in a fog chamber. This chamber study is thought to simulate a common tropospheric process, i.e., the condensation of water vapor onto nuclei to form fogs, plumes, and clouds in the presence of SO₂. Preliminary results of our experiments indicate that fog droplets containing soot nuclei are a very effective system for the oxidation of SO₂ to SO₄²⁻.

EXPERIMENTAL

A diagram of the experimental system is shown in Fig. 1. A flowstream of combustion particles (soot particles) was humidified and

Fig. 1. Diagram of the experimental system used to study the oxidation of SO₂ in fog droplets. (XBL 7812-13513)

subsequently cooled so that water vapor condensed onto the particles. The resultant fog droplets were drawn into a fog chamber and exposed to SO₂.

Soot particles from several types of sources were drawn through the system:

1. A propane diffusion flame (~125 ml/min propane) was produced by plugging the air holes in a Bernz-o-matic torch nozzle. Soot particles from this flame were forced into a 5-m³ polyethylene bag that had previously been inflated with filtered room air. The particles were permitted to coagulate in the bag for several hours, after which the bag was connected to the fog generator. For the remaining sources, the soot particles were collected from an 8 cm diameter x 40 cm tall stainless steel chimney into which the flames were introduced (Fig. 1).

2. A propane diffusion flame was produced as in (1) above.

3. A natural gas diffusion flame was produced by covering the air holes in a Fisher Bunsen burner located at the base of the chimney.

4. A natural gas premixed (fuel and air mixed before burning) flame from a Bunsen burner was introduced into the chimney.

Soot particles were optionally drawn through the fog generator or introduced directly into the fog chamber. Fog was produced by introducing water vapor from a flask of boiling water into a flowstream of particle-laden gases and subsequently cooling the humidified gases in a glass water-cooled distillation condenser (Fig. 1). When combustion particles were withdrawn directly from the chimney, an additional metal-finned water-cooled condenser, for cooling the combustion gases, was placed in the flowstream between

the chimney and the humidifier. The resultant fog droplets were 5-7 μ m in diameter as measured by sedimentation rates in the chamber. A mixture of 100 parts-per-million (ppm) SO₂ in N₂ could be introduced into the stream of fog droplets by means of a rotameter and valve. The resultant mixture of gases and particles was drawn into the top of a 60 cm D x 91 cm W x 122 cm H fog chamber. The chamber was constructed from 1.9-cm thick plywood with one of the 91 cm x 122 cm sides constructed from 1.9-cm thick plexiglass. The inside surface of the fog chamber was covered with a moisture-resistant paint.

Air samples were removed from the chamber through several closely spaced sampling ports located near the floor of the chamber. Two in-line 2.5-cm diameter stainless steel filters were connected to one of the sampling ports by means of a 1.9-cm diameter brass pipe Y. The Y and filters were heated by an electrical heating tape. Calibrated critical orifices were used to control the rate at which chamber air was drawn through the filters. Normally, identical orifices were used with the two filters, and particles from the chamber were collected simultaneously on a prefired quartz fiber filter and a 1.2- μ m pore Millipore filter. The temperature of the air which passed through the filters was monitored by a thermocouple located downstream from the critical orifices and the temperature was maintained at 50°C to prevent liquid water from being collected on the filters. This precaution avoided the possibility of chemical reactions involving liquid water taking place on the filter media.

An SO₂-specific monitor (Thermo Electron Co.) was connected to the heated manifold via a Teflon sampling tube. A dew-point sensor (thermo-electrically cooled mirror, General Eastern Corp.) was attached to a second sampling port. Formation of particulate SO₄²⁻ in the chamber

was monitored by filter analysis and/or flame photometry. A sulfur-specific flame photometric detector (FPD) (Model 285, Meloy Inst.) was attached to a third sampling port on the fog chamber. The instrument was modified slightly so that an air sample passed through only 10 cm of 0.32-cm diameter tubing before it entered the FPD. A diffusion scrubber was optionally inserted in the inlet line of the FPD. The use of an SO₂/H₂S diffusion scrubber (lead peroxide as the adsorbate) has been described in the literature as a selective way to remove sulfur gases from an air stream containing SO₂, H₂S, and particles.² The particles pass through the scrubber; if they contain sulfur, they are detected by the FPD. The Meloy instrument suffers from CO₂ interference, i.e., if CO₂ and SO₂ are present in an air sample, the CO₂ decreases the response to SO₂. This problem is particularly severe when the analyzer is used to measure sulfur in combustion gases which are characteristically enriched in CO₂. A new type of diffusion scrubber was designed to overcome the CO₂ interference problem. A 0.64 cm dia. x 19 cm long tube was constructed from 100-mesh stainless steel screening. This mesh tube was positioned axially inside a 1.7 cm diam x 19 cm long glass tube and sealed to the glass tube with appropriate tube fittings. The space between the mesh tube and the glass tube was filled with 8-20 mesh Ascarite (Matheson-Coleman and Bell, Co.). The Ascarite diffusion scrubber was capable of decreasing the CO₂ concentration in the chamber gases to 22 ppm from a presumably high value. The Ascarite scrubber was capable of removing 99+% of SO₂ from an air stream containing 5 ppm SO₂. This scrubber was also found to remove sulfur-containing gases from the chamber air which were not removed by lead peroxide scrubbers.

By placing a 2.5-cm diameter quartz fiber filter and the Ascarite scrubber in the sampling line of the FPD, gaseous and particulate sulfur were removed from the sample stream. The difference in FPD response with and without the filter in line is assumed to be due to particulate sulfur. A pressure drop associated with the filter was not responsible for this difference in FPD response because the same difference was observed when a larger filter was used. The lower limit of detection for particulate sulfur was 0.2 ppb as SO₂ or 0.8 µg SO₄²⁻/m³. It has also been reported in the literature that the sensitivity of the FPD to particulate sulfur is dependent upon the sulfur species and the temperature of the FPD burner. For example, at temperatures in excess of about 100°C, H₂SO₄ is vaporized and as much as 90% of this vapor is lost by reaction with metal parts in the FPD and escapes detection. Ammonium sulfate is not as easily vaporized and the FPD shows a greater response to ammonium sulfate than to equal concentrations of H₂SO₄. The sulfate concentrations as indicated by the FPD may be as low as 10% of the actual concentration because of the vaporization problem since the sulfate species is possibly H₂SO₄. This response factor must be kept in mind when extrapolating the results of this work to the ambient atmosphere. Attempts are being made to overcome the vaporiza-

tion problem and to determine the sulfate species produced.

The extent to which the fog droplets filled the chamber was determined by shining a 1-mW He-Ne laser beam through the plexiglass window to a mirror on the opposite chamber wall. By sitting along the reflected beam, crude measurements of light scattered in the forward direction by the particles and droplets were made. The beam was also used to probe the extent to which the fog filled other parts of the chamber.

Particulate samples collected on prefired quartz fiber filters (baked at 800°C for 12 hr) were analyzed for total combustible carbon. The CO₂ evolved from the combusted sample was detected by gas chromatography. The total carbon per m³ was then calculated from the CO₂ value and the volume of air drawn through the filter. Particulate samples collected on Millipore filters were analyzed by x-ray fluorescence (XRF) in a few cases for elements having Z > 14 but were normally analyzed only for sulfur. Electron spectroscopy (ESCA) was used to show that the sulfur was primarily sulfate. The light-absorbing properties of the filtered particles were determined by directing a 1-mW He-Ne laser beam through a loaded Millipore filter. By comparing the light transmitted by clean and loaded filters, a percent transmission value was calculated. From the percent transmission the optical attenuation, -100 ln I/I₀, was calculated.³

RESULTS AND DISCUSSION

To determine if combustion nuclei were encapsulated with liquid water, a small impactor, designed from a 2.5-cm diameter in-line filter holder, was used to collect fog droplets. A 22-gauge hypodermic needle was inserted through the center of the inlet to the filter holder and sealed in place with epoxy cement. The needle extended to within several mm of the grill, which normally supports the filter in such a filter holder. A small circle of gummed label was stuck onto the center of the grill and served as the impaction surface. By trial and error, the velocity of air through the needle was adjusted so that fresh combustion particles were not collected by this impactor and the fog droplets were impacted. Examination of the impaction spots indicated that many droplets contained black nuclei.

Propane Soot Particles

An initial series of chamber runs was conducted in which combustion particles were drawn from the 5-m³ bag into the fog generator and chamber. Filter samples of the particles were collected during these runs, but the FPD was not used. Figures 2 and 3 show the results of this series of runs. The presence of added SO₂ and fog increased the [SO₄²⁻] in the chamber. An average of 5.6 µg SO₄²⁻/m³ was observed in 18 soot-fog-SO₂ runs in which the [SO₂] was between 70 and 120 ppb. In 8 background runs, i.e., soot and fog or soot alone, an average

Fig. 2. A plot of sulfate formed versus carbon loading for fog droplets containing propane soot nuclei. The correlation coefficient for the two parameters was $r^2 = 0.25$. (XBL 7812-13512)

Fig. 3. A plot of sulfate formed versus optical attenuation ($-100 \ln I/I_0$) for fog droplets containing propane soot nuclei. (XBL 7812-13511)

of $1.8 \mu\text{g SO}_4^-/\text{m}^3$ was detected. Since the reaction time for the fog droplets was determined by the 15-min setting time, these results indicate a rather fast oxidation of SO_2 in the droplets.

Figure 2 shows that poor correlation ($r^2 = 0.25$) was obtained for the regression of total particulate carbon versus particulate SO_4^- . Soot particles, by definition, are composed of several components such as graphitic crystallites (source of black color) and various hydrocarbons. The amount of either of these components varies with the type of soot, and it is therefore not surprising that the production of SO_4^- was not well correlated with total particulate carbon.

A comparison of $\mu\text{g SO}_4^-$ versus the optical attenuation of the particle is presented in Fig. 3. Evidence from our laboratory has shown that the optical attenuation of filter deposits is proportional to the graphitic content of

Fig. 4. A plot of sulfate production versus mixing time in a chamber for fog droplets containing various types of nuclei. At $t = 0$ fog droplets and SO_2 were introduced into a chamber which had $\text{RH} < 50\%$ and a background concentration of SO_2 . (XBL 7812-13509)

the particles.⁴ Figure 3 thus shows that a relationship exists between the graphitic content of the particles and SO_4^- formation which agrees with the SO_2 oxidation mechanism reported by Chang et al.¹

An additional run was conducted in which propane diffusion flame particles were introduced into the fog chamber via the chimney. The results of this run are shown in Fig. 4 and are discussed later in this paper.

Natural Gas Soot Particles

In this series of experimental runs, the concentration of particulate SO_4^- was monitored by the FPD. Filter samples of the particles were not collected. Figures 4 and 5 show the results of these runs. At $t = 0$ (Fig. 4), an equilibrium concentration of combustion nuclei existed in the chamber and at this time the incoming stream of particles was diverted through the fog generator. SO_2 was also introduced into the fog stream at this time. Initially, the fog droplets evaporated rapidly in the chamber. As the relative humidity (RH) in the chamber increased, the lifetime of the droplets also increased so that the chamber was filled with fog in about 1-2 hr. At this time, the chamber RH was nearly 100% and the droplets did not evaporate before they settled to the bottom of the chamber. Reaction time in the droplets was limited to evaporation time during the initial 1-2 hr period or to settling time of the droplets (~ 15 min) after chamber RH was $\sim 100\%$. It is obvious from the curves in Fig. 4 that SO_4^- was produced even when the droplet reaction time was shorter than 15 min.

In Fig. 5 the steady state $[\text{SO}_4^-]$ for the runs in Fig. 4 are plotted versus the steady-state $[\text{SO}_2]$. The linear regression line drawn through the diffusion flame data points indicates

Fig. 5. A plot of sulfate formed versus SO_2 for fog droplets containing natural gas combustion nuclei. The $[\text{SO}_4^-]$ was obtained from the net steady-state $[\text{SO}_4^-]$ presented in Fig. 4.
(XBL 7812-13510)

a nearly linear dependence of $[\text{SO}_4^-]$ on $[\text{SO}_2]$. Previous investigations in our laboratory have indicated that the oxidation mechanism for SO_3^- in aqueous suspensions of soot is zero order with respect to SO_3^- .¹ The results reported here do not disprove the zero order mechanism since reaction rates were not measured. If one assumes a zero order reaction mechanism, the data reported here suggest that the oxidation of SO_2 in the droplet proceeds at a faster rate than the oxidation of SO_3^- in aqueous suspensions in soot. The rate may be fast enough so that all of the SO_2 in the droplet is oxidized in less than 15 min (settling time of droplets). In the zero order mechanism, the same amount of SO_4^- is produced after a fixed reaction time, for example, 15 min, regardless of the initial $[\text{SO}_3^-]$. If, however, the reaction rate in fog droplets is rapid enough to oxidize all of the SO_3^- that was present initially, it would mistakenly appear that the amount of SO_4^- produced was related to the initial $[\text{SO}_3^-]$. Future investigations will examine the rate of reaction and the reaction mechanism for the oxidation of SO_2 in a soot-fog- SO_2 system.

In addition to the runs conducted with fog droplets containing natural gas diffusion flame particles, single runs were conducted with natural gas premixed-flame particles or propane diffusion flame particles. The results of these two runs are presented in Figs. 4 and 5. The premixed natural gas combustion particles produced a smaller equilibrium $[\text{SO}_4^-]$ than was expected for diffusion flame particles in a similar $[\text{SO}_2]$. This was presumably due to the fact that premixed flames are less sooty than diffusion flames.⁵ The composition of the nucleus of a fog droplet appears to influence the oxidation of SO_2 in the experiments described here. The experimental run in Fig. 4 which was conducted with propane diffusion flame

particles supports the data in Figs. 2 and 3 and shows that soot particles, when encapsulated with liquid water, can oxidize SO_2 . The experimental run with propane particles is thought to have the highest $\mu\text{g C}/\text{m}^3$ of all the runs in Fig. 4 as judged by the density of the fog in the chamber. Thus the fact that the propane particle curve (3.7 ppm SO_2) rises above the natural gas diffusion particle curve (4.1 ppm SO_2) does not necessarily indicate that propane soot particles oxidize SO_2 more effectively than natural gas soot particles.

Evidence in our laboratory indicates that a large fraction of the particles in urban atmospheres are soot particles. These particles can act as sites for the condensation of water, and the lifetime of these droplets appears to be long enough to oxidize SO_2 to SO_4^- , even when the SO_2 concentration is low, i.e., several tens of parts-per-billion. Comparison of the relatively long reaction time permissible in natural fog to the 15-min reaction time in the fog chamber strongly suggests that oxidation of SO_2 by soot particles encapsulated with liquid water is an important tropospheric reaction.

The following conclusions were drawn from the data reported in this paper:

1. Soot can act as a nucleus for the condensation of water.
2. SO_2 is oxidized in the soot-fog- SO_2 system to form SO_4^- .
3. The presence of liquid water and soot in the system is critical.
4. The production of SO_4^- is poorly correlated with total particulate carbon, but more strongly correlated with the graphitic content of the particles.
5. Dense fogs could be produced with natural gas premixed and diffusion flame particles, but the fog containing the diffusion flame (sooty) particles appeared to oxidize SO_2 more efficiently.
6. The reactions appear to be rapid enough so that SO_2 oxidation in liquid droplets appears to be important in the ambient air.

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Kinetics and Mechanism of the Reaction of NO_x with SO_2 in Aqueous Solutions

S. B. Oblath, et al.

The oxides of nitrogen (NO_x) and sulfur dioxide (SO_2) are common and abundant air pollutants. The gas-phase interaction of NO_x and SO_2 has been widely studied.¹⁻⁴ So far the reaction between NO_x and SO_2 after dissolution in water droplets has been overlooked by atmospheric chemists. It is important to investigate the reaction in an aqueous medium because such circumstances occur frequently in fogs, clouds, rain, plumes, and the human respiratory system. In addition, deliquescent and/or hygroscopic salts, such as NH_4HSO_4 , $(\text{NH}_4)_2\text{SO}_4$ and NaCl , in atmospheric particulates can pick up liquid water at a low relative humidity.⁵

We have reviewed the literature⁶⁻⁹ and found that many concurrent and consecutive chemical reactions can occur as a result of the interaction between NO_x and SO_2 in liquid water. The kinetics and mechanisms of these reactions have not been well characterized. Nevertheless, it has been demonstrated that the products of the reaction depend on the concentrations of reactants, temperature, and acidity of the solution. For example, sulfuric acid is produced and NO_x is regenerated in the well-known lead chamber process where the reaction is carried out at very low pH and high concentrations of reactants. On the other hand, species such as N_2O , hydroxylamine sulfonates, amine sulfonates, and sulfuric acid are produced if the reaction takes place in a slightly acidic or neutral solution.

The purpose of this study is to determine the products, kinetics, and mechanisms of reactions occurring in the $\text{NO}_x\text{-SO}_2\text{-H}_2\text{O}(\ell)$ system under realistic atmospheric conditions and to assess the impact of these reactions on air quality. Preliminary results have indicated that the interaction of NO_x and SO_2 in an aqueous medium could be a very important source of sulfate and N_2O formation in the atmosphere.

Nitrous (III) and nitric (V) acids are produced in the aqueous phase after nitrogen oxides are absorbed into liquid water. Also, sulfurous (IV) acid is formed if SO_2 dissolves in water. The present study measured the reaction rate of nitrites with bisulfites in the pH region between 3 and 7, at 20°C. A mixture of sodium metabisulfite with sodium sulfite was used as the buffer solution for a pH of 7, while potassium biphthalate and sodium hydroxide was used for a pH of 5.5 and 4.5. In order to study the dependence of the reaction rate

on the nitrite and bisulfite concentrations, the initial concentrations of either nitrite or bisulfite were varied, while all other parameters, such as pH and temperature, were held constant. These kinetic experiments were carried out in an excess of bisulfite with respect to nitrite in order to keep the S(+4) concentrations nearly constant at the initial value throughout the course of the reaction. The concentration of nitrite was monitored spectrophotometrically during the course of the reaction using either a Beckman DU (358 nm) or a Bausch and Lomb Spectronic 20 (356 nm). Because the rate of disappearance of nitrite changes many orders of magnitude over the range of pH studied, the initial concentrations of the reactions are adjusted for the selected pH region. The typical initial conditions for pH = 7 were: nitrite, 0.01-0.02 M; bisulfate, 0.10-0.30 M; and sulfite, 0.10-0.25 M. The initial conditions for pH of 5.5 or 4.5 were: nitrite, 0.001-0.003 M; and bisulfite, 0.02-0.05 M.

The results of the experiments at pH 7, 5.5 and 4.5 are shown in Figs. 1, 2, and 3 respectively. The linear relationship between the logarithm of the nitrite concentration and the reaction time (Figs. 1a, 2a, and 3a) indicates that the reaction rate is first order with respect to the nitrite concentration in all three pH regions. The bisulfite dependence on the reaction rate is illustrated by the logarithmic plot of $(d \ln[\text{NO}_2])/dt$ vs. $[\text{HSO}_3^-]$ (Figs. 1b, 2b, and 3b). The slope of the line represents the reaction order of bisulfite, which is 2, 1.1, and 1 for pH = 7, 5.5, and 4.5, respectively.

We have also carried out a series of experiments to study the overall stoichiometry of the reaction at 20°C. In these experiments, similar initial concentrations of bisulfite and nitrite were employed. The sulfite concentration was determined by addition of excess iodine to quench the reaction and back-titration with thiosulfate. The nitrites were determined by visible spectrophotometry at 356 nm. The results are 2.5, 2.1 and 1.5 bisulfate per nitrite molecule reacted at pH of 7, 4.5, and 3 respectively.

Further studies to determine the dependence of the reaction rate on species such as sulfate and sulfite are being investigated. The reaction rate was found to be independent of the sulfate concentration at a pH of 7. An increase in sulfite concentration appears to slow down the rate of disappearance of nitrite.⁸ This

Fig. 1a. Nitrite concentration as a function of reaction time for various initial concentrations of nitrite at $\text{pH} = 7$. The initial bisulfite concentration is 0.20 M. (XBL 7812-13384)

Fig. 2a. Nitrite concentrations as a function of reaction time for various initial ones of nitrite at $\text{pH} = 5.5$. The initial bisulfite cones are 0.030 M. (XBL 7812-13389)

Fig. 1b. A plot of $(d \ln [\text{NO}_2^-])/dt$ versus bisulfite concentration at $\text{pH} = 7$. (XBL 7812-13386)

Fig. 2b. A plot of $(d \ln [\text{NO}_2^-])/dt$ versus bisulfite concentration at $\text{pH} = 5.5$. (XBL 7812-13385)

Fig. 3a. Nitrite concentration as a function of reaction time for various initial concentrations of nitrite at pH = 4.5. The initial bisulfite concentration is 0.022 M. (XBL 7812-13388)

Fig. 3b. A plot of the $(d \ln [\text{NO}_2^-])/dt$ versus bisulfite concentrations at pH = 4.5. (XBL 7812-13387)

may be due to a change in pH on addition of the sulfite.

These experimental results support the belief that there are several concurrent processes involved. The following diagram illustrates those reaction processes which have been indicated in the literature.⁶⁻⁹

Nitrous acid and bisulfite react to form nitrosulfonic acid, which then continues along one or more of three reaction paths:

1. Further sulfonation to produce hydroxylamine disulfonate and amine trisulfonate. These can hydrolyze to form sulfuric acid and reduced nitrogen species.

2. Hydrolysis to form sulfuric acid and hyponitrous acid. The latter decomposes to produce nitrous oxide.

3. Reaction with nitrous acid to yield sulfuric acid and nitric oxide. The extent to which these three different processes will contribute to the system depends on the pH, temperature, and concentration of nitrite and bisulfite species. It is believed that process 1 favors a neutral or mildly acidic solution. Processes 2 and 3 are expected to become increasingly important as the pH of the solution decreases.

Our experimental results appear to indicate that process 1 is the major process even at a pH as low as 4.5. The contributions from processes 2 and/or 3 are observed at a pH of 3 under the conditions of this investigation.

Further experiments are currently being carried out to determine the effect of the sulfite concentration and/or pH on the reaction rate. The results of these experiments will enable us to elucidate a mechanism which is consistent with all of the experimental data.

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Kinetics and Mechanism for the Catalytic Oxidation of SO₂ on Carbon in Aqueous Suspensions

R. Brodzinsky, et al.

INTRODUCTION

Soot particles, in addition to being a major constituent of the ambient particulate burden,¹⁻⁴ are a catalytically and surface chemically active material. For example, Novakov et al.^{1,5} have shown by photoelectron spectroscopy that SO₂ oxidation to sulfate can be catalyzed by combustion-generated soot particles. They reached the following conclusions:

1. Soot-catalyzed oxidation of SO₂ is more efficient at a higher humidity.
2. The oxygen in air plays an important role in SO₂ oxidation.
3. Soot-catalyzed oxidation exhibits a saturation effect.
4. The saturation level of sulfate produced is probably related to such properties of soot particles as size, active surface area, an adsorbed surface oxygen.

5. The sulfate produced on soot particles is water soluble and contributes to the acidification of the solution.

6. SO₂ can be oxidized on other types of graphitic carbonaceous particles, such as ground graphite particles and activated carbon.

Although these authors have shown that the soot-catalyzed oxidation of SO₂ is more efficient in prehumidified air rather than dry air, the specific role of water was not made clear in their experiments. The effects of liquid water are important because liquid water may condense on the soot particles in plumes, and soot particles may encounter liquid water in their passage through fogs and clouds. Also, hygroscopic and deliquescent materials associated with soot particles may hold significant amounts of liquid water, even at a comparatively low relative humidity.⁶

We have recently extended research on the role of soot particles as catalysts for SO₂

oxidation by studying the effect of liquid water on the soot-catalyzed reaction.⁷ In this report, we present a reaction rate law and propose a reaction mechanism for the catalytic oxidation of SO₂ on soot particles in an aqueous suspension. We also compare the soot-particle-catalyzed reaction with other reactions involving liquid water.

EXPERIMENTAL METHODS AND RESULTS

The reaction was studied in systems containing various concentrations of sulfurous acid and suspended carbonaceous particles. The carbon concentrations used in the suspensions ranged from 0.005% to 0.32% by weight, and the sulfurous acid concentration ranged from 1.5×10^{-4} M to 1.00×10^{-3} M. The concentration of sulfurous acid was monitored, using iodometric titrations during the course of the reaction. The concentration of sulfuric acid was followed by the turbidimetric method in some selected runs. Soots produced by the combustion of acetylene and natural gas, as well as by a diesel engine, were collected by impinging the effluent into water. These were used in this study and found to be efficient catalysts.

Figure 1 shows the typical reaction curves of the oxidation of H₂SO₃ by dissolved oxygen in aqueous suspensions of soot particles collected from acetylene and natural gas flames. The reaction occurs in two steps. The rate of the initial disappearance of H₂SO₃ is so fast that it could not be followed by the analytical technique used. The second process is characterized by a much slower linear reduction of H₂SO₃. The results obtained with these combustion-produced soots were essentially reproduced (Fig. 2) by suspensions of similar concentrations of activated carbon⁸ (Nuchar-C190)⁹; Table 1 shows its elemental composition. Figure 2 also shows that there is a mass balance between the sulfurous acid consumed and the sulfuric acid produced. Since it is difficult to prepare soot suspensions reproducibly, suspensions of Nuchar were used as a model system.

Fig. 1. H₂SO₃ concentration as a function of time for acetylene and natural gas soot suspensions. (XBL 7710-2065A)

Fig. 2. H₂SO₃ and H₂SO₄ concentrations as a function of time for activated carbon suspensions. (XBL 782-219)

Table 1. Elemental composition of Nuchar C-190 (% by weight).

C	74.7	K	0.091	Ni	0.001
O	23.6	Al	0.055	Cl	0.001
H	0.9	Ti	0.016	As	0.0004
N	0.1	Mn	0.013	Br	0.0004
Ca	0.221	Cr	0.002	Rb	0.0004
S	0.166	Cu	0.002	Zr	0.0004
Si	0.111	Zn	0.002	Pb	0.0004
Fe	0.117	Sr	0.002	Ga	0.0001

BET surface area = 550 m²/g.

C,H,N: Combustion

O: Difference

Other elements: XRF

To investigate the reaction rate and mechanism, a series of experiments was done with Nuchar as a model catalyst. We have previously reported⁹ the effects of the concentrations of carbon and sulfurous acid on the rate of oxidation of sulfurous acid. The amount of sulfurous acid oxidized, at a constant temperature, by the rapid first step process is linearly proportional to the concentration of the carbon particles. A linear relationship was found between the half-life of the second process and both the reciprocal of the carbon concentration, and the initial sulfurous acid concentration. This behavior suggests a first order reaction with respect to the carbon catalyst concentration and zeroth order with respect to the sulfurous acid concentration under the conditions of the experiment (Nuchar, between 0.005% and 0.32% by weight; sulfurous acid, between 1.5×10^{-4} and 10^{-3} M; pH, between 1.5 and 7.5).

Fig. 3. H_2SO_3 concentration as a function of time for various concentrations of dissolved oxygen at a fixed activated carbon concentration of 0.16% by weight. (XBL 782-299)

Fig. 4. The rate of formation of sulfuric acid versus dissolved oxygen concentration at a fixed activated carbon concentration of 0.16% by weight. (XBL 784-771)

Figure 3 shows the reaction curve at differing dissolved oxygen concentration. The rate of reaction with respect to the concentration of dissolved oxygen was found to be fractional order (0.69) in Fig. 4.

To assess the dependence of the SO_2 oxidation reaction on pH, a known volume of H_2SO_4 or NH_4OH was mixed into the sulfurous acid solution before adding Nuchar. This approach was used

Fig. 5. H_2SO_3 concentration as a function of time at an activated carbon concentration of 0.16% by weight at various pH values. The initial H_2SO_3 concentration was 8.85×10^{-4} M. (XBL 782-218)

for low pH. High pH's were achieved using an NH_4OH - Na_2SO_3 solution. The pH of the solution decreased during the course of the reaction. The change in pH varied from 0.05 to 1.0 pH unit, depending on the initial pH of the solution: the larger the initial pH, the larger the change. The results, represented in Fig. 5, demonstrate that the reaction rate does not depend on the pH of the aqueous suspension under the conditions of this investigation. The pH of these experiments

Fig. 6. H_2SO_3 concentration as a function of time at an activated carbon concentration of 0.15% by weight at various temperatures.
(XBL 782-300)

ranged from 1.45 to 7.5, which should cover the entire range of interest found in the atmosphere. The latter observation is very striking, as it differs from other heterogeneous reactions involving liquid water which are dependent on the pH of the liquid water.

The reaction is accelerated by temperature, as may be seen from the results shown in Fig. 6. The activation energy is 11.7 kcal/mole between 5.5°C and 50°C (Fig. 7).

In summary, the reaction occurs in two steps--an initial rapid oxidation followed by a much slower one. The rate of the first process is too fast to follow. The reaction of the second process has the following characteristics:

1. The reaction rate is first order, zeroth order, and 0.69th order with respect to the concentration of carbon, sulfurous acid, and dissolved oxygen, respectively.

2. The reaction rate is pH independent (between pH's of 1.45 and 7.5).

3. The activation energy of the reaction is 11.7 kcal/mole.

4. There is a mass balance between the consumption of sulfurous acid and the production of sulfuric acid.

DISCUSSION

Based on the experimental results, we propose the following section mechanism:

Fig. 7. A plot of the rate constant versus the reciprocal of the reaction temperature (the Arrhenius equation). The activation energy is calculated to be 11.7 kcal/mole.
(XBL 784-772)

where C_X = soot, $O_2(\ell)$ = dissolved oxygen molecule, Su = sulfite species, and SuO = sulfite species.

Equation (1) indicates that dissolved oxygen is adsorbed on the soot particle surface to form an activated complex. This adsorbed oxygen complex then oxidizes the sulfurous acid to form sulfuric acid according to Eqs. (2)-(4). If we assume that the reaction follows the condition of Langmuir adsorption equilibrium,¹⁰ the rate of acid formation is:

$$\begin{aligned} \frac{d[SuO]}{dt} &= 2K_4 [C_X \cdot O_2(\ell) \cdot 2Su] \\ &= 2k_4 [C_X] \left\{ \frac{K_1 [O_2(\ell)]}{1 + K_1 [O_2(\ell)] + K_W [H_2O] + K_{Su} [Su]} \right\} \\ &\quad \left\{ \frac{K_2 [Su]}{1 + K_2 [Su]} \right\} \left\{ \frac{K_3 [Su]}{1 + K_3 [Su]} \right\} \end{aligned}$$

where K_1 , K_2 , and K_3 are the equilibrium constants of reactions (1), (2), and (3) respectively. K_W and K_{Su} are the equilibrium constants of the adsorption of water and sulfite species on carbon particles respectively. If $k_2 [Su] \gg k_{-2}$ and $k_3 [Su] \gg k_{-3}$, the rate law simplifies to

$$\frac{d[SuO]}{dt} = 2k_4 [C_X] \left\{ \frac{K_1 [O_2(\ell)]}{1 + K_1 [O_2(\ell)] + K_W [H_2O] + K_{Su} [Su]} \right\}$$

If the power rate form of the Freundlich isotherm¹⁰ is used instead of the Langmuir form, the rate law becomes

$$\frac{d[SuO]}{dt} = k [C_X] [O_2(\ell)]^n,$$

which corresponds to the experimental results where $n = 0.69$. The activation energy (E_a) was determined to be 11.7 kcal/mole. The rate law as a function of temperature is

$$\frac{d[SuO]}{dt} = A [C_X] [O_2(\ell)]^n \exp\left(-\frac{E_a}{RT}\right)$$

where $A = 1.17 \times 10^5 \text{ mole}^{0.31} \text{ g}^{-0.7} \text{ sec}$, which is the average value determined for natural gas and acetylene soot.

We have ruled out the possibility that the oxidation of sulfurous acid is due to a reaction involving impurities such as iron in carbon particles. This was done by leaching a carbon sample with concentrated sulfuric acid for

about a week before it was used for the study. This sample contained less than one-third of the original iron content; however, it still exhibited the same reaction rate as all samples without this treatment.

The possibility that the outgassing of SO_2 from the solution might contribute to the disappearance of sulfurous acid is ruled out by the fact that there is a mass balance between the amount of sulfurous acid consumed and the amount of sulfuric acid produced and that no significant consumption of sulfurous acid was observed over a 30-min interval for a solution without the addition of carbon particles.

We have examined the role of dissolved oxygen on the behavior of the reaction. It is conceivable that the initial rapid consumption of sulfurous acid could be due to the depletion in the amount of dissolved oxygen in the solution. The second, slower rate of consumption would then be limited by the rate of diffusion of the oxygen into the solution. This hypothesis was ruled out by noting that the behavior and the rate of the reaction were not affected by bubbling air into the solution or by increasing the stirring speed. The reaction rate speeds up, however, if one increases the concentration of dissolved oxygen (Fig. 3). We therefore conclude that the reaction rate is not limited by the mixing rate of gaseous oxygen molecules into the solution, but rather by the rate of formation of the activated oxygen complex.

We have also carried out a preliminary investigation on the possibility of any chemical species in the atmosphere which might inhibit the soot-catalyzed process, since it is known that some organic substances retard the SO_2 aqueous oxidation by transition metal ions.¹¹ To explore these effects in a realistic atmosphere, liquid water was collected by condensing water vapor from the Berkeley atmosphere. This collection, used for the kinetic study, was found to have no effect on the oxidation rate of sulfurous acid. In a separate experiment, a gummy deposit taken from the wall of a highway tunnel was used for the study. The reaction rate of this sample is 50% faster than the same amount of Nuchar C-190. Therefore, no indication of inhibition from atmospheric contaminants has been observed so far.

The rate constants of several different types of carbon particles were studied and found to depend on the nature of the carbon particles. In principle, the reaction rate should be proportional to the concentration of carbon particles. The number of active sites per unit mass of carbon particles should vary from one type to the next¹² and is not necessarily proportional to the surface area. Using the electron paramagnetic resonance method, Sidelewski¹² has shown that free electrons on carbon particles can serve as active centers for the oxidation of SO_2 . The concentration of free electrons is related to the origin and thermal history of the carbon particles. The rate constant reported in this study represents

the average value between the values of natural gas and of acetylene soot particles produced under rich flame conditions. In a recent fog chamber study, Benner et al.¹³ have found that the reaction rate of soot particles generated from a natural gas diffusion flame can be considerably faster than the reaction rate reported here for aqueous soot suspensions.

Our observation that the reaction behaves independently of the concentration of sulfite species and the pH of the solution is expected as long as the following conditions are satisfied:

$k_2[\text{oxidizable sulfite species}] \gg k_{-2}$ and

$k_3[\text{oxidizable sulfite species}] \gg k_{-3}$,

where the oxidizable can be $[\text{SO}_2 \cdot \text{H}_2\text{O}]$, $[\text{HSO}_3^-]$, or $[\text{SO}_3^{=}]$. However the possibility that two or three sulfite species are oxidized cannot be ruled out.

We have also investigated the kinetics at a much smaller sulfite concentration and at a much higher pH of the solution. Preliminary results indicate that the oxidation rate is considerably slower at $\text{pH} > 7.6$. This behavior could indicate that a reaction mechanism, different from the proposed one, is operating. However, the proposed mechanism reproduces the results obtained under our experimental conditions. Further work is necessary to completely understand the actual reaction mechanism.

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A Carbon and Lead Emission Inventory for the Greater San Francisco Bay Area

A. D. A. Hansen, et al.

INTRODUCTION

The incomplete combustion of almost any fuel can result in the formation of trace particulates in the exhaust stream. Particulate carbon and lead are two of the most important anthropogenic contributions to the ambient aerosol and often reach large concentrations in urban situations under relatively stagnant atmospheric conditions. As discussed elsewhere in this report,¹ there has been controversy over the relative importance of particulates directly emitted from sources versus those formed from gaseous precursors in atmospheric reactions. Calculations originally presented by Friedlander² called for a dominant contribution of secondary carbonaceous material in the ambient urban aerosol of the Los Angeles air basin. In essence, this method considered that the major primary source of particulate carbon and lead was automotive emissions characterized by a [C/Pb] mass ratio of the order of 1. To account for an observed [C/Pb] mass ratio of the order of 6, a mass balance calculation was performed that required carbonaceous particulates of secondary origin to be present in quantities considerably exceeding the primary contribution. In this report we present emission factor estimates and a similar calculation to predict the inputs of particulate carbon and lead to the greater San Francisco Bay Area air basin. The results of this prediction are then compared with the results of the analysis of many ambient samples, and show that it is possible in principle to account for the observed ambient [C/Pb] ratio solely by proper consideration of source inputs.

SOURCES

The sources we consider here (with their contribution to the total energy consumption of the area³) are as follows: 1) domestic and commercial combustion of natural gas and refinery gas (61%); 2) vehicular use of gasoline (28%); 3) vehicular use of diesel fuel (4%); 4) aircraft use of jet fuel (2%) and 5) combustion of heavy fuel oil (5%). We further break down vehicular gasoline use into categories of high-speed (freeway) driving and start-stop driving.

Natural Gas Emission Factor

Although it had long been believed that natural gas is a "clean" fuel, we have found considerable emission of particulate carbon from poorly regulated combustors. Stack sampling was done on three combustors representative of the various classes used in the area in order to estimate an overall emission factor. The particulates were collected on prefired absolute quartz fiber filters from 1) a 50,000-lb steam generator on the UCB campus, 2) a 36,000-Btu/hr

domestic-type hot water heater (30 gal), and 3) a 300,000-Btu/hr boiler at LBL used for heating a laboratory building. During sampling of the steam generator, enough heat was transferred from the stack gases to the filter holder to prevent water condensation on the filter. For the boiler and water heater, the filter holder was heated to ~225°F with a length of electrical heating tape. The volumetric flowrate of stack gas from the steam generator was calculated from operating parameters supplied by the plant superintendent. The stack gas flowrate from the boiler and water heater were determined from pitot tube measurements. The filter samples were analyzed for carbon by a total combustion/CO₂ evaluation technique.⁴ The results shown in Table 1 show wide variation in emission rates and indicate that the generation of particles is not a constant process. As the flame in a burner ignites, a short-term production of particles occurs, probably due to improperly mixed gases in the burner. The initial puff of particles may account for a sizeable fraction of the entire amount of particulate carbon released during the burning cycle of a domestic unit. Even apart from this, the steady-state emission factor of the small units is much greater than that of the large steam generator. Commercial installations are usually well-monitored, continuously burning, and frequently maintained in order to obtain the best economic return. In contrast, domestic units are neither as well designed nor carefully maintained and burn in cycles. From the data we propose emission factors within the following limits: commercial use of natural gas, 0.003-0.007 µg C/Btu; domestic use of natural gas, 0.2-2.5 µg C/Btu.

Vehicular Gasoline Emission Factor

We use Refs. 5, 6, and 7 and some of our own measurements to estimate the range of automotive emission factors for particulate carbon and lead. In all cases, the figures quoted are corrected for the 3:1 preponderance of leaded gasoline used vs. unleaded fuel.

Emission rates for highway driving in the ranges of 0.03-0.08 g C/mile and 0.01-0.05 g Pb/mile can be found in the literature. These rates are consistent with a [C/Pb] ratio of 2.2 ± 0.35 observed by us on a set of particulate samples taken in the exhaust vent of a local freeway tunnel; so we propose emission rates per gallon of "composite" gasoline of 0.6-1.6 g C/gallon and 0.2-1.0 g Pb/gallon.

Driving under urban conditions involves acceleration, deceleration, and the use of the choke on a cold engine. These have a strong influence of the emission of particulates, especially carbon. Emission rates of 0.1-0.4 g C/mile and 0.03-0.08 g Pb/mile have been reported.

Table 1. Particulate carbon released during combustion of natural gas.

Source	g C/Btu	Comments
50,000-lb steam/hr generator, campus	0.005	Exhaust gas flowrate calculated from CH ₄ feed rate, stoichiometry, and 2% excess O ₂ , @ 310°F (pitot tube was not available at this time for Q meas.).
Domestic water heater, LBL Bldg. 44	2.81	Sample collection began ~5 sec after ignition.
"	1.85	Sample collection began 3.5 min after ignition.
Heating boiler, LBL Bldg. 73A	1.29	Sample collection began 1-2 min after ignition.
"	1.00	Sample collection included initial puff of particles at ignition but stack was warmer than usual.
"	0.27	Boiler had been running ~30 sec before sampling started.
"	0.15	Sample included initial puff of particles, but entire sample period = 4 min.
"	0.46	Average of 4 determinations in which the first 30 sec of the firing cycle was sampled.
"	0.20	Sample collection began 30 sec after ignition and extended for a total of 3.0 min.

These are consistent with a [C/Pb] ratio of 7.8 ± 2.5 observed by us on a set of particulate samples taken in an underground parking garage. We assume a reduced fuel economy for this type of driving and propose emission rates per gallon of "composite" gasoline of 1-4 g C/gallon and 0.3-0.8 g Pb/gallon.

Diesel Emission Factor

The dominant use of diesel fuel is by heavy trucks, whose emissions are almost entirely carbonaceous. Emission rates of 0.5-4 g C/mile can be found in the literature, which correlate with the findings in Ref. 8 that diesel trucks emit approximately 25 times as much particulate carbon per mile as automobiles. We therefore propose emission rates in the range of 2.5-20 g C/gallon.

Jet Fuel Emission Factor

Estimates of the emission rate of carbonaceous particles from jet engine exhaust range from 1 to 5 g C/kg fuel consumed^{9,*} under full-power (takeoff) conditions. For the present calculation we shall use emission rates in the range of 3-15 g C/gallon jet fuel.

Heavy Fuel Oil Emission Factor

Power plants account for the major use of heavy fuel oil in the Bay Area. An emission factor for carbonaceous particulates in the

range of 0.05-1 g C/gallon fuel oil is comparable to the emission factors for other liquid fuels' use and is consistent with the total particulate emission estimates of Ref. 3.

Emission Factor Table

The above emission factor estimates may be conveniently summarized in Table 2.

Emission Inventory

Fuel use data from Ref. 3 show the following approximate annual consumption in 1975: natural gas (commercial), 3.9×10^{14} Btu; natural gas (domestic), 1.8×10^{14} Btu; gasoline (total), 2.1×10^9 gallons; diesel fuel, 2.4×10^8 gallons; heavy fuel oil, 3.6×10^8 gallons; and jet fuel, 1.5×10^8 gallons. This last figure is an estimate of the fraction of the jet fuel sold in the area that is consumed within its air volume. We shall assume a gasoline consumption breakdown of 60:40 weighted toward "urban" driving conditions, and then multiply the emission factor estimates by the fuel use data to arrive at the following breakdown for yearly particulate inputs to the Bay Area air basin. (See Table 3)

PREDICTIONS OF MODEL

From the above estimates we may predict a range of properties that the ambient aerosol could possess if it were composed entirely

Table 2. Emission factor table.

Fuel	Use	Grams produced per unit of fuel			Unit
		Lead	Carbon		
Natural gas	Commercial	0	0.003-0.007		10 ⁶ Btu
Natural gas	Domestic	0	0.2-2.5		10 ⁶ Btu
Gasoline	Highway	0.2-1.0	0.6-1.6		gallon
Gasoline	City	0.3-0.8	1.4		gallon
Diesel		0	2.5-20		gallon
Jet fuel			3-15		gallon
Heavy oil			0.05-1		gallon

Table 3. Particulate input (10⁹ g/year)

Fuel	Use	Lead	Carbon
Natural gas	Commercial	0	0.001-0.003
Natural gas	Domestic	0	0.04-0.45
Gasoline	Highway	0.17-0.84	0.5-1.35
Gasoline	City	0.38-1.01	1.26-5.04
Diesel		0	0.6-4.8
Jet fuel		0	0.45-2.25
Heavy oil		0	0.02-0.36
Total (10 ⁹ g/yr)		0.55-1.85	2.87-14.25

of primary particulate material. Taking median values of the carbon and lead inputs, a [C/Pb] ratio of around 7.1 is predicted; by taking extrema, a wide range of values is covered. We also note that the automotive use of gasoline is estimated to contribute between 1760 and 6390 tonnes of particulate carbon per year, while other sources may account for between 1110 and 7860 tonnes per year; in other words, nonautomobile sources may well account for a large fraction of the total primary particulate carbon. The median value of the particulate carbon input estimate is 8560 tonnes/year. This quantity may be used in simple diffusion/dispersion models for the Bay Area air volume to predict mean particulate carbon loadings from primary emissions of the order of 10 µg C/m³.

As a corollary, we note that if primary material were predominant in the ambient aerosol, we would expect to measure a good correlation coefficient between daily average carbon and lead loadings. This would occur if both were simply proportional to anthropogenic input rates (reflecting an average daily fuel use cycle) divided by a factor dependent on ventilation and air transport. A poor correlation coefficient could indicate that fuel use patterns varied widely from day to day, that there were selective

scavenging mechanisms for carbon and lead aerosols, or that there were mechanisms capable of the substantial production of carbonaceous particulates whose contribution was not proportional to the lead input to the atmosphere.

RESULTS FROM AMBIENT AEROSOL SAMPLING PROGRAM

Routine analysis of 24-hr ambient aerosol samples has been in effect for many months at two sites in the Bay Area air basin: Lawrence Berkeley Laboratory, Berkeley, and the Bay Area Pollution Control District monitoring station, Fremont. The mean monthly average [C/Pb] ratios and carbon particulate loadings are as follows:

Berkeley	Jun 77-Mar 78	[C/Pb] = 8.8 ± 1.3	180 samples
Fremont	Jul 77-Feb 78	[C/Pb] = 12.9 ± 2.2	126 samples
Berkeley	Jun 77-Jul 78	$\bar{C}$ = 6.9 ± 1.2 µg/m ³	286 samples
Fremont	Jul 77-Aug 78	$\bar{C}$ = 11.7 ± 3.1 µg/m ³	295 samples

The correlation coefficients for particulate carbon and lead loadings on the 24-hr samples were high at both sites: Berkeley, $r = 0.84$; Fremont, $r = 0.83$.

CONCLUSIONS

The emissions factors we have presented are necessarily approximate, covering a wide range of values reported in the literature. However, we see that it is possible to construct a plausible model for the inputs of particulate carbon and lead which may account for the observed loadings of these constituents of the ambient aerosol by consideration of primary sources alone. This model does not set limits on the possible relative importance of primary and secondary contributions to the ambient aerosol, but it shows that one may account for phenomena observed in the Bay Area without the need for dominantly large quantities of secondary material. The wide ranges of reported emission factors, coupled with this demonstrated importance of primary particulate emissions, show that much more source sampling is necessary before better estimates of the probable composition of the ambient aerosol can be achieved.

FOOTNOTES AND REFERENCES

*An emission factor may be obtained from Ref. 3 by dividing total particulate input estimates by fuel use data.

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Relative Importance of Various Sulfate Production Mechanisms in Aqueous Droplets

R. Toossi, et al.

Atmospheric sulfate, a major constituent in ambient aerosol particles, is presumably formed by the oxidation of SO_2 . The dominant mechanisms responsible for this transformation have not yet been established. One set of mechanisms thought to be important involves the dissolution of SO_2 in water droplets. When liquid water is present, as in clouds, fog, and plumes, the atmospheric SO_2 can dissolve in the droplets and be oxidized to sulfate. The purpose of this paper is to compare the relative importance of various SO_2 oxidation mechanisms in aqueous droplets.

The systems considered in our box-type calculation are: $\text{SO}_2\text{-H}_2\text{O}(\ell)\text{-air}$; $\text{NH}_3\text{-SO}_2\text{-H}_2\text{O}(\ell)\text{-air}$; $\text{O}_3\text{-SO}_2\text{-H}_2\text{O}(\ell)\text{-air}$; $\text{NH}_3\text{-O}_3\text{-SO}_2\text{-H}_2\text{O}(\ell)\text{-air}$; $\text{Fe}^{+3}\text{-SO}_2\text{-H}_2\text{O}(\ell)\text{-air}$; $\text{NH}_3\text{-Fe}^{+3}\text{-SO}_2\text{-H}_2\text{O}(\ell)\text{-air}$; $\text{Mn}^{+2}\text{-SO}_2\text{-H}_2\text{O}(\ell)\text{-air}$; and soot- $\text{SO}_2\text{-H}_2\text{O}(\ell)\text{-air}$. The kinetics of each of these processes, other than the soot-catalyzed reactions, have been studied by many investigators. The results of Beilke et al,¹ Erickson et al,² Freiberg,³ and Matteson et al⁴ for oxygen, ozone, iron,

and manganese systems respectively were used in this calculation. The aqueous oxidation rate of SO_2 on soot is from the work of Chang et al.⁵ The following initial conditions were used in the calculation: liquid water, 0.05 g/m³; SO_2 , 0.01 ppm; O_3 , 0.05 ppm; and CO_2 , 0.000311 atm. For NH_3 a concentration of 5 ppb was used, which is higher than the highest equilibrium partial pressure of NH_3 over the United States as calculated by Lau and Charlson.⁶ Concentrations of particulate Fe and Mn of 250 ng/m³ and 20 ng/m³ respectively were assumed. However, only 0.13% of the total iron and 0.25% of the manganese are water soluble, according to Gordon et al.⁷ A soot particle concentration of 10 $\mu\text{g}/\text{m}^3$ was assumed. Tables 1 and 2 list the equilibrium equations and oxidation rate equations used for this comparative study.

The following assumptions were made in the calculations:

1. The size of liquid water drops suspended inside the box is so small that the absorption

Table 1. Chemical equilibria in SO₂-NH₃-CO₂-H₂O(l) system.^a

1. $\text{H}_2\text{O} \xrightleftharpoons{K_w} \text{H}^+ + \text{OH}^-$	$K_w = 1.008 \times 10^{-14}$
2. $\text{CO}_2(\text{g}) + \text{H}_2\text{O}(\text{l}) \xrightleftharpoons{H_c} \text{CO}_2 \cdot \text{H}_2\text{O}$	$H_c = 3.4 \times 10^{-2}$
3. $\text{CO}_2 \cdot \text{H}_2\text{O} \xrightleftharpoons{K_{1c}} \text{HCO}_3^- + \text{H}^+$	$K_{1c} = 4.45 \times 10^{-7}$
4. $\text{HCO}_3^- \xrightleftharpoons{K_{2c}} \text{CO}_3^{2-} + \text{H}^+$	$K_{2c} = 4.68 \times 10^{-11}$
5. $\text{NH}_3(\text{g}) + \text{H}_2\text{O}(\text{l}) \xrightleftharpoons{H_a} \text{NH}_3 \cdot \text{H}_2\text{O}$	$H_a = 57$
6. $\text{NH}_3 \cdot \text{H}_2\text{O} \xrightleftharpoons{K_a} \text{NH}_4^+ + \text{OH}^-$	$K_a = 1.77 \times 10^{-5}$
7. $\text{SO}_2(\text{g}) + \text{H}_2\text{O}(\text{l}) \xrightleftharpoons{H_s} \text{SO}_2 \cdot \text{H}_2\text{O}$	$H_s = 1.24$
8. $\text{SO}_2 \cdot \text{H}_2\text{O} \xrightleftharpoons{K_{1s}} \text{HSO}_3^- + \text{H}^+$	$K_{1s} = 1.7 \times 10^{-2}$
9. $\text{HSO}_3^- \xrightleftharpoons{K_{2s}} \text{SO}_3^{2-} + \text{H}^+$	$K_{2s} = 6.24 \times 10^{-8}$
10. $\text{HSO}_4^- \xrightleftharpoons{K_{3s}} \text{H}^+ + \text{SO}_4^{2-}$	$K_{3s} = 1.2 \times 10^{-2}$

^aConcentration in mole/l and gas pressures in atmospheres.

rate of gaseous species (SO₂ and NH₃) is governed by chemical reactions.

2. There is no mass transfer of any species across the box during the reaction. Therefore, the SO₂ (and NH₃) in each box is depleted with time. The mass balance of the sulfur and ammonia (i.e., $\Delta[\text{SO}_2]_{\text{g}} = \Delta[\text{SO}_2 \cdot \text{H}_2\text{O}] + \Delta[\text{HSO}_3^-] + \Delta[\text{SO}_3^{2-}] + \Delta[\text{HSO}_4^-] + \Delta[\text{SO}_4^{2-}]$, and $\Delta[\text{NH}_3]_{\text{g}} = \Delta[\text{NH}_3 \cdot \text{H}_2\text{O}] + \Delta[\text{NH}_4^+]$) is always maintained.

3. The growth of liquid water droplets due to the vapor pressure lowering effect of the sulfuric acid formed in the droplets is neglected.

The amount of sulfate formed as a function of time was calculated according to the following procedure:

1. Initially, the droplets achieve chemical equilibrium with CO₂, SO₂, and NH₃ at the partial pressures adopted. The $[\text{H}^+]$, $[\text{SO}_2 \cdot \text{H}_2\text{O}]$, $[\text{HSO}_3^-]$, $[\text{SO}_3^{2-}]$, $[\text{NH}_3 \cdot \text{H}_2\text{O}]$, and $[\text{NH}_4^+]$ are calculated when HSO₄⁻ and SO₄²⁻ are equal to zero.

2. Assuming a time step Δt , the $[\text{HSO}_4^-]$ and $[\text{SO}_4^{2-}]$ are calculated with the aid of the corresponding reaction rate law for each process.

Table 2. Rate of SO₂ oxidation by various mechanisms in aqueous droplets.

Mechanism	Reaction rate law
O_2	Rate = $\frac{H_s(k_2 + k_{10}K_w/[H^+])K_{2s}k_3}{k_{-2}[H^+]^2 + k_{-10}[H^+] + K_{2s}k_3} P_{\text{SO}_2}$
O_3	Rate = $\{k_4[\text{HSO}_3^-] + k_5[\text{SO}_3^{2-}]\}[\text{O}_3 \cdot \text{H}_2\text{O}]$
Fe^{+3}	Rate = $\frac{k_0 k_s^2 H_s^2 P_{\text{SO}_2}^2 [\text{Fe}^{+3}]}{[H^+]^3}$
Mn^{+2}	Rate = $3.67 \times 10^{-3} [X] - 1.17 \{ [\text{HSO}_4^-] + [\text{SO}_4^{2-}]^2 \} \{ [\text{Mn}^{+2}] - [X] \} \times [\text{H}_2\text{O}(\text{l})]^{-2}$ where $X = \frac{k_1 H_s P_{\text{SO}_2} [\text{Mn}^{+2}]}{k_1 \{ H_s P_{\text{SO}_2} + [\text{H}_2\text{O}(\text{l})] [\text{Mn}^{+2}] \times 10^{-6} \} + 0.17}$
Soot	Rate = $k_6 [C_x] [\text{O}_2]^{0.7}$ where $[\text{H}_2\text{O}(\text{l})]$ in cc/m ³ , concentration in mole/l, gas pressure in atm and time in sec. $k_0 = 151.69$ l/mole-sec, $k_s = 1.84 \times 10^{-2}$ mole/l, $k_1 = 8.12 \times 10^4$ l/mole-sec, $k_2 = 3.4 \times 10^6$ sec ⁻¹ , $k_{-2} = 2 \times 10^8$ l/mole-sec, $k_{10} = 2.9 \times 10^5$ l/mole-sec, $k_{-10} = 2.3 \times 10^{-7}$ sec ⁻¹ , $k_3 = 1.7 \times 10^{-3}$ sec ⁻¹ , $k_4 = 1.1 \times 10^5$ l/mole-sec, $k_5 = 7.4 \times 10^8$ l/mole-sec, $k_6 = 1.8 \times 10^{-4}$ l ^{0.7} ·mole ³ /gr·sec

Table 3. Comparison of the relative significance of various SO₂ conversion processes in aqueous droplets.

Mechanisms	1 hr		6 hr		12 hr		24 hr	
	SO ₄ ⁼ μg/m ³	% conv.	SO ₄ ⁼ μg/m ³	% conv.	SO ₄ ⁼ μg/m ³	% conv.	SO ₄ ⁼ μg/m ³	% conv.
Mn ⁺²	2.55x10 ⁻⁵	6.2x10 ⁻⁵	1.6x10 ⁻⁴	3.9x10 ⁻⁴	3.1x10 ⁻⁴	7.5x10 ⁻⁴	6x10 ⁻⁴	1.45x10 ⁻³
O ₂	1.8x10 ⁻³	4.3x10 ⁻³	9.6x10 ⁻³	2.3x10 ⁻³	1.8x10 ⁻²	4.4x10 ⁻²	3.4x10 ⁻²	8.2x10 ⁻²
Fe ⁺³	4.7x10 ⁻³	1.1x10 ⁻²	2.1x10 ⁻²	5x10 ⁻²	3.3x10 ⁻²	8.0x10 ⁻²	4.8x10 ⁻²	0.12
O ₃	0.13	0.33	0.27	0.66	0.35	0.85	0.47	1.13
O ₂ -NH ₃	0.52	1.26	1.54	3.7	2.02	4.89	2.50	6.1
Fe ⁺³ -NH ₃	2.3	5.6	3.2	7.76	3.6	8.75	3.9	9.45
O ₃ -NH ₃	4.51	10.94	5.14	12.5	5.28	12.8	5.28	12.8
C _x	1.8	4.4	10.8	26.4	21.6	52.4	41.25	100

Concentration: H₂O(l): 0.05 g/m³; SO₂: 0.01 ppm (10⁻⁸ atm); NH₃: 5 ppb (5x10⁻⁹ atm); O₃: 0.05 ppm (5x10⁻⁸ atm); Mn⁺²: 20 ng x 0.25%/m³; Fe⁺³: 250 ng x 0.13%/m³; C_x: 10 μg/m³; temp.: 10°C.

Fig. 1. Comparison of the relative significance of various SO₂ conversion processes in aqueous droplets. (XBL 782-4614)

3. Gaseous SO₂ and NH₃ are depleted. The remaining [SO₂] and [NH₃] are calculated using the mass balance equation.

4. Then the [H⁺], [SO₂·H₂O], [HSO₃⁻], [SO₃⁼], [NH₃·H₂O], and [NH₄⁺] are again calculated and the process is repeated until a 24-hour period is completed.

The results of this calculation are given in Table 3 and in Fig. 1. The conversion rate of SO₂ to sulfate by the soot process is 4.4%,

very close to the rate observed in many field studies. Aqueous oxidation of SO₂ by the Mn⁺², O₂, Fe⁺³, and O₃ processes does not appear to be important without the presence of a high concentration of NH₃. When there is a high concentration of NH₃ in the air, the O₃ and Fe⁺³ reactions can be important initially; but they slow down as the reaction proceeds because their reaction rates are inversely dependent on the acidity of the solution. From this comparison, we can conclude that the soot-catalyzed oxidation of SO₂ can be the dominant aqueous mechanism under realistic atmospheric conditions.

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SO₂ Oxidation in a Dispersing Plume

R. Toossi, et al.

INTRODUCTION

Theoretical prediction of the spatial distribution of pollutant concentrations and the ultimate fate of SO₂ oxidation in plumes is important in environmental impact studies. SO₂ oxidation reactions in plumes are governed by both chemical and dispersion processes, which cannot be treated separately. Under unstable or slightly stable atmospheric conditions, plume reaction rates may be controlled by the rate of mixing and dilution by ambient air. A first or second order reaction rate has usually been considered in studies of SO₂ oxidation in plumes. However, in a recent paper,¹ it is suggested that the rate of plume expansion and quenching has a controlling influence on the order of the reaction. Many homogeneous² and heterogeneous³⁻⁶ reactions are considered to be responsible for SO₂ oxidation in plumes. However, the role of soot particles emitted in large amounts by the combustion sources had been discounted until Novakov et al.⁷ showed that under certain conditions, these particles can be responsible for the major conversion of sulfur dioxide to sulfate. Chang et al.⁸ recently extended the research on the reactivity of these particles in aqueous solutions of pH between 1.45 and 7.4. The reaction was first order with respect to carbon concentration in the solution and was independent of pH and dissolved SO₂ concentration. A box-type calculation comparing the relative importance of "wet" soot-particle-catalyzed reactions with other catalytic reactions has been carried out. These calculations show that the soot-catalyzed oxidation of SO₂ can be the dominant mechanism under realistic atmospheric conditions (see R. Toossi et al., "Life time of droplets evaporating in ambient air" in this report).

Liquid water may condense on the soot particles when plumes of hot exhaust gases cool rapidly through mixing with ambient air or as they pass through fog and cloud banks. A model for SO₂ oxidation in a dry environment plume was presented earlier.⁹ The purpose of this study is to extend the model to predict the spatial distribution of sulfate concentration downwind from a plume resulting from aqueous oxidation of SO₂ catalyzed on soot particles.

MATHEMATICAL FORMULATION

The basic assumptions are:

1. Particulates are mainly fine soot particles which follow the streamlines of the gaseous pollutants and therefore can be treated as gases; i.e., $Ta \cdot Re_p \ll 1$, where $Ta = \rho_p \cdot r_p / \rho_g \cdot R$ is the Taylor number and $Re_p = \bar{u} \cdot r_p / \nu$ is the Reynold number based on particle radius r_p and gas kinematic viscosity ν .
2. Flow velocity perpendicular to the plume trajectory is neglected.
3. Plumes are ejected from stacks which are sufficiently high and have enough source strength to ensure that the intensity of atmospheric turbulence is much less than that associated with the turbulent plume.
4. Velocity, density, and pollutant concentration profiles are similar in all sections normal to the plume. The validity of this assumption is verified experimentally by Ooms.¹⁰
5. Boussinesq's approximation is valid, i.e., density variation affecting inertia is neglected. This assumption is valid when the initial fractional density difference $\rho_\infty - \rho_i / \rho_\infty$ is smaller than 0.5.¹¹
6. Molecular transport is neglected compared to turbulent transport.

The coordinate system is shown in Fig. 1, where v is the cross wind velocity, assumed constant with z for simplicity; u , ρ , and c_j 's are velocity, density, and species concentration respectively. The plume centerline makes an angle θ with the horizontal. The symbol s is the distance along the plume axis from the stack and b is the plume radius. We relate s and θ to the Cartesian coordinate by

$$z = \int_0^s \sin \theta \, ds \quad (1)$$

Fig. 1. Coordinate system. P , T , and u are the potential density, absolute temperature, and velocity; b is half the plume diameter, and V is wind velocity. (XBL 7710-2048)

and

$$x = \int_0^s \cos \theta \, ds \quad (2)$$

Governing equations consist of conservation of mass, momentum, energy, and chemical species as follows:

$$\text{Mass: } \frac{d}{ds} \int u \, dA = \epsilon \quad (3)$$

where $\epsilon = 2\pi b [\alpha |u - v \cos \theta| + \beta |v \sin \theta|]$ and α and β are entrainment coefficients determined experimentally.

Momentum along s direction:

$$\frac{d}{ds} \int u^2 \, dA = \frac{g \sin \theta}{\rho_1} \int (\rho_\infty - \rho) \, dA + \epsilon v \cos \theta \quad (4)$$

where g is acceleration of gravity.

Momentum in transverse direction

$$\frac{d\theta}{ds} \int u^2 \, dA = \frac{g \cos \theta}{\rho_1} \int (\rho_\infty - \rho) \, dA - \epsilon v \sin \theta \quad (5)$$

Energy:

$$d/ds \int \rho u C_p (T - T_\infty) \, dA = \rho_\infty \epsilon C_p (T - T_\infty) \quad (6)$$

where C_p is the specific heat.

Chemical species:

$$d/ds \int C_j u \, dA = \epsilon C_{j,\infty} + \int W_j'' \, dA \quad j=1, \dots, N \quad (7)$$

C_j is the concentration of species j inside the plume, W_j'' is the rate of production of species j , and N is the number of species examined. The subscripts ∞ and 1 denote the value in the background ambient condition outside the plume trajectory, and at the plume stack height.

Equations 1 through 7 can be solved numerically for $(N + 4)$ unknowns ρ , u , b , θ , C_1 , $C_2, \dots, C_N$. Initial conditions are values of the above parameters at the stack. The rate law can be written as

(8)

$$\frac{d[\text{sulfate}]}{dt} = W_{\text{sulf}}'' = A [C_X] [O_2]^n \exp \left(\frac{-5888}{T} \right)$$

where $A = 9.61 \times 10^4 \, \text{g}^n/\text{g} \cdot \text{sec} \cdot \text{mole}^{n-1}$. $[C_X]$ is soot concentration in gr/ℓ . $[O_2]$ is dissolved oxygen concentration in mole/ℓ and $n = 0.7$. Assuming all sulfate produced is in the form of sulfuric acid, Eq. (8) can be written

$$\frac{d[\text{sulf}]}{dt} = W_{\text{sulf}}'' = A' [C_X] [O_2]^n \exp \left(\frac{-5888}{T} \right) \quad (8')$$

with $A' = 9.42 \times 10^6$ when sulfate and soot concentrations are expressed in units of g/m^3 . The rate of SO_2 depletion is

$$W_{\text{SO}_2}'' = \frac{64}{98} W_{\text{sulf}}'' \quad (9)$$

Also note that carbon acts only as a catalyst and therefore no carbon is destroyed or produced. We then have

$$W_{\text{soot}}'' = 0. \quad (10)$$

The set of differential equations with appropriate initial conditions is solved, using Gear-Hindmarsh integration routine, to evaluate plume trajectory and concentration of inert and reactive pollutants in the plume. At each point the conversion rate is evaluated from the following equation:

percent conversion =

$$\frac{C_{\text{SO}_2} - C_{\text{SO}_2}(t=0)}{C_{\text{SO}_2}} = 100 \left(1 - \frac{\pi b^2 u C_{\text{SO}_2}}{\Gamma_{\text{SO}_2}} \right) \quad (11)$$

As an example of the use of this model, the rate of sulfate formation from the Keystone #1 plant described in the LAPPES¹² study is considered. The plant geometry and meteorological data on three different days, along with other assumptions made in the calculations, are listed in Table 1.

RESULTS

The data in Table 1 show that the plume is moderately stable for all three days of

Table 1. Meteorological data and plant conditions for three worked examples (Ref. 12).^a

		Example 1 (May 3)	Example 2 (Oct. 9)	Example 3 (Oct. 10)
Velocity of effluent at the stack	u_i (m/sec)	21	10	20
Stack height	H (m)	244	244	244
Stack radius	b_i (m)	4.1	4.1	4.1
Stack temperature	T_i (°C)	160	115	135
SO ₂ flux at the stack	Γ_{SO_2} (gr/sec)	3500	1500	2900
Wind velocity	v (m/sec)	10	3	4
Potential temperature gradient	$d\theta/dz$ (°C/m)	2.5×10^{-3}	3.5×10^{-3}	10^{-3}
Ambient temperature	T_∞ (°C)	20	20	20
Ambient temperature at stack height	T_1 (°C)	17.6	17.6	17.6

^aOther parameters assumed in calculations:

Soot concentration at the stack $C_{i,1} = 0.36$ gr/m³

Water vapor concentration at the stack $C_{i,3} = 10.0$ gr/m³

Sulfate concentration at the stack $C_{i,sulf} = 0.0$ gr/m³

Background concentrations $C_{\infty,sulf} = C_{\infty,1} = C_{\infty,2} = 0.0$ gr/m³

Fig. 2. Plume trajectory. The dotted line is the centerline. Note the periodic nature of the plume due to the stratification. The plume eventually stabilizes at its maximum rise. (XBL 7710-2155)

interest. It is assumed that the effect of inversions is neglected since stack height is greater than the ground-level inversion depth.¹² The plume trajectory is calculated for these plumes and plotted for the plumes of October 9 in Fig. 2. It can be seen that most dispersion occurs in the first 30 minutes within a kilometer of the source. Thereafter the plume is stable and can travel several kilometers before touching the ground.

The periodic nature of the plume trajectory can be explained on physical grounds. When a volume of air mass expands adiabatically to a new position, it cools. However, if the temperature decrease is less than the atmospheric

lapse rate, the air mass is colder than the ambient air and is driven back to its original position. Under these conditions, the restoring force is balanced by the acceleration, so that

$$\rho \frac{g}{T} \frac{d\theta}{dz} \Delta z = \rho \frac{d^2 \Delta z}{dt^2}$$

$1/T \, d\theta/dz$ represents the change in density per meter of rise and $\theta = T + 0.0098 z$ is the potential temperature. The solution of this equation leads to the general form for a harmonic oscillation with frequency $\omega = g/T \, d\theta/dz$. Numerical calculations show that temperature and velocity in the plume approach their ambient values as the plume rises to the equilibrium rise. The entrainment rate decreases, and the plume expands very slowly. Transport becomes negligible, and chemical reactions can be considered as they occur in a static batch reactor.⁹

A graph of the concentration of sulfate and the percent of total SO₂ conversion is plotted on the single graph against the distance downstream from the stack and the time of travel in Fig. 3. As the plume travels downstream from the stack, total sulfate conversion increases. However, in the first kilometer of transport, the plume is significantly entrained. When the plume reaches its maximum height, the entrain-

Fig. 3. a) Sulfate concentration; and b) fraction converted in the plume as a function of distance downstream of the stack. Parameters used in the calculations are given in Table 1. (XBL 7812-13506)

ment rate is insignificant and the chemical reaction is rate controlling. The result is a minima in the sulfate concentration curve at the point where the plume is appreciably bent. The conversion rate is 1.6% for the first hour and increases in a similar fashion to 40% in 24 hours at 250 km from the stack. The relative humidity has been taken as 100%, and therefore there is always some liquid water present for the wet mechanism to take place.

The effect of relative humidity on the rate of oxidation can be investigated by considering its effect on the lifetime of water droplets present in the plume gases. For this calculation we have assumed a surfactant layer on the droplet which reduces the evaporation coefficient to 10^{-6} . It has been shown that droplets of solution cannot theoretically evaporate completely if there is a formation of nonvolatile species inside the droplet. As the droplet evaporates, the concentration of nonvolatile species increases, which gradually reduces the vapor pressure of water at the droplet surface below that of ambience. Under these conditions, a droplet becomes so concentrated that the validity of the Henry, Raoulet Law and the Debye-Huckel theory¹³ becomes inadequate.

The lifetime of the droplets has been taken as the time in which the droplets reach this concentration, and therefore calculations have been stopped. At this point, we do not know how long the oxidation reaction proceeds thereafter. Research is under way to solve this problem.

The rate of oxidation is calculated for three examples and is tabulated in Table 2. These calculations show that although the reaction rate is independent of the liquid water concentration, total conversion inside the plume depends strongly on ambient humidity. As long as humidity is high enough to ensure the presence of enough

Table 2. Percent of SO₂ conversion under different meteorological conditions, $\alpha = 10^{-6}$, T = 20°C.

Example 1						
Time(hr)						
R.H.	1	2	4	6	12	24
100	1.6	3.1	6.1	9.0	17.8	35.6
95	1.6	3.1	6.1	9.0	17.8	
90	1.6	3.1	6.1			
80	1.6	3.1				
70	1.6	3.1				
60	1.6	3.1				
50	1.6					

Example 2						
Time(hr)						
R.H.	1	2	4	6	12	24
100	1.6	3.3	6.6	10.0	19.7	39.5
95	1.6	3.3	6.6	10.0	19.7	
90	1.6	3.3	6.6			
80	1.6	3.3				
70	1.6	3.3				
60	1.6					
50	1.6					

Example 3						
Time(hr)						
R.H.	1	2	4	6	12	24
100	1.8	3.5	6.9	10.4	20.8	40.8
95	1.8	3.5	6.9	10.4	20.8	
90	1.8	3.5	6.9			
80	1.8	3.5				
70	1.8	3.5				
60	1.8					
50	1.8					

liquid water around the soot nuclei, the wet mechanism prevails.

CONCLUSIONS

Based on the calculations presented in this report, it is concluded that under certain meteorological conditions, catalytic oxidation of SO₂ on soot particles, emitted as the natural products of incomplete combustion, can be very important, for the production of sulfate in plumes. The discrepancies on the data reported in the literature on the SO₂ conversion rate might be related in part to variations in particulate emissions and in ambient humidity.

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Lifetime of Liquid Water Drops in Ambient Air: Consideration of the Effects of Surfactants and Chemical Reactions

R. Toossi, et al.

INTRODUCTION

Heterogeneous reactions involving liquid water have recently been a subject of great interest to environmentalists and air pollution scientists. The degree of importance that the aqueous reactions play in the atmosphere depends on three factors: (1) rate of chemical reaction, (2) availability and nature of the condensation nuclei, and (3) lifetime of the liquid drops in the atmosphere. The rate of growth or depletion of the water droplets can be calculated by simultaneous solution of the diffusion and energy equations around the droplet.

$$\nabla^2 n(r) = 0 \quad (1)$$

$$\nabla^2 T(R) = 0 \quad (2)$$

where n is the concentration of the vapor molecule and T is the temperature at distance R from

the droplet center. Boundary conditions are given by the values of n and T at large distances from the drop and by assuming that the equilibrium between vapor and temperature holds at the droplet surface. Using this approach and assuming a hyperbolic vapor density distribution,

$$\rho = (\rho_r - \rho_\infty) \left(\frac{r}{R} \right) + \rho_\infty \quad (3)$$

Mason¹ derived the rate of growth or evaporation of a droplet of radius r for quasi-steady-state condition and a small Knudsen number as follows:

$$r \frac{dr}{dt} = \frac{P_\infty - P_s}{\frac{L^2 \rho_\ell P_s}{KR_V T^2} + \frac{R_V T \rho_\ell}{D}} \quad (4)$$

P_∞ and P_s are ambient vapor pressure and saturated vapor pressure over the droplet surface, D is the vapor diffusion coefficient, K is the thermal conductivity of the gas, L is the latent heat of condensation, and ρ_ℓ is the density of the liquid droplet. Equilibrium vapor pressure over a droplet's surface depends on its curvature and concentration of solute in the solution droplet and is given by²

$$P_s = P_s(\infty) \exp\left(\frac{2\sigma}{rR_v\rho_\ell T}\right) \cdot \left(\frac{n_0}{n+n_0}\right) \quad (5)$$

where $P_s(\infty)$ is the saturation vapor pressure over the bulk of the water, with surface tension σ at temperature T . n_0 and n are molar concentrations of water and solute. When a droplet is large enough for the Kelvin effect to be negligible, P_s will be independent of the radius; and Eq. (4) predicts a linear change in the surface area of the drop as a function of time. When the mean free path of escaping molecules is large compared with the droplet diameter (large Knudson number), the continuum theory as applied above fails, and the classical kinetic theory of gases can be applied to determine the evaporation rate.³ However, this condition applies only for submicron droplets or at reduced pressure, which is of little significance in atmospheric studies. Equation (4) approximates the rate of change of droplet surface area to a good accuracy for pure water droplets where diffusion in the gas phase is the rate controlling mechanism. For the atmospheric droplets, where a layer of surfactants is often present, resistance in the interphase is dominant and Eq. (4) underestimates the lifetime of drops up to many orders of magnitude. For example, according to Eq. (4), it takes only a fraction of a second for a 1.0- μm particle to vanish completely in an atmosphere saturated with water vapor. However, experiments of Gurdis et al.⁴ show that it takes 40 minutes for a drop of 4.0 μm size to reduce to 0.74 μm in a mixture of 70% hydrogen and 30% air. Similar results have also been found in our laboratory (see W. H. Benner et al., "SO₂ oxidation by water droplets containing combustion nuclei" in this report).

The evaporation rate of droplets containing insoluble monolayers for nonvolatile droplets ($L=0$) has been calculated elsewhere.⁵⁻⁶ According to these theories, the droplet evaporation occurs in a virtually vacuous spherical shell, of thickness Δ comparable to the mean free path of the diffusing molecule. The evaporation takes place in a Knudson flow. The second step is diffusion of the vapor shell at $r + \Delta$ (Fig. 1). Using the Maxwell equation of diffusion and making the mass balance between the molecules arriving at the shell surface at distance $r + \Delta$ and leaving by diffusion, the rate of evaporation can be written as

$$r \frac{dr}{dt} = \frac{P_\infty - P_s}{\rho_\ell R_v T \left(\frac{1}{r\alpha} + \frac{r}{r+\Delta} \right)} \quad (6)$$

Fig. 1. Model of a solution droplet of radius a covered by a thin layer of surfactant of thickness δ . Δ is the molecular flow layer thickness. R_ℓ , R_i , and R_g are resistance in the bulk of the liquid, at the interface, and in the gas phase respectively. (XBL 7812-13501)

where $v = \bar{v}/4$ and $\bar{v}$ is the velocity of the evaporating molecule calculated from the kinetic theory of gases, $\Delta = KT/AR$ is the distance between collisions. The collision cross section is $A = \pi(a_1 + a_2)^2$ where a_1 and a_2 are the radii of the diffusing and ambient gaseous molecules. The evaporation coefficient α is a function of the film thickness δ' and the degree of coverage and the nature of the monolayer. Deryaguin et al.⁸ determined a critical film thickness, beyond which a surface active material strongly suppresses any exchange of water vapor, either through condensation or evaporation.

FORMULATION OF THE PROBLEM

The general form of a governing equation describing evaporation and the growth of droplets can be derived by combining Eqs. (4) through (6). Assuming that resistance through the liquid drop is negligible, and taking $\rho_{eq}(\infty)$ as the equilibrium vapor density at large distances from the droplet, the evaporation rate for the drop shown in Fig. 1 can be written as

$$r \frac{dr}{dt} = \frac{\rho_{eq}(\infty)}{\rho_\ell} \cdot \frac{S - \frac{n_0}{n+n_0} \exp(2\sigma\rho_{eq}(\infty)/r\rho_\ell)}{R_i + R_g + R_k} \quad (7)$$

where $S = P_\infty/P_s$ is the saturation ratio,

$R_i = 1/r\alpha$ is the resistance in the interface,

Table 1. Chemical equilibria in a droplet system

Reaction	Equil. constant expression ^a	Value of equil. constant at 25°C
$\text{H}_2\text{O} \rightleftharpoons \text{H}^+ + \text{OH}^-$	$K_w = [\text{H}^+][\text{OH}^-]\gamma^+\gamma^-$	1.008×10^{-14}
$\text{SO}_2(\text{g}) + \text{H}_2\text{O} \rightleftharpoons \text{SO}_2 \cdot \text{H}_2\text{O}$	$H_s = [\text{SO}_2 \cdot \text{H}_2\text{O}] / P_{\text{SO}_2}$	1.24
$\text{SO}_2 \cdot \text{H}_2\text{O} \rightleftharpoons \text{H}^+ + \text{HSO}_3^-$	$k_{1s} = [\text{H}^+][\text{HSO}_3^-]\gamma^+\gamma^- / [\text{SO}_2 \cdot \text{H}_2\text{O}]$	0.0127
$\text{HSO}_3^- \rightleftharpoons \text{H}^+ + \text{SO}_3^{2-}$	$k_{2s} = [\text{H}^+][\text{SO}_3^{2-}]\gamma^+\gamma_2^- / [\text{HSO}_3^-]\gamma^-$	6.24×10^{-8}
$\text{NH}_3(\text{g}) + \text{H}_2\text{O} \rightleftharpoons \text{NH}_3 \cdot \text{H}_2\text{O}$	$H_a = [\text{NH}_3 \cdot \text{H}_2\text{O}] / P_{\text{NH}_3}$	57
$\text{NH}_3 \cdot \text{H}_2\text{O} \rightleftharpoons \text{NH}_4^+ + \text{OH}^-$	$K_a = [\text{NH}_4^+][\text{OH}^-]\gamma^+\gamma^- / [\text{NH}_3 \cdot \text{H}_2\text{O}]$	1.774×10^{-5}
$\text{CO}_2(\text{g}) + \text{H}_2\text{O} \rightleftharpoons \text{CO}_2 \cdot \text{H}_2\text{O}$	$H_c = [\text{CO}_2 \cdot \text{H}_2\text{O}] / P_{\text{CO}_2}$	0.034
$\text{CO}_2 \cdot \text{H}_2\text{O} \rightleftharpoons \text{H}^+ + \text{HCO}_3^-$	$K_{1c} = [\text{H}^+][\text{HCO}_3^-]\gamma^+\gamma^- / [\text{CO}_2 \cdot \text{H}_2\text{O}]$	4.45×10^{-7}
$\text{HCO}_3^- \rightleftharpoons \text{H}^+ + \text{CO}_3^{2-}$	$K_{2c} = [\text{H}^+][\text{CO}_3^{2-}]\gamma^+\gamma_2^- / [\text{HCO}_3^-]\gamma^-$	4.68×10^{-11}

^aThe activities follow the Davies relation $(21) \log \gamma_z = (-Az^2 \sqrt{I}) / (1 + \sqrt{I}) + 0.2IAz^2$, where I is the ionic strength, $I = 1/2 \sum_i |c_i|z_i^2$, and $A = 0.5085$ for water at 25°C.

$R_g = r/D(r+\Delta+\delta)$ is the resistance to mass diffusion,

The thermal conductivity and diffusion coefficient are approximated by the empirical relations

$R_k = bL/K$ is the resistance to heat diffusion,

and $b = L \cdot \rho_{\text{eq}}(\infty) / R_v T^2$ is the slope of the vapor density equilibrium curve $(\Delta V / \Delta T)$.

$$K(T) = 5.803 \times 10^{-5} \left(\frac{393}{T+120} \right) \left(\frac{T}{273} \right)^{3/2} \frac{\text{cal}}{\text{cm} \cdot \text{sec} \cdot \text{OK}}$$

$$D(T) = 0.226 \left(\frac{393}{T+120} \right) \left(\frac{T}{273} \right)^{5/2} \cdot \frac{1}{P} \text{ cm}^2/\text{sec}$$

Chemical Equilibrium in the Droplet System

It is assumed that the gaseous SO_2 , CO_2 , and NH_3 are in equilibrium with sulfite (IV), carbonate, and ammonium species in the aqueous droplet, as demonstrated by Beilke⁹ and Miller¹⁰. Table 1 lists the chemical equilibrium processes in the droplet-ambient system.

The latent heat of evaporation is also a function of temperature and can be approximated by the equation

$$L = -0.57 T + 753.1 \quad (L \text{ in cal/g and } T \text{ in } ^\circ\text{K})$$

RESULTS AND CONCLUSION

The rate of change of droplet size is found by solving Eq. (6) under different conditions. The molar concentration of solute n is taken as the summation of the total concentration of ions in the solution. Therefore it can be seen that this equation is coupled with the rate equation and other equilibrium equations used to explain the chemistry occurring in the solution droplet. It is assumed that the film thickness δ is much smaller than the droplet radius. Substituting for the values of the Boltzman constant and taking a_1 and a_2 as the radius of water vapor and air molecules, we have

$$\Delta = 4.86 \times 10^{-8} T/P \text{ cm}$$

$$v = 857 \sqrt{T} \text{ cm/sec}$$

between temperature range of interest, $253 < T < 313$. The value of $\sigma = 75$ dynes/cm and $\rho_0 = 1 \text{ gm/cm}^3$ is assumed for water. The values of σ strongly depend on the nature of the surfactants in the solution and can vary several orders of magnitude. For plain water, $\alpha = 0.034$. Reduction in the value of α to 6×10^{-6} resulted from coating the drop with a monomolecular layer of long-chain acids.¹¹ The importance of R_j relative to R in determining the rate of evaporation of droplets is reflected by the effect of trace impurities on the rate of evaporation. Table 2 gives the values of R_j and R_g in the limiting conditions for pure water droplets ($\alpha = 0.034$) and droplets containing a monolayer of insoluble surfactants ($\alpha = 10^{-6}$).

Thus a monolayer of a long-chain alcohol or acid should be able to reduce the rate of

Table 2. Comparison of the relative importance of the different film resistances to evaporation rate for different droplet size.

$T = 20^{\circ}\text{C}$, $\Delta = 1.425 \times 10^{-5} \text{ cm}$, $P = 1.0 \text{ atm}$, $b = 1.06 \times 10^{-6} \text{ }^{\circ}\text{K}^{-1}$				
$a \text{ (}\mu\text{m)}$	$R_i \text{ (sec}\cdot\text{cm}^{-2}\text{)}$		$R_g \text{ (sec}\cdot\text{cm}^{-2}\text{)}$	$R_k \text{ (sec}\cdot\text{cm}^{-2}\text{)}$
	$\alpha = 0.034$	$\alpha = 10^{-6}$		
0.1	200	6.02×10^6	1.60	10.08
1	20	6.02×10^5	3.41	10.08
10	2	6.02×10^4	3.84	10.08
50	0.4	1.2×10^4	3.88	10.08

evaporation by more than four orders of magnitude. The lifetime of a 10- μm drop in air of 80% relative humidity increased from 2.5 sec to 1300 sec¹² when α decreased from 0.04 to 1.5×10^{-5} . These results are based on the assumption that the solution effect is negligible. In practice the lifetime of these droplets can be longer because of the reduction in surface vapor pressure due to an increase in the solute concentration as the drop evaporates. This point will be discussed in more detail in the next section. Table 2 shows that for droplets of pure water smaller than 10 μm or at reduced pressure, R_g is small compared with R_i and R_k ; and therefore the rate is controlled by the rate of diffusion in the vacuum and by conduction. When a monolayer is present, however, a very small percentage of the water molecules striking the surface enter it, and a very high free energy of activation is needed to produce or find a hole in the liquid surface in which to be accommodated.

Figure 2 shows graphs of droplet lifetime as a function of ambient relative humidity

Fig. 2. Lifetime of droplets at different relative humidities. Different curves represent effects of surfactants on the lifetime. For a pure water droplet, $\alpha = 0.034$; and the lifetime is several orders of magnitude smaller than that of droplets covered by a thin film of surfactants. Other parameters used in the calculations are $T = 20^{\circ}\text{C}$, $R_0 = 5 \text{ }\mu\text{m}$, $P_{\text{SO}_2} = 10^{-8}$, $P_{\text{CO}_2} = 3 \times 10^{-4}$, and $P_{\text{NH}_3} = 5 \times 10^{-8} \text{ atm}$. (XBL 7812-13502)

Fig. 3. The effect of temperature on the lifetime of droplets. The lifetime is increased exponentially with a decrease in ambient temperature but varies linearly with inverse accommodation coefficient. R.H. = 80%, $R_0 = 5 \text{ }\mu\text{m}$, $P_{\text{SO}_2} = 10^{-8}$, $P_{\text{CO}_2} = 3 \times 10^{-4}$, and $P_{\text{NH}_3} = 5 \times 10^{-8} \text{ atm}$. (XBL 7812-13503)

and evaporation coefficients. These graphs show a strong moisture effect especially at relative humidities greater than 90%. The effect of temperature on the lifetime can be seen in Fig. 3. The evaporation rate is increased experimentally with an increase in temperature. When a slight amount of super-saturation is present, droplets start to grow. The rate of growth is a strong function of the supersaturation ratio and the nature of the surfactants. Fig. 4 shows the size that a 5- μm droplet reaches after it is exposed to 0.05% of supersaturation for 24 hr. When α is reduced most of the resistance is in the interface and since there is little chance of diffusing water vapor through this barrier, the droplet grows very slowly. When no surfactant is present, evaporation is diffusion controlled, the evaporation rate is independent of the evaporation coefficient α , and growth occurs very rapidly. The result is an S-shaped curve (Fig. 4).

When irreversible reactions lead to nonvolatile products in the droplet, their concentrations increase as the droplet evaporates and the solution effect eventually becomes important. This happens to many heterogeneous reactions occurring in atmospheric droplets. As an example,

Fig. 4. Growth of the droplets with supersaturation. Final radius of the droplets after 24-hr exposure in clouds with 0.05% supersaturation. $R_0 = 5.0 \mu\text{m}$, $T = 20^\circ\text{C}$, $P_{\text{SO}_2} = 10^{-8}$, $P_{\text{CO}_2} = 3 \times 10^{-4}$, and $P_{\text{NH}_3} = 5 \times 10^{-8}$ atm. (XBL 7812-13504)

catalytic oxidation of SO_2 on soot particles is considered here. The rate of reaction for this mechanism has been determined as¹³

$$\frac{d\{\text{HSO}_4^- + \text{SO}_4^{2-}\}}{dt} = A[\text{O}_2]^{0.7}[\text{C}_x]\exp(11500/R_v T) \quad (8)$$

where $A = 2.7 \times 10^{-13} \text{ mole}^{0.3}/\text{g} \cdot \text{sec}$, $[\text{C}_x]$ is the soot concentration, and $[\text{O}_2]$ is the dissolved oxygen concentration. This equation, together with the equilibrium relations listed in Table 1, the second dissociation step of the sulfuric acid,

Fig. 5. Change in the droplet size as a function of evaporation time when droplets contain soot particles and catalytic oxidation of SO_2 takes place in the liquid droplet. The dotted line represents the condition when equilibrium is present between the liquid and gaseous atmosphere. $R.H. = 80\%$, $T = 20^\circ\text{C}$, $\alpha = 10^{-6}$, $R_0 = 5.0 \mu\text{m}$, $P_{\text{SO}_2} = 10^{-8}$, $P_{\text{CO}_2} = 3 \times 10^{-4}$, and $P_{\text{NH}_3} = 5 \times 10^{-8}$ atm. (XBL 7812-13505)

and the charge balance

$$[\text{H}^+] = [\text{HSO}_4^-] + 2[\text{SO}_4^{2-}] + [\text{HSO}_3^-] + 2[\text{SO}_3^{2-}] + [\text{OH}]^- \quad (10)$$

has been solved at every point to calculate concentrations of products and the rate of evaporation of the droplet as a function of time. The dotted line in Fig. 5 represents the condition when the rate is assumed to be equal to zero. It is seen that as the droplet evaporates, solute concentration increases and eventually the vapor pressure reaches below the ambient level and the droplet starts to grow again (solid line). A short time later, the concentration of sulfate in the droplet is so high that, unfortunately, the validity of Henry's Law and the Debye-Huckel equations¹⁴ used in evaluating the activity coefficients failed and the calculations were stopped. Further research is under way to investigate the behavior of the droplets under highly concentrated conditions.

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Oil Shale Research

Strategies for the Abandonment of In Situ Oil Shale Retorts

P. Persoff, J. P. Fox, and P. K. Mehta

INTRODUCTION

Oil is produced from oil shale by the pyrolysis of kerogen at 500 C or higher in surface retorts or in situ. Porosity is introduced into the formation by fracturing (true in situ) or by mining 20-30% of the shale followed by explosive fracturing of the remainder (modified in situ). Mined oil shale from modified in-situ (MIS) retorts may be stockpiled or processed in surface retorts. In-situ retorting leaves behind large underground retorts of spent shale separated by pillars of raw shale and surface piles of raw or spent shale (MIS retorting).

In situ processing may result in a number of environmental problems including degradation of local surface and ground waters, low resource recovery, and subsidence. The target of present oil shale commercialization activities is the Mahogany zone in Colorado's Piceance Basin. The oil shale resource in this area is sandwiched between two confined aquifers. During mining and retorting, these aquifers are dewatered. When the site is abandoned, groundwater will reinvade the area and flow through the abandoned retorts, leaching potentially toxic or carcinogenic materials from the spent oil shale. This material may then be transported in local aquifers, withdrawn in wells, or discharged into the Colorado River system as base flow. This is shown schematically in Fig. 1.

The structural integrity of in situ oil shale retorts is presently a concern. Oil shale loses considerable strength during retorting. This has resulted in one collapse during retorting. The long term structural stability of the retorts is uncertain and inadequate pillar strength and spent retort porosity may result in retort creep and subsidence in the long term. Low resource recoveries have been experienced with the in situ process. This is due to technical problems with rubblization, and to the necessity to leave about 25% of the resource in place as pillars to provide structural strength.

The objective of this project is to develop techniques to prevent or mitigate the potential environmental effects described above. Many conventional techniques, such as grouting, may not be feasible because of the large volumes and high costs involved. Therefore, the focus of this program is on developing new technologies that exploit on-site waste products and oil shale chemistry.

This program is funded by DOE's Division of Environmental Control Technology and was started in June 1978.

ACCOMPLISHMENTS DURING 1978

A detailed assessment of environmental problems associated with in situ retorting and a literature

Fig. 1. Flow of leachates into gaining reach of a stream.
(XBL 791-178)

review on conventional control technologies used for related problems in other industries were completed. Preliminary estimates were made of the composition of leachate from in situ retorts and its probable dispersion and transport through local aquifers. These analyses indicated that it may take several centuries before significant degradation of local water resources occurs.

A variety of techniques has been used for flow blockage and strength development in underground formations in deep coal mining, oil field reservoir engineering, construction, and gas storage. An intensive literature survey was completed of the practices in these other industries and the resulting information interpreted in light of the unique problems facing in situ oil shale retorting. Conventionally, strength development and flow blockage are achieved by introducing a material called a grout into the formation. Materials used in these applications include portland cement, plastering agents, clays, emulsions, resins, gels, foams, and polymers. Preliminary cost estimates indicate that it could cost well in excess of several dollars per barrel of oil to apply these techniques to oil shale due both to the large quantity of material required to fill an in situ retort and to some rather unique problems in grout placement.

Cost analyses indicated that the only economically feasible solution would be one in which material costs were very low. This limited the range of possible solutions to those using on-site waste products or to novel approaches that do not require materials or difficult placement techniques. Possible solutions which have been identified include development of a hydraulic lime-pozzolan using surface retorted spent shale; placement of adsorbents, such as bentonite, into the abandoned retort; or formation of a CaCO_3 plug in situ using gas produced during retorting.

Production of a pozzolan from on-site waste materials is the most attractive option because it would simultaneously prevent surface and ground water disruption and provide for the disposal of surface spent shale. If sufficient strength could be developed, it might be possible to design retorts so that the pillars could be retorted, thus improving resource recovery. This technique is based upon the chemical similarity of spent shale and natural pozzolans which are siliceous and aluminous materials which combine with lime at ordinary temperatures to produce cohesive calcium silicate hydrates. Since spent shale has a substantial Ca content, true cementitious properties may be developed in spent shale by control of surface retorting conditions. A laboratory program has been initiated to determine the optimum cementitious properties that may be produced in spent shale. A summary of the proposed strategy under study is presented in Fig. 2.

- a. Add limestone before retorting if retorting temperature is high enough to calcine limestone.
- b. Add calcined limestone after retorting if retorting temperature is not high enough to calcine limestone.
- c. Portland cement addition only if strength development without it is inadequate.

Source: ref. 1

Fig. 2. Strategy for formation of a hydraulic lime-pozzolan from spent shale and its use for retort plugging. (XBL 791-248)

PLANNED ACTIVITIES FOR 1979

Laboratory studies will be conducted to determine how grouts may be prepared from available on site waste products. The production of a hydraulic lime-pozzolan and formulation of a CaCO_3 precipitate in situ will be studied. Grout distribution through a thousand feet of overburden in an area that includes fractures, fissures, large voids and micropores will be studied.

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Leaching of Organics from In Situ Spent Shale

W. G. Hall, R. E. Selleck, and J. F. Thomas

INTRODUCTION

In many areas of the oil shale region, particularly in the Piceance Basin in Colorado, groundwater aquifers surround oil shale deposits that are being considered for commercial development. During in situ retort preparation and retorting, groundwater levels adjacent to the development site will be lowered below the retorts by pumping. After oil recovery is complete, the returning groundwater may pass through the spent oil shale rubble and leach out organic and inorganic compounds. Some of these may be toxic or carcinogenic and may be transported through the aquifers to surface waters and wells.

The principal objective of this investigation is to develop reliable kinetic data for leaching of organic compounds from spent shale so that a predictive model of the in situ leaching process may be developed. This model will be used by the Oil Shale Research Group in the formulation and investigation of alternative schemes to mitigate the impact of the leachate from abandoned in situ retorts on the regional water resources. Total organic carbon (TOC) and total dissolved solids (TDS) are the principal parameters of interest, although specific organic and inorganic constituents present in the leachate will be identified. This program was initiated in June 1978 and is funded by the Department of Energy's Division of Environmental Control Technology.

A series of batch and continuous flow leaching experiments was completed in a previous LBL study by Amy and Thomas.¹ TOC and electrical conductivity (EC) were measured in leachates from four different in situ spent shales at various water temperatures, salinities and leaching times. A main conclusion was that the kinetics of leaching of TOC from the spent shale appear to follow the laws of mass transport in fixed bed reactors but that the TOC leaching isotherms were extremely non-linear.² This created difficulties in evaluating the magnitude of the external and internal liquid film transfer coefficients, and the rate limiting steps were not ascertained.

The approach of the present investigation is to pump tap water through tightly packed columns of spent shale of varying diameters and lengths (to accommodate three different sized particles). Approach velocities in the empty cross section are about 0.3 m per day. Samples of leachate are withdrawn from the columns at intermediate and terminal points and are analyzed for TOC and EC. Columns are operated continuously until the concentration of leached organics falls below the detection limit of the analytical method used. Estimates of the leachable organic isotherms will be obtained directly from the column studies.

These may be supplemented by batch studies as required.

Possible readsorption of leached organics in aquifer material will be investigated by placing columns containing crushed oil shale in series with the spent shale columns. The effects of high salt content on the leaching of organics will be evaluated by passing saline water through one of the smaller columns and then comparing the results with those obtained using tap water. The saline water will be dosed to simulate natural groundwater.

ACCOMPLISHMENTS DURING 1978

Fifty-five hundred kgs of spent shale were obtained from the Laramie Energy Technology Center's (LETC) 10-ton simulated in situ retort. The retort had been charged with 26 gallon-per-ton oil shale mined at Anvil Points, Colorado and ranging in size from fines to 60 cm. The maximum temperature reached during the run was 1200 F; steam was injected with the combustion air at a volume ratio of 67% air to 33% steam. Six leaching columns, 30 cm in diameter and 3 meters long, were constructed of standard galvanized corrugated steel culvert. Three smaller plastic columns with diameters from 10 to 15 cm were also constructed. A typical column is shown in Fig. 1. The columns are operated in the upflow mode with water entering the chamber at the bottom and leaving at the top. Sample taps of Tygon tubing are located at 15 cm intervals along the column so that leachate samples can be taken. Tap water is pumped from a reservoir by a variable speed Sigma pump set to deliver up to 10 ml per minute.

Results from one 220 hour long leaching run are shown on Fig. 2. A 10 cm diameter column was packed with spent shale particles having sizes from 0.3 to 1.3 cm. The shale column was 85 cm long. At the start of the run the column was filled rapidly with water and samples were taken immediately from each of the sample taps. Additional samples were then taken at intervals of 8 hours to 2 days. Figure 2 shows that the TOC concentration rapidly drops from the starting level to that of the influent in the time that it takes to pass six pore volumes of water. This suggests that it may be feasible to collect the leachate, treat it, and reinject it.

PLANNED ACTIVITIES FOR 1979

Additional column studies will be conducted to obtain data for development of a mathematical model of organic leaching. Two-media column studies will be conducted to study adsorption-desorption mechanisms during aquifer transport of the leachate. Detailed organic characterizations of the leachate will be performed using gas chromatography, mass spectrometry and high performance liquid chromatography.

Fig. 1. Large column experimental set-up for organic leaching and adsorption. (XBL 791-247)

Fig. 2. Effluent levels of total organic carbon in spent shale leachate. (XBL 791-246)

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Geochemical Studies of an Oil Shale Deposit

*B. Branstetter, R. D. Giauque, H. V. Michel, J. P. Fox,
R. B. Garrett, and L. Y. Goda*

INTRODUCTION

Oil shale is a marlstone that contains about 20% organic material. Green River oil shale was deposited from an ancient lake that covered parts of Colorado, Utah and Wyoming. This lake was probably permanently stratified. The upper portion may have supported an abundant microflora, and the lower layer was probably a sodium carbonate solution with a pH of 11 to 12. Oil shale was formed from constituents that entered this lake by overland runoff and atmospheric fallout of dust, pollen and volcanic ash. A complex series of geochemical processes produced the oil shale deposits that have appeared on the energy scene several times between 1850 and the present day.

The purpose of this program is to clarify the geochemistry of these deposits and develop information required to assess the deposits' commercial potential. The vertical variability of 45 major, minor and trace elements in the Green River Formation of Colorado is being determined by neutron activation analysis, x-ray fluorescence and other techniques. The results from these analyses will be used to assist in the evaluation of environmental impacts, environmental control strategies and to evaluate the recovery and utilization of some byproducts.

This program was initiated in June 1978 and is jointly funded by the Laramie Energy Technology Center (LETC), DOE's Division of

Environmental Control Technology and Division of Fossil Fuel Extraction, the U.S. Navy, and the Environmental Protection Agency.

ACCOMPLISHMENTS DURING 1978

Two cores from the Naval Oil Shale Reserve were sectioned and composited into 284 samples at 1, 2, 5, 25 or 50 feet intervals by LETC. The sample intervals selected were based upon presently known geologic stratigraphy and the type of technology likely to be used in commercial oil recovery (see Table 1). Sectioning of the cores was accomplished with a diamond saw. Each section was crushed and ground to 1/8 inch mesh particle size using a high-grade steel jaw crusher and a coffee-mill grinder. A standard splitting procedure was developed to randomly select representative 200 gram samples from composite samples weighing from 800 gm to more than 50 kg. Initially, analytical measurements were made on a number of sample splits to insure that the splitting procedure yielded representative, homogeneous samples. Analytical measurements were also made to insure that the samples were not contaminated by further grinding procedures preparatory to a complete analysis.

The analysis of the 296 samples is partially completed. Each sample is being analyzed for 45 major, minor and trace elements by several techniques yielding precisions of 0.1% to 5%. These include neutron activation analysis, x-ray fluorescence spectrometry, Zeeman atomic

Fig. 1. Vertical variation in As, Se, Zn, Cu and Pb in the Mahogany Zone, Core 25, Naval Oil Shale Reserve No. 1. (XBL 7811-12689)

Table 1. Core stratigraphy and compositing plan

Depth	Stratigraphy/ Technology	Feet of Core	Composite Interval In Feet	Number of Samples for Analysis
<u>Core Hole No. 15/16</u>				
856-1208	Overlying oil shale; vertical modified retorting	352	5	71
1244-1270	Mahogany bed; mining with surface retorting	26	1	25
1208-1346	Mahogany zone; excludes Mahogany bed; vertical modified retorting	138	2	57
1346-1372	B Groove	26	25	1
1372-1468	Rich oil shale; vertical modified retorting	96	5	18
1468-2019	Poor oil shale; commer- cial development not anticipated	551	50	11
	TOTALS	<u>1163</u>		<u>183</u>
<u>Core Hole No. 25</u>				
130-388	Solution cavity zone	258	50	5
388-634	Overlying oil shale; vertical modified retorting	246	5	49
634-705	Mahogany zone; excludes Mahogany bed; vertical modified retorting	50	2	25
670-690	Mahogany bed; mining with surface retorting	20	1	20
705-790	Poor oil shales	86	50	2
	TOTALS	<u>660</u>		<u>101</u>

absorption spectroscopy, and plasma emission spectroscopy. Partial results from the analysis of one core are shown in Fig. 1. This figure shows the variation of As, Se, Pb, Cu and Zn in the Mahogany zone. The variation in these elements is similar to that observed for most other elements except U. This data and other similar results indicate that Cu, Pb, Zn, and Ni, which are typically associated with sulfide minerals, probably exist as carbonates in oil shales. This is consistent with the postulated geochemical origin of the lake. Other analyses

suggest that the carbonate minerals act as diluent for other mineral phases.

PLANNED ACTIVITIES FOR 1979

Mineralogical studies including x-ray diffraction will be performed. Elemental analyses of the two cores will be completed. The resulting data will be statistically evaluated to identify vertical and lateral patterns and to clarify oil shale geochemistry.

Partitioning of Major, Minor and Trace Elements During In Situ Oil Shale Retorting

J. P. Fox, R. D. Giauque, A. L. Pacas, and J. F. Thomas

INTRODUCTION

Oil shale, a marlstone with about 20% organic material, contains measurable quantities of many elements and significant quantities of such environmentally troublesome elements as U, Th, Zn, Cu, Pb, As, Se, Hg, Cd, F, B and others. These elements can reach the environment by direct discharge, by leaching, or during refining and use of the oil.

The purpose of this program is to study the partitioning of fifty-one elements during in situ oil shale retorting. Oil shale retorting produces shale oil, a low BTU gas, a solid waste referred to as spent shale, and an aqueous effluent known as retort water. Elements initially present in the oil shale are partitioned to these products during retorting. In this program, products from pilot-scale and field-scale retorts are collected and analyzed for major, minor and trace elements using neutron activation analysis, x-ray fluorescence spectrometry, Zeeman atomic absorption spectroscopy and other techniques. The effect of retort operating conditions and oil shale source, grade and particle size on elemental partitioning are being studied. Isothermal kinetic studies are conducted on the raw oil shale to identify reaction mechanisms. The resulting data are used to complete elemental mass balances and to investigate the effect of operating conditions, such as temperature and input gas composition, on the distribution of the elements. Environmental implications of observed trends are determined and control of partitioning by modification of retorting parameters is explored.

This program was initiated in 1976 and is funded by DOE's Division of Fossil Fuel Extraction. The program is a collaborative effort with the Laramie Energy Technology Center (LETC). The majority of the retorting experiments has been conducted at LETC and the analytical work, data reduction and supporting laboratory measurements at LBL. The program has focused on products produced by LETC's controlled-state retort and Lawrence Livermore Laboratory's (LLL) pilot-scale retorts. Previously, products were collected from a few runs of these retorts and used to develop suitable sampling and analytical methods and to identify the variables that control elemental partitioning. These methods were then applied to new retorting experiments to determine partitioning trends and responsible reaction mechanisms. The following section describes this work.

ACCOMPLISHMENTS DURING 1978

Products from 18 runs of the LETC controlled-state retort and 9 runs of the LLL retorts were collected and analyzed. The effect of

a range of conditions on partitioning trends was studied including temperatures from 500 to 1000 C; nitrogen, air and steam atmospheres; isothermal advance rates from 0.7 to 7.3 m/day; shale grades from 25 to 248 liters per tonne; and shales from Colorado, Utah, Michigan and Morocco. Typical elemental data for one of these runs are summarized in Table 1.

In addition to these completed runs, four interrupted runs of the LETC retort were studied. In an interrupted run, retorting is stopped midway by cooling the reactor with a water quench, and products are collected as a function of depth in the retort. Partial results from one interrupted experiment are summarized in Fig. 1. This figure shows the concentration of organic carbon, Hg, Cd and Fe as a function of depth in the retort. Organic carbon is typical of elements that are volatilized and removed from the retort as gas, oil and water (N, S, H). The organic carbon located 7 feet into the shale bed was volatilized and swept out of the retort. However, below 7 feet, the temperature was not high enough to volatilize the organic carbon. Hg and Cd concentrations indicate a sharp maximum just below the point

Fig. 1. The vertical distribution of Fe, organic C, Cd, and Hg in an interrupted run of LETC's controlled-state retort. (XBL 791-238)

Table 1. Elemental abundances in products from a steam/combustion run of LETC's controlled state retort

	Raw Oil Shale ppm	Spent Oil Shale ppm	Shale Oil ppm	Retort Water ppm
Al	3.54 ± 0.06*	4.18 ± 0.08*	< 0.4	-
As	44.7 ± 1.8	52.5 ± 2.1	7.92 ± 0.40	9.36 ± 0.48
Ba	488 ± 14	580 ± 13	-	0.57 ± 0.07
Organic C	14.8 ± 0.1*	4.23 ± 0.01*	84.1 ± 0.1*	1.02 ± 0.01
Inorganic C	4.86 ± 0.01*	4.33 ± 0.01*	-	0.64 ± 0.01*
Ca	11.0 ± 0.1*	12.7 ± 0.1*	-	23.8 ± 1.2
Cd	0.82 ± 0.20	0.74 ± 0.05	< 0.014	0.0011 ± 0.0006
Ce	35.8 ± 0.6	48.6 ± 0.7	0.027 ± 0.005	0.0092 ± 0.0032
Cl	< 0.15*	< 0.15*	-	308 ± 4
Co	8.90 ± 0.17	11.7 ± 0.2	2.60 ± 0.02	0.469 ± 0.004
Cr	33.0 ± 0.6	39.6 ± 0.7	0.36 ± 0.02	0.31 ± 0.20
Cs	4.00 ± 0.12	6.51 ± 0.16	-	0.043 ± 0.001
Cu	33.8 ± 2.6	46.0 ± 3.0	0.52 ± 0.48	< 0.09
Dy	2.00 ± 0.08	2.76 ± 0.09	-	-
Eu	0.554 ± 0.009	0.723 ± 0.010	-	< 0.0001
Fe	1.90 ± 0.01*	2.36 ± 0.02*	63.2 ± 3.1	4.36 ± 0.22
Ga	7.8 ± 1.2	9.8 ± 1.4	< 0.48	0.05 ± 0.04
Ge	1.2 ± 1.0	2.2 ± 1.2	< 0.45	< 0.06
H	2.07 ± 0.01*	0.27 ± 0.02*	12.2 ± 0.1*	-
Hf	1.41 ± 0.05	1.99 ± 0.05	-	0.0049 ± 0.0003
Hg	0.062 ± 0.005	0.0095 ± 0.0021	0.029 ± 0.010	0.098 ± 0.005
K	1.38 ± 0.02	1.70 ± 0.02	-	36.1 ± 2.9
La	18.6 ± 0.5	24.7 ± 0.8	0.040 ± 0.003	-
Lu	0.146 ± 0.014	0.170 ± 0.015	-	-
Mg	3.5 ± 0.1*	4.4 ± 0.1*	29.2 ± 2.0	< 27
Mn	287 ± 6	360 ± 7	0.354 ± 0.003	0.019 ± 0.012
Mo	25.6 ± 2.1	31.0 ± 2.5	0.59 ± 0.12	0.65 ± 0.02
N	0.64 ± 0.01*	0.25 ± 0.03*	1.94 ± 0.01*	1.50 ± 0.01*
Na	1.69 ± 0.05*	2.26 ± 0.02*	124 ± 1	1283 ± 10
Nd	16 ± 1	18 ± 2	-	-
Ni	20.1 ± 3.4	26.4 ± 4.0	6.85 ± 0.68	6.95 ± 0.92
P	< 0.06*	< 0.06*	-	-
Pb	21.3 ± 1.8	29.3 ± 2.0	< 1.5	1.9 ± 1.2
Rb	57.2 ± 2.3	74.1 ± 3.0	< 0.69	1.1 ± 0.5
S	0.56 ± 0.01*	0.36 ± 0.01*	0.65 ± 0.01*	0.15 ± 0.01*
Sb	2.01 ± 0.14	2.68 ± 0.17	0.022 ± 0.002	0.158 ± 0.001
Sc	5.55 ± 0.15	6.71 ± 0.18	0.0019 ± 0.0002	0.0043 ± 0.0090
Se	1.6 ± 0.6	2.4 ± 0.6	0.93 ± 0.01	0.385 ± 0.004
Si	13.1 ± 0.1*	17.1 ± 0.1*	< 95	-
Sm	2.63 ± 0.13	3.47 ± 0.17	0.0020 ± 0.0005	-
Sr	733 ± 29	863 ± 34	-	0.21 ± 0.08
Ta	0.394 ± 0.004	0.513 ± 0.004	-	-
Tb	0.319 ± 0.088	0.396 ± 0.110	-	-
Th	6.01 ± 0.05	7.47 ± 0.06	< 1.3	0.0094 ± 0.0004
Ti	0.12 ± 0.02*	0.15 ± 0.01*	< 8.5	< 20
U	4.47 ± 0.04	5.63 ± 0.05	< 2.3	0.082 ± 0.001
V	118 ± 16	132 ± 15	< 5.2	0.40 ± 0.28
W	2.2 ± 0.6	2.6 ± 0.6	-	-
Y	8.7 ± 1.0	14.9 ± 1.0	< 0.99	< 0.15
Yb	1.21 ± 0.03	1.56 ± 0.03	-	0.0021 ± 0.0004
Zn	59.4 ± 2.4	80.9 ± 3.2	0.53 ± 0.13	0.63 ± 0.06

* Weight percent

Fig. 2. Summary of mechanisms that control elemental partitioning during in-situ oil shale retorting. (XBL 791-239)

at which retorting stopped. This is due to condensation of these elements in cool regions ahead of the reaction front. Fe concentration variations are typical of elements that are not volatilized from the oil shale (Ca, Mg, Na, Cu, Dy, Al). Above 7 feet, the Fe concentration is higher since approximately 20% of the original oil shale has been volatilized.

The data from these experiments have been analyzed and interpreted to determine reaction mechanisms that control partitioning patterns and to identify environmental implications. These studies have indicated that most elements in oil shale are not volatilized and therefore are present in the spent shale. This is in sharp contrast to coal technologies where many more elements are distributed among the byproducts because of the higher temperatures reached in coal combustion or conversion processes. The only elements that are distributed in significant amounts (>1 wt. %) from the oil shale to the water, gas and oil are Cd, Hg, As, Se, Ni, Co, S, N, H, C and the halogens.

This study has revealed that the principal factors controlling elemental partitioning are mineralogical residence, retorting temperature and atmosphere, residence time of the oil within the reactor, product collection system design, and contact time between the oil and water.

Elemental partitioning is controlled by chemical reactions in the reaction zone and in the cool zone ahead of the reaction zone. These reactions are summarized in Fig. 2. In the reaction zone, which consists of a combustion zone followed by a pyrolysis zone, the oil shale minerals are decomposed and oxides are formed (Eqs. 1-3). Some metal oxides are then reduced by carbon, CO and hydrogen in the pyrolysis zone (Eqs. 4-6). The resulting volatile metal species are swept ahead of the reaction front by the input gas and are either condensed in cool regions ahead of this front (Eq. 7), are adsorbed by oil mist, swept out of the retort, or are dissolved in the oil/water emulsion (Eq. 8). The water that condenses out of the gas stream in cool regions ahead of the reaction zone leaches some constituents from the unreacted shale in the cool regions (Eqs. 9-10).

PLANNED ACTIVITIES FOR 1979

Reaction mechanisms postulated to control elemental partitioning will be studied in laboratory isothermal kinetic programs. A field program will be initiated to test the applicability of laboratory studies to large-scale experiments.

Mobilization of Volatile Trace Elements During In Situ Oil Shale Retorting

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INTRODUCTION

Background

The most economically attractive method for the production of large volumes of oil from oil bearing shales is in-situ retorting whereby the shale is pyrolytically decomposed in its original geological setting. First, porosity is created in the shale bed; then heat for pyrolysis is supplied by combustion. The pyrolysis zone is driven down the shale bed in front of the advancing combustion zone by an introduced gas. The oil, water, and gases formed during the process also move down the bed, leaving behind a solid residue termed spent shale. In-situ retorting of one ton of moderately high grade shale would produce 25-30 gallons of oil, 10-660 gallons of water, and 70-14,000 SCF of gas.

Department of Energy commercialization goals call for the production of 100,000-250,000 barrels per day of shale oil by 1985. In order to achieve the lower limit of desired production, 175,000 tons per day of oil shale would have to be combusted. Processing of this quantity of shale could produce as much as 116 million gallons per day of retort water and two billion SCF per day of gas. These large volumes of waste materials are the focal point of environmental issues associated with the use of oil shale. The development of large-scale facilities to reduce toxic constituents to acceptable levels before the water and gas are released to the environment presents a major technological challenge.

Project Objectives

In October of this year, our group initiated a U.S. Environmental Protection Agency funded research project to study the partitioning of several toxic trace elements during simulated in-situ oil shale retorting. This project is specifically designed to determine how the potentially volatile elements As, Cd, Hg, Pb, Sb, and Se are distributed among the spent shale, oil, retort water and offgas by the retorting process. Emphasis will be placed on making careful gas phase measurements of these elements. A laboratory approach using a bench-scale retort has been selected for this investigation since field experiments are considerably more expensive and are complicated by contamination and sampling problems. The operation of the laboratory retort during the first and second years will allow us to develop the instrumentation, analytical methodologies and sampling strategies necessary for use in third year experiments with several pilot-scale retorts. In addition, the effects of retort operating parameters on the distribution of trace elements among oil shale products will be determined under controlled laboratory conditions.

This information can then be used to predict distributions for the field experiments. It is anticipated that this program will provide some of the information necessary to set emission standards for As, Cd, Hg, Pb, Sb, and Se for commercial in-situ oil shale processing plants. Additionally, it will develop monitoring strategies and analytical techniques suitable for determining compliance with standards or for making measurements at field installations for the purpose of acquiring additional data to set standards.

Trace Element Mobilization

The way in which elements initially present in raw oil shale are distributed among the products during in-situ retorting is presumably primarily controlled by retort operating conditions and the mineral phases of the elements in the starting material. The significant operating conditions are thought to be maximum retorting temperature, thermal advance rate, and input gas composition and flow rate. Temperature is a measure of the energy which controls for chemical reactions including pyrolysis, decomposition of carbonates and volatilization. Thermal advance rate controls the residence time of chemical species in the reaction zone. Gas composition and flow rate govern the chemical reactions that can occur at the gas-solid interface and in the gas phase.

Mobilization of trace elements during retorting is beginning to receive attention. Preliminary investigations of pilot-scale plants indicate that as much as 70% of the Hg present in raw oil shale may be released in the offgas. Comparable investigations have not yet been conducted for As, Cd, Pb, Sb and Se; however, limited mass balance data suggest that some of the As, Cd and Se may also be released to the atmosphere. No data are available for Pb and Sb.

If 100,000 bbl/day production is realized, uncontrolled emissions of volatilized trace elements could have major environmental impacts upon the lease tracts and surrounding areas. For example, Hg, which is the most toxic and volatile of the elements under investigation, occurs in the raw oil shales of the Piceance Basin, Colorado with an average concentration of about 100 ppb. If 70% of this Hg is volatilized and released with the offgas, the resulting Hg emission would be approximately four metric tons per year for a 100,000 barrel per day industry. Baseline studies of the Colorado lease tracts show that significant increases would likely occur in the Hg concentrations of the surface soils within one year if dispersal over the tracts was uniform. However, dispersal will almost certainly be non-uniform resulting in areas of more rapid and intensive impact.

The elemental composition of retort waters from a number of pilot scale retorts has been investigated; however, the data are inconclusive since large variability resulting from analytical problems has been encountered. Nevertheless, As appears to occur consistently at concentrations greater than 1 ppm. In addition to concentration, the chemical speciation of trace elements in retort and receiving waters must also be considered. Retort waters contain high levels of carboxylic acids and organonitrogen compounds, which can bind trace elements in organic forms and thus affect their biological availability.

ACCOMPLISHMENTS DURING 1978

The unique and innovative aspect of this program is the development of a continuous on-line monitoring technique for the elements of interest in gas streams containing high levels of organic compounds. The technique which we are employing is Zeeman atomic absorption (ZAA) spectroscopy which has been developed at LBL by Tetsuo Hadeishi. To date a ZAA instrument and furnace assembly for continuous Hg measurements has been constructed under a separate research contract described elsewhere in this Annual Report. Work is also continuing under a separate contract to develop stable light sources for As, Cd, Pb, Sb and Se. A laboratory scale, simulated in-situ retort has been designed and components are being evaluated. Development of analytical

methods to measure As, Cd, Pb, Sb and Se in oil and retort water samples has also been initiated. An ozonation cell equipped with an optional UV light source has been constructed to oxidize organic compounds which may interfere with trace element analyses in retort waters. The efficacy of this technique and its advantages over conventional oxidants have previously been demonstrated.

PLANNED ACTIVITIES FOR 1979

In 1979 we will complete the construction of the laboratory retorting apparatus and continue the development of analytical techniques for the measurement of As, Hg, Cd, Pb, Sb, and Se in gas, oil and retort water samples. Interlaboratory and multimethod comparisons will be used to validate the preferred techniques. In the case of the gas phase analyses, the comparison techniques will be conventional acidic or basic impinger trains and adsorption tubes, as well as innovative wet or dry chemical collection methods.

Experiments to determine the effect of temperature and input gas composition on trace element partitioning during retorting will also be initiated. In these experiments, retorting temperatures and input gas compositions will be varied to reflect present commercial options, while other variables such as shale grade, particle size and heating rate will be held constant.

On-Line Measurement of Mercury in Oil Shale Offgas Using Zeeman Atomic Absorption Spectroscopy

D. C. Girvin and T. Hadeishi

INTRODUCTION

Oil shale offgas is a complex and highly variable corrosive mixture containing significant quantities of entrained oil mist, hydrocarbons, CO₂, CO, H₂S and NH₃. Preliminary investigations of simulated in-situ oil shale retorts suggest that significant concentrations of mercury (Hg) may be present in this gas and emitted to the atmosphere during commercial oil shale retorting.¹

Major sampling and analytical problems have plagued previous investigators who have attempted to measure volatile trace elements in this gas with wet chemical collection devices, such as impinger trains, or with direct spectroscopic measurements. The purpose of this project is to determine the concentrations and fluxes of Hg in the product gases from several field experiments and to investigate the chemical mechanisms and physical processes controlling these fluxes. Zeeman atomic absorption spectroscopy will be developed to continuously analyze Hg and possibly other elements in these gas

streams. This program was initiated in August 1978 and is funded by the Environmental Protection Agency and DOE's Division of Environmental Control Technology.

Zeeman atomic absorption spectroscopy (ZAA) is a modification of conventional atomic absorption spectroscopy in which the light source is placed in a magnetic field. This splits the original resonance line into its linearly (π) and circularly (σ) polarized Zeeman components. The gas monitor being developed consists of four major components: a light source which provides a resonance emission line (π) and reference lines (σ) for background (smoke) correction; a furnace-absorption tube assembly where sample gas is thermally decomposed and swept into the light path of the detection and reference beams; a detector which converts changes in intensity of the transmitted detection and reference beams into an analog signal; and the signal processing electronics.

Prior to the initiation of this project in August, an existing Zeeman Atomic Absorption Spectrometer (ZAA), equipped with a R.F. source

and a furnace designed for batch analysis of liquids and solids, was used to make continuous on-line measurements of mercury in the product gas during an 80-hour burn of Laramie Energy Technology Center's (LETC) controlled-state retort.¹ This brief experiment demonstrated that ZAA can measure mercury and probably other elements in the presence of significant amounts of organics and smoke from incomplete combustion of entrained oil mist. This is due to the unique background correction ability of ZAA. It was also found that mercury concentrations in the gas stream vary by orders of magnitude during the retorting process. This variation is due to the successive volatilization and condensation of mercury as the retort reaction front propagates down the shale bed (Fig. 1). This kind of emission behavior can only be detected by continuous on-line analyses. No long-term direct gas measurements during field in-situ retorting experiments are available to corroborate these laboratory results. Verification of our LETC observations during a larger scale test is necessary so that control technology can be developed if necessary. This requires a significant improvement in instrumentation.

The primary objective during the first year of this project is to develop ZAA instrumentation capable of continuously measuring mercury concentrations in offgases on a real time basis under field and laboratory conditions. This will require modifications in the design of ZAA spectrometers. Light source and furnace assemblies must be redesigned to accommodate gas flows and severe field conditions. In addition, dynamic calibration methods and a gas sampling system capable of accurate metering and control of sample and calibration gases must be developed. Corrosion of the furnace due to sulfidation reactions will be investigated. When development and testing is completed, ZAA gas analyzers will be used to make long-term mercury measurements during laboratory and field retorting experiments.

ACCOMPLISHMENTS DURING 1978

A field ZAA spectrometer for on-line Hg analyses was designed and built during 1978.

This instrument incorporates some significant advances in state-of-the-art Zeeman atomic absorption spectroscopy and gas monitoring. These are discussed here.

Light Source

A new, low pressure, Hg, gaseous discharge lamp has been built and tested which will replace the R.F. excited electrodeless discharge lamp (EDL) previously in use. This "pen light lamp" (PLL) consists of a U-shaped quartz tube containing argon and a small quantity of Hg. Minute electrodes are sealed in each end of the tube. The outer diameter of the tube is 7 mm. The lamp is surrounded by a soft iron water jacket fitted with a quartz window. The lamp-water jacket assembly fits between the pole tips of the permanent magnet which produces the Zeeman splitting of the resonant lines. The argon plasma and Hg resonance lines are produced by a 1 kHz high voltage driver. The 2357 Å line intensity obtained with the PLL is approximately 50 per cent greater than that obtained with the EDL.

A major problem with the old EDL was the variation of intensity of the 2357 Å line and the variation of instrumental baseline with changes in ambient temperature. This represented a serious problem for field application where significant temperature fluctuations are likely to occur. However with the PLL this problem has been eliminated by coupling the water jacket to a constant temperature bath. Another problem with the EDLs was the R.F. pickup in adjacent instruments (e.g., thermocouples, and flow transducers) due to the R.F. excitation of the argon plasma. This problem has also been eliminated by the use of the PLL. Overall, the Hg PLL offers a significant improvement in ZAA versatility and performance.

Gas Sampling System

The gas sampling system is shown in Fig. 2. Sample gas is pumped into a heated stainless steel sample tube. To prevent condensation of mercury on the walls, this tube is maintained

Fig. 1. The distribution of total mercury in the offgas of a steam/combustion run of LETC's controlled-state retort. (Ref. 1) (XBL 784-711)

Fig. 2. Furnance assembly and gas sampling system of the Zeeman atomic absorption gas monitor. (XBL 792-480)

at approximately 200°C by joule heating. Oxygen is continuously introduced into the sample line to promote combustion of organics and thus reduce the level of smoke in the ZAA furnace. Calibration is achieved by introducing a carrier gas saturated with mercury vapor. Dilution gas is also introduced to the sample line to extend the calibration range. These gases are mixed and are then pumped into the combustion chamber of the furnace where they are heated to 900°C to atomize the mercury. The density of mercury atoms in the absorption chamber of the furnace is then measured by the ZAA. The gas leaving the furnace is cooled to reduce corrosion in the downstream pump and flow controller. Furnace temperature and the volumetric flow rate of gas through the furnace (Q) must be held constant between calibration runs. ZAA furnace temperature are maintained to within $\pm 10^\circ\text{C}$. Q is measured and held constant (2% of reading) by a flow controller. The flow controller is calibrated with a wet test meter downstream of the controller.

Furnace - Absorption Tube Assembly

Mercury and its compounds atomize (thermally decompose into individual atoms) below 900°C. To date we have succeeded in building a mercury

furnace capable of operating at 900°C for extended periods. The current design is shown in Fig. 2. Number 321 stainless steel tubing, 1/2 inch OD, is welded into a "T". The atomization chamber is filled with ceramic chips to break up the gas flow and increase the surface area for thermal contact. The adsorption and atomization chambers are separated by a narrow passage. Quartz windows pass the 253.7 nm resonance line of mercury while isolating the hot sample gas from the cooler ambient air. Temperatures of 900°C are attained in the atomization chamber by joule heating for gas flow rates as high as 10 l/min. Temperatures in the absorption chamber are lower since the current in each leg is 1/2 of that flowing through the walls of the atomization chamber. Current is supplied to the furnace via thin strips of 304 stainless steel welded to the tubing. When the furnace is at its maximum temperature, the outer ends of these variable cross section strips are cool enough so that resistive oxide layers do not build up on power connector surfaces. In addition, these strips act as furnace mounts providing both the rigidity to maintain optical alignment and the flexibility necessary to accommodate expansion during heatup.

The presence of H_2S in oil shale offgases creates a serious corrosion problem in the furnace. (H_2S concentrations can exceed several molar percent.) Sulfidation reactions are the main cause of this problem. In an attempt to inhibit corrosion and maximize furnace lifetime the stainless steel furnaces have been alonized. Alonization is a process whereby alumina is diffused into the surface of the tubing and welds. Based upon the work of others studying corrosion of stainless steel in oil shale atmospheres, this protective coating of alumina should significantly increase the lifetime of ZAA furnaces.

PLANNED ACTIVITIES FOR 1979

Corrosion tests will be conducted on alonized and untreated stainless steel furnace assemblies. The field mercury ZAA will be tested and used during laboratory retort experiments. Improvements resulting from these tests will be incorporated and the instrument will be used during at least one and perhaps several in-situ field experiments. The need for control technology to reduce mercury level will be assessed, based on these field measurements.

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The Biological Treatment of Oil Shale Process Waters

J. P. Fox, L. A. Tom, L. J. Tom, and D. E. Jackson

INTRODUCTION

Oil shale retorting produces from 0.10 to 22 barrels of water per barrel of oil. For a 500,000 barrel per day plant, which represents about 6% of the 1977 US crude oil production, this represents about 4 to 550 million gallons of water, depending on the type of process and plant location. This water, referred to as retort water, originates from combustion, mineral dehydration and groundwater. The waters are yellow to brown in color, have a pH that ranges from 8.1 to 9.4 and may contain high concentrations of HCO_3 , SO_4 , S_2O_3 , NH_4 , Na, and Cl and organic carbon. The organic constituents are primarily polar, and carboxylic acids comprise the principal group.

This water represents a potential resource for the arid areas in which oil shale is located if it can be upgraded. Work completed to date indicates that treatment of this water is particularly difficult due to the high levels and variety of constituents present. Any potential use of retort water will likely require the removal of some or all of the organic material. Work completed at other institutions indicates that conventional processes, including carbon adsorption, lime treatment, chemical oxidation, electrolytic oxidation and several aerobic biological processes are not suitable for the reduction of organics from retort waters.

The purpose of this study is to investigate the removal of soluble organics from retort water by anaerobic fermentation and activated sludge. The direct use of activated sludge to treat retort water is limited by oxygen transfer in the aeration tank (the BOD levels are very high) and by the presence of many toxicants. In this work, the use of anaerobic fermentation as a pretreatment step for activated sludge was investigated. Anaerobic fermentation is a two stage biochemical process. Organics in the waste are converted to carboxylic acids by a group of facultative and anaerobic bacteria referred to as the "acid formers". These acids are then converted into CO_2 and CH_4 by a group of anaerobic bacteria referred to as "methane formers". This process is particularly suited to wastes with high concentrations of carboxylic acids, such as retort water, as the bioconversion of these constituents is rapid. The process not only stabilizes a larger fraction of the organic matter than other biological processes, it also has lower nutrient requirements, produces less sludge, and is adaptable to intermittent loadings.

This program was initiated in 1977 and is funded by the Laramie Energy Technology Center. Previously, several digesters were set up and used to treat retort water. This work indicated that retort water must be pretreated to remove toxic constituents and to supplement nutrients.

Additional work was conducted during this period to verify these experiments, to identify and isolate toxic components and to investigate the use of activated sludge to biodegrade the organics in the effluent from an anaerobic digester. The results of this phase of the program are described below.

ACCOMPLISHMENTS DURING 1978

Four anaerobic digesters were acclimated and fed retort water from LETC's 150-ton retort and from a Geokinetics field experiment. The retort water was treated to remove oil and grease, suspended solids and ammonia, the pH was adjusted to 7, and the nutrients Ca, Mg and P were added. A schematic of the digesters used in these experiments is shown in Fig. 1. The composition of the 150-ton retort water is shown in Table 1. Daily measurements were made of the COD, TOC and volatile acids in the effluent and in the digester, and gas production and composition were determined. The result of one such experiment is shown in Fig. 2. This figure shows the effect of nutrient additions on the COD in the digester effluent. Prior to day 34, the volatile acids and COD levels in the effluent steadily increased suggesting that carboxylic acids produced by the "acid formers" were not being converted to methane. Both volatile acids and COD dropped to low levels after nutrient addition and remained there. Reductions in organic carbon obtained using this process ranged from 60 to 70% for hydraulic residence times of 30 to 50 days for the 150-ton retort water; the process failed when Geokinetic retort water was used. These long hydraulic residence times are not typical of anaerobic fermentation and limit the practical utility of the process for the treatment of large volumes of retort water.

It was postulated that the long residence times were due to an inhibitory effect of a constituent present in the retort water. Powdered activated carbon, which is an excellent adsorbent, was added to one digester. This did not improve the performance of the digester. The effect of SCN present in the retort water (525 mg/l) was investigated by dosing a control digester with artificial substrate spiked with SCN. Measurements of SCN in the influent, the digester and the effluent indicated that there was no conversion of SCN during anaerobic fermentation and that SCN was not toxic at levels present in retort water.

A series of experiments was conducted using the extended aeration activated sludge unit shown in Fig. 3. The effluent from one of the digesters was introduced into the activated sludge unit. This unit reduced the organic carbon by about 80%, which is considered excellent. In other experiments, the pretreated retort water was introduced directly into the activated

Fig. 1. Schematic of anaerobic acclimation system. (a) Digester's contents are mixed and kept at constant temperature ($35 \pm 10^\circ\text{C}$) by means of a hotplate-magnetic stirrer. (b) Fermented gas is introduced into a gas holder unit by means of a slight negative pressure created by the water column differential (h). The gas holder unit contains an acidified solution to prevent the dissolution of CO_2 . The gas, on entering the gas holder, displaces some of the acidified solution which is collected in the graduated cylinder. This volume of acidified solution is used to calculate the volume of gas produced. (c) The fermentation gas is recovered and the acidified solution level reset by lifting the graduated cylinder and properly operating the valves. (XBL 7710-2163)

Table 1. Composition of retort water from a combustion run (Run 13) of LETC's 150-ton retort (mg/l)

	Raw Retort Water		Raw Retort Water
Akalinity, Total (mg/l CaCO_3)	38,000	Magnesium	24
Aluminum	16.6	Manganese	0.22
Arsenic	1.4	Nickel	0.014
Barium	0.17	Nitrogen, Total NH_3 (as NH_3)	10,150
Biochemical Oxygen Demand, 5-day (BOD_5)	5,325	Nitrogen, Kjeldahl (as N)	11,000
Boron	3.4	pH	8.6
Bromine	1.5	Phosphorus (as P)	8.5
Calcium	3.3	Potassium	37
Carbon, Inorganic	5,850	Selenium	0.24
Carbon, Total Organic (TOC)	4,980	Silicon	25
Chemical Oxygen Demand (COD)	8,800	Sodium	655
Chlorine	57	Solids, Total Dissolved	4,210
Chromium	0.018	Solids, Total	-
Cobalt	0.31	Solids, Volatile	-
Copper	15.6	Solids, Suspended	-
Fluorine	26	Sulfate (as SO_4)	1,100
Hardness (as CaCO_3)	86	Sulfur, Total (as S)	406
Iodine	0.11	Vanadium	1.8
Iron	4.7	Volatile Acids (as CH_3COOH)	3,300
Lead	0.3	Zinc	6.4

Fig. 2. Time variation of total gas production, gas composition, volatile acids and chemical oxygen demand. (XBL 7710-2162)

Fig. 3. Schematic of extended aeration activated sludge system. (XBL 791-243)

sludge unit. This resulted in organic carbon reduction of about 30% which, again, indicates an inhibitory effect. Although good organic reductions were obtained by using anaerobic fermentation and activated sludge in series, the sequence is limited by the high hydraulic residence time of the digester, and therefore could not be effectively used in a large-scale treatment facility.

This study, to date, has indicated that biological treatment of retort water may be viable if the inhibitory and toxic effects of yet unidentified constituents can be resolved. This may be overcome by either

identifying the troublesome components and determining methods to remove them, or by developing a strain of bacteria which is immune to these constituents.

PLANNED ACTIVITIES FOR 1979

Other research has indicated that some types of bacteria proliferate in containers of retort water maintained at room temperatures. During the next fiscal year, a program will be initiated to determine if these bacteria can be acclimated and used to remove a significant fraction of the organics in retort water on a large scale.

Spent Shale as an Adsorbent for Organics

D. E. Jackson, R. N. Anaclerio, and J. P. Fox

INTRODUCTION

Oil shale retorting produces 0.10-22 gallons of retort water and about 70 pounds of spent shale for each gallon of oil, depending on plant location and retorting conditions. The retort water, which contains high levels of many organic and inorganic constituents, would be a valuable resource for the arid regions in which oil shale deposits are located, provided that effective and economical treatment methods can be found.

The goals of this project are to determine whether retorted oil shale can be used as an adsorbent to remove organic constituents from oil shale processing wastewaters (retort water) and, if so, to use it in a treatment sequence that includes biological processes. This program was initiated in June 1978 and is funded by DOE's Division of Environmental Control Technology.

Past attempts to adapt conventional treatment technologies such as anaerobic fermentation, trickling filters, activated sludge, carbon adsorption, or oxidation to remove organics from retort waters indicate that these methods have serious technical or economic limitations. However, an observation made at LBL during the course of other work suggested another solution. A normally non-adsorbing dye, pontacyl pink, was passed through a packed bed of spent shale in order to study the flow of water through the column; the experiment failed because the dye was adsorbed on the shale. This observation, supported by subsequent adsorption studies done elsewhere¹, suggested that spent shale might be used in a treatment step to reduce the level of organic constituents in retort waters.

Raw oil shale contains a complex organic component called kerogen that is imbedded in a mineral matrix. The pyrolytic decomposition of kerogen that occurs during retorting removes most of the organic material, leaving behind a complex system of pores and cavities that we think will provide the large surface area that is required for effective adsorption. Calculations from an isotherm obtained for the sorption of SO₂ on one spent shale² show that it has a specific surface area of roughly 5m²/g. Although this is more than two orders of magnitude lower than the specific surface area of activated carbon, we hope that the low cost and on-site availability of spent shale will compensate for its lower efficiency.

ACCOMPLISHMENTS DURING 1978

Since the project began in June 1978 we have completed the necessary preparatory work and have begun preliminary adsorption studies. We have collected samples of spent shales that have been retorted under various conditions and separated them by particle size, as well

as collecting and storing a variety of retort waters generated at the Laramie Energy Technology Center and Lawrence Livermore Laboratory.

Much effort has been devoted to developing a combustion-IR method of determining the levels of organic carbon in these waters that is free of interference by the other constituents. Following the elimination of carbonate, the samples are combusted in an O₂ stream at 950°C, and the CO₂ in the gas stream is determined with a non-dispersive IR spectrophotometer. The waters have been characterized, and their homogeneity and stability during storage have been investigated.

A few preliminary batch studies to determine the adsorptive capacity of the shales have been completed. The results of one of these experiments are summarized in Table 1. The batch studies were carried out on varying amounts of different spent shales and retort waters. The spent shale was weighed, placed in a 250 ml Erlenmeyer flask and then a measured amount of retort water was added. The flasks were sealed and placed on a mechanical shaker for varying amounts of time. Small samples were obtained by filtering a few milliliters of sample through a 0.45 µm Millipore filter, and analyzed for pH, organic carbon, inorganic carbon and conductivity. These studies indicated

Table 1. Batch adsorption experiment in which 50 g of 150-ton spent shale and 50 ml 150-ton retort water are contacted for 144 hrs.

Initial dissolved organic carbon, mg/l	3300
Final dissolved organic carbon, mg/l	2510
Percent reduction in dissolved organic carbon	24%
Specific adsorption, mg organic carbon/g shale	0.80
Initial pH	8.8
Final pH	10.1
Initial conductivity, µmhos/cm	36,000
Final conductivity, µmhos/cm	18,000
Percent reduction in conductivity	50%
Initial inorganic carbon, mg/l	6400
Final inorganic carbon, mg/l	340
Percent reduction in inorganic carbon	95%

that a 1:1 weight ratio between spent shale and retort water was necessary to observe measurable amounts of adsorption. Table 1 indicates that the dissolved organic carbon was reduced by 24%, the electrical conductivity by 50%, the inorganic carbon by 95% and the pH was elevated from 8.8 to 10.1 after contacting 150-ton water with 150-ton shale for 144 hours. The reduction in inorganic carbon is believed to be due to a process of exchange between carbonate in the water and hydroxide formed from the hydration of CaO or other metal oxides as follows:

These results verify the assumption that spent shale will remove organics from retort water. The organic carbon reduction of 24% is not as large as we anticipated. A series of studies has been initiated to determine if the adsorptive properties can be improved by chemically or physically treating the shale. Methods under study include heat treatment, acid leaching and pH adjustment. However, this may not be a serious limitation in light of the unexpected discovery that 95% of the inorganic carbon and 50% of the conductivity is removed.

The results of these batch studies were verified by passing retort water through packed columns of spent shale. Similar reductions in organic carbon and inorganic carbon and increases in pH were observed. In addition, the color of the retort water changed from brown to yellow on passage through the column. A difference spectrum between the untreated water and column effluents taken over the visible and ultraviolet wavelengths shows two separate regions where adsorption has taken place (Fig. 1). One is a broad, deep peak showing almost complete removal of a component or components with a maximum at 390 nm, which is the change responsible for the color change. Another peak in the ultraviolet around 215 nm indicates that other components may also be removed by the column. Further work will be done to identify the compounds responsible for these adsorption changes.

The simultaneous increase in pH and large decrease in inorganic carbon has important and immediate applications to the treatment of retort water. Carbonate alkalinity must be reduced in any treatment sequence designed to upgrade this water. These results indicate that a packed column of spent shale can be used in combination with a steam stripper to remove ammonia and carbonate alkalinity from the water. The increase in pH would enhance the removal of ammonia in the stripper. The nearly complete reduction of carbonate alkalinity through the spent shale column would allow the use of a smaller stripping tower. This represents a significant advance in the treatment technology for retort water, and it will considerably reduce the cost of retort water treatment.

Fig. 1. UV and visible difference spectra. Sample was 150-ton retort water and reference was the effluent of a 50 cm column packed with S-17 spent shale which was fed 150-ton retort water. Adsorption in this spectrum indicates the presence of compounds that have been removed by the column.
(XBL 795-1595)

PLANNED ACTIVITIES FOR 1979

We will continue batch studies in order to generate adsorption isotherms that will be used to identify the best adsorbers, study the effect of pH and temperature on the process, and determine the contact time necessary to reach equilibrium. We plan to measure some of the relevant physical variables such as pore volume, surface area, and carbon content of the shale. Work will also begin on oil and grease removal, a pretreatment required to prevent fouling of the columns. In cooperation with other groups in the Oil Shale Project, we will develop methods of fractionating and identifying the organic solutes in the retort waters so that we can obtain information about the specificity with which particular compounds or classes of compounds are removed from solution by spent shale. After the adsorption process is developed, we will use it in series with biological processes such as trickling filters, activated sludge and anaerobic fermentation to remove organics from retort water.

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Effect of Retort Water on Attached Microorganisms

P. P. Russell, A. J. Horne, and J. F. Thomas

INTRODUCTION

Production of synthetic crude from oil shale generates from 0.10 to 22 barrels of water per barrel of oil, depending on the specific process used. This water, referred to as retort water, originates from combustion, mineral dehydration and from groundwater intrusion (in situ processes only). The organic content of retort water may reach 3% while inorganic concentrations of as much as 5% are typical. The principal inorganic components of the wastewater are ammonium, sodium, and bicarbonate, with lesser but significant amounts of thiosulfate, chloride, sulfate and carbonate.

The goal of this project is to investigate the probable effects of accidental or intentional discharge of retort water on attached microorganisms (aufwuchs) and caddis fly larvae in streams of the oil shale region. Aufwuchs are sensitive indicators of the effect of a pollutant on the food chain. The aufwuchs community typically consists of an attached mat of algae, protozoa, bacteria, fungi, and some associated metazoans. The approach used was to employ laboratory scale model streams containing standardized growth surfaces upon which aufwuchs communities could develop. This program was initiated in 1977 and is funded by the Laramie Energy Technology Center (LETC). In 1977 four mutually isolated, parallel model streams, shown in Fig. 1, were constructed. These streams were used to study the effect of retort water on aufwuchs. This phase of the program is discussed here.

ACCOMPLISHMENTS DURING 1978

Two oil shale retort waters were studied. One sample came from a combustion run of Laramie Energy Technology Center's (LETC) 150-ton retort

facility (150-ton retort water). The other was produced during the Rock Springs Site 9 true in situ oil shale processing experiment (Omega-9 water) near Rock Springs, Wyoming.¹ These retort waters are not necessarily representative of waters which may be produced during other oil shale processing experiments, and the results obtained are strictly indicative of these waters only. Nevertheless, probable aufwuchs responses from the retort waters of future full scale oil shale processing can be estimated using this methodology.

Five experimental runs were performed using Omega-9 water, Omega-9 water filtered through a 0.4 μ m membrane (2 runs), 150-ton retort water, and an ammonium carbonate solution. Development and metabolism of aufwuchs on initially clean growth surfaces in the riffles of each stream were measured on the third, sixth and ninth day of each experiment. Assays of total solids, percent volatile solids, chlorophyll a, photosynthesis, respiration and adenosine triphosphate (ATP) were performed. The response of caddis fly larvae, *Gumaga nigricula* and *Dicosmoecus* sp., were confined to screened cages in the lower pools of each stream and their survival monitored.

Preliminary analysis of the results indicates that these effluents produce the greatest effect on the percent volatile solids of the aufwuchs. This response is typically illustrated by the results from runs using Omega-9 water (Fig. 2). The increase in percent volatile solids with retort water probably results from a reduced contribution of diatoms to the aufwuchs community.

Fig. 1. Model stream schematic. (XBL 779-1907A)

Fig. 2. Aufwuchs percent volatile solids vs. Omega-9 water dilution and growth period. (XBL 7811-12618)

Diatoms possess a silica shell or frustule which remains as a solid when the organic matter of the aufwuchs sample is volatilized. The fraction of aufwuchs comprised by green algae when retort water is present typically increases (Table 1). It is likely that the contribution of bacteria to the aufwuchs biomass also increases with the availability of retort water organics, although this fact was not confirmed directly. The increase in percent volatile solids was less pronounced when ammonium carbonate was tested alone.

Other significant results from preliminary analysis of the data suggest increased total biomass at low dilutions of retort water and decreased biomass at concentrations above about 1% retort water. This indicates that the stimulation by low effluent levels is supplanted by toxic effects at higher levels. Additionally, the ratio of gross photosynthesis to respiration tends to decrease with increasing retort water loadings. Evidently, the contribution of the photosynthesizing primary producers diminishes when retort water is present.

The concentrations of retort water examined had no significant effect on the caddis fly larvae. However, the sensitivity of Dicosmoecus sp. to ammonium carbonate (the only run in which it was employed) was more pronounced than that of G. nigricula. Perhaps a response to retort water would have been observed with Dicosmoecus if it had been available for the other experimental runs.

The consequence of shifts of species dominance in the streams of the oil shale region is controversial at this time. Aufwuchs is an important component of energy input to the food web. It is known that many insect species which graze on aufwuchs are quite selective with respect to palatability, caloric value and availability of the organisms in their diet. These insect grazers are in turn food for higher forms of aquatic life of economic importance to man, i.e., trout. Thus, there is significant potential for perturbations at the base of the food chain to be propagated widely.

PLANNED ACTIVITIES FOR 1979

Analysis of the data will be completed and published early in 1979. Confirmation of the results from this project must be obtained by use of the methodology in the field with oil shale related effluents. Valuable information could be obtained by applying higher concentrations of retort water to the model streams, as well as by examining other types of industrial wastes.

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Table 1. Community composition.

		Volume Percent									
		Navicula sp 1	Navicula sp 2	Navicula sp 3	Navicula sp 4	Nitschia	Diatoms	Closteridium	Microspora	Zygnema	Unid. Green Alga
Omega-9 Water	0	56	1	0	41	P	98	2	0	P	P
	1.06%	15	9	0	0	21	46	47	0	P	7
Filtered Omega-9 Water	0%	0	34	0	0	0	34	64	0	P	1
	2.12%	0	31	0	0	0	31	66	0	P	3
150 Ton Retort Water	0%	62	5	1	25	6	99	P	0	0	P
	0.67%	0	0	0	0	40	40	51	0	P	8
Ammonium Carbonate	0mM	43	18	0	36	7	95	P	1	P	3
	4mM	0	26	0	13	44	83	1	0	P	15

P = Present but less than 1%.

Potential Toxicants from In Situ Oil Shale Processing

M. J. Kland and J. P. Fox

INTRODUCTION

Increasing interest in in situ oil shale retorting as a means of augmenting our domestic fuel supplies raises the inevitable question of the potential for environmental and health impacts of this technology.

Consideration of possible deleterious environmental effects include - though they are not necessarily confined to - gaseous and particulate emissions to the atmosphere, particulate fallout to the ground and onto vegetation, and the consequent contamination of ground and surface waters.

Gases such as CO, SO₂, NH₃ and H₂S, which are known to be toxic to both plants and animals, are among the volatile emissions from in situ oil shale retorting. A variety of potentially toxic or carcinogenic hydrocarbons have been identified among the organic pyrolytic products emitted.¹

The handling of raw shales presents the usual occupational respiratory hazards of exposure to mineral dusts, including silicates, and adsorbed or occluded toxic trace metals. Contact with the kerogen and bitumen, which constitute the organic fraction of raw shale and contain possible oncogenic substances, is a further occupational hazard which will need to be addressed in greater depth. (See Ref. 1 for a number of excellent industrial hygiene references dealing with similar problems.)

Product oils collected in the retorting process contain a variety of hazardous substances: irritants capable of producing serious contact dermatitis, sensitizers and carcinogens. Among the oncogenic (tumorigenic) organic compounds identified are: benz(a)pyrene, benz(a)anthracene, other pyrenes, chrysenes and dibenzacridine(s).²

Residues from retorting include spent shale with concomitant dust and trace metals, as well as potential organic toxicants and carcinogens which may condense out on retort surfaces.

Although there are significant industrial hygiene and air pollution control problems connected with in situ oil production technology, the most serious environmental and public health concerns stem from process-related waters: their control and re-use, and the potential impact of the technology on increasingly scarce water resources.³ The remainder of this report will consider this aspect of the environmental problems anticipated in the event of large-scale in situ oil shale development.

Waters associated with in situ oil shale retorting are a major byproduct of this technology. They originate from combustion, dehydration of occluded and bound waters of shale minerals,

and injection water or steam associated with the retorting process. In addition, seepage of ground water occurs into the retorted zones (backflood water).

Waters derived from the in situ oil shale retorting process are heavily contaminated with organic and inorganic constituents.⁴ They are generally alkaline (ph 8-9.5) with primarily polar organic constituents (organic acids, amines, N-heterocyclics and organo oxygen and sulfur compounds). Inorganic anions include HCO₃⁻, CO₃⁻, F⁻, S₂O₃⁻, SCN⁻ and SO₄⁻; principle dissolved cations are Na⁺, NH₄⁺, Mg⁺, Zn⁺, Fe⁺, and amphoteric (Al, Si) which exist as complex anions under alkaline conditions. Trace elements of environmental concern include As, Hg, Se, Mo and B.

In addition to their own specific toxic potential for eco-systems, the hetero-organics may increase the mobilities of certain of the toxic trace elements (Cu, Cd, As, Se, F) by virtue of their complexing and chelating powers.⁵ It is not unusual for metals in organometallic form to exhibit enhanced toxicity toward fauna and flora because they may be more readily assimilated than the parent inorganic ions. Witness the far greater toxicity to fish and mammals of methyl and dimethyl mercury than the free metal or its relatively insoluble salt, Hg₂Cl₂.⁶

The purpose of this project is to identify specific organic and organometallic compounds in waters, oils and gases from in situ oil shale processes and to assess their environmental significance. The program was initiated in October 1978 and is funded by the Department of Energy.

ACCOMPLISHMENTS DURING 1978

A program has been initiated to determine organic and organometallic components in oils, waters and gases produced during oil shale retorting. A variety of analytical techniques, including Zeeman atomic absorption spectroscopy (ZAA), gas chromatography/mass spectrometry (GC/MS), high performance liquid chromatography (HPLC) thin layer chromatography (TLC) and UV-visible spectrometry, are being used to identify specific components.

Preliminary solvent extractions and analyses of shale waters from two sources have indicated the presence of a number of organonitrogen heterocyclics, phenols, organic thio derivatives, carboxylic acids and neutral hydrocarbons. Interestingly, x-ray fluorescence analysis of these extracts has also revealed the presence of As, Se, Zn and other metals.

Further separations and identifications are in progress, using GC-MS, UV-Vis spectro-

photometry, XRF and ZAA for metals. In addition to organic extraction techniques, we are experimenting with steam distillation in an alternative separation method. Ultimately, TLC and HPLC will also be used for the separation and confirmation of both the organic isolates and organometallics.

PLANNED ACTIVITIES FOR 1979

Techniques to measure organics and organometallics in complex aqueous matrices will be developed and applied to a range of retort waters. Spectrophotometric studies of interactions of pure heterocyclics with one or more of the trace metals will be conducted. A synthetic model organometallic compound will be used to gain further insight into the state in which metals exist in the organic fraction.

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Intercomparison Studies of Oil Shale Materials

J. P. Fox, F. Asaro, and R. D. Giauque

INTRODUCTION

Reliable chemical characterizations of oil shale materials have been difficult to obtain because of the lack of adequate standards and limitations of many available analytical methods. Concentrations of many constituents fall outside the recommended ranges for many methods, and chemical interferences produce inaccurate results.

The purpose of this investigation is to develop oil shale standards and to use these materials to identify/develop reliable analytical methods for the characterization of oil shale materials. This program was initiated in 1976 and is funded by the Laramie Energy Technology Center (LETC) and DOE's Division of Fossil Fuel extraction. The program is a collaborative effort with LETC, Battelle Pacific Northwest Laboratory and the Colorado School of Mines. Each collaborator prepared a series of standard reference materials which were distributed to various laboratories for analysis in 1977. The resulting data have been interpreted and recommendations advanced for suitable analytical methods for oil shale materials. This phase of the program is outlined below.

ACCOMPLISHMENTS DURING 1978

Fifty kilograms of 3 oil shales, 7 spent shales, 12,500 gallons of retort water and 5 liters of 2 oils were homogenized, split and submitted to various laboratories for

elemental analyses. A range of water quality parameters was determined in the retort water.

The results of the analysis of one oil shale standard are shown in Table 1. These data were analyzed to determine method/laboratory performance. Partial results of the performance analysis for each type of material are summarized in Table 2. This analysis indicated that reliable measurements of elemental abundances in raw and spent oil shales can be obtained using neutron activation analysis, x-ray fluorescence spectrometry and atomic absorption spectroscopy if laboratories are chosen that do careful work. Chemical techniques are limited by a number of interferences and should not be used unless careful methods development precedes analysis.

Less satisfying results were obtained for the oil and water. The statistics summarized in Table 2 indicate that the coefficient of variation for the normalized means was 26% for the oils and 33% for the waters compared with 9% for the solids. This large variation for the oils and waters is due to the low levels of many constituents and to uncorrected chemical interferences.

Significant analytical problems were encountered with the retort water. Large deviations were obtained for many elements (Al, P, Pb, Hg, Sr, Si, Cd) and water quality parameters (COD, phenols, CN, organic nitrogen, PO₄).

Table 1. Elemental composition of Anvil Points raw oil shale prepared by LBL, Raw 1B (ppm).

	Neutron Activation Analysis				X-ray Fluorescence Spectrometry				Other			Best value ¹	
	(D-1)	(D-2)	(A)(2)	(O)(1)	High energy (D)	High energy (A-1)(2)	High energy (J)(3)	Low energy (A-2)(1)	(D)	(A)(3)	(J)		
Al (%)	-	-	3.83±0.12	4.04±0.19	-	-	-	4.0±0.2	3.88±0.34 ^a	-	-	3.9±0.1	Al
As	54±1	62±1	45±4	39±1	38±3	37±1	40±9	-	-	-	33±3 ^a	47±10	As
B	-	-	-	-	-	-	-	-	108±11 ^g	-	-	(108±11)	B
Ba	540±50	-	498±26	479±19	-	-	520±36	-	-	-	-	495±27	Ba
Br	0.52±0.16	-	-	-	-	<1.5	0.55±0.01	-	-	-	-	0.55±0.02	Br
Ca (%)	8.25±0.6	-	10.3±0.5	9.41±0.12	10.5±0.8	-	11±1	9.2±0.5	10.0±0.5 ^a	-	-	9.5±0.9	Ca
Cd	-	-	-	-	-	-	-	-	-	0.72±0.07 ^b	-	0.72±0.07	Cd
Ce	46±2	-	44±2	41.2±0.6	-	-	-	-	-	-	-	42±2	Ce
Cl	-	-	<830	-	-	-	-	-	-	-	-	(<830)	Cl
Co	9.3±0.3	8.8±0.1	9.18±0.29	8.56±0.09	-	<31	-	-	-	-	-	8.7±0.3	Co
Cr	45±1	49±1	37±2	33.1±0.8	-	-	-	-	-	-	-	41±7	Cr
Cs	-	-	4.46±0.33	4.40±0.10	-	-	-	-	-	-	-	4.4±0.1	Cs
Cu	-	-	-	<98	43±4	40±3	34±3	-	-	40±4 ^b	-	39±4	Cu
Dy	-	-	2.48±0.13	2.13±0.14	-	-	-	-	-	-	-	2.32±0.25	Dy
Eu	-	0.59±0.03	0.63±0.02	0.59±0.01	-	-	-	-	-	-	-	0.60±0.02	Eu
F	-	-	-	-	-	-	-	-	-	-	990±20 ^g	(990±20)	F
Fe (%)	2.41±0.05	2.29±0.05	2.21±0.06	2.16±0.02	2.2±0.2	2.18±0.09	2.10±0.04	2.1±0.1	2.24±0.31 ^a	-	-	2.2±0.1	Fe
Ga	-	-	-	-	10.1±1.2	9.8±1.8	6.5±0.7	-	-	-	-	7.7±2.0	Ga
Ge	-	-	-	-	-	<2.4	-	-	-	-	-	(<2.4)	Ge
Hf	1.7±0.1	-	1.72±0.14	1.68±0.04	-	-	-	-	-	-	-	1.69±0.04	Hf
Hg	0.06±0.01	-	-	-	-	<4	-	-	0.086±0.005 ^a	0.077±0.008 ^b	-	0.08±0.01	Hg
In	-	-	<0.18	-	-	-	-	-	-	-	-	(<0.18)	In
Ir	-	-	<0.01	-	-	-	-	-	-	-	-	(<0.01)	Ir
K (%)	1.83±0.19	-	1.79±0.14	1.77±0.06	1.67±0.12	-	-	1.7±0.1	1.61±0.11 ^a	-	-	1.73±0.08	K
La	21.2±0.5	20.2±0.4	20.8±0.7	23.4±0.3	-	-	-	-	-	-	-	22±10	La
Lu	0.26±0.03	-	0.19±0.01	0.214±0.008	-	-	-	-	-	-	-	0.21±0.04	Lu
Mg (%)	-	-	3.5±1.6	3.6±0.09	-	-	-	3.5±0.2	3.52±0.10 ^a	-	-	3.5±0.1	Mg
Mn	-	-	343±12	334±2	350±30	341±21	300±8	-	395±70 ^a	-	-	333±31	Mn
Mo	-	-	20±2	19±1	21±2	-	20±2	-	-	-	19±2 ^c	20±1	Mo
Na (%)	1.54±0.01	1.58±0.01	1.56±0.04	1.53±0.01	-	-	-	1.7±0.1	-	-	-	1.55±0.02	Na
Nb	-	-	-	-	-	-	5.7±0.1	-	-	-	-	(5.7±0.1)	Nb
Nd	-	-	19±4	14±3	-	-	-	-	-	-	-	16±4	Nd
Ni	25±2	26±1	21±4	<36	23±3	20±4	29±1	<36	-	-	-	27±3	Ni
Pb	-	-	-	-	24.5±0.3	24±2	23±1	-	-	23±3 ^b	-	24±1	Pb
Rb	76±5	74±1	85±8	74±3	79±6	74±2	82±1	-	-	-	-	77±4	Rb
Sb	2.0±0.1	1.99±0.10	2.1±0.1	1.90±0.07	-	-	-	-	-	-	-	2.0±0.1	Sb
Sc	6.8±0.1	7.0±0.1	6.47±0.20	5.93±0.05	-	-	-	-	-	-	-	6.3±0.5	Sc
Se	2.6±0.3	2.6±0.1	-	2.38±0.30	2.2±0.5	2.1±0.7	-	-	-	-	-	2.6±0.2	Se
Si (%)	-	-	-	-	15.0±1.0	-	-	15.0±0.8	14.9±1.2 ^a	-	-	15.0±0.8	Si
Sm	3.6±0.1	3.5±0.1	3.08±0.12	3.19±0.07	-	-	-	-	-	-	-	3.3±0.2	Sm
Sr	840±50	740±15	-	683±29	-	698±19	798±4	-	720±60 ^a	-	-	789±61	Sr
Ta	0.55±0.02	-	0.46±0.02	0.47±0.04	-	-	-	-	-	-	-	0.50±0.05	Ta
Tb	0.37±0.04	-	0.40±0.07	0.36±0.02	-	-	-	-	-	-	-	0.36±0.02	Tb
Th	7.0±0.1	7.0±0.2	6.70±0.26	6.18±0.07	-	6.8±1.7	-	-	-	-	-	6.5±0.3	Th
Ti (%)	-	-	0.16±0.05	0.17±0.03	0.17±0.03	0.18±0.02	-	0.16±0.01	0.17±0.03 ^a	-	-	0.17±0.01	Ti
U	-	-	4.10±0.16	3.63±0.20	-	-	-	-	-	-	-	3.9±0.3	U
V	-	-	107±24	92±5	-	-	-	-	-	-	-	93±11	V
W	-	-	-	-	-	-	-	-	-	-	-	-	W
Y	-	-	-	-	12±2	13±1	12±1	-	-	-	-	12±1	Y
Yb	1.6±0.1	-	1.38±0.05	1.31±0.03	-	-	-	-	-	-	-	1.3±0.2	Yb
Zn	70±6	65±1	-	75±3	69±7	67±3	63±2	-	-	-	-	66±4	Zn
Zr	-	-	-	-	56±8	-	49±3	-	-	-	-	50±5	Zr

A = Lawrence Berkeley Laboratory, D = Battelle Pacific Northwest Laboratory, J = University of Colorado,
 O = Lawrence Livermore Laboratory, a = atomic absorption spectroscopy, b = Zeeman atomic absorption spectroscopy, c = colorimetric,
 d = fluorometric, e = delayed neutron, f = gamma-ray spectrometry, g = plasma emission spectroscopy.

¹ The following rules were used to determine best values: (1) The smallest upper limit is reported; (2) A range is reported if the coefficient of variation is greater than 100%; (3) Best values based on a single measurement are enclosed in parenthesis; (4) Best values based on two or more measurements are weighted averages computed following rejection of outliers. The reported errors are the larger of one standard deviation computed from the reported replicates or the smallest recorded analytical error.

Table 2. Normalized statistics for oil reference materials

	Normalized average	Coefficient of variation	Uncertainty in coefficient of variation
RAW OIL SHALE			
NAA (D-1)	1.04 ± 0.10	10%	1.4%
NAA (D-2)	1.04 ± 0.10	10%	1.8%
NAA (A)	1.02 ± 0.08	7.6%	1.0%
NAA (O)	0.97 ± 0.06	6.6%	0.80%
XRF (D)	1.02 ± 0.11	11%	2.0%
XRF (A-1)	0.98 ± 0.13	14%	2.7%
XRF (A-2)	1.00 ± 0.05	4.9%	1.3%
XRF (J)	0.98 ± 0.09	9.1%	1.7%
AA (D)	1.02 ± 0.08	7.6%	1.8%
SHALE OIL			
NAA (D-2)	1.27 ± 0.46	36%	7.5%
NAA (O)	0.92 ± 0.16	17%	3.5%
XRF (D)	0.92 ± 0.16	17%	4.7%
XRF (A)	1.26 ± 0.31	25%	7.4%
XRF (J)	1.13 ± 0.38	34%	9.2%
RETORT WATER			
NAA (A)	0.97 ± 0.22	23%	4%
NAA (B)	1.08 ± 0.34	31%	9%
NAA (C)	0.95 ± 0.17	18%	4%
NAA (D)	0.94 ± 0.19	20%	5%
NAA (O)	0.92 ± 0.19	20%	4%
XRF (A)	0.96 ± 0.21	22%	4%
XRF (D)	1.02 ± 0.31	30%	8%
SSMS (E)	1.30 ± 0.79	61%	9%
OES (F)	0.96 ± 0.49	51%	11%
PES (D)	0.88 ± 0.25	28%	6%
AA	1.03 ± 0.17	17%	3%
OTHER	1.15 ± 0.80	70%	15%

Letters A-J designate laboratories; NAA = neutron activation analysis; XRF = x-ray fluorescence spectrometry; AA = atomic absorption spectroscopy; SSMS = spark source mass spectrometry; OES = optical emission spectroscopy; PES = plasma emission spectroscopy.

The concentration of many elements was near the detection limit of instrumental methods. Acidification, which is conventionally used as a pretreatment step for metal analyses, resulted in the precipitation of elemental S and carboxylic acids which acted as an adsorbent for some elements, interfered with most analytical measurements, and resulted in an inhomogeneous sample. The performance of x-ray fluorescence, neutron activation, plasma emission and atomic absorption spectroscopy on the water was significantly better than that of spark source mass spectrometry, optical emission spectroscopy and other methods.

The study of water quality parameters demonstrated that standard methods, such as ASTM or EPA methods, cannot be used to accurately measure many of these parameters in these types of waters. The following methods were found to give incorrect results when used to analyze retort waters: (1) $\text{Hg}(\text{NO}_3)_2$ titration and

Technicon AutoAnalyzer methods for Cl; (2) titrimetric method without pretreatment for S^{2-} ; (3) gravimetric method for solids; (4) permanganate oxidation method for COD; (5) indirect method for TOC. Some existing chemical methods for the measurement of alkalinity, SO_4 , inorganic C, Na, SCN, As, and total S and methods developed in this work for CO_3 , HCO_3 and Cl may be adequate for routine analyses following limited additional laboratory testing.

PLANNED ACTIVITIES FOR 1979

The intercomparison studies initiated for oil shale materials will be extended to other synfuels including tar sands and coal gasification. Also additional work will be completed on oil shale retort waters. Other waters will be studied and work initiated to resolve the large number of chemical interferences found for standard analytical methods.

Advances in Soft X-Ray Fluorescence Spectrometry for Oil Shale Analyses

S. Flexser, H. R. Bowman, and J. M. Neil

INTRODUCTION

The low energy dispersive x-ray spectrometer developed at LBL has previously been used to determine the abundances of the major rock-forming elements in a variety of rock samples. Powdered samples are fused with a low-melting matrix (LiBO_2) to produce amorphous glass discs for analysis.

The purpose of this study was to apply this technique to the analysis of oil shale, which contains considerable volatile material, and to expand the suite of elements measured to include P, S, and Cl, which are generally minor constituents of rock samples. This involved the resolution of some particularly difficult technical problems, including sample crystallization on cooling, spectral background determinations, and loss of organics during fusion.

ACCOMPLISHMENTS DURING 1978

In order to determine the spectral backgrounds beneath the P, S, and Cl peaks, it was first necessary to evaluate the mutual interference of these adjacent peaks. Figure 1 shows the spectrum of a standard used in analyses of oil shales, excited by $\text{AgL}\beta$ x-rays. Peak interferences were studied using samples of individual elements as well as "blank" samples - discs of fused matrix alone. Past attempts to prepare such samples had failed due to crystallization on cooling, but this problem was circumvented by combining boric acid, in ratios up to 2:1, with the LiBO_2 matrix. This enabled us to observe the effect of crystallization on the x-ray spectra of blank discs. Figure

Fig. 1. X-ray spectrum of standard used in analysis of oil shales. Peaks of P, S, and Cl are shown. Exciting radiation is $\text{AgL}\beta$ x-rays resulting in peak to right of Cl. (XBL 791-241)

Fig. 2. X-ray spectra of blanks of identical composition with (a) no apparent crystallization and (b) considerable crystallization. Anomalous broad peaks in (b) are presumed diffraction peaks. Exciting radiation is $\text{MgK}\alpha$ x-rays, resulting in sharp peaks to the left. (XBL 791-240)

2 compares the x-ray spectrum for an amorphous blank disc (a), with that of a blank disc which crystallized considerably during cooling (b). Both samples were excited by $\text{MgK}\alpha$ x-rays, resulting in the sharp peaks shown. (Excitation by other radiation - e.g., by $\text{AgL}\beta$ x-rays - results in additional anomalous peaks and distortions of the spectrum which can interfere with fluorescence peaks. However, these anomalies are most apparent with $\text{MgK}\alpha$ excitation.) The anomalous peaks in (b) are presumed to be diffraction peaks resulting from crystallization. We hope to verify this by correlating these peaks with specific reflecting planes in the crystallized Li-borate compounds using diffraction techniques.

This investigation indicated that boric acid can effectively suppress crystallization during cooling of samples fused with a LiBO_2 matrix, and that such crystallization is likely to result in diffraction of x-rays.

PLANNED ACTIVITIES FOR 1979

The techniques developed to analyze oil shales will be applied to a range of samples to develop geochemical and environmental information.

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Methods for the Measurement and Analysis of Dissolved Gases in Complex Aqueous Mixtures

S. P. Lubic and A. S. Newton

INTRODUCTION

During the past year, methods were developed for the measurement and analysis of dissolved gases in water from wells and artesian springs and oil shale retort waters. In each method the water samples are degassed on a vacuum system and the evolved gas mixtures fractionated and collected in a series of low temperature traps. The amount of gas collected in each fraction is measured and the gas is transferred to glass sample bulbs for analysis by mass spectrometry.

ACCOMPLISHMENTS DURING 1978

Dissolved Gases in Well and Spring Waters

A method was developed to measure dissolved gases in well and spring waters without atmospheric contamination of the sample. A number of one liter stainless steel sample containers and associated valves and fittings were tested for vacuum tightness. After evacuating the sample containers, 20.0 torr of an internal standard gas mixture was added to each sample container. The gas mixture consisted of ^3He , Kr and CF_4 . The ^3He was used as an internal standard for the measurement of ^4He dissolved in the water. Kr was used to measure the efficiency of gas recovery from the water and sample container, and CF_4 acted as a carrier for gas transfer in the vacuum system and provided a suitable expansion volume for the water in the sample container. Atmospheric contamination of the sample was prevented by alternately evacuating and purging the sample line with CF_4 before water samples were aspirated into the sample containers.

The samples were transferred to the vacuum system by means of stainless steel lines connected to a two liter collection flask fitted with a large cold finger to prevent water contamination of the vacuum system (Fig. 1). The traps and two liter vessel were evacuated prior to sample introduction. The water was allowed to flow into the collection flask and then degassed. Evolved gases were collected in a series of traps. After degassing was completed the traps were isolated from the collection flask and vacuum manifold, connected to a Toepler pump, allowed to warm and the evolved gases transferred to a thermostatted gas buret. The gases were then transferred by mercury displacement from the gas buret into evacuated demountable sample bulbs and analyzed with a CEC model 21-103 mass spectrometer. Gas standards were run to determine mass fragmentation patterns and sensitivities. Analyses of various gas fractions were performed and the water basis determined. Results from a number of samples taken at the Hanford reservation in Washington are presented in Table 1.

Inorganic Carbon in Retort Waters

This method was developed to check the accuracy of the usual method which involves the evolution of CO_2 from an acid treated column of quartz chips maintained at 150°C followed by IR analysis of evolved CO_2 . Our method uses acid addition to shift the H_2CO_3 , HCO_3^- , CO_3^{2-} equilibrium such that H_2CO_3 is the predominant component. At low pH the solubility of H_2CO_3 is low and CO_2 will be evolved from solution. As the CO_2 is removed from solution, the equilibrium is further shifted until essentially all the

Fig. 1. Experimental setup used to measure dissolved gases in well and spring water. (XBL 791-245)

Table 1. Data summary for water samples for wells and artesian springs.^a

Component	Source					
	DC6	W1	SP1 (spring)	W2	DC6	DC2
H ₂	-	0.004	0.21	<0.00002	0.013	0.74
He	-	0.00027	0.00035	0.00052	-	-
O ₂	0.015	0.11	0.32	12	0.014	<0.02
N ₂	18	12	55	57	11	192
Ar	0.17	0.28	0.75	0.77	0.23	1.4
CO ₂	0.43	1.5	1.1	1.6	<0.016	0.0054
CH ₄	0.14	7.1	0.061	7.3	0.13	48
C ₂ H ₆	Sample DC2 only					0.01
Higher						<0.001
Hydrocarbons)						

^aAll values reported as ppm on a mole of gas per 10⁶ moles of water basis

inorganic carbon, originally present as HCO₃ and CO₃, is removed.

Five ml of an oil shale retort water sample were added to a 25 ml long neck, Pyrex flask; the flask was sealed and the contents immediately frozen in liquid nitrogen. One ml of concentrated H₃PO₄ was added to the solid sample and the flask connected to the vacuum gas transfer system. The whole system was then evacuated (Fig. 2). The flask was warmed and CO₂ was evolved as the H₃PO₄ mixed with the sample. The heat was removed and pumping continued until the solution began to freeze. At that point the sample flask and first trap were isolated from the rest of the system. The traps were warmed and the evolved gas transferred with a Toepler pump to a gas buret and analyzed by mass spectrometry. Analytical results for three retort waters are presented in Table 2.

Fig. 2. Experimental setup used to measure CO₂ in retort water. (XBL 791-244)

Table 2. Results for three oil shale retort water samples

Sample	# of analyses	mg/l inorganic C ^a
150 ton	3	6404 ± 43*
S-13	2	4042 ± 3
S-15	2	5358 ± 35
$\bar{x} \pm 1\sigma$		

The two methods differ primarily in the means of sample preparation and the choice of traps necessary to isolate the components of interest. For the analysis of well samples it was necessary to devise a method to minimize atmospheric contamination in sampling as well as in transferring the sample to the vacuum

system. Furthermore, since the amount of gas to be collected was small and the sample volume large, an internal standard was necessary to estimate the amount of gas recovered from the sample. For the analysis of the well samples it was necessary to use several traps to isolate all the components. In the analysis of the shale waste water sample, since evolved carbon dioxide was the only component of interest, the choice of trap was simple. By choosing liquid nitrogen, oxygen and nitrogen were not retained and the subsequent analysis was simpler. Finally, the two methods are general and with a few modifications, for example in the temperature of number of traps, could be applicable to other problems.

Instrumentation Development

Applied Laser Spectroscopy

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OVERVIEW

The research philosophy of our group is to apply advanced laser spectroscopy and condensed matter physics to energy and environmental problems. The narrow linewidth and tunability of lasers allow unsurpassed sensitivity and specificity in detecting trace contaminants of the atmosphere. The advanced state of condensed matter physics enables us to apply such knowledge effectively to energy production processes and to test novel methods for energy conversion, such as photovoltaic devices, super-ionic electrical energy storage devices, and the extraction of oil from oil shales with lyotropic liquid crystal emulsifiers.

LASER OPTOACOUSTIC MEASUREMENTS & CHARACTERIZATION

Laser optoacoustic spectroscopy is not only a powerful tool for the detection of trace contaminants in air and water, but is a means of investigating the fundamental properties of gaseous, liquid, or solid phases of matter. One of our goals in this project is to develop ultrasensitive multiparameter elemental and molecular detectors for the characterization of pollutants released during energy production and utilization. Another aim is to maintain a state-of-the-art capability in optoacoustic detection by fully understanding the physics of this technique. At the same time, we are active in developing new or modified laser systems compatible with our particular needs. Below we report on some results of our activities.

The Dependence of Acoustically Non-Resonant Optoacoustic Signal on Pressure and Buffer Gases*

The growing interest in optoacoustic spectroscopy has created the need for a better understanding of the processes involved in the generation of the observed signal. In particular, it is important to consider the role of the buffer gas and its thermodynamic and transport properties, to examine the dependence of the optoacoustic signal on pressure, and to include the microphone response and the detector geometry in the analysis. Molecular relaxations and energy transfer among the molecules involved should be taken into account in the case of acoustically resonant detector since the typical time scales at which these processes occur are comparable to the modulation frequencies of the exciting light (≥ 1 kHz). On the other hand, in the acoustically non-resonant case, bulk properties of gases constitute the dominant factors in determining the behavior of the detector. We report here on the dependence

of the non-resonant signal on pressure and on a wide range of buffer gas thermodynamic properties. The microphone response is taken into account for the first time. Our findings for the acoustically resonant case have been reported earlier.¹

The thermodynamic solid gas theory of Kerr and Atwood² provides a suitable starting point to analyze the optoacoustic signal strength. A weakly absorbing gas confined to a cylindrical cell is excited by radiation passing through on axis. This axial heating results in a negligible gas flow [$\Delta T(r=0) < 10^{-2}$ C], so that we may view the gas as a solid, determine the temperature everywhere in the cylinder and find the consequent local pressure rise, and then calculate the equilibrium pressure when the gas is allowed to shift. The temperature redistribution in the ensuing gas flow is of second order. A step rise in the onset of heating will cause a time-dependent pressure rise given by

$$p(t) = \beta(P_0) \frac{W}{L} \frac{P_0}{4\pi\bar{\kappa}T} \left\{ \sum_m D_m(b) \exp\left(-\bar{\alpha}\bar{\epsilon}_m^2 \frac{t}{a^2}\right) \right\} \quad (1)$$

where W/L is the power incident per unit length (z -axis) dependence is ignored), $\beta(P_0)$ is the fraction of W/L absorbed, P_0 and T are the equilibrium pressure and temperature within the cell, respectively; a is the radius of the cell, and $\bar{\epsilon}_m$ is the m th root of the zeroeth order Bessel function $J_0(\bar{\epsilon}_m) = 0$. In our case, $\bar{\kappa}$ is the effective thermal conductivity and $\bar{\alpha}$ is the effective thermal diffusivity of mixture. $D_m(b)$ are numerically calculated coefficients which depend on b , the ratio of the Gaussian beam waist to cell radius (0.189 in our case). The D_m are difficult to calculate for small values of b due to round-off error, but may be verified with the relation

$$\sum_m D_m(b) = 1 - b^2 + \frac{b^2 - 1/2b^2}{e^{1/b^2}}$$

Since in practice, the exciting light is approximately square-wave modulated, we may, from Eq. (1), determine the first harmonic lock-in amplifier output as

$$V = S(P_0, \bar{\gamma}, T) \times \beta(P_0) \frac{W}{L} \frac{P_0}{4\pi\bar{\kappa}T} \left\{ \sum_m \frac{D_m e^{i\theta_m}}{\sqrt{1 + \frac{\omega^2 a^4}{\bar{\alpha}^2 \bar{\epsilon}_m^4}}} \right\} \quad (2)$$

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where $S(P_0, \bar{\gamma}, T)$ is the sensitivity of the microphone, and $\tan \theta_m = (\omega a^2 / \bar{\alpha} \xi_m^2)^{-1}$. The

explicit dependence of the microphone sensitivity on P_0 , γ , and T is given by Eq. (3)

$$S(P_0, \bar{\gamma}, T) = S_{\text{rated}} \frac{1 + B}{1 + B \frac{P_0 \bar{\gamma} T_{\text{STP}}}{P_{\text{atm}} \gamma_{\text{air}} T}} \quad (3)$$

where $B \cong 1$, $\bar{\gamma} = (\bar{C}_V + R/\bar{C}_V; \bar{C}_V = x_i C_{pi} + (1 - x_i) C_{pj} - R$, and x_i is the molar fraction of i , the optically absorbing gas; the buffer gas is denoted by j . Equation (3) indicates that the microphone sensitivity increases as the pressure decreases.

In Figs. 1 and 2 we give graphic representations of the theoretical predictions of Eq. (2) for representative buffer gases.

The experimental configuration is shown in Fig. 3. A partial pressure of 10 torr CH_4 (the optically absorbing species) was maintained throughout the experiment. The 3.39μ line from a He-Ne laser served as the exciting light. The CH_4 relaxation time has been shown to be less than 0.2 msec for our case,⁴ too short to be noticed here. The thermodynamic properties of the cell were varied by the substitution of the following buffer gases: He, Ne, Ar, Kr, Xe, H_2 , CO, CO_2 , N_2O , and SF_6 . An external mixing chamber was used to ensure rapid and full gas mixing. Frequency and power fluctuations of the laser output proved to be the limiting factor in the data analysis.

The detector consisted of a 6-cm long cylindrical brass cell, 0.9-cm in diameter. Two Knowles Electronics miniature electret microphones (model BT-1759) were placed at the front end and one was placed at the rear. Except for the confirmation of the first longitudinal resource in SF_6 around 1000 Hz, little difference existed between microphones, and a single microphone was used throughout.

The 3.39μ output of the He-Ne laser lies in near coincidence with the ν_3 absorption band of CH_4 ;⁵ consequently, the power absorbed first rose, then fell with increasing pressure as the CH_4 line was broadened into the laser line. Since our laser operated in a multimode fashion, and due to the overlapping absorption lines at high pressure, it was judged appropriate to simply determine the pressure dependence of $\beta(P_0)$ from difference measurements with the power meter behind the cell. As expected, each buffer gas has a slightly different dependence due to differing molecular weights and sizes, as the curves in Fig. 4 indicate.

Typical experimental results are compared with theory in Figs. 1 and 2. The dependence of the optoacoustic signal on pressure for various buffer gases is in good quantitative agreement with the theoretical predictions

Fig. 1. Optoacoustic signal as a function of pressure for representative buffer gases. Solid lines are the theoretical predictions of Eq. (2). Modulation frequency is 50 Hz. κ and C_V were obtained chiefly from "Thermophysical Properties of Matter," Vols. 3 and 6, Y. Y. Touloukian, P. E. Liley and S. C. Saxena, editors (Plenum Press, N. Y., 1970); and C. Y. Ho, R. W. Powell, and P. E. Liley, J. Phys. Chem. Ref. Data 3, Suppl. 1 (1974). Vertical axis in arbitrary units. (XBL-789-2688)

Fig. 2. Optoacoustic signal as a function of modulation frequency for H_2 . Solid lines are the theoretical predictions of Eq. (2). Vertical axis in arbitrary units. (XBL-789-2690)

Fig. 3. Schematic of the experimental configuration. (XBL-789-2691)

Fig. 4. Percent of power absorbed as a function of pressure for the buffer gases of Figs. 1 and 2.

(XBL-789-2689)

of Eq. (2). We find that D_1 alone does not adequately describe the pressure dependence of the signal, particularly for low pressures, and that the number of terms required increases for gases of low molecular weights. Ten terms were used in our case. As anticipated, the signal strength is strongly influenced by the heat capacity of the gases involved. The many internal degrees of freedom associated with a large heat capacity, as in the case of SF_6 , compete for the exciting energy, thus depressing the optoacoustic signal. On the other hand, the noble gases produce the largest signals. Those gases with large thermal diffusivities yield their largest signals at higher pressures than those with smaller diffusivities.

The frequency dependence of the signal is clearly demonstrated by the set of curves for H_2 shown in Fig. 2. The dominance of the second term under the radical of Eq. (2) begins at lower P_0 with greater ω . The complicated pressure

dependence of the $\bar{\alpha}$ in the radical, together with the leading P_0 term, then eliminate the dip found at lower ω . No dip is shown for He, even at the lowest frequency; however, a small dip is expected to appear in a cell of smaller radius. The overall peak height increases with decreasing ω , due to the ω dependence under the radical. Furthermore, due to the P_0 dependence of the diffusivity, the peak will shift towards lower pressure with increasing frequency.

Some discrepancies do exist between the theory and the experimental results. The turn-over points tend to be shifted lower or higher in pressure than predicted, depending on whether the buffer thermal conductivity is lower or higher than that of the absorbing gas. Secondly, the actual curves tend to fall off with increasing pressure more than the theory predicts, particularly for CO, CO_2 , N_2 , N_2O , and H_2 . The differences, although not large, are most likely a result of a combination of factors, such as the effective thermal conductivity and thermal diffusivity. Since 50 to 90% of the incident power was absorbed in the experiment (Fig. 4), the z-dependence may improve the accuracy of the model slightly, but a more gas-dependent mechanism is a likelier cause for error. Also, the adequacy of Eq. (3) in describing the microphone sensitivity has not been experimentally verified. Finally, we use a multimode laser with no attempt made to stabilize its frequency, leading to fluctuations in the power absorbed at lower pressures.

A practical consequence of our results is that if one were to optimize the S/N of an acoustically non-resonant detector, the following should be taken into account: the second term under the radical in Eq. (2) must be kept on the order of one or smaller for as high a pressure as possible. Since α is proportional to $\kappa/(P_0 \cdot C_V)$, the first term eventually drops out, the P_0 dependence cancels, the κ dependence cancels, and the signal becomes proportional to $1/C_V$. Until this happens, however, the

signal rises with pressure. Ideally then, one requires a small κ and a large α in the buffer gas. Both this and the high-pressure dependence mentioned above point toward as small a C_V as possible, indicating the selection of a noble gas. Within the noble gases, the choice is not as clear. Argon worked well, and this may be due to the near match in diffusivity with the absorber. In particular, we find that a higher signal may be obtained with an absorber-buffer mixture than with any amount of absorber alone.

One may also moderate the increase of the second term under the radical by varying the other factors. One should use as low a modulation frequency as possible, although the $1/f$ noise of the electronics limits the benefits of this approach. A reduction in the cell's radius would be particularly effective since this enters as a factor to the fourth power. Here, to, a trade-off exists as the D_m falls with increasing b . In front of the brackets we find that reducing the temperature enhances the signal as well as (within limits) lowering the electrical noise.

In conclusion, we have demonstrated that a small-radius, non-resonant optoacoustic detector operating at low frequencies has a S/N ratio that compares well to the acoustically resonant case. It generates its largest signal at low pressure whereas the resonant detector operates best at high pressures.⁶ Low pressure operation has the advantage of better spectroscopic line resolution and lower background signal.⁶ The non-resonant signal, furthermore, is relatively independent of molecular relaxation times and viscosity effects, unlike the resonant signal. Advantages of such a detector include compactness and flexibility, since it lacks the restriction of a particular resonant frequency.

Many of the advantages of the optoacoustic technique are shared by the two types of detectors. For example, our findings point to the optoacoustic detector's potential as a quick means to determine the thermal conductivity and diffusivity of an optically non-absorbing gas or gas mixture. One may non-invasively study chemical reactions by monitoring the thermal conductivity and power absorbed. One may also invasively investigate laser-induced photophysical and photochemical processes.

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Optoacoustic Characterization of Hydrogenated Amorphous Silicon

Recently, there has been great interest in the generation of electric power by the use of solar cells. Because of the requirements of chemical purity and crystalline integrity, the cost of solar cells is prohibitive. These requirements can be fulfilled and the cost can be reduced by use of amorphous films. By using a new spectroscopic technique, optoacoustic spectroscopy, we hope to understand the properties of these films.

It has been shown that solar cells of reasonable efficiency can be made by passing an rf discharge through silane gas (SiH_4). The resulting material is a mixture of hydrogen and silicon which has semiconducting properties similar to those of crystalline silicon. It is believed that the hydrogen bonds to the vacancies and defects, tying up dangling bonds. These dangling bonds are responsible for trapping the electrons excited by the sunlight, preventing them from reaching the electrodes, and thereby limiting the efficiency of the device.

The role of hydrogen in determining the electronic band structure and absorption characteristics of hydrogenated amorphous silicon is not well understood. One of the most useful methods for investigating the material is to look at the optical absorption of its traps and defects. By measuring the number and location of these trapping states through absorption, one can hope to minimize their effects on the solar cell.

There is a problem, however. The films are 1μ thick, and are irregular, with pits and voids. The trapping states absorb very little since they are in the energy gap of the material. Consequently, traditional optical absorption techniques such as reflection and transmission are inadequate. The technique of optoacoustic spectroscopy, which detects a pressure wave caused only by the absorbed energy, is both very sensitive and unaffected by inhomogeneities of the sample. In optoacoustic spectroscopy, a laser is modulated on and off by a mechanical chopper. This beam is focussed on a sample where the absorbed energy causes expansion and contraction at the same frequency as the chopper. These oscillations in the sample are detected by a piezoelectric transducer attached to the sample. The output of the transducer oscillates in time with the chopped

laser beam and is fed into a lock-in amplifier which detects only signals at the chopping frequency. By changing the frequency of the laser, the absorption of the sample changes and therefore the magnitude of the stress wave in the solid changes. By plotting the output of the lock-in amplifier vs the laser frequency, one has spectra similar to an optical absorption spectra, with the difference that the sample's thermal and acoustical properties also affect the spectrum.

The first phase of our experiment was to develop piezoelectric transducer (PZT) handling techniques. We cut the PZT's using a sharp knife and soldered leads to the silver electrodes on each side. The PZT is glued to a glass slide using nonrigid epoxy to protect it. The sample is attached using Eastman 910, a very low viscosity glue, to give a thin glue layer. The samples tested have been thin 0.002 cm foils of copper, tantalum, and tungsten with and without a layer of black spray paint, tinted glass, and various lengths of black coated glass rod.

We have found that the sample's thermal and mechanical properties can significantly affect the signal. By comparing the signal from different lengths of glass rod, we observed the effect of sample length. The width of the sample does not seem to affect the signal significantly. According to the theory of elasticity, one can expect of thermally thin samples (their thicknesses are much less than the thermal length $[\kappa/\omega\rho c]^{1/2}$) where κ is the conductivity, ω is the chopping frequency, ρc is the heat capacity/volume) that $S \propto \alpha_t/k$ where α_t is the linear coefficient of expansion and k is the thermal diffusivity. We found that this relation is roughly true, i.e., copper gives a lower signal than tantalum because of its high diffusivity. However, the quality of the sample coupling to the PZT can be even more important. Finally, there can be as much as a 10% variation of the signal over the face of the PZT and the sample so that the beam cannot be positioned arbitrarily.

We have also investigated characteristics of the signal depending on the intensity of the incident light. The signal is linear in the absorbed power over 4 orders of magnitude. We have been able to detect as little as 0.1 μW of power, thus demonstrating the sensitivity of this technique. The limitation of the sensitivity have been found to be equipment electronic noises. This can be reduced if a better signal to noise ratio is required. If we vary the chopping frequency, we find that for thermally thick samples the signal is inversely proportional to the chopping frequency. This is predicted by the theory of elasticity. For thermally thin samples, the signal goes initially as $1/\omega^{3/2}$ and later as $1/\omega$. Finally, we have found that focussing of the beam only slightly increases the signal. Through these observations we have an empirical understanding of some of the factors affecting the signal.

The next phase of our research will involve taking spectra and comparing them to conventional optic spectra. We plan to look at known crystalline systems such as GaP and Si. By comparing the optoacoustic spectra to conventional optical spectra, we can determine the effect of the energy deposition profile in the sample vs the optoacoustic signal. The crystalline silicon spectra will provide a comparison for the hydrogenated amorphous silicon. Finally, we plan to take spectra of hydrogenated amorphous silicon and develop an understanding of the physics involved in this important substance.

Development of a Versatile, Inexpensive, Easily Constructed Waveguide Laser*

Last year we reported preliminary results on a new waveguide CO₂ laser design employing an alumina tube as an optical waveguide, swage-type tube fittings as electrodes, and a grooved, water-cooled aluminum block as a heat sink.¹ At that time we reported an output of 4.6 W from a laser tube 11.75 in. long with a 3.2 mm bore. We now report on our investigations of shorter and smaller-bore waveguide lasers, and grating-tuned operation.

We first attempted operation of a laser of the same design as previously described,¹ but with a waveguide 11 in. long and with a 2.4 mm bore. The smaller bore results in a larger divergence of the beam emerging from the end of the waveguide, and short radius of curvature concave mirrors are needed to refocus the beam into the ends of the waveguide if large losses are to be avoided. We obtained a copper high reflector and a ZnSe output coupler (reflectivity 94% at 10 μm), both with radii of curvature of about 34 cm. The maximum output power is 8.5 W occurred when the mirrors were spaced a distance about equal to their radius of curvature from the ends of the waveguide. Since for free-space modes this constitutes an unstable cavity, there is no question that our tube is acting as a true waveguide (an issue of uncertainty with our earlier, 3.2 mm bore laser). The gas mixture, as before, was 70% He, 20% CO₂, and 10% N₂; the optimum average (of inlet and outlet) pressure was 67 torr, and the differential across the tube was about 5.5 torr. The current was 10 ma, and the tube voltage drop was 11.5 KV. We operated the tube average pressures up to 103 torr, and estimate that it should continue lasing up to at least 125 torr.

Good output power of 4.8 W can be obtained using more readily available flat mirrors placed close to the ends of the waveguide.

We replaced the concave copper mirror with a grating placed as close as possible to the end of the waveguide. We were able to obtain single-line operation on P(6) through P(42) and R(4) through R(38) in the 10 μm band, and on P(10) through P(30) and R(10) through R(28) in the 9 μm band. The maximum single-line power was 1.1 W. When this laser was operated without any wavelength selection,

power was very insensitive to flow rate, but in single-line operation, a fast flow rate was found to be necessary. Also, optimum currents were found to be several ma lower than observed without wavelength selection.

We built an even further miniaturized laser with a waveguide 12 cm long and with a 1.6 mm bore. This laser, with its shorter length, could employ a cavity of larger free spectral range, and the smaller bore resulted in a higher optimum pressure of about 100 torr, and consequently a broader laser linewidth. Operation at pressures up to 146 torr was achieved. At optimum pressure the optimum current was 7.3 ma, and an output of 2.5 W was observed. However, we had frequent problems with damage to the windows of this laser, and have chosen to continue using the 2.4 mm bore laser.

A few miscellaneous points may be of interest to prospective waveguide laser builders. First, we found that as long as flowing gas operation is to be used, RTV is preferable to epoxy for attaching the windows, due to its greater flexibility. Use of a finned heat sink on the cathode, and fans to cool both electrodes, is probably essential. With our 1.6 mm bore laser we compared the performance of brass and stainless steel electrodes, and observed rapid window degradation with the former material. Finally, if special concave mirrors are to be used, it would be advisable to design the output mirror as a positive meniscus lens to collimate the output beam. This is especially important as one goes to small bore lasers, which produce very divergent beams, and for which (in many applications) an external collimating lens may be needed if collimation is not accomplished by the output mirror. Finally, we have operated this laser with other molecular gases, the details of which are awaiting patent office clearance.

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*A complete version of this work has been submitted for publication in Optics Letters.

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APPLICATIONS OF LIQUID CRYSTALS

The liquid-crystalline state of matter is characterized by a spontaneous anisotropic order and by fluidity. The anisotropic order leads to anisotropy in the physical properties of the medium, and the fluidity makes it easily susceptible to external perturbations. Such perturbations can be in the form of electric or magnetic fields, temperature or pressure. In addition, we have demonstrated that certain gaseous organic pollutants change the liquid-crystalline structure. This change, which is readily detectable, is the basis for an inexpensive and sensitive 1 ppm personal dosi-

meter for some organic pollutants. Two other applications of liquid crystals are described below.

Liquid Crystal Magnetometer

The purpose of this project is to develop a sensitive (fraction of a gauss) and simple dosimetry technique for occupational exposures to magnetic fields in fusion plants. Our approach will involve the use of ferro-nematic¹ and ferro-cholesteric² liquid crystals.

The physics behind the proposed device is that incorporating non-spherical magnetic grains into the liquid crystal matrix allows the nematic and cholesteric molecular orientation to be coupled to a very weak external magnetic field. The coupling, which is mechanical in nature, is due to the elastic properties of the liquid-crystalline phase. This coupling is what we propose to exploit as the basis for our magnetic dosimeter.

Specifically, the orienting effect of the "host" liquid-crystalline matrix upon the "guest" magnetic grains will result in a net magnetization in the absence of an applied field, and this remnant magnetization will provide the mechanism for coupling to the external magnetic field. At zero external field, the ferro-liquid crystal will exhibit certain optical properties. In the case of ferro-cholesterics, a specific wavelength of light will be selectively reflected. For ferro-nematics, a given light intensity will be transmitted through the birefringent sample.

Upon the application of an external magnetic field (as weak as one gauss), the coupling of the spontaneous magnetization to the field will induce the disruption of the liquid-crystalline order causing the optical properties of the matrix to change: (1) in the case of ferro-cholesterics the wave length of the selectively reflected light will vary as a function of the applied field, and at a critical field strength, complete disruption of the cholesteric order will occur; (2) in the case of ferro-nematics, as the external field increases, the matrix birefringence will change and the intensity of light transmitted through crossed polarizers will vary. As in the case of ferro-cholesterics, at a certain critical external field, total disorder of the nematic phase sets in.

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Novel Applications of Lyotropic Liquid Crystal for Energy Production*

We recently proposed the use of lyotropic liquid crystals for the efficient extraction

of oil from oil shale deposits. Typical lyotropics are organic molecules with an ionic end which is hydrophilic and an aliphatic tail which is hydrophobic. Depending on the solvent in which these molecules can be dissolved, and on the temperature they exhibit structural polymorphism which can be exploited for technological purposes. The simplest of these structures is the insoluble monolayer, which has been used to purify water and to recycle rare organic substances. In the case of oil shale application, a better understanding of the properties of the lyotropic monolayer is required if efficient extraction methodology is to be achieved.

The conventional techniques for investigating insoluble monolayers include the Langmuir-Adam and the Wilhelmy balance methods¹ where static surface pressure is measured as a function of the surface area per molecule. Dynamic properties such as dilatation viscosity (dynamic surface tension) and surface viscosity are typically deduced from studies of flow through slits, damping of oscillations of concentric cylinders, and damping of macroscopic surface waves.^{1,2} The results of these experiments are difficult to interpret because of the rather gross perturbations used to probe the experimental system.

Our experimental approach was to probe the spontaneous, thermally excited surface waves, the so called ripplons, by light scattering.³ The strength of this technique is that both static and dynamic properties of the monolayer can be elucidated in a reliable fashion and with minimum perturbation.

Our experimental arrangement is shown in Fig. 5. A beam, 2 mm in diameter, from an Ar⁺ laser (4880 Å) or a He-Ne laser (6328 Å) probed the air-water interface from the water side. To maximize the signal, the angle of incidence was slightly greater than the angle for total internal reflection.⁴ Reflected light was then collected with a 30 cm focal length lens, and the scattering wave vector was selected by a pinhole in the focal plane of the lens moving perpendicularly to the plane of the drawing. Light passing through the pinhole was collected on the photocathode of an FW 130 photomultiplier tube and the resulting photocurrent, after pulse shaping and amplification, was analyzed with a 4-bit real time digital correlator. Stray light scattered elastically by windows and other optical components served as the local oscillator. Instrumental linewidth was determined from measurements on pure water and comparing the results with existing theories.^{5,6}

Since ripplons on surfaces form dynamic gratings which phase modulate the reflected beam,^{7,8} the scattered light will then be frequency shifted by an amount equal to the ripplon frequency. Due to the small amplitude of the ripplons (few angstroms), light is scattered effectively only in the grating's first order, thus allowing for the investigation of one q -vector at a time.

Fig. 5. Experimental set-up.

(XBL-786-9199)

L- α -dipalmitoyl phosphatidyl choline (DPPC) was obtained from Sigma Chemical Co. ($\geq 98\%$ purity) and was used without further purification. The monolayers were deposited on the interface by spreading from a 9:1 hexane:ethanol solution (reagent grade). Demineralized distilled water was used for the experiments. The pH was 5.2 ± 0.2 and the sample temperature was stable to better than 0.1°C . The air over the interface was routinely purged with nitrogen to minimize DPPC oxidation.

We have extended the hydrodynamic theory of ripplons^{5,6,9} in insoluble surfactants at interfaces. We take into account the following monolayer parameters: the static surface tension $\pi(c)$ as a function of surface coverage c ; the dilatational viscosity $\beta(c)$ which takes into account the change in surface tension due to the rate of surface change ($\dot{c}$); the intrinsic surface viscosity $\eta_s(c)$; and the slip friction coefficient $\mu(c)$ which accounts for the difference in the velocity of the lipid film and the water.¹⁰ We assume the interface to be in the x - y plane and no motion in the y direction.

The following set of equations then describe an insoluble monolayer:

1. $\nabla \cdot \vec{v} = 0$ (water incompressibility)
2. $\rho \partial_t \vec{v} = -\nabla p + \eta \Delta \vec{v}$
(Navier-stokes equation of motion for water)
3. $c \partial_t v_L = \partial \pi / \partial c \partial_x c + (\beta + 2\eta_x) \partial_x^2 v_L - \mu (v_L - v_x(z=0))$
(equation of motion of the monolayer)
4. $\partial_t c + c \partial_x v_L = D \partial_x^2 c$
(Continuity equation for surface layer)
5. $v_z(t, x, z=0) = \partial_t \xi(t, x)$
(velocity boundary condition)
6. $p(z=0) - 2\eta \partial_z v_z(z=0) + \pi \partial_x^2 \xi + \beta \partial_x^2 \partial_t \xi = 0$
(boundary condition on normal force acting on interface).
7. $-\eta (\partial_x v_z + \partial_z v_x)(z=0) + \mu (v_L - v_x(z=0)) = 0$
(boundary condition on tangential force acting on interface).

where ξ = ripple amplitude
 $\vec{v}$ = water velocity
 v_L = lipid velocity in the x,y plane
 D = molecular surface diffusion coefficient
 p = hydrostatic pressure
 η = water viscosity
 ρ = water density

We look for a solution of the form

$$\xi(x,t) = \xi(t) e^{iqx}$$

Following general lines of Ref. (6), we can solve the above equation in terms of its time-Laplace transforms. The result is

$$\tilde{\xi}(s) = - \frac{\xi(t=0)}{s}$$

$$\left[\frac{\left(\sigma + \frac{1}{x} \frac{E(x)}{x+d} \right) (1 - m(x) + \theta x) + 1}{D(x)} - 1 \right]$$

where

$$D(x) = [1 + (x+y)^2 - y^2 m(x) + Bx]$$

$$\cdot \left[1 + \theta \left(cx + \frac{E(x)}{x+d} \right) \right]$$

$$+ \left(\sigma + \frac{1}{x} \frac{E(x)}{x+d} \right) [(1 - m(x))(1 + Bx) - x^2 m(x)]$$

$$x = S/\omega_0$$

$$\omega_0 = \sqrt{\pi q^3 / \rho}$$

$$y = 2\eta q^2 / \pi_0 \rho$$

$$m(x) = \sqrt{1 + 2 \frac{x}{y}}$$

$$E(x) = \frac{\partial \pi}{\partial c} \frac{c}{\pi} + 2\eta_s q^3 (x+d) / \pi_0 \rho$$

$$d = Dq^2 / \pi_0$$

$$B = \beta_0 / \pi$$

$$\sigma = cq / \rho$$

$$\theta = \rho \omega_0 / \mu q$$

The power spectrum of the ripples, which is the Fourier transform of the experimentally measured correlation function is then given (6) by

$$P(\omega) = \frac{\langle |\xi(t=0)|^2 \rangle}{\pi \omega}$$

$$\text{Im} \left\{ \frac{1}{D(x)} \left[1 + \left(\sigma + \frac{1}{x} \frac{E(x)}{x+d} \right) \cdot (1 - m(x) + \theta x) \right] \right\}_{s=-i\omega}$$

Computer calculations showed that in the range of the parameters of interest, the resulting power spectrum is very nearly Lorentzian and thus the experimental correlation data were fitted to the form

$$C(\tau) = C(0) e^{-\Gamma \tau} \cos(\omega \tau + \phi)$$

where the additional phase ϕ was needed to account for most of the deviation from Lorentzian shape.

RESULTS AND DISCUSSION

To a first approximation^{11,12} one expects that for a free surface $\omega = (\pi q^3 \rho)^{1/2}$ and $\Gamma = 1\eta q^2 / \rho$; therefore our data (Fig. 6) are plotted as apparent surface tension $\pi = \omega^2 \rho / q^3$, and relative damping constant $g = \Gamma / 2v q^2$. For surface coverage larger than 0.01 molecule/Å², the surface tension rapidly decreases as the number of molecules per unit area is increased until the transition region between the expanded and condensed phases of the film is reached. This is exhibited by an abrupt change in the slope of the apparent surface tension vs coverage curve at the low coverage side, while at the high coverage end of this region the transition to the condensed phase is gradual. Further increase of surface coverage results in a rapid decrease in the surface tension. Once the full monolayer is reached, addition of more molecules does not change the value of the observed surface tension.

The behavior of the damping constant is qualitatively similar to that of the apparent tension. It should be noted that at lower temperatures the shoulder corresponding to the expanded-condensed transition becomes much less pronounced.

The theory described above is a function of several dissipation parameters the relative importance of which can now be estimated.

We estimate the slip parameter μ to be the ratio of the water viscosity η and the mean distance between the lipid molecules; i.e., $\sim 10^5$ poise/cm. For our range of wave vectors, calculations show that Γ was independent of μ for $\mu > 10^3$ poise/cm. The slip is unimportant in our case. We can also neglect the dilatational viscosity since in our range of q 's the results show no q^3 dependence for Γ which would be the case if dilatational viscosity were important.

Fig. 6. Apparent surface tension and damping as a function of surface coverage for 32.4 °C. (XBL 786-9203)

Published values for surface viscosity of the expanded phase fall in the range of 10^{-4} and 10^{-3} surface poise, and for the condensed phase they are on the order of 1 surface poise.^{13,14} From our data, we estimate the surface viscosity for the expanded phase to be $<10^{-5}$ surface poise; otherwise the theoretical q -dependence of the damping constant will be in large disagreement with the observed values and we could not account for our high damping values at low coverage. The damping in the expanded phase is thus due to a particular combination of surface compressibility and surface tension.

Our results in the condensed phase are consistent with the behavior of an incompressible values derived from our surface tension data are too large to account for an incompressible behavior, we are lead to conclude that surface viscosity is an important damping mechanism in the case of the condensed phase and that it is $>10^{-3}$ surface poise. To verify this conclusion, data are needed at smaller q 's than we have been able to achieve.

In Fig. 7 we give the q -dependence of the relative damping coefficient for two coverages at 26°C. Figure 8a shows the results for a coverage of 0.0135 molecules/Å² with a surface tension of 60.5 dynes/cm. The theoretical curve is for zero surface viscosity and a film compressibility of 0.02. In Fig. 8b we give the results for a coverage of 0.0223 molecules/Å²

with corresponding surface tension of 39 dynes/cm. For q values above 10^3 cm⁻¹, the experimental results agree with the theoretical fit for both coverages. The systematic discrepancy between theory and experiment for the lower q 's is caused in part by an overestimate of the instrumental linewidth due to our inability to completely isolate low frequency mechanical vibrations for our experimental set-up.

In Fig. 8 we present a summary of the temperature dependence of the real surface tension, the relative damping coefficient, and the area per molecule for both a full monolayer and for the low coverage side of the expanded-condensed transition region. It can be seen that the low coverage results extrapolate to the full monolayer values at ~42°C.

We observe no increase in the compressibility of the monolayer at the onset of the expanded--condensed transition as the temperature increases. This and the jump in area per molecule lead us to conclude that the system does not exhibit critical behavior.

It is known that a second phase transition, the so called pretransition, occurs in bulk DPPC systems at 34.5°C.¹⁶⁻¹⁸ We observed such a transition in the monolayers. Our evidence for that is the abrupt change in the slope of the surface tension vs temperature isochore as shown in Fig. 9.

Fig. 7. Wave vector dependence of relative damping coefficient at 26°C. (a) coverage of 0.0135 molecules/Å² (expanded phase), (b) coverage of 0.0223 molecules/Å² (condensed phase); the solid lines are theoretical fits for zero surface viscosity and for an incompressible film, respectively. (XBL-786-9202)

Fig. 8. Temperature dependence of monolayer parameters. Solid circles are for full monolayer, open circles for the low coverage side of the expanded-condensed transition region. (XBL 786-9201)

Fig. 9. Surface tension isochore showing the "pre-transition." Only some of the data points are shown. The solid line represents the average behavior of data. (XBL 786-9220)

FOOTNOTE AND REFERENCES

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FUTURE DIRECTIONS

In the area of laser optoacoustic detection, work will continue in the direction of developing ultra-sensitive detectors for NH_3 , NO_x , HCN , and H_2CO . We plan to extend optoacoustic detection to water pollutants, with specific emphases on nitrates, sulphates and organic contaminants. Efforts will be given to the elemental detection and analysis by a tunable laser optoacoustic spectrometer. Our collaboration with the Atmospheric Aerosol Research Group at LBL will continue on the optical properties of carbonaceous particulates.

Research on the optical characterization of amorphous silicon will center on a careful investigation of the nature of the "band gap" and the possibility of the existence of excitons. De-excitation mechanisms of the photoexcited amorphous films will be investigated and optoacoustic spectra of hydrofluorinated amorphous silicon will be obtained. As has been the case this year, our prime motivation is to explore optically means of achieving higher conversion efficiencies from these devices.

Various applications of liquid crystals will continue to be explored. Optimization and comparison of ferro-nematic and ferro-cholesteric magnetometers will be made, and prototypes will be constructed; with the actual field tests conducted in magnetic fusion experimental areas. Work on gaseous organic detectors will aim at investigating the fundamental mechanism responsible for the observed effect; sensitizers will be incorporated in the liquid crystal detector to adjust the concentration threshold. Finally, in the case of lyotropic monolayers, work will be extended to the oil-water interface, and investigation of emulsification and vesicle formation will be carried out.

Fission Effects in Neutron Activation Analysis

F. Asaro and H. V. Michel

Several of the nuclides produced in the neutron-induced fission of ^{235}U interfere with the measurement of gamma (γ) rays utilized in neutron activation analyses. This article delineates quantitative methods for evaluating fission effects and making corrections in unknowns and standards.

The mass-yield curve for ^{235}U slow-neutron induced fission is a double-humped distribution with somewhat broad maxima at about masses 95 and 140. Below mass 89 and above mass 144 the mass yield rapidly becomes progressively smaller. In between the humps, the mass yield drops by over two orders of magnitude. More

energetic neutrons show the same general type of distribution, but with a more shallow valley between the two humps. The nuclides, either used for neutron activation analysis at LBL or expected to be used, which would be directly affected by fission, are ^{153}Sm , ^{147}Nd , ^{141}Ce , ^{140}La , ^{139}Ba , $^{117\text{m}}\text{Sn}$, ^{99}Mo , ^{95}Zr and ^{95}Nb . Although ^{131}Ba is not produced by fission, the measurement of one of its γ rays at 496.23 keV (particularly useful for neutron activation analysis) is complicated by the 497.08 keV γ ray of ^{103}Ru which is produced by fission. The rather sensitive measurement of Ba abundances by the $K\alpha$ x-rays of Xe ($^{131}\text{Ba} \rightarrow ^{131}\text{Cs} \rightarrow ^{131}\text{Xe}$) can also be difficult because of the interference of the 29.97 keV γ ray of the ^{140}Ba fission product.

The relationship between the abundance of the γ rays from the fission product daughter can be determined explicitly from the relative masses produced by the ^{135}U fission, the relative counting efficiencies of the detector system for the different γ rays, and the decay properties of the radioactive nuclides produced by fission or neutron irradiation.

The general equation of relative amounts of radioactivity produced in fission expressed as ppm of the different elements with normal isotopic abundances is:

$$\frac{\text{Abundances of element x in ppm}}{\text{Abundances of element y in ppm}} =$$

$$\frac{D_x}{D_y} \frac{I_y}{I_x} \frac{FY_x}{FY_y} \frac{\sigma_y}{\sigma_x} \frac{AW_x}{AW_y}$$

where I_y and I_x are the isotopic abundances of the isotopes which produce the radioactive nuclides by n, γ reactions; AW_x and AW_y are the corresponding atomic weights; σ_x and σ_y are the corresponding neutron activation cross sections; FY_x and FY_y are the cumulative relative yields, from the neutron induced fission, of the nuclides being measured; and D_x and D_y are functions of the half lives of the measured nuclides and their fission produced parents. The value of D for a measured radioactive nuclide with a fission parent of significant half life, for no direct production of any daughter of that parent, and for times of irradiation and counting which are short compared to the time between irradiation and counting, is approximated by:

$$D = \frac{\lambda_1}{\lambda_2 - \lambda_1} (e^{(\lambda_2 - \lambda_1)T} - 1)$$

where λ_2 is the half life of the measured γ ray radioactive, λ_1 is the half life of the fission parent and T is the time between the midpoint of the irradiation and the midpoint of the γ ray count. If the half lives of all of the fission-chain parents are not significant (i.e., they are very short), $D = 1$.

Although the relative fission yields of masses between fission humps in the mass yield curve will be sensitive to neutron energy, the others, which include all of those in this study, will be relatively insensitive. The principal variables are then the relative neutron activation cross sections, and these can be measured with standards, provided the relative γ ray counting efficiencies for the measurement system as a function of γ ray energy are known. The LBL neutron activation analysis procedure measures such relative cross sections for each neutron irradiation, and they are proportional to the product of the literature values (which are used as computer input) and quantities f_i (or flux $_i$) which are derived in the computer calculations. The equation then becomes:

$$\frac{\text{Abundances of element x in ppm}}{\text{Abundances of element y in ppm}} = \frac{f_y}{f_x} \frac{C_y}{C_x} \frac{D_x}{D_y}$$

where f_y and f_x have the meanings given above, and the C_i have the following values: Mo (140 keV γ rays of $^{99\text{m}}\text{Tc}$), 0.021; Nd (91 keV γ of ^{147}Nd), 0.082; ^{141}Ce 145 keV γ , 0.059; 329 keV ^{140}La γ , 1.09, 478 keV ^{140}La γ , 0.924; ^{153}Sm 103 keV γ , 231. Errors in the γ ray counting efficiencies and abundances used for computer input were compensated by changes in the C_i values. The D_i have values of 1 for the nuclides considered except for ^{140}La where

$$D_{\text{La}} = 0.152(e^{0.359(t+[t_{\text{irr}}+\Delta t]/2)} - 1)$$

and t = length of time in days between the end of irradiation and the start of the γ count, t_{irr} = length of irradiation in days and Δt = length of the γ count in days. D_i would have values different from 1 for a number of elements not considered in this article, e.g., ^{95}Nb (due to the ^{95}Zr parent) and ^{131}Ba as measured by the 496 keV γ (due to ^{103}Ru interference). The value of D for Mo has been incorporated in the value of C as its time dependence is negligible.

The fission effect could be rigorously measured absolutely from the gamma rays of 12.8 day ^{140}Ba or those of 1.68 day ^{140}La after essentially all of the latter activity produced by the n, γ reaction has decayed away. Alternatively two measurements of ^{140}La gamma rays at different times could be used to evaluate the fission component. In any event the equations given in this article would determine the fission contribution to the other nuclides considered. In the LBL neutron activation analysis procedures the apparent abundance of Mo produced by fission in a sample is approximated by assuming that it is 65% of the uranium abundance in the sample, and the other fission produced nuclides are determined relative to that value. Periodic measurements on uranium samples indicate this approximation is accurate to about 10%. This approximation would not be valid for samples with depleted or enriched ^{235}U . The Mo value used at LBL for the standard (Standard Pottery) includes both the Mo abundance and the fission effect and so needs no further correction. When

corrections for other elements are necessary in an unknown sample, they are also necessary in the standard.

The calculations for La, Nd and Ce were checked on geochemical samples or waters from oil shale production and found to give valid answers within the uncertainties. The amount

of fission-produced Sm was studied with Sm Kx-rays produced in the irradiation of normal uranium and was found to be negligible as indicated by the equations.

Further work is necessary to check the validity of the treatment for ^{95}Zr , ^{95}Nb and 496 kev γ of ^{231}Ba .

Instrumentation for Environmental Monitoring

*Y. C. Agrawal, N. M. Amer, R. McLaughlin, G. L. Morton,
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The "Instrumentation for Environmental Monitoring" volumes are an attempt to place in one convenient source much information about environmental monitoring. This material is being written in such a manner as to be understandable and interesting to the nonspecialist, as well as providing new information for the expert.

Analytical instrumentation development today is occurring at an ever increasing rate. Traditional wet chemical methods are being replaced by sensitive instrumental methods. Commercial instrumentation is constantly undergoing modification to increase multiple parameter capability, lessen interference, improve sensitivity, incorporate data processing and achieve automatic operation. Choosing an analytical instrument is becoming a more difficult task because of the large variety of instruments offered and the ever increasing financial investment. The instrumentation survey provides valuable information by comparing the features of almost all commercially available instruments used in environmental monitoring. During the present fiscal year, instrument notes on atomic absorption spectrometers, atomic emission spectrometers and ultraviolet-visible absorption spectrophotometers were updated. Information on monitoring radiation by radiation type (alpha, beta, gamma, and neutron) has been updated. Also, new sets of instrument notes have been prepared for the sampling of particulates and the calibration of instruments used for particulate sampling.

In addition to summarizing product literature in commercial instrumentation, the survey contains up to date description of developments in the environmental monitoring field. During the past year several new sections have been written and several old sections have been updated. In the AIR volume a section devoted to the sampling of particulates in air has been completed. A section describing the calibration of equipment used for particulate sampling has been written and is now undergoing review. Also, a section on the remote monitoring of air particulates is nearing completion.

In the WATER volume, the metals-in-water section has been rewritten, enlarged and updated. The discussion of atomic absorption spectroscopy has been expanded to include interferences and the use of the deuterium arc and Zeeman atomic absorption as a means to lessen the effects of background absorption. The discussion of atomic emission spectroscopy now includes a description of the rf and dc plasma arcs as well as information on commercial inductively coupled and dc plasma instruments. A new subsection on anodic stripping voltammetry has been included and the Introduction has been rewritten to include an expanded section on water pollution law. The metals-in-water and Introduction sections are now being prepared for the printer.

In the RADIATION volume, changes are being made to keep pace with rapid changes resulting from public and political concern with nuclear energy. This has led us to completely rewrite sections on nuclear reactors, fuel reprocessing plants, mining and milling of uranium ores, and natural radiation background. In addition, the introduction to this volume which contains new sections on biological effects of radiation and basic radiation detection methods is being rewritten and enlarged.

Four new sections have been added to the BIOMEDICAL volume: arsenic, beryllium, nickel and gaseous organics. These sections discuss the biological effects that result from the ingestion, inhalation and absorption of these materials by man and animals. What is known of the physio-chemistry of these effects is almost described. The remarks concerning the effects of inhaled aromatics, in the gaseous organics section, are particularly timely because of the substitution of these compounds for tetraethyl lead in gasoline. In addition instrument notes for the detection of metals discussed in this volume have been updated.

The accomplishments of the last fiscal year are summarized in Table 1.

Table 1. Accomplishments of Instrumentation Survey Group during FY 78.

<u>Volume 1 AIR</u>	<u>Status</u>
Sampling for Particulates in Air	completed
Calibration of Particulate Sampling	undergoing review*
Remote Monitoring of Particulates in Air	draft completed
Instrument Notes (for above sections)	in progress
<u>Volume 2 WATER</u>	
Introduction	completed
Metals in Water	completed
Instrument Notes	completed
<u>Volume 3 RADIATION</u>	
Introduction (biological effects, basic radiation detection)	undergoing review
Nuclear Reactors	undergoing review
Fuel Reprocessing Plants	draft completed
Mining and Milling of Radioactive Ore	in progress
Natural Radiation Background	undergoing review
Particle Accelerators	in progress
Sources of X-Radiation	in progress
Instrument Notes	complete
<u>Volume 4 BIOMEDICAL</u>	
Arsenic	complete
Beryllium	complete
Nickel	complete
Gaseous Organics	complete
Instrument Notes	complete

*This indicates material has been completed in draft form and has been sent to experts in the field for critical comment.

Operation of a Gas Chromatograph/Mass Spectrometer of Environmental and Fossil Energy Samples

A. S. Newton and W. Walker

The Finnigan model 4023 GC/MS has been in operation with a high degree of success for a little longer than one year. The operating duty cycle is estimated to be greater than 80%, and almost all problems of maintenance of the hardware have been solved at the local level. The life expectancy of expendable components, the electron multiplier detector and the ion source filaments has been about as expected from other users' experience, with the ion source giving less trouble than expected owing to the extreme care taken in its operation. The first multiplier lasted 1.3 years and failed dramatically with a loss in gain of 10^4 during an experimental chemi-ionization experiment. The longest down time was caused by failure of a memory chip in the computer. The procedure for locating the exact chip which had failed was not documented, and this increased the time necessary for repair.

Because this instrument is not used for routine work with the same type samples run every day, it has been necessary to fit the GC column to the type of sample under investigation. For packed column operation this change represents no difficulty, and several different columns can be used each day (though this is not good practice). Complex samples requiring the maximum resolution must be investigated using capillary columns. We have used the wall coated open tube type, 0.25 mm I.D., 30 m in length. These are more difficult to prepare and install. Owing to the difficulty in obtaining ferrule materials which will operate at high temperature, be flexible enough to seal the column outlet to the connecting lead to the mass spectrometer without breaking the fragile capillary, and thermal cycle with temperature programming of the column without developing leaks, the column outlets have been straightened, bent through

the separator oven, and connected directly to the transfer line to the ion source. The relatively constant temperature of the separator oven has greatly reduced leakage due to thermal cycling of the connecting ferrule. The difficulty of installing a column in this manner makes one loath to change to another column unless absolutely necessary. Fortunately the excellent resolution of a capillary column is such that a given column coating such as OV-101 yields an excellent RIC (reconstructed ion chromatogram) on most samples, even though a column coating of higher polarity would be preferred for some applications.

Some 150 samples have now been analyzed in addition to the many test mixtures which have been studied to adjust the system parameters. The experimental samples fall into several categories as described below.

In the first category are samples of the products of model compound studies in some coal liquefaction processes. These samples can be moderately complex as shown by the RIC in Fig. 1. This shows the total ion chromatogram of the products of phenanthrene with cyclohexane as a solvent in the presence of a Friedel-Crafts reagent. A packed column was used: 3% OV225 on 80-100 mesh Chromosorb W, HP; 2 mm x 2 m glass column. Figure 2 shows the effect of computer enhancement on this chromatogram. About 3/4 of the chromatographic peaks in Fig. 2 were identified by computer comparison of the mass spectrum of each chromatographic peak with the mass spectra of the 25,000 compounds in the library supplied with the data system. Obviously not all possible compounds are represented in the library nor will all compounds in the sample be necessarily separated in the chromatogram.

Another type of energy related samples has been gas samples from the hydrogenation of coal under various conditions. These samples

Fig. 1. Reconstructed total ion chromatogram of the products of Friedel-Crafts reactions of phenanthrene in cyclohexane. (XBL-792-331)

Fig. 2. Enhanced reconstructed ion chromatogram of the data shown in Fig. 1. (XBL-792-332)

Fig. 3. Reconstructed ion chromatogram of the products of the Fischer-Tropsch synthesis of hydrocarbons. 30m, Ov-101 capillary column. (XBL-792-330)

have been quantitatively analyzed for the light gases, H_2 , N_2 , Ar, CH_4 , CO , CO_2 , C_2H_6 , C_3H_8 , C_4H_{10} , dimethyl ether, and methyl chloride using the CEC 21-103 analytical mass spectrometer. In this analysis there is always a small residue of unaccounted intensity on various mass peaks. These residuals are obviously a mixture of alkanes. When a sample of the gas was run on the GC/MS, the identity of these trace hydrocarbons was established. Owing to the extreme discrimination for light molecules in the GC/MS, this procedure is only qualitative; but once identified, quantification on a gas chromatograph with a flame ionization detector is relatively simple. The products were found to be predominately branched alkanes.

Samples of products produced in the catalytic hydrogenation of CO by the Fischer-Tropsch process have been studied. As shown in Fig. 3, the principal products consist of a series of n-alkanes C_8 - C_{17} with smaller yields of branched alkanes and alkenes.

Products of purely synthetic organic reactions have also been studied. The mass spectrum of each product and the chemistry involved serve to identify the products even though the compounds are not in the library. The compounds so identified have been, in fact, added to our own library.

A series of studies have been made on samples resulting from engineering studies on new types of physics equipment. Materials of construction which might evolve gases with positive electron affinity are suspected. GC/MS studies of gases evolved on heating various materials in vacuum and of films condensed on vacuum chamber walls show that many materials contain plasticizers, mainly butyl and octyl phthalates (widely used with PVC). Materials of high electron affinity have not been observed, and if present may be transient and low boiling.

Extracts of waste waters from coal liquefaction processes and oil shale retorting processes have been briefly investigated. Phenols in the acid fraction from coal wastewaters have been identified, but polyfunctional products must be derivatized before successful GC/MS identification is possible. The neutral and basic fraction from shale waste water yielded many identifiable nitrogenous compounds. For better identification, more effort must be given to preparing suitable samples for the GC/MS.

Many environmental samples from marine sources have been studied. Various fractions of pollutants separated from seawater or mussels (*Mytilus californianus*) have been investigated, all using capillary GC/MS. The mussel samples were part of the mussel watch program, a world wide program to monitor pollution by studying the chemical species concentrated from water by the ubiquitous filter feeding mussel, *Mytilus* sp. Samples derived from either sea water or mussels are usually quite complex as illustrated by the chromatogram shown in Fig. 4. This was a saturated hydrocarbon fraction extracted from mussels collected at Carmel Bay, a relatively clean coastal area. The chromatogram, made using a 30 m, OV-101, capillary column and an FID detector, shows the presence of 167 peaks as well as a well defined manifold of unresolved components. Many of the components were identified by GC/MS, the n-alkanes from C₁₂ to C₃₂, and the biomarker hydrocarbons pristane and phytane. The identification of more compounds by use of mass chromatograms of compound-specific ion masses and multiple ion detection of mass numbers which are specific for given types of compounds is now being pursued.

Fig. 4. Gas chromatogram of the saturated hydrocarbon fraction extracted from the mussel *Mytilus californianus* from Carmel Bay.

Development and Application of X-Ray Fluorescence Analytical Methods

R. D. Giaque, R. B. Garrett, and L. Y. Goda

INTRODUCTION

The development and application of x-ray fluorescence (XRF) analytical methods is an ongoing program within the Chemical Analysis Group. The methods are applied to support programs which require trace multielement chemical analysis.

Over the past year we have contributed significantly to oil shale research programs. Raw and spent oil shales, shale oil, and retort waters have been analyzed to study the distribution and material balance of trace elements in products from in-situ oil shale retorting experiments. These chemical analyses assist in assessing potential environmental control problems associated with shale oil production.

A variety of liquid and solid industrial waste materials have been analyzed as part of a program designed to study potential waste management problems and assess possibilities of reclamation. Additionally, x-ray methods have been applied to support several programs in the Earth Sciences Division, including a program designed to locate a site suitable for disposal of radioactive waste materials.

ACCOMPLISHMENTS DURING 1978

A method for the direct determination of trace elements in light element matrices has

been established.¹ It takes advantage of the fact that the incoherent mass scattering coefficient for 17.4 keV Mo K α radiation is relatively constant for the elements Li (Z=3) $\rightarrow$ Ca (Z=20). Consequently, incoherent scattered Mo K α excitation radiation, corrected for matrix absorption, can serve as an internal standard which compensates for variations in sample mass, x-ray tube output, and sample geometry. Samples of ~ 0.5 g are prepared in the form of thin specimens (~ 0.08 -cm thick) in a cell between two 0.0006-cm thick polypropylene windows. Standardization for most elements is achieved using standard aqueous solutions diluted to ~ 100 ppm. Data obtained from simultaneous transmission measurements for several x-ray energies is used to calculate matrix absorption corrections. For 15-minute analysis periods, results are typically accurate to within $\pm 10\%$ when x-ray counting statistics are not the limiting factor. Sensitivities of 2 ppm or better are realized for 16 of the 22 elements determined (Ti $\rightarrow$ Zr, Hg, Pb, Th, and U).

Tables 1 and 2 list the results for NBS Standard Reference Material 1632 Coal and for a shale oil sample and serve to illustrate the capability of this method. Our Pb result for the coal is about a factor of two lower than the NBS certified value. However, our result for Pb has been substantiated by another analytical technique, Zeeman atomic absorption spectroscopy.²

Table 1. Elemental concentrations in NBS SRM 1632 coal ($\mu\text{g/g} \pm 2\sigma$)

Element	XRF	NBS	NAA (3)
Ti	951 $\pm$ 53	(800)	1040 $\pm$ 110
V	24 $\pm$ 8	35 $\pm$ 3	36 $\pm$ 3
Cr	22 $\pm$ 8	20.2 $\pm$ 0.5	19.7 $\pm$ 0.9
Mn	39 $\pm$ 3	40 $\pm$ 3	43 $\pm$ 4
Fe	7790 $\pm$ 360	8700 $\pm$ 300	8400 $\pm$ 400
Co	8.5 $\pm$ 4.2	(6)	5.7 $\pm$ 0.4
Ni	14.5 $\pm$ 1.2	15 $\pm$ 1	--
Cu	17.7 $\pm$ 1.5	18 $\pm$ 2	--
Zn	35.7 $\pm$ 9.9	37 $\pm$ 4	30 $\pm$ 10
Ga	6.1 $\pm$ 0.3	--	--
Ge	2.9 $\pm$ 0.2	--	--
As	4.7 $\pm$ 1.0	5.9 $\pm$ 0.6	6.5 $\pm$ 1.4
Se	3.1 $\pm$ 0.2	2.9 $\pm$ 0.3	3.4 $\pm$ 0.2
Br	17.5 $\pm$ 0.3	--	19.3 $\pm$ 1.9
Rb	20.1 $\pm$ 0.6	--	21 $\pm$ 2
Sr	151 $\pm$ 4	--	161 $\pm$ 16
Y	7.9 $\pm$ 0.6	--	--
Zr	33 $\pm$ 4	--	--
Hg	<1.1	0.12 $\pm$ 0.02	--
Pb	13.6 $\pm$ 6.5	30 $\pm$ 9	--
Th	2.7 $\pm$ 0.7	(3.0)	3.2 $\pm$ 0.2
U	<2.3	1.4 $\pm$ 0.1	1.41 $\pm$ 0.07

Table 2. Comparison of XRF and NAA elemental results for shale oil, S-09 ($\mu\text{g/g} \pm 2\sigma$)

Element	XRF	NAA (4)
Fe	40.3 $\pm$ 2.0	38 $\pm$ 3
Ni	4.5 $\pm$ 0.6	4.2 $\pm$ 0.2
Cu	4.9 $\pm$ 0.6	4.6 $\pm$ 1.8
Zn	3.3 $\pm$ 0.3	2.4 $\pm$ 0.4
As	18.2 $\pm$ 1.0	18.2 $\pm$ 1.0
Se	0.8 $\pm$ 0.3	0.7 $\pm$ 0.1

PLANNED ACTIVITIES FOR 1979

X-ray fluorescence techniques which permit improved sensitivities to be obtained for the determination of trace elements in liquids will be investigated. Current methods for the analysis of liquids and solids will be expanded to cover a wider range of elements.

X-ray fluorescence methods will be applied to support (1) oil shale research programs, (2) a study designed to characterize the occurrence of uranium in a region of east-central Utah, and (3) a study of industrial liquid and solid waste management problems.

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Chemical Characteristics of Medieval Brasses*

H. V. Michel, F. Asaro and A. L. Norberg

As part of the study of Plate of Brass¹ two (presumably rolled) medieval brasses of known origin and age were analyzed by neutron activation analysis (NAA), x-ray fluorescence (XRF) and emission spectroscopy (ES).

It was anticipated that the abundance of elements other than Cu and Zn would reflect the method of refining and impurities in the ores. A brass Astrolabe, which style indicated it was made by Arsenius in Louvain about 1570 A.D., was generously supplied by Rod and Marjorie Webster from the Adler Planetarium in Chicago, Illinois. The plates were ~11 inches in diameter and ~.06 inches thick. The Horizon Plate and Tympan 51 of the Astrolabe were each carefully drilled in three areas and the resulting samples were analyzed by NAA, XRF and ES. The methods of measurement have been previously described.²

The composition of the two Astrolabe pieces is shown in Table 1. In order to place these elemental abundances in perspective as to time and/or origin of manufacture, the composition of several medieval brasses has been treated in the following manner. The average ratio of the abundance in medieval brass to the Plate of Brass was summed for eight elements, As, Ni, Sb, Au, Pb, Sn, and Fe. These elements

Table 1. Composition of astrolabe

	ASTR-1 (Horizon Plate)	ASTR-2 (Tympan 51)
Cu	68.5 $\pm$ 1.5	68.4 $\pm$ 1.5
Zn	30.6 $\pm$ 1.2	30.9 $\pm$ 1.1
Ag ppm	278 $\pm$ 12	260 $\pm$ 11
As ppm	470 $\pm$ 43	392 $\pm$ 36
Sb ppm	304 $\pm$ 5	67 $\pm$ 1
In ppm	< 0.5	1.3 $\pm$.3
Au ppm	1.5 $\pm$.3	1.3 $\pm$.3
Sn	.53 $\pm$.10	1.00 $\pm$.10
Ni ppm	2598 $\pm$ 33	2413 $\pm$ 22
⁴ Fe	.080 $\pm$.005	0.140 $\pm$.005
Cd	< 171	<179
² Pb	1.2 $\pm$.1	1.4 $\pm$ 0.1
Mg ppm	7 $\pm$ 2	5 $\pm$ 2

1. Composition in % unless indicated ppm.
2. XRF measurements done by Lily Goda and Robert Giaque.
3. 20% uncertainty due to flux monitor calibration.
4. Emission spectroscopy done by George V. Shalimoff.

can be much more abundant in old brass than in modern brass. Lead and tin can also be additives to brass besides being impurities. Table 2 shows the abundances of these elements in eight medieval brasses four from Italy (16th-17th C.), one from the Rhineland (18th C.), one possibly from France or Spain (14th C.), and the two Astrolabe samples (16th C.). The last column is the average ratio of the abundances with respect to the Plate of Brass (19th or 20th C.). In Table 2 and Table 3 it can be seen that the impurity or additive levels in the Astrolabe are about 30 times higher than the Plate of Brass and are similar to those of the 18th C. Rhineland brass.

It was previously shown that the impurities in the Plate of Brass were only consistent with Cu available in the 19th or 20th Centuries. A factor of 30 increase in these levels, which is large indeed, indicates sources of Cu or refining techniques of earlier periods.

Iron is not an additive used to improve the quality of brass, and the level in the Rhineland piece is much higher than the Astrolabe pieces. This may be associated with the casting

process of the Rhineland piece. This work suggests further studies are desirable to determine if the general level of impurities observed may be characteristic or be a lower limit for German-Belgium brass of the 16th-18th centuries. The impurity or additive levels for the 14th century French/Spanish and the 16th-17th century Italian brasses are on the average about 200 times higher than the Plate of Brass. (See Table 2 and 3). Further work may indicate if this may be characteristic or a lower limit for Italian brasses of that period.

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* This work was funded by the Bancroft Library of the University of California at Berkeley.

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Table 2. Trace element composition⁽¹⁾ of brasses

Sample	Date	As	Ni	Sb	Ag	Au (ppm)	Sn	Pb	Fe	Average Ratio (to Plate of Brass)
Astrolabe:										
Horizon Plate	1570	.047	.26	.0304	.028	1.5	.53	1.2	.08	27
Tympan 51	1570	.039	.24	.0068	.026	1.3	1.00	1.4	.14	33
Rhineland	18th C.	.036	.09	.033	.020	2.0	1.40	2.8	1.0	48
France/Spain	14th C.	.22	.19	.76	.11	5.6	1.07	6	1.2(2)	167
Italy	16th C.	.33	.63	.71	.23	67	1.45	2.7	.5	217
Italy	17th C.	.41	.33	.83	.06	18	1.41	3.1	.3	198
Italy	17th C.	.41	.42	.55	.12	35	2.5	3.5	.5	193
Italy	17th C.	.24	.34	.43	.21	72	2.25	4.3	.5	186
Plate of Brass	19-20C.	.005(2)	.012	.0083	.0048	.21	.006	.10	.027	1

(1) Abundances are in percent except for those of gold which are in parts-per-million (ppm).

(2) One half of upper limit was used in calculation

(3) Average ratio = $\frac{\sum_{i=1}^I (\text{Abund. Brass})_i}{\sum_{i=1}^I (\text{Abund. Plate of Brass})_i} \div I$ where i = elements 1-I

Table 3. Summary of average ratios of old brasses.

Geographic area	Date (century A.D.)	No. of artifacts	Mean	RMSD ¹
Belgium-Rhineland	16-18	3	36	11
Italy	16-17	4	198	13
France, Spain	14	1	167	
Plate of Brass	(19-20)	1	1	

¹Root - means square deviation of the mean.

Characterization of Mesoamerican Obsidian*

F. Asaro, F. H. Stross, R. Sidrys and H. V. Michel

Obsidian is a volcanic glass which can be chipped to form a very sharp edge for use as a cutting tool. It was much used by ancient peoples for this purpose, and a study of the distribution of obsidian from various source areas leads to a better understanding of ancient trading and cultural patterns. Because of their glassy nature, obsidian deposits from a given volcanic eruption can be chemically very homogeneous. However, because of the complexity of geochemical processes, the rhyolitic magmas (which lead to obsidian) vary somewhat in chemical composition in different areas. Both of these characteristics enable the high-precision neutron activation analyses performed at Lawrence Berkeley Laboratory to serve as powerful tools for distinguishing different obsidian source areas. In these measurements about 40 elements are detected, about 30 are measured with good precision, and 15-25 are used for characterization purposes. As obsidians from new sources are measured, the data are incorporated into a growing data base of reference sources. Part of this project involves cross-calibrations with other laboratories which are making or have made such measurements and incorporation of their information into the data base.

In a recent paper¹ a detailed record of compositions of several outcrops and workshops in the El Chayal area, northeast of Guatemala City in Guatemala, and some data in the Ixtepeque, Rio Pixcaya, and the Tajmulco sources (also in Guatemala) were given. This study makes available more detailed information on the Ixtepeque and Rio Pixcaya areas, which resulted from an extensive study and sampling of these areas.² It was found that different outcrops in the Ixtepeque region are similar in composition but are definitely distinguishable by high-precision methods. At least two of the different outcrops in the San Martin Jilotepeque - Rio Pixcaya area, however, are not readily distinguishable by these methods. Also included is an analysis of obsidian from Palencia, a village located within a few kilometers from the El Chayal source area, and possibly a part of it.

ARTIFACTS

Between the Ixtepeque (Guatemala) and the Santa Ana (El Salvador) volcanoes, which are about 60 km apart by air, there are several archaeological sites. A group of five worked samples was analyzed, which were collected² near the village Desague on the Lago de Guija, about 25 km southeast of Ixtepeque. The village is in El Salvador but close to the border with Guatemala. Three samples were obtained in the village of Chalchuapa near Santa Ana Volcano.² The samples were said to have come from Laguna Seca, a nearby obsidian workshop.

DISCUSSION

In Table 1 are listed the compositions of three outcrops in the Ixtepeque source area, which are designated 2-1, 2-2 and 2-4. Also listed are the compositions of the artifacts from Desague and Chalchuapa.

The three outcrops while apparently related, can be readily distinguished by our methods. One of the samples, however (942k) shown as having been collected at outcrop 2-2, matches in composition the six samples from outcrop 2-1, and not the other samples collected at outcrop 2-2. This suggests that this sample fell, or rolled, or was otherwise transported from the higher level of outcrop 2-1 to the locality 2-2 below. The artifacts from El Salvador, both those from Desague and from Chalchuapa matched in composition the Ixtepeque sources, specifically outcrop 2-1. Obsidian from the Santa Ana volcano has been measured by others,³ and the Ba abundance (~605 ppm) is much lower than found in Ixtepeque obsidian. If the Chalchuapa obsidian is indeed characteristic of that found in the Laguna Seca obsidian workshop, then bulk obsidian was transported from Ixtepeque rather than the nearer Santa Ana volcano.

The results relating to the Rio Pixcaya source area are listed in Table 2. These values may be compared with data obtained and published earlier¹ on samples from the same source area but whose specific outcrop association was not known. The two sets of samples match very well. Also listed in Table 2 are compositions⁴ of relevant artifacts from the Palaeoindian site of Los Tapiales in Guatemala. It is seen that all compositions form tight, coherent groups which cannot be differentiated by our methods.

The composition of the Palencia (see Table 3) sample is similar to but distinguishable from the El Chayal¹ compositions. It is consistent with less detailed data reported by other workers.^{5,6}

The sample analyzed from La Esperanza (see Table 3) is of interest particularly because it is the easternmost of Mesoamerican obsidian sources we have analyzed to date, and because its existence had been questioned. Its composition pattern is distinct from those of the nearest source, which we have analyzed, i.e. the Ixtepeque volcano. It cannot yet be distinguished from earlier less detailed and precise data taken by other workers³ on obsidian from the Santa Ana Volcano.

Table 1. Elemental abundances* of samples from Ixtepeque, Jutiapa, Guatemala source area.

Element	----- Source Samples -----				----- Artifacts from: -----	
	Outcrop 2-1 (6 samples)	Quequexque Village (1 sample)†	Quequexque Village (3 samples)	Agua Blanca (4 samples)	Desaque El Salvador (5 samples)	Chalchuapa, El Salvador (3 samples)
Al %	7.24±.20	7.09±.10	6.93±.13	7.15±.15	7.11±.23	7.27±.14
Ba	1022±19	1037±19	975± 18	1042±36	1077±23	1031± 36
Ce	43.3±.9	43.4±.9	42.7±.7	42.9±.5	42.9±.5	43.1±.7
Co	1.05±.08	1.10±.06	0.46±.04	0.79±.14	0.98±.05	1.10±.10
Cs	2.71±.17	2.81±.09	2.42±.07	2.47±.18	2.67±.09	2.78±.08
Dy	2.30±.11	2.25±.09	2.33±.10	2.36±.09	2.35±.11	2.35±.11
Eu	0.540±.013	0.558±.013	0.513±.008	0.540±.010	0.540±.009	0.551±.010
Fe %	0.923±.019	0.90±.02	0.74±.01	0.89±.07	0.91±.02	0.92±.02
Hf	4.44±.12	4.52±.10	3.60±.08	3.91±.07	4.52±.07	4.47±.05
K %	3.61±.26	3.93±.25	3.57±.25	3.61±.25	3.67±.29	3.38±.45
La	23.5±.9	24.1±.5	23.9±.5	23.6±.5	23.5±.5	23.2±.9
Mn	449±9	455±9	481±9	528±11	454±9	456±9
Na %	3.05±.05	3.06±.06	3.03±.06	3.15±.06	3.07±.06	3.08±.06
Rb	103±6	108±5	103±4	102±5	109±5	105±4
Sb	0.19±.04	0.23±.04	0.16±.04	0.23±.10	0.21±.04	0.24±.05
Sc	2.11±.05	2.12±.02	1.79±.02	1.95±.12	2.07±.04	2.17±.02
Sm	2.65±.03	2.72±.03	2.65±.03	2.64±.03	2.68±.03	2.66±.03
Ta	0.76±.02	0.81±.01	0.75±.01	0.71±.01	0.75±.01	0.76±.01
Th	7.17±.10	7.14±.07	6.98±.07	6.66±.09	7.13±.07	7.19±.07
U	2.30±.05	2.33±.03	2.14±.03	2.01±.03	2.29±.03	2.25±.02
Yb	1.81±.04	1.87±.04	1.82±.09	1.78±.05	1.86±.07	1.81±.02

See Ref. 1.

†The uncertainties are about 1 σ values of the precision.

*The abundances are in parts-per-million (ppm) except for those of Al, Fe, K and Na, which are in percent (%). The uncertainties are standard deviations (>1 sample). The measurements were calibrated vs. Standard Pottery.⁷ The accuracies of the measurements must incorporate the uncertainties in the Standard Pottery calibration.⁷

Table 2. Elemental abundances of samples from Rio Pixcaya (San Martin Jilotepeque), Chimaltenago, Guatemala source area.

Element	----- Source Samples -----			Artifacts from: Los Tapiales (7 samples)
	SMJ Outcrop 3-4 (2 samples)	SMJ Finca Durazno (4 samples)	SMJ* (2 samples)	
Al %	7.00±0.34	6.98±0.18	7.15±0.13	6.92±0.14
Ba	1103±30	1122±29	1073±22	1059±28
Ce	47.4±0.6	47.6±0.6	47.3±0.5	47.4±0.8
Co	0.33±0.05	0.39±0.07	0.39±0.04	0.42±0.07
Cs	3.29±0.10	3.46±0.10	3.29±0.10	3.32±0.16
Dy	2.03±0.14	2.00±0.10	2.10±0.11	2.13±0.11
Eu	0.532±0.008	0.547±0.008	0.547±0.007	0.543±0.012
Fe %	0.65±0.02	0.65±0.02	0.67±0.01	0.65±0.04
Hf	3.25±0.15	3.15±0.07	3.28±0.06	3.16±0.09
K %	3.54±0.35	3.45±0.24	3.71±0.24	3.56±0.27
La	26.4±0.5	26.4±0.5	26.0±0.6	26.6±1.0
Mn	530±11	519±10	521±10	521±10
Na %	2.94±0.06	2.95±0.06	2.92±0.06	2.94±0.06
Rb	122±5	120±5	125±9	125±12
Sb	0.41±0.06	0.37±0.05	0.34±0.05	0.47±0.11
Sc	1.98±0.06	2.00±0.02	1.98±0.02	1.93±0.03
Sm	2.68±0.03	2.69±0.03	2.69±0.03	2.71±0.03
Ta	0.76±0.01	0.76±0.01	0.75±0.01	0.76±0.01
Th	9.15±0.09	9.33±0.09	9.14±0.09	9.01±0.16
U	2.78±0.03	2.84±0.05	2.76±0.03	2.77±0.05
Yb	1.42±0.02	1.40±0.03	1.39±0.02	1.40±0.03

*See Ref. 1, Table 3.

FOOTNOTES AND REFERENCES

*This work is funded by programs at the University of California at Berkeley, the University of Texas at San Antonio, the University of Pennsylvania, and the University of Colorado at Boulder.

Table 3. Elemental abundances* of samples from Palencia, Guatemala and La Esperanza, Honduras source areas.

	Palencia	La Esperanza
Al %	7.02±0.09	7.58±0.29
Ba	874±21	772±25
Ce	42.5±0.7	49.8±0.6
Co	0.72±0.06	0.56±0.06
Cs	6.28±0.10	4.95±0.12
Dy	2.22±0.13	2.45±0.10
Eu	0.476±0.008	0.454±0.008
Fe %	0.738±0.014	0.83±0.02
Hf	3.54±0.06	3.54±0.07
K %	3.72±0.24	4.28±0.24
La	20.8±0.4	28.5±0.5
Mn	474±9	437±9
Na %	2.93±0.03	2.90±0.06
Rb	155±5	169±6
Sb	0.60±0.07	0.18±0.04
Sc	2.10±0.02	2.59±0.03
Sm	2.31±0.02	3.05±0.03
Ta	0.93±0.01	0.973±0.010
Th	11.2±0.1	12.50±0.12
U	4.03±0.04	3.60±0.04
Yb	1.59±0.03	1.47±0.02

*See Table 1.

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Combustion Research

Introduction

Continued expansion of research on combustion processes has occurred both nationally and at Lawrence Berkeley Laboratory (LBL). The principal programmatic research goal is to reduce the level of pollutant emissions associated with the combustion of fossil fuels, while at the same time conserving our natural resources through high combustion efficiency and low capital investment.

The research programs described in the following are aimed at developing a better understanding of the various fluid mechanical and chemical processes which are thought to be of critical

importance in reducing pollutant formation. The principal program areas are the interaction of fluid mechanical turbulence with combustion reactions, important phenomena and pollutant generating processes associated with internal combustion engines, fire safety and flame spread, and diagnostics and formation mechanisms associated with the generation of nitrogen containing pollutants. Most of these programs are closely associated with the University of California Department of Mechanical Engineering faculty, and the training of graduate students is an important aspect of the research.

Internal Combustion Engine Heat Transfer*

R. Greif, K. Chu, H. Heperkan, M. Nikanjam, and T. Namba

INTRODUCTION

The determination of the unsteady heat transfer in an internal combustion engine represents a problem that is of considerable practical importance as well as being one of fundamental interest. For example, heat transfer processes are critical to the quenching of wall reactions leading to high hydrocarbon emissions, the durability of engine components, the loss of energy leading to decreased efficiency, the reliability of calculations for cylinder pressure, etc. The transient, variable volume (moving surface), variable pressure aspects of the compression-expansion process result in complex phenomena that are difficult to appraise and predict.

ACCOMPLISHMENTS DURING 1978

In order to study reciprocating engine processes under well controlled laboratory conditions simulating the operation of a spark ignition engine, a single-pulse, compression-expansion apparatus was built by Oppenheim et al.¹ Measurements have been carried out in this system during the compression stroke (of a single pulse). In particular, experimental and theoretical studies have been completed of the unsteady wall heat transfer in nonreacting gases,^{2,3} as discussed below.

The temporal variation of the pressure of the compressed gas was recorded by using a pressure transducer that was placed in one of the ports in the test section. The variable displacement of the piston was obtained by using a steel rack that moved with the piston and interrupted a magnetic pickup during the

motion. The temperature of the wall was measured as a function of time by using a thin-film resistance thermometer. The resistance thermometer consisted of a thin platinum film on an insulated backing and was mounted flush with the wall to avoid disturbing the flow; it was connected as the active element in a d-c bridge. The increase in wall temperature during compression then caused a change in resistance of the platinum film which caused an unbalance in the bridge. The determination of the resistance versus time variation then yielded the desired variable wall temperature variation.

Based on the above measurements, the wall heat flux is obtained during piston compression. Specifically, the result is based on a solution of the conduction equation in the solid wall (insulated backing) subject to a variable surface temperature, and the heat flux is expressed as a Duhamel integral in terms of the variable surface temperature and the wall properties.²

An alternative approach for the determination of the wall heat flux is based on a solution of the conservation equations in the gas as applied to the thin boundary layer near the wall. Neglecting viscous dissipation and taking the pressure to be uniform yields the appropriate equations of continuity and energy. These equations have been solved to obtain a heat flux based on the gas properties.^{2,3}

Typical results for the unsteady heat flux as determined from both the solution of the conduction equation in the solid and the solution of the laminar boundary layer conservation equations in the gas, are presented in Fig. 1. The results for the heat flux from these two

Fig. 1. Heat flux variation. (XBL 793-9047)

independent methods are seen to be in good agreement. Results for the heat transfer coefficient have also been obtained and exhibit a nonmonotonic variation. Detailed analyses have also been made of the thermal boundary layer thickness, the induced convective transport resulting from the drop in the gas temperature near the wall, and the conditions near both end and side walls.

In conclusion, note that the studies provide a rigorous and useful method for determining the heat transfer to a steel wall during piston compression (when there is no insulated backing present). Indeed such calculations have been carried out by solving simultaneously the conduction equation in the steel wall and the boundary

layer equations in the gas subject to the required matching of the temperature and the heat flux at the surface.³ The results should prove to be useful in a number of applications.

PLANNED ACTIVITIES FOR 1979

A basic effort in the next year will be the study of the heat transfer in the presence of reacting gases. This will also entail a contribution to the energy transport by thermal radiation. We also plan to carry out measurements in shock tubes since the transport in the wall region is directly related to the phenomena in the piston-cylinder configuration.

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Wall Quenching Processes

J. W. Daily

INTRODUCTION

Unburned hydrocarbons remain in an automobile engine due to incomplete chemical reactions within the cylinder, along the cylinder walls, and in any small gaps in the piston crevices where the flame quenches and the fuel is left unburned. The flow patterns within the engine cylinder that affect the combustion process are extremely complicated. Both the intake process and the compression stroke introduce turbulence into the flow field, the former by the jet action from the intake valve, and the latter due to the vortex roll-up phenomena and any other piston induced motion. The flame must propagate through this flow field, and the nature of the turbulence and its location within the cylinder can have a profound effect on the degree to which reactions are completed.

In addition, flow changes near the spark plug have been postulated to be a major cause of cycle to cycle variations.

ACCOMPLISHMENTS DURING 1978

We have been studying the effect of engine configuration and operating conditions on unburned hydrocarbon emissions. The experiments have been conducted utilizing a pneumatically operated compression-expansion machine with square cross section and quartz side windows. Previous visualization experiments have been performed under conditions which allowed only a top view of the piston, whereas we are able to observe the combustion process from the side. Optical observations have been made by taking high speed schlieren movies of the test section. Hydrocarbons are measured by means of a gas chromatograph.

In a previous publication we have reported observations of unburned hydrocarbons for several piston configurations and have shown for our machine that the roll-up vortex and wall turbulence can play a critical role in determining combustion efficiency. The schlieren observations have shown a significant effect of piston shape and cycle timing on the flow field through which the flame must propagate. Even without the bulk turbulence that an intake process might introduce, wall turbulence can be generated during the compression stroke, both because of the roll-up vortex, and because of the unsteady boundary layers along the side walls. For complex piston shapes, large scale bulk motions are also induced.

The hydrocarbon measurements reveal a general trend of decreased combustion efficiency with retarded timing, and with total unburned fuel percentages much higher than that predicted by laminar quenching correlations.

PLANNED ACTIVITIES FOR 1979

Unfortunately, the gas chromatograph measurements provide no information about the dynamics of the quenching process. As the next stage in the investigation we would like to make spatially and time resolved optical measurements of methane concentration during the compression and expansion cycle. These measurements are to be performed by observing absorption of the HeNe 3.391 μ laser line by the methane. The square piston machine is ideally suited for such measurements.

Time and spatially resolved methane concentration measurements will allow identification of major hydrocarbon source areas and will enable comparison of measurements with appropriate theoretical models.

Lean Combustion in a Model I.C. Engine*

O. I. Smith,[†] R. F. Sawyer and C. K. Westbrook[‡]

INTRODUCTION

Requirements for the operation of internal combustion engines under conditions resulting in both high efficiency and low emissions of carbon monoxide, oxides of nitrogen and unburned hydrocarbons have resulted in increased interest in the combustion of very lean premixed gases. In general, lean combustion processes satisfy the first three criteria rather well; however, many studies show that unburned hydrocarbon emissions from internal combustion engines increase as the mixture is leaned from stoichiometric. This behavior may be attributed to three processes: misfire, wall quenching of the flame inside the thermal boundary layer, and quenching outside the thermal boundary layer (due to chamber expansion, for example), the so called "bulk quenching." Since the lean and rich flammability limits for premixed combustion approach stoichiometric values as the temperature and pressure of the unburned gas is lowered (due to adiabatic chamber expansion), it seems likely that the bulk quenching mechanism will assume increasing importance relative to wall quenching as the mixture approaches the lean flammability limit.

ACCOMPLISHMENTS DURING 1978

The experimental measurements have been carried out in a square-piston, single-pulse compression-expansion machine with schlieren quality glass side windows. The principal diagnostics for the present study were high-speed schlieren movies, and chemical analysis of the burned fuel mixture.

The results of the experimental investigations in premixed laminar methane-air flames

have been described and compared with those of the corresponding theoretical investigations.^{1,2} Both aspects of the studies were initiated in 1977. The experimental investigation allows one to estimate the role of bulk quenching in internal combustion systems, while the theoretical study provides an interpretation of the process on a molecular level.

The experimental studies have identified the two major contributions to bulk quenching as flame stretch, the process of flame kernel growth in a diverging (non-planar) geometry, and the magnitude (not the rate) of combustion chamber expansion.

The role of flame stretch in bulk quenching is well characterized by the Karlovitz number K , which serves as a measure of the net heat deficit due to divergent flame front propagation. The Karlovitz number depends on both mechanical properties (ignitor geometry) and the physical and chemical properties of the combustible mixture (specific heat, density, thermal conductivity and laminar flame speed) as well as the flame kernel diameter. For a laminar methane-air flame, flame stretch was found to play an important role if, at the beginning of chamber expansion, the flame kernel Karlovitz number is greater than 0.2. For $K < 0.2$, chamber expansion dominates and a one-dimensional (plane wave) model is likely to be satisfactory. Since K is inversely proportional to the flame kernel diameter, this principle indicates from a practical viewpoint that bulk quenching due to flame stretch will eventually become dominant as ignition timing is retarded. Further, within the limits of the Karlovitz number as a similarity variable, the condition for negligible flame stretch ($K < 0.2$) should apply to any combustible mixture, ignitor geometry, etc.

For bulk quenching processes where flame stretch is negligible, a one-dimensional theoretical analysis utilizing a 56 reaction chemical mechanism indicates that density decrease is ultimately responsible through its effect on both chemical and transport processes. Calculations indicate that bulk quenching occurs when H, O and OH radicals diffuse out of the flame zone faster than they can be consumed by the predominant chain propagation reactions. Volume expansion produces this effect because the rates of the bimolecular propagation reactions decrease quadratically with density while those of the diffusion processes decrease in proportion to the density. Thus this conclusion is in agreement with the experimentally observed correlation between amount of volume expansion and the point of bulk quenching, and suggests that for $K < 0.2$, simple heat loss models are unlikely to describe the process adequately. It also suggests that bulk quenching in I.C. engines should be much more sensitive to compression ratio than to engine speed.

Although the experimental and theoretical work emphasized quenching in a flame propagating through a laminar flowfield, it was observed experimentally that turbulence, from whatever source, minimizes the effect of bulk quenching. In fact, bulk quenching was never observed once the flamefront had penetrated a turbulent flowfield. This limits the application of the conclusions discussed previously to practical I.C. engines since turbulence is always present from the intake valve and piston motion during the compression stroke.

PLANNED ACTIVITIES FOR 1979

No further work is planned in this area, although extension of the bulk quenching characterization to the turbulent regime (very difficult both experimentally and numerically) should be very useful to the design of lean burn I.C. engines. Other useful extensions involve development of correlations between bulk quenching and degree of volume expansion for more realistic fuels and experimental confirmation of our contention that the criterion for flame stretch influence ($K \sim 0.2$) applies to a wide range of different fuels, ignitor geometries, etc.

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Jet Ignition Studies*

*A. K. Oppenheim, F. C. Hurlbut, F. A. Robben,
K. Teichman, K. Hom, and H. E. Stewart*

INTRODUCTION

The goal of these studies is to explore the fundamental features of the process of ignition of lean gaseous fuel-air mixtures using jets of radicals. The jets are generated either by an electric discharge, creating a plasma, or by combustion in a small prechamber producing a non-equilibrium mixture of products. The results of the study are of particular importance to the development of internal combustion engines operating on lean mixtures. Such engines should have the attributes of high efficiency and at the same time relatively clean exhaust gases.

ACCOMPLISHMENTS DURING 1978

The major effort was directed towards the investigation of the effectiveness of various seed gases in the plasma jet ignition system. This was accomplished by introducing different gases into the plasma jet generator cavity. In order to insure reliable data, main chamber

methane-air mixtures of an equivalence ratio $\phi = 0.6$ were used, while the orifice diameter of the plasma jet generator was kept at 2.4 mm. This work has resulted in a Ph.D. thesis¹ now being edited for publication as an LBL Report. As an illustration of the results obtained in the course of this study, some practical aspects are described below.

Figures 1, 2, and 3 are excerpts from high speed schlieren movies and pressure transducer records taken at the same time for three plasma jet igniter cases--methane seed, no seed, and nitrogen seed respectively. The time interval indicated under each print is the delay after discharge in the igniter, expressed in milliseconds. The pressure and time scales for each oscillogram are 10 psi per division and 20 msec per division, respectively.

Figure 4 shows the evolution of the volume of gas burned determined from the cinematographic records, while Fig. 5 compares the pressure

Fig. 1. Cinematographic schlieren photographs and pressure transducer record for plasma jet ignition ($\phi = 0.6$) -- CH₄ seed. (XBL 793-1047)

Fig. 2. Cinematographic schlieren photographs and pressure transducer record for plasma jet ignition ($\phi = 0.6$) -- no seed.
(XBL 794-1046)

Fig. 3. Cinematographic schlieren photographs and pressure transducer record for plasma jet ignition ($\phi = 0.6$) -- N_2 seed.
(XBL 794-1045)

in the explosion vessel as a function of time for the three plasma jet igniter cases. These results demonstrate clearly the superiority of methane seed over the others. The evolution of the mass burned in the explosion vessel evaluated from these data is displayed in Fig. 6, while the variation of the corresponding mass averaged flame speed, S_u , is shown in Fig. 7. In all three cases, the maximum value for S_u occurs at 4 msec (the starting point for the computations) and decreases continuously. The maximum value

of S_u for the methane seeded case is 34.7 cm/sec, while those for the no seed case and nitrogen case are respectively 33.4 cm/sec and 33 cm/sec, all significantly higher than the classical laminar flame speed of 8 cm/sec for a methane-air mixture at room temperature and an equivalence ratio of 0.6. This indicates conclusively the positive effects due to turbulence created by the jets in the enhancement of the combustion process they are capable of initiating.

Fig. 4. Volume burned as a function of time for three cases of plasma jet ignition -- CH₄ seed, no seed, and N₂ seed. (XBL 7812-13316)

Fig. 6. Mass burned as a function of time for three cases of plasma jet ignition -- CH₄ seed, no seed, and N₂ seed. (XBL 7812-13326)

Fig. 5. Pressure as a function of time for three cases of plasma jet ignition -- CH₄ seed, no seed, N₂ seed. (XBL 7812-13315)

Fig. 7. Mass averaged flame speeds as a function of time for three cases of plasma jet ignition -- CH₄ seed, no seed, N₂ seed. (XBL 7812-13328)

PLANNED ACTIVITIES FOR 1979

With results of our preliminary investigation providing the necessary background, we intend to concentrate upon the basic features of the processes involved in the generation of free and active radicals and their performance as multi-point ignition sources. This will be accomplished by two parallel and closely related programs[†] of study. One, under the direction of Professor F.C. Hurlbut, will be concerned mainly with the measurement of time resolved local concentration of chemical species in the jets using a molecular beam sampling technique with a quadrupole mass spectrometer serving as the primary sensing element. The other, under the direction of Dr. F. A. Robben, will concentrate upon non-intrusive optical measurements using at first conventional emission and absorption spectroscopy and later, as they become available, laser induced fluorescence and scattering tech-

niques. This strategy is based upon the premise that the most appropriate research tools for this purpose, laser-based instruments, are not yet developed to a point where they could provide a reliable means for studying the chemical reactions of these ignition processes. Hopefully they will become available in time to make a contribution to our experiments.

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Flame Propagation in a Turbulent Flow*

R. G. Bill, Jr., I. Namer, F. A. Robben, and L. Talbot

INTRODUCTION

The inability of classical techniques of analysis to resolve problems in turbulence may, to a large extent, be interpreted as a result of the wide spectrum of length scales that are associated with these flows. The importance of the scale of turbulence in turbulent flame propagation is attested to by numerous studies in which flame speed is correlated with the scale and intensity of turbulence. Recent reviews of such studies were given by Andrews et al² and Abdel-Gayed and Bradley.¹ Despite the large number of studies devoted to this problem, few studies exist for which sufficient measurements of turbulent parameters have been reported to provide a clear understanding of the effect of turbulence on flame propagation.

Smith and Gouldin^{4,5} investigated the effects of turbulence on the flame speed of unconfined V-shaped, stabilized methane-air flames in a flow with a grid generated turbulence. Local flame speeds were measured employing hot film and laser anemometry as well as fine-wire thermocouples. Over a narrow range of test conditions, flame speeds were found to increase with increased macroscale and rms. velocity fluctuation level. Unfortunately, due to instrumentation difficulties, only relatively cool regions of the flame were investigated. Although the studies demonstrated the importance of local measurements of flame speed in turbulent flows, more measurements over the entire flow field are needed to expand our knowledge of the effect of turbulence on flame propagation.

We are presently investigating V-shaped, stabilized, propane-air flames using Rayleigh scattering and laser Doppler anemometry for

two upstream flow conditions: 1) flow with grid generated turbulence and 2) flow in which a cylinder generates a Kármán vortex street in an otherwise laminar flow. Our objective in the first experiment will be to compare our measurements of flame speed to correlations with the turbulent Reynolds number based upon integral scales or Taylor microscales. The evolution of length scales upstream and through the flame front will help to quantify the effect of eddy size on the transition of the wrinkled laminar flame to a disrupted flame sheet and on the production of turbulent kinetic energy. Development of probability density functions should be helpful in determining the effect of eddy size on the mixing of burnt and unburnt gases. Furthermore, the shape of these distributions may give some insight into conditional sampling techniques necessary to isolate coherent structures in the flame propagation process.

In the second experiment, the regularity of the Kármán vortex street will enable us to use phase locked signal averaging to obtain the density and flow fields associated with the disturbed flame. For this purpose a reference hot wire probe is used in the wake of the cylinder to monitor the oscillatory patterns of the Kármán vortex street.

ACCOMPLISHMENTS DURING 1978

A computerized data acquisition system has been completed based upon a Digital Equipment Corporation (DEC) PDP 11/10 computer with 28 K words of memory. The computer system is run under a DEC RT-11 operating system using an RK05 disk with 1.25 million words of storage. Eight channels of 12 bit A/D conversion are

available. Samples may be acquired at a constant sampling rate through clock control (the maximum clock frequency being 1 MH) or individual samples may be initiated by a separate control voltage input by the user. In the latter mode, the time between samples is continuously monitored by the clock. In addition to these data acquisition capabilities, an interface has been added to the PDP 11/10 to provide for control of stepping motors to be used to move flow field positions through the laser optical path for Rayleigh scattering and laser anemometry measurements. The stepping motor controls have been completed and tested under computer control.

In order to overcome previous problems encountered in making Rayleigh scattering measurements (Namer et al³), a coaxial combustor was built and tested. The flow of the combustible mixture is limited to the inner jet while air flow in the outer jet shields the flow from mixing associated with interaction with the stagnant surroundings. The wake formed behind the wall of the inner nozzle is smoothed using #200 mesh screen.

The use of conventional hot wire probes and probe supports in the second experiment would introduce disturbances in the flow similar to that of the Kármán vortex street; hence, these probes can not be employed. A hot wire probe design was constructed which incorporated a cylindrical tube both as the probe holder and as a wake generator. The wire sensor, 0.02 mm diameter gold plated tungsten, is welded to 0.5 mm diameter platinum wire supports 6 mm apart. The sensor position is fixed at 1 cm above the cylinder and offset to the side by one cylinder radius.

PLANNED ACTIVITIES FOR 1979

Rayleigh scattering and laser anemometry measurements will be used to measure mean and fluctuating values of density and velocity in the turbulent flow with a V-shaped, stabilized flame. Parameters to be varied will include flow velocity equivalence ratio and grid mesh size. The combustor to be used is that described above, adapted for use with grid-induced turbulence. Flame speed and flow divergence will be locally determined at the flame front. Distributions of length scale as indicated by autocorrelation functions and power spectra will be computed.

Probability density functions will be calculated to give insight into mixing processes both before and after the flame front.

The development of the Kármán vortex street as it moves downstream in the flow will initially be mapped in detail using a hot wire anemometer. The hot wire will also be used to test and verify the computer algorithm used for signal averaging measurements of the vortex street. Following this, Rayleigh scattering and laser anemometry measurements will be used to analyze the interaction of the vortex with the V-shaped stabilized flame. In particular, the distortion of the flame front by the vortex, and the intensity of the vortex after passing through the flame front, will be carefully investigated.

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Combustion in a Turbulent Boundary Layer*

R. K. Cheng, R. G. Bill, Jr., F. Robben, L. Talbot

INTRODUCTION

The interaction of turbulence with the combustion process is an important element of almost all practical combustion systems. The combustion intensity, the degree of completion of combustion, and the generation of gaseous pollutants are profoundly affected by the nature and degree of turbulence. Considerable progress has been made recently in numerically modeling turbulence, and the results have been applied to turbulent combustion with varying degrees of success. In order to assist in the formulation of suitable approximations for turbulent combustion, and to critically evaluate the results of these numerical models, laboratory scale experiments are required on suitable turbulent combustion geometries capable of detailed diagnostic studies. In this program we study a heated flat plate boundary layer with induced turbulence in which premixed combustion can occur.

This classical geometry was chosen because of the extent of theoretical and experimental work dealing with laminar and turbulent boundary layers. A heated boundary layer is well suited for the study of combustion for it can support combustion under a wide range of equivalence ratios ranging from stoichiometric to very lean by proper control of the wall temperature and free stream velocity. The change in the scale and intensity of turbulence as a result of combustion heat release can be investigated over a much wider range of conditions than in conventional combustion systems such as flames. Furthermore, the combustion heat release can be adjusted to occur throughout the boundary layer permitting detailed study of the evolution of turbulence through each stage of the exothermic process.

ACCOMPLISHMENTS IN 1978

Several pieces of experimental equipment have been completed and tested in the last year. An existing PDP 11/10 computer with an LPS 11 peripheral system was expanded so as to have 28 K of memory, a programmable clock, 4 channels of buffered analog inputs, an RK 01 hard disc, Tektronix 4025 terminal, Telecorporation line printer and a communication link to a central PDP 11/45 computer. Two three axis stepping motor drives for the 2.5 cm and 10 cm channel combustion tunnels were constructed and interfaced to the computer. Software has been developed and is operational for program development, file management, and operation of the experiment to take laser Doppler velocimeter and Rayleigh scattering data. This includes plotting of the data on the terminal and calculation of simple statistical parameters.

A device to generate approximately 2 micron particles for LDV measurements has been constructed, tested and found to be reasonably

satisfactory. It is based on the burning of magnesium ribbon to form MgO particles.

A 2.5 cm square channel, 10 cm long, has been built to fit onto an existing stagnation chamber and traversing mechanism. One wall of this channel consists of thin strips of Kanthal, a high temperature iron based heating alloy, over which combustion takes place. It is being used for initial measurements and as a prototype for the 10 cm combustion channel.

Construction is nearly complete on a tunnel which will give 20 m/s velocity of combustible gas in a 10 cm square channel up to 1 m long. This combustion tunnel is driven by a centrifugal pump and is mounted on a 3-axis stepping motor controlled traverse mechanism.

All results to date have been obtained in the 2.5 cm square channel, which gives a Reynolds number of approximately 3×10^5 at the channel exit at the maximum flow velocity of 22 m/s. This is too low for a fully developed turbulent boundary layer, but high enough for transition type disturbances created by an obstacle or by a non-uniform surface. The initial design of the heated surface, using Kanthal strips, is rather uneven and thus we find a fairly high degree of unsteady motion in the boundary layer. Fairly extensive measurements have been made in this channel using a hot wire anemometer with an unheated wall, laser Doppler velocimetry for an unheated and heated wall, and Rayleigh scattering for a heated wall. Further, interferograms of the integrated density across the channel have been made using differential interferometry.

The development of combustion in the boundary layer as a function of surface temperature, fuel equivalence ratio and flow velocity has been qualitatively determined from the interferograms. Some judgment on the intensity of the turbulence can also be made; it appears that the introduction of combustion, with all other factors remaining approximately the same, results in a decrease in the turbulent intensity. Detailed statistical measurements of the velocity and density fields have had to await the completion of computer controlled data acquisition, and at present new data has been recorded but not yet analyzed.¹

The primary measurement techniques, laser Doppler velocimetry and Rayleigh scattering, have considerable inherent fluctuation, or noise, and methods for extracting the turbulent flow fluctuations from these signals have not yet been treated properly in the literature, if at all. The corrections for root-mean-square fluctuation, and the auto-correlation and power spectral density appear fairly straightforward, while the corrections for the probability density function are more complex. We have developed a model for this purpose which has yet to be

implemented and verified. These are important problems in the analysis of turbulent flow data, and advances are valuable in a broad area of research.

The motion of small (2 micron) particles in a thermal boundary layer has been studied in some detail. It was found necessary to investigate this problem in order to properly apply the laser Doppler velocimeter technique to thermal boundary layers, and the end result is a significant contribution to the field of thermophoretic motion of particles as well as to laser Doppler velocimetry. Our data, taken at much larger thermal gradients than previous studies, is quite precise, and is analyzed by full consideration of the fluid mechanics and particle trajectories. From the results we are able to distinguish between several theories of thermophoretic motion; presentation of our results with a review of other measurements and theoretical results is in draft form.

PLANNED ACTIVITIES FOR 1979

Final analysis of the results obtained from the 2.5 cm square channel will be made. This will require the development of proper methods for extracting the probability density and the power spectral density of the fluid from the data. This analysis will characterize the turbulence properties in the disturbed boundary layer, and give the effect of boundary layer combustion upon these properties.

Measurements in the 10 cm square channel will initially concentrate on the same statistical turbulence properties (density and velocity) as measured in the small channel. Both larger Reynolds numbers and lower flow velocities will be investigated, and the effect of combustion in the boundary layer on these properties will be determined. The experimental results will be compared with available numerical modeling results, and extension of present numerical modeling techniques to heated boundary layer combustion will be undertaken.

There are considerable uncertainties in the use of the laser Doppler velocimeter technique for fluctuating velocities, and investigation

will be necessary in order that the quality of our measurements can be assured. There are problems with control over the size and rate of particle seeding, with thermophoretic motion of particles in the heated boundary layer, and with the processing of the Doppler bursts to give the velocity.

At least one of several possible extensions of the diagnostic measurements will be undertaken. Simultaneous measurement of two components of velocity is relatively straightforward and will enable the evaluation of the mean Reynolds stress in the fluid. The introduction of a periodic disturbance into the boundary layer will enable phase-locked measurements to be made of the coherent disturbance. This could be a very powerful technique to assess the effect of combustion on a coherent disturbance in the boundary layer. The other contemplated diagnostic extensions involve simultaneous measurement of velocity and density at one point and simultaneous measurements of either velocity or density at two different points. The first of these measurements allows evaluation of v correlations and the use of Favre averaging; the second establishes the spatial correlation functions and the spatial scale of the turbulent fluctuations.

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Turbulence Modeling of Heat and Momentum Transport Processes

B. E. Launder

Research in 1978 proceeded on two principal fronts. One of these was the development and testing of a second-order closure for heat and momentum transport processes in two- and three-dimensional flows. The work has been fully documented,¹ while journal articles on the research are under review² and in preparation. This work has, we believe, carried forward closures based on transport equations for the turbulent heat fluxes as far as is practical without introducing independent turbulent time scales for the velocity and temperature fluctuations. Indeed, devising a workable and reliable scheme for obtaining the thermal-turbulent time scale is a major goal of the writer's research work during the present year and the next.

The thermal-time-scale work will be aided by studies currently underway aimed at devising models for momentum transport (not heat transport) that adopt multiple independent time scales. This is the second of the fronts mentioned above. The modeling consists of dividing the

Reynolds stress spectrum into more than one slice and devising characteristic time scales for each part. The work, still in its development stages, has nevertheless succeeded in widening the range of flows that can be predicted with a single set of equations and coefficients. Chief among these is the round jet in stagnant surroundings for which single-time-scale models usually predict a rate of spread that is 50% too large.

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Chemically Reacting Turbulent Free Shear Layer*

B. Pitz, J. Keller, M. Houser, and J. W. Daily

OBJECTIVES

Most flames of industrial interest today burn in a free shear layer that is turbulent. Premixed flames are stabilized by heat recirculation involving the recycling of hot combustion products which are mixed with the cold reactants in a free shear layer. Diffusion flames are controlled by the rate at which fuel and oxidizer mix in a free shear layer. Free shear layers play such a controlling role in the development and propagation of flames that it is important to understand them in detail.

Because of the strong current interest in prevaporized/premixed combustion caused by the NO_x air pollution problem, we have been conducting a study of the premixed flame stabilized by mixing of cold reactants with hot combustion products in a turbulent free shear layer. This flow is typical of that occurring in the stabilization region of premixed combustors, and knowledge of its characteristics is needed to establish stability and flame spread rates.

Although there has been extensive and thorough research on turbulent flame propagation and stability in the past,^{1,2} investigation of these processes in light of recent research

on large eddy structures in turbulent shear flows has given a new direction to studies in this field.³⁻⁷ The basic findings of such studies have established the importance of coherent large scale structures in turbulent shear flows. This leads to a deterministic approach to the description of the flow field, according to which large eddies are formed first in quasi-orderly fashion and then are carried through the mixing layer, growing by coalescence and engulfment. Fine mixing inside the eddies occurs by the action of small scale turbulence and viscosity.⁷ These structures have been observed in geometrically simple, nonreacting flows; primarily two dimensional free shear layers and round jets, with some evidence of their existence in boundary layers and wakes.

RECENT WORK AND ACCOMPLISHMENTS

Our studies have been conducted in a two dimension premixed burner equipped with fused quartz windows on the side and top for optical access to the combustion zone. Preliminary work by Gangi and Sawyer⁸ shows that although long exposure schlieren photographs illustrate apparently well defined regions of flame propagation and recirculation, in fact both are controlled by the dynamics of large scale eddies. High

speed schlieren movies confirm a pattern of large scale structures in the form of rolled up eddies and reveal the eddy formation rate, growth rate, coalescence and intermittent intrusion into the recirculation zone.

Given the qualitative nature of the flow field, we have made detailed measurements of conventional turbulence parameters and used these in conjunction with the schlieren movies to increase understanding of the interaction between the fluid mechanics and combustion process.

The measurements include:

(1) Hot wire anemometry measurements of the inlet flow field, including mean and rms fluctuating velocities, autocorrelations, power spectral, and probability distribution functions.

(2) Laser anemometry measurements in the body of the flow field with the same quantities obtained as in (1) above.

(3) Rayleigh scattering total density measurements in the body of the flow field, including mean and rms fluctuating density, auto-correlations, power spectra, and probability density distribution functions.

(4) Laser schlieren power spectra.

(5) Schlieren movies of the entire flow field.

The measurements have been used to study the effect of inlet velocity, temperature, and turbulence state on the shear layer structure.

The measurements reveal a number of interesting trends including:

(1) There is strong acoustic coupling between the combustor configuration and the shear layer behavior.

(2) Temperature affects the shear layer stability as expected through a variation in sonic velocity and transport properties.

(3) The beautiful two-dimension nature of the shear layer is lost when the incoming boundary layer becomes turbulent although the large structures do not disappear.

(4) The effect of combustion on the shear layer structure is surprisingly small.

PLANS FOR THE COMING YEAR

The current combustor stabilized the flame on a rearward facing step. In the coming year we will install a two stream free shear layer combustor and continue our studies with this new configuration.

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Fundamental Features of Lean Premixed Prevaporized Combustion*

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INTRODUCTION

An experimental study of lean, premixed turbulent flames has been undertaken in recognition that basic understanding of the fluid dynamics and chemistry of these types of flames is a major step in the application of premixed prevaporized combustion to gas turbines.

The use of lean, premixed combustion is one possible approach for the reduction of oxides of nitrogen and particulate emissions, and for the improvement of turbine inlet temperature patterns. On the other hand, some related problems including stability, flashback, and auto ignition must be solved before the application of the concept to the gas turbine combustor becomes feasible. The advantages and problems for the application of premixed combustion to gas turbine combustors have been discussed in detail in Ref. 1.

Although there has been extensive and thorough research on turbulent flame propagation and stability,^{2,3} investigation of these processes in light of new findings in turbulent flow research has attained renewed interest. Recent research on large eddy structures in turbulent shear flows has led to a new direction to fluid mechanics research in this field.⁴⁻⁸ This work has established the concept of coherent large scale structures in turbulent flows. This results in a rather deterministic approach to the description of turbulent flow, according to which large eddies formed first in quasi-orderly fashion are then carried through the mixing layer and grow through coalescence and engulfment. Fine mixing inside the eddies occurs by the action of small scale turbulence and viscosity.⁸ Such structures have been observed in geometrically simple, nonreacting flows, primarily two dimensional free shear layers and round jets, with some evidence in boundary layers and wakes.

The problem of turbulent combustion in shear layers is far more complicated in the sense that fluid dynamics and chemical reaction are coupled phenomena governing the propagation and growth of the flame. In order to clarify some fundamental aspects of this problem, a unique experimental facility has been constructed in our laboratory. Its primary function is to provide a two dimensional premixed burner 17.3 cm wide, 5.1 cm high, and 22 cm long equipped with fused quartz windows on the sides for optical access to the combustion zone. The flame is stabilized behind a step which is streamlined in the upstream direction and has a blockage ratio of 0.5. Uniform mixing of propane and air and uniform velocity are attained by the time the flow reaches the entrance to the test section. The flame is initiated at the edge of the holder and propagates toward the top of the combustion chamber, while a "recirculation zone" is established behind the step, and extends to the bottom of the combustor. The experimental apparatus is shown in Fig. 1.

ACCOMPLISHMENTS DURING 1978

Work carried out last year was concerned primarily with the following two aspects of experimental investigations.⁹

- 1) Flow field visualization and characterization for both the stable mode of operation of the burner and for the unsteady processes of flashback and blowout.
- 2) Pollutant formation processes through the use of conventional probe techniques.

A schlieren system was used for taking both still photographs and high speed (6500 frames per second) motion pictures (in black-and-white as well as in color). Pt/Pt-Rd fine wire (.076 mm)

EXPERIMENTAL APPARATUS

Fig. 1. Two dimensional combustor test section.
(XBL 794-9131)

thermocouples and aerodynamically quenched quartz microprobes were used to measure the space resolved (but time averaged) temperature and species concentrations inside the flame. Pointwise combustion efficiency was determined from these measurements.

Reynolds numbers based on the reference flow velocity have been in the range of 0.5×10^4 to 1.5×10^4 corresponding to reference flow velocities of 7.5 to 22.5 m/sec at ambient temperature. Studies have been conducted for equivalence ratios of 0.40 to 0.67 at atmospheric pressure and inlet temperatures of 300 K to 600 K.

The system has a narrow range of stability between lean blowout and lean flashback, compared to results presented in Refs. 2 and 3. Flashback occurs when the equivalence ratio is increased above a certain value (depending on initial velocity and inlet temperature). It leads to "chugging" -- a non-steady mode of operation manifested by cyclic flow variation associated with a static pressure oscillation inside the chamber. Temperature measurements show a sharp drop across the flame close to the edge of the step while the corresponding change from fully reacting to nonreacting fluid a few centimeters downstream of the step is quite gradual, demonstrating that the apparent sharp flame front observed in conventional (long exposure time) pictures of the flame does not actually exist; instead the flow field is dominated by large scale turbulent mixing which obliterates the effects of sharp flame fronts.

Analysis of the still pictures and high speed motion pictures reveal the following features of the flow field:

- 1) Long exposure (20 msec) schlieren pictures show a well defined region immediately behind the step (commonly referred to as a recirculation zone) and a well defined region of flame propagation (usually associated with the shear mixing layer).
- 2) Short exposure time ($< 1 \mu\text{sec}$) shadowgraph and schlieren pictures show a pattern of large eddies which grow downstream to a size of the order of the chamber height and intrude into the recirculation zone (see Fig. 2).
- 3) High speed schlieren movies confirm the pattern of large scale structures in the form of roll up eddies as observed in the still pictures and reveal additional details, both qualitative and quantitative, including the formation of eddies, their shedding frequency spectrum, shedding position spectrum, convection velocity, growth rate, coalescence, and intermittent intrusion into the recirculation zone. The above phenomena have been investigated for different operating conditions (equivalence ratio, entrance velocity, and inlet temperature) for both reacting and nonreacting flows.

Fig. 2. Spark shadowgraph of the flame (exposure time $< 1 \mu\text{sec}$). The flow is from left to right and the flame is stabilized at the edge of the step (left). (Experimental conditions: reference velocity = 13.3 m/sec, equivalence ratio = 0.6, inlet temperature = 300 K).

- 4) Schlieren movies show that the process of flashback corresponds to overgrowth of the eddies behind the step until the flame is lifted from the edge of the step and enters the throat above the step. Flashback leads to a "chugging" mode generated by the growth of a single eddy behind the step until it fills out the test section and is subsequently blown out. The reactants are then again reignited by the products of combustion in the recirculation zone behind the step and the process repeats itself.

The primary accomplishments and conclusions of this research are:

- 1) Demonstration of a two dimensional facility for the study of premixed turbulent combustion processes with surprisingly high optical quality.
- 2) Confirmation that the quasi-orderly large scale eddy structures which have been observed in simple, nonreacting flows also exist in nonreacting and reacting flows behind a step.
- 3) Establishment of the fact that combustion is confined to these large structures and that the "flame front" and the "recirculation zone" are intermittent in character, being dominated by the transport of large scale eddies.
- 4) Attainment of optical records of turbulent combustion, and the processes of flashback and blowout which provide new insights for the modeling of turbulent combustion.
- 5) Evaluation of stability, efficiency, temperature, NO , NO_2 , CO , and HC concentrations inside the above described flames.

PLANNED ACTIVITIES FOR 1979

The program of work to be carried out next year consists of the following items:

- 1) Establishment of the turbulent properties of the flow fields based on point measurements of density and velocity fluctuations using Rayleigh scattering, hot wire anemometry, and laser Doppler velocimetry (under the direction of J.W. Daily).
- 2) Experimental study of the mechanism of flashback and the non-steady chugging mode of combustion it triggers (under the direction of A.K. Oppenheim).
- 3) Computational analysis of the non-steady flow phenomena associated with a flashback and chugging (under the direction of A.K. Oppenheim).

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Blast Wave Studies*

A. F. Ghoniem, R. H. Guirguis, S. A. Berger, and A. K. Oppenheim

INTRODUCTION

Explosions are manifested by blast waves: the non-steady flow fields generated at the center by an explosive source and bounded on the periphery by a shock front. The effects of the latter are readily observable. The objective of our studies is to elucidate the evolution of the driving force at the source as these effects are produced. This can be attained only by theoretical analysis, for experimental insight into processes occurring at the center is practically impossible. One has to develop proper techniques for an analytical insight into the structure of blast waves, furnishing information about the link between the processes occurring at the center with the motion of the wave front.

So far the only means available for this purpose have been numerical computations based

on finite difference techniques. Besides their inherent limitation to a single specific example at a time, and a relatively high cost, these techniques are deficient for three fundamental reasons:

- 1) The results are fuzzy since the data have to be smoothed out over a number of computational cells so that information on discontinuities, which are the essential elements of the structure, are lost.
- 2) The effects of transport phenomena cannot be assessed because they are obscured by those of the numerical diffusivity.
- 3) The conditions at the center cannot be properly evaluated for, as a rule, they are at a singularity which has to be avoided in order to assure convergence of the numerical scheme.

ACCOMPLISHMENTS DURING 1978

We have developed an analytical technique, the Phase Space Method, that is capable of treating conditions at singularities in the center with great precision. An analysis based on this method is applicable to point, line, or plane symmetrical blast waves, yielding an asymptotic solution; that is, one permitting exact results to be approached as closely as one wishes depending on the number of steps taken in their evaluation.

We have derived analytical solutions for a complete class of self-similar blast waves driven by the deposition of variable energy at the front. Of particular interest is the clarification of non-unique type of solutions that may have locally either sonic or supersonic flow immediately behind the front. Such situations can arise in the case of laser-driven explosions.

Some results of our studies have been reported in Ref. 1-3; results described in Refs. 4 and 5 are in press, while the remainder of our results are being prepared for publication in the form of Ref. 6-8.

No work is planned in this area in 1979.

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Numerical Analysis of Flow Fields Generated by Accelerating Flames*

J. Kurylo, H. A. Dwyer, and A. K. Oppenheim

INTRODUCTION

This research program concerns the evaluation of the gasdynamic effects in explosive clouds--a subject which is of particular interest today in connection with the transportation of large quantities of LNG, as exemplified by a number of papers presented at the last Combustion Symposium.^{1,2,3} The particular question to which the study has been addressed can be stated as follows: A flame emanating from the center of the cloud at a steady velocity has been established. At a given moment its speed increases abruptly due to some turbulent disturbances. One is interested to find out the consequences of this event.

ACCOMPLISHMENTS DURING 1978

The planned analysis of this problem has been completed and published in an LBL Report,⁴ and the main aspects of the work have been described in a paper presented at an AIAA meeting.⁵

Specific results have been obtained for the following case representing conditions typical of a hydrocarbon-air mixture close to its stoichiometric composition:

- Specific volume ratio at initial pressure:
 $v_F = 7$
- Specific heat ratio of unburned medium:
 $\Delta_u = 1.3$
- Specific heat ratio of burned gases:
 $\Delta_b = 1.2$
- Ambient pressure:
 $p_a = 1 \text{ atm}$
- Velocity of sound at ambient conditions:
 $a_a = 331 \text{ m/sec}$

The flame burning speed S_u , is expressed in terms of a law based on experimental evidence,⁶⁻¹⁰

$$S_u = S_0 \left(\frac{p}{p_a} \right)^{0.5} \left(\frac{a}{a_a} \right)^{4.6}$$

where subscript o denotes the initial flame speed, while subscript a refers to conditions of the ambient atmosphere into which the flame propagates initially.

The initial conditions for the computations are provided by the solution of the pressure wave generated by a flame propagating with constant burning speed, S_0 .¹¹ When the flame is at a radius $X = 1$, its speed is suddenly increased by a finite increment, ΔS . The ensuing development of the process is determined using our computational technique.

A time-space wave diagram of the solution is presented in Fig. 1. Here we have $S_0 = 9.6$ m/sec and $\Delta S = 14.6$ m/sec, while the flow was considered to be plane symmetrical ($j = 0$). A solution obtained under similar circumstances for the same initial flame speed but with $\Delta S = 19.0$ m/sec is displayed in Fig. 2. On both diagrams dashed thick lines represent the trajectories of deflagrations, solid lines refer to shocks, the thick solid line corresponds to detonation, and the thin broken lines indicate the particle paths.

In the first case, the imploding shock, generated when the flame speed was suddenly increased at $x = x_0$, was reduced to a sound wave after eight reflections from the center and interactions with the deflagration. In the meantime the propagation speed of the deflagration increased to 37.2 m/sec while the Mach number of the shock at the front of the pressure wave was augmented from 1.1 to 1.4. The process took about $240 x_0$ m/sec while the deflagration traveled a distance of $53 x_0$ meters, where x_0 is expressed in meters. Thereupon the whole wave system settled to a steady state corresponding to a self-similar solution obtained for the final propagation speed of the deflagration.

In the second case, however, as demonstrated in Fig. 2, the process escalated to detonation propagating finally at a speed of 2250 m/sec. Its onset occurred at a radius of $20.3 x_0$ meters and the time of $76 x_0$ milliseconds. Associated with this was the generation of a retonation wave traveling at a speed of 1250 m/sec, corresponding to a local Mach number of 1.29, into the burned medium.

Details of the wave interaction processes associated with the onset of the detonation and retonation waves are shown in Fig. 3. This is, in effect, an enlargement of a part of the solution delineated by a small rectangle on Fig. 2. Added here for clarity of exposition are the characteristics. As it appears here, the onset of detonation is associated also with the formation of a centered rarefaction wave. Its front edge is at the Chapman-Jouguet state propagating with the detonation front, while its trailing edge is identified on the diagram by a chain-double-dotted line.

There are thus two possibilities: a steady solution culminated by a constant velocity flame driving a pressure wave or an unsteady solution associated with transition to detona-

Fig. 1. Wave diagram of stable solution obtained in the case of subcritical burning speed increment. (XBL 781-6814)

Fig. 2. Wave diagram of unstable solution obtained in the case of supercritical burning speed increment. (XBL 781-6815)

Fig. 3. Details of solution presented by Fig. 2 depicting the onset of detonation. (XBL 781-6816)

tion. The distinction between the two is governed solely by the value of the initial flame speed and the flame speed increment. The demarcation line between the two regimes of these parameters is presented in Fig. 4. For initial conditions corresponding to a point below the line, a stable solution, like that of Fig. 1, is obtained; for points above the line the solutions are unstable as exemplified by Fig. 2.

For stable cases similar solutions to that of Fig. 1 were obtained by our Cloud Code¹² -- a Lagrangian computational scheme for blast waves employing the von Neumann-Richtmyer artificial viscosity with Wilkins' modification. However, when the unstable conditions associated with transition to detonation were approached, the computations became excessively unstable. This feature manifested itself so distinctly that it was actually exploited to check the demarcation line of Fig. 4. With the use of the Cloud Code such lines were determined by spherical as well as planar flow fields. The difference between them turned out to be so small that the line presented in Fig. 4 could be considered to be valid irrespective of the geometry of the flow field.

Noted on the diagram are a number of specific points marked by crosses. That indicated by S corresponds to the solution of Fig. 1; the point denoted by U specifies initial conditions for the solution presented in Figs. 2-3. Points indicated by W refer to experimental results obtained by Dörge et al.¹³ with the use of acetylene-air mixtures. Subscript S denotes cases when the flame, after passing the screen barrier, settled to a new steady propagation velocity. Subscript U refers to the unstable case associated with transition to detonation which was observed when air was enriched with oxygen. The numerals in the subscripts indicate

Fig. 4. Regimes of initial conditions for stable and unstable solutions.
(XBL 781-6821)

the number of turbulence generating screens used in the experiment. As it appears the increase in flame burning speed could be practically doubled by the use of three screens instead of one. However, the addition of oxygen to air was so effective in triggering the transition to detonation that evidently one screen was in this case quite sufficient.

PLANNED ACTIVITIES FOR 1979

No work is planned in this area in 1979.

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Catalytic Combustion in a Boundary Layer*

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INTRODUCTION

Interest in the use of catalytic surfaces to promote combustion reactions has increased greatly over the past several years due to the potential improvements in combustor efficiency and the greatly reduced pollutant levels which have been demonstrated. Much of the work to date has involved parametric investigations of prototype catalytic combustor configurations. Such work is necessary to the development of practical catalytic combustors and the results have been quite promising. However, such studies are somewhat limited in terms of obtaining a more fundamental understanding of catalytically supported combustion. Two such areas where a greater knowledge would be desirable are the role of internal heat and mass transfer in the catalytic combustion process, and the role of homogeneous as opposed to catalytic surface reactions. An understanding of these and related processes such as pollutant generation is necessary for the optimum evaluation and application of the surface catalysis concept to practical combustion system design.

The approach of the present investigation has been to examine catalytically supported combustion in a well characterized system in which most of the important physical and chemical processes found in larger scale catalytic combustors are present. The geometry chosen consists of combustion in the boundary layer of a heated catalytic flat plate. This system provides a suitable geometry for both experimental and numerical modeling studies. The operation of such a system under a suitably selected range of conditions greatly facilitates determination of the roles of the various processes involved. The parallel development of a numerical modeling program has aided considerably in the analysis of the experimental results and will provide a means with which to extend these results to more practical combustion systems.

Since initiation in 1976 the experimental system has been constructed and several measurement techniques have been developed. These include optical pyrometry to measure surface temperature, Rayleigh scattering and differential

interferometry to measure gas temperatures in the boundary layer, and the measurement of surface energy release rates from plate heating strip power inputs. A numerical finite difference scheme was also developed for boundary layer flows which includes detailed gas phase kinetics and realistic transport properties. A simplified model was proposed for surface reaction based on the limiting case of an equilibrium surface condition.

ACCOMPLISHMENTS DURING 1978

A detailed study was completed of boundary layer behavior under combustion conditions for lean H_2 /air mixtures flowing over a platinum catalytic surface.^{1,2} Regions were identified in which only surface reaction was present and, at higher equivalence ratios and surface temperatures, in which both surface reaction and stable boundary layer combustion occurred simultaneously. At the highest equivalence ratios and surface temperatures, the combustion zone moved upstream toward the plate leading edge where the primary reaction zone developed into a flamelike structure characterized by steep temperature gradients which extended well out into the free stream. These results are summarized in Fig. 1.

Surface energy release rates were measured over a range of conditions for both H_2 /air³ and C_3H_8 /air mixtures. Under all conditions investigated the surface reactions rapidly became diffusion limited downstream of the plate leading edge, thus limiting the catalyst reaction rate. From the data it was possible to derive expressions for the surface reaction rate based on simplified surface reaction mechanisms. The determination of high temperature surface reaction rate data such as this is necessary for the development of future catalytic combustor design criteria.

A more realistic model was developed for catalytic surface reactions which included surface oxidation of H_2 to H_2O and radical recombination at the plate surface. The H_2 surface oxidation rate was based on experimentally measured values and the rates for

Fig. 1. Combustion regions for H_2 /air mixtures over a heated platinum plate. $U_\infty = 1.5$ m/s, $T_\infty = 293K$. (XBL 784-7918)

radical recombination were derived from a kinetic theory surface collision model assuming a reaction probability of unity for each collision.

The effect of various surface reaction models on the combustion process was investigated for lean H_2 /air mixtures. The surface boundary conditions considered were based on 1) the limiting case of an equilibrium surface at which species concentrations are driven instantaneously to their equilibrium values, 2) a condition which includes finite rate surface oxidation of H_2 to H_2O , and 3) a condition which includes radical recombination at the plate surface in addition to surface oxidation of H_2 . A detailed reaction mechanism for gas phase combustion which included 13 reactions and 8 species was used in the calculations. A comparison of the above models for a catalytic surface with results for a noncatalytic plate is presented in Fig. 2 where the thermal boundary layer thickness, δ_T , is shown as a function of distance along the plate. An increase in δ_T over that found for the case of no combustion indicates the presence of gas phase heat release. These results show the strong quenching effect that surface reaction has on the initiation of gas phase combustion in the boundary layer, due to the depletion of H_2 near the plate surface and the quenching of radical species generated in the gas phase. This results in a significant reduction in gas phase heat release rates over that found with a noncatalytic plate surface.

The numerical calculations for a catalytic plate surface predicted higher gas phase heat release rates than were found experimentally for lean H_2 /air mixtures flowing over a platinum plate. Possible causes for this discrepancy are uncertainties in the surface reaction model and uncertainties in the gas phase kinetic mechanism. A series of sensitivity tests were carried out which indicated that uncertainties

Fig. 2. The effect of surface boundary condition on thermal boundary layer thickness. H_2 /air combustion. $\phi = 0.1$, $T_s = 1100K$, $U_\infty = 3.17$ m/s. Case 1. Total equilibrium surface; Case 2. Surface oxidation of H_2 ; Case 3. Surface oxidation of H_2 and radical recombination. (XBL 792-8363)

in the gas phase kinetic mechanism are the most likely cause of the high predicted heat release rates.

PLANNED ACTIVITIES FOR 1979

The above work in catalytic combustion is currently being extended into several areas. Studies similar to that done for H_2 will be conducted for typical hydrocarbon fuels. These studies will include mapping out the various combustion zones for these fuels over a variety of catalyst materials, obtaining surface reaction rate data, and developing models for surface and gas phase reactions. Data over a noncatalytic plate would improve our understanding of the effect of surface reaction on gas phase combustion. An area of particular interest with respect to catalytic combustion is the burning of fuels with a high fuel bound nitrogen content since future energy needs will require an increasing reliance on fuels of this type. Preliminary results indicate that catalytic combustor operation under fuel rich conditions could be very effective in reducing the conversion of fuel bound nitrogen to NO_x . Our studies to date have concentrated on fuel lean operation. During the coming year catalyst operation under fuel rich conditions will be investigated with the emphasis on soot formation characteristics and its effect on catalyst performance.

FOOTNOTES AND REFERENCES

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Characterization of NO_x Removal Through Ammonia Addition*

*N. J. Brown, R. F. Sawyer, T. S. Eitzen,
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INTRODUCTION

Control of nitrogen oxides emissions is most desirable since these compounds result in atmospheric nitrogen dioxide, photochemical smog formation, nitrate formation and perhaps other compounds whose role in air pollution is less well defined. Combustion sources both of the mobile and stationary types are recognized as the primary sources of the oxides of nitrogen. The two principal sources of nitrogen oxides in the combustion of conventional fuels are oxidation of atmospheric molecular nitrogen (thermal NO_x) and oxidation of nitrogen containing compounds in the fuel (fuel nitrogen NO_x). The latter classification of NO_x increases with the nitrogen content of the fuel and may account for more than half of the nitrogen oxides emitted from the combustion of high nitrogen content oil or coal in power plants. While the formation mechanism of thermal NO_x is quite well understood, the mechanism of fuel NO_x formation is not understood. Fuel NO_x production appears favored under conditions different from those which enhance thermal NO_x production. Consequently, the various control strategies used in the United States to meet NO_x emission standards, namely the modification of the combustion processes to reduce thermal NO_x production, are ineffective in reducing fuel NO_x .

A new NO_x control technology has been patented by Exxon Research and Engineering Company which selectively removes NO_x from combustion effluent gases through homogeneous reaction with ammonia and oxygen. This process is distinctly different from other technologies in that it does not prevent or limit NO_x formation but rather removes the NO_x through reaction after its formation. Thus, the process offers the possibility of removing both thermal and fuel NO_x . This process has been proposed for the control of oxides of nitrogen from stationary sources in California. It is of major importance to assess its potential for secondary pollutant formation, especially at operating conditions different from those which are considered optimal for reduction of oxides of nitrogen.

In recognition that NO_x removal through NH_3 addition appears to be a viable control strategy, the California Air Resources Board is sponsoring a research program at the Lawrence Berkeley Laboratory. This research is directed toward characterizing the NH_3 addition/ NO_x removal process for secondary pollutant potential, and providing a framework to assist the California Air Resources Board in assessing utilization of this control process. This research is being conducted in a laboratory scale combustion tunnel which is a well controlled experimental environment. Experimental variables which are being considered are: 1) equivalence ratio, 2) temperature of the combustion products prior to ammonia addition, 3) ammonia concentration, 4) NO_x concentration, and 5) type of fuel nitrogen added. Propane is being used as a fuel and nitrogen addition is being used to control the gas temperature at the point of ammonia addition.

ACCOMPLISHMENTS DURING 1978

A stainless steel combustion tunnel has been constructed and characterized to ascertain that the performance is consistent with that required to evaluate the NH_3 addition/ NO_x control process. Composition and temperature measurements have been performed at various radial and axial positions downstream of combustion under various operating conditions. Temperatures are measured with thermocouples and radiation corrections are made with suction pyrometry; CO and CO_2 concentrations are measured with non-dispersive infra-red analyzers and NO and NO_2 are measured using a chemiluminescent analyzer. Figure 1 is an illustrative plot of CO_2 concentration as a function of radial position downstream of the NH_3 injector. Agreement among the measurements at the various points is indicative of good mixing and completeness of combustion. Analysis of the various measurements indicate that stable, steady state and reproducible combustion occurs in the tunnel over a range of experimental variables, and that mixing lengths are relatively short. Since the quantity of ammonia injected into the product combustion gases is an important

Fig. 1. Spatial variation in dry CO₂ concentration for propane/air combustion at an equivalence ratio of 0.8. (XBL 794-9135)

experimental parameter, a series of experiments has been performed to determine a satisfactory ammonia injection technique. Ammonia was found to decompose catalytically in a stainless steel inlet system at elevated temperatures; however, a quartz injector system was found satisfactory.

The literature associated with currently used NO_x reduction techniques has been surveyed and a report¹ summarizing the findings has been written. In addition the literature associated with combustion sources of nitrogen compounds has been reviewed and a paper² has been written which describes potential sources of non-criteria nitrogenous pollutants.

PLANNED ACTIVITIES FOR 1979

This work is to be completed during 1979. A series of measurements will be performed to determine NO_x reduction levels under conditions deemed optimum for NO_x removal through

NH₃ addition and for a set of conditions that are less than optimum. Gas chromatography and mass spectroscopy will be used to determine possible nitrogen-containing by-products. CO/CO₂ will be monitored over the range of experimental variables. A light distillate oil containing nitrogen will be substituted for propane and a series of characterization studies will be performed.

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Characterization of Emissions from the Combustion of Alternative Fuels

N. J. Brown, W. K. Chin, T. Hadeishi, A. S. Newton,
R. F. Sawyer, and R. W. Schefer

INTRODUCTION

Increased reliance on heavier alternate and fossil fuels derived from coal and shale to supply future energy requirements has associated environmental impacts of potentially serious consequences. One of the more serious problems associated with utilization of these fuels is pollution formation resulting from their combustion. Alternative and fossil fuels pose a substantially more serious threat to air quality than natural gas and distillate oils since they contain nitrogen and sulfur chemically bound to hydrocarbon chains and aromatic rings of the fuel. While sulfur removal via fuel pretreatment or product scrubbing appears to be an economical solution to the sulfur emissions problem, analogous removal procedures do not appear promising for nitrogen chemically bound in the fuel. Thus initial stages of this proposed research will be concerned with the characterization of nitrogen emissions from alternative and fossil fuels. This is important since it is a crucial step in the sequence which leads to the determination of source emissions and an assessment of health effects of pollutant species.

To date consideration of nitrogen compounds as air pollutants has focused upon the nitrogen oxides, NO and NO₂, with occasional interest in ammonia. The so-called technology for assessing nitrogen emissions reflects this in that it is specialized with regard to NO_x and even more specifically to the NO_x evolved from the oxidation of atmospheric nitrogen (thermal NO_x). It now appears that fuel nitrogen will become a significant and even dominant source of NO_x with combustion of alternative and fossil fuels. Moreover, a potentially more dangerous and difficult problem exists since combustion processes involving these fuels are likely to emit, in addition to oxides, a host of other nitrogen compounds (e.g.: ammonia, hydrogen cyanide, amines, nitriles, isocyanides, cyanates, isocyanates).

The importance of the potentially serious fuel nitrogen pollution problem associated with increased alternative and fossil fuel utilization has not been assessed since all the nitrogen containing combustion products have neither been identified nor quantified. It is, however, reasonable to assume that these compounds are at least as reactive as oxides of nitrogen and should be of similar concern on an equal mass basis. The major problem associated with assessing and controlling the nitrogen containing combustion products is lack of suitable analytical techniques. The analyses are complicated by adsorption and reactions in sampling systems and interferences from other species.

A coordinated research program is underway to determine measurement techniques suitable for nitrogen compound quantification in combustion environments. This effort involves the close

collaboration of researchers in combustion, pollution chemistry, mass spectrometry and modern laser spectroscopy, and consists of the following four tasks:

- Task 1: Measurement of nitrogeneous emissions from prototype alternative fuels in premixed laminar flat flames.
- Task 2: In situ detection of nitrogen and sulfur compounds from alternative and fossil fuel combustion.
- Task 3: The identification and quantitative determination of nitrogen containing combustion products by mass spectroscopy and GC/MS.
- Task 4: Analysis of nitrogen compound emissions from coal and coal derived fuels using the opposed flow diffusion burner.

ACCOMPLISHMENTS DURING 1978

A flat flame apparatus has been constructed and characterization experiments have been performed to determine which portions of the flame are suitable for comparative diagnostic measurements. Hot wire anemometry has been used to determine velocity profiles of cold gases flowing through the burner and temperature profiles have been determined for stoichiometric, methane/air flames at various heights above the burner surfaces. Figure 1 is an illustrative plot of the maximum temperature measured at a fixed axial distance above the burner as a function of radial distance from the centerline to burner edge. Characterization studies indicate that the current apparatus is suitable for diagnostic measurements in the post-flame zone. A chemiluminescent analyzer, suitable for NO and NO_x measurements has been constructed.

An optical technique has recently been developed at Lawrence Berkeley Laboratory which is suitable for the quantitative determination of trace amounts of small molecular species. An atomic line source (e.g. cadmium) is placed in a variable magnetic field, and through utilization of the Zeeman effect, two closely spaced atomic emission lines, a σ^+ and σ^- component, are obtained which can be tuned by varying the field strength so that one component corresponds to an absorption line of the species to be measured. The differential absorption between the two components is then proportional to the concentration of that species and is very insensitive to most other disturbances. Calibration experiments have been conducted so that the technique can be used to measure NO and NO₂ in a mixture of combustion gases.

Work is underway to determine suitable separation techniques for qualitative and quantitative analyses of low molecular weight nitrogen compounds from combustion environments. A sampling system

Fig. 1. Maximum temperature as a function of reduced radial distance (r/R), $R = 29.5$ mm, measured from burner centerline, at the axial position corresponding to the maximum temperature of a premixed stoichiometric methane/air flame. Flame velocity at the burner surface is 117.9 mm/sec and x and o designate different radii. (XBL 794-9136)

has been constructed to probe the nitrogen containing products of combustion from the test section of a combustion tunnel. In addition, a sampling system has been designed for sample extraction from the products of coal combustion, produced in the opposed flow diffusion burning of nitrogen containing coals.

PLANNED ACTIVITIES FOR 1979

Various diagnostics will be used to measure NO and NO_2 produced in premixed laminar flames. Experimental variables will be: 1) fuel type 2) equivalence ratio, and 3) fuel nitrogen concentration. Samples will be: 1) extracted with different probe types and measured with chemiluminescent analysis, 2) extracted with different probe types and measured spectroscopically in an absorption cell, and 3) measured

in situ spectroscopically. A new burner will be constructed which gives proper one dimensional behavior in the pre-flame and flame zones. Effects of probe disturbances to the flames will be characterized.

Analysis schemes for chromatographic separation of low molecular weight nitrogen compounds present in combustion gases will be devised for use under a variety of experimental conditions. These techniques will be used for nitrogen compound measurement in coal combustion, in premixed flame experiments with prototype alternative fuels, and is assessing non-criteria nitrogen pollutants formed in the NH_3 addition/ NO_x reduction process. Measurements of low molecular weight nitrogen compounds formed in the combustion of coal in the opposed flow diffusion flame will be conducted for a variety of coal types.

Application of Unimolecular Rate Theory to Combustion Science

N. J. Brown

INTRODUCTION

Combustion science is concerned with chemistry and fluid mechanics and the coupling between them. Our ability to understand the multistep chemical mechanisms characteristic of combustion processes is made difficult since they are of the chain type and individual reactions are difficult to isolate for experimental study. Relative to the considerable experimental effort, the application of theory to the kinetics of combustion chemistry has been rather limited. Applications of theory can be used to eliminate potential reaction steps in a proposed chemical mechanism. Theory is also useful in evaluating rate coefficients, predicting reaction pathways, and in experimental interpretation of rate data. In addition it should find considerable use in predicting non-Arrhenius behavior and in minimizing errors in the extrapolation of low temperature data to the high temperature regime germane to combustion. One such theory that has benefitted from recent progress is that associated with unimolecular reactions. Unimolecular rate theory can be applied to dissociation, recombination and isomerization reactions. These reactions play an important role in combustion initiation, fuel pyrolysis, radical quenching, and pollutant formation and destruction reactions. Unimolecular reactions are governed by a complex competition between collisional energy transfer and intramolecular energy redistribution. The kinetics are of the second-order type at low pressure where collisional intermolecular energy transfer is rate controlling and first order in the high pressure regime which is rate limited by intramolecular energy transfer. Between the high and low pressure limits, the kinetics are complicated by the coupling between the intermolecular and intramolecular processes, and this intermediate area is termed the fall-off regime.

This research program which was initiated in mid 1978 is concerned with formally extending current theories of unimolecular reactions. These extensions will then be applied to generate kinetic data for reactions that are important in combustion processes.

ACCOMPLISHMENTS DURING 1978

Work associated with the remaining two parts of a four part study of the $H_2 + D_2$ bimolecular exchange reaction was completed. Three potential energy surfaces were computed using valence bond theory to generate simple model wavefunction. A semi-empirical evaluation of the various electronic integrals was undertaken to obtain a tractable analytical form for the H_4 potential surface and its derivatives. A parametrization of the integrals was chosen to give proper asymptotic limits. The remaining parameters governing the repulsive four-atom effects are chosen to give agreement with *ab initio* calculations of the H_4 potential. The similarities and differences among these three surfaces and their comparison with *ab initio* results are discussed in a paper¹ soon to be presented for publication. A paper² summarizing the results of a comparative scattering study investigating reactivity and energy transfer on the three valence bond surfaces and on a London surface has been written and will soon be submitted for publication.

The current scientific literature associated with unimolecular reaction-rate theory has been reviewed.

PLANNED ACTIVITIES FOR 1979

An improved description of centrifugal effects will be sought for small molecule reactions. Bond fission reactions occurring at or near the high pressure limit will be investigated and fully rotationally averaged rate coefficients will be determined.

PUBLICATIONS IN PREPARATION

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2. N.J. Brown and D.M. Silver, "Comparison of reactive and inelastic scattering of $H_2 + D_2$ using four semi-empirical potential energy surfaces."

Laser-Induced Fluorescence Spectroscopy Applied to Turbulent Combustion Flow*

J. W. Daily and C. Chan

INTRODUCTION

Due to large fluorescence cross-sections, laser induced fluorescence spectroscopy has been shown to be a very promising diagnostic technique for combustion systems. The method consists of illuminating the gas with a laser source tuned to an absorption line of the species of interest. The molecules are excited and then reradiated spontaneously, and the resulting fluorescence is measured. The beam diameter and the collection optics define the spatial resolution which may be as fine as 0.1 to 0.5 mm.

ACCOMPLISHMENTS DURING 1978

The primary difficulty with using laser induced fluorescence spectroscopy to make species density measurements has been that collisional de-excitation of the excited state completely dominates radiative de-excitation, causing fluorescence quenching. For atomic species like sodium, we have demonstrated that this difficulty can be overcome by using a laser source of sufficient intensity to saturate the exciting transition. A linear curve of growth for sodium atom concentration has been obtained. The dynamic range of the measurement is approximately two orders of magnitude, limited at low number densities by detectability limit considerations and at high densities by radiative trapping. For diatomic molecules the more complex molecular structure means that the intensity required to saturate is several orders of magnitude higher than that for atomic species. If one cannot attain saturation conditions, the quenching rate must be known in order to interpret the fluorescence signal.

The quenching of OH under flame conditions has been studied and a detailed model of rotational relaxation and quenching for the excited molecules has been developed. The success of this model is reflected in the comparison between the predicted fluorescence spectrum and experimental results. A typical comparison between the computed spectrum and the experimental results is shown in Fig. 1. One of the adjustable parameters for the model is the quenching rate which can be obtained through an iterative procedure. The quenching rate of OH is found to be about $5.0 \times 10^{-9} \text{ sec}^{-1}$ for a methane/air premixed flame at an equivalence ratio of 1.03. We are presently studying the dependence of the quenching rates on temperature, equivalence ratio and diluent ratio.

As mentioned above, one problem that exists for atomic fluorescence spectroscopy is that fluorescence trapping severely limits the dynamic range. One method for overcoming this limitation is to observe the enhanced Rayleigh scattering near resonance, rather than the fluorescence signal itself. If the laser is detuned from

Fig. 1. A comparison between computed spectrum (top) and experimental results (bottom). (XBL 794-1143)

resonance slightly, then the spectrum of the scattered light consists of a Rayleigh scattering line at the laser frequency, a fluorescent signal which is caused by collisional redistribution of energy to the resonant state, and perhaps a three photon signal if the laser intensity is sufficiently large. We have observed the Rayleigh and the resonance peaks in sodium in flames. We have demonstrated that the Rayleigh component is not significantly trapped at number densities much higher than that for which fluorescence trapping becomes important.

Other useful information can also be obtained by laser induced fluorescence spectroscopy. If the characteristic decay time of the excited species is of comparable length to the exciting pulse, chemical decay may be observed directly. We have observed and made measurements of such decay on sodium for a range of flame conditions.

FOOTNOTE

* This work was supported by the Air Force Office of Scientific Research through the Engineering Office of Research Services, University of California, Berkeley.

Combustion of Coal and Coal Related Fuels in an Opposed Flow Diffusion Flame*

W. K. Chin and R. F. Sawyer

INTRODUCTION

The growing and renewed importance of coal as a primary energy source has motivated our study of the fundamental combustion characteristics of coal and coal derived fuels. Initiated in Fall 1976, this project is based upon utilization of an existing opposed flow diffusion flame (OFDF) burner for experimental investigation on burning characteristics of coal and coal related fuels (solvent refined coal [SRC], coke, carbon and graphite). Research has included: comparison studies among these five fuels, determination of the relative importance of O_2 and CO_2 on surface oxidation, measurement of pollutant formation, and extraction of physical properties under burning conditions.

The utility of the OFDF apparatus for laboratory study of the combustion of gaseous, liquid, and polymer fuels has been demonstrated by a number of researchers. We have employed this configuration to study the steady state combustion of graphite, pulverized coal, and SRC in an opposed flow of oxygen/nitrogen or oxygen/argon. The advantages of this geometry lie primarily in the ability to observe the combustion of coal and coal related fuels in a particularly well controlled environment. While the heating rates, which are known to be important to the pyrolysis and combustion of coal, are considerably less than is typical of the burning of pulverized coal, they are in the range of applicability to the in-situ, fluidized bed, and possibly stoker fed combustion of coal. Moreover, this experimental technique provides a means of observing the combustion of these fuels under comparable combustion conditions. In previously completed work, the experimental program has demonstrated the suitability of the OFDF technique to the study of the combustion of graphite and pressed pulverized coal samples, even in cases where there is a substantial ash fraction, 6% by weight. Porosimeter measurements indicate void and pore characteristics in the pressed samples which are consistent with reported properties of the pulverized coal. Regression rate under steady state condition was measured and solid phase temperature distribution in coal and SRC were obtained by an imbedded fine thermocouple.

ACCOMPLISHMENTS DURING 1978

The OFDF apparatus is contained in a 10 cm diameter pyrex cross to eliminate external disturbances, Fig. 1. The oxidizer is metered through the rotameter and enters the nozzle above the sample. A He-Ne laser and a photodiode is used to sense the sample surface, providing a signal to a stepping motor which automatically positions the fuel sample. Linear regression rate measurements are obtained directly from an electronic counter.

Fig. 1. Opposed flow diffusion flame apparatus.
(XBL 784-7996)

The burning characteristics of pulverized coal and SRC in the OFDF were investigated by measuring the regression rate dependence on oxygen concentration and oxidizer flow velocity. Both fuels have shown roughly the same power dependence on oxygen mole fraction at oxidizer velocity of 3.81 m/s. This similarity of burning characteristics suggests that the rate limiting process for both may be established by char oxidation.

To investigate the relative importance of carbon dioxide and oxygen on surface oxidation, pulverized char was obtained by heating pulverized coal at the rate of 280°C/min to 700°C in an oven purged with nitrogen gas. Coke samples were pressed into cylindrical rods.

Carbon electrodes also have been studied. The regression rates in mixtures of oxygen and nitrogen and in mixtures of oxygen, carbon dioxide and argon were compared. No clear indication of the effect of carbon dioxide on regression rate has yet been observed.

PLANNED ACTIVITIES FOR 1979

The relative importance of CO_2 and O_2 on surface oxidation will be investigated further. Gas phase product composition will be measured and gas phase

temperature profiles determined. Experimental results will be analyzed to provide a comparison of the combustion of the several fuels studied and a final report of this phase of work will be completed.

FOOTNOTE

* This work was supported by the LBL Director's Office Fund. Lawrence Berkeley Laboratory, Berkeley, California.

Condensation of Ash and Trace Metals from Pulverized Coal Combustion*

R. Greif, J. Pennucci, F. Robben, and P. Sherman

INTRODUCTION

All indications point to a greater use of pulverized coal and in all probability greater use of coal of lower quality. This trend enlarges the concern in recent years over the environmental effects of the particulates emitted by coal combustion. The effects on the atmosphere of new power plants, even with improvements in clean-up devices, such as electrostatic precipitators, remains a serious problem. New regulations for particulates from power plants provide an added incentive for exploring new and more efficient ways of decreasing emissions.

It had been thought that the very small ($<0.5\mu$) particles emitted during coal combustion were neither prevalent nor detrimental. However, more recent studies show that there are indeed many submicron particles¹ and furthermore, that the smallest particles are the ones which are deposited in the pulmonary region of the respiratory system. In addition, there are indications that toxic trace elements are concentrated in the smaller particles^{1,2} and these are particularly hazardous when ingested. There now are also indications that crops may be affected by the particulate emissions; further, the way in which the smaller particles effect the formation of larger ones to create "smoke" is just being investigated.

Although the submicron particulates may represent only a small fraction of the total mass of particulates emitted, they do represent a large fraction of the total number of particulates emitted. Cleanup devices remove the larger particles most easily; cleanup of the smaller particles is much more costly.

It is clear that it would be preferable to generate a smaller number of larger particles instead of a larger number of smaller particles. One possibility for doing this is by modifying the combustion process. Variations in the combustion process, such as changes in temporal and spatial temperature histories, have a profound effect on the combustion products. It is therefore of interest to consider the feasibility of controlling the generation of small (50Å to 5000Å) particulates from pulverized coal combustion by varying the combustion and heat transfer parameters. This work initiated last year is directed toward investigating that possibility.

ACCOMPLISHMENTS DURING 1978

A preliminary laboratory arrangement has been designed and built. For convenience and simplicity a Bunsen burner type of arrangement was chosen to burn the pulverized fuel. Provision was made for auxiliary gaseous fuel, oxygen and air for support combustion. (Stoichiometric methane-air temperature is 2236°K while stoichiometric methane-oxygen temperature is 3053°K.) The gaseous fuel, oxygen and air are injected radially at the bottom of a 1/2" diameter mixing tube. The coal/air mixture is delivered through a 1/8" diameter tube and injected vertically on the center line of the mixing tube. The main disadvantage of the burner arrangement is the flow velocity limitation due to flash back. However, reasonable velocity limits can be found using methane, air, and oxygen keeping an equivalence ratio well below 1.0. The limits using hydrogen are more restrictive.

Emphasis of the program is on particulates in the 50Å to 1000Å range. An appropriate sampling device should therefore collect and disaggregate the small particles for examination. It must also eliminate any larger particles which may obscure the small ones. Sampling can be done isokinetically, using an impacting surface, using a sonic orifice, or by various electro-magnetic or diffusion schemes. The initial design chosen was a streamlined wedge shaped chamber with a sonic orifice (0.03" dia.). A vacuum pump evacuates the chamber so that sonic conditions are maintained at the sampling orifice. With sonic flow a maximum flow rate for the given orifice size is maintained. In addition, the streamlines are forced to curve, sucked inward toward the sampler orifice. As a result of their inertia, the larger particles tend to travel in a straight path in their initial direction. Most of them therefore bypass the sampling orifice. The small particles with much less inertia follow the curved streamlines into the sampler orifice. The collecting surface geometry inside the sampler should remove any large particles which may have entered, and it should further spread out the particles collected. The design employed provides for two kinds of collection surfaces. One is a thick flat plate with a rounded leading edge. The leading edge catches the large particles and the small ones are spread out over the flat surface. The other collection surface

that fits into the sampler is a hexagonal cylinder which permits collection of particles at different angles to the flow. The design has proven effective. Large particles by-pass the orifice, and the submicron particles are distributed over the collection surface.

Examinations of very small particles of the order of 100Å requires the use of the transmission electron microscope (TEM). It permits a magnification greater than any other kind of microscope so that very small particles can be photographed and their morphology determined. The resolution of most TEMs permit observation of particles down to 20Å. The substrate required, however, must be transparent to the electron beam of the microscope and must also be microscopically flat and clean. A technique which meets these requirements is a thin carbon film supported on a strip of mica. The mica is cleaved along its lattice surface so that it is microscopically smooth. A layer of carbon is deposited on it by surface condensation in an evaporator kept at very low pressure. After particles are collected on the coated mica, they are "shadowed" in the evaporator by depositing a thin film of chromium (or platinum-palladium) at an angle to the surface of the mica. The chromium layer is opaque to the electron beam so that shadows are created which give a three-dimensional character to the image. The higher the particle stands above the surface, the longer the shadow. If grain size of the opaque shadowing material is kept fine by proper use of the evaporator, good photographs are obtained at greater than 100,000 magnification.

Figure 1 shows an example of the photographs taken. The darkest parts of the photographs are particles. The grey background is the shadowing material. The light "tails" are the shadows where no shadowing material falls.

PLANNED ACTIVITIES FOR 1979

The preliminary work done has demonstrated in a general way the feasibility of the laboratory approach. Refinements of the equipment and the experimental techniques hold the promise of significant results. Modifications to the equipment should be made to insure substantial progress.

The changes presently considered are:

- a new coal hopper section for steadier flow of fine coal dust
- an improved mixing tube geometry to remove the boundary layer
- a cleaner sampler inlet with filtered bleed-in,
- addition of a positioning device for locating the sampler
- a heated flame holder ring for wider flame stabilization conditions

Fig. 1. Micrograph of shadowed particles

Flow rates: coal ~ 2.7 gms/min
methane ~ 2.7 liters/min
oxygen ~ 5.8 liters/min
air ~ 20.3 liters/min

Run time ~ 10 minutes
Sampler orifice ~ 21 1/2" from mixing tube exit.

- added instrumentation:
thermo-couples and pyrometers to obtain the temperature field; laser light absorption or scattering to measure the coal dust flow rate.

In addition, an alternate burner approach should be investigated. In the open flame arrangements now employed, the free jet mixing process and resultant temperature and concentration fields, although somewhat predictable, cannot be independently controlled. A flame enclosure with walls which can be heated or cooled would provide for better control of heat transfer and mixing with secondary air.

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Polymer Combustion and Flame Chemistry*

N. J. Brown, R. F. Sawyer, R. W. Schefer, and W. J. Pitz

INTRODUCTION

New energy technologies and conservation measures have resulted in an increased use of polymeric materials. Although they are advantageous from the perspective of energy considerations, polymeric materials sometimes create a fire hazard. In order to assess their potential risk, it is important to characterize the flammability of these materials. For this reason a combined experimental and theoretical program is underway to investigate steady state polymer combustion, gas phase flame inhibition, and flame chemistry. Fundamental combustion characteristics of polymeric materials, including burning rates, mass transfer numbers, extinction limits, and flame structure, are determined in a series of opposed-flow diffusion flame experiments with the objective of relating the basic physical and chemical properties of the polymer to flammability. A complementary study of flame inhibition is underway, and the results will be used to explain the chemical inhibition of polymer combustion.

Flame inhibitors are broadly classified as being either of the physical or chemical type. The former is believed to act simply as a physical diluent while the latter is thought to participate directly in the reaction mechanism important to flame propagation. Although no general consensus exists regarding the mechanism(s) of chemical inhibition, it is recognized that certain molecules have been observed to retard flame propagation out of proportion to their thermal influence which leads to the supposition that this type of inhibition is directly linked to chemical reactivity. Since effective, rapid suppression of unwanted fires is most desirable, theoretical and experimental studies of flame chemistry and flame inhibition have been undertaken to determine combustion characteristics and chemical kinetic mechanisms which are important in understanding inhibition.

ACCOMPLISHMENTS DURING 1978

Extinction measurements have been performed on uninhibited and inhibited polyethylene samples burning in the opposed flow diffusion flame apparatus.¹ The contrasting cases of oxidizer inhibitor addition and fuel inhibitor addition have been investigated, and in the former case various concentrations of the inhibitor HCl have been added to the (N₂/O₂) oxidizer stream.

Since polyvinyl chloride differs chemically from polyethylene by the substitution of a chlorine atom for a hydrogen atom in the monomer, the polyvinyl chloride may be thought of as inhibited polyethylene and was used for the set of extinction measurements where the inhibitor was added to the fuel. In comparing the extinction data for the addition of chlorine to the oxidizer with its addition to the fuel, it is important to compare only cases with identical amounts of chlorine in the flame zone and suitable data for comparison are shown in Fig. 1. The results of such a comparison suggest that inhibition is more effective when the inhibitor is added to the fuel side; however, the differences in physical properties of polyethylene and polyvinyl chloride and presence of impurities in each polymer preclude a definite conclusion. Further studies are currently underway with pure samples.

A numerical boundary layer model was developed to aid in analyzing extinction data from opposed flow diffusion flame experiments. The model relates overall kinetic parameters to various extinction data and may indicate the influence of inhibitors on overall kinetics. In addition, an improved aerodynamically designed nozzle was built which yields a more uniform laminar velocity profile in the flame zone of the opposed flow burner and gives a closer match between experiment and numerical model. Preliminary gas composition measurements with a quartz microprobe have been performed to determine characteristics of the flame chemistry close to extinction.

Work has been completed on the construction and demonstration of a two zone flame model which is largely based on flame chemistry and is suitable for computing flame propagation velocity and average properties of the radical generation region and fuel attack region of a flame.² An experimental study of low pressure hydrogen/oxygen flames concerned with the flame structure analysis of lean, near stoichiometric and rich flames has also been completed.³

A computational study of flame inhibition has been made using the model of the perfectly stirred reactor. The flame system selected for study was hydrogen/oxygen/argon and the inhibitors studied were Ar, N₂, HCl and HBr. The variables considered in this study were 1) H₂/O₂ mechanism, 2) pressure, 3) equivalence

Fig. 1. Comparison of extinction curves and adiabatic flame temperatures of PVC with N_2/O_2 mixtures and PE with $N_2/O_2/HCl$ mixtures where $\eta_{HCl}/\eta_{O_2} = 1/3$. (XBL 784-4832)

ratio and 4) inhibitor type and concentration. The perfectly stirred reactor equations were solved for a series of residence times, and the corresponding compositions and temperatures between the blowout condition and thermodynamic equilibrium were obtained. An inhibition parameter was defined to characterize inhibition in a perfectly stirred reactor.

The blowout parameters: residence time, temperature, composition, reaction rate and heat release rate were especially sensitive to inhibitor type and concentration in the perfectly stirred reactor calculations. Radical concentrations were also found to be sensitive to the variables considered. Figure 2 illustrates the effect of HBr on the radical pool fraction for a lean H_2/O_2 mixture. A paper⁴ describing the cases of HBr, N_2 and Ar inhibition has been written and another contrasting the inhibitors HCl and HBr is in preparation.⁵ Computational studies of HBr inhibition in plug flow and HBr inhibition of wet CO/O_2 mixtures in the perfectly stirred reactor are in progress.

Fig. 2 Radical pool fraction as a function of residence time for 2 and 8 mole percent HBr for lean $H_2/O_2/Ar$ mixtures reacting via mechanisms I and III at one atmosphere. (XBL 784-7962)

PLANNED ACTIVITIES FOR 1979

This project is to be completed during 1979 and planned activities are:

- 1) Completion of the experimental studies of polymer inhibition in the opposed flow diffusion apparatus.
- 2) Determination of the composition and temperature profiles of polyethylene/oxygen/nitrogen opposed flow diffusion flames for various oxidizer velocities and compositions.
- 3) Completion of the computational studies of HBr inhibition of hydrogen/oxygen/argon

mixtures in plug flow and of wet carbon monoxide mixtures in the perfectly stirred reactor.

Papers describing this work will be submitted for publication.

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Soot Radiation in Foam Polystyrene Flames*

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INTRODUCTION

The flaming properties of plastics have become an increasingly important concern in fire safety considerations. Several recent studies have been devoted to the radiative properties of plastic flames.¹⁻³ Of particular interest is the soot contribution to thermal radiation from these flames, which is quite significant but little understood. A good understanding requires detailed information on soot characteristics, such as optical properties, size, shape and number density, as well as how they vary with fuels and flaming conditions.⁴⁻⁷ Soot optical properties have been studied for different soots in combustion systems,⁸⁻⁹ but information on soot size, shape and number density in different flames is comparatively scarce.

Assuming that the characteristic size of soot particles is small compared to the characteristic wavelength of thermal radiation, soot radiation can be analytically described by Rayleigh absorption, the limit for small, absorbing particles in the general Mie theory.¹⁰ In this limit, the analytical description is greatly simplified in that detailed information on soot size, shape and number density becomes unnecessary, and soot radiation depends only on the soot volume fraction and the optical properties of soot.^{4,5} Indeed, it is found experimentally that the soot size in solid-plastic flames is much smaller than the characteristic radiation wavelength,³ and the soot extinction coefficient follows closely that due to Rayleigh absorption.¹¹ It is on this simple model that most calculation methods for luminous flame radiation have been developed,⁴⁻⁶ and a useful tabulation of soot volume fractions for different diffusion flames is presented.⁶

The present work reports experimental results of soot radiation in foam polystyrene flames, which exhibit radiation characteristics distinctively different from Rayleigh absorption as previously observed in solid polystyrene flames.¹ This interesting, but surprising, finding not only provides valuable information in the fire-safety analysis of widely-used foam plastic materials, but also suggests the general use of the full Mie theory in analysing soot radiation.

EXPERIMENT

The experimental system for infrared transmission and emission measurements is essentially the same as that used by Buckius and Tien.¹ Foam polystyrene samples (National Bureau of Standards Special Reference Materials GM 48) of size 20(H) x 8 x 5 cm were each placed in aluminum foil trays of size 0.7(H) x 8 x 5 cm with the short side along the path of the light beam emitted from the source unit. The light path was 2 cm above the burning surface. The present measurements show that the radiative properties of foam polystyrene plastic during solid-foam and liquid-pool burnings display essentially the same characteristics, but for convenience, most data were taken during the pool burning period. Each test was run at a fixed wavelength from 1.6 to 5.0 μm , and the pathlength was determined photographically.

DATA ANALYSIS

Away from the absorbing bands of gases, a beam of monochromatic radiation is attenuated along a homogeneous polydisperse aerosol according to

$$I_{\lambda}(L) = I_{\lambda}^0 e^{-\kappa_{\lambda} L} \quad (1)$$

where I_{λ}^0 and I_{λ} are the initial and transmitted intensities respectively, L the optical pathlength, and κ_{λ} the spectral aerosol extinction coefficient. In terms of particle parameters, κ_{λ} can be expressed as^{11,12}

$$\kappa_{\lambda} = \int_0^{\infty} \pi r^2 N(r) Q_e(r) dr \quad (2)$$

where r is the particle radius, $N(r)$ the particle size distribution, and Q_e the single-particle extinction efficiency. For spherical particles, Q_e has been analytically expressed and numerically tabulated in terms of the particle size parameter, $\alpha = 2\pi r/\lambda$, and particle optical properties.¹⁰

The particle size distribution $N(r)$ is often represented by the following three-parameter distribution^{3,11}

$$N(r) = ar^{b-3}e^{-cr} \quad (b \geq 3, c > 0) \quad (3)$$

and the constants a , b and c are related to the basic distribution parameters as

$$a = \frac{N_0 c^{b-2}}{(b-2)}, \quad b = 2 + c^2 \sigma^2, \quad c = \frac{b-3}{r_m} \quad (4)$$

where N_0 is the total number of particles, σ the standard deviation, and r_m the most probable radius. The soot volume fraction is thus

$$f_v \equiv \int_0^\infty \frac{4}{3} \pi r^3 N(r) dr = \frac{4}{3} \pi a \frac{\Gamma(b+1)}{c^{b+1}} \quad (5)$$

Based on the experimental values of K_λ , an iterative least-squares fit to equation (2), with $N(r)$ given by equation (3), and the appropriate optical constants⁸ and Q_e ¹⁰ were employed to determine a , b , and c , and thus the basic distribution parameters.

RESULTS AND DISCUSSION

The spectral variation of the soot extinction coefficient for foam polystyrene flames is shown in Fig. 1, along with those for solid polystyrene flames. The bars represent the upper and lower bounds of the experimental data. The solid polystyrene data of Buckius and Tien¹ clearly show an

inverse wavelength dependence, denoting that scattering is negligible, soot particles are small, and the Rayleigh absorption limit can be applied. The distinctively different spectral variation for foam polystyrene implies that scattering is appreciable, particles are large, and the full Mie theory must be employed. The results in Fig. 1 show that the spectral soot extinction coefficients are generally higher for foam than solid polystyrene due to the larger size of soot in foam polystyrene flames. This means, of course, that the total emissivity or radiance of foam polystyrene flames is accordingly higher than that of solid polystyrene flames.

Analysis of the present soot-radiation data yields $a = 6.224 \times 10^{-4} \mu\text{m}^{-5}$, $b = 4$, and $c = 7.5 \mu\text{m}^{-1}$, which correspond to $r_m = 0.133 \mu\text{m}$ and $f_v = 2.64 \times 10^{-6}$. In comparison, the solid polystyrene results indicate a comparable value of f_v (4.6×10^{-6} (ref. 3) and 4.2×10^{-6} (ref. 1)) and a much smaller r_m ($0.021 \mu\text{m}$ (Ref. 3)). The basic cause for this interesting, but surprising, disparity in soot size is subject to anyone's conjecture, since there exists so little information on the basic mechanisms of soot formation and conglomeration. It appears, however, that one plausible cause is the differing interweaving arrangement of long-chain polymer molecules resulting from different manufacturing processes.

The soot size distribution obtained in this study is much broader than that measured by Pagni and Bard³ using a laser-optical method. Their distribution with $a = 1.073 \times 10^3 \mu\text{m}^{-7}$, $b = 6$, and $c = 49.2 \mu\text{m}^{-1}$, which gives a smaller r_m ($0.061 \mu\text{m}$) and a slightly higher f_v (4.7×10^{-6}), does not yield the soot extinction coefficient in agreement with the present experimental results. The difference in the soot sizes is probably due to the larger ventilation rate used in their experiment which induces more complete combustion.

Fig. 1. Spectral variation of soot extinction coefficient for foam and solid polystyrene flames.
(XBL 794-1094)

The different sample sizes (7.5 cm vs. 5 cm in the present study) might have some effect on the value of f_v . For solid polystyrene flames, Markstein² obtained for larger samples a higher f_v than that obtained by Pagni and Bard³ and Buckius and Tien¹ for smaller samples.

CONCLUSION

The soot extinction coefficient determined from the measured infrared transmittance of foam polystyrene flames shows a wavelength dependence distinctively different from the inverse wavelength dependence of Rayleigh absorption as reported for solid polystyrene flames. The data analysis based on the full Mie theory yields the soot size distribution which indicates larger soot sizes in foam polystyrene flames. Consequently, soot and flame radiation of foam polystyrene flames is larger than that of solid polystyrene flames.

FOOTNOTES AND REFERENCES

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Fire Modeling*

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INTRODUCTION

The overall goal of this project is to develop physical and mathematical models of the detailed combustion phenomena which control a fire's growth within a compartment of origin and its subsequent propagation through a structure. These experimental studies and theoretical analyses attempt to provide bases for eventual development of test methods and predictive capabilities for evaluation of the real fire hazard of specific materials and configurations. This work is divided into three broad categories: (1) extensions and applications of excess pyrolyzate concepts, (2) soot volume fractions in diffusion flames, (3) flat flame burner designs and experiments.

ACCOMPLISHMENTS DURING 1978

Excess Pyrolyzate

Several papers have been published describing the effects of fuel which is not consumed locally in the flame that produced it.^{1,2,3,4,5} In preparation for applying this concept to compartment fires, the well-defined, steady, two-dimensional, laminar, opposed flow, diffusion flame was considered.⁶ Predictions of flame heights and excess pyrolyzate have been obtained for axisymmetric and two dimensional geometries. Agreement within ten percent with preliminary flame height experiments using PMMA in an OFDF apparatus previously described by Sawyer and co-workers has been

obtained. The problem of a fuel jet impinging on a noncombustible plate with an oxidizing ambience has also been considered. Order of magnitude extension of laminar flame heights due to this impingement is predicted. In addition, experimental flame heights for PMMA were measured over a wide range of ambient oxygen concentrations in a forced flow apparatus. Agreement with predictions within twenty percent is obtained.

Soot Volume Fractions

Experimental values of the volume fraction of small turbulent diffusion flames occupied by combustion generated carbon particulate are listed in Table 1 for some of the common fuels tested.

Table 1. Sample soot volume fractions.

Fuel	Polystyrene (Foam)	Polystyrene (Solid)	Polyurethane (Foam)	PMMA (Solid)	Acetone (Liquid)
$f_v \times 10^6$	4.7	4.6	0.80	0.31	0.18

Since scattering appears to be important for flames with volume fractions greater than 3×10^{-7} , a multi-wavelength technique was required to determine accurate soot volume fractions. Measurement of the attenuation at several wavelengths of monochromatic laser beams passing through a flame determines, in addition to f_v , approximate detailed size distributions of the carbon particles within the flame.⁷ Calculations of flame radiation back to polyurethane fuel in a pool fire geometry yields good agreement with experimental mass burning rates.⁸

Flat Flame Burner

The detailed temperature and velocity field around a cooling coil embedded in a porous plug burner have been predicted assuming a low Reynolds number media. The results indicate that the maximum extension of the coil wake beyond the front stagnation point is 5 coil diameters and that as the distance between the coils decreases, the length of the coil wake also decreases to a limit of approximately two diameters. The governing nondimensional groups have been identified and the character of the solution over their full range has been examined. Flat flame burners have been designed and built based on these results.⁹

Additional Accomplishments

Other studies of flame spread in opposed flow, excess pyrolyzate in compartments and heat and mass transfer in wet concrete are in preparation.¹⁰

Successful comparison between excess pyrolyzate and flame height predictions and laboratory data have been obtained in a wide variety of systems. The effects of physical and chemical parameters on flame height have been clearly delineated. A technique for measuring the volume fraction of soot in flames in situ has been developed, and data on f_v and detailed size distributions of combustion generated carbon particles have been obtained for

several common solid, foam and liquid fuels. Temperature and velocity fields within water cooled flat flame burners have been predicted and apparatus are available designed according to these analyses.

Flame radiation is now well accepted as the dominant heat transfer mode in full scale fires. This radiation is in turn controlled by the amount of soot in the flame which now can be measured in both laboratory and full scale flames by the techniques developed here. Criteria to be included in ranking material hazard may develop from our studies of excess pyrolyzate. In addition, similar analyses may have utility as sub-program components in compartment fire prediction models under development elsewhere. The flat flame burner described here is now in use in several laboratories and will permit useful comparisons of detailed flame structure experiments.

PLANNED ACTIVITIES FOR 1979

In the second year of this grant the present program will be continued with more emphasis on modeling compartment fires.

Further applications of excess pyrolyzate calculations in systems with both external and flame generated radiation, vitiated ambience and feedback from compartment configurations are under development. Experiments are continuing to obtain data on flame lengths for comparison with predictions. The multi-wavelength laser technique for in situ measurements carbon particulates in flames will be refined to give more accurate particle size distributions for a wide variety of fuels. The effects of flame scale and the variation of the size distribution in space and time will be explored.

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Event Logic Models and Fault Tree Analysis of Fires

R. B. Williamson

INTRODUCTION

There has been a continuing interdisciplinary research project since 1971 at the University of California, Berkeley on "Fire Safety in Urban Housing". The original project was initiated through the College of Engineering on the campus, and the continuing research program was shifted to the Energy and Environment Division of Lawrence Berkeley Laboratory during 1978. The original sponsor was the National Science Foundation--Research Applied to National Needs (NSF-RANN) with additional support from the Department of Housing and Urban Development. In 1976 the fire research mission was shifted from the National Science Foundation (NSF) to the U.S. Fire Administration and the Center for Fire Research (CFR) at the National Bureau of Standards (NBS), and the sponsorship of the Berkeley projects was also shifted to those agencies. A variety of topics have been studied in the overall project and the specific subjects discussed here started several years ago before they were shifted to LBL.

The object of this portion of the fire research project has been to develop event logic models for fire and then incorporate fault tree methodology in their analysis. This has led to the development of a state transition model (STM) of fire growth and spread, as well as the identification of four submodels which make up the total fire event model.

The submodels are constructed to answer the following questions:

1. What is the extent of fire growth with time?
2. What is the extent of spread of combustion products (smoke) from the fire as a function of time?
3. What are the roles of people with the fire in causing its ignition, in fighting it and possibly in becoming its victims?
4. What fire protection techniques can be expected to prevent the fire spread of fire and smoke?

The first question is answered by the Fire Growth Model (FGM), the second by the Smoke Spread Model (SSM), the third by a Human Response Model (HRM), and the fourth by a Fire Protection Model (FPM). As mentioned above, the emphasis has been placed on developing the FGM with particular attention to the utilization of both deterministic calculation and experimental data to quantitatively validate the modeling techniques.

The potential impact of fire can be characterized by (1) the probability of ignition, (2) the probability distribution of fire growth as a function of time and (3) the conditional probability distribution of losses given that a fire has broken out. The total fire model should have the capacity to allow quantitative assessment of the potential temperature of a fire, and there should be sufficient generality to make it applicable to new types of fire situations. For instance, there are fire situations in new occupancies, such as nuclear reactors or wide-bodied airplanes, which have not yet generated a sufficient number of case histories to identify the many possible fire scenarios. Yet a fire situation in these cases could be disastrous. It would therefore seem important for such cases to take data from other occupancies where people are performing similar tasks, and the same behavior pattern of both people and equipment could be reasonably expected. For instance, the data from restaurants and theaters might be analyzed to see what might be expected in wide-bodied aircraft which has many of the same activities and equipment as restaurants and theaters. Similarly nuclear power plants might be compared with conventional power plants for fire that started with a common activity. These data and subsequent fault tree analyses would help to predict and hopefully prevent potentially dangerous fires.

ACCOMPLISHMENTS DURING 1978

The FGM for the room of origin is shown in Fig. 1. It follows the state transition format introduced by Williamson.⁶ The events shown are not necessarily the only events which could be chosen, but they represent observable phenomena that are useful in quantifying full-scale fire tests. The histograms and cumulative distribution

Fig. 1. Fire growth model for fire in a room. (XBL 794-9177)

Fig. 2. A simple form of the fault tree for the original ignition process. (XBL 794-9178)

functions (CDF's) for the observed state durations can be directly utilized as probabilities of the end event for tested materials.¹

One of the special features of the state transition model in Fig. 1 is that it spans the entire duration of fire in the room of origin, and subsequently, in adjacent spaces, the fire growth process starts from a new state J where the flames emerging from the room of origin can be considered the ignition source. This is schematically represented by the symbol (R') in Fig. 1.

The events which mark the beginning and end of the states shown in Fig. 1 can be considered as the top event in a fault tree. The goal of fault tree construction is to model the system conditions that can cause the undesired

event at the top of the tree. When fault trees are constructed for the fire protection system of a whole building, they are quite large and complex; when they are applied to the limited number of state transition events, they can be relatively simple and the very important time factor is automatically taken into account. An example of a fault tree is shown in Fig. 2 where the ignition event is the top event and the four principal sources of actual fire ignitions are connected to ignition through an "or" gate.

An analysis has been performed on the origin of fires in kitchens and was published for the Fall 1978 meeting of the Western States Section of the Combustion Institute.² As shown in Fig. 2, the original ignition of unwanted fires has four principal causes: loss of control of wanted fire, arson, spontaneous combustion

and malfunction of equipment. Loss of control refers to ignitions which start with a planned or wanted ignition, but which, due to human error causing a sufficient heat transfer to the target fuel, results in unwanted spread. Malfunction refers to equipment failures such as overloaded electrical circuits or exploding heaters. A more detailed fault tree than Fig. 2 was constructed to reflect the findings of the National Household Fire Survey (NHFS) which found kitchens to be the origin of 65% of the 2,017 residential fires reported by the respondents.³ There was sufficient quantitative information in the NHFS to estimate that the probability of human error in causing the heat transfer for loss of control to be 0.1. This would indicate that in nine out of ten incidences the heat source and the fuel were right for a fire, but the heat transfer did not occur to cause fire.

The fault tree on ignition of fire gives not only a graphical representation of the top event, but also a ranking of the scenarios according to their probabilities of occurring since the minimum cut sets of the fault tree are a listing of the possible fire scenarios to which probability of occurrence can be quantitatively assigned by using fire statistics from the field.

PLANNED ACTIVITIES FOR 1979

The NBS-CFR sponsors have shifted their emphasis for 1979 to the fire growth experiments leading toward a standard room fire test (see

below), and thus major activities on this project will require new sponsorship. There are a number of potential avenues of research that should prove interesting and important. The Fire Growth Model (FGM) can be further developed to specifically treat the spread beyond the room of origin and the Fire Protection Model (FPM) can be constructed to control that spread. The concept of "defense in depth" can be quantitatively evaluated from the imposition of the FPM and the effects on the FGM beyond the room of origin. Standard fire test data on suppression systems, fire walls, fire doors and other fire protective devices and/or assemblies can serve as the pool of quantitative information to make the FPM meaningful.

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