LA--9394-SR

DE83 003994

LA-9394-SR
Status Report

UC-41
Issued: October 1982 ✓

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Industrial Hygiene Group Annual Research Report,

FY 1981

Compiled by
J. O. Jackson
H. J. Ettinger

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INDUSTRIAL HYGIENE GROUP
ANNUAL RESEARCH REPORT

FY 1981

Compiled by

J. O. Jackson and H. J. Ettinger

ABSTRACT

Field studies have been performed at several oil shale facilities to identify unique industrial hygiene problems and provide input to inhalation toxicology studies aimed at evaluating the hazards of materials associated with this developing technology. Aerosol physics support has also been provided to develop aerosol generation and animal exposure techniques for evaluating the toxicity of oil shale materials and manmade mineral fibers. As part of the Department of Energy effort to assure a safe, orderly, and timely development of various synfuels, field evaluation of indicator-sampling procedures was performed, and industrial hygiene work practices for two synfuel technologies are being prepared. Respirator studies are used to evaluate the performances of special devices (some of which are not in the existing government approval schedules) and of a proposed test procedure for self-contained breathing apparatus. We are developing an approval procedure for air-purifying respirators required for protection against radioiodine, evaluating the adequacy of respirator programs at the Nuclear Regulatory Commission licensee facilities, and developing a program for respirator use under emergency situations. A new aerosol size-characterization stack sampler has been designed, and potential instrument changes to aerosol size monitoring for filter testing are being evaluated. Material permeability tests have identified the protection afforded by protective clothing materials, and improved analytical procedures have been developed for pentachlorophenol and plutonium.

OUTLINE OF PROGRAM

The primary responsibility of the Los Alamos National Laboratory Industrial Hygiene Group is to assure that Laboratory employees are adequately protected when working with potentially toxic chemicals or physical stresses. In support of these efforts, the Group has developed considerable expertise in the areas of applied industrial hygiene studies, respiratory protection, aerosol physics, personnel protective clothing, and analytical chemistry. Because our expertise constitutes a national resource, the Group has directed part of its efforts to a variety of research projects funded by the Department of Energy (DOE), other government agencies, and industry.

The diverse research activities at the Laboratory frequently result in unique industrial hygiene concerns, which may be forerunners of problems to be faced in the future by various industries. In the past, this has led to research studies by the Group involving respirable-dust sampling; definition of protection factors for respirators; development of test methods and analytical procedures, instrumentation, and training programs for respirator fitting; aerosol filtration studies; plutonium aerosol studies; and testing of materials used for personal protective clothing.

During FY 1981, the program focused on the following areas of concern to DOE and other funding organizations:

- evaluation of potential health protection problems associated with the development of oil shale, solvent-refined coal technologies, and other synfuel activities of interest to DOE;
- evaluation of respirator performance, use and approval procedures for devices of special interest to the DOE, the Nuclear Regulatory Commission (NRC), the Bureau of Mines (BM), and the Department of Defense (DoD);
- development and evaluation of methods for aerosol size characterization and filter testing;

- evaluation of materials used for personal protective clothing in various industries;
- aerosol physics support for inhalation toxicology studies of interest to energy-related industries; and
- development of improved analytical chemistry procedures for highly toxic materials of special interest.

Several of the individual projects constituting this total program were performed in conjunction with other Los Alamos organizations, such as the Life Sciences Division, Occupational Medicine Group, and Waste Management Group. Whereas projects are designed to satisfy the specific requirements of the funding organization, overlapping interests frequently result in increased benefits to several organizations. All of these programs directly relate to protecting workers, the public, and the environment by applying the scientific skills previously noted and by using the special facilities and equipment developed.

James O. Jackson
Group Leader

Harry J. Ettinger
Project Leader

ORGANIZATION CHART

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I. INTRODUCTION AND OVERVIEW

The Industrial Hygiene Group (H-5) is responsible both for operational industrial hygiene at the Los Alamos National Laboratory and for applied research and development studies. As a result, various projects and funding organizations are involved. Funding organizations include the DOE, Office of Health and Environmental Research (OHER), Office of Operational Safety (OOS), Airborne Waste Management Program Office (AWMPO), Laramie Energy Technology Center (LETC), Los Alamos National Laboratory-Indirect Budget, Nuclear Regulatory Commission (NRC), National Institute for Occupational Safety and Health (NIOSH), Environmental Protection Agency (EPA), Bureau of Mines (BM), US Air Force, and industry [Thermal Insulation Manufacturers Association (TIMA)].

Over the past several years, Group H-5 has developed technical expertise in many areas of industrial hygiene. These include field studies, respiratory protection, aerosol generation, sampling and characterization, filtration, personal protective clothing, support for inhalation toxicology, and analytical chemistry development. In addition to the typical laboratory and field instrumentation needed to support research in these areas, the Group has also obtained a considerable amount of highly specialized equipment and facilities to perform unique studies. These include a 30-m wind tunnel, walk-in aerosol test chambers, scanning electron microscope, gas chromatograph/mass spectrometer, and fluorescent single-particle aerosol spectrometer.

A major effort is evaluation of potential hazards associated with development of oil shale as a source of liquid fuel. This includes field studies to characterize the contaminants of concern so that toxicology studies can be designed to best evaluate the hazards associated with this developing industry; support for inhalation toxicology studies (performed by the Los Alamos Life Sciences Division) using oil shale materials; and

assistance in the application of a laboratory scale oil shale retort for inhalation toxicology exposures. Field studies are also concerned with the development of industrial hygiene work practices for the solvent refined coal and aboveground oil shale technologies, evaluation of air sampling for indicator compounds at coal gasification facilities, and an assessment of the potential industrial hygiene problems at the LETC.

Efforts directed at respirator problems include an evaluation of (1) a new stress-test procedure proposed by the BM, (2) the proposed military respirator, and (3) various respiratory equipment of special interest to the nuclear industry. Respiratory programs at various NRC licensee facilities were evaluated to provide a background for preparation of a Manual for Respiratory Protection in Emergency Situations, and a test method has been developed to permit approval of air-purifying respirators used for protection against radioiodine. This newly developed technology will be transferred to NIOSH during FY 1982.

Aerosol studies have included the evaluation of aerosol size-characterization instrumentation used for filter quality-assurance testing, calibration of a "real time" impactor, and development of a new size-separating stack sampler. Work in the area of personal protective equipment focused on determining the permeability of various materials used to provide protection against skin contact with selected organic compounds of concern and on preparing (through a subcontract) a status report and guidance document regarding selection of protective clothing. In addition to the previously noted oil shale inhalation toxicology support, a multiyear joint program with the Los Alamos Life Sciences Division is proceeding to evaluate the carcinogenicity of manmade mineral fibers.

Analytical chemistry efforts were directed at developing new analytical methods to (1) better quantify the presence of pentachlorophenol (PCP) and its associated decomposition products and (2) improve the analytical procedures for measuring plutonium in urine.

II. APPLIED INDUSTRIAL HYGIENE

A. Oil Shale Workers' Health Study (Industrial Hygiene Activities)

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Funding Organization

DOE/OHER

The Industrial Hygiene Group participates in three areas of the Los Alamos National Laboratory Oil Shale Health and Environmental Research Program. These areas are (1) field studies to identify and evaluate unique hazards in the developing oil shale industry and provide input to the Los Alamos toxicology studies in progress; (2) participation in the Oil Shale Task Force, which assists the DOE in establishing program direction and priorities for the health and environmental studies associated with development of oil shale recovery processes; and (3) aerosol generation and characterization support and operation of a laboratory-scale oil shale retort for animal inhalation toxicology studies. Items (1) and (2) are discussed in this section. Item (3) is discussed in Sec. VII.

The Oil Shale Workers' Health Study includes components of both industrial hygiene and occupational medicine. Industrial hygiene activities involve field studies that provide information to determine if unique health hazards are associated with alternate oil shale technologies, to assist in the design of toxicological studies, and to provide bulk material for use in these studies. Occupational medicine aspects of this study will be discussed in the H-Division Annual Research Report.

Industrial hygiene field studies and medical worker evaluations were previously conducted on the Paraho aboveground retort and underground mine at the DOE Anvil Points oil shale facility. Industrial hygiene studies have also been performed

at Occidental and Rio Blanco facilities during the burn of underground modified in situ (MIS) retorts. Emphasis has been placed on the retorting unit operation because this phase appears most likely to produce unique hazards.

During FY 1981, industrial hygiene field studies were conducted at the Geokinetics true in situ (TIS) oil shale facility and at the Rio Blanco MIS facility during the burn of a second and larger retort. Medical evaluations were carried out on employees at the Geokinetics TIS site. A proposal was developed for a comprehensive study during the simultaneous burn of two commercial-size MIS retorts at the Occidental Logan Wash facility during FY 1982. Continuing support was provided to the DOE Health and Environmental Oil Shale Task Force.

1. Geokinetics. An industrial hygiene study was conducted during the burn of Retort 24 at the Geokinetics oil shale facility. Retort 24 was the first commercial-size horizontal TIS retort burned. Preparation of the in situ retort involves drilling a pattern of blastholes from the ground surface through the overburden and into the oil shale bed. Blasting uplifts the overburden, creating a zone of broken (rubbled) shale which constitutes the in situ retort and contains void spaces necessary to make the shale permeable to gas flow.¹ Surface facilities installed (Fig. 1) include blowers and pipes for injection and removal of air and offgases, pumps for removal of retort oil and water, demisters, storage tanks, and a thermal incinerator.

A flame front is established at one end of the retort with burning charcoal. Oil shale is retorted ahead of the flame front by the hot combustion gases as they flow through the retort. Condensed vapors flow to sumps and are pumped to the ground surface. Retort offgases are drawn from the retort, passed through demisters to remove oil mist, and burned in a thermal incinerator.

Industrial hygiene sampling was conducted during early, middle, and late phases of the 9-month burn of Retort 24. We sampled workplace air in areas of expected maximum air contaminant concentrations rather than measuring actual employee exposures. This identifies air contaminants of greatest concern, as well as critical

Fig. 1. Surface facilities, Geokinetics Retort 24.

areas or operations where employees might spend extended time in a commercial-scale facility consisting of 10 or more retorts. Air samples were collected for analysis of dusts and selected gases and vapors, and limited noise measurements were made. Limited air sampling for dusts was also conducted during the drilling of blastholes for another retort.

Results of total, respirable, and size-analysis dust sampling using filters, cyclone pre-samplers, and an Andersen eight-stage cascade impactor are presented in Table I. Respirable dust samplers were operated to match the American Conference of Governmental Industrial Hygienists (ACGIH) criteria for respirable dust.² Dust concentrations were very low during retorting (generally $<0.1 \text{ mg/m}^3$ for total dust). Particle size ranged from 3.3 to 4.7 μm mass median aerodynamic diameter (MMAD), indicating a substantial respirable fraction. Alpha-quartz content determined by x-ray diffraction ranged from 2 to 7 per cent (cristobalite and tridymite were not detected). The limited sampling during the drilling of blastholes indicated high dust concentrations in the immediate vicinity of the drilling operation. However, personal samples of the drilling employees showed their exposures were not

excessive because the employees worked within an enclosure or spent only limited periods of time in the area of highest dust concentrations.

Carbon monoxide, hydrogen sulfide, oxygen, and mercury vapor were measured by direct-reading instruments. Organic gases and vapors (amines and selected aliphatic and aromatic hydrocarbons) were collected on solid sorbents and analyzed by gas chromatography. Ammonia, hydrogen cyanide, formaldehyde, methyl mercaptan, carbon dioxide, sulfur dioxide, nitrogen dioxide, and arsine were measured by length-of-stain gas detector tubes. Ammonia, nitrogen dioxide, sulfur dioxide, and mercury vapor were also measured by passive dosimeters.

Gas and vapor sampling showed air concentrations well below established Threshold Limit Values (TLVs) in breathing zones above the retort, indicating that leakage of retort gases through the retort overburden was not a problem. Higher concentrations of carbon monoxide (up to 300 ppm) and hydrogen sulfide (up to 10 ppm) were observed around the blower that removed offgases from the retort. These data indicate that careful maintenance of blowers and seals will be required in commercial operations to minimize fugitive emissions.

The condensation of organic materials onto particles is a possible concern due to the presence of potentially carcinogenic polynuclear aromatic hydrocarbons (PAHs) in the retort. Glass fiber/silver membrane filters with Tenax solid sorbent backup were used to sample for particulate and vapor-phase PAH around the retort. Filters and Tenax samples were extracted with cyclohexane in an ultrasonic bath and analyzed by high-performance liquid chromatography for seven specific PAHs (anthracene, benzo(a)pyrene, chrysene, fluoranthene, fluorene, phenanthrene, and pyrene). Aliquots of the extracts were also analyzed gravimetrically to obtain total cyclohexane extractables. Air concentrations of the seven PAHs over the area above the retort were less than the limit of detection in most samples, indicating that fugitive emissions through the retort overburden were not a problem. Detectable PAH air concentrations were observed in the area of the leaking fan and demister. Extracts from a charcoal tube and a Tenax tube with prefilter, analyzed by gas

TABLE I
PRELIMINARY RESULTS OF DUST SAMPLING AND ANALYSIS
GEOKINETICS TIS FACILITY

Parameter and Location	No. of Samples	Concentration			Av Particle Size	
		Max.	Mean	Unit	MMAD (μ m)	σ
<u>Total Dust</u>						
Above Retort	30	0.54	0.06	mg/m ³	4.0	3.8
Offgas Blower	11	0.30	0.12	mg/m ³	3.3	4.8
Drilling						
Area Sample	3	85.1	32.2	mg/m ³		
Personal Sample	1	--	0.79	mg/m ³		
<u>Respirable Dust</u>						
Above Retort	1	--	0.02	mg/m ³		
Drilling						
Area Sample	1	--	3.40	mg/m ³		
Personal Sample	1	--	0.04	mg/m ³		
<u>Cyclohexane Extractable Material</u>						
Above Retort	12	3.5	1.5	μ g/m ³		
Offgas Blower	7	89.0	31.8	μ g/m ³		
<u>Sum of 7 PAH</u>						
Above Retort	12	0.03	<0.01	μ g/m ³		
Offgas Blower	6	2.82	0.61	μ g/m ³		
<u>Free Silica Content</u>						
Above Retort	2	7	5	per cent		
Drilling	3	4	3	per cent		

chromatography/mass spectrometry, indicated the presence of a very complex mixture of more than a hundred organic compounds.

These sampling data indicate that the retort can be operated without significant fugitive emissions. Dust levels around the drilling operation indicate that dust suppression and/or personal protective equipment may be required.

Noise levels in the immediate vicinity of blowers ranged from 85 to 95 dBA, indicating that engineering controls and/or personal protective equipment may be required if workers spend major portions of a workshift in those areas.

Airborne organic materials, such as those collected around the leaking fan and demister, have not been well defined or characterized and are extremely complex. Although no Occupational Safety and Health Administration (OSHA) standards or TLVs exist for most of these compounds and little is known regarding their toxicology as pure compounds or complex mixtures, many of these compounds are potentially carcinogenic. Because of the uncertainty, the health significance of air

contaminants detected at this facility is not known. Additional work on characterization and toxicology of such airborne materials is required.

2. Rio Blanco. Industrial hygiene sampling was initially conducted at the Rio Blanco Oil Shale Company's facility during the latter half of 1980. Air samples were collected at the lower level of the mine before and during the burn of the company's first MIS oil shale retort (Retort 0).³ A second field study was conducted in September 1981, during the burn of a larger MIS retort designated as Retort 1.

Air sampling was again conducted on the lower level of the mine, and limited sampling was conducted around process units located on the ground surface. Limited noise monitoring was also conducted in the mine and on the surface. Surface facilities at the Rio Blanco operation (Fig. 2) include a demister, fans, incinerator, sulfur dioxide scrubber, pumps, and storage facilities.

Observed levels for total dust were always less than 0.5 mg/m³--well below the TLVs for respirable and total dust containing 5 to 10 per

Fig. 2. Rio Blanco Surface Facilities.

cent quartz. This was probably due to the fact that all mining activity had ceased before initiation of the burn, and there were also no dust-generating activities on the surface. Gravimetric analysis of aliquots of cyclohexane extracts of filter samples showed no detectable levels on most filters. Cyclohexane extracts of filters and Tenax solid sorbent samples were analyzed by high-performance liquid chromatography for eight specific PAHs (acenaphthene, anthracene, benzo(a)pyrene, chrysene, fluoranthene, fluorene, phenanthrene, and pyrene). No detectable levels of PAH were observed on the filters, but the Tenax samples from both the mine and surface showed a mean of $0.1 \mu\text{g}/\text{m}^3$ for the sum of the eight PAHs analyzed. This indicates that the PAHs were present in low quantities in the vapor phase.

Samples were obtained for selected inorganic and organic gases and vapors. Inorganic gases and vapors analyzed consisted of carbon monoxide, hydrogen sulfide, hydrogen cyanide, carbon dioxide, carbon disulfide, ammonia, sulfur dioxide, nitrogen dioxide, arsine, and mercury vapor. Analyses of samples for organic species (including amines,

formaldehyde, n-hexane, dodecane, benzene, toluene, xylenes, pyridine, cresol, and phenol) have not been completed.

In samples analyzed to date from the mine, concentrations of gases and vapors were all well below existing TLVs and in most instances were below the minimum detectable limit of the sampling and analytical methods employed. Surveys for carbon monoxide (CO) and hydrogen sulfide (H_2S) around process units on the surface using a direct-reading monitor showed no detectable levels of either gas except in the immediate area of the sour-water pumps where a peak of ~10 ppm of CO only was observed. No detectable concentrations of either CO or H_2S were observed on the ground surface above Retort 1 (where air and boiler flue gases were injected into the retort) or in the area where the pipe carrying retort offgases came through the ground surface.

Noise levels in the mine exceeded 90 dBA near booster fans and in both mine water and product pump areas. The noise level in a large area around the demister and the fan handling retort offgases on the surface was also above 90 dBA.

Analyses of air samples indicate no concentrations of dusts or gases and vapors that should be of concern. Noise levels in some areas indicate that engineering controls and/or personal protective equipment may be required if employees spend major portions of a workshift in these areas. Although analyses of samples for organic constituents are not completed, based upon previous work at the Rio Blanco facility and other oil shale facilities, the expectation is that the analyses will show a complex mixture of organic components. The health significance of such mixtures is not known, and additional work on characterization and toxicology of airborne materials at oil shale facilities is required.

3. Occidental Logan Wash Facility.

Occidental Oil Shale, Inc., has prepared two vertical MIS test retorts (Nos. 7 and 8) at Logan Wash, Colorado. These MIS retorts are commercial size and are expected to be burned simultaneously for approximately 8 months starting in December 1981. These operations may provide the basis for future operations at the C-b federal lease tract.

Commercial operation of the MIS process will involve the concurrent development, operation, shut-down, and abandonment of many MIS retorts at the same time, thus presenting the potential for exposure of workers to retort products.

Previous industrial hygiene sampling during the burn of Retort 6 at Logan Wash⁴ was primarily for dusts, with little emphasis on vapors and gases that may be of concern during a retort burn. An industrial hygiene study during the burn of Retorts 7 and 8 will provide information regarding contaminants not previously addressed and the first opportunity to sample during a period when two commercial-size retorts are burning.

In cooperation with personnel of Occidental Oil Shale, plans have been developed to perform air sampling during (1) the initial period of the burn, (2) toward the end of the burn, and (3) during the retort abandonment period for Retorts 7 and 8. Samples will be collected near the retorts and in other areas of the mine in which workers may be exposed to air contaminants resulting from the burn of the retorts or the handling of retort products.

Table II presents a summary of the proposed methods of sampling and analysis. Samples will be collected for a number of gases and vapors, with emphasis on organic compounds, to better characterize the quality of the air for use in design of toxicological studies, as well as to determine whether there appear to be exposure problems unique to the oil shale retorting process.

4. Support for Oil Shale Task Force. The DOE Oil Shale Task Force formulates research plans for health and environmental studies associated with development of the oil shale industry. This research planning provides coordination among researchers, industry, and government (local, state, and federal). Research plans include data development for assessment of potential health and environmental impacts, studies on methods to mitigate adverse impacts, and coordination with engineering development schedules.

The task force meets periodically to review and discuss research results, status of the

industry, oil shale processes, and research needs of those involved with or concerned about oil shale development. The task force also provides summary progress reports of the research conducted on various processes or at process sites.

Four staff members from the Los Alamos National Laboratory are members of the oil shale task force. During 1981, the task force member from the Industrial Hygiene Group participated in (1) several meetings to develop research plans for studies during the burning of MIS retorts at the Occidental oil shale site at Logan Wash, Colorado, and the Rio Blanco oil shale site (C-a) near Rangely, Colorado; (2) a meeting on the oil shale risk analysis being conducted by I. W. G. Corporation, San Diego, California; (3) a scientific exchange on health and environmental effects of oil shale use in Tallin, Estonia, USSR; and (4) preparation of a progress report on studies conducted during the burning of Retort 0 at the Rio Blanco oil shale facility on the C-a federal lease tract.⁵

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TABLE II
PROPOSED SAMPLING AT OCCIDENTAL RETORTS 7 AND 8

Type of Sample	Contaminant or Parameter of Concern	Method of Analysis
Direct-Reading Instruments	Carbon Monoxide and Hydrogen Sulfide Mercury Vapor	Electrochemical Cell Ultraviolet-Light Absorption Total Organic-Vapor Flame-Ionization Detector
Solid Sorbent Tube (Alumina, Charcoal, Silica Gel, Tenax)	Formaldehyde Selected Aliphatic and Aromatic Hydrocarbons and Amines Selected PAHs	Colorimetry Gas Chromatography High Performance Liquid Chromatography (HPLC)
Passive Dosimeters	Ammonia, Nitrogen Dioxide, and Sulfur Dioxide Selected Aliphatic and Aromatic Hydrocarbons Mercury Vapor	Colorimetry Gas Chromatography Conductivity
Detector Tubes	Ammonia, Sulfur Dioxide, Nitrogen Dioxide, Carbon Dioxide, Hydrogen Cyanide, Carbon Disulfide, Formaldehyde, Methyl Mercaptan, and Arsine	Length-of-Stain
Various Filters	Total and Respirable Dust Organic Content Selected PAHs Free Silica Content Various Elements	Gravimetric Analysis Cyclohexane Extraction HPLC X-Ray Diffraction Proton-Induced X-Ray Emission (PIXE) Analysis
Cascade Impactors	Particle-Size Distribution	Gravimetric Analysis

B. Industrial Hygiene Task Force

Participating Staff Members

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Technical Assistance

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Funding Organizations

DOE/OOS and LETC

The Industrial Hygiene Task Force provides the OOS with comprehensive technical support on unique and special industrial hygiene problems associated with operational programs and the development of energy technologies. In FY 1981,

activities centered on developing work practice guidelines for the Solvent Refined Coal-II (SRC-II) demonstration plant; initiating efforts for the development of work practices for the aboveground oil shale technology, reviewing Environmental Impact Statements (EISs) for the SRC-I and SRC-II facilities, completing a study to evaluate the use of indicator compounds for monitoring airborne contaminants in coal gasifiers, responding to several requests for field assistance involving unique industrial hygiene problems faced by DOE contractors, and assisting the LETC in evaluating any industrial hygiene problems and in expanding their industrial hygiene program. One special short-term study was the evaluation of aerosols that might be used in place of di(2 ethylhexyl) phthalate. This was jointly funded by DOE/OOS; NRC; and the Los Alamos—Indirect, and the results are reported in Sec. IV.A.

1. Support for DOE Synfuel Activities.

Experience with direct coal liquefaction has indicated that stringent measures may be necessary to protect the health of coal liquefaction workers. A draft manual of health protection guides (work practices) has been prepared for the planned SRC-II Demonstration Facility. This manual, "Work Practices for the Solvent Refined Coal-II Demonstration Plant-Guides for the Protection of Worker's Health," identifies potential hazards specific to the demonstration facility, details the SRC process, characterizes the hazards associated with the various parts of the process, discusses the toxicology of chemicals of major concern, reviews control measures, and outlines generic industrial hygiene, medical surveillance, biological monitoring, and recordkeeping programs for facilities of this type.

An outline has been prepared for "Health Hazard Evaluation and Recommended Industrial Hygiene Practices for Aboveground Oil Shale Retorting." This document will outline the requirements to ensure that workers in aboveground oil shale retorting facilities are adequately protected against potential industrial hygiene hazards and will be similar to the Work Practice Guide covering SRC-II. It will discuss the several aboveground commercial processes, identify the health hazards associated with each process unit operation, discuss the health effects and toxicology of chemicals of major concern, and outline the requirements for a generic occupational health program including a discussion of engineering controls, monitoring, training, personal protection, medical surveillance, biological monitoring, and recordkeeping.

Draft and final EIS on both SRC-I and SRC-II demonstration facilities were critically reviewed to provide input for the DOE/OOS review. The topics that were reviewed included public health as well as occupational health and safety.

2. Indicator Sampling Study. The recent development of fossil energy conversion processes has brought about a corresponding development of techniques to monitor worker exposure in these facilities. The NIOSH has presented an indicator method of exposure monitoring for use at coal conversion facilities. This method estimates

airborne levels of PAH compounds from airborne levels of more easily monitored substances, such as CO or H₂S.

Airborne levels at two coal gasifiers were monitored to evaluate the correlation between various airborne contaminants. The contaminants studied include CO, H₂S, both particulate and vapor cyclohexane extractables, and particulate and vapor levels of six PAH fractions. The six PAH fractions studied are listed in Table III along with PAH compounds potentially present in the fractions. The air contaminants were sampled simultaneously using conventional industrial hygiene techniques.

The correlation among levels of all the airborne contaminants measured was determined using a computer program that calculates the linear sample correlation coefficient and tests its significance at the 95 per cent confidence interval. Because of the log-normal character of the air contaminant concentrations, two types of correlation analyses were applicable: (1) linear sample correlation analysis using the logs of the data and (2) a rank correlation analysis using ranked data. The former was chosen to preserve the interval information contained in the data.

Insufficient data existed to test the correlation between H₂S levels and other air contaminants because H₂S levels at both gasifiers were found to be below minimum measurable limits of 0.5 ppm. Measured time-weighted average levels of CO at both gasifiers ranged from 0.5 to 15.2 ppm. However, no significant correlation was found between these CO levels and levels of the other air contaminants studied. Both particulate and vapor

TABLE III

PAH FRACTIONS STUDIED AND A PARTIAL LIST OF COMPOUNDS POTENTIALLY PRESENT IN THESE FRACTIONS

Fraction	Compound
Acenaphthene	Acenaphthene
Fluorene	Fluorene
Phenanthrene	Phenanthrene
	Anthracene
Pyrene	Pyrene
Fluoranthene	Fluoranthene
Benzo(a)pyrene	Benzo(a)pyrene
	Benzo(e)pyrene
	Perylene

cyclohexane extractable levels failed to significantly correlate with the other air contaminant levels. Significant correlation was found between levels of many of the six PAH fractions studied. In general, particulate PAH fraction levels correlated best with levels of other particulate PAH fractions; vapor PAH levels, with other vapor PAH levels. No significant correlation was found, however, between particulate and vapor PAH fractions. Some significant correlations were found between individual PAH fraction levels and the sum of specific PAH fraction levels.

These results indicate that the NIOSH indicator method is not applicable for these coal gasifiers, but additional, more sophisticated studies, may be warranted. Correlations found between various PAH fractions suggest that potential indicator relationships may exist among these fractions. However, the use of PAH fractions as indicators may not be feasible for routine industrial hygiene monitoring because of the sophisticated instrumentation and technical capability required for PAH analysis.

3. Industrial Hygiene Study at LETC. At the request of LETC, an industrial hygiene survey of four selected areas at LETC was performed to provide recommendations for work practices and engineering controls to ensure employee exposures are as low as practicable.

The four areas studied were (1) the Fisher Assay Laboratory, (2) the sample preparation annex, (3) the water warehouse, and (4) the 10- and 150-ton retorts. In addition, an evaluation the ventilation system in the main laboratory building and a review of proposed modifications to the ventilation system were performed. Unfortunately, the scheduled run of the 150-ton retort in September was cancelled, deferring this effort until FY 1982.

Air samples for carbon monoxide, sulfur dioxide, arsine, hexane, formaldehyde, and carbon dioxide were collected with direct-reading detection tubes. Eight-hour time-weighted average personnel exposures were estimated using passive organic vapor badges. The organic vapor badges were analyzed for benzene, toluene, hexane, phenol, acetone, methylene chloride, and pyridine.

Tenax, charcoal, and silica gel sorbent tubes were used to collect samples for laboratory analysis. The sorbent tubes were analyzed by gas chromatography/mass spectroscopy to identify all organic materials present. Direct-reading instruments were used to sample for CO, H₂S, and mercury. Total and respirable dust exposures were evaluated gravimetrically with personal sampling pumps and cyclone personal samplers.

Local exhaust ventilation systems in the main laboratory building and the sample preparation annex were evaluated with air velocity meters. The results from air sampling indicate no significant worker exposure. These results together with the evaluation of the existing ventilation system, review of the proposed ventilation system, and recommendations concerning ventilation requirements, control of carcinogens, limited egress/confined space practices, and elements of a respirator program have been forwarded to OOS and LETC.

III. RESPIRATOR

A. Technical Assistance, Support, and Performance Testing for NRC

Participating Staff Members

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Technical Assistance

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Funding Organization

NRC, Office of Research

This project's primary objective is to provide the NRC with information on respiratory protective devices and programs for their licensee personnel. During FY 1981 this involved:

- (1) completion of the NUREG-0041 manual revision;
- (2) completion of a set of NRC video tape training aids;

- (3) development of a Manual of Respiratory Protection in Emergency Situations (RPES), which required numerous site visits to NRC licensee facilities and Three Mile Island; and
- (4) evaluation of respirator products and instrumentation.

1. Manual of Respiratory Protection Against Radioactive Materials (NUREG-0041). This manual was originally developed at Los Alamos in 1976. Because of the many advances since that time in respiratory protection, the NRC requested that the manual be revised and updated. Main emphasis was placed on chapters relating to medical considerations, breathing-air quality, fitting selection, and equipment use. Recommendations concerning medical criteria are currently being reviewed by licensees.

2. Video Tapes. The final training video tape was developed and produced for the NRC. The tape, "Acceptable Practices for Respirator Cleaning and Maintenance," and its accompanying handbook completed a series of four video tapes developed to aid NRC licensees in adequately training their employees in the correct use and care of respiratory protection devices.

3. RPES Manual. We visited NRC licensee facilities including Three Mile Island to collect information regarding the emergency use of respiratory protection and to provide the background information for development of an NRC Respiratory Protection Emergency Situations Manual. A working outline of the RPES manual was prepared and submitted to NRC. A draft of the manual will be prepared during FY 1982.

A survey was also performed to evaluate the Respiratory Protection Program (RPP) at NRC licensee facilities. Five uranium mills, eight power reactors in addition to Three Mile Island, and two research reactors were visited. Without exception, every licensee visited cooperated with the survey team in allowing full access to any records, answering any questions, and touring all respirator program facilities. A report detailing this survey and submitted to NRC suggests that

licensees communicate more among themselves on health protection matters and consider establishing a network to aid each other in unusual or emergency situations. Use could also be made of the services of professional societies and consultants in upgrading respirator programs.

4. Evaluation of Respirator and Associated Equipment. A portion of the technical assistance provided to the NRC involves the testing of certain respiratory equipment to determine the adequacy of protection afforded the user. Seven closed-circuit breathing apparatuses (CCBAs) were worn by a panel of anthropometrically selected test subjects to determine the protection afforded by each. The protection was quantified by placing the test subject in a challenge atmosphere of diethylhexyl sebacate (DEHS) aerosol and measuring the concentration outside and inside the facepiece. The types of CCBA tested included those that supply breathing gas continuously, or on demand, or a combination of both. Table I summarizes the protection factors (PFs) obtained by facial size. These data indicate that many CCBAs provide relatively low PFs, probably due to the negative pressure produced within the facepiece during the breathing cycle. The Biomarine units, which are designed to maintain a positive pressure in the facepiece; the Chemax Ultravue; and the Draeger devices provide the highest PFs for large and medium faces.

An evaluation of three types of powered air-purifying respirators was also conducted. One design appears to be highly suitable for use in atmospheres contaminated with radioactive particulates and would be of significant interest to the NRC. This device became the object of a special study when the NIOSH, which is responsible for the approval of such devices, discovered apparent failures in field use and recommended revoking approval for this device.

Based on Los Alamos data obtained in attempting to duplicate the apparent failures, we recommended to the NRC, NIOSH, and users that, with precautions, the use of the device be continued. Since that time, the planned public hearing to institute revocation of approval has been cancelled.

TABLE I
NUMBER OF SUBJECTS ACHIEVING STATED PROTECTION FACTOR
WEARING CLOSED-CIRCUIT BREATHING APPARATUS (CCBA)

<u>Apparatus</u>	<u>10</u>	<u>20</u>	<u>50</u>	<u>Protection Factors</u>						
				<u>100</u>	<u>500</u>	<u>1K</u>	<u>2K</u>	<u>5K</u>	<u>10K</u>	<u>20K</u>
Aerorlox										
L ^a				11			10	9	8	4
M (B 7) ^b	12		11				10	9	8	4
S(B 6,7,9,9,10)	5	4	3	2					1	
Biomarine 45										
L				11	8	6	4			
M				13	5	4	3			
S	10	8	7	6						
Biomarine 60										
L								11		10
M						13		12		9
S		10		9		7	6	5		1
Chemox Ultravue										
L (B 2)				10	9	8	6			
M				13	.	12	6	1		
S					10	9	4			
Chemox Dual Vision										
L (B 1,2,4)	8			7			4	1		
M (B 4,7,7,7,7)	8			7		6	4			
S (B 6,7,7,7,7,9,10,10)	2						1			
Drager BGL74										
L					11	10	8		7	2
M (B 7)		12			10	8	7		5	3
S (B 7,9)	8	6		4	3		2		1	
McCaa Ultravue										
L		11		10	4	1				
M		13		12	4	1				
S		10		9	2					
McCaa Dual Vision										
L	11	10		8	5	3				
M (B 7)	12	11	8	7	3	1				
S (B 7)		9	7	6	2		1			
Scott 900050										
L			11	10	6	2				
M				13	7	3	1			

^aProtection factors by facial size: L = large, 11 test subjects; M = medium, 13 tests subjects; and S = small, 10 test subjects.

^bNumbers in parentheses are the boxes in which the terminated tests occurred. B7 is the terminated test in box 7.

The potential human carcinogenicity of di-ethylhexyl phthalate (DEHP) [also known as di-octylphthalate (DOP)] aerosol used for respirator-fit testing led the NRC to request assistance in the search for replacement materials. A number of

substitute compounds have been tested and found to produce an acceptable particle size. We have recommended the use of DEHS as a temporary substitute for DEHP. This material can be used in existing equipment for testing respirator fit, respirator

cartridge and HEPA filter quality assurance, and in-place filter performance. This effort was also supported by funding from DOE/OOS and the Los Alamos—Indirect.

B. Respirator Studies for DOE/OOS

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Funding Organization

DOE/OOS

This program ensures that DOE and contractor personnel are adequately protected by personal respiratory protective equipment. Support included (1) technical consultation to DOE and DOE contractors, (2) acceptance testing of special respiratory protective equipment that cannot be approved by the existing NIOSH/Mine Safety and Health Administration (MSHA) approval procedures, and (3) special short-term respirator studies as directed by the OOS. Laboratory testing evaluated the capabilities and limitations of respiratory protective equipment, and information was disseminated through publications, consultations, and visits to contractor sites.

1. Acceptance Testing of Unapprovable Devices. Three DOE contractor devices were submitted, tested, and accepted by the Respirator Advisory Committee (RAC) during FY 1981.

The Los Alamos Supplied-Air Suit was resubmitted for testing of a modified air distribution system designed to reduce noise within the suit to an acceptable level. Test data indicated the sound pressure levels to be 68 to 76 dBA, well below the 80 dBA maximum outlined in the "Specifications and Test Procedures for Airline-Type Supplied-Air Suits (LA-5958-MS).¹ The RAC has recommended to DOE/OOS that this suit is acceptable for use at Los Alamos.

The Savannah River Plant Supplied-Air Hood was tested for acceptance following the outline and schedules prescribed in the specification and test procedures for airline supplied-air

suits.¹ This procedure was modified, in part, to make it more applicable to hoods. Test data indicates that this hood provides PFs of at least 20 000 for the three test subjects at airflows of 8, 9, and 20 cfm. Sound pressure levels using 25- and 50-ft lengths of air hose are well below the RAC acceptable level of 80 dBA. Testing of the supplied-air hose for crush, pull, and kink indicates the hose is of excellent quality that meets or exceeds all requirements. The RAC has recommended to the DOE/OOS that this hood is acceptable for use at Savannah River.

The Rocky Flats Plant Supplied-Air coverall type suit, with a removable hood and rear entry opening, was also tested in conformance with existing procedures.¹ The hood is attached to the body suit with ridged neck rings and clamp assembly, and the entry opening is sealed with a pressure-sensitive adhesive. One size suit fits all wearers because it has internal adjustable waist band and suspenders. The suit provided PFs of 20 000 or higher for all tests performed, and the sound pressure levels were well below the 80 dBA minimum. All associated equipment such as supplied-air hoses and fittings met all existing requirements. The RAC recommended to the DOE/OOS that this suit is acceptable for use at Rocky Flats.

2. Testing of Commercial Devices. Ten supplied-air devices were tested, and data from nine of these devices were forwarded to the RAC for review and recommendations. One device failed to meet existing acceptance criteria for airline-type supplied-air suits considered for use by DOE contractors.¹

Of the devices tested, three were constructed of polyvinyl chloride (PVC). Of these, two were one-piece coverall type, the other a two-piece jacket and pants design. Two of these devices indicate protection factors of 10 000 or better at airflows above 10 cfm, and one device did not satisfy existing acceptance criteria.

Five of the devices were constructed of basic Tyvek spunbonded olefin, with various types of seam construction (i.e., double stitching, rolled seams, laminated seams, or Varicon laminated on the Tyvek material). All of these devices were of a one-piece coverall design, with the hood and

facepiece permanently attached. Four of these suits satisfied all acceptance requirements¹ using airflows of 10 cfm or higher. One suit, which failed to meet the criteria during an exercise, will be retested.

Because most commercial supplied-air suits are purchased without an air distribution system and each user must design and construct his own system, most of the problems in the testing and acceptance of a device are associated with the air distribution system. Using the expertise obtained in previous testing, a universal air distribution system was designed and constructed using commercially available parts. This system will interface with any commercial covering and will meet all requirements for airflow and sound levels.

A complete report for each of the 12 devices tested was formulated and submitted to the RAC for evaluation and recommendations. These evaluations and the development of a universal air distribution system should assist DOE contractors in the selection of suits for their facilities, reduce the cost of providing this type of respiratory protection, and assure a high level of protection for the user.

3. Respirator Advisory Committee. The RAC met and recommended the following actions (1) acceptance of the Los Alamos and Rocky Flats supplied-air suits, and the Savannah River hood, (2) review of test data for commercially available supplied-air suits, (3) acceptance of a revised charter for the RAC,* and (4) acceptance of a modified supplied-air suit test procedure that details revised test methods for evaluating the air hose, noise levels, escape procedures, contaminated suit removal, and flammability.

4. Medical Criteria. Criteria for determining the physiological stress of pulmonary-impaired subjects were developed by the Texas College of Osteopathic Medicine under a subcontract from Los Alamos. Previous medical considerations offering guidance to physicians in granting medical approval for the use of respiratory protective equipment were not adequately definitive.

Consequently, a study was conducted with the aid of physiologists, to establish more definite criteria for this purpose.

This study recommended that the following three primary factors be determined in classifying a potential respirator user: the individual's previous medical history, the workload ventilation rates of the job to be performed, and the employee's maximum voluntary ventilation (MVV) rate. Using this information the employee classification in terms of respirator usage can be (1) no restrictions on tasks or devices; (2) limited use only, specifying the limitations; or (3) restricted from the use of respiratory protective equipment. These recommendations, currently being reviewed, will provide the information relevant to the physical consequences of respirator usage and the primary basis for selecting/approving personnel to use respirator protective equipment. Because of the complexity of this study and the many ramifications, further studies in this area may be required before the development of final medical acceptance/approval criteria.

Reference

1. W. H. Revoir, J. A. Pritchard, T. O. Davis, C. P. Richards, and L. D. Wheat, "Specifications and Test Procedures for Airline-Type Supplied-Air Suits," Los Alamos Scientific Laboratory report LA-5958-MS (May 1975).

C. Evaluation of New 30 CFR 11 Self-Contained Breathing Apparatus Tests

Participating Staff Members

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Funding Organization

BM

The specified self-contained breathing apparatus tests using human subjects listed in the BM approval regulations, 30 CFR 11, may be inadequate to evaluate breathing apparatuses. Research has suggested that the stress levels listed in the existing approval tests may be significantly lower

*Accepted by DOE/OOS, the major change in the charter allows contractors to submit respiratory protective devices, other than supplied-air suits, for acceptance testing.

than the stresses imposed on mine rescue personnel during actual use. At present all test parameters are measured only during test periods between exercises. The Bureau has proposed a new series of tests that incorporates higher work levels and continuous monitoring of key parameters. Los Alamos is evaluating a variety of different self-contained breathing apparatuses on a number of test subjects using the new higher stress levels.

The seven different breathing apparatuses tested are: a 30-min pressure demand, open-circuit; a 1-h pressure demand, closed-circuit; a 4-h demand, closed-circuit; a 4-h pressure demand, closed-circuit; a 3-h liquid oxygen, demand, closed-circuit; and two 1-h closed-circuit, self-rescuers, one a chemical oxygen type and the other a compressed oxygen type. During each test, a volunteer subject performs various tasks while several continuous measurements determine how well the apparatus functions. In general, the following are measured and recorded: temperatures of the air in the inhalation tube, the air exiting the sorbent canister, and the surface of the canister; pressure in the face mask and in the gas supply cylinder; concentrations of oxygen and CO_2 in the mask and in the inhalation tube; and the volume of excess gas vented from the apparatus.

These test procedures have been approved by the Los Alamos National Laboratory Human Studies Review Committee. Each volunteer is required to successfully complete a maximal stress test conducted by a cardiologist before participating in this program. To date, approximately 30 of approximately 70 evaluation tests have been completed. Whereas no definite conclusions can be drawn from this limited number of tests, the following tentative conclusions are indicated.

1. Measured inhalation air temperatures are higher than 40°C in some tests at high humidities with certain apparatuses. Because air is saturated with water vapor in some mine environments, use of such devices in

very warm environments, such as a mine fire, may cause the body to gain enough heat to be physiologically unsafe.

2. One of the present certification requirements deals with the CO_2 concentration of the air entering the face mask. It appears that an equally or possibly more important factor may be the ratio of the volume of air that enters the mask during inhalation to the volume in the mask itself. At the start of each breath, previously exhaled air, which fills the mask and has a relatively high CO_2 concentration, is inhaled first. If the volume of this air is an appreciable fraction of the air withdrawn from the inhalation tube, the total CO_2 inhaled will be much larger than would be expected from considering only the concentration in the inhalation tube and may present a problem. It may be necessary to modify the certification procedure to take this into account.
3. With pressure demand apparatuses, there is a possibility for loss of breathing gas caused by poor face mask fit. With long-duration apparatus, like that worn by mine rescue personnel, poor fit could cause a dangerous situation. This indicates the need for a device to warn that such a condition exists.

English translations of existing foreign self-contained breathing apparatus approval criteria are also being reviewed. This will permit possible incorporation of appropriate foreign procedures in US regulations.

Potential future work for the Bureau includes physiological determinations of upper limits for temperature and CO_2 concentrations of inhaled air, determination of mask leakage during heavy work, and testing of a metabolic simulator (breathing machine) to replace some of the present man tests.

D. Criteria and Test Methods for Certifying
Air-Purifying Respirators Against Radioiodine

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Funding Organization

NRC, Office of Research

The effectiveness of air-purifying respirator cartridges and canisters for methyl iodide (CH_3I) removal was studied under various conditions of humidity and temperature. The goal of these studies was to provide the NRC with data and recommendations for defining guidelines for approval of air-purifying respirators for airborne radioiodine. Previous work demonstrated the usefulness of CH_3I as the most penetrating form of iodine vapor giving results equivalent to the use of methyl radioiodide. Coincidental with these studies has been test apparatus development and documentation with a view toward establishing a testing and certification program at NIOSH.

Humidity is one of the most significant parameters that affects the efficiency, service life, and wearability of a cartridge for gases or vapors. Effects of humidity on efficiencies of triethylenediamine- (TEDA-) impregnated charcoal cartridges were studied in detail. At equilibrium with the airflow (32 L/min), temperature (27°C), and relative humidity (50-91 per cent), penetration of 0.13 ppm CH_3I challenge vapor was consistent with a simple competitive mechanism where water vapor reacts with TEDA, making it unavailable for CH_3I removal. Humidity effects on service life and t_p , the time required to reach a selected unacceptable penetration, were found to be related by linear log-log plots of t_p versus water vapor pressure (or RH) with slopes between 2 and 3 (Fig. 1). This was true whether the cartridges or canisters contained 5 per cent TEDA charcoal or unimpregnated activated charcoal. For a certification program, these results allow extrapolation of test results to other humidities not as easily accessible experimentally (e.g., 100 per cent RH).

Fig. 1. Effects of water vapor and relative humidity on cartridge and canister service lives for methyl iodide.

Another measured effect of high humidity was the heating of air passing through the sorbent bed from water vapor adsorption. Dew points and temperatures of air entering and leaving test cartridges were measured and correlated to calculate heats of adsorption of 4-9 kcal/mol. Temperature increases up to 10°C at 85 per cent RH were observed at about 5 min from initial exposure (Fig. 2). Measurable heating continued for up to 6 h. This widely neglected effect of humidity is important to the user, because it makes the respirator less comfortable to wear. It also adds a complicating parameter to the modeling of cartridge and canister performance. Excessive temperature increases may limit the conditions under which a unit can be approved for use.

Temperature is another environmental parameter whose significance in determining cartridge efficiencies and service lives has been underestimated. Ambient air temperatures for applications of air-purifying respirators can vary widely from the $25 \pm 2.5^\circ\text{C}$ specified for bench tests of gas and vapor cartridges. The range of test temperature ($\pm 2.5^\circ\text{C}$) allowed indicates little expected temperature effect on cartridge efficiencies and service lives. One calculation, based on temperature dependence of an adsorption isotherm, has estimated a

Fig. 2. Air heating upon passage through a charcoal cartridge at several humidities.

1-10 per cent decrease in service life for every 10°C rise in temperature. However, we found that temperature effects can be more complicated and more significant than this.

One series of experiments used a TEDA-impregnated charcoal cartridge equilibrated at air temperatures of 26 to 38°C and dew points of 15 to 26°C (50-75 per cent RH). Dew point was a more useful parameter than relative humidity, because it, unlike relative humidity, is not a function of air temperature. At constant dew point, i.e., at constant water concentration, equilibrium penetration of CH_3I decreased with increasing ambient temperature. This was due to an enhanced reaction rate of CH_3I with the TEDA impregnant. However, at constant relative humidity, equilibrium penetration actually increased at higher temperatures. This was due to the higher water vapor concentrations for fixed relative humidity at higher temperatures. The greater amount of water vapor bound more TEDA, making it less available for CH_3I removal. An activation energy of 6 kcal/mol was calculated for the chemisorption of CH_3I by TEDA.

Of perhaps more concern are the effects of temperature on cartridges freshly opened and not equilibrated with ambient humidity. Methyl iodide breakthrough curves for several types of cartridges and canisters showed increased penetrations for increased temperatures at all experimental

times. When logarithms of percentage penetrations were plotted against temperature, apparent straight lines resulted (Fig. 3). Whether the cartridges contained 5 per cent TEDA-impregnated charcoal or unimpregnated charcoal, the temperature effects corresponded to approximately doubling the penetration (halving the protection factor) for each 5°C rise in temperature. The empirical relation discovered between temperature and penetration will allow certification testing at selected convenient temperatures and data extrapolations to extremes.

Service life, as well as efficiency, was reduced for higher temperatures and fixed relative humidity. For example, CH_3I service lives (1 per cent penetration) for one TEDA-impregnated charcoal cartridge, freshly opened, at 32 L/min airflow and 50 per cent RH decreased from 180 min at 29°C to 40 min at 38°C. We observed similar large temperature effects for several cartridges and canisters containing variously impregnated and unimpregnated charcoals in differing bed dimensions. The results from all these temperature studies demonstrate that more than one temperature, as well as more than one humidity, must be included in a certification testing program.

On the basis of these and previous experimental studies and discussions with NRC,

Fig. 3. Dependence of CH_3I penetrations of freshly opened canisters on temperature for selected times.

NIOSH, and respirator manufacturers, we have proposed a set of testing conditions:

Test vapor,	CH ₃ I;
Concentration,	1 ppm;
Relative humidities,	50 per cent and 85 per cent;
Temperatures,	25°C and 30°C;
Airflow,	64 L/min (32 L/min for cartridges used in pairs); and
Preparation,	freshly opened.

The criteria for acceptance and certification are still under review.

An apparatus for performing tests of cartridges and canisters at these conditions has been developed and improved. The final version is pictured in Fig. 4. It contains in one unit on wheels: (1) air flow, humidity and temperature control, (2) CH₃I generator, (3) sampling pumps and automatic samplers, (4) dual column gas chromatograph with sampling valves and electron capture detector, and (5) data integrator with chart recorder. It requires (1) compressed air, (2) distilled water, (3) argon/methane carrier gas, and (4) electric power for operation.

Future work for this project includes studies of effects of humidity, airflow rate, and cyclic flow (representative of breathing patterns). Additional documentations and consultations will lead to establishing a certification testing program at the NIOSH Testing and Certification Branch.

E. Testing and Evaluation of Military Respiratory Equipment

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Funding Organization

US Air Force, Life Support Systems Program Office

In the event of an overt action utilizing airborne chemical agents, air crews and ground crews of the United States Air Force (USAF) may be exposed to hazardous atmospheres that can cause a temporary impairment of eyesight or can be toxic

Fig. 4. Photograph of the apparatus developed for testing radioiodine cartridges and canisters.

to the respiratory system. Several systems, which must be compatible with aircraft and provide high levels of protection, are presently undergoing various tests and investigation by the USAF, which asks that we perform respirator fit tests to define the protection provided to wearers of various types of respiratory protective equipment. This requires each unit to be tested against an anthropometrically selected panel representing the various facial dimensions of potential users of this equipment. Studies quantitatively evaluate protection provided in the areas of the eyes, forehead, and neck of individuals wearing the devices.

To quantitatively and realistically determine the protection afforded by each device, the test program was designed to:

- (1) obtain data in a nontoxic atmosphere simulating that which may be expected in an overt action;
- (2) obtain data quantitatively defining protection afforded to the eyes, respiratory zone, and neck or shoulder areas;
- (3) provide data while the test subject is performing specific movements similar to those that a pilot, crew member, or others may perform in carrying out their required duties; and
- (4) include experimental procedures sufficiently sensitive to permit quantitative evaluation of protection factors up to 100 000.

During late FY 1981, details of the experimental program were developed in cooperation with the USAF. Initial activities have included an extensive series of anthropometric facial measurements to supplement the conventional use of face width and face length to distinguish among small, medium, and large faces. Because these devices must provide high protection factors (up to 100 000 for positive-pressure devices), the single-particle counter laser-aerosol spectrometer (LAS-X) has been adapted for application to the test program using diethylhexyl sebacate (DEHS) as the test aerosol. A test panel and fit test exercises have been identified, and preliminary testing has been initiated.

The USAF must make a major respirator procurement decision during early calendar year 1982, requiring completion of Phase I of the project by December 1981. During the latter part of FY 1982, additional devices will be evaluated to provide guidance to the USAF regarding the performance levels and adequacy of existing protective equipment.

IV. APPLIED AEROSOL STUDIES

A. Aerosol Support for the Filter Test Stations

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Funding Organization

DOE, Airborne Waste Management Program Office

High-efficiency particulate air (HEPA) filters are routinely quality assurance (QA) tested at DOE Filter Test Stations (FTSs) prior to installation.¹ This QA test includes evaluation of filtration efficiency against a 0.3- μ m monodisperse aerosol to assure that the minimum filtration efficiency criterion of 99.97 per cent is satisfied. In the past, this test used diethyl hexyl phthalate (DEHP) aerosol, instrumentation (OWL) measuring depolarization angle to determine particle size, and a light scatter photometer to determine aerosol concentration upstream and downstream from the filter to permit calculation of efficiency. The assumption was made that the 0.3- μ m monodisperse aerosol represented the most difficult size to filter, resulting in a conservative QA test. Recent designation of DEHP as a potential carcinogen resulted in the need to consider alternative test aerosols. At the same time it was considered desirable to evaluate the potential advantages of using simpler aerosol generation techniques and more modern instrumentation to measure aerosol size and determine filtration efficiency.

This study could develop an aerosol test system that avoids problems associated with using an aerosol material (DEHP) that has been determined

to be a potential carcinogen and provides a more meaningful HEPA filter QA test. During FY 1981, the program focused on assisting the FTS in evaluating the effectiveness of the OWL for monitoring aerosol size and developing a data base that might permit using a single-particle aerosol spectrometer to reliably monitor particle size.

Aerosol size may be characterized by the median diameter (d) and geometric standard deviation (σ_g) if the aerosol has a log normal size distribution. One way to determine these size distribution parameters is to use a single-particle aerosol spectrometer to measure the light scattered by individual particles as they pass through a laser beam and use these data to generate a frequency histogram.

The single-particle aerosol spectrometer used was the LAS-X manufactured by Particle Measuring Systems, Inc., Boulder, Colorado. By incorporating an aerodynamically focused aerosol flow, a helium neon laser beam as a probe, and a parabolic mirror, the LAS-X collects the light scattered from single particles over a polar angular range from 35 to 120 degrees. Detection of the scattered light intensity is used to determine particle size from 0.1- to 3.0- μm diam. These data are in turn used to generate histograms defining the aerosol size distribution. Because the LAS-X is unable to handle the high concentrations present in the FTS test systems, a 1000:1 aerosol diluter was constructed for use with the LAS-X at each FTS. With the diluter, the LAS-X can sample the DEHP aerosol size distributions at the 100- $\mu\text{g/L}$ concentrations used in the FTS test systems. Use of the LAS-X would be a major change for the FTS. However, this type of instrumentation is already being used by some filter manufacturers.

Several potential limitations of the LAS-X were evaluated. These include whether the detector response is sufficiently monotonic that calibrations with polystyrene latex microspheres can be extrapolated reliably to the QA test aerosols, which have different refractive indices, whether the channel-to-channel differential nonlinearity is sufficiently small for our purposes, whether the size distributions obtained by the LAS-X are insensitive to aerosol concentration (count rate),

and whether the LAS-X reliably monitors aerosol size during QA filter testing and permits the operator to reliably control size of the test aerosol.

Figure 1 shows the theoretical LAS-X scattered light detector response as a function of spherical particle diameter for three different particle indices of refraction corresponding to polystyrene latex microspheres ($n = 1.5905$), DEHP ($n = 1.485$), and DEHS ($n = 1.4496$), which is being used as a replacement for DEHP at one FTS. Different scattering intensities are produced by particles of the same size having different refractive indices. Because the instrument is calibrated in terms of particle size using polystyrene latex microspheres, an algorithm based on Fig. 1 can be used to permit direct indication of the diameters of the test aerosols for the aerosol size of concern (median diameter 0.2-0.3 μm ; $\sigma_g < 1.2$).

To accommodate the nonlinear scatter detector response function in Fig. 1, the signal voltage increment for each size interval can be set at a different value. The question of system response as a function of particle concentration will be addressed during FY 1982 by collecting data over a wide range of concentrations.

Test aerosol size distribution data were obtained at each FTS during routine QA testing of 1000 and 575 cubic feet per minute (CFM) HEPA filters. Calibrated aerosol diluters and LAS-X instruments were installed at each FTS. In each case, the aerosol generation system (Q107) was adjusted by the operator to deliver smoke of 0.3- μm geometric mean diameter according to the mechanical analyzer (OWL). Figures 2, 3, and 4 show the aerosol size parameters as measured over several days at the three FTSs. These data indicate that the QA aerosol mean diameter is smaller than 0.3 μm , with a σ_g well in excess of the requirements for a monodisperse aerosol.

The LAS-X can give the operator useful real-time information for measuring and controlling the mean diameter and standard deviation of the smoke used in filter testing to permit a better match of existing criteria for QA testing.

In Phase II of this project, a microprocessor will be interfaced to the LAS-X so that the instrument operator can obtain a nearly continuous

Fig. 1. LAS-X response as a function of particle diameter for three different indices of refraction.

display of median diameter and standard deviation during startup of the Q107 and during actual filter testing. The operator will then be able to control the aerosol size distribution precisely so that every FTS can operate with an aerosol having the same mean diameter and standard deviation. Phase II will also evaluate use of the LAS-X to measure the downstream-size distribution and measure filter efficiency as a function of particle size for each filter tested.

B. Health Related Aerosol Studies--Particle Resuspension

Participating Staff Members

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Technical Assistance

L. D. Wheat

Funding Organization

DOE/CHER

An automatic readout cascade impactor was purchased for size measurement of airborne particles in wind tunnel studies of particle resuspension. The impactor (California Measurements, CMCI) was evaluated and calibrated during 1981. This 10-stage impactor classifies and collects particles by inertial impaction onto grease-coated collection surfaces. Unlike other impactors, the 10-stage has the collection surfaces that are

Fig. 2. Size distribution of DEHS aerosol used at Hanford FTS.

Fig. 3. Size distribution of DEHP aerosol used at Rocky Flats FTS.

Fig. 4. Size distribution of DEHP aerosol used at Oak Ridge FTS.

vibrating quartz crystals. Deposited particles produce a change in the frequency of vibration of the crystals proportional to the mass of the deposited particles. A microprocessor then calculates the size distribution with respect to mass in near real time. The mass sensitivity of each quartz crystal (~ 800 Hz/ μ g) provides measurement of as little as 10^{-8} g per impactor stage. Thus, with a sampling rate of 240 cc/min, the impactor can adequately sample an aerosol of 1 μ g/L concentration in about 30 s. Another 30 s are required for the sample to pass entirely through the CMCI stack, after which the distribution data and a size histogram are printed.

The effective cutoff aerodynamic diameters (ECADs) (for which the collection efficiency is 50 per cent) of the 10 stages were determined experimentally. The impactor was challenged by aerosols of known size during short sampling periods. The mass on each stage (obtained from the printout) was converted to a percentage of the total mass collected to determine the collection efficiency of each stage as a function of particle size (Fig. 5). A log normal distribution curve was then calculated from each set of collection efficiency data. The ECAD of each stage is the median particle size of this log normal distribution.

The CMCI calibration was determined with relatively monodisperse ($\sigma_g < 1.3$), challenge aerosols of polystyrene latex (PSL), Eosin-Y fluorescent dye (E-Y), and pollens of ragweed and mulberry. The pollens and PSL were nebulized from

water suspensions, whereas the E-Y was generated from the a Berglund-Liu vibrating orifice generator. The pollens were used to calibrate the upper stages ($D_{ae} > 10\text{-}\mu$ m); the other aerosols, the lower stages. Nucleopore filter samples were taken for size analysis, and a laser particle spectrometer (PMS LAS-X) was used to indicate monodispersity or satellite presence for aerosols $< 3\text{ }\mu$ m. Size distributions were determined by light microscope for the pollens and by scanning electron microscopy (SEM) photomicrographic techniques for the PSL and E-Y particles.

The calibration results are shown in Table I where the experimental ECADs are listed, compared with theoretical ECADs,² and the percentage difference noted. The large difference between theoretical and experimental ECADs for the first two impactor stages may be due to scatter of large particles on the collection crystal. That is, particles collected outside the sensitive (electrically conductive) area of the crystals may not be detected. Microscopic examination of deposits on crystals from stages 1 and 2 revealed that, in fact, particles were deposited or rolled after deposition to positions outside the crystals' sensitive areas.

A particle-loss analysis indicated that losses for particles $< 0.4\text{-}\mu$ m and $> 3\text{-}\mu$ m D_{ae} were severe. Wall deposition losses were approximately 50 per cent for particles in the size range 10- to 20- μ m D_{ae} and approximately 30 per cent for particles $< 0.3\text{-}\mu$ m D_{ae} . These losses, as determined, were cumulative for the entire impactor

Fig. 5. Calibration data showing impactor collection efficiency as a function of aerosol aerodynamic size.

TABLE I
CMCI STAGE ECADs

Stage	Theoretical (μm)	Experimental (μm)	Difference (%)
1	24.0	14.7	-39
2	9.4	12.2	30
3	9.2	7.7	-16
4	4.6	3.8	-17
5	2.3	1.7	-26
6	1.3	1.2	- 8
7	0.58	0.64	10
8	0.37	0.34	- 8
9	0.21	0.26	24
10	0.13	0.14	8

rather than for any particular stage. However, microscopic examination indicated that most of the large particle losses were in the impactor inlet and above stage 3. No particle bounce and reentrainment were observed microscopically, which suggests the losses were due to sedimentation and impaction of large particles and diffusion of small particles. Very low flow velocities caused by the large interstage volume in the impactor could have produced the observed wall losses.

The resuspension project, of which this study was a part, will not be funded in FY 1982.

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C. A Virtual Impactor for In-Stack Particle-Size Measurement

Participating Staff Member

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Funding Organization

EPA

The collection of representative samples from exhaust stacks is complicated by the variety of conditions that may be encountered. A wide

range of gas velocities, temperatures, and mass loadings may be encountered depending on the process being exhausted and the location of the sampler. Characterization of the exhaust requires different types of samples and instruments depending on the parameter of interest. The aerodynamic size of the particulate material in the exhaust is a parameter of interest. The distribution of aerodynamic diameters is important information in the prediction of suspension times, transport, inhalation potential, and deposition on surfaces and in the respiratory tract.

Aerodynamic diameter is frequently measured by projecting the particle at a collection surface at a high velocity in the presence of an airflow normal to the collection surface. Particles having sufficient momentum to penetrate the normal flow will impact on the collection surface. The remaining particles are entrained in the normal flow and are swept away. Subsequent impactor stages operate at higher velocities to collect the smaller particles.

A disadvantage of impactor collection is the limited mass of material that can be collected on the impaction surface before the collection characteristics change or material breaks loose and is swept to lower stages. This disadvantage may be circumvented by use of a virtual impaction surface. The virtual impaction surface normally consists of a volume of still air or air that is moving at a much lower velocity than the particle acceleration jet air. The particles that project into the volume are normally swept away by a low flow rate for collection on a filter. Use of a virtual impactor permits collecting a large mass of each size fraction.

A two-stage virtual impactor has been designed to collect samples in exhaust stacks. The impactor incorporates a variable area inlet to provide near isokinetic sampling over a range of stack velocities. A cross-sectional view of the impactor is shown in Fig. 6. The variable area is achieved by a central flow divider. Dividers of different lengths are used to change the cross-sectional area of the inlet. Three inlets are shown in Fig. 6. The inlet shown with the cross-sectional view of the impactor provides the maximum inlet area, thus, the lowest inlet velocity for a fixed flow rate.

Fig. 6. Two-stage virtual impactor.

Individual flow dividers that provide the minimum inlet area and an intermediate inlet area are also shown.

The impactor is designed to operate at an inlet flow rate of 50 L/min. The dust-laden air enters the impactor through the annulus around the flow divider. Most of the airflow is diverted toward the centrally located second-stage jet. Approximately 10 per cent of the initial airflow is diverted through the large particle filter. The diverted airflow will be enriched in large particles. This enrichment results from the momentum of the large particle carrying these particles out of the main flow as the flow diverts toward the second-stage jet. Behind the second-stage jet, the majority of the air flows through the small-particle filters. Approximately 10 per cent of the second-stage flow is drawn through the intermediate-particle filter. The sample is thus divided into three fractions according to particle size.

The sharpness of the separation (particle sizes or overlaps in each fraction) is dependent on the collection efficiency curve for each stage. The design of the impactor is based on a model of virtual impactor performance developed by Marple and Chien.¹ The model is developed for flow diverging from a round jet with the collection stage directly below the jet (similar to stage two). The flow through the first stage of

this impactor is in the opposite direction (converging after leaving the accelerating jet). Several assumptions were made in determining the correct dimensions for stage one. The validity of these assumptions to provide a 50 per cent collection efficiency for particles with aerodynamic diameters of 15 μm needs to be checked by calibration.

Two impactors have been constructed for initial evaluation. One impactor employs external filters and easily removable jets that can be modified or changed. The second impactor uses internal sieve filters made by cutting the end from standard thimble filters. Evaluation of these impactors and development of a final design were planned for FY 82. However, current budget allocations will not permit this work to be performed.

Reference

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V. PERSONAL PROTECTIVE CLOTHING

A. Quantitative Evaluation of Personal Protective Equipment

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Technical Assistance

M. J. McLeod and A. M. Martinez

Funding Organization

NIOSH

Workers in the chemical, rubber, and other industrial environments, and individuals responsible for hazardous waste sites and chemical spills may be exposed to hazardous chemicals either by inhalation and/or dermal contact. Protective equipment must be provided to minimize such exposures. Available information concerning the ability of garment materials to protect against skin exposure to liquid contaminants is scarce, and most of what is available is of a qualitative nature. To permit the industrial hygienist to select the proper protective equipment, there is a

need to obtain quantitative data on protective clothing permeation rates. There is also a need for predicting the suitability of a given protective garment material for various chemicals of concern.

The permeation of at least 10 different materials by 8 different chemicals is being determined. This includes many of the more common materials (surgical, nitrile, neoprene, and butyl rubber, polyvinyl alcohol and polyethylene); some less common materials (Viton and Teflon); and two composite materials (polyethylene-coated Tyvek and Saranex-coated Tyvek). The challenge chemicals include a polychlorinated biphenyl (PCB), trichlorobenzene (TCB), a mixture of this PCB with TCB, a mixture of PCB with paraffin oil, two chlorinated ethenes, ethylene dibromide, and epichlorohydrin.

The permeation tests are conducted by clamping a sample of the garment materials in the center of a permeation cell. The challenge chemical is added to one-half of the cell and water is placed in the other half. If the challenge chemicals are insoluble in water, a layer of liquid, which is insoluble in water but in which the challenge compound is soluble, is floated on top of the water. Periodically during the permeation test, an aliquot of the water, or the layer on top of the water, is taken and analyzed for the challenge substance. These analyses are carried out by spectrophotometer or by gas chromatography.

Besides these permeation tests, each of the materials is soaked in each of the challenge substances to determine any weight or volume changes that may occur from absorption. The results of these tests are correlated with the permeation data. Previous work has shown a moderately good correlation, such that the penetration of a given substance tends to be more rapid for those materials that show the largest weight and volume increase. This correlation is not adequate to predict exactly when the challenge substance will first penetrate the material. However, with the exception of polyvinyl alcohol (PVA) and polyethylene, it does indicate those materials that offer little chance of providing protection. As a rule of thumb, those materials that show a 100 per cent or greater weight or volume increase should

not be used with the chemical producing that change. (PVA may not fit this correlation because it is degraded in the presence of water.)

This interagency agreement was initiated late in FY 1981 and limited data are available. To date, we have determined the weight and volume changes of 10 to 13 materials with TCB, paraffin oil, and trichloroethylene. Permeation tests with TCB have been completed, and we are presently measuring the permeation of a mixture of 42 per cent TCB and 58 per cent PCB through 12 different protective garment materials. In light of the preliminary status of data collection, no conclusions are available.

B. Guidelines for Selecting Personal Protective Clothing

Participating Staff Members

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Funding Organization

EPA

Knowledge concerning the protection afforded by Personal Protective Clothing (PPC) is quite limited relative to the highly complex and variable mixtures of toxic chemicals that workers encounter at hazardous waste sites and environmental spills. Furthermore, there does not exist a unified and comprehensive set of guidelines for workers to use in choosing appropriate PPC.

Recognizing the need for the EPA personnel and associated workers to be protected when working at hazardous waste sites, EPA has requested Los Alamos to provide such guidelines for actual field use. A user's matrix will be developed to assist in the choice of appropriate PPC for field wear. The following specific tasks will be accomplished to develop this matrix.

- (1) Categorize personal protective clothing into general groups, such as gloves, aprons, and other particular garments. The guidelines will identify and discuss (a) commercially available clothing, (b) the more exotic clothing currently being used and developed by the military where this information is not

classified, and (c) to a limited extent, that information concerning foreign manufacturers with commercially available PPC.

- (2) Review available information dealing with the validity, constraints, and background upon which the ratings tables of vendors' literature and technical publications are based.
- (3) Discuss the existing bases of the vendors' evaluations and information; determine how they might be used in future PPC evaluations.
- (4) Review the phenomenological aspects of how solubility relates to chemical permeation and breakthrough of liquid, vapor, and particulate phase chemicals and how material thickness affects permeation.
- (5) Detail the limitations of various types of PPC and how pinholes, seams, imperfectly sealed seams, and/or other material flaws will affect the predicted performance of PPC.
- (6) Discuss training and orientation requirements for users.
- (7) Develop evaluation criteria concerning the protocol(s) by which experimental data may be obtained for chemical permeation through PPC materials.

A subcontract for this work should be awarded and the project initiated during the first half of FY 82.

VI. AEROSOL SUPPORT FOR INHALATION TOXICOLOGY STUDIES

A. Manmade Mineral Fiber Inhalation Toxicology Study

Participating Staff Members

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Technical Assistance

B. Isom and J. Martinez

Funding Organization

TIMA

A study is being conducted to assess the potential long-term effects in laboratory animals by inhaled manmade mineral fibers (MMMFs). Female Osborne-Mendel rats and male Syrian golden hamsters are being exposed in a "nose only" confinement mode to aerosols produced from various commercially available MMMFs.* Fibrous materials being tested include three different types of fibrous glass, one mineral wool, and one ceramic fiber. Crocidolite asbestos has been included as a positive control aerosol material. All test aerosols are being produced using a Los Alamos modified Timbrell type fibrous aerosol generator,¹ which relies on the controlled feeding of a fibrous plug compact into a rotating blade assembly for aerosol production. Fibers are shaved from the end of an advancing plug and a moving air stream exhausts the shaved fibers from the generator to the exposure chamber. Eleven exposure chambers, each of which can accommodate 64 rats or 90 hamsters are currently being operated 5 h/day, 5 days/wk. Aerosol exposure concentrations are measured by daily gravimetric sampling procedures, and airborne fiber sizing is accomplished on a regular basis using scanning electron microscopy (SEM). These data serve to monitor and characterize the exposure aerosols.

Groups of 64 rats and 80 hamsters are currently being chronically exposed to (1) 0.45- μ m mean diam glass fiber, high- and low-concentration levels; (2) fibrous glass, "Blowing Wool," with a 3.1- μ m mean diam; (3) fibrous glass (binder-coated building insulation), with a 6.1- μ m mean diam; (4) crocidolite asbestos, positive controls; and (5) a sham control group. All exposures are longevity studies, designed for 24 months active exposure. During FY 1982, three more animal groups

*"Nose only" refers to the fact that only the animals' noses protrude through the anterior end of animal-holding tubes into the aerosol exposure chamber.

will be exposed to aerosols produced from a flame-attenuated fibrous glass, a mineral wool, and a ceramic fiber.

Aerosol characteristics for each exposure material are listed in Table I. High-level 0.45- μm mean diam glass fiber exposures are being maintained at mass concentrations of $3.0 \pm 0.6 \text{ mg/m}^3$ and low-level chambers at $0.3 \pm 0.1 \text{ mg/m}^3$. These mass concentration levels correspond to ~2500 and ~250 fibers/cc for the high- and low-level exposures, respectively. High-level microfiber exposures will conclude December 1981. Low-level exposures will cease February 1982. Glass fiber "Blowing Wool" chambers are being maintained at ~10 mg/m^3 or ~100 fibers/cc. Chamber concentrations of binder-coated building insulation fiber are maintained at ~9 mg/m^3 (~25 fibers/cc). This is a large diameter (6.1- μm mean diam) material coated with a phenol-formaldehyde binder that is available as a commercial home insulation material. Crocidolite exposures continue at ~7 mg/m^3 (~3000 fibers/cc). Asbestos exposures, under way for 12 months, will continue for another calendar year. The sham control group is handled like the experimental group but is exposed only to clean air. Aerosol samplings from 50 different

ports indicate that the aerosol mass distribution within these exposure chambers is within ± 10 of the mean over a 10 h exposure. MMADs range from 2.0 μm for the glass microfiber aerosol to 4.5 μm for the fibrous glass "Blowing Wool" fibers, with σ_g 's ranging from 2.1 to 2.5. These aerodynamic size parameters (MMAD, σ_g) are determined by cascade impactor sampling and define the "respirable" fraction of each dust when related to the ACGIH standards.^{2,3}

A prime objective of this study is to expose animals to high airborne concentrations of long thin fibers ($\leq 3\text{-}\mu\text{m}$ diam; $> 10 \mu\text{m}$ in length). Special interest in these fiber sizes relates to observed biological effects produced by intra-pleural implantation of this category of fibers in experimental animals. Fiber-sizing data for the current exposure aerosols are summarized in Table II. These data indicate that both the glass microfiber and glass "Blowing Wool" aerosols meet this objective and would constitute a respirable aerosol. The glass microfiber aerosol has ~15 per cent of all airborne fibers in the desired long-thin category. This corresponds to ~375 fibers/cc at total aerosol concentration levels of 2500 fibers/cc. The glass "Blowing Wool" aerosol has >90 per cent of all airborne fibers $> 10 \mu\text{m}$ long

TABLE I
FIBROUS AEROSOL CHARACTERISTICS

Material	Mass Conc (mg/m^3)	Fiber No Conc (f/cc)	Fiber Diam Range (μm)	Mean Fiber Diam (μm)	Impactor Characterization		"Respirable" ^a Fraction ACGIH Criteria (%)
					MMAD (μm)	Geometric Std Dev (σ_g)	
Glass Microfiber (High)	~3.0	~2500	0.05 - 2.5	0.45	2.0 ± 0.2	2.1 ± 0.1	~70
Glass Microfiber (Low)	~0.3	~250	0.05 - 2.5	0.45	2.0 ± 0.2	2.1 ± 0.1	~70
Glass Fiber "Blowing Wool"	~10	~100	0.3 - 10	3.1	4.5 ± 0.7	2.5 ± 0.4	~38
Binder Coated ^b Bldg. Insulation	~9	~25	0.3 - 12	6.1	---	---	---
Crocidolite	~7	~3000	---	---	2.5 ± 0.2	1.9 ± 0.1	~65

^aCalculated based on Ref. 3.

^bAerodynamic characterizations tests not complete.

TABLE II
FIBER-SIZING DATA

Material	Fiber Length Distribution (Per Cent by Count, μm)				Mean Fiber Diameter (μ)
	>5	6-10	10-20	>20	
Glass Microfiber	-55	-30	-10	-5	0.45 - 0.2
Glass Fiber "Blowing Wool"	<1	-8	-26	-62	3.10 $\pm$ 2.6
Binder-Coated Fibrous Glass	--	--	-13	-87	6.10 $\pm$ 2.6
Crocidolite	-97	-2	-1	--	---

with a significant proportion of these fibers in the $\leq 3\text{-}\mu\text{m}$ diam range. The binder-coated fibrous glass aerosol has an abundance of long fibers, but most fibers are $>3\text{-}\mu\text{m}$ physical diam resulting in an aerosol that would not be considered "respirable." The crocidolite aerosol--considered short fibered by similar standard (i.e. $<5\text{ }\mu\text{m}$ long)--was selected for a positive control aerosol material because of its known ability to provoke biological response in experimental animals.

All inhalation experiments are longevity studies, designed to continue until each animal group has completed 24 months of active exposure to each fibrous aerosol material. Details of the toxicological results will be included in the annual report of the Los Alamos Life Sciences Division.

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B. Health-Related Aerosol Studies--Oil Shale and Toxicology

Participating Staff Members

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Technical Assistance

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Funding Organization

DOE/OHER

In conjunction with the previously detailed oil shale industrial hygiene field studies, the Los Alamos Industrial Hygiene Group provides support for aerosol generation and characterization and the development of a laboratory-scale retort for animal inhalation studies.

1. Aerosol Support. Using the vast American oil shale resource requires determination of possible health effects associated with inhalation of consequent airborne materials. Inhalation toxicology studies require (1) characterization of airborne process materials at operating oil shale facilities (discussed in Sec. II) and (2) small-animal inhalation exposures to representative airborne materials. Such exposures (Fig. 1) are being carried out in the "nose only" mode on a 6-h/day, 4-day/wk schedule. "Nose only" refers to animals' noses protruding through the anterior end of animal-holding tubes into the aerosol exposure chamber. Current or recently suspended studies

Fig. 1. Animal-holding tubes in an exposure chamber with animals' noses protruding.

include 7 groups initially composed of 62 animals each. All animals in a group are exposed simultaneously in one chamber (Fig. 2). The exposure aerosols are shown in Table III. The six oil shale inhalation exposure groups and the types of study involved are (1) Paraho spent shale longevity study, (2) Paraho raw shale longevity study, (3) Paraho raw shale, serial sacrifice study, (4) Paraho raw shale low-level longevity study, (5) Paraho raw shale intermediate-level longevity study, and (6) Estonian raw shale longevity study. The Estonian raw shale was obtained by a mutual study agreement with Russia. In addition, a positive control group has been exposed to a pure α -quartz aerosol dispersed by nebulizer from a water suspension. The other aerosols are dispersed with the Wright Dust Feed.¹ Two control groups are used: (1) a sham control group, which is handled like the experimental group relative to chamber time, but breathes only clean air and (2) a colony control group, which is not placed in exposure chambers, but lives under the same cage and feeding conditions as the experimental group.

Two groups of animals recently completed 2 years before exposures were suspended. The surviving members of each group will be allowed to live out their lives. Exposures of the Paraho spent shale group and Paraho raw shale longevity

Fig. 2. Oil shale aerosol exposure chamber.

group were suspended after 24 months. Exposures of a third group, the Paraho raw shale serial sacrifice group, were terminated after 22 months. The quartz silica group exposures were terminated after 19 months because of poor health of the animals. Health effects and pathology will be detailed in the Life Sciences Division Annual Report.

Oil shale aerosols for these studies are prepared by crushing and ball milling the bulk materials. Fines which pass a 270-mesh (53- μ m) screen are then packed under pressure into a plug for dispersal by the Wright Dust Feed. The material is scraped from the surface of the plug with a carbide-tipped blade and entrained in the airstream for passage through a ⁸⁵Kr deionizer for particle charge neutralization before entering the exposure chamber.

Concentration measurements are made daily by gravimetric analysis of material collected on Gelman DM800 filters. Particle-size characteristics are determined biweekly by an Andersen cascade impactor.

TABLE III
AEROSOLS FOR OIL SHALE INHALATION TOXICOLOGY STUDIES

Material	Aerosol Concentration (mg/m ³)	MMAD (μm) ^a	Particle Size ^b σ _g	Respirable ^c Fraction
Paraho spent shale	178 ± 49 ^d	2.6 ± 0.3	2.0 ± 0.1	0.60 ± 0.05
Paraho raw shale	170 ± 21	2.7 ± 0.2	1.9 ± 0.1	0.57 ± 0.04
Paraho raw shale, s.s. ^e	168 ± 26	2.6 ± 0.2	2.0 ± 0.1	0.58 ± 0.04
Paraho raw shale	4.0 ± 1.3	2.4 ± 0.1	2.0 ± 0.1	0.76 ± 0.07
Paraho raw shale	27 ± 5.0	2.5 ± 0.2	2.0 ± 0.1	0.61 ± 0.05
Estonian raw shale	64 ± 12	2.6 ± 0.2	2.2 ± 0.1	0.58 ± 0.04
Silica	14 ± 3.2	2.3 ± 0.3	1.6 ± 0.2	0.80 ± 0.09

^aMass median aerodynamic diameter.

^bGeometric standard deviation.

^cRespirable fraction according to the deposition curve of the ACGIH.

^dThe range shown is 1 std dev.

^eSerial sacrifice.

Mass concentrations and particle-size distributions for the various aerosols are detailed in Table III. The aerosol of Paraho spent shale had a MMAD of 2.6 μm and a mean concentration of 178 mg/m³. Paraho raw shale aerosol averaged 2.6-μm MMAD with mass concentrations (for the initial raw shale longevity and serial sacrifice groups) of ~170 mg/m³. The low- and intermediate-concentration raw shale groups averaged 4.0 and 27 mg/m³, respectively. Estonian raw shale aerosols had a 2.6-μm MMAD and a concentration of 64 mg/m³, whereas the silica aerosols averaged a 2.3-μm MMAD and 14-mg/m³ concentration. Respirable percentages, based on the deposition curve of the ACGIH,³ ranged from 57 to 76 per cent for the shales and to 80 per cent for the silica. The low-level, intermediate-level, and Estonian shale exposures are continuing with preparations under way to add some low- and intermediate-level spent shale groups to the study.

2. A Laboratory-Scale Retort. To more nearly simulate mixed aerosols, such as may be encountered in an oil shale processing facility, a small, laboratory-size retort has been installed and is being tested. Effluents from the oil shale extraction process will be administered by nose only exposure to small animals at various dose levels. Long-range plans include injection of oil shale dusts as condensation nuclei into the retort effluent stream for additional inhalation exposure studies. Details on retort design, modifications,

and preliminary testing follow. Details of this program are discussed below.

The complex mixture of organic and inorganic compounds produced during the retorting of oil shale makes it difficult to completely characterize potential inhalation exposures. A sampling method coupled with an analytical procedure that eliminates the possibility of chemical reactions between the compounds collected before analysis is not available. In addition, the toxicology associated with inhalation of complex mixtures of organics is largely unknown, making it impossible to select the significant mixtures for toxicology studies. Many of the problems associated with the design of toxicology studies based on characterization of potential exposures and generation of realistic exposure atmospheres can be avoided by exposing animals to the effluent from an oil shale retort. A laboratory retort will permit operation over a wide range of conditions. The exact operating conditions of commercial-scale retorts cannot be achieved in laboratory-scale systems, and no attempt will be made to match any process currently in use or being considered for commercial use.

A laboratory-scale retort designed and built at the LETC was loaned to Los Alamos for use in the oil shale toxicology studies. The original retort was modified into two shorter retorts (each 150 cm long). A schematic of one retort is shown in Fig. 3. The retort is constructed from

stainless steel pipe with an outside diameter of 8.9 cm and an inside diameter of 7.6 cm. Eight independently controlled electrical resistance heaters surround the retort. Each heater is 15 cm high and is covered with an insulator. Temperatures in the retort are monitored by means of a thermocouple well consisting of a stainless steel pipe of 1.6-cm diam, located in the center of the retort. There are 16 thermocouples located in the central well (2 per heating zone).

Eight thermocouples are located on the outer wall of the retort (one per heating zone). Gas flow through the retort is from top to bottom with provisions for using nitrogen, compressed air, or any combination of these two gases. The annulus between the thermocouple well and the retort wall is filled with shale crushed and sieved to pass a 1.3-cm (1/2-in.) screen and not pass a 0.6-cm (1/4 in.) screen.

The retort can be operated in the indirect-heated mode by heating with the electric heaters while passing nitrogen gas through the crushed shale. The retort can also be operated in the direct-heated mode by igniting the shale with air passing through the crushed shale. Ignition is accomplished by adding burning charcoal or by electrical heating with a high air flow (~6 L/min). Retort temperatures have been ~550°C in the combustion zone. Normal gas flow through the retort is 3 to 3.5 L/min in the direct-heating mode. When retorting in the direct-heated mode, the electrical heaters are used to heat the walls of the retort to approximately the center line temperature. This reduces heat loss through the walls of the retort. The progress of the retort can be followed by monitoring the center line temperature. In addition to center line temperature, gas temperature is monitored in the liquid trap; inlet gas flow rate is monitored; and the exhaust gases are continuously analyzed for CO and H₂S. Periodic grab samples are collected to determine the concentration of specific compounds and total organic carbon (TOC).

To provide sufficient airflow for inhalation chamber operation, the effluent is diluted with filtered room air. Concentration measurements for all compounds are taken at the exit of the dilution chamber. A summary of the concentrations

Fig. 3. Schematic of laboratory-scale oil shale retort.

observed during indirect- and direct-heated runs is given in Table IV. Continuous concentration measurements for CO and H₂S were made with an Ecolyzer using electrochemical detectors. The TOC concentration was measured with an organic vapor analyzer (OVA) using a hydrogen flame ionization detector. The organic vapor analyzer was calibrated with known concentrations of methane. Grab samples were collected in evacuated bottles and analyzed by gas chromatography/mass spectrometry or gas chromatography with a flame ionization detector. The concentrations of CO and TOC measured in the grab samples were somewhat higher than the concentrations measured by the Ecolyzer and the OVA. Compounds identified in the grab samples and the range of concentrations observed in ppm are shown in Table V. The characterization of the retort effluent is continuing to determine what compounds are present and what compounds can be monitored to provide an indication of retort performance.

Inhalation exposures of small animals to retort effluents will begin during the first quarter of calendar year 1982.

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TABLE IV

RETORT OPERATING CONDITIONS WITH CORRESPONDING GAS AND VAPOR CONCENTRATION

Retort Heat Method	Inlet Gas		Average Temperature		Effluent Material Concentrations		
	Flow Rate		Center Line (°C)	Liquid Trap (°C)	CO (ppm) ^a	H ₂ S (ppm) ^a	TOC ^b (ppm) ^a
	Type	(L/min)					
Indirect	N ₂	2.0	~540	~24	200-2500 ^c 2250 ^e	85 ^c 53 ^e	600-1500 ^d 2600 ^e
Direct	Air	3.0-4.0	~500	~25	750-2500 ^c 5537 ^e	22 ^c 45 ^e	140-950 ^d 500 ^e

^aparts per million.^bTotal organic carbon.^cConcentration measured with ecolozer.^dConcentration measured with organic vapor analyzer (OVA) calibrated with methane.^eGas bottle samples measured with gas chromatography/mass spectrometer.

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VII. ANALYTICAL CHEMISTRY DEVELOPMENT

A. Development of Analytical Methods for Pentachlorophenol and Its Possible Combustion Products

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Analytical methods for PCP were developed in support of research on the combustion of PCP-treated wood. Two types of samples were submitted for analysis: chips of the original wood and toluene/isooctane solvents from impingers used to collect vapors from offgases of the combustion processes. PCP was extracted from the wood chips by 24-h refluxing in toluene in a Soxhlet extractor. Impinger solvents were filtered to remove carbon particles. Aliquots of impinger samples were concentrated by a factor of 50 by evaporating to dryness at 40°C under vacuum and reconstituting to

TABLE V

COMPOUNDS OBSERVED IN GRAB SAMPLES FROM LABORATORY-SCALE RETORT OFFGASES

Compound	Concentration (ppm)
Carbon Dioxide	1700-6000
Carbonyl Sulfide	20-220
Sulfur Dioxide	40-125
Nitrogen Oxides	20-100
Ammonia	80-350
Methane	50-1500
Ethene	8-100
Propane	5-190
Propene	5-100
Butanes	5-230
Pentanes	5-25
Benzene	<1
Toluene	<1
Xylenes	<1
Phenols	<1
Cresols	<1
Napthalene	<1
Resorcinol	<1
Thiophene	<1

500 μ L with isooctane/toluene containing 1-fluoro-2,4-dinitrobenzene as an internal standard. Triplicate spiked samples containing 1 ppm PCP were concentrated simultaneously with recoveries of 70 $\pm$ 20 per cent.

The primary analyte to determine extent of combustion was PCP. Possible toxic combustion products of concern were 2,3,7,8-tetrachlorodibenzo-p-dioxin (TCDD) and 2,3,7,8-tetrachlorodibenzofuran (TCDF). The approach taken was to develop at least one analytical method for PCP, with the hope that TCDD and TCDF could be determined simultaneously. Preliminary gas chromatography/mass spectrometry analysis using a 30-m WCOT SE-54 fused silica column, which is temperature programmed from 100°C to 250°C at 16°C/min, showed no PCP, TCDD, or TCDF present in the original impinger samples above the 20-ppm detection limit. Our needs required a reduction of the detection limit at least to 1 ppm for the PCP and 0.1 ppm for the TCDD and TCDF. Therefore, it was necessary to develop analytical methods by the alternate techniques of HPLC and gas chromatography/electron capture detection (GC/ECD).

Successful analysis with HPLC was achieved with a 30-cm Partisil PXS 10/25 ODS-2 column. It was operated isocratically at 1.5 mL/min with a solvent of 99 per cent cyclohexane, 0.97 per cent acetic acid, and 0.03 per cent acetic anhydride. The ultraviolet detector was set at a wavelength of 300 nm to minimize absorption by toluene solvent. The injection volume was 90 μ L. 1-Fluoro-2,4-dinitrobenzene was used as an internal standard. Under these conditions the 95 per cent confidence detection limit was 0.5-ppm PCP but only 10 ppm for TCDD or TCDF.

From the duplicate toluene extracts of the wood used in the combustion, we determined that the wood had contained 0.104 $\pm$ 0.004 per cent by weight of PCP. This compares well with the estimate of 0.1 per cent we had been given by the suppliers of the wood.

Only 3 of the 27 impinger samples had measurable amounts of PCP, and none of them had measurable amounts of TCDD or TCDF. The PCP results are shown in Table I. The concentrated samples could not be quantified because of an interfering unknown.

TABLE I
PCP CONTENT OF IMPINGER SAMPLES

Sample No.	PCP Concentrate ^a (ppm)	
	Methods	
	HPLC	GC/ECD
22	1.64 $\pm$ 0.16	1.96
46	0.41 $\pm$ 0.24	0.89
50	5.09 $\pm$ 0.67	3.39

^aAs received.

The most successful analysis using GC/ECD was with a Varian 2800 GC and a Valco Model 140B wide-range ECD. The 5-ft by 1/8-in. o.d. stainless steel column was packed with Tenax GC (60/80 mesh). Column temperature required was 280°C at which evidence of PCP decomposition was seen. Carrier gas flow was 38 mL/min 9:1 argon:methane. A 2- μ L injection gave a detection limit of 0.5 ppm PCP. Good agreement with the HPLC was obtained, as seen in Table I. Neither TCDD nor TCDF was seen in the samples at a detection limit of 0.05 ppm.

The HPLC method has the advantage over the GC/ECD method in that the analyte does not have to be heated to vaporize it. This heating can lead to thermal decomposition of the analyte, particularly in the case of high boiling analytes like PCP. However, ECD has the advantage of specificity for chlorinated compounds, which can greatly reduce the interference problems.

Additional work is planned to obtain lower detection limits for TCDD and TCDF by cleaning up the samples by removing phenolics, such as PCP, and by concentrating. Lower detection limits are desirable because of the very high toxicity of these two compounds. It is also desirable to identify an unknown present in some of the samples to determine whether it is a contaminant or a combustion product.

B. Plutonium Urinalysis Study

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Los Alamos—Indirect Budget

A simplified analytical method for the analysis of plutonium in urine at the 0.15-pCi detection level has been developed. Plutonium is separated from urine by a calcium oxalate coprecipitation and then isolated by anion exchange methods without wet-ashing or washing treatments of the precipitate, as described by Campbell¹ and Kressin.² With modifications, the oxalate precipitation procedure has been placed into routine use for the Los Alamos plutonium bioassay program. The results (90 ± 10 per cent, 1 σ) obtained from the analysis of over 1000 urine samples spiked with ²⁴²Pu tracer (2 pCi per sample) were equal to or better than recovery data (82 ± 17 per cent) obtained from use of the alkaline-earth-phosphate coprecipitation wet-ashing method of Campbell.¹

The need for wet ashing, which is expensive and time consuming, is eliminated entirely. The need for transfer from the precipitation beaker (1000 cm³), centrifuging, and washing of the precipitate as described by Kressin² is also unnecessary. The small amount of supernate solution remaining after decanting the bulk of the supernate is evaporated by heating the solution on low heat (75–90°C). The dried precipitate is easily dissolved in 7.8M nitric acid (HNO₃). Filtering the solution at the time of the loading onto the anion exchange resin (Bio Rad AG 1 x 4–100–200 mesh) achieves the necessary removal of flocculent organic material.

In the early stages of the development of the ashless oxalate procedure, erratic results were obtained. The cause was associated with the poor adsorption of the ²⁴²Pu tracer on the anion exchange resin. Samples that were spiked with plutonium after precipitation and before dissolution and heating of the 7.8M-HNO₃ solution gave 100 per cent recovery, whereas samples spiked with the same plutonium solution after dissolution and heating gave erratic (10–50 per cent) tracer recovery. The anion exchange separator procedure requires that the plutonium be in the ionic +4 valence state for quantitative adsorption onto the

anion exchange resin. We concluded that the ²⁴²Pu tracer solution contained polymeric Pu +4 that may have been formed at the time of preparation by dissolution with water. Rainey³ states that Pu +4 polymer is formed when solutions of plutonium are diluted with water because of the existence of transient regions of high pH. No studies were performed to determine in what form Pu exists after the alkaline precipitation, but Rainey³ states that polymeric +4 Pu should be suspected whenever the acid concentration of a plutonium solution is below 0.5M.

Evidence to support the conclusion that Pu +4 polymer may be present in the samples after the alkaline precipitation is suggested by the results that show increasing higher tracer recovery as a function of heating time of the 7.8M-HNO₃ sample solution. Castanzo and Biggers⁴ showed that depolymerization of plutonium is very slow at room temperature in moderate acid concentrations. The depolymerization is increased by heating. Tracer recovery without heating of the 7.8M-HNO₃ solution was 38 per cent, 50 per cent with 60-min heating, and 95 per cent with 90-min heating. From this study, we concluded that it is necessary to heat (to 75–90°C) the dissolved precipitate for at least 90 minutes for quantitative adsorption of plutonium onto the AG 1 x 4 anion exchange resin. This heating was the most critical step for quantitative recovery of plutonium from urine without wet-ashing treatments. Studies using urine containing excreted plutonium and plutonium added as a tracer gave equal recovery data upon such heating.

The presence of the chelating agent diethylenetriaminepentaacetate (DTPA) in urine, following personnel treatment to enhance plutonium excretion, did not interfere with the plutonium recovery by the method described here.

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