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**Fossil-Energy Program
Quarterly Progress Report
for the Period Ending
June 30, 1983**

L. E. McNeese

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*Fossil
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FOSSIL-ENERGY PROGRAM
QUARTERLY PROGRESS REPORT FOR THE
PERIOD ENDING JUNE 30, 1983

L. E. McNeese
Program Director

Date Published — August 1983

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- ORNL-5049, Coal Technology Program Quarterly Progress Report for the Period Ending March 31, 1975
- ORNL-5069, Coal Technology Program Annual Interim Report for Fiscal Year Ending June 30, 1975
- ORNL-5093, Coal Technology Program Quarterly Progress Report for the Period Ending September 30, 1975
- ORNL-5120, Coal Technology Program Quarterly Progress Report for the Period Ending December 31, 1975
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- ORNL-5861, Fossil Energy Program Quarterly Progress Report for the Period Ending December 31, 1981
- ORNL-5877, Fossil Energy Program Quarterly Progress Report for the Period Ending March 31, 1982
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ORNL-5944, Fossil Energy Program Quarterly Progress Report for the
Period Ending December 31, 1982

ORNL-5955, Fossil Energy Program Quarterly Progress Report for the
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FOSSIL ENERGY PROGRAM QUARTERLY PROGRESS REPORT
FOR THE PERIOD ENDING JUNE 30, 1983

L. E. McNeese, Program Director

ABSTRACT

This quarterly report covers the progress made during the period March 31 through June 30 for the Oak Ridge National Laboratory research and development projects that are carried out in support of the increased utilization of coal and other fossil fuels as sources of clean energy. These projects are supported by various parts of DOE including Fossil Energy, Basic Energy Sciences, Office of Health and Environmental Research, Office of Environmental Compliance and Overview, the Electric Power Research Institute, and by the Tennessee Valley Authority and the EPA Office of Research and Development through inter-agency agreement with DOE.

1. SUMMARY

1.1 Coal Conversion Development

During the first part of this reporting period for physical properties, rheology measurements were attempted on a slurry prepared from Lummus ITSL solvent. Due to continuing operational problems, efforts were switched to thermal conductivity studies using Wilsonville solvent and Illinois No. 6 coal. Thermal conductivities of the solvent and slurry have been measured up to 500 K. A CSD feed quality monitoring system designed to be used in the laboratory was installed at Wilsonville during the latter part of May. The instrument, in addition to operating troublefree, appears on the basis of initial data to be tracking CSD operation. A comparison of relative radical concentrations for nine Wilsonville solvents was unable to either validate or invalidate a correlation between solvent quality as measured by the microautoclave assay and relative radical concentration determined by ESR. This is primarily due to the fact that the range in solvent quality for most of the

solvents was too small, being from 67 to 75 for seven of the nine solvents.

1.2 Chemical Research and Development

Pyridine is an ideal medium in which to carry out chemical modifications of coal. However, it is strongly retained by the product and interferes with subsequent spectral characterization methods. A simple efficient method has been developed to remove most of the pyridine and consists of washing with aqueous tetrahydrofuran.

1.3 Materials Technology

The investigation to develop iron and nickel aluminides for use as critical components in fossil energy conversion systems continued. Mechanical properties data indicate that boron-doped nickel aluminides containing 10 ± 2 at. % Fe have the best cold fabricability. Also, carbide-strengthened aluminides seem to have the best strength at temperatures to 700°C ; above that temperature hafnium-modified aluminides appear to be the strongest. We are continuing to investigate the weldability of the aluminides. In addition, a test was conducted to assess the resistance of Ni_3Al and Fe_3Al to the oxidation-sulfidation reactions caused by CaSO_4 .

We continued our investigation of materials performance in coal conversion systems, including studies of corrosion and combined erosion-corrosion mechanisms. The equipment to be used for the in situ scanning electron microscope study of erosion-corrosion was tested by firing particles at gold foil and examining the resulting impact craters. In addition, two papers on corrosion in coal liquefaction plants were completed this quarter.

The study of the effect of cyclic oxidizing and reducing atmospheres on the rate of corrosion of a heated metal specimen is continuing. The oxidation-sulfidation of nickel was studied under cyclic conditions. The results indicate that a rapidly cycling environment does not affect the rate of oxidation-sulfidation.

We continued our study of the mechanisms that control the corrosion of anode and cathode current collectors in molten carbonate fuel cells. Work progressed toward the determination of phase equilibria and thermodynamic data for the Fe-LiKCO₃ and Cr-LiKCO₃ systems to assist in understanding the differential thermal analysis experiments. Three solid phases were identified in the Li-Fe-O and Li-Cr-O systems, respectively, and the standard enthalpies and entropies of formation were obtained for each phase. The relative stabilities of these compounds at fuel cell operating temperatures and oxygen partial pressures were examined.

In the task to evaluate materials for use in ceramic heat exchangers, several new batches of colloidal-silica-pitch gel SiC and colloidal-silica-sugar gel SiC were synthesized and characterized. Also during this quarter, transmission electron microscopy of silicon carbide powders was initiated, and agglomerates composed of fine particles and crystals of SiC were observed. Studies of hot pressing particulate-reinforced SiC composites continued. In the task to investigate and characterize fiber-reinforced ceramic composites, the slurry, vacuum-molding equipment was tested during this quarter by molding a part from carbon fibers. In addition, moldings were made from three sources of silicon carbide fibers, and the results were characterized. In our work on structural ceramics, fracture toughness and slow crack growth measurements were performed on several SiC ceramics with dispersed-phase additions. Also in this quarter, posttest microscopic analyses of the ceramic heat exchanger tubes tested in the Ceramic Recuperator Analysis Facility Test 4 revealed no major reactions between the coal slag and the tubular surface.

In our work on advanced pressure vessel materials technology, initial tempering studies were completed on three weld metals produced in 2 1/4 Cr-1 Mo steel plate by the submerged arc method. In the electroslag component casting task, chemical analyses were performed on three electroslag cast valve bodies, which were received this quarter.

In our assessment of materials needs for advanced steam cycle pulverized coal plants, a study of advanced system design was completed. The results of this study showed that the most effective measures to improve plant efficiency were significant increases in steam throttle and reheat conditions and design improvements in the turbine.

1.4 Basic Energy Sciences — Fossil Energy Materials Program

Modification of the surface properties of ceramics by ion implantation is being investigated at ORNL. Knoop microhardness, indentation fracture toughness, and scratch-wear resistance of TiB_2 were increased 50 to 100% by implanting 1-MeV Ni^+ ions. Fundamental processes in the sulfidation of iron-base alloys are being investigated in studies designed to determine the effect of alloying elements on the point defect concentration in sulfide scales and, thus, on the kinetics of sulfidation.

Microalloying Ni_3Al with 0.025 to 0.2 wt % B produced ingots that could be fabricated into sheets by cold rolling. Deviation from stoichiometry to nickel-rich compositions increased the room-temperature ductility, whereas deviation to the aluminum-rich side decreased ductility.

1.5 Technical Support to Major Liquefaction Projects

Technical support is provided by Oak Ridge National Laboratory and Union Carbide Nuclear Division Engineering to the major liquefaction projects being managed by DOE Oak Ridge Operations--SRC-I Demonstration Plant, H-Coal Pilot Plant, and the Exxon Donor Solvent (EDS) Project. Activities are reported in five broad categories--engineering and design review, liquefaction technology, process analyses, materials, and environmental and health.

Activities in the area of engineering and design review have continued at a low level toward completion of remaining tasks. DOE comments have been received on the draft report dealing with Application of the Rand Corporation Estimating Techniques. SRC-I design materials have been reviewed in both the Expanded Bed Hydrotreater area and the Gasification and Gas Treatment area. The draft report of H-Coal reactor vessel thermal/fatigue analysis has been submitted for review.

In the area of liquefaction technology, remaining activities are also winding down. An operational test of the VSB viscometer was performed, but plans to install the unit at a pilot plant have been curtailed. The quality monitor for feed to the Wilsonville CSD unit has been delivered and appears

to be performing well. Thermal conductivity measurements in the flow system have been completed for SRC-I solvent and feed slurry to 500 K; measurements to 700 K will be attempted next quarter. We have submitted a plan for radiotracer measurements of residence time distribution in the Wilsonville dissolver.

Three activities are in progress in the area of process analysis. Our model of the SRC-I DEA system for purification of recycle hydrogen is nearing completion. Analysis of vapor-liquid equilibrium predictions with the ASPEN physical property code indicates that the precision of estimates of critical temperature may have to be high for mixtures involving hydrogen and aromatics. The H-Coal material balance yield calculations have been reviewed, and some questions have been raised about certain data adjustments; the rationale for these adjustments should be documented by ASFI/HRI.

Significant effort continues in the materials area. Two advanced trim materials--some TiB_2 coatings and a sintered $\beta\text{-SiC}$ --appear attractive in comparison with 701 cemented carbide after erosion testing. During the next quarter we will complete work on SA-387, grade 22, class 2 pressure vessel material and weldments and recommend a design methodology for flawed heavy-wall structures operating above 700°F. SRC-I, H-Coal, and EDS materials information is being assessed; the most recent fractionator corrosion experience at the H-Coal pilot plant has raised some puzzling questions.

Efforts related to environmental and health concerns also continue at a significant level. Polishing wastewater treatment studies have been completed at Wilsonville, and results are being analyzed. Likewise, sample analyses from the earlier operations at Catlettsburg have been completed and a final report is being prepared. The final draft of our report "Guideline for SRC-I Industrial Hygiene Monitoring and Research" has been submitted for publication. Several activities are underway in our assessment of environmental, health, and safety lessons learned and remaining R&D needs.

1.6 Component Development and Process Evaluation

All program plan documents for advanced gasification component development are being processed for publication.

1.7 Process Analysis and Engineering Evaluations

The DLTAS Task 1 draft report was completed and issued to DOE reviewers. The final four segments of this task were completed during this work period.

Modeling of an indirect coal liquefaction flowsheet has been completed using the ASPEN process simulator. Individual components of the flowsheet were modeled in modular form so that they will have application to a number of different process alternatives. Simulation of the Tri-State Synfuels Project showed good agreement with the base design.

1.8 Effluent Control Technology

Work in the Chemical Technology Division on the assessment of effluent control technology for indirect liquefaction processes continued with emphasis being placed on zero-discharge options for Lurgi-based processes. Wastewater treatment studies on polishing processes and on biooxidation processes continued in Wilsonville and in ORNL laboratories, respectively. An assessment of current solid waste management practices was concluded by the Chemical Technology and Environmental Sciences Divisions.

1.9 Fossil Energy Environmental Analysis

In the Fossil Energy Support area, major efforts during this reporting period focused on the finalization of Draft FE Order 3790.1 "Fossil Energy Occupational Safety and Health Programs for Federal Employees," continuation of technical support to the Bartlesville Energy Technology Center and assistance to the Morgantown Energy Technology Center in the development of an Environment, Safety and Health Information and Data Management System.

In the Synfuels Project, the Energy Division continued to participate with Chemical Technology Division in R&D studies involving ORNL's mobile wastewater treatment PDU located at the Advanced Coal Liquefaction R&D Facility in Wilsonville, Alabama.

1.10 Tennessee Valley Authority (TVA) Fluidized Bed
Combustion (FBC) Demonstration Plant Program
Technical Support

ORNL is continuing to provide support to TVA in evaluating the AFB pilot plant data. Most of the effort this quarter has been spent in reviewing the summary reports from Runs 5 and 6, Campaign I and Series I, Campaign II. As a result of this review, detailed recommendations have been made to TVA regarding performance calculations, sample analysis, and sulfur capture modeling.

The final report for the Tubular Flow Reactor Experiment has been reviewed and approved by TVA. The report is now being prepared for publication.

1.11 Health and Environmental Applications

Environmental and health-related studies are being conducted for the DOE/FE Office of Coal Processing (OCP), with support from the Gas Research Institute and the DOE/Office of Health and Environmental Research. They include implementation of several monitoring and testing components for the Gasifiers in Industry Program and investigation of hydrotreatment as a method to mitigate biological effects in coal-derived liquid products. Specifically, progress is described in the preparation of documentation for the University of Minnesota-Duluth gasifier and the studies of the Westinghouse fluidized bed gasifier and in the study of the chemical, physical, ecological, and biological properties of liquid products [from the SRC-II, H-Coal, and Exxon Donor Solvent (EDS) processes] upgraded by hydrotreatment.

1.12 FBC Program Planning and Analysis

Final reports on the PFBC component development plan and PFB industrial boiler are in preparation. Work has been resumed on the PFB control methodology task.

1.13 Coal Preparation and Waste Utilization

The wet HGMS pilot plant was delivered from Muscle Shoals to Paradise on April 12; ORNL personnel joined TVA engineers for shakedown tests on April 26-29. Several equipment modifications resulted from this work, and a test plan tailored to the actual physical configuration was developed. Results are presented for desliming cyclone characterization tests.

The Dense Medium Sample Separator was delivered and demonstrated to the operations staff at Paradise. Two more units are being fabricated to make a three unit DMSS facility at Paradise for routine float-sink analysis.

1.14 Basic Chemical Engineering Studies

Initial experiments with a low-power laser (5 mW) have demonstrated capabilities of the proposed technique for using light scattering to measure fluid viscosities. Measured viscosities of pure fluids at low temperatures (0-90°C) and atmospheric pressures were normally within $\pm 2\%$ of values reported in the literature. These experiments have been used also to test seed particles for use with the different fluids of interest. Both suitable organic polymers and inorganic particles have been found, and it now appears that suitable seed particles will be available for all of the fluids and fluid mixtures of immediate interest. A new cell capable of measurements at high pressures (and temperatures) has been designed and is being fabricated.

1.15 Fossil Energy Information Center

FEIC continues to concentrate on work in support of the Fossil Energy Technology Environment Program. Preparation of two topical papers has been completed. Approximately 700 responses to requests for service have been made during the quarter.

1.16 Generalized Equilibrium Models of Liquid and Gaseous Fuel Supplies

Under the sponsorship of the Division of Policy and Strategic Planning (DOE/FE), Oak Ridge National Laboratory, together with its subcontractors Decision Focus, Inc. and Lewin and Associates, is developing computer models of liquid and gaseous fuel supplies. The objective is to enable quantitative assessment of competitive supply technologies and thus contribute to the development of the knowledge base required for reducing the U.S. energy supply vulnerability to the economic and security implications of reliance upon scarce and increasingly expensive conventional petroleum resources. The Division of Energy Security (DOE/PPA) is simultaneously sponsoring a complementary effort at ORNL to develop a world oil model, through expansion of the U.S. model supported by Fossil Energy to include world energy supply regions. ORNL's Engineering Physics Division has the lead responsibility for the program. The April to June 1983 activities are reviewed.

2. COAL CONVERSION DEVELOPMENT

B. R. Rodgers

Coal conversion development activities are carried out in the Chemical Technology Division. This section discusses three projects conducted for the U.S. Department of Energy and managed by the DOE's Oak Ridge Operations. The projects are (1) Physical Properties of Coal Liquids, (2) Instrumentation for Measurement of Critical Solvent Deashing Feed Quality, and (3) On-Line Monitoring of Hydrogen Donor Solvent Quality Using Electron Spin Resonance Spectroscopy.

2.1 Physical Properties of Coal Liquids

D. D. Lee and J. H. Wilson

2.1.1 Summary

During the first part of the quarter, attempts to determine the rheology of a slurry prepared with Lummus ITSL solvent were unsuccessful due to plugging problems. CLFS operations were switched to thermal conductivity studies using Wilsonville solvent and Illinois No. 6 coal. Thermal conductivities of the solvent and of slurry were determined at temperatures from 295 to 500 K. Measurements at temperatures to 700 K will be made next quarter.

2.1.2 Introduction

Knowledge of the physical properties (e.g., viscosity, density, thermal conductivity, and heat capacity) of coal liquids under process conditions is essential for proper design of heat transfer equipment, preheaters, reactors, separation units, and process piping systems in liquefaction processes. The high hydrogen pressure--high temperature conditions present in coal-solvent slurry liquefaction and hydroprocessing schemes, as high as 31 MPa (4500 psig) and 810 K (1000°F), prevent measurement of physical properties of the process fluids with conventional instruments. Physical properties may be strongly influenced by the effect of dissolved hydrogen and/or by the effects of ongoing liquefaction-hydrogenation reactions; therefore, flowing stream

measurements are essential, and the test fluid must be quenched, sampled, and chemically characterized to provide a basis for ultimately correlating physical properties with chemical composition and physical conditions.

Instruments for measuring the viscosity and density of flowing streams of coal liquids at process conditions have been incorporated into the Coal Liquids Flow System (CLFS). A thermal conductivity instrument is presently being installed and a heat capacity unit is to be installed at a later date. The CLFS is a bench-scale continuous flow, high hydrogen pressure, high temperature system capable of processing both coal-solvent slurries and solids-free, coal-derived liquids at up to 31 MPa (4500 psig) hydrogen pressure and 810 K (1000°F) and measuring their physical properties under processing conditions. The unit can simulate coal-solvent slurry preheating and liquefaction conditions prior to physical property measurements. A detailed description of the Coal Liquids Flow System and the physical property instruments are included in an earlier report.¹

2.1.3 Discussion

During the first month of this quarter, attempts were made to determine the rheology of a slurry of Lummus ITSL solvent and Illinois No. 6 coal at a solvent-to-coal (S/C) weight ratio of 1.2:1. Measurement temperatures of 478 and 617 K were utilized. In all cases, the unit plugged shortly after introduction of slurry into the preheater. Just before plugging, high pressure drop in the preheater was observed. As reported last quarter, a coking run with a 2:1 S/C weight ratio slurry was made which lasted for over 5 h. The slurry viscosity at the higher coal content apparently is too high for CLFS operation. Because of the difficulties experienced in processing slurries containing Lummus solvent, in both coking and rheology tests, the decision was made to switch to thermal conductivity studies using Wilsonville solvent.

The thermal conductivity instrument, which had been mounted onto the CLFS rack last quarter, was piped into the unit between the preheater outlet and the high pressure letdown valve. To facilitate

installation and to eliminate some operational problems experienced during static tests, the sand bath (used to control the thermal conductivity cell temperature) had been replaced by a "metal bath." The latter was a 12.7 cm (5 in.) ID section of pipe into which the conductivity cell was placed and then small diameter copper shot was added to fill the void space. Strip heaters were mounted on the outside surface of the pipe and the entire assembly was insulated. In previous quarterly reports, the theory of operation, the design of, and the results of measurements on toluene and a coal liquid with the thermal conductivity instrument have been discussed in detail.^{2,3}

Thermal conductivity measurements were made on Wilsonville solvent (Sample V-178, Tray 8, March 28, 1983) and a slurry comprised of the same solvent and Illinois No. 6 coal at a S/C weight ratio of 2:1. The measurements covered a temperature range of 295 to 500 K. The results are presented in Tables 2.1 and 2.2 and in Figure 2.1. Also, data from Battelle are shown in Figure 2.1. The Battelle data were obtained with Kentucky No. 9 coal and Wilsonville solvent, the slurry also prepared at a S/C ratio of 2:1.

As seen from Tables 2.1 and 2.2, the precision of the measurements is good, the average standard deviation expressed as a percentage of the thermal conductivity being 3%. Previously, in static measurements using toluene at temperatures up to 358 K, results were obtained which were within 2% of one set of literature values and within 5% of another set. Tests with toluene will be conducted on the CLFS to confirm the accuracy of the measurements (assuming that these literature values are themselves accurate).

From Figure 2.1, the thermal conductivities of the solvent and of the slurry are seen to approximate corresponding values obtained by Battelle at room temperature. However, ORNL data demonstrate a significantly greater temperature dependence than those of Battelle. At 500 K, the ORNL slurry thermal conductivity is only about three-fourths that of the Battelle value. Also, the slope of the conductivity vs temperature curve for the ORNL solvent is closer to that for toluene (up to 400 K) than is the slope of the Battelle solvent curve. This is an observation

Table 2.1 Solvent^a thermal conductivity

Temperature (K)	Thermal conductivity [mW/(cm K)]	Standard deviation
296	1.229	0.005
338	1.264	0.003
375	1.124	0.015
438	0.93	0.07

^aSample V-178, Tray 8, Wilsonville SRC-I pilot plant March 28, 1983.

Table 2.2 Slurry^a thermal conductivity

Temperature (K)	Thermal conductivity [mW/(cm K)]	Standard deviation
295	1.58	0.08
339	1.44	0.09
374	1.298	0.004
438	1.13	0.03
498	0.918 ^b	-
505	1.02	0.01

^aSolvent prepared from solvent in Table 2.1 and Illinois No. 6 coal at a solvent-to-coal weight ratio of 2:1.

^bOne determination only.

only, as no prediction of the thermal conductivity-temperature relationship for the solvent has been made. The change in conductivity of the slurry with temperature could be due in part to the change exhibited by the solvent. A change in the coal thermal conductivity could also be occurring. Actually, the conductivity of the slurry appears to be decreasing just as rapidly as that of the solvent, indicating that

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Fig. 2.1. Thermal conductivity versus temperature.

significant physical and/or chemical changes in the coal are taking place. This is rather surprising considering the relatively low temperatures involved. If the coal is undergoing such changes at these temperatures, the primary cause may be the use of a solvent with a high hydrogen donor capacity. This Wilsonville solvent was produced in the integrated two-stage liquefaction mode, whereas the Battelle solvent was produced in the single-stage non-catalytic SRC-I mode. As temperature is increased, the behavior of the slurry conductivity as more and more of the coal is solubilized will be of interest. A crossing of the solvent and the slurry conductivity temperature curves may result when very high molecular weight components are produced from the coal. Also of interest is the minimum value of thermal conductivity that will be attained by the slurry. The conductivities measured thus far have been considerably lower than those from theoretical calculations or from other experimentation. As the heat transfer coefficient is proportional to the thermal conductivity to the two-thirds power, a significant effect on the feed slurry preheater design would be expected.

2.1.4 Future Work

The thermal conductivities of solvent and slurry will be attempted at temperatures up to 700 K. After completion of this work in July, the CLFS unit will be converted for the study of the rheology of Lummus short-contact-time solvents and slurries.

2.2 Instrumentation for Measurement of CSD Feed Quality

J. E. Mrochek and S. R. Dinsmore

This work element has two concurrent objectives. The first is to fabricate, test, and install in the Wilsonville pilot plant laboratory a system for measurement of feed quality to the Kerr-McGee Critical Solvent Deasher (CSD). The second objective is to fabricate and test a self-contained, automated, instrumental system to monitor on-line, or near-on-line, that same feed quality. The latter system is to be suitable for installation at Wilsonville or at a demo plant, should one be built.

2.2.1 Summary

The system for the analysis of CSD feed quality in the laboratory is based upon the two-solvent elution of a CSD feed sample (dissolved in pyridine, 0.1 g to 10 ml) which is dispersed on a 50 x 1.2 cm column filled with sea sand. Chloroform and pyridine are employed to elute two fractions consisting of (approximately) oils + asphaltenes and preasphaltenes. These two fractional components are monitored by an optical detector having a broadband uv source (centered around 360 nm) and a photoconductive detector. The analog output from this detector is plotted and integrated by a peak integrator and the normalized peak area percent is used to follow CSD feed quality.

Initial testing of the new detector versus the detector used in the prototype system (in series) indicated a lack of reproducibility for the new detector. Excessive offset in the baseline before and after the pyridine-eluted peak were believed to be a contributing factor. The cell position was adjusted to minimize this offset and this, together with sonication of the pyridine-solubilized sample just prior to introduction into the sample loop, sharply improved system reproducibility. The completed laboratory system, installed in the Wilsonville control laboratory on May 23, has been operating in a troublefree manner. Results obtained to date have apparently tracked CSD operation quite closely and initial results seem to indicate that the assay may be useful in predicting CSD operation.

2.2.2 CSD Feed Quality Monitor

The laboratory version of the CSD feed quality monitoring system is illustrated in Fig. 2.2 with a schematic diagram shown in Fig. 2.3. The completed system consists of two Laboratory Data Control (HDC) HPLC pumps, a Hewlett-Packard (Model 3920) integrator-plotter, an ORNL-developed optical detector, Rheodyne sample injection valve, a 50 x 1.2 cm sand column, and a μ Data Trak programmable timer. As illustrated in Fig. 2.2, four light emitting diodes (LED) have been incorporated into the panel which supports the programmable timer to provide the operator with timely information concerning system operation.

Fig. 2.2 CSD feed quality monitoring system.

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CSD FEED QUALITY MONITOR

Fig. 2.3. Schematic diagram of CSD feed quality monitoring system.

The programmable timer controls complete system operation, only requiring the operator to rotate the injection valve twice, first to start the system and then to inject the sample. The sample goes through its entire cycle, sample elution and regeneration, in 13 min and 16 s and shuts itself down after regeneration (return to initial solvent conditions). The timer controls five external events and outputs two voltage signals to control the pumping rate of both pumps. The program profile which is entered into the timer's memory by means of the keyboard shown in Fig. 2.2 is illustrated in Table 2.3. The timer, equipped with a battery backup, can retain its program in memory for 4 h in case of a power failure. The integrator must be reprogrammed after a power failure; however, a few simple entries on its keyboard accomplish this.

Table 2.3. Program profile

Segment	1	2	3	4	5	6	7	8	9	10	11
E1 ^a (valve)	Off	On	Off	- ^b	-	-	-	-	-	-	-
E2(valve)	Off	-	-	-	-	-	-	-	-	-	On
E3(integrator)	Off	On	Off	-	-	-	On	Off	-	-	-
E4(READY LED)	On	-	Off	-	-	-	-	-	-	-	-
E5(RUN LED)	Off	-	On	-	-	Off	-	-	-	-	-
SP1(pump A)	41.5 ^c	-	-	0	-	41.5 ^c	-	61.5 ^c	-	0	-
SP2(pump B)	0	-	-	40.0 ^c	-	0	-	-	-	-	-
Time ^d	1 s	1 s	3 min	5 s	5 min	5 s	1 s	1 s	5 min	1 s	1 s
Next Point	2	3	4	5	6	7	8	9	10	11	1

^aE1-E5 are external events, either off or on.

^bDashes indicate repetition of the previous segment's condition.

^cIndication is percentage of full flow (22.5 ml/min).

^dTime indicated is duration of each program segment.

During initial testing at ORNL of the new system, problems were encountered with reproducibility. Even multiple injections of the same

sample were not reproducible. The old detector from the prototype system was placed in-line with the new detector. Results on the old detector were better but not entirely satisfactory. It was noted that the offset generated on changing the eluent from chloroform to pyridine seemed to be excessive for the new detector. An electronic reference is provided and the detector is zeroed using the initial solvent, chloroform, thus changes in the absorption of the solvent do affect the baseline. Since a frontal elution is performed, the baseline before the second peak is that of chloroform and after the peak it is pyridine. The peak integrator was drawing a baseline from the beginning of the peak to its internally determined end of the peak and results were quite variable. Correcting this problem involved two changes: (1) The cell was rotated to reduce the amount of light incident on the cell window (effectively decreased the aperture) and this minimized baseline offset due to pyridine; and (2) The second peak was "declared a solvent peak" which effectively allowed longer integration on solvent "tails" and integration was terminated at a set time. In addition, we found that sonication of the pyridine-solubilized sample immediately prior to filtration and loading of the sample loop improved the reproducibility of results. These factors sharply improved system reproducibility and precision and enabled us to transport the system to the Wilsonville pilot plant for installation. A short (8 page) operating manual was written to assist in familiarizing operating personnel with the instrument and its operation.

The CSD feed quality monitor was installed in the control laboratory of the Wilsonville pilot plant on May 23, 1983. Initial results, obtained by Wilsonville operating personnel, are listed in Table 2.4. Note that chloroform solubles (approximately the oil + asphaltene fraction) were quite uniform through May 30, averaging 64.3% with a standard deviation of 1.1. Results increased to a maximum of 70.8% chloroform solubles over the period May 31 to June 3 whereupon the Critical Solvent Deasher was shut down because of excessive ash carryover in the overhead product. It appears as though the feed quality monitor was indicating a change on May 31 with the loop increase

Table 2.4. Initial analytical data from Wilsonville using
ORNL CSD feed quality monitor

Date	Chloroform soluble, %		SRC recovery, %		Energy ^a rejection, %
May 23	65.6	64.3 <u>+1.1</u>	91.7	90.7 <u>+1.2</u>	22.6
24	65.6		91.3		21.1
25	63.3		90.4		24.7
26	65.8		88.6		25.7
27	63.3		90.9		-
28	63.4		89.1		-
29	63.9		91.7		-
30	63.8		91.6		22.3
31	66.3		90.7		23.6
June 1	65.8		91.5		23.3
2	68.6	61.2 <u>+1.8</u>	91.5	89.0 <u>+0.7</u>	-
3	70.8 ^b		-		-
4	61.3		90.4		-
5	61.6		89.2		27.5
6	61.4		88.7		25.9
7	57.4		88.6		29.8
8	61.4		88.3		30.7
9	62.5		89.1		29.9
10	62.7		88.8		-

^aEstimate of feed coal heating value rejected to the CSD ash concentrate.

^bCSD unit was shut down because of excessive carryover of ash to second stage.

from 63.8 on May 30 to 66.3 on May 31. The CSD unit was started again after the shutdown but at a lower level of chloroform solubles, averaging 61.2 with a standard deviation of 1.8 for the next 7 days (stable operation). You will note that chloroform solubles show an average reduction of 3.1% with a corresponding average reduction of 1.7% in SRC recovery for the two periods of operation. Energy rejection which is estimated feed coal heating value lost with the ash concentration, is too high during the June 5 to June 9 period. The CSD unit is considered to be operating well when energy rejection is in the range of 20 to 22%.

These results and the lack of operational difficulties with the CSD feed quality monitor are preliminary indications of a useful analytical system. The early results seem to be tracking CSD operation and later data even suggest that changes in feed coal may be detected.

2.3 On-Line Monitoring of Hydrogen Donor Solvent Quality Using Electron Spin Resonance Spectroscopy

J. E. Mrochek, R. Livingston,* H. Zeldes,* and S. R. Dinsmore

The objective of this program is to establish feasibility, and then develop high temperature, high pressure electron spin resonance (ESR) instrumentation to monitor relative free radical concentrations at or near on-line process conditions. The major objective is to provide a measure of donor solvent quality which is both timely and amenable for use in feedback control of coal liquefaction processes.

2.3.1 Summary

A Wilsonville solvent, reportedly chemically and physically identical to a previously obtained solvent except for conditions of storage, showed rather uncharacteristic behavior at temperatures in excess of 300°C at 10.5 MPa in the ESR sample cell. The sample, stored in a sealed can at refrigerator temperatures, displayed 2 to 4 times the relative radical concentration of the supposedly identical sample stored under

*Chemistry Division.

normal ambient temperature conditioning in a large tank. In addition, at higher temperatures ($>300^{\circ}\text{C}$) a heteroatom-containing polymer was apparently formed which prevented critical coupling of microwave power to the sample.

Reviewing ESR results on nine Wilsonville solvents covering a solvent quality range from 62 to 86, we were unable to validate or invalidate a correlation between microautoclave solvent quality and ESR-measured free radical concentrations. Most of the solvents are clustered too close together in solvent quality to enable a clear cut decision to be made (seven solvents in the range of 67 to 75). A question is posed concerning whether microautoclave solvent quality as currently performed using a standard coal to assay a solvent not derived from that coal, is a valid and true measure of the ability of that solvent to liquefy coal.

2.3.2 ESR Applied to a Series of Wilsonville Solvents

A fifth Wilsonville solvent,* thoroughly characterized by the carefully standardized procedures developed by Dr. F. K. Schweighardt and reported to be identical to solvent "C" described in the previous quarterly report,⁴ was received from ICRC and analyzed by ESR. Solvent "C" was a blend of three drums of solvent from a single Wilsonville pilot plant run, stored in a 900-gal tank under normal ambient conditions. The sample, on receipt, was found to contain water and required additional filtering to remove the water. The supposedly identical solvent was from a single one of the barrels and had been stored in a sealed can at refrigerator temperatures. Although no physical or chemical method was capable of distinguishing these samples, ESR showed the refrigerated sample to have 2 to 4 times the free radical concentration of the 3-barrel blend (see Table 2.5). In addition, at temperatures in excess of 300°C at 10.5 MPa, the solvent stored at refrigerator temperatures coated the walls of the capillary with a strongly diamagnetic coating which destroyed critical coupling within the cavity and prevented further

*Sample courtesy of Dr. F. K. Schweighardt, Air Products and Chemicals, Inc., Allentown, PA.

Table 2.5. Comparison of relative radical concentrations for two reportedly identical^a Wilsonville solvents

Temperature	Relative radical concentration	
	a	b
74	0.7	1.4
100	1.6	1.8
149	2.2	4.5
198	2.4	8.7
247	2.8	11.0
289	3.0	12.2
337	2.7	11.0
382	1.6	- ^b
427	1.2	
423	1.4	

^aSamples were a blend of three barrels of solvent from a single run stored at ambient conditions in a 900-gal tank (sample a) and a sample of one of those barrels stored in a sealed can at refrigerator temperature (sample b).

^bDiamagnetic coating on cell walls prevented critical coupling of microwave power and caused run to be terminated.

measurements at temperatures above 337°C. The rapidity and extent to which the Q of the cavity (a ratio of microwave power reflected to microwave power absorbed) was degraded and the fact that rinsing with hot pyridine did not remove the diamagnetic coating, suggested that a heteroatom-containing polymer had been formed. Critical coupling was restored after cleaning the cell with 6 M nitric acid at 228°C and 7 MPa for one hour. Differences such as were observed between these two supposedly identical solvents would seem to have some bearing on their ability to liquefy coal which could be advantageously utilized if such differences could be quantified.

A total of nine Wilsonville solvents, all believed to have emanated from Fies coal, have been analyzed by ESR. They span a range of solvent

quality (all measured with Wilsonville standard Indiana V coal) from 62 to 86. Unfortunately, seven of these solvents are within the solvent quality range of 67 to 75 and two of these seven behaved uncharacteristically. That is, one carbonized, plugging the ESR cell, and one formed a diamagnetic coating on the cell wall at elevated temperatures — both conditions prevented completion of ESR measurements over the full temperature range (see samples footnoted e and f in Table 2.6). Five of the Wilsonville solvents listed in Table 2.6 were analyzed by Schweighardt's standardized microautoclave assay⁵; however, two of these must be discounted because of their previously mentioned uncharacteristic behavior during ESR analysis. The remaining three solvents (solvent quality 62, 67, and 70 in Table 2.5) display decreasing relative radical concentration with increasing solvent quality. Radical concentrations determined for the Wilsonville-analyzed solvent (SQ = 69 in Table 2.6) seem to fit in properly for temperatures $\leq 149^{\circ}\text{C}$; however, above this temperature, its radical concentrations exceed those of the lower quality (SQ = 67) solvent except at the highest temperature. On the other hand, solvents having SQ's of 69 and 75 (determined at Wilsonville) have virtually the same free radical concentrations (see Table 2.6).

In general, the results are certainly not conclusive in either direction, i.e., validating or invalidating a relationship between microautoclave solvent quality and ESR-measured free radical concentrations. The nature of the assay, the skills required to obtain reproducible and precise results with it, and the narrow range covered by this group of solvents do not permit a clearcut decision on the utility of the ESR measurement based on comparisons with the microautoclave assay. The outcome of the microautoclave assay is strongly dependent on the time-temperature relationship during heatup and the overall solubility of the standard coal in a solvent which was not derived from that standard coal. Schweighardt⁶ suggests that, as an analytical test, microautoclave-determined solvent quality has a precision of ± 2 . He also points out in his analysis of Wilsonville data, high gas production (an undesirable product in coal liquefaction because of increased usage of expensive hydrogen) cycles with each new coal type introduced into the

Table 2.6. Comparison of relative radical concentrations for Wilsonville solvents

Temperature (°C)	Relative free radical concentration								
	62 ^a	67 ^{a,b}	69 ^c	70 ^{a,d}	70 ^a	72 ^a	75 ^c	75 ^c	86 ^c
24	4.8	2.0	0.9	0.7	1.4	1.9	0.9	1.1	0.6
100	7.6	4.2	2.1	1.6	1.8	4.2	1.8	1.8	0.7
149	12.6	4.7	4.1	2.2	4.5	4.5	4.3	4.4	1.2
198	16.8	5.5	6.0	2.4	8.7	4.7	6.3	6.1	
247	14.8	5.0	6.8	2.8	11.0	^f		6.2	
289	14.0	5.3		3.0	12.1			6.5	
337	9.6	4.6	7.2	2.7	11.0			5.9	
382	5.4	4.1	5.8	1.6	^e			3.2	
427	4.1	3.9	4.3	1.2				1.7	
473	3.6	4.7	2.3	1.4				2.3	

^aSolvent quality by ICRC microautoclave method, Indiana V coal from Catalytic at Wilsonville 8:1 solvent/coal, 750°F, 10 min.

^bSolvent quality by microautoclave using Indiana V coal from Conoco was 79.

^cSolvent quality by Catalytic at Wilsonville, method as in footnote a.

^dSolvent quality by microautoclave using Indiana V coal from Conoco was 83.

^eDiamagnetic deposit on capillary walls prevented further measurements because of loss of critical coupling.

^fFormation of carbonaceous material plugged system preventing further flow-through operation.

pilot plant. This, of course, raises an interesting question concerning the validity of microautoclave assays of solvent quality using a non-solvent-derived coal, the standard Indiana V. Schweighardt says, "As used at Wilsonville, the solvent quality test does not appear to provide an absolute or relative measure of liquefaction."⁶ In conjunction with SRC-I liquefaction, he further suggests that the solvent is a primary product of a feed coal whose composition is controlled (1) by the coal's structure, (2) by processing conditions, and (3) by external material

addition. This philosophy seems to be confirmed by his analysis of the Wilsonville pilot plant operation over a period of four years.

2.4 References for Section 2

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3. CHEMICAL RESEARCH AND DEVELOPMENT

M. L. Poutsma

This Section has previously contained reports of chemically oriented studies sponsored by the Office of Fossil Energy. These studies are now terminated. However, this Section will continue to provide occasional reports from coal research in the ORNL Chemistry Division sponsored by the Office of Basic Energy Sciences.

3.1 Displacement of Retained Pyridine from Coals by Aqueous Tetrahydrofuran

R. R. Chambers, Jr. and D. R. McKamey

Solvent extraction of coal represents one of the most common methods for obtaining coal-derived materials whose structure closely resembles that of the entire coal.¹ These extracts are ideal for further study since they are soluble in at least one solvent and they lack a high mineral content which can interfere with some analytical techniques such as NMR. Within the coal community, pyridine has been the solvent of choice for extraction because of its ability to dissolve a substantial portion of the coal, as much as 30% for a bituminous vitrain. In addition, the excellent swelling properties of pyridine make it an ideal medium for performing various chemical transformations on coal such as acylation² and trimethylsilylation³ of phenolic hydroxyls. The major disadvantage, however, associated with the use of pyridine is the difficulty in completely liberating the coal of residual amine which clings tenaciously even after extended periods under high vacuum.

Collins et al⁴ demonstrated that large quantities (12-20% by weight) of ¹⁴C-pyridine are retained both by the pyridine extract and residue from an Illinois No. 6 vitrain after 48 h under high vacuum. And, although all but 0.2-1.7% of the labeled amine could be exchanged with unlabeled pyridine, repeated benzene extractions removed only 20-25% of the ¹⁴C-pyridine from the solutes.

Two recent reports from the Ames Laboratory describe a method, using supercritical carbon dioxide, for the removal of retained pyridine from

Illinois No. 6 and Kentucky No. 9 extracts.⁵ The amount of pyridine removed by this method agrees well with the amount of reversibly bound pyridine as found by Collins. Of interest is the finding that water is an essential co-solvent for complete extraction. The authors have suggested that carbon dioxide's ability to penetrate the coal extract and displace the pyridine makes it an effective extracting medium.

We report here a useful alternative to supercritical CO₂ extraction for producing pyridine-free coals which avoids the use of high pressure equipment. The method involves repetitive washing with a dilute aqueous THF solution. For this study, an Illinois No. 6 vitrain and its O-methylated derivative were used.⁶ The O-alkylated coal was prepared according to the general procedure outlined by Liotta⁷ in which phenolic hydroxyls and carboxylic acids are converted to methyl ethers and esters by treatment with tetrabutylammonium hydroxide and methyl iodide.

The pyridine-retained coal samples were prepared by refluxing 1 g of coal (<100 mesh) and ¹⁴C-pyridine (5-10 mL, 3 mCi/mole) for 20 hrs under argon. The excess pyridine was distilled off and the sample placed under vacuum (6.6 Pa, 23°C, 24-48 h). Carbon-14 assay revealed that Illinois No. 6 and the O-methylated derivative retained 10.7% and 7.9% (W/W) pyridine, respectively.⁸ The decrease in retained pyridine upon O-methylation is consistent with the notion that hydrogen bonding contributes to the affinity of coals for amine solvents.⁹

A portion of the labeled coals (30 mg) was placed on a funnel, stirred for five minutes with a 5% (V/V) aqueous THF solution (0.75 mL) and then filtered. This was repeated a total of ten times. After drying (110°C, 2.9 kPa) for 18 hrs, the samples were assayed for their carbon-14 content. The Illinois No. 6 vitrain retained only 1.3% pyridine while the O-methylated derivative retained 1.9% pyridine, in agreement with Collins' finding that most of the pyridine is not bound irreversibly to coal. To rule out the incorporation of large quantities of THF during this procedure, the two coals were treated as above with an aqueous ¹⁴C-THF solution and dried. Neither coal retained more than 1.2% (W/W) THF.¹⁰

The same extraction process was carried out on a large (1 g) amount of coal containing unlabeled pyridine to monitor weight losses. The results are presented in Table 3.1, from which it is clear that only small amounts of coal are lost throughout this procedure.

Table 3.1. Weight losses during aqueous THF extraction

Coal	Before Extraction (g)	After Extraction (Theory) (g)	% Coal Lost
Ill. No. 6	1.0034 ^a	0.8150 (0.8432) ^b	3.3
O-Methylated Ill. No. 6	1.0287 ^a	0.9172 (0.9187) ^b	0.16

(a) The general procedure is as follows: 5.0 g of dry (110° C, 2.9 KPa, 18 h) coal is refluxed for 2 h with 50 mL of purified (over BaO) pyridine. The excess pyridine is removed by distillation and the sample placed under vacuum (23°C, 6.6 Pa, 18 h). The Ill. No. 6 vitrain and O-methylated derivative retained 15.96% and 10.69% (W/W) pyridine, respectively, under these conditions.

(b) Each sample was washed ten times with 25 mL of a 5% (V/V) aqueous THF solution as before and then dried (110°C, 2.9 KPa, 18 h).

3.2 References for Section 3

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6. Ill. No. 6 vitrain: C, 73.83; H, 4.99; N, 1.55; S, 2.02;
Ash 6.12 wt %.
O-Methylated Ill. No. 6: C, 74.06; H, 5.80; N, 1.77; S, 1.64;
Ash 5.04 wt %.
7. R. Liotta, Fuel 1979, 58, 724; R. Liotta, K. Rose, and E. Hippo,
J. Org. Chem. 1981, 46, 277.
8. The ^{14}C assays are expressed on an ash-free basis and are within
 $\pm 0.6\%$.
9. I.G.C. Dryden, Nature 1950, 166, 561; Chem. Ind. 1952, 30, 502.
10. Specific activity of ^{14}C -THF: 4.1 mCi/mole. Coal assays are
expressed on an ash-free basis and agree to within $\pm 1\%$.
Ill. No. 6: 1.16% (W/W) THF
O-methylated Ill. No. 6: 0.65% (W/W) THF.

4. MATERIALS TECHNOLOGY

R. A. Bradley

This section describes research and development performed on the Advanced Research and Technology Development (AR&TD) Fossil Energy Materials Program and the Surface Gasification Materials Program. The AR&TD Fossil Energy Materials Program includes tasks on the development of iron and nickel aluminides, materials research for liquefaction systems, corrosion of atmospheric fluidized-bed combustor (AFBC) materials, corrosion of materials for molten carbonate fuel cells, development of structural ceramics, and an assessment of materials needs for advanced steam cycle pulverized-coal plants. The Surface Gasification Materials Program includes tasks on advanced pressure vessel materials technology, electroslog component casting, and materials application and development. This section also includes work sponsored by the Pittsburgh Energy Technology Center (PETC) on high-temperature ceramic heat exchangers.

4.1 Development of Iron and Nickel Aluminides*

C. T. Liu

The objective of this task is to develop new structural materials based on Ni,Fe aluminides for use as critical components in fossil energy systems such as coal gasifiers and fluidized-bed combustors. Nickel aluminides based on Ni_3Al are strong and resistant to air oxidation at elevated temperatures, but they are extremely brittle in polycrystalline forms. Our previous study of microalloying at Oak Ridge National Laboratory (ORNL) indicated that additions of a few hundred parts per million of boron dramatically improved the fabricability and ductility of polycrystalline Ni_3Al . The boron-doped Ni_3Al thus serves as an attractive basis for the development of ductile and strong structural aluminides. Current efforts of this alloy development task focus on optimization of iron content in the nickel aluminides. The function of adding iron is to lower the nickel content in Ni_3Al and to improve its mechanical and metallurgical properties further.

*Work sponsored jointly by the AR&TD Fossil Energy Materials Program (AA 15 10 10 0) and the DOE Conservation Energy Conversion and Utilization Technologies Program (EG 05 00 00 0).

4.1.1 Basic alloy development — C. T. Liu and E. H. Lee

A series of Ni,Fe aluminides based on Ni₃Al was prepared, in which nickel and aluminum atoms were partially replaced by iron atoms. All the aluminides were doped with 500 ppm B for ductility improvement. The alloy ingots were homogenized at 1000°C and fabricated by repeated cold rolling at room temperature, with intermediate anneals at 1000 and 1050°C. The aluminides with 10 ± 2 at. % Fe have the best cold fabricability. The sheet fabrication with iron content above that level became increasingly difficult. The aluminide containing 20 at. % Fe showed some degree of surface and end cracking during fabrication and was difficult to roll into sheet material.

Metallographic examination indicated that the solubility limit of iron in Ni₃Al having the fcc ordered crystal structure (L1₂-type) depends on the aluminum concentration. The solubility of iron in the aluminide containing 20 at. % Al is less than 15 at. %. The aluminide can dissolve up to a maximum of about 20 at. % Fe in solution at a lower aluminum concentration. These observations clearly suggest that iron atoms occupy both the nickel and aluminum sublattice sites available in the fcc ordered crystal structure.

Boron-doped Ni₃Al showed a light spalling during cyclic oxidation above 900°C. To improve the adhesion between aluminum oxide scale and base metal, a small amount of alloy additions was added to nickel aluminides containing 23.5 to 24.5 at. % Al. The modified aluminide with 24.5 at. % Al cracked during cold rolling, but the aluminides with 24 (IC-49) and 23.5% Al (IC-50) were successfully fabricated into sheets. The oxidation behavior of IC-49 and -50 was determined by exposure of samples to air at 1000°C. The samples were removed from a furnace after each 25-to 75-h exposure. Figure 4.1 is a plot of weight gain due to oxidation in sample IC-50 as a function of exposure time at 1000°C. The modified aluminide showed a parabolic oxidation and exhibited no apparent spalling. The total weight gain was 0.6 mg/cm² after a 571-h exposure. The oxidation rate of the aluminide was much lower than that of stainless steels and commercial superalloys. The good oxidation resistance of IC-50 resulted from formation of aluminum oxide films, which protect the base metal from excessive oxidation.

Fig. 4.1. Weight gain in sample IC-50 as a function of exposure time at 1000°C in air.

The modified aluminide was further alloyed with 10 at. % Fe, which was designated as IC-63. This aluminide was readily fabricated into 0.8-mm-thick sheets by repeated cold rolling, with intermediate anneals at 1050°C. Tensile properties of IC-63 were determined as a function of test temperature. Figure 4.2 compares the yield strength of IC-63 with boron-doped Ni₃Al (500 ppm B), iron-modified IC-14, and carbide-strengthened IC-32. The yield strength of commercial wrought alloys, such as Hastelloy X and type 316 stainless steel, is also included in the plot for comparison. The yield strength of the aluminides increased as the temperature rose and peaked around 600°C. As a result of this increase, the aluminides were much stronger than the commercial alloys at elevated temperatures. Figure 4.2 shows that Ni₃Al can be effectively strengthened by macroalloying. The carbide-strengthened aluminide IC-32 has the best strength at temperatures to 700°C; above that temperature the modified IC-63 is the strongest of the aluminides.

Fig. 4.2. Comparison of yield strength as a function of temperature of the aluminide alloys (IC-14, -63, and -32) with boron-doped Ni₃Al and commercial wrought alloys Hastelloy X and type 316 stainless steel.

Structural features in modified IC-63 were studied by transmission electron microscopy (TEM). The specimens were well recrystallized before thinning by electropolishing. Preliminary results indicate no second-phase particles were formed in this modified aluminide.

4.1.2 Weldability of aluminides — W. Jemian* and S. A. David

We are continuing to investigate the weldability of aluminides to understand the development of weld microstructure, to understand cracking behavior, and to seek the means to overcome cracking. As reported earlier, successful full penetration welds in IC-25 (Ni-10.7 Fe-9.8 Al-0.5 Mn-0.5 Ti-0.05 B, wt %) can be made in a very narrow range of welding speeds and focusing conditions by the electron beam welding (EBW)

*Auburn University, Auburn, Alabama.

process. Recent work has shown that this narrow range of welding conditions for successful welds can be expanded by using a preheat of 450°C during welding, as indicated by the dashed line in Fig. 4.3. Efforts are also under way to conduct interrupted solidification and phase stability experiments to determine the development of microstructure in IC-25 aluminide when subjected to weld thermal cycles. These experiments will be followed by thermal simulation experiments with the Gleeble thermo-mechanical test system, and the results will be correlated with those of the interrupted phase stability experiments.

Fig. 4.3. Weldability of alloy IC-25 as a function of welding speed and beam defocusing number. Dashed line indicates that preheated material did not crack.

4.1.3 Corrosion of aluminides in sulfidizing environments — H. Inouye

Limestone is added as a sulfur acceptor with combusting coal to keep the sulfur emission low in AFBCs. At bed temperatures of about 900°C, the limestone calcines to CaO, then reacts with SO₂ to form CaSO₄. Deposits of CaSO₄ are reported to cause accelerated oxidation-sulfidization of in-bed components.

An initial test was conducted to assess the resistance of Ni_3Al and Fe_3Al to the oxidation-sulfidization reactions caused by reagent grade CaSO_4 . Because this CaSO_4 simulates but does not duplicate the CaSO_4 deposits from an AFBC, control specimens of common alloys were also tested under the same conditions to permit a comparative evaluation. Alloy strips measuring about $0.6 \times 3 \times 12.25$ mm were preoxidized 96 h in air, encapsulated with dehydrated CaSO_4 in evacuated quartz capsules, then heated for 168 h at 871°C (1144 K). Under these conditions the CaSO_4 dissociates to CaO , SO_2 , and O_2 . The equilibrium partial pressures of SO_2 , O_2 , and S_2 , based on literature data, are 0.253, 0.131, and 2.53×10^{-18} Pa (2.5×10^{-6} , 1.3×10^{-6} , and 2.5×10^{-23} atm), respectively.

The corrosion resistance in terms of postexposure weight changes and room-temperature bend tests is summarized in Table 4.1. The results show that both the high-nickel aluminides had the highest weight gains and were completely embrittled by the CaSO_4 . The brittle behavior of Fe_3Al is a characteristic of the alloy and is not caused by the CaSO_4 exposure. Future tests will include alloys with various Ni,Fe contents and other test conditions.

Table 4.1. Corrosion of alloys by CaSO_4 at 871°C (1144 K)

Alloy	Weight change (10^{-4}g/cm^2)		Bend angle (deg)	
	Control	Control + CaSO_4	Control	Control + CaSO_4
Hastelloy X	1.9 ^a	1.9	180	180
Type 304 SS	3.0 ^a	-9.4	180	180
Fe_3Al	1.3 ^a	2.0	0	0
Modified Ni_3Al ^b	6.0 ^c	19	180	0
$\text{Ni}_3\text{Al} + 10\text{ Fe}$ ^d	11.2 ^c	431	180	0

^aOxidized 96 h at 800°C .

^bAlloy IC-50.

^cOxidized 96 h at 1000°C .

^dAlloy IC-63.

4.2 Materials for Coal Conversion

R. R. Judkins

4.2.1 Mechanisms of erosion-corrosion in coal conversion environments — P. J. Ficalora and J. R. Keiser

The purpose of our investigation is to understand the process of erosion under conditions that exist in coal conversion environments. The experiment involves the use of a scanning electron microscope (SEM) to observe in situ the damage on a metal caused by single-particle impacts. The particles are 0.0343-cm-diam ($0.0135^{+0.00001}_{-0.00000}$ -in.) tungsten carbide balls shot at the metal surface (in the SEM) from a miniature air rifle. The experimental variables include the metallurgical nature of the metal (surface), impact velocity, impact angle, gaseous environment, and temperature. To date, the following has been accomplished:

1. The SEM was installed, and the unit is fully operational.
2. A miniature air rifle, whose principle of operation is based on a rotary breech mechanism, was constructed and tested. The feed mechanism is based on the gravity feed of a single particle from a hopper into a cylindrical breech. A 90° rotation of the breech puts the particle in line with the gun tube: a 0.0406-cm-ID (0.016-in.) stainless steel syringe tube. A high-pressure gas pulse is then used to fire the particle. When this air rifle was tested, we encountered difficulties during the loading sequence; the particles would not gravity feed into the cylindrical breech because of the static charge on the particles, which caused them to adhere to the wall of the hopper. To provide for a feed mechanism in which a particle could be pushed into a breech, a second air rifle was designed, constructed, and tested. The air rifle consists of a set of dovetail blocks. The gun tube (0.0406-cm syringe tube) and particle chamber (0.0406-cm syringe tube) are mounted on one of the dovetail blocks in the same plane. This plane is perpendicular to the direction in which the blocks can be translated. The second block contains the breech, which is in the same plane as the gun tube and particle chamber. To load the rifle, the particle chamber is filled with particles, and a plunger is placed in the tube behind the last particle loaded. The block containing the gun tube and chamber is translated until the particle chamber comes

into coincidence with the breech. At that time one particle is pushed into the breech, which can accommodate only one particle. The block is then translated to bring the gun tube into coincidence with the breech, and the gun is fired. The entire air rifle will be mounted inside the SEM chamber, and a rotary feedthrough and a set of bevel gears will provide the necessary motion for loading.

To test this gun, the trigger system from a commercial air pistol was adapted so that it could provide the gas pulse necessary to fire a particle. A 6.2-MPa (900-psi) gas pulse was used. Particles were successfully loaded and fired at a gold foil at a normal impact angle.

An examination of the impact craters on the surface of the gold foil indicated that the particle velocity was not very high. The system for measuring the particle velocity is not yet constructed, so the above conclusion is very qualitative. A calculation of the cross-sectional areas of the particle and the gun tube bore showed that the particle occupied only 70% of the tube area. Hence, there was a 30% blow-by. The gun tube was changed to a 0.0368-cm-ID (0.0145-in.) syringe tube. This change decreases the blow-by to 10%. Figure 4.4 shows impact craters on a gold surface created under 30% (*right side*) and 10% blow-by conditions.

M-16956

Fig. 4.4. Craters on a gold surface caused by the impact of 0.0343-cm-diam tungsten carbide balls under 10% (*left side*) and 30% (*right side*) blow-by conditions.

The velocity of the particle will be measured by determining the flight time between two light beams separated by a known distance. This system is being designed and constructed by the ORNL Instrumentation and Controls Division.

4.2.2 Investigation of corrosion in coal liquefaction plants — J. R. Keiser and A. R. Olsen

During this quarter, a paper entitled "Corrosion Sample Studies in Coal Liquefaction Pilot Plants" was presented at the National Association of Corrosion Engineers Corrosion/83 conference, and an article on coal liquefaction plant fractionator corrosion was published in the U.S. Department of Energy (DOE) newsletter, *Materials and Components in Fossil Energy Applications*. For the first of these papers, corrosion sample data from four pilot plants were collected, and results for similar vessels were compared. The data for nine vessel types were published in the paper, but the results for only four of the vessel types are described here.

The reactor and reactor effluent separator generally operate under similar temperature and pressure conditions, so the results shown in Fig. 4.5 for the reactor are typical of both vessels. The sulfur content of the bituminous coals processed at the liquefaction pilot plants is generally 3 to 4%; consequently, sulfidation was a potential problem for low-chromium alloys above 260°C (500°F). Figure 4.5 shows that corrosion rates for alloys containing 12% Cr could be as high as 0.6 mm/year (24 mils/year); to ensure a corrosion rate below 0.25 mm/year (10 mils/year), it is necessary to use a steel with 18% or more chromium.

The overhead product from the reactor effluent separator is fed to a high-pressure condensate drum, in which temperatures remain above 260°C (500°F). Figure 4.6 shows that 12% Cr alloys could have an unacceptably high corrosion rate, but austenitic stainless steels have demonstrated corrosion rates of less than 0.3 mm/year (12 mils/year). The elevated temperature and relatively high concentrations of sulfur and chlorine compounds make this a very corrosive environment.

Fig. 4.5. Corrosion rate versus chromium content for samples exposed in reactor vessels of coal liquefaction pilot plants.

Fig. 4.6. Corrosion rate versus chromium content for samples exposed in high-pressure condensate drums at coal liquefaction pilot plants.

The underflow from the reactor effluent separator fed a lower pressure flash drum. Because a fairly high-melting slurry was being handled, the temperature was kept above 370°C (700°F). Although the temperature was high, most of the corrosive gases were flashed off in a previous separation, so corrosion rates for a given chromium concentration (Fig. 4.7) were lower than in previous vessels. From the limited data shown, the slurry appears to be less corrosive than the vapor.

Another area in which a large number of data have been collected is the 215 to 260°C (420–500°F) region of the fractionation column. This is the area in which the amine hydrochloride corrosion problem has been most severe. Unlike most other areas of the plant, the corrosion rate does not have a direct relationship with the chromium content of alloys tested. Instead, there is a regular pattern between the nickel and molybdenum content as shown in Fig. 4.8. The one exception to this pattern is the data point for Incoloy 800.

Fig. 4.7. Corrosion rate versus chromium content for samples exposed in intermediate-pressure flash drums at coal liquefaction pilot plant.

Fig. 4.8. Corrosion rate versus nickel plus molybdenum content for samples exposed in the 215 to 260°C region of fractionation columns at coal liquefaction pilot plant.

4.3 Investigation of Gas-Metal Reactions in Cyclic Oxidizing and Reducing Atmospheres and the Effect of Sulfate Deposits on Corrosion

J. H. DeVan and P. J. Ficalora

The experiment to determine the effect of a cyclic oxidizing-sulfidizing environment on the rate of corrosion of a heated metal specimen is continuing, and the measurement system is completely functional. The oxidation-sulfidation of nickel was studied under the following conditions:

Specimen: nickel

Specimen temperature: 600°C

Gas temperature: 600°C

Gas pressure: $P_{\text{SO}_2} = 13 \text{ kPa (100 torr)}$

$P_{\text{O}_2} = 13 \text{ kPa (100 torr)}$

Gas pulse time: 0.3 ms/s for each gas

Background pressure: reaction chamber, 1.3 mPa (10^{-5} torr)
beam chamber, 4.5 Pa

Measurement interval: 10 min

Exposure per interval: 3.6 s per interval

Total number of intervals: 300

Total exposure: 18 min

The data were converted into the plot function for a parabolic process,

$$[x_0 - C/R]^2 ,$$

where

- x_0 = the specimen thickness at $t = 0$,
= 0.018 cm,
- C = $\rho L/W = 1.6 \times 10^{-5} \Omega \cdot \text{cm}$,
- $\rho_{600^\circ\text{C}}(\text{Ni})$ = resistivity = $37.86 \times 10^{-6} \Omega \cdot \text{cm}$,
- L = distance between voltage taps,
= 1.417 cm,
- W = specimen width,
= 0.338 cm,
- R = measured resistance.

The plot function gave an excellent linear fit with time (Fig. 4.9). The slope gave a rate constant k_p of $5.0 \times 10^{-6} \text{ cm}^2/\text{s}$. Assuming that the density of the product is equal to the average of the densities of NiO (7.45 g/cm^3) and Ni_3S_2 (5.82 g/cm^3), the rate constant can be converted to

$$k_p = 1.1 \times 10^{-7} \text{ g}^2/(\text{cm}^4 \cdot \text{s}) .$$

The oxidation-sulfidation of nickel has been determined under normal conditions of flowing premixed sulfur dioxide and oxygen over a specimen. The parabolic rate constant, measured under similar temperature (603°C) and pressure [$P_{\text{SO}_2} = 21 \text{ kPa}$ (163 torr), $P_{\text{O}_2} = 10.5 \text{ kPa}$ (81 torr)] conditions is 1.0 to $4.5 \times 10^{-8} \text{ g}^2/(\text{cm}^4 \cdot \text{s})$ (ref 1). The agreement of the

Fig. 4.9. Oxidation-sulfidation rate of nickel.

value obtained in this work and the literature value is quite good. This leads us to conclude that a rapidly cycling environment does not affect the rate of oxidation-sulfidation.

4.4 Materials for Molten Carbonate Fuel Cells

P. T. Carlson

The purpose of this task is to define and study the mechanisms that control the corrosion of anode and cathode current collector materials in molten carbonate fuel cells. The major objectives of the program are to

- (1) identify the reaction products formed between carbonate salt and

iron, nickel, and chromium under oxidizing conditions (cathode side) and (2) measure the solubilities of iron oxide in the carbonate salt under acidic (cathodic) and basic (anodic) conditions. Our approach to the first objective uses differential thermal analysis-thermogravimetric analysis (DTA-TGA) to establish the phase relationships between Li_2CO_3 - K_2CO_3 and iron, nickel, and chromium, respectively. The second objective requires the construction of an enclosed furnace and crucible for solubility studies of iron oxide in carbonate salt in the presence of air and CO_2 (oxidizing conditions) and $\text{H}_2 + \text{CO}$ (reducing conditions).

4.4.1 Investigation of the mechanisms of molten salt corrosion of candidate materials for molten carbonate fuel cells - J. H. DeVan and J. R. Keiser

We have continued the DTA-TGA experiments to study phase equilibria and reaction kinetics involving structural metals (viz., chromium and iron) and the reference fuel cell salt (62 mol % Li_2CO_3 -38 mol % K_2CO_3). The tests are being conducted in nickel crucibles lined with gold foil at temperatures between the salt melting point (480°C) and the proposed fuel cell operating temperature (650°C). Aliquots of finely divided metal are mixed with granular Li_2CO_3 - K_2CO_3 , and time-temperature traces are being recorded under two conditions of controlled oxygen partial pressures, air and flowing CO - CO_2 mixtures, at atmospheric pressure.

Data on the phase equilibria and other thermodynamic properties of the Fe-LiKCO_3 and Cr-LiKCO_3 systems are required to interpret the DTA experiments now under way. As a first step we have examined information available on ternary compounds lying within the composition field bounded by Li , Me , Li_2O , and Me_xO_3 , where Me designates either Fe or Cr . Literature searches identified the list of compounds and melting temperatures shown in Table 4.2 (refs. 2-6). The standard enthalpies and entropies of formation of the compounds are listed in Table 4.3 (refs. 7-8). Data in the Li-Cr-O system were taken from the recent thermodynamic review by Lindemer, Bessman, and Johnson;⁷ we also applied

Table 4.2. Composition and melting temperature of solid phases formed in the Li-Fe-O and Li-Cr-O systems

Compound	Melting temperature (°C)	Source
Li ₅ FeO ₄	1135	<i>a</i>
LiFeO ₂	1617	<i>b</i>
LiFe ₅ O ₈	1600	<i>b</i>
Li ₂ CrO ₄	516	<i>b</i>
LiCrO ₂	>1500	<i>c, d</i>
Li ₃ CrO ₄	750	<i>e</i>

^aH. Takeshita et al., "Mass Spectrometric Study of the Evaporation of Li₅FeO₄ as a Corrosion Product in the Compatibility Experiment of Li₂O Pellets with Fe-Ni-Cr Alloys," *J. Nucl. Mater.* **78**, 281-88 (1978).

^bE. M. Levin, C. R. Robbins, and J. F. McMurdie, *Phase Diagrams for Ceramists*, American Ceramic Society, Columbus, Ohio (1964).

^cT. Kurasawa et al., "Reaction of Several Iron- and Nickel-Based Alloys with Sintered Li₂O Pellets," *J. Nucl. Mater.* **80**, 48-56 (1979).

^dG. Izquierdo and A. R. West, "Phase Equilibria in the System Li₂O-Cr₂O₃-SiO₂," *J. Am. Ceram. Soc.* **62**, 136-237 (1979).

^eK. Niki and H. A. Laitinen, "Stability of Li₃CrO₄ and Ba₂CrO₄ in KCl-LiClMeH," *J. Inorg. Nucl. Chem.* **37**, 91-95 (1975).

their calculational techniques to enthalpy and entropy determinations for compounds in the Li-Fe-O system for which we could find no published values.

Table 4.3. Thermodynamic properties of ternary compounds in Fe-Li-O and Cr-Li-O systems

Compound	Property		Source
	Enthalpy (ΔH_{298}°) (kJ/mol)	Entropy (ΔS_{298}°) [J/(mol·K)]	
Li ₅ FeO ₄	-1950	-412 ^a	b
LiFeO ₂	-750	-186 ^a	c
LiFe ₅ O ₈	-2550 ^a	-741	c
Li ₂ CrO ₄	-1394	-346	b
LiCrO ₂	-928	-193	b
Li ₃ CrO ₄	-1669	-390.7	b

^aEstimated by authors.

^bT. B. Lindemer, T. M. Besmann, and C. E. Johnson, "Thermodynamic Review and Calculations - Alkali Metal Oxide Systems with Nuclear Fuels, Fission Products, and Structural Materials," *J. Nucl. Mater.* **100**, 178-226 (1981).

^cD. D. Wagman et al., "Compounds of Uranium, Protactinium, Thorium, Actinium, and the Alkali Metals," in *Selected Values of Chemical Thermodynamic Properties - Series 1*, National Bureau of Standards Technical Note 270-8 (PB 81-223463), 1981, table 98, p. 21.

The compatibility of Li₂O with Fe-Cr-Ni alloys is important to the development of fusion reactors. Experimental studies supporting this development have shown that LiCrO₂ is the primary reaction product when Li₂O is exposed to austenitic stainless steel to at least 800°C (refs. 4,9). The oxygen partial-free energies of the ternary lithium compounds are compared in the Ellingham diagram in Fig. 4.10. At 650°C LiCrO₂ is stable in the presence of Li₂O over the oxygen pressure range 2×10^{-35} Pa $\leq P_{O_2} \leq 2 \times 10^{-1}$ Pa, a range that is germane to the anode

Fig. 4.10. Ellingham diagram showing oxygen partial free energy (μ_{O_2}) for Li-Cr-O compositions lying between lithium and CrO_3 . (Note that $\mu_{O_2} = RT \ln P_{O_2}$). The melting temperatures of solids are shown at the top of the figure, and isobars for lithium pressure are shown as dashed lines. Source: T. B. Lindemer, T. M. Besmann, and C. E. Johnson, "Thermodynamic Review and Calculations — Alkali Metal Oxide Systems with Nuclear Fuels, Fission Products, and Structural Materials," *J. Nucl. Mater.* **100**, 178–226 (1981).

side of the carbonate fuel cell. However, at higher oxygen pressures at the cathode side, the Li_3CrO_4 and Li_2CrO_4 compounds should be predominant. On the basis of the melting temperatures shown in Table 4.2, the latter compound will be liquid at the 650°C fuel cell operating temperature. Figure 4.11 shows a phase diagram for the Li-Cr-O system based on the Ellingham diagram in Fig. 4.10. Experiments of Izquierdo and West have confirmed the calculated equilibrium of Li_2O and Cr_2O_3 - LiCrO_2 (ref. 5). Also, the calculated equilibrium of Li_2O and chromium with LiCrO_2 is in agreement with the experiments of Kurasawa et al.⁴

Fig. 4.11. Li-Cr-O ternary equilibrium diagram for $T < 789$ K. Source: T. B. Lindemer, T. M. Besmann, and C. E. Johnson, "Thermodynamic Review and Calculations — Alkali Metal Oxide Systems with Nuclear Fuels, Fission Products, and Structural Materials," *J. Nucl. Mater.* **100**, 178–226 (1981).

The properties in Table 4.3 were used to calculate phase equilibria for the Fe-Li-O system between 750 and 1100 K. On the basis of the Ellingham diagram in Fig. 4.12, at the 650°C fuel cell temperature, the compounds Li_5FeO_4 and LiFeO_2 are stable only at oxygen pressures below 10^{-19} Pa (10^{-24} atm) and 10^{-22} Pa (10^{-27} atm), respectively; however, the compound Li_5FeO_3 will coexist with LiFeO_2 at an oxygen pressure as low as

Fig. 4.12. Ellingham diagram showing oxygen partial free energy for Li-Fe-O compositions lying between lithium and Fe_2O_3 .

10^{-19} Pa (10^{-24} atm) and with Fe_2O_3 at 10^5 Pa (1 atm). None of these compounds melt within the fuel cell operating range. The phase diagram for the Fe-Li-O system at 650°C is shown in Fig. 4.13. Note that all the ternary compounds in this system lie on a tie line between Li_2O and Fe_2O_3 ; therefore, iron in all cases is in the +3 oxidation state. As shown in Fig. 4.11, the equilibrium of LiFeO_2 with FeO at 650°C gives rise to an equilibrium of iron with LiFe_5O_8 at temperatures not exceeding 630°C .

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Fig. 4.13. Li-Fe-O ternary equilibrium diagram for $T = 923$ K (650°C).

We expect to complete the DTA-TGA experiments this fiscal year, at which time we will begin solubility studies of structural metal oxides (e.g., Fe_2O_3 and Cr_2O_3) in the reference fuel cell electrolyte. The design of the solubility apparatus has been completed, and procurement of the needed components has started. Potentiometric techniques will be used to measure and control the oxidizing potential (oxide ion activity) of the salt. An electrochemical cell with a solid-state electrolyte conductive to sodium ions has proved effective in measuring the Na_2O activity in Na_2SO_4 and Na_2CO_3 salts. We are designing a similar cell that is conductive to lithium ions to measure the Li_2O activity in the Li_2CO_3 - K_2CO_3 salt. The cell uses an Li-Na β -alumina solid electrolyte and a reference junction of molten Li_2CO_3 - K_2CO_3 maintained under a controlled mixture of CO_2 and O_2 . Studies are under way to evaluate the compatibility of the proposed electrolyte with the Li_2CO_3 - K_2CO_3 salt at temperatures up to 650°C .

4.5 Ceramics for Heat Engines and Heat Recovery

R. A. Bradley

4.5.1 Silicon carbide powder synthesis* — G. C. Wei, L. A. Harris, and C. R. Kennedy

Synthesis and characterization of silicon carbide continued, and a paper was drafted on the synthesis of powders by the gel processes. As previously reported, the colloidal-silica-pitch process produced sinterable SiC powders (batch 512) comparable to the commercial Starck SiC[†] and Fujimi's Acheson SiC[‡] powders.¹⁰ Two new batches (516 and 517) of the colloidal-silica-pitch gel SiC powder were synthesized. The processing and formulation parameters of these batches were essentially the same as those of batch 512 except that the boron dopant content was varied and the firing atmosphere was changed from nitrogen (used in batch 512) to argon.

*Work sponsored jointly by the AR&TD Fossil Energy Materials Program (AA 15 10 10 0) and the Office of Vehicle and Engine R&D, Conservation and Renewable Energy (EE 01 04 00 0).

[†]Starck SiC, grade A-10; product of Hermann Starck Company, Goslar, Federal Republic of Germany.

[‡]GC10k SiC, product of Fujimi Abrasive Supply Company, Ltd., Nagoya, Japan.

The specific surface areas of these two batches were determined as 25.5 and 9.5 m²/g, respectively. Since "large" (~20-μm) spherical agglomerates consisting of ultrafine SiC particles observed in the colloidal-silica-pitch SiC powder might be detrimental to sinterability, we attempted to remove them by using a centrifugal classifier.* Initial results showed that, although sizing above about 10 μm was possible, most of the sub-micron SiC particles were carried to the filter bag. Adjustment in the classifier wheel speed and air flow rate may help to minimize the loss of submicron particles in subsequent runs. Sinterability of the classified colloidal-silica-pitch SiC powder (samples S-65-1 and -3 in Table 4.4) was insufficient, probably because of the loss of the submicron-size particles.

New batches of colloidal-silica-sugar gel SiC with various silica-to-sugar ratios and polymeric precursor SiC powders doped with boron and carbon were made (Table 4.5). Sintering results are shown in Table 4.4. The colloidal-silica-sucrose SiC powder (batch G16A) was sintered to over 95% density (sample S-61-9), comparable to that of the Starck SiC powder. Scanning and transmission electron microscopic analysis of the colloidal-silica-sucrose SiC showed round submicron SiC particles (Fig. 4.14). The microstructure of the sintered colloidal-silica-sucrose SiC (2100°C for 2 h in Ar) consisted of elongated SiC grains (~50 μm), with residual pores at grain boundaries (Fig. 4.15).

In the case of polycarbosilane SiC powder (batches T-15 and -16), the HF acid treatment reported previously did not reduce the oxygen content (~10 wt %) (ref. 11). However, doping with resin in acetone followed with reduction at 1600°C for 30 min in argon did reduce the oxygen content of this powder to less than 0.5 wt %. The surface area of the purified powder was 3 m²/g. The polycarbosilane SiC so purified and doped with 0.8 wt % B and 1 wt % C densified to over 99% when hot pressed at 2000°C and 62 MPa (sample SC-111 in Table 4.5). The microstructure consisted of elongated grains (~50 μm) in a fine-grained matrix (Fig. 4.16).

*Centrifugal classifier; model 100 MZR, Alpine American Company, Notick, Mass.

Table 4.4. Sintering response of various SiC powders

Sample	SiC	Density (% of theoretical)	Remarks
S-59-1	G16A	90.1	<i>a, b</i>
S-59-2	G16B	74.2	<i>a, b</i>
S-59-3	G16C	80.0	<i>a, b</i>
S-59-4	G16A	94.1	<i>a, c</i>
S-59-5	G16B	75.0	<i>a, c</i>
S-59-6	G16C	87.4	<i>a, c</i>
S-59-7	A-10	89.0	<i>a, c</i>
S-61-1	G16A	76.9	<i>d</i>
S-61-2	G16B	67.6	<i>d</i>
S-61-3	G16C	64.1	<i>d</i>
S-61-4	G16A	94.5	<i>d</i>
S-61-5	G16B	67.9	<i>d</i>
S-61-6	G16C	80.6	<i>d</i>
S-61-7	A-10	94.2	<i>d</i>
S-61-8	G16A	90.8	<i>d, e</i>
S-61-9	G16A	95.3	<i>d, f</i>
S-62-1	I15	57.6	<i>d</i>
S-62-2	I15	58.5	<i>d</i>
S-63-1	I16	46.9	<i>a</i>
S-63-2	I16	47.6	<i>a</i>
S-64-1	G17A	68.1	<i>a, g</i>
S-64-3	G17B	71.0	<i>a, g</i>
S-65-1	516	70.4	<i>a, g, h</i>
S-65-3	516	70.1	<i>a, g, i</i>
SC-111	I15	99.1	<i>j</i>

*a*Fired at 2050°C in argon for 2 h.

*b*Boron, 0.8 wt %.

*c*Boron, 0.8 wt %, and resin, 2 wt %.

*d*Fired at 2100°C in argon for 2 h.

*e*Sample S-59-1 refired.

*f*Sample S-59-4 refired.

*g*Resin, 2 wt %.

*h*Classified, <2 μm .

*i*Classified, <5 μm .

*j*Hot pressed at 2000°C and 62 MPa for 45 min.

Table 4.5. Processing parameters and surface areas of SiC powders

Parameter	G16A	G16B	G16C	G17A	G17B
$\text{CH}_3\text{Si}(\text{OCH}_3)_3$, mL	0	0	0	72	72
H_2O , mL	100	100	100	120	120
Colloidal silica, g	30	30	30	0	0
Sucrose, g	45	45	45	31.5	31.5
Boric acid, g	3.4	3.4	3.4	0.64	0.64
NH_4OH , mL	0	0	0	35	35
Drying	Freeze	Freeze	Freeze	Freeze	Freeze
Calcination (in Ar), °C	400	400	400	400	400
Reaction (in Ar), °C/h	1400	1500	1600	1400	1500
	1600	1600		1600	1600
Surface area, m^2/g	13.8	17.7	10.7	4.1	3.7

(a)

Fig. 4.14. (a) Scanning electron micrograph of the colloidal-silica-sucrose SiC powder (batch G16A). (b) Transmission electron micrograph of the colloidal-silica-sucrose SiC powder (batch G16A).

(b)

Y-190423

Fig. 4.15. Microstructure of sintered colloidal-silica-sucrose SiC (sample S-61-9).

Y-190421

Fig. 4.16. Microstructure of hot-pressed polycarbosilane SiC (sample SC-111).

The particle sizes and distribution of various SiC powders were measured by sedimentation (the particle size actually refers to agglomerate size). The results are shown in Fig. 4.17. The colloidal-silica-sucrose powder has an average particle size smaller (but with a wider distribution) than that of the Starck A-10 powder. We believe that the wide particle size distribution in the colloidal-silica-sucrose or -pitch and polycarbosilane gel SiC powders results in the elongated grains observed in the sintered specimens. Since the SiC particle size is primarily determined by the carbon particle size, ways to control the particle size distribution of carbon in the raw reactants must be established.

Dispersion of Starck SiC powder in a variety of liquids was investigated. A synthetic lubricating oil produced good dispersion. This synthetic oil may be used in sedimentation classifying to remove coarse particles and in centrifugal casting to produce uniform, high-density green bodies.

Fig. 4.17. Particle size distribution of various SiC powders: A, Starck A-10; B, batch G16A; C, batch 512; D, batch G2; and E, batch I15.

Characterization of the spherical agglomerates formed in the ultrafine colloidal-silica-pitch SiC powders is continuing. These agglomerates were present even in the precursor material after carbonization at 500°C. This is the material that is subsequently heated to 1600°C and results in ultrafine SiC powders. The formation of these spherical agglomerates is thought to be a consequence, at least in part, of the pyrolysis of the pitch with the attendant evolution of gas bubbles and the formation of semicoke via mesophase production. Additional studies are planned to explore this thesis for spherical agglomeration in colloidal systems.

During this quarter, TEM of SiC powders was initiated. Specimens for TEM analysis were prepared by depositing the powders on carbon substrates supported on standard TEM grids. It should be noted that, since the TEM SiC powder specimen probably excludes large particles and/or agglomerates ($>5-10\text{ }\mu\text{m}$), size analyses based on TEM are biased. However the TEM of SiC powders does permit detailed analysis of the submicron particle fraction. The TEM characterization is currently being performed on a 1-MV high-voltage electron microscope. Electron diffraction is used to identify the specific SiC polymorph comprising the powders.

To date three SiC powders have been examined by TEM, namely, A-10 batch 2503, G1, and G16A. Agglomeration has been observed in all three powders. Typically, these agglomerates are composed of fine particles and crystals of SiC. Figure 4.18 is a transmission electron micrograph of such an agglomerate that consists exclusively of submicron-size particles. In addition to the agglomerates and individual particles shown, we have seen unusual looking fibers (Fig. 4.19). These fibers almost appear to have grown as miniature boules that "neck" down and then continue growing. Electron diffraction data obtained from these fibers are being studied; plans are under way to characterize all in-house SiC powders by the above techniques.

C-26325

Fig. 4.18. Transmission electron micrograph of submicron SiC particles agglomerated together. Preliminary electron diffraction data suggest that particles are individual crystals.

C-26320

Fig. 4.19. Transmission electron micrograph of unusual SiC fiber in SiC powder.

4.5.2 Ceramic fabrication and microstructure development* — G. C. Wei

Studies on hot pressing of particulate-reinforced SiC composites (using Starck A-10 SiC matrix) were continued. Second-phase particles were added to the SiC powder, either from solution or by solid-state mixing. Three different types of toughening agents were investigated: metal (molybdenum, tungsten, etc.), ceramic (TiC or BN), and transformation ($\text{Al}_2\text{O}_3\text{-ZrO}_2$). Hot-pressing results are presented in Table 4.6.

Table 4.6. Results of fabrication of particulate-reinforced SiC composite

Sample	Additives (wt % of SiC)	Density (Mg/m^3)	Theoretical density (%)	Hot-press temperature (°C)
SC-112	B, 0.8; resin 2	3.1918	99.4	2000
SC-113	TiC, 2.5; BN, 5	2.5797	81.4	2000
SC-114	TiC, 2.5; BN, 5	2.6719	84.3	2000
SC-115	TiC, 1; B, 0.8; resin, 2	3.2044	96.2	1975
SC-116	$\text{Al}_2\text{O}_3\text{-ZrO}_2$, 25	3.2724	96.2	1975
SC-115A	TiC, 1; B, 0.8; resin, 2	3.2026	96.2	2000
SC-117	Mo, 2; B, 0.8; resin, 2	3.2387	99.6	2000
SC-119	$\text{Al}_2\text{O}_3\text{-ZrO}_2$, 5	3.1375	96.3	1975

Samples of SiC dispersed with low concentrations of molybdenum (sample SC-117) and with a low concentration of TiC (sample SC-115) and high concentrations of $\text{Al}_2\text{O}_3\text{-ZrO}_2$ (samples SC-116 and 119) were almost fully dense. All the specimens listed in Table 4.6 were made by hot pressing with a graphite die assembly, which consisted of semicylindrical inserts and rectangular punches instead of the conventional cylindrical die cavity and punches. This die minimizes machining and facilitates fabrication of near-net-shape bar specimens for the mechanical property characterization

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being performed in cooperation with P. F. Becher and M. K. Ferber (Sect. 4.5.4). The mechanical properties of these specimens at ambient and high temperatures are presented in that section; they are noted only briefly below. The four-point bend strength of the SiC-Mo system is appreciably (~15%) higher than that of sintered- α SiC, probably because of the residual stress produced by the thermal expansion mismatch between SiC and molybdenum. However, the fracture toughness of the SiC-Mo, SiC-W, Si-Ir, and SiC-TiC systems is not significantly higher than that of sintered- α SiC. This is probably because of the low concentration (<2 vol %) of the dispersed phase in SiC. As previously reported, silicon carbide with high concentrations of tungsten or molybdenum particles (samples SC-84, -84A, -85, and -85A) has densities that are less than 90% of theoretical and would not have sufficient strength.¹² The densification problem with high concentrations of metal particles dispersed in SiC is believed to be caused by the formation of metal borides that essentially deplete the boron required for densification of SiC polycrystals. This problem may be minimized by changing the sintering dopant from boron to aluminum. However, most refractory metals form alloys with aluminum, which would again deplete the sintering aid. In summary, stabilizing the higher concentration of metal particles in SiC, which is required for significant improvement in toughness and in dense SiC, depends on minimizing the reaction of the sintering aids with the metal.

The microstructure of SiC dispersed with a relatively low concentration of molybdenum particles (Fig. 4.20) (sample SC-117 in Table 4.6) consists of very fine (<1- μ m) metal particles in a fine-grained SiC matrix. The very fine metal particles were produced through the use of the solution addition described before.

It should be noted that SiC doped with a high concentration (20 vol %) of $\text{Al}_2\text{O}_3\text{-ZrO}_2$ showed a fracture toughness ($5 \text{ MPa}\cdot\text{m}^{1/2}$) nearly double that ($3\text{--}4 \text{ MPa}\cdot\text{m}^{1/2}$) of sintered- α SiC. The microstructure of the SiC doped with 20 vol % $\text{Al}_2\text{O}_3\text{-ZrO}_2$ consists of $\text{Al}_2\text{O}_3\text{-ZrO}_2$ distributed in a fine-grained SiC matrix (Fig. 4.21).

Y-191297

(a)

10 μm

Y-191298

(b)

10 μm

Fig. 4.20. Microstructure of an SiC-Mo composite (sample SC-117).
(a) As-polished. (b) Etched.

Fig. 4.21. Microstructure of an $\text{SiC-Al}_2\text{O}_3\text{-ZrO}_2$ composite (sample SC-97). Etched.

4.5.3 Fabrication of fiber-reinforced composites — A. J. Caputo, W. J. Lackey, and W. B. Stines

The purpose of this new task is to develop a ceramic composite having higher than normal strength and toughness yet retaining the normal ceramic attributes of refractoriness and high resistance to abrasion and corrosion. The ceramic fiber-ceramic matrix composites will be fabricated by infiltrating fibrous structures with vapors, which deposit on and between the fibers to form the matrix of the composite.

Background — Fiber composites are currently in the limelight as a result of exceptionally high toughness values recently achieved for silicon carbide fiber-reinforced glass ceramics. Since use of ceramics is frequently restricted because of inadequate toughness, any progress in the toughening of ceramics will greatly expand their potential market. However, a generic problem that must be overcome is that normal ceramic

fabrication processes tend to damage the fibers mechanically and chemically when they are consolidated within a ceramic matrix. The purpose of this task is to form the matrix by a comparatively low-stress low-temperature chemical vapor deposition (CVD) infiltration process that will avoid the pitfalls of conventional ceramic processing.

As reported previously, others have used CVD infiltration for fabricating ceramic composites.¹³ The vapor consolidation technique has been used to prepare fiber composites with matrices of carbon and ceramics such as SiC, Si₃N₄, B₄C, BN, and TiB₂.

Approach — Our initial goal is to demonstrate that a high-density ceramic composite matrix can be deposited by use of materials of high interest to the fossil community. After an initial brief assessment to identify the most promising fiber-matrix compositions, we will assess the preferred fiber dimensions, geometry, packing density, binder type and concentrations, and other processing variables.

Initial experimental efforts will be on the use of a vacuum-forming molding process to fabricate a low-density fiber bed suitable for vapor infiltration. Once the fiber bed is formed and dried, the matrix of the composite will be formed by CVD in a high-temperature furnace. We hope that a novel scheme of forcing the coating gases to flow through the fiber bed will substantially increase the deposition rate over the rates normally obtained in flowing the deposition gases across the surface to be coated. Important variables of the CVD process, such as temperature, gas composition, flow rate, and pressure, will be systematically altered to maximize matrix density and to obtain a microstructure consistent with the goal of fabricating high-toughness high-strength ceramic composites.

Status of experimental work — The installation of the vacuum forming equipment was completed last period. During this period the equipment was first tested by molding a part from carbon fibers. This part was acceptable, so the equipment appeared to be functioning properly. However, one modification was made to permit more uniformity in the molded parts. Since this system produced parts about 16.5 by 16.5 cm (6.5 by 6.5 in.), we decided that a smaller forming system was needed with the

limited amount of fibers and binder for the initial cursory formings. A standard laboratory-type funnel and filtering setup proved too small and too slow for producing uniform parts without laminations. Thus, an intermediate-size system was fabricated, which successfully produced uniform parts about 7.6 cm (3 in.) in diameter.

During this reporting period, delivery was completed of the previously ordered silicon carbide fibers. We now have silicon carbide fibers from three sources: SILAR brand from Arco Company, TOKAMAX from Tokai Carbon, and NICALON brand from Nippon Carbon. The SILAR and TOKAMAX materials are really whisker-type, being about 0.5 μm in diameter and 10 to 200 μm long, and the NICALON material is 10- to 15- μm -diam filament that has been chopped into 3-, 6-, or 9-mm lengths. We have also received limited quantities of the SiC-type binder (polycarbosilane) needed for the moldings. The larger amount (1 kg) of Nippon binder had different properties from the small quantity of experimental material received from another source. Not only did it contain large chunks rather than a uniform powder, but it appeared to be less soluble in various solvents (toluene and hexane). In addition, it had a more erratic weight-loss profile in a thermogravimetric analysis (TGA) in an argon atmosphere. The weight loss occurred between 350 and 800°C, compared with 200 to 700°C for our experimental binder, but the total loss was only 32% compared with 64%. A more striking difference was the comparison of the data when the TGA was run in an air atmosphere. The profile for our experimental binder was about the same as in argon, but the total weight loss was only 46% compared with 64% in argon. However, the Nippon binder had a substantial weight gain (could not be measured because it went off scale) between 200 and 350°C and essentially no weight gain or loss after that up to 1000°C. We concluded that the behavior of the binder in air at about 250°C was important because, as will be discussed below, the NICALON fibers gave a firm formed part when heated in air at 250°C but gave a soft, powdery part when heated in air to 130°C.

Initial moldings were made from all three fiber sources. When we used the SILAR whiskers, the polycarbosilane binder was dispersed in

methanol and added to the methanol-fiber slurry. After air drying to 100°C, the parts were quite fragile, and the solid binder dispersion was readily visible throughout the part. After heating to 1200 or 1500°C in argon, the parts were still quite fragile and powdery and were therefore unacceptable for infiltration. Dispersing the binder in methanol did not give a uniform binder content throughout the part.

TOKAMAX brand SiC whiskers from Tokai Carbon were used to fabricate parts with either a polycarbosilane or a phenolic resin-type binder. A part was formed from a 50-50 wt % mixture of whiskers and binder with the polycarbosilane binder dissolved in toluene. Adding this dissolved binder to the methanol-whisker slurry resulted in a much finer dispersion of the binder throughout the part. Other parts were formed with either a 5 or 50 wt % phenolic resin binder in a water slurry. The parts with 50% of either binder were firm enough to permit handling after air drying, but the part with 5% phenolic binder was fragile and powdery. After heating to 1200°C in argon, the parts with 50% of either binder were still firm, and the part with 5% binder was still fragile and powdery.

First attempts to fabricate parts from the NICALON fibers from Nippon Carbon were unsuccessful. These fibers were the filaments that had been chopped into 3-, 6-, or 9-mm-lengths. Thus, the fibers were very long (3000 to 9000 μm) compared with the whisker-type SiC (10 to 200 μm). Apparently, the high length-over-diameter ratio of the NICALON fibers (>200) prevented an acceptable dispersion of the fibers and resulted in severe "clumping." A typical food-type blender with a shearing blade was used to reduce the fiber length, which permitted an acceptable dispersion of the shorter fibers. Thus, a part was made with the blender and the NICALON fibers (starting length of 3 mm) with conditions previously used for the shorter SiC whiskers. This included dissolving the polycarbosilane binder in toluene and adding to the fiber-methanol slurry. In this case, the binder level was 25 wt %, since previous work showed 5% binder gave a fragile part and 50% gave a reasonably firm part. This part was successfully vacuum formed and air dried at 130°C, but the formed part was quite fragile and could not be picked up without damage to it. When a

portion of this material was heated to 1200°C in argon, it was reasonably firm. A portion of the soft material dried at 130°C was heated to 250°C in air in an attempt to cure some of the binder and thus give the part some firmness. This appeared to be successful because the part was quite rigid. Further processing of all the material will be done.

The installation of the CVD furnace is essentially complete. The glass reservoirs for the feed material were replaced with stainless steel reservoirs, which will operate at a slight pressure [21 to 35 kPa (3–5 psi)] and are surrounded by a constant-temperature water bath. If the water should inadvertently come in contact with SiCl_4 feed material, it would produce fumes of hydrochloric acid. The hydrogen and argon gas flows through the reservoirs and controls the flow rate of the feed material. Thus, the size and consistent operation of these metering valves are quite critical. The originally installed valves were unacceptable, but the replacement valves appear to be acceptable. A new, solid-type (soda-lime) vapor trap was installed to remove the corrosive off-gases in place of the cold trap-type scrubber for ease of operation. Thus, the furnace was assembled and is undergoing shakedown tests. Various vacuum leaks have been repaired, various water-flow switches have been replaced, and the temperature control system is now being checked out.

4.5.4 Mechanical behavior and strength of structural ceramics – P. F. Becher and M. K. Ferber

Several composite ceramic materials developed under the Work Breakdown Structure (WBS) Task Element ORNL-5.11(A) were evaluated. This included fracture toughness and slow crack growth measurements at 22°C. The materials studied included several SiC ceramics with dispersed-phase additions.

The first set of dispersed-phase-toughened SiC included small additions (typically <2 wt %) of dispersed fine (<2- μm) refractory metals or TiC particles. On the basis of toughening models involving crack deflection¹⁴⁻¹⁵ or bowing¹⁶ by second-phase particles, one expects that additions of 10 vol % or greater are needed to effect substantial toughening. As can be seen in Table 4.7, the critical fracture toughness

Table 4.7. Initial data showing sensitivity of critical fracture toughness of dispersed second phase in SiC to second-phase content

	Hardness (GPa)	K_{IC} indent (MPa·m ^{1/2})	K_{IC} , double cantilever beam specimen (MPa·m ^{1/2})
SiC			3.0–3.5
SiC–2 wt % Mo >99% TD	24.57	3.1 ± 0.4	
SiC–2 wt % W >99% TD	24.00	3.3 ± 0.6	
SiC–2 wt % Ir >99% TD		3.3 ± 0.2	
SiC–1 wt % TiC 95.8% TD	21.08	3.5 ± 0.5	3.2 ± 0.3
SiC–2.5 wt % TiC 97.1% TD	21.33	3.4 ± 0.2	
SiC–10 wt % [Al ₂ O ₃ –20 vol % (ZrO ₂ ·2 mol % Y ₂ O ₃)]	18.54	3.2 ± 0.2	
SiC–25 wt % [Al ₂ O ₃ –20 vol % (ZrO ₂ ·2 mol % Y ₂ O ₃)]	19.51	5.5 ± 0.3	5.4 ± 0.1

K_{IC} values of the dense SiC ceramic containing small amounts of a dispersed phase are comparable to those of conventional SiC ceramics. This is what the toughening models predict and indicates that larger dispersed-phase contents are needed. In the preparation of initial composites, Wei found that it was difficult to fully densify SiC with such levels of second-phase particle additions.^{17–18} Perhaps this was caused by the fact that boron as well as carbon must be added to SiC to achieve densification and that the refractory metals and possibly TiC readily form borides. This could deplete the boron level available to effect sintering of the SiC. This will be addressed in future processing studies.

The second group of dispersed-phase-toughened ceramics involved stress-induced phase transformation toughening^{19–21} by incorporating ZrO₂

particles. To prevent reaction between SiC and ZrO₂, the ZrO₂ particles were incorporated into Al₂O₃, and the mixed Al₂O₃-20 vol % (ZrO₂-2 mol % Y₂O₃) particles were dispersed in the SiC. Note that the Y₂O₃ is added to the ZrO₂ to control the stress-induced phase transformation in ZrO₂. Again, the amount of Al₂O₃-ZrO₂(Y₂O₃) added to the SiC will influence the toughness achieved, as illustrated in Table 4.7, which shows that K_{IC} increases with an increase in dispersed-phase content. It should be pointed out that alumina additions to SiC are effective densification aids but, when combined with certain impurities, increase the oxidation rates of SiC (refs. 22-23). The Al₂O₃-ZrO₂(Y₂O₃) addition also improves the densification of SiC (ref. 24). Preliminary oxidation tests at 1300°C suggest that this increased oxidation may not occur in these composites. Note that, in the absence of iron, potassium, sodium, and other impurities, alumina silicates are quite refractory and would not exaggerate the oxidation behavior of SiC (ref. 25).

4.5.5 High-temperature ceramic heat exchangers — V. J. Tennery and M. K. Ferber

During this reporting period the posttest analyses of the ceramic heat exchanger (HX) tubes tested in the Ceramic Recuperator Analysis Facility (CRAF) Test 4 were essentially completed. These analyses included both the microstructural examinations and the C-ring strength studies. In this test ten tubular ceramic elements were exposed to the combustion products of an acidic-ash coal (base-to-acid ratio of about 0.10) carried in a crude-derived No. 6 fuel oil. The use of the coal-oil mixture (COM) provided a convenient means for burning the coal in the existing combustion chamber of the Refractory Test Facility (RTF) (ref. 26). Initially, we anticipated that the highly refractory nature of the coal ash, as reflected by both the low base-to-acid ratio and high ash fusion temperature ($>1482^{\circ}\text{C}$), would produce a fairly erosive combustion environment with minimal fouling. However, significant coal slag deposits formed on all tubes during the high-temperature exposure.

Five of the ten tubular elements used in CRAF Test 4 were closed on one end (COE) and pressurized to about 689 kPa gage (100 psig). These pressurized tubes were included in the test to simulate the conditions

expected in advanced energy systems employing a pressurized high-temperature HX to isolate a hot gas turbine from relatively dirty combustion environments. In such systems a pressurized secondary working fluid (such as air, helium, or argon) heated by the HX is used to operate the turbine. The remaining five ceramic tubes in Test 4 were open on both ends (OBE) so that an internal air flow could be maintained through their inside diameters during the exposure. This latter configuration was used to approximate actual HX elements in a cross-flow configuration.²⁷ The specific materials included two tubes each (one COE and one OBE) of α -SiC, KT SiC, SC-2 SiC, and NC-430 SiC. An Si_3N_4 -bonded E10 tube (OBE), designated as CS SiC, and an AD 998 Al_2O_3 tube (COE) were also tested. Table 4.8 summarizes all tubular elements examined in CRAF Test 4.

Posttest microscopic analyses of all ceramic tubes revealed no major reactions between the coal slag and the tubular surface. However, the microstructure of the slag at the ceramic-slag interface varied significantly on the different tubular elements. For example, the slag remaining on the alumina tube contained two types of crystals dispersed in a glassy matrix (Fig. 4.22). The first type had a blocklike morphology and contained high concentrations of iron and nickel. These results were similar to those obtained for the Al_2O_3 exposed in CRAF Test 2 (ref. 28). The second crystal type was needlelike in appearance. The presence of silicon and aluminum in these crystals (as detected by energy-dispersive x-ray analysis) suggested that they were composed of an aluminosilicate compound. This conclusion was further substantiated by results of the x-ray diffraction studies, which revealed the presence of mullite ($3 \text{ Al}_2\text{O}_3 - 2 \text{ SiO}_2$) within the slag.

The slag remaining on the α -SiC tube also consisted of small crystals dispersed in a glassy matrix (Fig. 4.23). However, the blocklike crystals observed in the slag on the Al_2O_3 tube were almost entirely absent. The energy-dispersive x-ray spectrum of slag matrix [Fig. 4.24(a)] revealed major concentrations of silicon and aluminum and smaller amounts of potassium, titanium, and iron. These latter constituents were probably

Table 4.8. Materials, dimensions, and sources of ceramic tubes exposed in
Ceramic Recuperator Analysis Facility Test 4

Material	Tube designation ^a	Dimensions ^b (mm)			Source
		Length	OD ^c	ID ^c	
Siliconized SiC	KT-1 (COE)	431.8	26.01 ± 0.07	13.05 ± 0.04	Carborundum Resistant Materials Co., Niagara Falls, N.Y.
	KT-2 (OBE)	306.4	26.03 ± 0.06	13.33 ± 0.08	
	SC-2 SiC-1 (COE)	420.7	24.18 ± 0.53	18.96 ± 0.05	Coors Porcelain Co., Golden, Colo.
	SC-2 SiC-2 (OBE)	403.2	24.17 ± 0.10	16.92 ± 0.04	
	NC-430-1 (COE)	431.8	25.04 ± 0.05	18.72 ± 0.21	Norton Co., Worcester, Mass.
	NC-430-2 (OBE)	408.0	25.13 ± 0.08	18.72 ± 0.09	
Si ₃ N ₄ -bonded SiC	CS (OBE)	406.4	24.91 ± 0.15	14.89 ± 0.03	Norton Co., Worcester, Mass.
Pressureless- sintered SiC	α-SiC-1 (COE)	428.4	25.40 ± 0.05	18.90 ± 0.02	Carborundum Resistant Materials Co., Niagara Falls, N.Y.
	α-SiC-2 (OBE)	304.8	25.49 ± 0.10	18.82 ± 0.05	
High-purity alumina	Al ₂ O ₃ (COE)	431.8	25.58 ± 0.09	19.21 ± 0.05	Coors Porcelain Co., Golden, Colo.

^aCOE, closed on one end; OBE, open on both ends.

^bFor each tubular element, several measurements of the inner and outer diameters (ID and OD, respectively) were made at tube end used for air inlet during the actual exposure. The OD was also measured at several positions along each tube.

^cThe first number is the average, and the second is the standard deviation.

Fig. 4.22. Scanning electron micrograph of ceramic-slag interface associated with Al₂O₃ tube.

Fig. 4.23. Microstructural characteristics associated with ceramic-slag interface on α -SiC tube. (The cracks in the α -SiC tube reflect a polishing artifact.)

Fig. 4.24. Energy-dispersive x-ray spectrum for (a) slag matrix and (b) slag crystals shown in Fig. 4.23.

present as oxides in the glassy slag matrix. Finally, as indicated in Fig. 4.24(b), the slag crystals were apparently composed of an aluminosilicate compound.

The pretest and posttest C-ring fracture strengths were measured for the α -SiC, CS SiC, NC-430 SiC, and Al_2O_3 tubes. The test samples were loaded to failure at room temperature in air with an Instron* machine operating at a crosshead speed of 21.2 $\mu\text{m/s}$ (0.05 in./min). The exposed samples were oriented such that fracture occurred from the region that exhibited the greatest apparent reaction between the ceramic and the coal slag. The results (shown in Fig. 4.25) revealed no significant differences between the pretest and posttest strengths for either the α -SiC, NC-430 SiC, or Al_2O_3 . However, the strength of the CS SiC exhibited a significant increase after the test exposure. It is possible that the glazelike slag formation that remained on the CS SiC tube substantially reduced the severity of the intrinsic porosity. Such porosity was probably responsible for the low strength of the as-received material.

Fabrication of a laboratory-scale High Temperature Corrosion Facility (HTCF) was also completed this reporting period, and high-temperature strength tests were initiated. The HTCF is used to study high-temperature corrosion (including mechanical degradation) of C-ring samples exposed to various slag environments. This facility (shown in Fig. 4.26) is considerably more flexible than is the CRAF since strength measurements can be performed at elevated temperatures. The HTCF can also facilitate the collection of data related to the kinetics of the high-temperature corrosion processes. Initial studies are aimed at developing a better understanding of the corrosion mechanism(s) that were observed in the ceramic tubular elements exposed in CRAF Test 3 (ref. 29). Such information is essential if one is to establish in-service limitations for structural ceramics in HX applications involving coal combustion environments.

* Product of Instron Corporation, Canton, Mass.

Fig. 4.25. Summary of pretest and posttest C-ring data for tubes exposed in CRAF Test 4.

Fig. 4.26. Overview of high-temperature corrosion facility.

Table 4.9 gives the 1250°C C-ring fracture strength results for exposure times of 0 and 24 h in both air and basic slag environments. The data, although limited, revealed a strengthening trend in both environments. Subsequent strength measurements for exposure times of one week should yield further insights into this behavior.

Table 4.9. Summary of C-ring fracture strength obtained for α -SiC at 1250°C

Exposure time (h)	Fracture strength ^a [MPa (ksi)]	
	Air environment	Slag environment
0	327 $\pm$ 55 (47.5 $\pm$ 8.0)	
24	389 $\pm$ 55 (56.6 $\pm$ 8.0)	389 $\pm$ 35 (56.1 $\pm$ 5.0)

^aNumbers following $\pm$ sign represent standard deviations.

4.6 Surface Gasification Materials Program

R. R. Judkins

4.6.1 Advanced pressure vessel materials technology — R. W. Swindeman, J. F. King, and W. J. Stelzman

The objective of this program is to qualify a high-strength chromium-molybdenum steel for use in the construction of gasifier pressure vessels that will experience pressures, temperatures, or environments that restrict the use of the alloys currently approved in Sect. VIII, "Unfired Pressure Vessels," of the *American Society of Mechanical Engineers Boiler and Pressure Vessel Code*. We believe that the development of the fabrication technology for an alloy with 15 to 25% more strength than the current candidate alloy (SA-387, grade 22, class 2) will be of considerable economical benefit to the Surface Gasification Materials Program. Additional payoff will be for vessels in the hydrogenation section of direct coal liquefaction plants. Finally, an advanced alloy designed to meet domestic

melting and fabrication capabilities will benefit U.S. industry in competing with foreign manufacturers for new vessels required by the petroleum and petrochemical industries.

Assessment report — During this reporting period the second draft of the assessment report on the need for an advanced chromium-molybdenum steel for gasifier pressure vessels was completed and distributed to several industrial and university personnel for technical review.³⁰ A meeting in Pittsburgh is planned for August to complete the review process.

Work on 2 1/4 Cr-1 Mo steel — The first round of tempering studies was completed on three weld metals produced in 2 1/4 Cr-1 Mo steel plate by the submerged arc process. The welds and their deposited chemistries were described previously.³¹ The welds consist of three filler metal-flux combinations. The room-temperature ultimate tensile strength data obtained from some of the heat-treated specimens taken from the welds are plotted against the tempering parameter in Fig. 4.27. Also shown in the

Fig. 4.27. Ultimate strength versus tempering parameter for three weld metals produced in 50-mm (2-in.) plate of 2 1/4 Cr-1 Mo steel.

figure are the trends for the base metal and the scatter band for base metal established by Erwin and Kerr.³² Our data show that specimens from the two "advanced" weldments (types 306/308 and 310) produced data that fall well within the scatter band for base metal and that specimens from the "standard" weldment (307) produced data of lower strength. The data also suggested that the tempering parameter must be maintained below 35,000 (Rankine scale) but above 34,000 to produce an ultimate tensile strength in the range of interest for an advanced alloy [620 to 758 MPa (90–110 ksi)]. Additional samples have been heat treated for elevated-temperature tests, but work has been deferred until the information is needed.

The Charpy V impact energies are plotted in Fig. 4.28 against the test temperature for several tempering conditions. Data are for the strongest of the advanced weldments (306/308). Results indicate that the upper-shelf energy increased with increasing parameter. However, it was necessary for the tempering parameter to exceed 36,000 to decrease the transition temperature.

Fig. 4.28. Charpy energy versus temperature for 2 1/4 Cr-1 Mo welds in 0.2-m (8-in.) plate.

In the next quarter we plan to finish our studies of the strength and toughness response to tempering of heat-affected zone material.

Work on 3 Cr-1.5 Mo-0.1 V steel — A heat of 3 Cr-1.5 Mo-0.1 V steel was melted, and ingots are being rolled to produce 100-mm (4-in.) plate. The chemistry came very close to the aim, as indicated in Table 4.10. We expect to receive delivery of the plate from Lukens Steel in late June or early July.

A contract has been placed with Climax Molybdenum Company to produce submerged arc welds in the plate and to conduct evaluations of the strength and toughness as a function of tempering parameter.

Table 4.10. Chemistry of Climax
3 Cr-1.5 Mo-0.1 V steel plate
produced by CarTech for
Lukens Steel Company

Element	Aim (%)	Limits	Achieved (%)
C	0.10	±0.02	0.10
Mn	0.90	±0.10	0.87
Si	0.20	0.30 max	0.27
Ni	0.20	0.40 max	0.12
Cr	3.00	±0.20	2.92
Mo	1.45	±0.10	1.48
V	0.10	±0.02	0.10
S		0.01 max	0.001
P		0.012 max	0.011
Al		0.025 max	0.006
Sn		0.020 max	0.004
Sb		0.007 max	0.001
Cu		0.12 max	0.06
N	100 ^a	50-200 ^a	130 ^a

^aParts per million.

4.6.2 Electroslag component casting — V. K. Sikka and R. L. Heestand

The Surface Gasification Materials Program electroslag casting (ESC) task is directed to the development of ESC technology for use in coal conversion components such as valve and pump housings. The purpose is to develop a sufficient data base to permit acceptance of ESC as an ASME Code material and to transfer the ESC process technology to private industry. The task has four major areas of emphasis: (1) advancement of ESC technology, (2) preparation of castings (by commercial vendors), (3) testing (by ORNL) of commercial ESCs for mechanical properties, and (4) participation with industrial component fabricators to demonstrate the ability to produce representative components for coal conversion systems by the ESC process.

During this period we procured three ESC valve bodies from the University of British Columbia, Vancouver, British Columbia, Canada. Two of the castings were of modified 9 Cr-1 Mo steel, and one was of 2 1/4 Cr-1 Mo steel (Fig. 4.29). One ESC each of 2 1/4 Cr-1 Mo and 9 Cr-1 Mo are shown as photographed after sandblasting in Fig. 4.30. These figures show the excellent surface finish expected for the ESC components. Table 4.11 gives the chemical analysis of the modified 9 Cr-1 Mo electrode, two modified 9 Cr-1 Mo castings, and one 2 1/4 Cr-1 Mo casting. All chemical analyses are near the bottom edge of the ESC. This table shows the following:

1. The silicon content of ESC1 of modified 9 Cr-1 Mo is an order of magnitude lower than that in the electrode. A similar reduction in silicon content was also observed in 2 1/4 Cr-1 Mo casting. Lower silicon in these castings is believed to come from the use of basic slag and the absence of deoxidation during casting. We believe that silicon was oxidized and absorbed by the basic slag, and we plan to control the slag chemistry in future castings to obtain the desired casting composition.

2. The chromium content of both 9 Cr-1 Mo castings is lower than its value in the electrode. We believe that this is caused by the dilution effect in the mild steel base plate used during these castings; however, we can correct this situation by using a base plate of electrode composition during future castings.

Y-190722

Fig. 4.29. Three electroslag cast valve bodies procured recently from the University of British Columbia, Vancouver, Canada. Two of the castings are of modified 9 Cr-1 Mo steel and one is of 2 1/4 Cr-1 Mo steel.

Y-190726

Fig. 4.30. Electroslag castings of 2 1/4 Cr-1 Mo and modified 9 Cr-1 Mo after sand blasting. Note the excellent surface finish obtained.

Table 4.11. Chemical analysis of various
electroslag castings

Element	Analysis (wt %)			
	Modified 9 Cr-1 Mo			2 1/4 Cr-1 Mo ^a
	Electrode	ESC1 ^a	ESC2 ^b	
C	0.083	0.098	0.12	0.084
Mn	0.51	0.49	0.29	0.52
P	0.018	0.019	0.019	0.009
S	0.002	0.001	0.010	0.001
Si	0.28	0.02	0.25	0.03
Ni	0.15	0.20	0.16	0.16
Cr	9.25	8.41	8.36	2.11
Mo	1.01	0.94	1.16	1.00
V	0.215	0.173	0.25	0.006
Cb	0.056	0.020	0.03	0.002
Ti	0.001	0.001	0.001	<0.001
Co	0.022	0.021	0.025	0.013
Cu	0.08	0.10	0.09	0.11
Al	0.014	0.009	0.004	0.005
B	<0.001	<0.001	<0.001	<0.001
W	0.02	0.03	0.25	<0.01
As	0.004	0.005	0.007	0.007
Sn	0.003	0.005	0.004	0.005
Zr	<0.001	<0.001	<0.001	<0.001
N	0.038	0.034	0.037	0.004

^aBasic slag used during casting.^bNeutral slag used during casting.

Detailed chemical analyses were also conducted on the 1/2-thickness slices of each of the 2 1/4 Cr-1 Mo and 9 Cr-1 Mo castings. For 2 1/4 Cr-1 Mo, specimens were taken 25 mm apart from the top to the bottom and from the left to the right of the castings. Data from these analyses are presented in Figs. 4.31, 4.32, and 4.33. Figure 4.31 shows that all elements were uniformly distributed in the 2 1/4 Cr-1 Mo casting. Chromium, molybdenum, and vanadium showed strong gradients near the bottom of the casting in the modified 9 Cr-1 Mo steel (Fig. 4.32). We believe

ORNL-DWG 83-11952

Fig. 4.31. Plot of element weight percent as a function of distance from the top to the bottom of the electroslag cast valve body of 2 1/4 Cr-1 Mo steel.

ORNL-DWG 83-11951

Fig. 4.32. Plot of element weight percent as a function of distance from the top to the bottom of the electroslag cast valve body of modified 9 Cr-1 Mo steel.

ORNL-DWG 83-11950

Fig. 4.33. Plot of element weight percent as a function of distance from the left to the right of the electroslag cast valve body of modified 9 Cr-1 Mo steel.

that these gradients are due to transfer of these elements into the mild steel base plate. As mentioned above, we plan to correct this situation by using the base plate of the electrode composition. Figure 4.33 shows that the amount of various elements from the left to the right of the casting is nearly the same. The microstructural evaluation and mechanical testing of these castings is in progress and will be presented in the next report.

4.6.3 Plant materials surveillance tests — J. P. Hammond

The purpose of this pilot plant materials testing program (MPC, Phase II) is to provide a critical assessment of potential corrosion problems in various coal gasification environments and, in conjunction with laboratory tests (Phases I and IV), to increase confidence in materials selection and corrosion-rate prediction in coal gasification plants. The effort is being carried out by the Illinois Institute of Technology Research Institute (IITRI) under contract with The Metal Properties Council, Inc. (MPC), in pilot plants operated for DOE.

Fabricated assemblies of metal and refractory coupons are exposed to diverse environments at preselected locations having significant corrosion potential. The gasifier locations for metal testing generally include coal pretreatment, gasification, and quench systems, but the locations for refractories are confined to gasification. In selecting test materials, we have tried to choose candidates that are metallurgically suitable for the environment and that are both lower and higher in corrosion resistance than that expected of the construction material. The metals generally range from carbon steel to ferritic and austenitic stainless steels for the coal pretreatment and quench system locations; the materials consist of highly alloyed iron-, nickel-, and cobalt-base heat-resistant alloys for the gasification locations.

Status of Phase II testing — The scope and status of the Phase II pilot plant testing program as of June 1, 1983, are outlined in Table 4.12. Exposure 1 in the Gegas Process Development Unit (PDU) was completed in May, and exposure 2 in the Westinghouse PDU will be completed soon. Testing in Gegas had accumulated 400 h, mainly with Pittsburgh

Table 4.12. Status of Phase II pilot plant surveillance testing

Pilot plant	Number of test locations		Exposure in progress	Number of exposures completed
	Metals	Refractories		
Bi-Gas	7 + 2 ^a	1	3d ^b	2
Westinghouse	7	1	2d ^c	1
Gegas	5	0	0 ^d	1
Mountain Fuel Resources	5 ^e	0	1	0

^aTwo new test racks added (locations 5 and 6) in lines 401 and 601 in Bi-Gas process.

^bTest runs expected to resume in June, and corrosion specimens will be reinserted.

^cExposure begun second week of March 1982 will be completed in June.

^dCorrosion specimens being analyzed.

^eTwo additional test locations may become available in the future. Exposure began in February.

No. 8 bituminous coal in the form of briquettes. Construction of the Mountain Fuel Resources PDU was completed in February, and exposure 1 was initiated in it. As of May 1983, the third exposure in the Bi-Gas plant had accumulated an estimated 200 h of operational exposure with Pittsburgh No. 8 bituminous coal as feedstock. However, shortly thereafter the plant was temporarily shut down pending resolution of funding to continue testing. Operation of the Bi-Gas was resumed in June of 1983, with the use of Illinois No. 6 coal as feedstock; the test racks of exposure 3 will be reinserted. At the end of 1982, testing in the Westinghouse PDU was interrupted for repairs to the plant. However, five test locations of exposure 2 had been exposed 800 h, during which time a variety of coals was gasified. Also, two test locations in the first gas cooler were still in the first period of exposure, with an accumulated time of 1900 h.

During the past quarter the main activities consisted of analytical work performed on the corrosion specimens removed from tests and preparation of manuscripts of reports and papers. A paper entitled "Materials Requirements for Coal Base SNG Production" by Ray Yurkewycz was accepted for presentation at the International Gas Research Council Meeting in London in June 1983.

In future surveillance testing, the major emphasis will be on long-term exposures and interpretive studies designed to explain test results that have varied significantly from those of the laboratory corrosion-erosion tests of MPC, Phase IV. New racks for exposure 3 in the Westinghouse PDU will be prepared, and tests will employ lignite and Eastern coals as feedstock.

Highlights of tests - Results of the Phase II program to date are summarized below. Information on experimental methods and a more detailed account of results have been published.³³ Phase II pilot plant testing conducted on metals showed several high-temperature alloys to be suitable for gasifier internal applications.

Alloys acceptable for gasifier environment service at 871 to 982°C (1600-1800°F) are limited to Fe-Cr-Ni and Fe-Cr types, with more than about 25% Cr (e.g., type 310 stainless steel, HL-40, and E-Brite 26-1), the higher chromium cobalt-base alloys (e.g., 6B), and nickel-base alloys with chromium at about 49% (e.g., IN-671). At temperatures below 871°C (1600°F), the list of acceptable materials broadens to include several alloys of somewhat lower levels of chromium (e.g., type 309 stainless steel, IN-800, IN-825, Hastelloy X, 22-13-5, and RA-333). In contrast, nickel-base alloys containing comparatively low or no chromium, including IN-600 and Monel 400, showed consistently unacceptable corrosion rates [>0.51 mm/year (>20 mils/year)] and are regarded as unsuitable for gasifier internals. These results suggest that high-nickel weld filler metals such as IN-82 may not be acceptable.

The diffusion zone formed by pack aluminizing IN-800 and type 310 stainless steel has shown some promise for corrosion protection, but the coating itself incurs many cracks from thermal cycling. The cracks form

short-circuit corrosion paths up to the diffusion zone, thereby undermining the corrosion protection of the Al_2O_3 coating. In the Conoco Coal regenerator (nongasifier environment), pack-aluminized alloys outperformed their uncoated counterparts.

Accumulated Phase II data for coal pretreatment and gasifier quench systems show that uncoated carbon steel and other iron-base alloys (2 1/4 Cr-1 Mo, silicon iron, cast iron, Ni-Resist, Ni-Cu Resist) corroded at unacceptable rates [$>2.54 \times 10^{-4}$ m/year (>10 mils/year)] in almost all low-temperature pilot plant locations. To date, stainless steel types 329, 316, 304, and 18-18-2 and E-Brite 26-1 appear to be more acceptable than stainless steel types 430 and 410, the latter two being susceptible to deep localized corrosion in many test locations.

A variety of liner materials from numerous refractory manufacturers have been exposed in six pilot plants under nonslagging conditions at 816 to 1065°C (1500–1950°F). In general, the alumina-base refractories with greater than 60% Al_2O_3 and less than 30% porosity have experienced little deterioration. Materials bonded with both calcium aluminate and phosphate alike withstood attack. An exception to the above observation was that Alfrax bubble alumina, with greater than 30% porosity, showed no significant deterioration. Silicon carbide refractories bonded with silicon nitride and oxynitride deteriorated badly.

4.6.4 Process plant materials review, evaluation, and support – J. P. Hammond, A. R. Olsen, and R. R. Judkins

The purpose of this task is to conduct materials assessments of gasification pilot plants and PDUs sponsored by the Office of Coal Processing and to provide other appropriate materials services to plants as required. The task makes maximum use of findings of the ongoing AR&TD Fossil Energy Materials Program. The assessments are being conducted by reviewing materials and components performance with the plant operators and designers. Problems of long-life performance of materials and plant scaleup are stressed, and recommendations are made to fill gaps in technology where they appear. The results of the assessments and of materials surveillance tests in the plants that are not otherwise published are reported as an engineering data base for future reference.

During the last quarter, we reviewed the Corrosion Control/Materials Evaluation Program Plan for the Great Plains Gasification Project, submitted to ORNL March 24 by DOE. The results of this review were transmitted to the Morgantown Energy Technology Center (METC) April 14. Other contributions to the review, evaluation, and support task included evaluations made of AR&TD program proposals to DOE on heat exchangers for coal gasification application. Some of the salient points with reference to the materials test plan reviewed for the Great Plains Gasification Project are summarized below.

1. The adequacy of the corrosion coupon and probe locations could not be determined from the tabular data presented. The materials flow diagrams referenced in the program plan were requested. These diagrams are expected to supply information on locations and operating conditions needed to resolve this question.

2. We concurred with the program need for flow stream analyses throughout the plant and recommended that analyses be made of halogens, particularly chlorine and fluorine, since these elements can have a significant effect on materials performance.

3. For general corrosion tests, we recommended that the gravimetric method now proposed be augmented by the metallographic method. The metallographic method should include metal recession by scaling, pitting, and substrate penetration (e.g., attack along grain boundaries by void or sulfide formation).

4. Electrical isolation of each corrosion coupon from adjacent coupons and the metallic support unit was recommended to ensure against galvanic corrosion. We suggested the use of dense Al_2O_3 for the insulation construction material.

5. With reference to analyses of exposed corrosion coupons, we suggested that special care be taken to ensure against ambiguous information as a result of coupon cleaning. The use of descaling by pickling was recommended for the gravimetric method of analysis.

6. We recommended that corrosion racks include test specimens of the same materials employed for the vessel construction and suggested duplication of specimens to the extent practicable.

7. Suspect locations such as weldments, elbows, liquid-vapor interface regions, impingement surfaces and heat exchanger tubes were singled out as being important in the nondestructive test evaluation.

8. It was recommended that particular attention be given to the method of applying the U-bend in the stress-corrosion cracking tests. Elastic stressing should be maximized, and relaxation by springback during mounting should be avoided. Because of the tendency of weldments to stress-corrosion crack, we recommended that welded U-bend specimens be included in the tests and cautioned that weld deposits should be perpendicular rather than parallel to the specimen axis to maximize residual tensile weld stresses.

9. With regard to the materials contained in the corrosion test matrix, several additions were suggested. These included Corten low-alloy steel (copper-containing alloy of U.S. Steel) and types 316 and 310 stainless steel in a number of the flange locations. Alonized carbon steel was suggested for several locations. Also, Incoloy 800, type 310 stainless steel, and alonized type 310 stainless steel were suggested for the incinerator location. For the numerous applications involving liquids and wet vapors below 66°C (150°F), we suggested that more consideration be given to organic coatings over carbon steel.

4.7 Assessment of Materials Needs for Advanced Steam Cycle Pulverized Coal Plants

P. L. Rittenhouse

Advanced steam cycle coal plants with ultrasupercritical steam conditions offer the potential for large economic benefits. This task is contributing to such a goal by assessing the materials technology required to operate plants reliably under these advanced conditions.

A study of advanced system designs was completed by R. L. Graves (Engineering Technology Division). The effect of major design parameters on plant efficiency was examined, and the most effective measures to improve the efficiency were found to be significant increases in steam throttle and reheat conditions and design improvements in the turbine.

The reference advanced system defined in this study produces steam at 37.9 MPa (5500 psig), 649°C (1200°F), and has two reheats to 593°C (1100°F). Net plant efficiency is calculated as almost 44%. It appears, however, that the maximum tube metal temperature in the superheater will approach or exceed 704°C (1300°F) under such conditions.

Members of the assessment team (G. M. Goodwin, J. C. Griess, Jr., and P. L. Rittenhouse) met R. M. Curran and R. Lindinger of the General Electric Company Large Steam Turbine-Generator Department. Their conclusion from earlier studies is that a plant with 31.0 MPa (4500 psig), 538°C (1000°F) steam, and reheats to 552 and 566°C (1025 and 1050°F) is optimal economically (i.e., lowest busbar cost). Their standard plant today is 16.5 MPa (2400 psig), 538°C (1000°F), with a single reheat to 538°C (1000°F). General Electric has designed and built a 31.0-MPa (4500-psig) 621°C (1150°F) system, but fatigue problems have occurred in the stainless steel rotor of the high-pressure turbine; a new rotor material, perhaps A-286, would need to be qualified for advanced systems. In the opinion of these General Electric people, reheat piping and valves are also potential problem areas.

An Electric Power Research Institute-sponsored workshop on failure and nondestructive evaluation of boiler tubes was attended by K. V. Cook. Boiler tube failure is the number one availability problem for utilities, with more than 16,000 outages from such failures documented over the past decade. Almost 50% of boiler tube failures were in the furnace wall or superheater; erosion and corrosion account for the majority of all failures.

Plans were made to visit the Fossil Power Systems group of Babcock & Wilcox at Barberton, Ohio. Visits to the Westinghouse turbine plant and to Cameron are being negotiated.

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5. BASIC ENERGY SCIENCES — FOSSIL ENERGY MATERIALS PROGRAM

C. J. McHargue

The Basic Energy Sciences — Materials Sciences Program of the Metals and Ceramics Division has a number of tasks that have been developed to support the applied research and development activities of various fossil energy systems. This report describes progress in studies of hard erosion-resistant ceramic materials, the fundamentals of sulfidation processes in iron-base alloys, and intermetallic alloys.

5.1 Properties of TiB_2 Implanted with 1-MeV Nickel

C. J. McHargue and M. B. Lewis

A series of studies has recently been undertaken at Oak Ridge National Laboratory (ORNL) to determine the effect of ion beam treatments on the surface structure and properties of ceramics. A variety of techniques (Rutherford backscattering-channeling, analytical electron microscopy, transmission electron microscopy, x-ray diffraction, scanning transmission electron microscopy, and Raman spectroscopy) have been used to determine the structure of the implanted or ion-beam-mixed layer, in particular the defect configurations or radiation damage produced by the energetic ions. Surface mechanical properties have been evaluated by microhardness, indentation fracture toughness, and scratch-wear measurements.

Polycrystalline TiB_2 specimens were prepared from powder that initially contained about 1 wt % O as the major impurity (H. Starke Company, Berlin). Samples having 98.4% theoretical density were produced by vacuum hot pressing at 2050°C under 25-MPa uniaxially applied pressure for 4 h; the grain size ranged from 50 to 100 μm . Specimens of appropriate size were cut from these compacts and polished mechanically to a surface finish of less than 25 nm. The implantation of 1-MeV Ni^+ ions was carried out in the ORNL 5-MeV Van de Graaff facility. The fluence was

1×10^{17} ions/cm². This procedure resulted in a nickel-to-titanium ratio of about 0.12. The calculated composition was made on the assumption that the nickel ions were uniformly distributed in the region centered around the peak in the distribution and were contained within the calculated half-width.

The hardness of the samples was measured by the Knoop microhardness technique. With a 0.147-N (15-g) load, this procedure creates indentations that are about 250 to 300 nm deep. The implanted ion concentration peaks in these specimens at about 450 nm; thus, the hardness values may reflect a contribution from the underlying unmodified lattice. The hardness values are reported only as relative values, expressed as the ratio of the hardness of the implanted area to that of an unimplanted region on the same specimen, which indicates the magnitude of hardness changes rather than absolute hardness values. Unimplanted areas are retained on all implanted specimens by selective masking to allow the implanted-to-unimplanted hardness ratio to be determined on specimen volumes having identical histories. Since TiB₂ is hexagonal and exhibits anisotropic physical and mechanical properties, measurements were made in individual grains that overlapped the edges of the implanted and unimplanted (masked) areas.

Indentation fracture toughness values were determined from Vickers hardness indentations. Vickers indentations produced by 0.49- and 0.98-N loads generated cracks at the corners of the indenter impressions. The crack lengths and indentation diagonals were measured and used to calculate an apparent fracture toughness value by the methods of Evans and of Marion.^{1,2} The fracture toughness values determined from the two methods differ somewhat, but the ratios of the values for implanted to unimplanted material were comparable.

An evaluation of the response of the surface to simulated mechanical abrasion was made by a scratch test. In this test, a stylus is slowly translated across the surface under normal loads of 0.098 to 0.49 N while the tangential force on the stylus is continuously measured. The scratch

origin was positioned to cause the stylus to cross the unimplanted-implanted interface during the traverse of the surface. The stylus is a Vickers diamond indenter, positioned to move at a velocity of 28 $\mu\text{m/s}$ over the sample surface, with one of the pyramid faces normal to the direction of motion.

Significant hardening resulted from implantation of TiB_2 with nickel. Figure 5.1 shows the relative hardness (implanted to unimplanted) for two implanted samples and one sample annealed for 2 h at 1450°C after implantation. The hardness of this already very hard material was increased by 70 to 100% (hardness ratios of 1.7 and 2.0). The value of the latter specimen exceeded that of cubic boron nitride (generally accepted as the second hardest substance to diamond). The hardness ratio decreased only from 1.7 to 1.6 for the sample annealed for 2 h at 1450°C.

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Fig. 5.1. Relative hardness of TiB_2 implanted with 1 MeV Ni.

The indentation fracture toughness was increased from 40 to 80%. Variations in the apparent K_{IC} from grain to grain suggest an orientation effect on both hardness and K_{IC} . In general, the higher values of K_{IC} were associated with the higher hardness values.

The scratch-wear test gives an indication of the wear resistance under gouging or abrasive action for material removal. At a given value of normal force, the tangential force divided by the cross-sectional area of the groove gives the specific energy of material removal or the energy required to remove a unit volume of material. Specimens of TiB_2 implanted on one-half of a polished face were evaluated by measuring the change of tangential force and cross-sectional area of the scratch as the measuring stylus moved across the interface between unimplanted and implanted regions. The shape and cross-sectional area of the grooves (scratches) were determined from surface profilometer (Dektak) measurements with a 2.54- μ m-diam stylus.

The tangential force, at 0.098-N (10-g) or 0.196-N (20-g) normal force, did not change during the traverses; however, the cross-sectional areas of the scratches did. Table 5.1 contains a summary of the measurements for two samples. The specific energy of material removal for the implanted portion of the specimens was 50 to 90% greater than was that for the unimplanted regions.

Table 5.1. Results of scratch wear tests

Specimen	Relative hardness	Normal force (N)	Tangential force (N)		Cross section of groove (μm^2)		Ratio of specific groove energy
			Unimplanted	Implanted	Unimplanted	Implanted	
1	1.7	0.098	0.015	0.015	2.96	1.91	1.54
		0.196	0.025	0.025	5.74	3.80	1.51
2	2.0	0.098	0.012	0.015	3.00	1.58	1.90
		0.196	0.020	0.025	5.75	3.10	1.85

5.2 The Linear Gradient Approximation for Diffusion-Controlled Growth of Iron Sulfide Scales

R. E. Pawel and J. V. Cathcart

As part of our research program to investigate the reaction kinetics and defect behavior of iron and dilute iron-base alloys in sulfur-containing gases, we have performed calculations that permit a test of the common "linear gradient approximation" for layer growth in such highly defective reaction products.³

Although it is clear that a growing product layer will always involve a nonlinear concentration gradient of the diffusing species leading to its growth, the extent of this deviation for compound formation is generally considered to be small and is therefore neglected in most diffusion-related considerations. The above reaction of iron or its alloys produces reasonably uniform layers of iron sulfide, $\text{Fe}_{1-\delta}\text{S}$, where δ represents the fraction of vacant cation sites in the sulfide lattice. With some complications, the reaction proceeds under diffusion control, with iron diffusion via cation vacancies being the dominant mode of mass transport. The chemical diffusion coefficient is virtually independent of the defect concentration,^{4,5} at least for values of δ up to about 0.15.

We assessed the extent of possible departure from idealized behavior by considering the iron sulfidation reaction in terms of a simplified single-layer moving-boundary problem with constant diffusivity. This method relates the effective chemical diffusion coefficient to the growth constant and, in addition, defines the concentration gradient across the growing layer. The latter result permitted a convenient appraisal of the linear-gradient approximation. For example, a mass balance at the layer-gas interface yielded the following equation:

$$k_p = \tilde{D} \frac{\Delta C_L}{C_{L/G}} \left\{ \left(\frac{2k_p}{\pi \tilde{D}} \right)^{1/2} \frac{\exp(-k_p/2\tilde{D})}{\text{erf}[(k_p/2\tilde{D})^{1/2}]} \right\}, \quad (1)$$

where

- k_p = parabolic rate constant for growth of $\text{Fe}_{1-\delta}\text{S}$ layer,
 $\tilde{D}$ = chemical diffusion coefficient,
 $C_{L/G}$ = iron concentration in sulfide layer at sulfide-gas interface,
 ΔC_L = iron concentration difference across sulfide layer.

The factor in braces in Eq. (1) is the "slope factor" (the ratio of the actual concentration gradient to that defined by the linear approximation) at this interface. This slope factor, as well as its counterpart at the sulfide-metal interface, is independent of time and depends only on the relative values of the parabolic rate constant and the chemical diffusivity. For $k_p:\tilde{D}$ ratios up to about 0.1, the slope factors are essentially unity, and a linear gradient is thus a good approximation; as the ratio increases above 0.1, a significant "droop" develops in the concentration profile for the diffusing species.

It can also be shown that the $k_p:\tilde{D}$ ratio depends (for cation diffusion) directly on the defect concentration at the sulfide-gas interface. For compound scales having relatively small numbers of defects, the ratio is approximately equal to the defect fraction δ . Therefore, for the case of iron sulfide growth, a linear concentration gradient is a good approximation for all reaction conditions. Even at high temperatures and high sulfur pressures, where the maximum defect concentration approaches 0.2, the gradient will vary by less than 10% from the linear value at each interface.

5.3 High-Temperature Alloy Design

C. T. Liu and C. L. White

The Ni_3Al alloy containing 24 at. % Al was microalloyed with various amounts of boron (0 to 0.4 wt % B) to study the ductilizing effect of boron additions. The boron-doped ingots were prepared by arc melting and drop casting, using pure aluminum and nickel metals and an Ni-4 wt % B

master alloy. The cast ingots were homogenized at 1000°C and fabricated by repeated cold rolling at room temperature, with intermediate anneals at 1000 and 1050°C. The aluminides doped with 0.025 to 0.2 wt % B were successfully fabricated into sheets, but those with 0 and 0.4 wt % B cracked during fabrication.

The effect of alloy stoichiometry on fabricability was studied with a second series of Ni_3Al aluminides containing 24 to 26 at. % Al. The 24% Al aluminide was doped with 0.05 and 0.10 wt % B, and other aluminides were doped with 0.05 wt % B. The results in Table 5.2 indicate that sheet fabrication becomes increasingly difficult as the aluminum content increases and that the aluminides with equal or greater than 25% Al (i.e., Al-rich deviations from stoichiometry) cannot be successfully fabricated into sheets by cold rolling.

Table 5.2. Effect of alloy stoichiometry on fabricability of boron-doped Ni_3Al

Aluminum concentration (at. %)	Boron concentration (ppm by weight)	Fabricability
24.0	250-2000	Sheets fabricated
24.5	500	Sheet fabricated with difficulty
24.8	500	Sheet fabricated with difficulty
25.0	500	Sheet fabricated with considerable difficulty
25.2	500	Ingot cracked
26.0	1000	Ingot cracked

The room-temperature ductility of boron-doped Ni_3Al aluminides was determined as a function of boron concentration and alloy stoichiometry. Figure 5.2 is a plot of the total elongation of 24 at. % Al aluminides doped with various boron concentrations. The ductility of the aluminides with greater than or equal to 0.025 wt % B was measured from tensile tests of sheet specimens, and the ductilities of aluminides with 0.005 and 0.01% B (which were unfabricable) were estimated from cold rolling. Undoped Ni_3Al exhibited very little ductility at room temperature. Figure 5.2 indicates a sharp increase in ductility from about 10 to 43.8%

Fig. 5.2. Tensile elongation of boron-doped Ni_3Al (24 at. % Al) as a function of boron concentration.

as boron levels increase from 0.01 to 0.025 wt % in Ni_3Al . Ductility continues to increase with higher boron levels, reaching 53.8% for the 0.1% B alloy. This is the highest tensile ductility ever achieved in polycrystalline aluminides. With further increases in boron content, the ductility appears to decrease gradually to 39.8% at 0.2% B. Since the 0.4% B aluminide cannot be fabricated, its ductility must be quite low, less than 6%. Undoped Ni_3Al fractured completely by grain boundary separation [Fig. 5.3(a)], but aluminides doped with 0.025 to 0.2% B failed predominantly in a transgranular mode [Fig. 5.3(b)].

Table 5.3 shows the effect of deviation from stoichiometry on the room-temperature tensile properties of boron-doped Ni_3Al . Both tensile elongation and yield strength decrease with increasing aluminum concentration above 24 at. %. Actually, the ductility of the aluminide doped with 0.05 wt % B drops from 49.4 to 6.0% as the aluminum content increases from 24 to 25% (stoichiometric composition). The results in Tables 5.2 and 5.3 clearly indicate that small deviations from stoichiometry strongly influence the ductility and fabricability of boron-doped Ni_3Al aluminides.

Fig. 5.3. Scanning electron microscopic fractiographs of Ni_3Al aluminides (24 at. % Al) fractured at room temperature. (a) Grain boundary fracture of undoped Ni_3Al . (b) Transgranular fracture of Ni_3Al doped with 0.05 wt % B.

Table 5.3. Effect of deviation from stoichiometry on tensile properties of Ni_3Al doped with boron

Alloy	Al (at. %)	B (ppm by weight)	Yield stress (MPa)	Elongation (%)
IC-6	24	1000	322	53.8
IC-15	24	500	291	49.4
IC-22	24.8	500	240	18.5
IC-54	25.0	500	227	6.0

To understand the effect of boron dopant on the ductility and fracture behavior of Ni_3Al , the compositions of fracture surfaces were determined by Auger electron spectroscopy (AES). Table 5.4 shows the results of AES analysis of 24 at. % Al aluminides in terms of "peak-height-ratios" and atomic ratios relative to nickel atoms. The AES analysis was made on cast samples homogenized for 20 h at 1200°C . In this condition, undoped aluminide samples showed only grain boundary fracture, but boron-doped samples failed in a mixed fracture mode. Auger spectra show no indication of segregation of oxygen and carbon to Ni_3Al grain boundaries. Comparison of Auger spectra in Fig. 5.4 reveals a strong segregation of boron to grain boundaries in boron-doped Ni_3Al . The boron concentration in 2- to 3-atom-layer-thick grain boundary regions is estimated to be about 10 at. % B. Sulfur, an impurity in Ni_3Al , is also present at the boundaries at a level of less than 1 at. % (Fig. 5.4 and Table 5.4). The presence of sulfur at the grain boundaries indicates that the primary function of boron is not to scavenge sulfur from the boundary region. The

Table 5.4. Results of Auger electron spectroscopic analysis on fracture surface of Ni_3Al aluminides

Aluminide composition	Type of fracture surface	Peak-height-ratio (min/max)		Atomic ratio (min/max)	
		S,150 eV	B,180 eV	S,150 eV	B,180 eV
		Ni,102 eV	Ni,102 eV	Ni,102 eV	Ni,102 eV
Ni-24 at. % Al	Grain boundaries	0/0.202	0/0.158	0/0.006	0/0.028
Ni-24 at. % Al- 0.1 wt % B	Grain boundaries	0.153/0.246	0.980/1.081	0.005/0.008	0.174/0.192
	Transgranular regions	0/0.047	0.097/0.157	0/0.002	0.017/0.028

intensity of boron segregation to Ni_3Al grain boundaries appears to depend on the deviation from stoichiometric composition. Preliminary analysis indicates that the grain boundary concentration of boron in the 26 at. % Al aluminide is only about half of that in the 24 at. % Al aluminide.

Our results strongly suggest that the presence of a sufficient amount of boron at the grain boundaries reduces the tendency toward intergranular fracture in substoichiometric Ni_3Al and thereby increases ductility and

Fig. 5.4. Partial Auger spectra from a grain boundary area in (a) Ni₃Al doped with 0.1 wt % B and (b) undoped Ni₃Al.

fabricability. Recently Messmer and Briant proposed an electronic model to explain the effect of alloying elements on grain boundary cohesion in metals.⁶⁻⁷ According to their model, the embrittling elements (such as sulfur) are those that are more electronegative with respect to base metals (such as nickel and iron). These elements draw charge from the neighboring metal atoms onto themselves; consequently, less charge is available to participate in the metal-metal bonds, and they are weakened. The beneficial elements (such as boron) are those that are less electronegative with respect to the base metals. These elements do not draw charge from the base metal atoms and thus do not weaken the metal-metal bonds. In addition, these elements share electrons with the metal atoms (i.e., form homopolar bonds) and thus enhance bonding in the grain boundary. Messmer and Briant verified their model to a certain extent by use of quantum-mechanical cluster calculations. Thus, the beneficial effect of boron dopants in Ni₃Al may be attributed to a strong grain boundary segregation of boron, which increases bonding between nickel atoms

and results in improvement of grain boundary cohesion and in reduction of the tendency toward brittle intergranular fracture. Boron additions have less effect in ductilizing Ni_3Al when aluminum concentrations approach or surpass the stoichiometric composition, 25% Al. This is probably related to the fact that less boron segregates to grain boundaries in hyperstoichiometric Ni_3Al , as indicated by our AES analysis. Further studies are needed to understand how alloy stoichiometry influences the mechanism(s) by which boron additions segregate to grain boundaries in Ni_3Al .

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6. TECHNICAL SUPPORT TO MAJOR LIQUEFACTION PROJECTS

H. D. Cochran

Technical support is provided by Oak Ridge National Laboratory and Union Carbide Nuclear Division Engineering to the major liquefaction projects being managed by DOE Oak Ridge Operations-SRC-I Demonstration Plant, H-Coal Project, and the Exxon Donor Solvent (EDS) Project. Activities are reported in five broad categories--engineering and design review, liquefaction technology base, process analysis, materials, and environment and health.

6.1 Engineering and Design Review

This section reports on reviews, evaluations, and analyses of processes, engineering, and designs presented in project documents for major coal liquefaction projects managed by the DOE Oak Ridge Operations Office (ORO). The objectives are to assess conformance of project technical elements with the data bases, to identify data gaps and technical problems, and to investigate anomalies and problems as directed and/or authorized by DOE-ORO. The scope of the Engineering and Design Review activities applicable to the coal liquefaction projects managed by the DOE Oak Ridge Operations Office is summarized below:

- Project technical documents are reviewed for objectivity, adequacy, and accuracy in areas of interest requested or authorized by DOE.
- Engineering design is reviewed for technical adequacy and conformance with the data base at review sites designated by ORO.
- Relevant project meetings are monitored as requested by ORO as an aid in assessing project progress, status of issues, and problem areas, and to make presentations deemed useful by ORO.

- Technical status studies, analyses, and evaluations requested or authorized by ORO are performed on specific engineering design subjects focused on project problems affecting plant design or operability.

The status summaries of activities within this scope are presented below under the applicable project titles.

6.1.1 SRC-I Project Engineering Support

This project involves the design, construction, and operation of a coal liquefaction plant for the production of clean solid boiler fuel, upgraded liquid fuels for transportation, and anode coke for aluminum reduction cells. Marketable by-products include sulfur, ammonia, and LPG.

The detail design phase of the SRC-I project is cost-shared by the U. S. Government and the International Coal Refining Company (ICRC).

Status Summary - The DOE-ORO comments on the UCC-ND draft report on the Application of Rand Corporation Estimating Techniques were received in June and resolution and incorporation are planned for next quarter.

The design materials reviews completed this quarter include:

- 1) materials design selections for the proprietary Expanded Bed Hydrotreater (EBH) process area
- 2) appropriate materials performance monitoring provisions for the entire Parsons Design area (gasification and gas treatment processes), the EBH process area and the coker and calciner areas.

An outstanding area of materials concern has been the suitability of carbon steel for equipment and piping that handles process solvent at temperatures above 505K (450°F). A compromise approach agreed upon this quarter is to change most of the material selections to austenitic stainless steel or a 5 Cr-1 Mo alloy while leaving one line in a series of four parallel lines of heat exchangers carbon steel with appropriate

corrosion monitoring equipment. In addition, ORNL received and commented on an ICRC proposal to obtain additional experimental data on the corrosivity of process solvent as a function of temperature.

The material information compilation and assessment effort for the SRC process area has continued with all of the revisions entered in accordance with the revised baseline designs.

The development of similar files to record pilot plant and laboratory corrosion data and component performance information has been initiated.

A meeting on Synthetic Fuel Components on May 10th and 11th, and the Technical Status Review of June 1, 1983, were attended by UCC-ND Engineering and trip reports were provided to DOE-ORO documenting the results.

6.1.2 H-Coal Project

This H-Coal Pilot Plant, cost-shared by the U. S. Government with several industrial participants, and operated by Ashland Synthetic Fuels, Inc. (ASFI), involves the direct liquefaction of coal using the H-Coal ebullated bed process for producing either syncrude or boiler fuel.

Status Summary - The draft summary report on the thermal/fatigue analysis of the reactor vessel was issued to DOE-ORO for comment this quarter with publication planned for next quarter.

6.2 Liquefaction Technology Base

B. R. Rodgers

This section reports on five work elements with the overall objective of accumulating, evaluating, and maintaining a broad base of technical information on coal liquefaction.

6.2.1 VSB Viscometer - J. H. Wilson, D. A. McWhirter, and B. R. Rodgers

Introduction

In a coal liquefaction process, the bottoms from the vacuum distillation column may be gasified, fed to a solids/liquid separation unit, or as in Exxon's EDS process, charged to a Flexicoking unit. Unlike similar product streams in refinery processes, the VSB (vacuum still bottoms) from coal liquefaction contains a high amount of solids, up to 50%, approximately 25% ash, and is relatively susceptible to further reactions, such as irreversible polymerization or coking. Since operability will undoubtedly be a major factor in the economics of coal conversion processes, it will be important to monitor specific properties of the VSB streams for indications of potential problems with controlled feeding of the VSB to the following process step. Viscosity obviously will have a major effect upon pumpability. Thus, this project, which has as an objective the development of an on-line viscometer for VSB streams, will contribute to the successful operation of coal liquefaction plants. It will also produce generic information heretofore unavailable on high solids content streams typical of coal conversion processes, e.g., the first stage bottoms from the Kerr-McGee CSD unit.

The flow sheet of the viscometer which has been constructed is shown in Fig. 6.1. The basic concept is to measure the pressure drop that results from pumping VSB at a calibrated rate through a length of capillary tubing which has a diameter of 3.18 mm (0.125 in.). VSB from the process will be metered by a Bran-Lubbe pump through the capillary tubing and returned to the process. Heavy distillate will be available from the process for flushing purposes. To maintain the VSB above its fusion point [422 to 478 K (300 to 400°C)], all equipment and piping which contain VSB are installed within an insulated and heated enclosure. A process control computer is supplied to (1) make changes in pump settings, temperature set-points, etc., while recording pressure drop across the capillary as a function of flow rate and temperature, (2) calculate and print out values of viscosity vs shear rate, (3) provide proper sequencing of valve openings and closings in order to flush

Fig. 6.1. VSB viscometer flow diagram.

the system either routinely or upon operator command, and (4) take appropriate steps in emergency situations. The entire viscometer system is mounted upon a base for ready transportation to a coal liquefaction pilot plant. On site, the only process hook-ups required are the VSB and the flush solvent supply and return lines. Utilities required are electricity, water, air, and nitrogen.

Discussion

As discussed last quarter, a 24-h test at ORNL was planned before shipment of the viscometer to Wilsonville. When attempted, the test was terminated after approximately 14 h due to failure to maintain flow of VSB. Apparently, plugging of the pump check valves occurred, a problem experienced several times previously. No other mechanical operating problems were experienced during the test period. Furthermore, the computer programs, in the multitasking mode of the Macsym 2 computer system, performed the roles of data acquisition and process control satisfactorily. Although the 24-h run time was not achieved, based on its overall performance, the VSB viscometer system is believed to be ready for on-line evaluation at Wilsonville. As pointed out previously, plugging should not be a major problem in continuous operations. In the ORNL laboratory tests, degradation, and consequently solids formation, of the VSB likely occurs due to the batch-type feed system, whereas in the Wilsonville plant fresh feed will always be supplied to the viscometer.

After the 24-h test, a decision was made by DOE-ORO to discontinue work on this project and transfer the remaining funds to the Coal Liquids Flow System for thermal conductivity studies.

Future Plans

Other sources of funding for the continuation of this project will be sought.

6.2.2 CSD Feed Quality - J. E. Mrochek, S. B. Dinsmore, and B. R. Rodgers

The economics of the SRC-I process are sensitive to SRC recovery from the Kerr-McGee Critical Solvent Deashing (CSD) unit which is, in turn, dependent on the asphaltene/preasphaltene (ASP/PASP) ratio of the feed. The ASP/PASP ratio may be controlled to some degree through control of the

severity of treatment in the dissolver. Process feedback control is not possible using present methods of determining the ASP/PASP ratio; on-line sampling and analysis would permit process control much closer to optimum.

Two prototype systems were to be designed and fabricated. Automated solvent elution chromatography employing two-solvent elution of CSD feed samples from a sand column was selected as the basis for both systems. The first system, similar to our current prototype system, was to be fabricated as quickly as possible and installed in the control laboratory at the Wilsonville pilot plant for use by laboratory personnel. The second system, to be designed and fabricated concurrently with the first, is to be suitable for automated, on-line or near-on-line operation at a pilot or demo plant. Installation of the first laboratory system at Wilsonville was completed on May 23, 1983.

The system for the analysis of CSD feed quality in the laboratory is based upon the two-solvent elution of a CSD feed sample (dissolved in pyridine, 0.1 g to 10 ml) which is dispersed on a 50 x 1.2 cm column filled with sea sand. Chloroform and pyridine are employed to elute two fractions consisting of (approximately) oils + asphaltenes and preasphaltenes. These two fractional components are monitored by an optical detector having a broadband uv source (centered around 360 nm) and a photoconductive detector. The analog output from this detector is plotted and integrated by a peak integrator and the normalized peak area percent is used to follow CSD feed quality.

Initial testing of the new detector versus the detector used in the prototype system (in series) indicated a lack of reproducibility for the new detector. Excessive offset in the baseline before and after the pyridine-eluted peak was believed to be a contributing factor. The cell position was adjusted to minimize this offset and this, together with sonication of the pyridine-solubilized sample just prior to introduction into the sample loop, sharply improved system reproducibility. The completed laboratory system, installed in the Wilsonville control laboratory on May 23, has been operating in a troublefree manner. Results obtained to date have apparently tracked CSD operation quite closely and initial results seem to indicate that the assay may be useful in predicting CSD operation. Some initial results from Wilsonville are presented in Section 2.2 of this report.

6.2.3 CLFS Studies - D. D. Lee, J. H. Wilson, T. L. Sams, and
D. A. McWhirter

In any coal liquefaction process, knowledge of the physical properties (e.g., viscosity, density, thermal conductivity, and heat capacity) of coal liquids and slurries under process conditions is required for proper design of the processing equipment. Conventional instrumentation for physical properties measurements will not operate at the high temperatures and pressures [31 MPa (4500 psig) and 810 K (1000°F)] that can be reached in various liquefaction schemes. In addition, the physical properties may be strongly influenced by dissolved hydrogen, ongoing reactions, mixing and holding conditions of the slurry before liquefaction, and residence time above the onset of reaction temperature. For these reasons, flowing stream measurements of the reacting mixtures are required.

The Coal Liquids Flow System (CLFS) has been designed as a versatile instrument to measure the viscosity and density of flowing streams of coal liquids or slurries at process conditions and while the slurry is undergoing reaction. A thermal conductivity instrument is presently being installed and a heat capacity unit is to be added later. The CLFS is capable of measuring slurry rheology and density at high temperature and pressure, with and without hydrogen present, under a variety of different slurry mixing and holding conditions prior to actual reactions, and at contact times under reaction conditions ranging from 10 s to 2 min. Detailed descriptions of the CLFS are included in previous reports.

The thermal conductivity instrument which had been installed previously was piped into the CLFS unit. Measurements were made at temperatures from 295 to 500 K using a Wilsonville solvent and a slurry prepared from this solvent and Illinois No. 6 coal at a solvent-to-coal weight ratio of 2:1. With increasing temperature, the thermal conductivities varied from 1.58 to 1.0 mW/(cm K) and from 1.23 to 0.93 mW/(cm K) for the slurry and the solvent, respectively. Initial results from these thermal conductivity experiments may be found in Section 2.1 of this report. Measurements at temperatures up to 700 K will be

attempted. Afterwards, a study of the effects of slurry mix tank temperature and residence time on slurry rheology at preheater conditions will be performed.

6.2.4 Wilsonville Tracer Study - R. L. Jolley

Objective: The objective of this work element is to prepare a study plan for implementation at the Wilsonville SRC pilot plant to measure the slurry residence time in the dissolver using radioactive tracers.

Progress: Stimulus-response measurements using radiotracers have been used to measure residence time distributions (RTD) and hydrodynamic parameters for the preheaters and dissolvers at the Ft. Lewis and the Exxon Donor Solvent coal conversion pilot plants. We have proposed a plan for a similar series of radiotracer RTD studies at the Advanced Coal Liquefaction facility at Wilsonville, Alabama. The objective of the proposed plan is to measure the residence time distributions for the preheater and dissolvers in the SRC-I mode. Xenon-133 and gold-198 (on carbonized resin or as an aqueous suspension of colloidal gold) will be used as tracers for the gas and slurry, respectively. Four experimental phases are recommended for the RTD tracer studies: (1) preheater; (2) dissolver with 100% takeoff; (3) dissolver with 100% takeoff and solids withdrawal; and (4) dissolver with 50% takeoff. Eighteen gas tracer and 22 slurry tracer injections are projected to accomplish the four experimental phases. The experimental design and projected time schedule, including procurement of necessary components, preparation of the radiotracers, assembly and testing of tracer injection apparatus and detection systems, onsite work and tracer injections, laboratory experimentation, data analysis, and report writing are included in the plan. The total estimated cost of the proposed plan is \$221,483. The final draft report has been prepared and reviewed and is currently being edited.

6.2.5 Wilsonville Support - J. H. Wilson

The Wilsonville Technical Review and the Planning and Scheduling meetings were attended on May 4 and June 15, 1983. During the reporting periods, Run 243, operated in the integrated two-stage liquefaction (ITSL) mode, was in progress. The thermal dissolver was operated initially with 50% and later with 25% volume in service. No substantial difference was apparent between the yield structures of Run 243 and Run 242 which was an ITSL run with the dissolver bypassed. Two options for Run 244 are catalytic hydrotreatment of light SRC with subsequent recycle of atmospheric flash bottoms to the thermal stage (in contrast to hydrotreating all of the CSD unit SRC product) and evaluation of a new catalyst presulfiding technique which should increase catalyst sulfur level from about 5 to 10%.

6.3 Process Analysis

John M. Begovich, Oran L. Culberson, Philip J. Johnson,
and Ashfaq A. Khan

Accurate process calculations are necessary for rational design and operation of process equipment. Process analysis support to DOE/ORO includes the following: (1) support for ICRC's SRC-I steady-state modeling program, (2) analysis of the SRC-II physical property data base using the ASPEN simulator program, and (3) independent verification of the H-Coal pilot plant material balance calculations.

6.3.1 SRC-I Steady State Modeling Support

ORNL is responsible for providing support to DOE/ORO in reviewing the development of a steady-state model of the SRC-I process by the International Coal Refining Company (ICRC). ORNL initiated this effort in a meeting at ICRC in February, 1983. During the course of this meeting, it became evident that ICRC's modeling of the SRC-I product area using the ASPEN (Advanced System for Process Engineering) simulator was proceeding smoothly. To facilitate detailed ORNL understanding of

ICRC's modeling activities and to ensure a productive contribution, it was mutually agreed that ORNL would attempt, in a limited 4-month effort, to develop an ASPEN model of the hydrogen sulfide removal plant in the SRC-I hydrogen recycle system compatible with the ICRC ASPEN models.

In the SRC-I plant, H_2S will be scrubbed from the H_2 recycle stream using diethanolamine (DEA) units. These units combine physical absorption with chemical reaction to remove H_2S so that the scrubbed stream, composed primarily of hydrogen, can be recycled back to the hydrogenation reactor. A unit operation block for absorption with chemical reaction does not presently exist in ASPEN. The existing blocks, ABSBR and RADFRC, handle physical absorption only. While it may be possible to use a chemical reactor block such as RGIBBS to simulate the DEA system, such an approach will require coupling RGIBBS blocks in series to simulate multiple stages and knowledge of the extent of conversion (which is a function of the concentration of each species) for each stage. In this work, it was felt that a more tractable approach would involve the use of ABSBR or RADFRC along with activity coefficient parameters regressed from vapor-liquid equilibria (VLE) data for the quaternary H_2S - CO_2 -DEA- H_2O system.

Since it was recognized that modeling of an H_2S -DEA scrubber would be a challenging task, the effort was divided into several parts. This report describes the development of a simplified flowsheet model where the absorption units were simulated using ASPEN SEP blocks. This model was based on existing flowsheets and would be sufficient, in the event of failure to put together a rigorous scrubber model, of closing the hydrogen recycle loop. Sections describing our experience in using ABSBR and RADFRC as physical absorbers with the H_2S - CO_2 -DEA- H_2O system and an ideal system (CH_4 - C_5H_{12} - $C_{14}H_{30}$) will be reported in the next report, as will compilation of the physical properties required for DEA and regression of the VLE data for the quaternary system and the use of these data with ABSBR.

Simplified flowsheet - An ASPEN mass and energy balance simulation model was constructed for the Area 15 - DEA Unit of the SRC-I Demonstration Plant. The flowsheet developed by the Ralph M. Parsons Company under contract to ICRC for the DEA section of the plant was used as the basis for the ASPEN simulation.

The block-flow diagrams for the ASPEN simulation are shown in Figures 6.2a through e. Stream and block identifications for the simulation were made consistent with the Parsons flowsheet whenever possible. This included dividing the overall flowsheet into the five sections depicted in Figs. 6.2a-e.

Stream parameters needed in the simulation (temperatures, pressures, and entering stream flowrates and compositions) were obtained from the material balance summary tables included with the Parsons flowsheet. The unit operation parameters needed were also taken from the Parsons flowsheet. These included heat exchanger outlet temperatures, pump outlet pressures, drum outlet pressures and split fractions for various streams.

The ASPEN general component splitter/separator model SEP was used to simulate the performance of the six towers included in the design (H.P. water wash column, L.P. water wash column, H.P. DEA absorber, L.P. DEA absorber, caustic wash column, and DEA regenerator). The separations of the components were based on data presented in the Parsons material balance tables.

Due to problems with the ASPEN compressor/turbine model COMPR, the two-phase flash model FLASH2 was used to model the DEA hydraulic turbine, HT-15301 [Fig. 6.2(c)]. The principal source of the problem was that COMPR does not allow for any vapor to be present in the feed stream to the block. In this simulation, a small amount of vapor (0.3 per cent) was predicted to be in the feed stream; this resulted in an ASPEN error being generated, and the block being bypassed when COMPR was utilized.

The ASPEN stoichiometric reactor model RSTOIC was used to account for the following reactions occurring in the caustic wash column:

Fig. 6.2(b). ASPEN block diagram of the SRC-I DEA Unit Area, based on Parsons flowsheet No. 00-15-01302D.

Fig. 6.2(c). ASPEN block diagram of the SRC-I DEA Unit Area, based on Parsons flowsheet No. 00-15-01303D.

Fig. 6.2(d). ASPEN block diagram of the SRC-I DEA Unit Area, based on Parsons flwsheet No. 00-15-01304D.

Conversions of CO_2 and H_2S in the above reactions were taken to be 0.79, 0.18, and 0.80, respectively. These conversions were determined from material balance data taken from the Parsons tables.

Physical properties for NaOH , Na_2CO_3 , NaHCO_3 and NaHS are not included in the ASPEN pure component data bank. Values needed to account for the presence of these components in the flowsheet were determined and entered into the ASPEN input language.

Results - A comparison of the Parsons and ASPEN simulation values for the compositions of the high pressure DEA absorber overhead and bottoms streams is presented in Table 6.1. A similar comparison is shown in Table 6.2 for the low pressure DEA absorber overhead and bottoms streams. The ASPEN results are in good agreement for both columns.

It should be noted that this ASPEN simulation does not account for boiling point curve cuts, and thus no comparison of results can be made for these components.

Table 6.3 presents the comparison of the Parsons and ASPEN simulation values for the treated gas compositions, and Table 6.4 shows the comparative results for the acid gas stream. Again, the results of the simulation are in good agreement with those of Parsons.

6.3.2 VLE Analysis of the SRC-II Data Base with ASPEN

The objective of this task is to evaluate the SRC-II physical property data base by utilization of the unique features of the ASPEN simulator program and to examine applicable vapor-liquid equilibrium (VLE) techniques. Validated thermodynamic methods for handling the SRC-II data will be incorporated into ASPEN and will be made available to DOE and its contractors.

Table 6.1. Comparison of the Parsons and ASPEN simulation values for the composition of the high pressure DEA absorber overhead and bottoms streams

H.P. DEA Absorber Overhead (Stream 6305)			H. P. DEA Absorber Bottoms (Stream 6315)		
Component	Parsons	ASPEN	Component	Parsons	ASPEN
H ₂	9937.95 lbmol/hr	9938.05	H ₂	9.11 lbmol/hr	8.95
N ₂	598.62	598.58	N ₂	0.34	0.36
Ar	95.92	95.92	Ar	0.06	0.06
CO	690.36	690.38	NH ₃	0.02	0.02
CO ₂	6.73	6.73	CO	0.57	0.55
H ₂ S	0.05	0.04	CO ₂	88.10	88.12
C ₁	1381.37	1381.48	H ₂ S	217.07	217.12
C ₂	409.48	409.55	C ₁	1.45	1.38
C ₃	190.74	190.77	C ₂	0.46	0.41
C ₄	85.97	85.97	C ₃	0.23	0.19
C ₅	27.00	27.00	C ₄	0.03	0.03
C ₆ - 250°F	46.00	*	DEA	465.76	465.79
250 - 300°F	1.00	*	H ₂ O	7812.89	7871.10
H ₂ O	14.57	14.98			

*Boiling point curve cuts not included in ASPEN simulation.

Table 6.2. Comparison of the Parsons and ASPEN simulation values for the composition of the low pressure DEA absorber overhead and bottoms streams

L.P. DEA Absorber Overhead (Stream 6314)			L. P. DEA Absorber Bottoms (Stream 6317)		
Component	Parsons	ASPEN	Component	Parsons	ASPEN
H ₂	115.65 lbmol/hr	115.49	H ₂	0.46 lbmol/hr	0.46
N ₂	17.52	17.54	N ₂	0.02	0.02
Ar	1.76	1.76	NH ₃	0.02	0.02
CO	18.24	18.22	CO	0.03	0.03
CO ₂	2.73	2.70	CO ₂	90.42	90.47
H ₂ S	0.10	0.09	H ₂ S	228.52	228.59
C ₁	232.98	232.91	C ₁	0.07	0.07
C ₂	83.24	83.19	C ₂	0.02	0.02
C ₃	4.30	4.30	C ₃	0.01	0.22
C ₃	55.42	55.17	C ₄	0.01	0.03
C ₄	3.30	3.30	DEA	529.50	529.50
C ₄	51.87	51.59	H ₂ O	8682.65	8742.13
C ₅	1.50	1.50			
C ₅	17.90	17.90			
C ₆ - 200°F	15.50	*			
200 - 250°F	1.30	*			
250 - 300°F	0.40	*			
300+	0.10	*			
H ₂ O	11.82	13.13			

*Boiling point curve cuts not included in ASPEN simulation.

Table 6.3. Comparison of the Parsons and ASPEN simulation values for the treated gas compositions

Treated H.P. Gas to Hydrogen Purification (Stream 6307)			Treated H.P. Gas to Hydrogen Compression (Stream 6308)	
Component	Parsons	ASPEN	Parsons	ASPEN
H ₂	6299.96 lbmol/hr	6290.16	3636.89 lbmol/hr	3646.9
N ₂	379.50	378.86	219.08	219.66
Ar	60.80	60.71	35.10	35.20
CO	437.64	436.97	252.64	253.34
CO ₂	0.08	0.13	0.05	0.07
H ₂ S	<0.01	<0.01	trace	<0.01
C ₁	875.67	874.39	505.51	506.95
C ₂	259.57	259.22	149.85	150.29
C ₃	120.91	120.73	69.80	69.99
C ₄	54.33	54.42	31.37	31.55
C ₅	17.11	17.09	9.87	9.91
C ₆ - 250°F	29.14	*	16.82	*
250 - 300°F	0.63	*	0.37	*
H ₂ O	6.12	11.79	3.48	6.84

*Boiling point curve cuts not included in ASPEN simulation.

Table 6.4. Comparison of the Parsons and ASPEN simulation values for the acid gas stream composition

ACID GAS TO S.R.U.		
(Stream 6334)		
Component	Parsons	ASPEN
H ₂	0.46 lbmol/hr	0.464
N ₂	0.02	0.018
NH ₃	0.02	0.02
CO	0.03	0.029
CO ₂	84.07	84.14
H ₂ S	213.51	213.51
C ₁	0.07	0.07
C ₂	0.02	0.02
C ₃	0.01	0.22
H ₂ O	18.11	20.73

Status — The flowsheet for the computer program developed to interface with the ASPEN simulator is shown in Fig. 6.3. Data which describe a boiling point curve are fed into the program, as is the choice of physical property correlations. After fitting the boiling point curve, it is broken into the desired number of cuts, or pseudocomponents, and for each cut the physical properties required in ASPEN are obtained. The program outputs the necessary information in a format that is directly compatible with ASPEN.

The effect of changing the boiling cut size, which is used to define the average properties of a pseudocomponent, was examined using the boiling point distillation curve for SRC-II liquid given by Henry.¹ Physical property correlations developed by Wilson² were utilized with the chosen cut sizes to simulate isothermal flashes with ASPEN at temperatures ranging from 400 to 700°F and at low and high pressures (215 and 2015 psia). The results are shown in Table 6.5. Both hydrogen and methane were mixed with the coal liquid before flashing. For the hydrogen-to-coal-liquid-feed ratios considered, the vapor fraction flashed was found to be relatively insensitive to cut size for cuts smaller than 100°F, but it was very sensitive to the hydrogen-to-coal-liquid-feed ratio. The methane-to-coal-liquid-mass ratio was held constant. The conclusions may not apply to other systems. These ASPEN simulations were performed using the Redlich-Kwong-Soave (RKS) equation of state.

The main program for interfacing thermodynamic property correlations with ASPEN has been made more flexible so that any given set of physical property correlations (which are written in separate subroutines) can be invoked to write an ASPEN input program. A correlation proposed by Wilson for calculating Antoine vapor pressure coefficients was added to the computer subroutines. Also, some physical property correlations which were examined by ASPEN Technology, Inc.,³ were programmed as a subroutine and connected with the overall computer program.

The effect of perturbations in critical temperatures on the vapor fraction in an isothermal flash and the phase envelope was examined for pure component mixtures. The mixture pairs chosen were hydrogen/

Fig. 6.3. Flowsheet of physical properties program developed to interface with ASPEN.

Table 6.5. Effects of cut size on coal liquid
vapor mole fraction flashed

Number of Cuts:	1	2	10	20	50
Cut Size (°F):	1000	500	100	50	20
Temperature °F	Vapor Mole Fraction, P = 215 psia				
400	0.5911	0.6046	0.6254	0.6241	0.6236
500	0.6003	0.7954	0.7336	0.7324	0.7320
600	0.6342	0.9323	0.8822	0.8826	0.8827
650	0.6728	0.9518	0.9455	0.9464	0.9465
700	0.7414	0.9684	0.9871	0.9879	0.9879
	Vapor Mole Fraction, P = 2015 psia				
400	0.5462	0.4793	0.4916	0.4914	0.4913
500	0.5371	0.4818	0.4974	0.4969	0.4967
600	0.5276	0.5081	0.5185	0.5176	0.5172
650	0.5233	0.5418	0.5396	0.5385	0.5381
700	0.5199	0.6015	0.5729	0.5715	0.5712

toluene and methane/n-decane. The reason pure components were chosen for this study was to estimate possible effects of inaccuracies in the critical temperature correlations on the vapor fraction calculated by ASPEN. This approach was taken after discussions with Dr. M. Brule of the University of Oklahoma.

Hydrogen/toluene mixtures have been extensively studied experimentally by Chao et al.⁴ and S. Laugier et al.⁵ The ASPEN isothermal flash simulations were carried out at a temperature of 269°C and a pressure of 249.8 atmospheres using the Redlich-Kwong-Soave equation of state. It was found that the K values obtained from the simulation matched those from Chao's experiments to within 1%. However, when the critical temperature of toluene was perturbed by 10%, the simulation failed to converge. Thus, it was concluded that the precision of the physical property correlation for critical temperature may have to be high in order to simulate systems such as hydrogen/toluene.

At the request of DOE/PETC, a review has been made of the work on physical property correlations done by ASPEN Technology, Inc.³ Plans for next quarter include the following: (1) Runs will be made to simulate P-99 flash and separation units using the data of S. T. Mathias;⁶ (2) Transport property correlations will be examined. (3) Quality checks will be continued on the computer programs using the ASPEN data base.

6.3.3 H-Coal Material Balance Calculations

The objective of this work is to enable the DOE, independently, to reproduce material balance yield calculations for the H-Coal Pilot Plant based on information available in the McAuto data base and other information available to DOE and referenced in the Final Technical Report of the H-Coal Pilot Plant.

Status — The computer program MATBAL, as received from ASFI/HRI and supplemented by McAuto and ORNL, has been successfully compiled and executed. The entire Pilot Plant process and analytical data file was obtained from McAuto, placed in storage on the ORNL computer system, and is accessible via the MATBAL program.

MATBAL was then executed in three steps. In the first step, the raw data were retrieved for the period 7/7/82 to 7/8/82 (Run 10 with Wyodak coal). The three matrices printed (raw hourly stream flows, raw elemental analyses for flows, and raw compositional analyses for flows) agreed identically with the printout provided by ASFI/HRI for the same time period. This agreement confirmed the correctness of the process and analytical data received from McAuto.

In the second step, the special adjustments identified by ASFI/HRI were used to modify the raw data of the above three matrices. The third step then consisted of making actual material balance calculations using the adjusted matrices. The results of this third step essentially duplicate those of ASFI/HRI.

The transference of these results to tables in the topical report and the use of the special adjustments, however, raise several concerns. As described in an interim report to DOE/ORO, a large number of adjustments were made to the raw data. These include changes in the flow rates and compositions of the major feed input and product output streams. While the explanation for these special adjustments may be quite straightforward, the substantial changes made to the raw data cause some uncertainty about the reported yields. The reasons for making adjustments to the raw data need to be clearly explained by ASFI/HRI so that their reasonableness can be evaluated.

ASFI/HRI has been asked to provide detailed answers to the questions raised in this work. Specifically, these questions concern the special adjustments made to the three matrices of the raw input data and the manner in which MATBAL output results are reported in the topical reports. ORNL will be able to determine the reasonableness of these adjustments once their rationale has been explained.

If valid future mass balances are to be made for any other periods of Run 10, Run 8, or Run 11, all of the special adjustments necessary for those calculations must be documented and explained by ASFI/HRI. Once their reasonableness has been verified, DOE might well find it more convenient to have the modified matrices stored rather than the raw input matrices.

6.4 Materials

This section reports on five subtasks in materials technology: materials support for improved slurry valves in direct coal liquefaction plants, mechanical properties for pressure vessels, solvent refined coal (SRC)-I liquefaction project support — materials, materials testing for H-Coal, and materials testing for the Exxon Coal Liquefaction Pilot Plant.

6.4.1 Materials support for improved slurry valves in direct coal liquefaction plants — A. J. Caputo

The objectives of this activity are to characterize the more popular commercial trim materials, to obtain candidate advanced trim materials for screening tests, and to submit samples to Battelle Columbus Laboratories for erosion testing. Funding for this task was authorized in February 1981, and work was initiated on characterizing the commercial trim materials more commonly used in letdown valves. Letdown valve trim samples received from Wilsonville and Fort Lewis were included in the characterization studies.

Candidate advanced letdown trim samples are being supplied by commercial vendors for incorporation into this activity. In addition, a number of samples have been fabricated at ORNL and Sandia National Laboratory, Albuquerque.

During this reporting period candidate advanced trim materials were erosion tested at Battelle Columbus Laboratories. The results, which ranged from good to bad, are summarized in Table 6.6.

When the results of Table 6.6 are compared with the crater depths (1.6–2.9 μm) obtained on the reference 701 cemented carbide material, a portion of the ORNL TiB_2 coatings and the General Electric Company sintered $\beta\text{-SiC}$ are the only materials that showed substantial improvement. It is interesting that the TiB_2 coatings deposited at 900°C showed essentially no wear but that those deposited at 800°C were completely penetrated by the coal-oil jet stream, although the coating thickness ranged from 4 to 25 μm .

Table 6.6. Results of erosion tests on advanced trim materials

Source	Specimen	Material	Crater depth (μm)
General Electric, Houston	GE-H1	Sintered $\beta\text{-SiC}$	0.7
ORNL	Z-65	Hot-pressed B_4C -10% Co	6.9
ORNL	SC-68	Hot-pressed Al_2O_3 -20% SiC	3.8 ^a
ORNL	SC-68	Hot-pressed Al_2O_3 -20% SiC	14.0 ^b
ORNL	160	Hot-pressed CrB-8% Fe	101.6
ORNL	161	Hot-pressed CrB-8% Ni	127.5
ORNL	162	Hot-pressed CrB-8% Co	133.1
ORNL	163	Hot-pressed CrB-10% Fe	49.0
ORNL	164	Hot-pressed CrB-10% Ni	198.1
ORNL	165	Hot-pressed CrB-10% Co	66.6
Nilsen	MS	Partially stabilized ZrO_2 (MgO)	30.5 ^c
Nilsen	MS	Partially stabilized ZrO_2 (MgO)	7.4 ^d
Nilsen	TS	Partially stabilized ZrO_2 (MgO)	8.5 ^c
Nilsen	TS	Partially stabilized ZrO_2 (MgO)	24.6 ^d
ORNL	AJC-401	4 μm CVD TiB_2 on WC-Co (GE-370)	5.2 ^e
ORNL	AJC-394	7 μm CVD TiB_2 on WC-Co (GE-370)	11.4 ^e
ORNL	AJC-402	5 μm CVD TiB_2 on WC-Co (GE-370)	8.7 ^e
ORNL	AJC-425	13 μm CVD TiB_2 on WC-Co (GE-370)	23.6 ^e
ORNL	AJC-422	25 μm CVD TiB_2 on WC-Co (GE-370)	33.0 ^e
ORNL	AJC-426A	20 μm CVD TiB_2 on HP TiB_2 -Ni	30.5 ^e
ORNL	AJC-411	22 μm CVD TiB_2 on WC-Co (GE-370)	~0 ^f
ORNL	AJC-391	29 μm CVD TiB_2 on WC-Co (GE-370)	~0 ^f
ORNL	AJC-404	24 μm CVD TiB_2 on WC-Co (GE-370)	~0 ^f

^aParallel to surface polish direction.^bNinety degrees to polished surface.^cAs-fabricated surface.^dAs-cut surface.^eDeposited at 800°C; CVD, chemically vapor deposited.^fDeposited at 900°C.

The partially stabilized ZrO_2 appears to be sensitive to whether the fabricated or the cut surface is being tested, but it is not consistent. The Al_2O_3 -SiC composites seem to be sensitive to whether the jet stream hits the sample in a plane parallel to or at 90° to the direction in which the surface had been polished. The results on the B_4C -Co sample are not as promising as were earlier results. The results of the CVD with iron, nickel, and cobalt binders are not encouraging.

6.4.2 Mechanical properties for pressure vessels — R. W. Swindeman and B. C. Williams

The objective of this activity is to produce the mechanical properties data for reliability and safety analyses of SRC dissolver vessels. Time-dependent data for construction materials have been collected and assessed according to the criteria established in Sect. VIII, Div. 1, and Sect. VIII, Div. 2, of the *ASME Boiler and Pressure Vessel Code*. We found that, at the design temperatures of the SRC-I dissolver vessel, time-dependent properties should dictate the allowable design stress intensities. Values for the pressure vessel material (SA-387, grade 22, class 2) were recommended.⁷

We have developed isochronous stress-versus-strain curves that allow an elastic analysis to be used in conjunction with a limit strain derived from the shape of the creep curve, temperature, and design life of the component and have recommended a program that would lead to the verification of this approach for design problems.⁸

We believe that, if there are fatigue problems in the dissolver, they will occur in weldments. Hence, our experimental work on 2 1/4 Cr-1 Mo steel emphasizes tests on welds. Testing of weldments produced by the hot-wire narrow-groove gas tungsten arc (GTA) process was completed at $482^\circ C$ ($900^\circ F$), and results were described in the last progress report.⁹ However, we have initiated additional testing at room temperature to obtain information about the behavior of weldments at temperatures currently covered for design by Sect. VIII, Div. 2, of the *ASME Boiler and Pressure Vessel Code*. Preliminary data suggest that fatigue life improves with decreasing temperature.

Fatigue testing has started on specimens machined from a submerged arc weldment produced at ORNL. Testing data at 482°C (900°F) indicate that this material has better fatigue properties than does the GTA weld. Even so, defects and large differences in the weld metal and base metal strengths produce strain concentrations that greatly reduce fatigue life.

Work has started on collecting and interpreting fatigue crack growth data produced on SA-387, grade 22, class 2, and its weldments. We hope to complete this work in August and draft a report that recommends a program leading to a design methodology for flawed heavy-wall structures operating above 371°C (700°F).

6.4.3 SRC-I liquefaction project support -- materials -- A. R. Olsen, J. R. Keiser, and G. M. Caton

The objectives of this work element are to assist in the review of contractor documents for materials selection, to review and provide input to materials testing and failure analysis plans, and to compile materials information for specific processing steps for use by designers in making appropriate materials choices.

SRC-I design materials reviews -- During this quarter several revised baseline designs for various portions of the SRC-I demonstration plant have been released for comment. The review of materials design selections for the proprietary expanded bed hydrotreater (EBH) process area was completed. The entire Parsons design area incorporating gasification and gas treatment processes, including the revised design documents and the piping and instrumentation drawings, was reviewed in Oak Ridge and Allentown. The primary objective of this review was to ensure the incorporation of appropriate materials performance monitoring, including corrosion probe and corrosion coupon racks, in the design documentation, although a cursory review of modified materials selections was also included. Materials performance monitoring locations were also reviewed for the EBH process area and the Coker and Calciner areas, and the review is essentially complete for the SRC process and critical solvent deashing areas of the plant. We have also reviewed and commented on International Coal Refining Company's (ICRC's) response to our earlier comments on the materials selections for the critical solvent deashing unit.

In the SRC area an important concern has been the suitability of carbon steel for piping and equipment to handle the process solvent above 230°C (450°F). In a meeting at Allentown, a compromise solution for this problem in the design baseline was reached. Most of the materials selections will be changed to austenitic stainless steel or a 5 Cr-1 Mo alloy, but one line in a series of four parallel lines of heat exchangers will remain carbon steel with appropriate corrosion-monitoring equipment. This decision was based on limited available corrosion data and economic considerations. We also reviewed and commented on an ICRC proposal to obtain additional experimental data on the corrosivity of process solvent as a function of temperature.

Materials information compilation and assessment -- During this quarter we continued to collect the design data for the SRC process area. With the exception of the proprietary critical solvent deashing area, all the revisions in accordance with the revised baseline designs have been entered on the appropriate forms. We have also initiated the development of similar files that are suitable for computer entry to record pilot plant and laboratory corrosion data and component performance information. Although these data have been used to review the design materials selections, the new format will make the data more readily accessible.

6.4.4 Materials testing for H-Coal — J. R. Keiser, A. R. Olsen, and R. R. Judkins

The chemical analyses of selected feed coal and flaker samples collected at the H-Coal Liquefaction Pilot Plant were completed this quarter. We attended a meeting in Catlettsburg, at which pilot plant personnel described the performance of plant components and materials.

The last operating period at the H-Coal Pilot Plant, run 11, was from August 12 to November 19, 1982. Operation with Illinois No. 6 coal continued from the start of the run until October 31, when a switch was made to Kentucky No. 9 coal. According to engineers at the plant, during Illinois coal operation, corrosion probes indicated negligible corrosion in the fractionation column.

About the time the switch was made to Kentucky coal, an instrument failure prevented the collection of corrosion probe data for several days. When data collection resumed, appreciable corrosion had occurred in the middle portion of the fractionation column, and significant corrosion continued until the end of the run. Chemical analyses of column liquids were reported to show increasing chlorine content during operation on Kentucky coal. In an effort to determine the cause of this apparent difference in corrosivity, we requested, received, and analyzed samples of feed coal and the flaker product. Along with many samples of Illinois and Kentucky feed coal, we received one sample of Wyodak coal. Results of analyses of the feed coals are given in Table 6.7. These results show that the Wyodak coal had the lowest nitrogen, sulfur, and chlorine contents. Although the Illinois coal apparently caused less corrosion in the fractionation column, its chlorine content was considerably higher than was that of the Kentucky coal.

Table 6.7. Feed coal analysis results

Coal type	Number of samples analyzed	Average content						
		N (%)	S (%)	Cl (μg/g)	Na (μg/g)	Mg (μg/g)	K (μg/g)	Ca (μg/g)
Illinois No. 6	10	1.25	3.31	622	483	935	1,610	4,468
Kentucky No. 9	13	1.48	3.40	114	139	731	1,438	1,223
Wyodak	1	0.79	0.87	27	717	2,650	422	12,100

As suggested in previous work, we thought that the chemical form of the chlorine in the feed coal might be the key in explaining why a low-chlorine coal (Kentucky) was more corrosive than a higher chlorine coal (Illinois).¹⁰ Of the salts that might be present in the feed coal, NaCl would not be expected to hydrolyze under liquefaction plant conditions, CaCl₂ would at least partially hydrolyze, and MgCl₂ would hydrolyze appreciably. Table 6.7 shows that the Illinois coal has more sodium, which, if present as NaCl, would tend to prevent formation of HCl.

However, the Illinois coal also has more magnesium and calcium, which would tend to promote HCl formation. Obviously, the apparent greater corrosivity of the Kentucky No. 9 coal cannot be explained simply on the basis of Cl, Na, Mg, and Ca contents.

The importance of amines and phenols in this corrosion process is well established,^{10,11} but we were not able to obtain samples of fractionator liquids to analyze for these components. The nitrogen content of the Kentucky feed coal was 15 to 20% higher than that of the Illinois coal, but that does not necessarily relate to the amine content of the fractionator liquids.

Analyses were performed on several samples of flaker product to determine if the unreacted mineral products could provide clues to explain the difference in corrosivity of the Illinois and Kentucky coals. The results in Table 6.8 show that, compared with the feed coal, a proportionately greater amount of chlorine was contained in the Illinois flaker product than in the Kentucky flaker product. The chemical form of the chlorine is not known, nor are the rates of production of the flaker products. If we assume that the flaker production rates were equal for the two coals (and coal feed rates were equal), we can say that proportionately more of the chlorine in the Illinois coal reached the flaker than was the case for the Kentucky coal. This chlorine could have been removed with the gaseous products as HCl or with the water as NH_4Cl . Or it could have reached the fractionator as an amine hydrochloride. Insufficient data are available for us to trace the path of the chlorine for each coal type completely or to determine why the low-chlorine coal is apparently more corrosive than the higher chlorine coal.

Table 6.8. Flaker product analysis results

Coal type	Number of samples analyzed	Average content					
		N (%)	S (%)	Cl ($\mu\text{g/g}$)	Na ($\mu\text{g/g}$)	Mg ($\mu\text{g/g}$)	K ($\mu\text{g/g}$)
Illinois No. 6	3	1.20	1.91	1622	913	370	3077
Kentucky No. 9	3	1.54	2.02	143	287	184	3267

6.4.5 Materials testing for Exxon Coal Liquefaction Pilot Plant —
J. R. Keiser, R. J. Gray, and A. R. Olsen

Metallographic examinations are currently being performed on 14 pieces of piping and components from the Exxon Coal Liquefaction Pilot Plant. Examination has been completed for three components: a fractionator tray clip, a hydrotreater reactor bubble cap, and some solvent hydrogenerator condenser tubing. Results of all the examinations will be summarized in the next quarterly.

6.5 Environment and Health

R. K. Genung

Projects which were active in the environment and health areas during this reporting period included field wastewater treatment studies at the SRC-I plant; continued work on occupational health risk assessment for SRC-I; and work on the assessment of lessons learned and remaining R&D needs in the areas of environment, health, and safety for direct liquefaction technologies while emphasizing experience from the Ft. Lewis project.

6.5.1 Studies of Wastewater Treatment Polishing Processes at the
Wilsonville, Alabama, Advanced Coal Liquefaction R&D Facility —
C. H. Brown, M. T. Harris, R. D. Roop, J. C. Rose, and
J. D. Hewitt

The objective of this project is the field evaluation of carbon adsorption, ozonation, and reverse osmosis as polishing processes in treating coal conversion wastewaters generated at the Advanced Coal Liquefaction R&D Facility (ACLF) in Wilsonville, AL. It is being supported by DOE/Fossil Energy through DOE/ORO. Laboratory studies at ORNL, supportive to the field work, were also conducted as part of this project.

Status Summary - The second and final operating campaign at the ACLF in Wilsonville, AL was conducted during the period May 13-27, 1983. A summary of tests conducted during this campaign is given below. In

order to stabilize the concentration of contaminants in the ACLF wastewater treatment plant equilization basin the flow of water from the liquid waste sump (LWS) was diverted to the "A" biotreater feedbox. This stream normally is introduced in the equilization basin and, since a major constituent of the LWS water is runoff due to rainfall, it results in large concentration fluctuations during periods of heavy rainfall.

Carbon absorption - Before startup of the carbon unit the optimal feed pH was determined to be 7.5 based on batch adsorption tests performed in a shaker-flask system. In these batch tests the removal efficiencies of TOC, COD, phenol, and color were measured at a fixed carbon dosage and variable pH. Subsequent to these batch tests a bed-depth/services-time test was performed using equilization basin wastewater diluted to a TOC concentration of 150 to 200 mg/L. Wastewater feedrate to the unit was 63 mL/s (1 gpm) and initially three columns were operated in series using degassed regenerated Darco activated carbon. During this operating period contaminant removals were 30%, 85%, 100%, and 70% for COD, color, phenol, and TOC, respectively. After ~55 h of operation the pH control system on the carbon adsorption feed tank failed, resulting in a pH excursion from the control point of 7.5 to approximately pH 10. Readjustment of the pH to 7.5 resulted in plugging of the lead carbon column by a tar-like material which precipitated from the feed water. This tarry substance is soluble at high pH (~10) and much less soluble at pH 7.5. A sample of this material was obtained and is being analyzed by members of the Analytical Chemistry Division. The carbon adsorption unit was shut down temporarily to modify operating procedures. Upon restart the number 2 and 3 columns were operating in series and the feed pH was controlled between 10 and 10.5. The unit operated in this manner for 93 h at which time the number 3 column became plugged. An explanation of this plugging has not yet been deduced. During the second run period nominal removal levels for COD, color, phenol, and TOC were 30%, 65%, 97%, and 60%, respectively. For the remainder of the campaign (25 h), the unit was operated with only the number 2 column online.

The data taken during operation of the unit will be analyzed to determine height and rate of movement of the mass transfer zone for each component.

Ozonation - Several different types of experiments were performed with the ozonation unit during this campaign. The data obtained complement the data gathered earlier. The tests and preliminary results are outlined below.

I. Tests with water obtained from the equalization basin

1. A batch test was performed in which a captive volume of wastewater was stripped with air (no ozone generated). Results indicate that after 30 min of air stripping, 10% of the TOC and 3% of the COD were removed.
2. A second batch test was performed in which a captive volume of wastewater was ozonated for 5 h to determine ultimate TOC and COD removal capabilities. Preliminary results indicate complete removal of color and phenol within 6 min, these species were initially at 780 cu and 8 mg/L, respectively. In three hours of reaction time TOC was reduced from 125 to 45 mg/L and COD decreased from 600 to 80 mg/L. During the final two hours of ozonation, COD and TOC remained unchanged. During the test, pH decreased from 10 to 3.5 passing through two inflection points (similar to a titration curve for a diprotic acid).

II. Tests with water obtained from the "A" clarifier

1. A matrix of continuous ozonation experiments was performed with various combinations (following a fractional factorial design) of pH, ozone dose rate, and hydraulic

residence time. The range of values for these variables was:

O ₃ Dose Rate	3.6 - 6.6 mg O ₃ /L-min
pH	3.2 - 9.8
Hydraulic Residence Time	10 - 50 min

2. Carbon adsorption isotherms were measured for selected sets of conditions in 1 above. The results indicate adsorption to be less efficient after ozonation. Interpretation of the data is complicated by the very low values for many of the parameters.

Reverse Osmosis - The reverse osmosis (RO) unit was operated during the entire campaign on water obtained from the "A" clarifier. Pretreatment of this water consisted of pH adjustment to 5.5, filtration to 5 μ m, and addition of antiscalent. The membrane tested was an Osmonics, Inc. spiral wound cellulose acetate membrane. The unit was initially operated at 50 and 70% recoveries. Plugging of the control valves downstream of the module and partial plugging of the RO membrane occurred at 70% recovery. After cleaning, the unit was restarted at 60% recovery and was operated at this recovery for 89 h. The total elapsed time for this test was 235.8 h during which the unit was operated for ~71 h on tap water, ~161 h on wastewater, and ~4 h on cleaning solutions. A summary of the feed water to the RO unit is given in Table 6.9. Component rejection data are summarized in Table 6.10. Measurements made for COD and calcium are not included in this table. COD was below detectable limits and an interference was present in the calcium analysis causing poor mass balance closure.

The RO unit was operated using tap water as feed to facilitate measurement of permeate rate at fixed conditions. This was done initially, after the unit was cleaned subsequent to the blockage occurring at 70% recovery, and at the termination of the run. The conditions for the test were: 50-55% recovery, 26-28°C circulation temperature, and 2.76 MPa feed pressure. The tap water permeate rate is plotted as a function of time in

Table 6.9. Pretreated RO feedwater characteristics averaged during campaign W-2

pH	5.2
Conductivity	4475 μ S/cm
TDS	3125 mg/L
Calcium	62 mg/L as CaCO_3
Magnesium	42 mg/L as CaCO_3
Sulfate	1940 mg/L
Alkalinity	25 mg/L as CaCO_3
COD	56 mg/L
TOC	24 mg/L
Phenol	0.8 mg/L

Table 6.10. Summary of component rejection data

Component	Feed ^a concentration	Rejection (%)	
		Range	Average
TOC	19-37	76-95	86
Color	110-280	89-99	95
Phenol	0.5-1.3	56-95	76
Hardness ^b	84-118	82-100	94
Sulfate	1300-4700	85-100	94
Alkalinity	15-50	55-95	71
Conductivity	3600-6400	87-92	89
TDS	2500-4400	92-98	95

^aAll values mg/L except color is given in color units and conductivity is given as μ S/cm.

^bAs CaCO_3 .

Fig. 6.4. As shown in this figure, the permeate rate appears to decrease with time. A linear fit of the data yields

$$P = 12 - .0086 t \quad (1)$$

where P is the permeate flowrate in mL/s and t is operating time in hours. Equation 1 indicated a 20% decrease in flux in 280 h of operation. Manufacturer's data indicate a 7% decline in permeate flux in 280 h due to membrane compaction. With this assumed to be correct, there still remains a 13% decrease in flux which is probably due to fouling. The RO module will be sectioned and analyzed for foulants. Samples were taken of the cleaning solutions and of the feed, permeate, and concentrate streams during operation which will further help in identifying the RO foulants.

6.5.2 Occupational Health Risk Assessment - P. J. Walsh

The objectives and scope of this project are to provide a quantitative analysis to supplement design and implementation of industrial hygiene programs for SRC-I and to integrate health, engineering, chemical and biological data in order to prioritize possible concerns and minimize further testing requirements.

Status Summary - We have received final review comments on the report "Guideline for SRC-I Industrial Hygiene Monitoring and Research" from Dr. Kelly representing ICRC. The comments and suggestions were acceptable to the authors, and a final report will be published as an ORNL Technical Memorandum. Dr. Kelly and Dr. Cochran of ORNL contributed substantially to the presentation of data and major conclusions. We will acknowledge their efforts and the reviews and suggestions of others in the report.

The report now provides a consensus view of monitoring and research needs for the SRC-I demonstration plant based upon present information. Research needs were identified in three major areas.

1. Monitoring for exposures to materials of concern.
2. Prediction of source emissions and worker exposure factors.

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Fig. 6.4. Membrane productivity decrease during campaign W-2.

3. Biotesting to improve understanding of the possible range of effects resulting from various levels of exposure.

Research in these areas will improve the data base for assessment of the technology. In addition, recommendations for monitoring will help guide the design of an effective industrial hygiene program for the demonstration facility staff. This project was effectively concluded during this reporting period.

6.5.3 SRC Environmental, Health, and Safety Assessments - R. K. Genung

The objectives of this work, which will emphasize experience from the Ft. Lewis project, are to document the lessons learned and to prioritize remaining data and information needs in the areas of environment, health, and safety (EH&S). The data/information used in these assessments and the data/information generated by these assessments will be preserved in an expandable computer-based information system designed for public accessibility with appropriate consideration for classification and protection of its contents.

Status Summary - During this period, the scope of this program was modified to delete studies of socioeconomics and water availability and usage. The duration of the project was extended from September 30, 1983 to December 31, 1983. Deliverables for the following specific tasks which are now in progress are due at the conclusion of the project:

- Process Analyses for Source Terms
- Characterization, Monitoring, and Measuring Guidelines for Unregulated Materials
- Worker Registry Studies
- Occupational Health and Industrial Hygiene Studies
- Public Health Effects
- Solid Waste Management Studies
- Environmental Transport, Fate and Effect Studies
- Evaluation of Compliance Source Monitoring Programs

- Evaluation of Ambient Monitoring Programs
- Integrated Lessons Learned and Remaining Needs Report

The design of an information system and the selection of appropriate hardware and software is now in progress.

6.5.4 Studies of Wastewater Treatment Polishing Processes at the H-Coal Pilot Plant Site - C. H. Brown

Field evaluation of wastewater treatment polishing processes was conducted at the Catlettsburg H-Coal site during FY 1982 in a 60 mL/s (~1 gpm) PDU consisting of mobile, modular ozonation, carbon adsorption and reverse osmosis systems with associated feed storage and surge tanks. Efforts during FY 1983 focus on the development of material balances for priority pollutants.

Status Summary - The ORNL wastewater treatment process development unit (WWT-PDU) was operated at the H-Coal pilot plant during the period September 4-17, 1982. The WWT-PDU was used to treat the clarified effluent from the H-Coal activated sludge biotreater. The processing sequence consisted of the series combination of multimedia filtration followed by ozonation, carbon adsorption, pH adjustment, and reverse osmosis (RO). During the operating campaign two suites of samples, consisting of influent and effluent from each unit, were taken, preserved, and returned to ORNL for trace element analyses. The inorganic analyses were performed by personnel in the Analytical Chemistry Division at ORNL and consisted of metal cation and complementary anion analyses. These analyses were performed on only the reverse osmosis samples. Organic analyses were performed by Chemical Technology Division personnel. These analyses were performed on the first suite of samples and included the use of chromatographic sample concentration and analysis by high performance liquid chromatography (HPLC) and gas chromatography (GC). Some limited molecular identifications were made with the aid of gas chromatography-mass spectrometry (GC-MS).

Material balances based on the analyses for inorganics suggest barium and iron as possible precipitant-type RO foulants. Comparison of permeate

quality with drinking water standards indicates no components present in anything near hazardous amounts (mercury and arsenic were not analyzed). Data for cation rejection by the RO membrane are presented. Organics analyses indicate very efficient performance of the 3-module PDU. By HPLC analysis the carbon adsorption effluent is not distinguishable from distilled water; however, with the use of the more sensitive GC several differences were detected. Purge and trap analyses indicated the presence of purgeable nonpolar organics in the feed to the ozonation unit. Analysis of the RO permeate by GC showed two minor components (as compared to four in the feed) which are possibly inorganic in nature.

A draft final report was issued during this period to conclude the project. A final report (ORNL/TM-8775) will be issued later this year.

6.6 References for Section 6

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7. COMPONENT DEVELOPMENT AND PROCESS EVALUATION

D. M. Eissenberg

The objective of component development and process evaluation activities is to ensure that coal conversion (liquefaction, gasification, pyrolysis) processes, subsystems, and components are available which have satisfactory performance, lifetime, reliability, and safety for their intended applications, and that sufficient component and subsystem performance data are available to permit design optimizations. Activities to be carried out include performance and cost analysis; assessments of operating plants; field tests; operation of test loops; and the development of advanced processes, subsystems, and components.

Present component development activities include development of advanced components for use in gasification processes, reviews and analyses of the design and liquefaction plants, and fundamental research aimed at an improved understanding of the functional performance of critical components.

7.1 Advanced Gasification Component Development

D. M. Eissenberg and W. L. Greenstreet

Objective

Advanced gasification component development activities aim to provide reliable, durable, economic, advanced design critical components for application to coal gasification processes. This work covers slurry pumps, hot dirty gas heat exchangers, hot dirty gas compressors/expanders, hot dirty gas valves and coal preparation equipment. For each component or subsystem, the activities will result in the development of an R&D plan for advanced concepts and identification of test facilities.

Results from the program are contained in the following documents:

1. "Program Plans for Development of Hot Dirty Gas Compressors/Expanders for Coal Gasification Systems," M. E. Lackey.

2. "Program Plans for Development of Slurry Pumps for Coal Gasification Systems," M. E. Lackey.
3. "Program Plan for Development of Hot Dirty Gas Valves for Coal Gasification," W. K. Kahl.
4. "Program Plan for Development of Coal Preparation Equipment for Coal Gasification Systems," J. R. Horton.
5. "Program Plan for Development of Hot Dirty Gas Heat Exchangers for Coal Gasification Systems," E. L. Churnetski.

Each of these is in draft form and is being processed for publication as an ORNL/TM report.

7.2 Gasification Process Plant Review, Evaluation, and Support

W. L. Greenstreet and J. R. Horton

The objective of this task is to provide a means to guide and integrate component programs for coal gasification processes and to provide engineering support, as required, to pilot and demonstration plant projects.

This task has been completed.

7.3 Scoping Study of Technology Needs For Coal Liquefaction Critical Components

R. P. Krishnan

Objective - The purpose of this task is to identify scaleup-related technology gaps in coal liquefaction slurry pumps and slurry letdown valves. An assessment of the scaleup factors anticipated for commercial plants, the data gaps, and the development needs will be made for these two components.

Background - Slurry pumps and slurry letdown valves serve very important functions in the front end (i.e., coal processing sections which include preparation of the coal/oil slurry, preheating the slurry,

converting the slurry to oil at high temperatures and high hydrogen pressures and separating the reacted mixture into gas and liquid streams) of coal liquefaction plants. The successful operation of commercial-size coal liquefaction plant and plant availability are directly affected by the performance and reliable operation of these components. Also, from an economic standpoint, their impact is significant since the downtime in a commercial size coal liquefaction plant would prove very expensive in terms of both low productivity and high operation and maintenance costs for the plant. It is imperative that reliable components be installed to maximize plant availability.

The technical data on performance of these components have come primarily from the direct coal liquefaction pilot plants, viz the SRC-I, SRC-II, H-Coal, and EDS pilot plants, and to a limited extent from process development units and laboratories. Although the data gathered is extensive, it is believed that there are some important gaps in these data, particularly if they are to be used for reliable scale up to commercial sizes and for eliminating component-related bottlenecks in the major direction liquefaction processes. Current design of these components is largely based on state-of-the-art knowledge with due consideration of the limitations of present hardware. The emphasis in the selection and design of these components has been mainly to demonstrate their operability and reliability leaving scope for improvements and development for future applications in commercial size plants.

The component technology data base, as it currently exists, has been developed to meet the near-term needs of the coal liquefaction demonstration plants. It is not adequate to meet the long-term needs for future commercial plants in which the selection and sizing of those components have to be such that, in addition to operability and reliability, they would also have to be cost effective.

Status Summary - During this quarter just ended, the draft report on slurry pumps was completed. The significant findings are:

- The existing data base on slurry pumps for coal liquefaction pumping systems is adequate to specify functional pumps in the three pump services (coal slurry recirculation and pressure boosting, high pressure slurry feeding and vacuum bottoms pumping) considered in this study.
- Among the three types of pumps specified for the pumping services, the centrifugal pumps can be considered low risk and a sufficiently mature technology compared to the positive displacement pumps in the coal liquefaction application.
- The degree of scale-up indicated for the demonstration/pioneer commercial plant pumps with features demonstrated in the pilot plants is of the order of 10:1 or less. The scale-up factor appears reasonable from the standpoint of specifying and designing pumps in the required sizes for the larger plants with available technology.
- The on-stream factors anticipated in the larger plants are much higher for the low-head centrifugal pumps than for the positive displacement plunger pumps. A service life of 8,000 hours or greater for the centrifugal pumps, and 2,000 hours for the reciprocating pumps is projected in the larger plants. The experience on the screw pumps is extremely limited and is not adequate at the present time to predict the service life of the larger pumps.
- Testing of prototype pumps in all three pump categories (centrifugal, reciprocating, and rotary screw) in the demonstration plants or in a realistic test loop is imperative to optimize the design and operation parameters, to determine the practical limits on these parameters, and the sensitivity of pump performance to process parameters.

- Limitations in the existing data bases have led to conservative designs, use of high quality non-expendable type pumps, and extra redundancy compared to normal industrial practice. Additional work in pump component development and testing identified in this study can result in less conservative design, minimum sparing, improved pump service life, and reduced operation and maintenance needs.
- The potential benefits of revised pump designs and alternate technologies for the pumping services which have been mentioned in the literature, should be investigated in sufficient detail to consider their usage in future commercial plants.

This report is presently being reviewed internally and by DOE.

The draft report on the slurry pressure letdown valves is in preparation. The scope of this report will be much limited compared to the report on slurry pumps because there is very little information in terms of valve selection and specification for the larger demonstration and commercial plants.

The trade-off study performed by Catalytic on the slurry pressure letdown system for the SRC-I demonstration plant has some information on the projected sizes and the technical uncertainties in the scale-up of letdown valves. Both H-Coal and EDS are in the process of issuing their final reports which will contain the experience on the letdown valves in their pilot plants, the commercial readiness, and the recommended valve specification for the larger plants.

Completion of the draft report on valves during the next quarter, will essentially complete the activities under this task.

7.4 Surge Leg Pump Oscillating Flow Characterization

J. C. Conklin

Objective - The overall objective of this task is to investigate the flow and heat transfer characteristics of oscillating columns, particularly those containing liquid-liquid or liquid-slurry interfaces. The results

are intended to increase the technology base needed for the design and operation of surge leg reciprocating pumps for use in coal liquefaction plants.

The task will involve experimental and analytical approaches. The experimental work will utilize an existing 2" O.D. oscillating U-tube apparatus capable of maintaining oscillating columns of pure liquids, solutions, or slurries over a range of amplitudes and frequencies. Slurry particle migration in an oscillating flow inside a vertical tube will be of specific interest.

Status Summary - The effects of varying the frequency and stroke for an oscillating column were investigated for a trial mixture of aluminum particles in water during the quarter. For a given frequency, there is a critical value of stroke above which the entire column of liquid up to the free surface appears completely mixed with solid particles. At and below this critical value of stroke, an interface is formed above which the liquid is clear with all the solids being entrained below this interface. As the oscillation frequency is decreased, this critical stroke increases. The frequencies investigated to date were on the order of 1 Hz.

The liquid viscosity and solids volume fraction were also varied. The varied liquid viscosity had a more pronounced effect on the critical stroke than did the solids volume fraction. Future work will further investigate the effects of solids volume fraction, frequency, stroke and viscosity upon the value of the critical stroke.

Before draining the oscillating test column of the aluminum particle/water slurry, a portion of the slurry was saved. Experimental determination of the aluminum particle static settling rate has begun for correlation with the particle migration behavior observed for oscillating flow. An apparent tap water/aluminum particle gas generating chemical reaction may complicate such a correlation. This chemical reaction also probably caused cleaning problems with the oscillating flow test apparatus upon concluding the preliminary aluminum particle slurry tests. The glass test section had to be removed from the apparatus and be mechanically cleaned in order to remove all traces of the aluminum. Cationic resin exchange beads have been

identified as an alternate solids material. These beads have a size and density distribution comparable to those of coal slurries and have been obtained from local sources. No apparent chemical reaction between tap water and cationic resin exchange beads has been observed for the static case. Static settling rate experiments have begun.

Experimentally determined settling rates of the beads in water at a volumetric liquid fraction of 61%, comparable to that of coal slurries, have agreed with settling rates calculated from an empirical relationship observed from published static settling rate experiments with cationic resin exchange beads having smaller diameters.

A theoretical analysis of effective solids diffusion for an oscillating slurry flow where body forces are important is being developed in order to predict the effect of solids volume fraction and other important parameters upon the critical stroke value.

8. PROCESS ANALYSIS AND ENGINEERING EVALUATIONS

H. D. Cochran

Engineering Evaluations are being prepared for the DOE Fossil Energy Office of Planning and Environment. This effort includes evaluations of most of the coal conversion and utilization processes. The program objective is to provide, on a consistent basis, technical and economic evaluations of competing processes and systems for coal conversion and utilization. Current effort focuses on technical assessment of direct liquefaction.

Process analyses are provided for the DOE/FE-Morgantown Energy Technology Center. The effort includes: the development of analytical tools for use in the evaluation of processes and equipment and particularly development of ASPEN simulation models and ASPEN enhancements.

8.1 Liquefaction Technology Assessment (LTAS)

A. R. Irvine, O. L. Culberson, J. F. Fisher,
and R. Salmon

The objective of Liquefaction Technology Assessment is to provide technical information, cost information, and economic evaluations needed by the Department of Energy (DOE) to assist in the decision-making process. Direct coal liquefaction technology is being assessed for readiness for commercial application. The work is broken down into two major elements; the first element (Task 1) deals with the several direct coal liquefaction processing steps which involve major amounts of developing technology. The second element (Task 2) is concerned with an assessment of the capability to operate an integrated facility made for the new technology areas plus the areas of conventional technology. The areas of developing technology examined included the following:

- Dissolver
- Preheater, fired and unfired
- Vapor/liquid separation
- Vacuum distillation of residues
- Handling and utilization of residues
- Product upgrading
- Solid/liquid separations

- Slurry makeup
- VLE data base
- Critical components

During the previous quarter work was completed on all the above except for the last four. Summary information relative to these last four topics from recently completed draft reports is presented below. Also presented below is information on the status of Task 2, on which work was initiated during this report period.

8.1.1 Solid/liquid separations

Adequate process performance of the Kerr-McGee critical solvent deashing (CSD) process is contingent upon compatability of liquefaction process products with deashing system conditions, which include deashing solvent (DAS) composition, feed/solvent flow ratio, temperature, and pressure. At this time it is necessary that this compatibility and the deashing conditions be determined experimentally by use of prototypical, small scale equipment. In order for CSD to be a commercially applicable process, the prototype tests must demonstrate sufficient insensitivity of the CSD process to normal variations in coal liquefaction process product composition such that these variations will not result in process shutdown or other unacceptable results. The results obtained at the Wilsonville pilot plant when operating under demonstration plant conditions indicate that sufficient latitude is available under those conditions for satisfactory CSD operation; certain other pilot plant operations indicated that some liquefaction process conditions allow very little latitude in CSD operation.

Commercial scale equipment is expected to reduce problems with first stage settler plugging problems because the larger pipes and discharge valve ports will pass particulates and agglomerates with much greater facility than could the small equipment used in the pilot plant. Further, available instrumentation for detection of interface level and deposition of solids on settler walls can allow corrective action to be taken prior to the onset of operational difficulty. (This is in contrast to the situation that obtained during the bulk of the runs conducted at Wilsonville.) In addition, commercial scale operation is

assumed to be predicated upon use of operating conditions which are sufficiently far from boundary line (for operability) conditions that overextraction is highly unlikely. Commercial scale operation also implies consistent operations from day to day, in contrast to the general pilot plant experience.

The capability to produce fluffy ash powder (K-MAC) of a consistent character on a routine basis is not demonstrated even on the pilot plant scale. Because it is believed that the fundamentals governing this operation are understood, we are led to believe that a satisfactory commercial scale system can be devised.

The pilot plant experience indicates reasonable capability to produce SRC products having an ash content ≤ 0.16 wt per cent. While there is no direct experience with rework of high ash content products, it appears reasonable that either of two available rework systems could function adequately. In addition to these rework methods, it may be possible to blend the high ash products with products containing significantly less than the permissible ash content such that little or no product will require reworking. Furthermore, ash contents greater than 0.16 wt per cent may be acceptable with little penalty when two stage liquefaction is employed.

Pilot plant loss of DAS has been in excess of the amount that would be acceptable for a commercial scale plant. The indications are that this performance reflects the nature of the pilot plant equipment and is not indicative of performance which could be achieved in well designed commercial scale equipment.

Filtration

There is no filtration technique which we can consider as being technically ready for use in a commercial scale direct liquefaction plant. No technique has been tested on a pilot scale in this country which regularly produced specification grade product. The rotary drum precoat filter is not adequately developed for this application and is non-competitive with other filter types. The vertical leaf filter is not adequately developed for this application, particularly with respect

to filter leaf construction, and only occasionally met product specifications with regard to maximum ash content of filtrate. The candle filter, as manufactured by Bergbau/Boll and Kirch, has some potential for significantly improved performance over that of the leaf filter, but is not proven in direct liquefaction service.

Antisolvent Deashing

The level of development of this deashing process is insufficient to warrant consideration for application in commercial use.

H-Coal recycle slurry treatment

Hydroclones are proposed for use in reducing the solids content of H-Coal's heavy recycle liquids. Commercial hydroclones, in somewhat similar service, have performed predictably and without excessive maintenance. In the H-Coal pilot plant, however, conditions were not favorable (and probably could not have been) for hydroclone performance representative of a commercial installation. The less than ideal conditions which existed at Catlettsburg were:

- (1) varying feed rate/pressure, including full cessation of flow
- (2) varying overflow/underflow ratio
- (3) hydroclone bank enclosure design and flow arrangement permitted accumulation of solids in feed and overflow chambers (except for the final 2 days operation).
- (4) liquid temperature at about 550°F instead of 650°F which was available at the feed tank
- (5) limited clean oil flushing capability
- (6) low velocities plus some static regions in feed supply pipes
- (7) poorly functioning instrumentation

None of the above conditions need exist in a commercial scale facility.

The apparent primary cause of the erratic performance of Catlettsburg's hydroclones was plugging of outlet ports, which was related in large part to process interruptions. However, providing for

uninterrupted hydroclone feed and discharge flows can be readily accomplished in a commercial scale plant. It is difficult to understand how hydroclone plugging can happen in a steadily operating system that is designed to prevent accumulations of sediment and that is being fed with prescreened liquids. While it is not practical to install a screen at the inlet to each individual hydroclone, it is feasible to provide a screen at the inlet to each bank of hydroclones and to arrange flow through the hydroclone bank feed zone such that accumulation of agglomerated particulates is improbable. It is also practical to orient the hydroclones in a horizontal position and to provide bottom outlets from the overflow and underflow chambers. Hence, there appear to be practical means to remove the known impediments to satisfactory hydroclone bank operation.

The manufacturer of the hydroclones used at the H-Coal pilot plant is no longer fabricating units of the alumina used at Catlettsburg; instead, assemblies of mullite are being supplied. Limited pilot plant experience with these units indicates acceptable performance.

Thus, with respect to the state of technical readiness of hydroclones for commercial use in an H-Coal plant, we can be sure that a significant reduction in solids content of recycled heavy coal liquids can be achieved through use of hydroclones, but the reliability and maintenance costs for the system cannot be predicted. Hydroclone performance at a commercial scale should surely be no poorer than was experienced in the pilot plant. Because the same size units, simply more of them, will be used in a commercial plant as were used in the pilot plant, there is no problem associated with scaleup. If the system design is such that uncontrolled interruptions of hydroclone feed are avoided and that it employs all other reasonable means to remove known obstacles to satisfactory performance, it is conceivable and perhaps probable that commercial scale experience will be much better than was the pilot plant experience.

8.1.2 Slurry preparation

1. Existing technology and operating experience appear to be adequate for the design of operable commercial-scale slurry mixing systems with an acceptable degree of technological risk. Some problems may be expected during the initial operations of a first commercial plant, but, assuming that conservative design procedures have been followed, it appears likely that such problems will be of a minor nature and can be successfully corrected during the first year of operation.

2. Both gas-swept mill (GSM) drying and slurry drying systems appear to be operationally feasible for large-scale commercial plant designs. The choice between the two systems can be made on the basis of relative economics. Slurry drying may allow use of some low grade process heat and may offer process advantages over GSM drying (by avoiding reductions in coal convertibility that occurs under some conditions with GSM drying).

3. The slurry mixing temperatures selected by Exxon and Ashland Synthetic Fuels for the EDS and H-Coal conceptual commercial designs, 350°F and 450°F respectively, both appear to be feasible based on the data available. Based on laboratory test results, the 450°F temperature used by Ashland Synthetic Fuels appears to be sufficiently below the range of rapid viscosity increase. A mix tank temperature of 430°F was successfully achieved during operation of the H-Coal pilot plant at Catlettsburg.

4. The principal problems encountered in the pilot plants, aside from purely mechanical failures, were erratic operation of the coal feeding and weighing system and loss of suction of the centrifugal slurry circulation pumps. The causes of these difficulties appear to have been adequately identified, and corrective measures have been taken in the commercial designs. Obtaining adequate wetting and mixing does not appear to have been a problem.

8.1.3 VLE data base

The purpose of this study was to assess the adequacy of the vapor/liquid equilibrium (VLE) data and correlations for use in design of a commercial scale plant.

Lummus Co. compared results obtained by use of a Grayson-Streed correlation (applicable for high pressures and temperatures) modified for use with coal liquids with experimentally determined values. The average absolute deviation of calculated results for ~300 experimental data points for hydrogen, nonpolar solvents, and heteroatom-containing solvents was of the order of 20%. Further, good agreement ($\pm 5\%$ on material balance) was reported between calculational results and pilot plant data.

For use in predicting performance of near atmospheric and subatmospheric pressure distillation systems, Lummus modified and tested for use with coal liquids a much simpler correlation. A computer simulation based upon use of this correlation was found to be in excellent agreement with results obtained with the Wilsonville vacuum tower and atmospheric pressure solvent fractionator.

Gulf Research and Development Co. also modified the Grayson-Streed correlation for use in SRC-II process design. It is reported that agreement is very good for fractions having a normal boiling point $< 600^{\circ}\text{F}$, and reasonable for those having a boiling point between 600 and 700°F when the error in gas chromatographic simulated distillation technique is considered. The SRC-II Process Data Book contains the following statements concerning the applicability of the modified Grayson-Streed correlation for design of the demonstration plant.

- Computer calculated material balances around the coal reaction portion of the P-99 unit have shown good agreement with measured flow ratios.
- Computer simulation of the P-99 unit vacuum flash vessel operation has modeled the degree of vaporization satisfactorily.

Other industrial organizations, such as Exxon, no doubt have a VLE data base for coal liquids, but we were not able to obtain access to that information.

On the basis of the available information and within the constraints of the scope of this effort, we cannot reach a fully supportable conclusion as to the adequacy of the available VLE data. However, inasmuch as the pilot plants operated with no reported difficulties due to inaccurate VLE data, it seems reasonable that the available VLE data and correlations are adequate for design of a commercial-scale pioneer plant. The indicated error bands using the best available correlations appear to be relatively narrow. We have not, however, performed calculations to determine the magnitude of the impact on plant cost that might be associated with an error of a particular magnitude. Such uncertainties as exist in VLE data, we believe, will not result in failure of a direct coal liquefaction facility, but instead may be manifest by either a reduced plant capacity or unwarranted capital expenditure.

8.1.4 Critical components

The technical status of the various critical components has been the subject of other reports and conferences. Five of these component categories are discussed briefly here for completeness.

Pumps

There are three major categories of slurry pumps: reciprocating, rotary screw, and centrifugal. The abrasiveness of the slurry pumpage results in a limited life for wearing parts in each of these types. The experience with these slurry pumps will be described briefly below.

Reciprocating pumps suffer greatest wear at the packing-plunger interface. By use of a clean purge fluid and a throat bushing substantially longer than the pump stroke, the population of abrasive particles at the packing/plunger interface has been minimized to the extent that packing and rod lives of one month or more have been obtained. Exxon reports that several weeks to one year of operation may be expected

between overhauls. Surge legs (a substantial volume between plunger and check valves) have been used successfully in other industries and at the Bottrop plant for increasing packing life, but were not used in any of the U.S. pilot plants. Texaco used this technique at its Montebello facility for pumping coal liquefaction residues to a test gasifier. The cycle rate for reciprocating pump operation is limited in part by check valve operation, as higher speed operation results in lower volumetric efficiencies. Acceptable check valve operation also depends on limiting the maximum coal particle size to less than 1/4 in. Long valve life has been obtained.

Rotary screw pumps are useful for handling very viscous fluids such as vacuum bottoms. For the more viscous fluids, reciprocating and centrifugal pumps are not applicable. The rotary screw pump has a limited operating temperature range; thus this type pump must be near normal operating temperature prior to rotation even though the liquid in the pump may be fluid at a much lower temperature. Packing trouble (attributable mostly to operational errors) were encountered with the ECLP rotary screw pump; also significant wear of the rotors and casing was observed. The ECLP pump used a design which placed the packing under pressure for reasons which turned out to be largely immaterial. A mechanical seal system probably would operate more reliably than packing in this service. The sum of the experience with the ECLP unit led Exxon to the conclusion that this type of pump can be employed satisfactorily, but that it should not be used if a centrifugal unit can serve.

Centrifugal pumps are abraded in the area of the pump casing in general, but particularly in the cutwater area, and at the tips of the impeller. Lifetimes for the wearing parts of about one year (8000 hrs) are said to be achievable provided impeller tip speeds are appropriately limited and abrasion resistant liners and impellers are used. The use of hardened materials to resist abrasion requires that thermal stresses be minimized by avoiding rapid temperature changes. This presents a problem with pumps that operate at elevated temperature, requiring that the spare pump be maintained at or near operating temperature at all times. Pump seals will perform satisfactorily if an adequate flushing system is used to keep abrasive particles away from the seal faces.

Block Valves

The peculiar requirements for block valves used in direct coal liquefaction service pertain to one or more of the following fluid or operating conditions.

- Abrasive solids which settle
- High temperature
- High melting points
- High pressure, operating and/or differential

Valves of a number of different designs have been tested, both at ECLP and the H-Coal pilot plant, as well as at smaller capacity installations. ECLP experience is shown in Table 3.8.2. Catlettsburg experience was largely limited to several designs for the metal seated ball valve, some of which performed well. ECLP experience with the through-conduit valve was very good. It seems to be suitable for all the different conditions mentioned above, and is reported to be substantially less costly than are the metal seated ball valves.

Letdown Valves

Letdown valves of various designs have been employed. Exxon's streamlined design valve worked very well with relatively long life (up to several months). The H-Coal pilot plant tested a number of different letdown valves. These include a Masoneilan prototype, a Masoneilan Sasol, a Hammel Dahl, a Kieley-Mueller, two Cameron units, and a Paul valve by Continental Disc Corp. Exxon feels that it has a sufficiently good understanding of the effects of the various parameters that a relatively long life valve can be tailored to the particular conditions that prevail for a given mode of operation. In any event, valves are available that will provide in excess of one month's service life, and these valves can be replaced while in operation, such that plant shutdown need not result from failure or wear-out of a let-down valve. These valves are quite costly per unit, yet their cost would not constitute an overwhelming economic penalty if their lifetime is as much as one month.

Instruments

Many problems with instruments in the pilot plants concerned more-or-less conventional liquid and flow measurements. These problems were generally traceable to failure of the purge system. The characteristics of workable purge systems are known and documented, but great care is required in both design and construction of every installation.

Some of the streams have highly non-Newtonian properties and are quite viscous, resulting in very low Reynolds numbers. In this case, the conventional primary flow metering devices (orifices and venturis) give a non-linear response. Wedge type orifices have been tested under conditions involving low Reynolds numbers and found to give an accuracy in the range of $\pm 5\%$. A Doppler flow meter is not yet fully developed, but offers some promise for this type of service. If it can be made to function adequately, it will be more desirable than the wedge because of the Doppler meter's non-intrusive character.

Fractionator Corrosion

Atmospheric pressure fractionators at all four pilot plants suffered severe corrosion when operating on high chlorine content feed coals. The most severe corrosion occurred where the temperature was $\sim 500^\circ\text{F}$. This high corrosion zone has been shown to be coincident with high chlorine concentrations in the process fluids found at that zone.

Type 321 stainless steel and more corrosion resistant alloys such as Hastelloy C-276 have been shown to be much more resistant to attack in this zone of the fractionator than is carbon steel, which was used in the original installations. Hastelloy C-276 will surely be adequate for use in a commercial scale plant, and 321 stainless steel may suffice.

Process modifications to reduce the amount of chlorine-bearing compounds reaching the fractionator have been proposed. One method, involving water washing of the condensate recovered from the high pressure separator overhead stream, received limited testing at Ft. Lewis and was found to be of benefit. Other methods for selectively volatilizing chlorine compounds, followed by water washing the chlorine out of the organic have been proposed but have not been definitively tested.

Removal of chlorine from the process streams before it can exit in a product stream is appealing in concept; however, the significance of early removal is not established.

8.1.5 Plant integration

Task 1 of the DLTAS study was an assessment of the state of technical readiness of the major sections of a coal liquefaction facility; these sections were considered as separate process entities. The problems involved in combining these sections into an integrated facility will be considered in Task 2. This task will address the integration of critical process loops and operations such as solvent recycle, vacuum bottoms recycle and gasification, hydrogen supply and recovery, gas treatment, etc.

Following a meeting with DOE representatives to clarify the content of the task, a revised work statement was submitted and approved.

Background material and references have been collected and are being analyzed. Initial efforts will be directed at assembling a report chapter on the topic of hydrogen production, including the utilization of vacuum bottoms by partial oxidation and the integration of these operations with those of other major parts of the liquefaction plant.

8.2 Process Modeling

John M. Begovich and James H. Clinton*

Overall process model of the Tri-State Project

The Tri-State Project was originally conceived as an indirect liquefaction plant producing approximately 56,000 barrels of oil equivalent per day of transportation fuels and chemicals from Kentucky coal. The preliminary design of this plant was co-funded by the Department of Energy (DOE) and the industrial participants. Within DOE, the Morgantown Energy Technology Center (METC) has the role of technical lead for gasification systems to DOE-funded projects.

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This work has consisted of developing models of the various systems comprising the Tri-State project and integrating the models in a consistent fashion with recycle streams to produce an overall process model using the ASPEN computer code. Although the Tri-State project has been terminated, the ASPEN models and special purpose subroutines developed for this work should be applicable to many indirect liquefaction flowsheets.

Status

The final Tri-State Synfuels Project block flow diagram, entitled "Case 13 - Coal to Gasoline - Quarter Size Plant,"¹ was used as the baseline Tri-State case for checking the developed ASPEN models in an overall simulation performed by sequential execution of the major groups. To demonstrate the range of operability of these models, overall simulations were also performed using feed of Illinois No. 6 coal and the original full-scale feed rate of Kentucky No. 9 coal to the plant.

Results

In the baseline Tri-State case, 240 tons per hour of Kentucky No. 9 coal would be converted to transportation fuels and chemicals. The simulation results of the baseline case were discussed in the last quarterly report.² In the full-size Tri-State case, 960 tons of coal per hour would be fed to the Lurgi gasifier. This case was simulated to ensure that the models developed could operate over a range of flow rates. The intermediate simulation results are shown in Table 1. Comparison with the baseline case shows that each component of the gasifier output streams have been increased by a factor of 4, the same factor that the coal feed rate has been increased. Similarly, the Rectisol output streams have been increased by a factor of 4 as compared to the baseline case. The H_2S content of the gas stream has been reduced by 99.86% so that the total gas stream contains only 24 ppm H_2S . The amount of methanol produced, 10,680 tons/d, is also a factor of 4 times the baseline case value of 2670 tons/d.

The predicted product rates for this case are shown in Table 2. As would be expected, since methanol is being converted to gasoline, the predicted gasoline production rate of 341,600 lb/h is 4 times the baseline value of 85,400 lb/h. The estimated isobutane, SNG, and LPG rates are also 4 times the baseline values. Thus the change in coal feed rate proportionally changed all the output product rates, showing the rangeability of the ASPEN models developed in this study.

Demonstrating such versatility and range of operability is very important for any process simulation since it shows whether the models developed have been sufficiently generalized. In this case, specific values for certain feeds, splits, and outputs were replaced with ratios, often using FORTRAN blocks to set initial estimates. Similar tests of any new models that are developed should be made to assure generality.

The baseline Tri-State case (i.e., 240 tons of coal fed per hour) was next simulated using Illinois No.6 coal as feed to the Lurgi gasifier. The chemical and physical characteristics of this coal, shown in Table 3, were taken from test data.³ The amount of clean tar produced (shown in Table 4) was kept the same as used previously.

The composition of the dry gas produced using the Illinois No.6 coal, using the same REAL vector and reaction temperatures as previously, is very similar to that predicted for the Kentucky No.9 coal. Higher percentages of carbon monoxide and methane are predicted for the Illinois coal, while a slightly lower percentage of hydrogen is expected. Because of its lower sulfur content, the amount of H_2S predicted is considerably less than that predicted using the Kentucky No. 9 coal.

The intermediate simulation results are shown in Table 5. A comparison with the baseline case shows that the gasifier outputs are very similar and that the Rectisol unit again removes over 99% of the H_2S from the gas stream. The fact that some H_2S is predicted to remain in the synthesis gas stream for each of these simulations indicates that zinc oxide guard beds should probably be used prior to methanol synthesis to avoid poisoning of its catalyst. The predicted amount of methanol produced, 2772 tons/d is 3.8% greater than the baseline case value.

The estimated outputs, given in Table 6, show that more SNG, LPG, isobutane, and gasoline would be produced using Illinois No.6 coal, as compared to the use of Kentucky No.9 coal. The SNG produced is again composed of 95% methane, with the major impurity being nitrogen. The major reason for the increased product rates using the Illinois coal is its lower ash content (9.0% as opposed to 15.4% for the Kentucky coal).

Conclusions

The ASPEN process simulator has been used to model the Tri-State indirect coal liquefaction process. Individual components of the Tri-State flowsheet were developed in modular form so that they will have application to a number of different process alternatives. Models developed in this study include the following: Lurgi gasifier, Texaco gasifier, synthesis gas cooling, Rectisol, methanol synthesis, methanol-to-gasoline, CO shift, methanation, and naphtha hydrotreating. In addition, an enhancement has been made to ASPEN to allow for the direct input of coal heat of combustion values, and three FORTRAN programs were developed to handle the devolatilization and decomposition of coal in a gasifier and the handling of boiler feed water.

Simulations were made of three cases: (1) the baseline Tri-State flowsheet with Kentucky No.9 coal fed in at 240 tons/h; (2) a full-size Tri-State case with Kentucky No.9 coal fed in at 960 tons/h; and (3) the baseline Tri-State case with Illinois No.6 coal fed at 240 tons/h. Prediction of the synthesis gas composition produced by the Lurgi gasifier was calibrated using the SASOL coal test data. For the first case, the simulation was forced to match the production rates of methanol, LPG, isobutane, and gasoline as indicated by the Tri-State Case 13 flowsheet. This was accomplished by (1) using a recycle ratio of 1.63 in the methanol synthesis model, and (2) modifying the MTG reactor yield structure. Quadrupling the coal feed rate of the first case, the second case indicated that exactly four times as much SNG, LPG, isobutane, and gasoline would be produced. The use of Illinois No.6 coal in the third case resulted in outputs slightly higher than those predicted by Kentucky No.9 coal. The anticipated isobutane, LPG, and gasoline production

rates are 3.8% higher for the Illinois coal, while the SNG production would be expected to be 12% higher. A comprehensive report on this project will soon be issued.⁴

8.3 References

1. *Tri-State Synfuels Project Review*, Contract 835504, Tri-State Synfuels Company (June 1982).
2. L. E. McNeese, *Fossil Energy Program Quarterly Progress Report for the Period Ending March 31, 1983*, ORNL-5955, pp. 161-168 (June 1983).
3. *Trials of American Coals in a Lurgi Gasifier at Westfield, Scotland*, FE-105, Woodall-Duckham, Ltd. (Dec. 1972-Nov. 1974).
4. R. E. Barker, J. M. Begovich, J. H. Clinton, and P. J. Johnson, *ASPEN Modeling of the Tri-State Indirect Liquefaction Process*, ORNL/TM-8611 (in publication).

Table 1. Intermediate simulation results for full-size Tri-State case

Component	Gasifier and cooling output, Rectisol input (lb-mol/h)	Rectisol output, MeOH synthesis input (lb-mol/h)	MeOH synthesis output, MTG input (lb-mol/h)
H ₂	66,334	66,131	1.6
CO	30,641	30,204	2.8
CO ₂	47,292	5,764	481
CH ₄	13,840	13,222	54
C ₂ -C ₄	1,333 ^a	-	-
C ₆ H ₆	400 ^b	-	-
N ₂	1,671	1,647	0.9
H ₂ S	2,044	2.8 ^a	-
COS	25 ^a	-	-
H ₂ O	693	-	1,138
NH ₃	245 ^a	-	-
CH ₃ OH	-	3 ^a	27,781 ^c

^a Output stream component, but not used in input stream.

^b Used as an input stream only.

^c MeOH synthesis = (27,781 lb-mol/h)(32.042 lb/lb-mol)(24 h/d)/(2000 lb/ton) = 10,680 tons/d.

Table 2. Predicted outputs for full-size Tri-State case as compared to the baseline case

Production	Baseline	Full-size
SNG, MMSCFD	39.5	158
LPG, lb/h	4,300	17,200
Isobutane, lb/h	4,760	19,040
Gasoline, lb/h	85,400	341,600

SNG from Full-Size Case

Component	lb-mol/h	%
H ₂	118	0.68
N ₂	822	4.74
CO	5	0.03
CH ₄	16,376	94.55
Total	17,321	100.00

Heat of combustion (HHV) = 956 Btu/SCF

Table 3. Chemical and physical characteristics of Illinois No.6 coal

Ultimate analysis (as received coal)	%
Ash	9.0
Carbon	64.3
Hydrogen	5.5
Nitrogen	1.2
Sulfur	2.8
Oxygen	<u>17.2</u>
	100.0
Proximate analysis	%
Moisture	10.3
Fixed carbon	46.0
Volatile matter	34.7
Ash	<u>9.0</u>
	100.0
Heat of combustion = 12,770 Btu/lb (dry coal)	

Table 4. Lurgi gasifier output using Illinois No.6 coal as compared to Kentucky No. 9 coal

	Ill. No. 6 coal	Ky. No. 9 coal
Clean tar produced, as % MAF coal fed:	5.9	5.6
Dry gas composition, %		
Hydrogen	40.3	41.4
Carbon monoxide	16.0	15.4
Carbon dioxide	30.7	30.8
Methane	10.0	9.1
C ₂ +	1.0	0.9
Nitrogen	1.0	1.0
Hydrogen sulfide	<u>1.0</u>	<u>1.4</u>
	100.0	100.0

Table 5. Intermediate simulation results using Illinois No.6 coal

Component	Gasifier and cooling output, Rectisol input (lb-mol/h)	Rectisol output, MeOH synthesis input (lb-mol/h)	MeOH synthesis output, MTG input (lb-mol/h)
H ₂	16,949	16,897	0.4
CO	8,399	8,279	1
CO ₂	12,379	1,448	124
CH ₄	3,940	3,764	15
C ₂ -C ₄	374 ^a	-	-
C ₆ H ₆	100 ^b	-	-
N ₂	427	421	0.2
H ₂ S	407	0.5 ^a	-
COS	6 ^a	-	-
H ₂ O	189	-	196
NH ₃	63	-	-
CH ₃ OH	-	-	7,211 ^c

^aOutput stream component, but not used in input stream.

^bUsed as an input stream only.

^cMeOH synthesis = (7,211 lb-mol/h)(32.042 lb/lb-mol)(24 h/d)/(2000 lb/ton) = 2772 tons/d

Table 6. Predicted outputs using Illinois No.6 coal as compared to Kentucky No. 9 coal

Production	Kentucky No. 9	Ill. No. 6
SNG, MMSCFD	39.5	44.3
LPG, lb/h	4,300	4,460
Isobutane, lb/h	4,760	4,940
Gasoline, lb/h	85,400	88,600

SNG produced using Ill. No. 6 coal

Component	lb-mol/h	%
H ₂	13.0	0.27
N ₂	210.2	4.32
CO	0.4	0.01
CH ₄	4,640.4	95.40
Total	4,864.0	100.00

Heat of combustion (HHV) = 964 Btu/SCF

9. EFFLUENT CONTROL TECHNOLOGY

R. K. Genung

The assessment of environmental control technology for Lurgi-based processes continued with an emphasis on zero-discharge options. A draft report on material balance studies on key priority pollutants in H-Coal wastewater samples was issued, and field wastewater treatment studies at the SRC-I site in Wilsonville were continued. In other wastewater treatment studies being conducted at ORNL, studies regarding the kinetics of phenol degradation in fixed-film, fluidized-bed bioreactors were continued.

9.1 Indirect Liquefaction Environmental Control Technology Assessment (ILECTA)

J. F. Fisher and S. P. N. Singh

9.1.1 Objective

The objective of the project is to examine the impact of two wastewater treatment scenarios for a conceptual Lurgi-based indirect coal liquefaction plant located at a generic site in the eastern U.S. and processing a generic eastern U.S. bituminous (Illinois No. 6) coal. The process examined consists of Lurgi dry-ash coal gasification followed by Imperial Chemical Industries' (ICI) methanol synthesis with subsequent conversion of the methanol to gasoline using Mobil's methanol-to-gasoline (MTG) process. The project is funded by DOE/Fossil Energy through the Pittsburgh Energy Technology Center (PETC).

The two wastewater schemes to be examined are called base case and zero wastewater discharge case. In the base case, plant wastewaters are treated to meet effluent regulations for allied industries such as petroleum processing, power plants, and coke ovens. However, in the zero wastewater discharge case, no aqueous effluent is discharged from the plant, per se; water is returned to the environment only as water vapor.

For each scheme, the assessment will consist of the following major elements:

1. Unit processes will be described briefly. Wherever possible, references will be provided to enable the reader to obtain more detailed process information.
2. Resultant emissions and their hazard potentials will be estimated.
3. Preliminary process economics for the two wastewater schemes will be evaluated. The two schemes will be treated as battery-limits installations for evaluating the economics.

The assessments will be based on published information supplemented by vendor-supplied data where necessary. Auxiliary information developed in the assessment such as stream flows, compositions, unit sizes, etc. will be included in the report. In addition, uncertainties and data gaps in the state-of-knowledge will be addressed together with suggestions to reduce the uncertainties in the available data base.

Information to permit the base case design assessment will be obtained from previously completed studies at ORNL such as the Liquefaction Technology Assessment¹ and the Environmental Controls Cost Study,² and the recently available Tri-State Synfuels Project Review reports.³

This assessment will, among other things, highlight the impact and the potential cost of designing plants to meet zero wastewater discharge requirements.

9.1.2 Status Summary

The assessment is nearing completion. Much of the base information for the assessment was obtained from Reference 3 which reported on the results of gasifying western Kentucky No. 9 coal in a commercial scale, stirred Lurgi-dry-ash gasifier at SASOL. In the report, the gasifier condensate has been quantified, reasonably well assayed, and subjected to the typical treatment sequence, namely solvent extraction (Phenosolvan),

volatiles stripping, biotreatment and activated carbon treatment. However, some steps in the treatment were not entirely representative of commercial conditions.

The Lurgi condensate after the biotreatment step was reported to be toxic to the fathead minnow. Activated carbon treatment reduced this toxicity. The meaning of these tests may have been distorted by the very high residual ammonia in the treated waters.

The design base used in the present assessment assumes that the nitrogen is in the less toxic nitrate form based on Zimpro's success in nitrating the ammonia in H-Coal wastewaters.⁴ However, denitrification of these types of wastewater has never been demonstrated.

The interface between the surface discharge case and the zero wastewater case is assumed to be the carbon treated process condensate. The environmental impact of this wastewater containing 10-40 ppmw of unknown TOC, 300 ppmw of NO_3^- and 30 ppmw of F^- is not known. Surface disposal of these waters is assumed to be viable despite the unexpected toxicity of the treated waters noted above.

In the zero wastewater discharge case, process condensate reuse is based on the separation of relatively pure cooling tower feed water by reverse osmosis, and concentration of the brine by vapor recompression evaporation. This assumption coupled with the use of EPA's clay-lined hazardous waste landfill for 800,000 tons of very soluble salts rich in toxic trace elements leads to a zero wastewater discharge cost only about 20 to 25% above the surface water discharge case.

The wastewater may have to be denitrified and defluorinated before discharge to surface waters. Reverse osmosis may have to be replaced by vapor recompression evaporation. EPA's landfill is not a permanent (>500 years) means of disposal. Unfortunately, the only alternates - deepwell or ocean disposal - had to be rejected because of technical and/or regulatory uncertainties.

Too little is known about the chemistry of the wastewaters to evaluate such logical alternates as detoxification of the salt brine and disposal of the brine in the ocean.

9.2 Studies of Wastewater Treatment Polishing Processes at the Wilsonville, Alabama, Advanced Coal Liquefaction R&D Facility

C. H. Brown, M. T. Harris, R. D. Roop,
J. C. Rose, and J. D. Hewitt

9.2.1 Objective

The objective of this project is the field evaluation of carbon adsorption, ozonation, and reverse osmosis as polishing processes in treating coal conversion wastewaters generated at the Advanced Coal Liquefaction R&D Facility in Wilsonville, AL. It is being supported by DOE/Fossil Energy through DOE/ORO. Laboratory studies at ORNL, supportive to the field work, will also be conducted as part of this project.

9.2.2 Status Summary

The second and final operating campaign at the ACLF in Wilsonville, AL was conducted during the period May 13-27, 1983. A summary of tests conducted during this campaign is given below. In order to stabilize the concentration of contaminants in the ACLF wastewater treatment plant equilization basin the flow of water from the liquid waste sump (LWS) was diverted to the "A" biotreater feedbox. This stream normally is introduced in the equilization basin and since a major constituent of the LWS water is runoff due to rainfall it results in large concentration fluctuations during periods of heavy rainfall.

Carbon absorption - Before startup of the carbon unit the optimal feed pH was determined to be 7.5 based on batch adsorption tests performed in a shaker-flask system. In these batch tests the removal efficiencies of TOC, COD, phenol, and color were measured at a fixed carbon dosage and variable pH. Subsequent to these batch tests a bed-depth/services-time test was performed using equilization basin wastewater diluted to a TOC concentration of 150 to 200 mg/L. Wastewater feedrate to the unit was 63 mL/s (1 gpm) and initially three columns were operated in series using degassed regenerated Darco activated carbon. During this operating period contaminant removals were 30%, 85%, 100%, and 70% for COD, color, phenol, and TOC respectively. After ~55 h of

operation the pH control system on the carbon adsorption feed tank failed, resulting in a pH excursion from the control point of 7.5 to approximately pH 10. Readjustment of the pH to 7.5 resulted in plugging of the lead carbon column by a tar-like material which precipitated from the feed water. This tarry substance is soluble at high pH (~10) and much less soluble at pH 7.5. A sample of this material was obtained and is being analyzed by members of the Analytical Chemistry Division. The carbon adsorption unit was shut down temporarily to modify operating procedures. Upon restart the number 2 and 3 columns were operating in series and the feed pH was controlled between 10 and 10.5. The unit operated in this manner for 93 h at which time the number 3 column became plugged. An explanation of this phenomena has not yet been aimed at. For the remainder of the campaign (25 h) the CA unit was operated with only the number 2 column online. During the second run period nominal removal levels for COD, color, phenol, and TOC were 30%, 65%, 97%, and 60% respectively.

The data taken during operation of the CA unit will be analyzed to determine height and rate of movement of the mass transfer zone for each component.

Ozonation - Several different types of experiments were performed with the ozonation unit during this campaign. The data obtained complement the data gathered earlier. The tests and preliminary results are outlined below.

I. Tests with water obtained from the equalization basin

1. A batch test was performed in which a captive volume of wastewater was stripped with air (no ozone generated). Results indicate that after 30 min of air stripping, 10% of the TOC and 3% of the COD were removed.
2. A second batch test was performed in which a captive volume of wastewater was ozonated for 5 h to determine ultimate TOC and COD removal capabilities. Preliminary results indicate complete

removal of color and phenol within 6 min, these species were initially at 780 cu and 8 mg/L respectively. In three hours of reaction time TOC was reduced from 125 to 45 mg/L and COD decreased from 600 to 80 mg/L. During the final two hours of ozonation, COD and TOC remained unchanged. During the test, pH decreased from 10 to 3.5 passing through two inflection points (similar to a titration curve for a diprotic acid).

II. Tests with water obtained from the "A" clarifier

1. A matrix of continuous ozonation experiments was performed with various combinations (following a fractional factorial design) of pH, ozone dose rate, and hydraulic residence time. The range of values for these variables was:

O ₃ Dose Rate	3.6 - 6.6 mg O ₃ /L-min
pH	3.2 - 9.8
Hydraulic Residence Time	10 - 50 min

2. Carbon adsorption isotherms were measured for selected sets of conditions in 1 above. The results indicate adsorption to be less efficient after ozonation. Interpretation of the data is complicated by the very low values for many of the parameters.

Reverse Osmosis - The RO unit was operated during the entire campaign on water obtained from the "A" clarifier. Pretreatment of this water consisted of pH adjustment to 5.5, filtration to 5 μ m, and addition of antiscalent. The membrane tested was an Osmonics, Inc. spiral wound cellulose acetate membrane. The unit was initially operated at 50 and 70% recoveries. Plugging of the control valves downstream of the module

and partial plugging of the RO membrane occurred at 70% recovery. After cleaning, the unit was restarted at 60% recovery and was operated at this recovery for 89 h. The total elapsed time for this test was 235.8 h during which the unit was operated for ~71 h on tap water, ~161 h on wastewater, and ~4 h on cleaning solutions. A summary of the feed water to the RO unit is given in Table 9.1. Component rejection data are summarized in Table 9.2. Measurements made for COD and calcium are not included in this table. COD was below detectable limits and an interference was present in the calcium analysis causing poor mass balance closure.

The RO unit was operated using tap water as feed to facilitate measurement of permeate rate at fixed conditions. This was done initially, after the unit was cleaned subsequent to the blockage occurring at 70% recovery and at the termination of the run. The conditions for the test were: 50-55% recovery, 26-28°C circulation temperature, and 2.76 MPa feed pressure. The tap water permeate rate is plotted as a function of time in Fig. 9.1. As shown in this figure, the permeate rate appears to decrease with time. A linear fit of the data yields

$$P = 12 - .0086 t \quad (1)$$

where P is the permeate flowrate in mL/s and t is operating time in hours. Equation 1 indicated a 20% decrease in flux in 280 h of operation. Manufacturers data indicates a 7% decline in permeate flux in 280 h due to membrane compaction. With this assumed to be correct there still remains a 13% decrease in flux which is probably due to fouling. The RO module will be sectioned and analyzed for foulants. Samples were taken of the cleaning solutions and of the feed permeate and concentrate streams during operation which will further help in identifying the RO foulants.

Table 9.1. Pretreated RO feedwater characteristics averaged during campaign W-2

pH	5.2
Conductivity	4475 μ S/cm
TDS	3125 mg/L
Calcium	62 mg/L as CaCO_3
Magnesium	42 mg/L as CaCO_3
Sulfate	1940 mg/L
Alkalinity	25 mg/L as CaCO_3
COD	56 mg/L
TOC	24 mg/L
Phenol	0.8 mg/L

Table 9.2. Summary of component rejection data

Component	Feed* concentration	Rejection (%)	
		Range	Average
TOC	19-37	76-95	86
Color	110-280	89-99	95
Phenol	0.5-1.3	56-95	76
Hardness**	84-118	82-100	94
Sulfate	1300-4700	85-100	94
Alkalinity	15-50	55-95	71
Conductivity	3600-6400	87-92	89
TDS	2500-4400	92-98	95

*All values mg/L except color is given in color units and conductivity is given as μ S/cm.

**As CaCO_3 .

ORNL DWG 83-695

Fig. 9.1. Membrane productivity decrease during campaign W-2.

9.3 Development of Fixed-Film, Fluidized-Bed Bioreactors as Biooxidation Processes for Coal Conversion Wastewater

T. L. Donaldson and G. W. Strandberg

9.3.1 Objective

The objective of this project is to develop a biooxidation process for the treatment of coal conversion wastewaters which would have significant advantages over existing technologies such as the activated sludge process. In particular, a fixed-film, fluidized-bed bioreactor will be designed, assembled, inoculated, and tested on a feed characteristic of coal conversion wastewaters. The objectives include the definition of process design parameters, the identification and evaluation of operating parameters to be used for process control, and the demonstration of steady-state operation for extended periods.

9.3.2 Status Summary

The main bioreactor has been operated successfully for over 13 months. The fixed films on the coal support continue to be stable: there has been no sign of difficulty in maintaining the biologically active films under a variety of operating conditions. During May and June, the main bioreactor has been successfully operated with a complex synthetic wastewater influent based on the Singer et al. recipe described in previous reports. The performance is summarized in Table 9.3. Phenol degradation rates have remained comparable to rates obtained with monohydric phenol alone, and have been greater in some cases. The concentration of organics has been increased gradually throughout the month, as can be seen in Table 9.3. There is good removal of organic acids, although the loading rate is relatively low compared to phenolics. Most of the COD removal appears to be associated with degradation of phenolics.

The nature of the fixed films has changed in response to the new influent. The films appear more dense, and there is less bed expansion and carryover of particulates than occurred with monohydric phenol alone. This new behavior is an improvement and contributes to stable operation. As mentioned above, biological activity has remained constant.

Table 9.3. Typical performance of the fixed-film, fluidized-bed bioreactor with Singer synthetic wastewater ^a

Date	Concentration (mg/L)					
	Phenols (4-AAP)		Total Organic Carbon ^b		Chemical Oxygen Demand	
	Influent	Effluent	Influent	Effluent	Influent	Effluent
5/4	26	7	32	11.5	71	23
5/12	22	11			74	48
5/17	33	15			140	90
5/23	46	2.2			212	63
5/25	43	6				
6/1	49	6			187	60
6/16	57	25	104	53	203	107
6/24	81	16	126	57	391	113
6/27	90	21	161	67		

^aFlowrate was 0.85 – 1.2 L/min, bed volume was ~2.2 L.

^bTOC analyzer was unavailable the latter part of May.

Table 9.4. HPLC assay

Compound	Influent (mg/L)	Effluent (mg/L)
Phenol	63	6.3
Resorcinol	29	7.9
Catechol	31	<2
Total	123	14.2

The 4-aminoantipyrine (4-AAP) assay remains our method of choice for daily determination of phenolics. However, this assay exhibits slightly different responses for the various phenols, so our "phenol" concentration is a lumped value. Influent and effluent samples are being submitted periodically to our Analytical Chemistry Division for more extensive characterization of phenolics and other compounds. One set of results are shown in Table 9.4. A thiocyanate assay is currently under development to eliminate apparent interferences.

Microbial characterization work has shown that the commercial Sybron culture appears to contain four bacterial species; however, five bacterial strains and one "filamentous" yeast have been isolated from our bioreactor after four months of operation. The bacteria have been tentatively classified, but several additional tests are required for verification. The yeast has proven difficult to identify, and the assistance of the ARS Culture Collection, Peoria, IL has been solicited for this purpose. Several isolates have been recovered from the other (Polybac) bioreactor and are undergoing taxonomic study.

Limited agitation of biomass-laden coal particles with a vortex mixer appears to be a rapid and effective means of removing biomass from coal particles. Treatment with alkaline hypochlorite plus mild agitation is also effective in removing and solubilizing cellular material. We are currently examining a variety of methods to quantify the recovered biomass. Wet packed cell volume, dry weight, nitrogen content (total and protein), and carbon (total and organic) are being examined. The reaction of partially solubilized cell mass (extracted with 4 M NaOH) with the protein-reactive Biuret reagent gives a linear colorimetric response with dry weight of cell mass.

During the past quarter, batch kinetic experiments have been carried out with both cultures at low phenol concentrations from ~10 mg/L to <1 mg/L. The objective of these experiments has been to estimate K_M in a Michaelis-Menten-type rate equation. We have previously found that the kinetics are zero order in phenol concentration above 20 mg/L, which indicates that K_M is less than ~20 mg/L. An estimate for K_M is necessary

for reactor design and scale up since the reaction rate will decrease as the phenol concentration becomes comparable in magnitude to K_M .

The K_M for the Sybron culture appears to be approximately 10 mg/L. In contrast, results to date with the Polybac-derived culture indicate a K_M of 1-5 mg/L. Thus it appears that the Polybac culture may have somewhat better kinetic properties at low phenol concentrations; however, the difference is rather small, and removal rates for other species in addition to phenol may be a significant factor in the choices of a culture.

The temperature dependence of the reaction rate was investigated with the Sybron culture in batch experiments. The agitation rate was 200 rpm, which has been shown to give maximal rates and minimize mass transfer and mixing effects. Pure oxygen was sparged through the liquid to maximize the availability of oxygen. The initial reaction rates at ~50 mg/L of phenol are shown in Table 9.5. These rates suggest an activation energy of ~10 kcal/g-mol, which is a reasonable value for this type of reaction. A weaker temperature dependence has been found for the continuous bioreactors, due to mass transfer limitations at low liquid flowrates.

The degradation of ^{14}C -labeled phenol was studied in shake flasks. $^{14}\text{CO}_2$ was identified in the off-gas by trapping the CO_2 in an organic base. It was also found that low concentrations of phenol in the liquid (<5 mg/L) can be easily measured. This technique may be quite useful for degradation studies at low concentrations.

We believe that the reaction kinetics are sufficiently well-characterized to allow reactor design and scaleup to a system to handle 1 gpm. The process can be designed to produce an effluent having <1 mg/L of phenol. To demonstrate this design capability, we identified a phenol concentration which could be treated to reduce the concentration to <1 mg/L at a flowrate of 1 L/min in the present reactor system. The volumetric removal rate was assumed to be 8 mg phenol/L bed·min. On this basis, an influent stream containing 16 mg/L could be treated at 1 L/min, or a stream containing 32 mg/L could be treated at 0.5 L/min using the existing 2-L bed. Experiments were then run as shown in Table 9.6. It can be seen that the design effluent quality of <1 mg/L is achieved. In

Table 9.5. Temperature dependence of initial reaction rate for Sybron culture

Temperature (°C)	Reaction rate (mg phenol/L coal·min)
20	30
25	46
30	65
35	65

Table 9.6. Experimental confirmation of design performance ^a

Flowrate (L/min)	Phenol concentration (mg/L)	
	Influent	Effluent
0.98	20	1.0
0.99	16	1.0
0.51	38	2.0
0.51	32	0.1
0.81	16	<0.1
0.81	18	<0.1

^a Bed volume = 2 L, temperature = 30°C.

order to treat influent streams having higher phenol concentrations, a longer residence time would be needed — a taller column or perhaps several shorter columns in series. The current hydraulic residence time in the bed is ~2 min at a flowrate of 1 L/min.

During June a significant "bloom" of fixed films was seen in the Sybron culture bioreactor. The usual 2-3% cell dry wt/coal wt increased to 8-9% over a period of several days. The phenol degradation rate remained constant at 4-5 mg/L·min at the "maintenance" flowrate of ~0.4 L/min. The cause of this bloom is not known.

Throughout the past year we have used several preservation techniques to save small quantities of coal-biomass particles for future use as inocula for new reactors. A reliable inoculation and start-up procedure is critical to successful implementation of this technology. In mid-June a new bioareactor was initiated using fresh coal and a freeze-dried inoculum of coal-biomass particles which had been collected on December 12, 1982. Preliminary data indicate that this culture preservation and start-up test is successful.

Arrangements have been made to obtain several hundred liters of wastewater from the coal gasifier at the Holston Army Munitions Plant at Kingsport, TN during the first week of July. This water, appropriately diluted, will be fed to the bioreactor. The raw water is expected to have approximately 25,000 mg/L COD, 30,000 mg/L total solids, 5,000 mg/L ammonia, and 2,000 mg/L total phenols.

T. L. Donaldson attended the Third Biennial Synfuels Wastewater Workshop, June 15-16, 1983, Morgantown, WV and gave a brief project report. R. K. Genung attended the Advanced Gasification Projects Contractors Review Meeting, June 28-30, 1983, Morgantown, WV and gave a project report.

9.4 Solid Waste Management Studies

C. W. Francis and J. S. Watson

9.4.1 Objective

The objective of this task is to assess the status of on-going research and development relative to the utilization and disposal of fossil energy related solid wastes. The work is being funded by DOE/FE through METC.

9.4.2 Status Summary

A draft document has been prepared that outlines the current state-of-the-art for utilization and disposal of fossil energy solid wastes, describes current research and development efforts, and suggests areas in which further studies might be warranted. This report is currently being reviewed by METC, and will be available following any revisions required by METC.

9.5 References for Section 9

1. R. M. What et al., Liquefaction Technology Assessment — Phase 1: Indirect Liquefaction of Coal to Methanol and Gasoline Using Available Technology, ORNL-5664, February 1981.
2. P. J. Johnson et al., The Impact of Environmental Control Costs on an Indirect Coal Liquefaction Process, ORNL-5722, August 1981.
3. Tri-State Synfuels Company, Tri-State Synfuels Project Review, prepared for U.S. DOE under cooperative agreement No. DE-FC05-81OR20807, June 1982.
4. B. M. Churton, H-Coal Pilot Plant, Zimpro's Biophysical Treatability and Characterization Study on H-Coal Wastewater, Topical Report, DOE/ET/10143-T24, November 1982.

10. FOSSIL ENERGY ENVIRONMENTAL ANALYSIS

C. R. Boston

Environmental support is provided to DOE/Fossil Energy and DOE/Economic Regulatory Administration. The effort includes (1) preparation of environmental assessments related to synfuels programs and fuel conversion implementation; (2) programmatic environmental studies that are critical to the early realization of advanced fossil technologies and minimization of the use of petroleum and natural gas; and (3) general environmental technical assistance.

10.1 Fossil Energy Support

C. R. Boston

Specific work areas include:

Environment, Health and Safety Support - Under this project ORNL provides technical support to the Environment, Health and Safety Branch (EHSB), Office of Management and Planning in evaluating and improving the status of environmental, health and safety programs at both Fossil Energy Headquarters and the Energy Technology Centers (ETCs). Initial efforts directed toward program planning and evaluation and the issuance of program guidance are nearing completion and emphasis is shifting to support of the ETCs in improving the effectiveness of their ESH programs.

Regulatory and legislative reviews - Provides a continuing review of all regulatory and legislative items, present and planned, and their effects on fossil energy programs.

10.1.1 Environment, Health and Safety Support - R. C. Martin

This project provides technical support to the Division of Planning and Environment. The FTP/A provides for nine general support tasks.

1. Technical review of reports, orders, and standards to assist FE in responding to regulatory changes and new developments.
2. Development of a system for continuing evaluation of the status and needs of the program and preparation of appropriate guidance documents.
3. Implementation of a system for evaluating the compliance of ASFE activities with applicable OSH/IH requirements.
4. Implementation of a system to assure that OSH information is collected, analyzed, and utilized.
5. Implementation of budget procedures to assure that ESH budget requirements are identified.
6. Technical assistance to the ETCs in improving their OSH programs.
7. Review of institutional plans to assure technical and resource adequacy.
8. Review of program plans to identify OSH/IH issues.
9. Special studies as requested.

Major efforts during this reporting period focused on the finalization of the Draft of FE Order 3790.1, "Fossil Energy Occupational Safety and Health Programs for Federal Employees," (Task 2); continuation of technical support to the Bartlesville Energy Technology Center; and assistance to the Morgantown Energy Technology Center in the development of an Environment, Safety and Health Information and Data Management System.

An approval copy of the proposed FE Order was submitted to the Office of Planning and Environment on June 7 and the document is now in the approval process.

Completion of the supplemental analysis of modified risk reduction alternatives at BETC continues to be deferred. At this time, it appears that FE has elected to upgrade the existing building rather than relocate the laboratory facilities to either a new or an existing building. ORNL is continuing to provide technical support in the evaluation of both interim and permanent risk reduction measures. Personnel from ORNL and A. F. Meyer and Associates (AFMA) visited BETC on June 21-22 to assist in evaluation of a prototype emergency laboratory exhaust system recommended by the headquarters review panel. A representative of AFMA returned to BETC on June 29-30 to provide assistance in evaluating the need for industrial hygiene monitoring in Building 6 and in the storage and handling of reactive metals and perchloric acid.

In the development of the ES&H information system, the initial tasks are for the evaluation of available commercial data management systems and for the development of detailed user specifications. An initial evaluation of commercial systems has been completed and meetings with the vendors of the two systems which appear to be most appropriate have been scheduled for mid-July. In conjunction with these meetings, preliminary user specifications will be reviewed with METC support contractor personnel.

10.1.2 Regulatory and Legislative Review - R. D. Roop

The purpose of this project is to provide DOE/FE with an informal tri-weekly newsletter that concisely reviews noteworthy technical, regulatory, and legislative actions that have occurred in the environmental field during a given three week period. During the third quarter of FY 1983 the "Environmental and Regulatory Legislative Update" was delivered to the Planning Division, Office of the Assistant Secretary for Fossil Energy, Department of Energy, on April 15, May 6, May 27, and June 17. During the quarter one notable development with regard to air quality was the proposal of several pieces of legislation designed to limit emissions of sulfur dioxide in attempts to control

acid precipitation. Water quality and wetlands may be affected by the Corps of Engineers' proposed new rules which modify the procedures for issuance of dredge-and-fill permits. In a move to accelerate the clean-up of hazardous waste disposal sites, the EPA ordered its regional administrators to reevaluate which abandoned sites should get immediate attention. Also noteworthy was the adoption of interim monitoring guidelines by the Synthetic Fuels Corporation; these guidelines were criticized by both environmental groups and by industry groups as being too broad and vague.

10.2 Synfuels Project

This project provides DOE with program assistance in the performance of environmental assessment functions related to the expansion of fossil energy conversion technologies, performs assigned technical assistance tasks, and conducts programmatic environmental investigations that are critical to the early realization of advanced fossil energy technologies.

10.2.1 Coal conversion projects

Liquefaction projects - R. D. Roop

This activity is reported in Chapter 6.

11. TENNESSEE VALLEY AUTHORITY (TVA) FLUIDIZED BED
COMBUSTION (FBC) DEMONSTRATION PLANT PROGRAM
TECHNICAL SUPPORT

C. S. Daw

Tennessee Valley Authority has assumed a lead role in the demonstration of FBC technology for application in large utility boilers. ORNL is providing technical support and services to TVA in FBC systems. This work is to support TVA's objective to develop FBC systems for utility electric power generation which will burn high-sulfur coal and meet environmental emission standards.

TVA is the lead agency in this work and will reimburse DOE for the work to be performed by ORNL. This work is being conducted by ORNL under the terms and conditions of the Interagency Agreement between TVA, DOE, and ORNL regarding support for FBC research (reference: Agreement TV-48296A, Subagreement 5).

11.1 Tubular Flow Reactor Experiment - Task 13

C. S. Daw and R. P. Krishnan

11.1.1 Objective

The goal of this program is to develop reliable kinetic expressions for the combustion of devolatilized Western Kentucky No. 9 coal (a swelling bituminous coal) in an atmospheric fluidized bed combustor. A series of small-scale experiments will be run to identify the key variables that affect char combustion and to provide the data needed for a quantitative model.

11.1.2 Status Summary

TVA has reviewed and approved the draft of the final report. The report is now being prepared for publication as an ORNL-TM.

11.2 Analysis of the TVA Pilot Plant - Task 15

C. S. Daw, M. E. Lackey, J. Wells

11.2.1 Objective

The objective of this task is to provide technical support and assistance to TVA in evaluating and interpreting the data from the AFB pilot plant.

11.2.2 Status Summary

We have completed review of the run 5 and run 6 summary reports which together cover operational data from February 4 to April 6, 1983. We are currently reviewing the summary report for Campaign II, Series 1 which covers data from April 7 to May 12.

As a result of these reviews, the following concerns have been discussed with TVA:

- There appeared to be occasional contamination of as-fed coal samples with limestone and vice versa. If not allowed for, such contamination could lead to significant errors in the overall mass balances. We recommended that standard analyses of Ca, Mg, and CO₂ (as determined by acid dissolution) be made of "off-the-pile" coal and limestone so that contamination of the as-fed solids could be detected and allowed for.
- Lack of accurate measurements for char, bed drain, and baghouse solids flows made overall material balances questionable at best. Mass balances appeared to improve significantly after the measurement system for char solids become operational. There still appear to be some problems with the measurement systems for the bed drain and baghouse solids.
- The flue gas orifice measurement is erratic and generally appears to be reading low. This measurement is particularly important in measuring the gaseous emissions levels. TVA has found that the original coefficient used in calculating flows for this orifice was in error, and the correct coefficient

is being determined. We are continuing to check the orifice readings to see if the problem has been resolved. Until it is, we have recommended to TVA that they estimate the flue gas flows from input flows and approximate combustion efficiency and calcination values.

- It is clear the the limestone is not being completely calcined, even during recycle operation. Of course this proportionately reduces the amount of sorbent available for sulfur capture. For no-recycle operation, it appears that only about 80% of the inlet limestone is actually calcined. About 90-95% is calcined during recycle conditions. The reasons for this are not certain, but we have hypothesized that it is primarily due to the short residence times of the elutriating limestone particles. We are currently exploring this problem in detail.
- The presence of uncalcined limestone in disposal solids samples greatly complicates the measurement of the effective heating values of such samples. These measurements are critical in evaluating overall combustion efficiency. Until the analysis problems can be resolved, we have concurred with TVA that the best procedure would be to estimate heating values from the burnable carbon contents.
- The elutriation rates for the TVA bed are rather high. Typically, about 75 to 80% of the solids leaving the bed leave in one of the elutriate streams (i.e., char to disposal or baghouse dust). This indicates a high level of fines in the input solids and/or a high degree of attrition. This is another indication that the lack of complete calcination is an elutriation problem.
- Bed drain samples have the potential for providing a lot of information about the bed mixing patterns, the bed time constants and the accuracy of the steady-state model in predicting the bed composition. We have recommended that multiple bed samples be taken simultaneously (i.e., as nearly simultaneous as possible) from different sample points to get an indication of the relative homogeneity of the bed. Such sampling would be

be especially informative under transient or non-standard conditions (e.g., when one coal or limestone feeder is off).

- Feed line erosion and pluggage (during underbed-feed operation) are clearly the most significant operating problems associated with AFB technology (i.e., other equipment problems occurred, but they involved conventional technology). As expected, most erosion problems have occurred in "input" zones on the branch lines and at the splitter outlets. Some of the splitter erosion patterns indicate uneven distribution of solids into the branch lines. Most plugs occurred in or downstream from the splitters, and many were associated with wet or oversize solids or possibly with erosion leaks. We are continuing to follow the progress by TVA in this area.
- The acid solubilization test for carbonates in solids samples has proven to be a very valuable analytical tool. It appears to be more accurate than thermogravimetric analysis for measuring CO_3 content. The standard volatiles measurement for limestone appears to be useless.
- There is some evidence for biasing of solids samples due to segregation effects. This is particularly evident when comparing char to disposal samples and recycle samples. Normally these samples should be almost identical in composition and size distribution. We have recommended using the char to disposal samples in all calculations as they appear to be more representative of the cyclone downleg solids.
- The high dust loading in the freeboard makes it extremely difficult to make visual observations of the bed fluidization behavior and the presence (or lack) of coal volatiles plumes. We have suggested the testing of high temperature borescopes as a means of better visualizing the bed and also as a method for making measurements such as solids level. One borescope vendor, Diaguide, Inc., has agreed to provide a demonstration borescope for testing at the pilot plant. The test is now expected to take place in late July.

Our current efforts are focused on improving the ability of the steady-state computer model to simulate calcination and sulfur capture, especially with regard to the effects of recycle. The ultimate goal is to determine how calcium utilization can be improved.

12. HEALTH AND ENVIRONMENTAL APPLICATIONS

K. E. Cowser

Environmental and health-related studies are being conducted for the DOE/Fossil Energy, with support from the Gas Research Institute and the DOE/Office of Health and Environmental Research. They include implementation of several monitoring and testing components for the Gasifiers in Industry Program and investigation of hydrotreatment and other refinery practices to determine the effects of upgrading on the biological properties of coal-derived liquid products. Specifically, progress is described in the preparation of documentation for the University of Minnesota-Duluth Development Organization (CAN-DO) gasifier; in the studies involving the Westinghouse fluidized bed coal gasification process development unit; and in the study of the chemical, physical, ecological, and biological properties of liquid products [from the SRC-II, H-Coal, and Exxon Donor Solvent (EDS) processes] upgraded by hydrotreatment.

12.1 Coal Gasification Demonstration Plants

Efforts during this reporting period have continued to focus on completion of documentation associated with the University of Minnesota-Duluth (UMD) project. In addition, environmental, health, and safety (EH&S) monitoring activities were conducted during maintenance operations at the Westinghouse fluid bed gasification process development unit and plans were developed for similar studies during routine operation of the gasifier.

12.1.1 University of Minnesota-Duluth Coal Gasification Project -
 (S. D. Van Hoesen,¹ R. M. Cushman,² W. G. Dreibelbis,³ J. L. Epler,⁴
 H. R. Meyer,⁵)

UMD project efforts continue to be focused on completing UMD documentation. "Environmental Evaluation of the University of Minnesota-Duluth Coal Gasifier" (ORNL/TM-8552) was published March 1983. Two documents, "Personnel and Plant Area Monitoring at the University of Minnesota-Duluth Gasifier" and "Biological Response to Products and Effluents from the University of Minnesota-Duluth Gasifier," were circulated for external review. Comments have been received and are being incorporated into the documents in preparation for publication. A final draft document, "University of Minnesota-Duluth Gasifier Health Risk Assessment," was also circulated for external review. Additional efforts will be required to respond to comments received. Discussions are under way with DOE/OHER to determine the extent of revisions to be made.

12.1.2 Environmental Health and Safety Studies at the Westinghouse Fluid Bed Gasifier Process Development Unit (PDU) - (S. D. Van Hoesen,¹
 J. M. Evans,⁶ W. Menzies⁷)

The U.S. Department of Energy (DOE) and the Gas Research Institute (GRI) are jointly funding a program to develop environmental, health, and safety (EH&S) data for process modules and streams at the Westinghouse fluidized bed coal gasification process development unit (PDU) in Madison, Pennsylvania. The Radian Corporation is under contract to perform the bulk of the work. ORNL was requested by GRI to utilize several newly developed monitoring and analytical techniques during the EH&S

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- 1. Central Management Offices
 - 2. Environmental Sciences Division
 - 3. Health Division
 - 4. Biology Division
 - 5. Health and Safety Research Division
 - 6. Gas Research Institute
 - 7. Radian Corporation

study to develop additional information on the potential for production of and exposure to polycyclic aromatic hydrocarbon (PAH) compounds. Three discrete sampling periods have been planned: gasifier maintenance activities conducted in January 1983 (preliminary results described in this report); gasifier operation on bituminous coal (scheduled for June 1983); and gasifier operation on lignite in July 1983.

The measurements conducted by ORNL involve the following instruments and techniques.

The spill spotter is a portable instrument designed to detect and measure surface contamination from PNA containing process materials. The instrument is based on the principle that PNA materials are highly fluorescing when excited by appropriate wavelength UV light. The instrument contains a UV light source which is directed at the surface being evaluated. The resulting fluorescence is measured by a photo multiplier tube in the instrument providing a measure of the amount of PNA material present on the surface.

The derivative ultra-violet absorption spectrometer (DUVAS) is a semi-portable, real-time area monitor designed to detect and measure mono- and diaromatic hydrocarbon vapors, such as benzene, toluene, naphthalene, cresol, etc. A wavelength modulated UV light beam is passed through a multi-pass sampling cell which contains the gaseous sample being analyzed. The second derivative of the absorption of the UV light beam is measured producing an electrical signal proportional to the concentration of the absorbing compounds in the gas sample. The DUVAS can also be operated in a second mode to analyze water samples for phenol content.

Synchronous luminescence (SL) analysis will be utilized to rank process samples provided by Radian according to their aromatic content and to qualitatively indicate the relative concentration of aromatic compounds of various ring size. The technique utilizes synchronous scanning of the excitation and emission wavelengths with a fixed wavelength difference. This enhances detection and selectivity for the fluorescent compounds such as the PNAs.

The PNA dosimeter is used to determine the concentration of higher ring PNA vapors that may be present in ambient areas. The

technique utilizes a specially treated filter paper to absorb the PNA vapors which are then measured using room temperature phosphorescence analysis. The dosimeters can be utilized in a passive mode, for example as personal dosimeters, or in an active mode, with a sampling pump to perform ambient atmosphere measurements.

The following discussion briefly describes the measurements conducted in conjunction with Radian Corporation and the preliminary results obtained during the maintenance activities evaluated in January 1983. A more detailed description of these activities and those to be conducted in June and July will be prepared at the conclusion of the program.

ORNL's involvement in the maintenance activities involved approximately one day of time on site and were primarily to develop experience in utilizing the PNA dosimeters in the active mode and to train Radian in the use of the spill spotter. The spill spotter was then loaned to Radian for about two weeks for their use during the remainder of the maintenance activity evaluations.

The PNA dosimeters were utilized to develop information on worker exposures during a steam cleaning of the recycle gas compressor filter holders. Three dosimeters were utilized on the worker performing the steam cleaning operation--two in the passive mode and one in the active mode. Radian collected personal samples during the operation with a teflon filter and XAD-2 resin cartridge and Tenax cartridge sampling train. The dosimeters were exposed for approximately one hour during the operation.

Results of the work with the PNA dosimeters indicated that the readings from the exposed dosimeters were comparable to those from blank dosimeters. In addition, results from the passive and active badges were comparable. These results suggest that no PNAs were present during the operation or, if present, were less than the detection limit for the PNA dosimeter. Estimated dosimeter detection limits for selected compounds, for example, are 2 ppb/hr for pyrene and quinoline. Additional work with the PNA dosimeters will be undertaken during the June and July operating periods.

The spill spotter was utilized to evaluate surface contamination from PAH-containing material in selected process areas, on selected pieces of equipment, on worker protective clothing, and to provide training and experience to Radian personnel in its use. Several locations on the ground floor in the process area were surveyed. The flanges on the manifold for the recycle gas compressor filter holders did not exhibit any obvious level of contamination. Slightly elevated fluorescence readings were noted on areas of the flange where a white material, possibly gasket or sealing compound, was present. The areas in and around the separator pit/sludge elevator were also evaluated. Fluorescence levels were generally quite low with isolated spots having intensities less than 2 times the general background levels.

Surveys were also conducted on selected pieces of equipment which were undergoing maintenance. The recycle gas compressor filter holders were surveyed before and after cleaning. Fluorescence readings were actually higher after the steam cleaning than before the cleaning. This is thought to be due to the fact that dried, caked coal/ash material, which experience has shown tends to mask fluorescence, was removed during the steam cleaning operation. Levels after cleaning were consistent with readings at the filter manifold. Several of the dirty filter elements were surveyed after removal from the filter housing. Levels of fluorescence were 10-30 times higher than those measured on the inside of the clean filter holder assemblies. A make-up scrubber water pump was surveyed and no fluorescence contamination was noted. Several tools utilized during disassembly of the filter holders were surveyed. Fluorescence levels on the tools were low with no hot spots being noted.

Extensive surveys of several sets of worker protective coveralls were conducted to establish background fluorescence levels. These coveralls were then monitored by Radian after being worn by Westinghouse personnel during maintenance operations to evaluate whether fluorescence contamination from PAH materials was occurring. Fluorescence levels on the clean coveralls were fairly uniform both from one coverall to the next as well as from location to location on a particular coverall. One set of coveralls worn by an operator was surveyed after the recycle gas compressor filters were steam cleaned. Contamination of the coveralls with a black stain was visibly noted in several areas, particularly on

the lower pants legs. The contamination appeared to result from the black liquid (coal/ash materials suspended in water) produced during the steam cleaning operation. Surveys with the spill spotter suggested that fluorescence levels on most areas of the coveralls were at background levels. Elevated fluorescence readings (four to five times background) were associated with the visible contamination described earlier.

Radian Corporation conducted additional surveys with the spill spotter and performed chemical analysis of both clean and contaminated areas of the coveralls. The results of these activities will be documented in the final Radian report describing their EH&S activities at the Westinghouse gasifier.

Plans are currently being made to conduct additional measurements during gasifier operations planned for June and July. It is anticipated that additional surveys with the spill spotter will be performed to evaluate levels of surface contamination from PAHs. Passive PNA dosimeters will be used to monitor selected personnel, and active PNA dosimeters will be used to evaluate ambient levels at several locations where fugitive emissions may be experienced. The DUVAS will be utilized to evaluate both ambient and process gas samples for mono- and diaromatic hydrocarbons. Several samples (either liquid samples or extracts of particulate samples) will be evaluated for aromatic content using the synchronous luminescence analysis technique.

12.2 Hydrotreatment of Coal Liquids

12.2.1 Sample Management and Chemical Characterization - (W. H. Griest, B. A. Tomkins, and C. -h. Ho⁸)

In this reporting period, an extension to the hydrotreatment study has been arranged, and one of the three additional samples for that study has been received. At the request of DOE/FE, we are arranging for a chemical analysis, biological and ecological assay comparison of the samples listed in Table 12.1. These samples include ACD Nos. 931, 934, and 935, which correspond to the H-Coal blend after water washing, and the medium and high severity hydrotreated, water-washed blend,

8. Analytical Chemistry Division

Table 12.1 Hydrotreated H-Coal Samples and Petroleum Reference
Materials for Study

ACD Sample No.	Supplier Sample No.	Description
931	WOW-4747 ^a	H-Coal Blend After Water Wash
934	SGQ-8031 ^a	H-Coal Blend HDT to 2650 ppm N
935	SGQ-8014 ^a	H-Coal Blend HDT to 0.2 ppm N ("Fuel Oil")
936	4378-89 ^b	H-Coal Reformed Naphtha ("Gasoline")
-	-	Petroleum Home Heating Oil ^c
-	-	Petroleum Gasoline ^c

^aChevron Research Company

^bUniversal Oil Products, Inc.

^cTo be supplied by American Petroleum Institute

respectively. The ACD No. 936, a reformed naphtha, was supplied in this reporting period by Universal Oil Products, Inc. (UOP). UOP catalytically reformed a water washed H-Coal blend which had been hydrotreated twice by Chevron. The first stage of hydrotreatment was identical to that of ACD No. 935. The petroleum reference materials are expected to be received from the American Petroleum Institute (API) in the near future. The other samples have been distributed for this study.

Chemical/physical characterization of ACD Nos. 931, 934, and 935 were reported in a previous progress report.¹ Most of the tests have been completed for ACD No. 936. These data are compared in Table 12.2 with those for ACD No. 935, which represents a less-refined "precursor" for ACD No. 936. The second stage of hydrotreating and catalytic reforming have resulted in a much more volatile, less dense, and less viscous sample. Number 936 is more aromatic in character than No. 935, which is necessary to achieve its octane rating. The H/C ratio is lower, the neutral mono-/diaromatics class fraction is higher, and the benzo(a)pyrene (BaP) content has been increased noticeably. The latter result was higher than expected, and precautions were taken to check the results. Both No. 935 and 936 were reanalyzed side-by-side along with a blank to verify the relative results and the absence of a background contribution to the BaP measurement. The BaP result was confirmed by another chromatographic method. The present study will be completed when the petroleum-derived samples are received from the API and have been analyzed. An ORNL/TM is being prepared to detail the current status of the project.

12.2.2 Mammalian Genetics Studies (W. M. Generoso⁹)

12.2.2.1 Acute toxicity determination. Preparatory to the planned genetic studies, we conducted acute toxicity studies in male and female mice to determine the maximum tolerated dose for single intraperitoneal injection (i.p.). The mixtures were dissolved in corn oil. The volume injected was adjusted to the weight of each mouse but never exceeded 0.5 ml. Body weights and survival data were obtained during a 30-day observation period. Survival data are given in Table 12.3.

Table 12.2 Comparison of Results for H-Coal Blend Hydrotreated to 0.2 ppm N ("Fuel Oil") and Reformed Naphtha

Parameter, Units	Results for Sample	
	No. 935 HDT to 0.2 ppm N	No. 936 Reformed Naphtha
-Ultimate Analysis-		
H/C Ratio	1.85	1.67
N/C Ratio x 10 ³	<0.10	<0.10
S/C Ratio x 10 ³	<0.01	<0.0004
-Physical Parameters-		
Density, g/cm ³ @ 25°C	0.867	0.781
Viscosity, cSt @ 25°C	2.68	0.60
Pour Point, °C	-40	<-30
Flash Point, °C	28	<-10
-Simulated Distillation-		
Initial BP, °C	84	78
Avg. BP, °C	241	102
Final BP, °C	363	362
-Chemical Analysis-		
Benzo(a)pyrene, µg/g	0.2	1.4
-Chemical Class Distribution-		
Volatiles, %	-	58
Ether-Soluble Acids	0.48	0.59
Ether-Soluble Bases	0.72	0.13
Insoluble	<0.1	<0.1
Neutral Saturates	58.9	0.44
Neutral Mono/Diaromatics	8.32	13.1
Neutral Polyaromatics	0.52	0.09
Neutral Residue	0.08	0.01
Total Recovery	69.0	72.4

Table 12.3 Acute Toxicity in Male and Female Mice

Mixture	Stock of mice	Sex treated	Dose (mg/kg)	No. of Mice treated	No. of survivors*
SRC-II 915	(C3H x 101)F ₁	Male	2000	12	5
			1500	12	12
	(SEC x C57BL)F ₁	Female	1500	36	24
SRC-II 919	(C3H x 101)F ₁	Male	5000	12	10
			3000	12	12
	(SEC x C57BL)F ₁	Female	4000	36	15
H-Coal 931	(C3H x 101)F ₁	Male	3000	12	1
			2500	12	11
			2000	12	12
	(SEC x C57BL)F ₁	Female	2500	12	12
			2000	12	12
H-Coal 935	(C3H x 101)F ₁	Male	7500	12	6
			6250	12	12
			5000	12	12
	(SEC x C57BL)f ₁	Female	7000	12	12
			6000	12	11

*Observation period was 30 days.

Samples tested included ACD No. 915 (SRC-II blend before water wash), ACD No. 919 (SRC-II blend hydrotreated to 505 ppmN), ACD No. 931 (H-Coal blend after water wash), and ACD No. 935 (H-Coal blend hydrotreated to 0.2 ppmN).

12.2.2.2 Dominant-lethal tests in male mice. Male (C3H x 101) F_1 mice (11-12 weeks old) were given single i.p. injection of the mixtures dissolved in corn oil. For each mixture, the maximum tolerated dose, determined from the acute toxicity studies, was used. Control mice were given 0.5 ml of corn oil each. Each male was caged soon after injection with two (C3H x 101) F_1 females. Females were checked for presence of vaginal plugs each morning. Plugged females were separated and replaced by fresh ones.

Dominant-lethal data are shown in Tables 12.4 and 12.5. Results show that SRC-II 915 and H-Coal 931 have no statistically significant demonstrable dominant-lethal effects in male germ cells. These two samples have been shown in other studies to be more toxic and more mutagenic than the samples derived from them after hydrotreatment, namely, SRC-II 919 and H-Coal 935, respectively. Because of this finding and because of the negative dominant-lethal response observed in the present study, dominant-lethal studies with the post-hydrotreatment samples were concluded to be unnecessary.

12.2.2.3 Total reproductive capacity tests in females. The mouse ovary is generally known to be sensitive to even relatively slight insult from known mutagens. The total reproductive capacity test in females detects both dominant-lethal and cell-killing effects in female germ cells as well as nongenetic effects associated with alterations in female physiology. The test is done by simply determining the lifetime production of offspring of females exposed to the sample and mated continuously to fertile males. Ten to twelve weeks old (SEC x C57BL) F_1 females were given single i.p. injection of the test mixtures dissolved in corn oil. For each mixture the maximum tolerated dose was used - i.e., 1200 mg/kg, 3000 mg/kg, 2500 mg/kg, and 3500 mg/kg for SRC-II 915, SRC-II 919, H-Coal 931, and H-Coal 935, respectively.

Experiments with SRC-II samples have already been completed. Experiments with H-Coal samples, on the other hand, are still in progress and data are available only for a period up to 119 days

Table 12.4 Dominant-Lethal Test in Male Mice with H-Coal 931

Treatment	Treatment to fertilization interval (days)	No. of mated ♀♀	No. of pregnant ♀♀	No. of implantations (per preg. ♀)	No. of living embryos (per preg. ♀)	% Dead implants
H-Coal	1/2-1	7	6	8.2	7.3	10.2
	2 1/2-3 1/2	21	19	9.0	8.3	8.2
	4 1/2-5 1/2	10	10	7.3	6.3	13.7
	6 1/2-7 1/2	16	15	7.7	6.9	9.6
	8 1/2-9 1/2	11	10	7.5	7.1	5.5
	10 1/2-11 1/2	12	12	6.6	6.0	8.9
	12 1/2-13 1/2	8	8	7.3	6.8	6.9
	14 1/2-15 1/2	14	14	7.6	7.1	7.5
	16 1/2-17 1/2	10	10	7.2	6.1	15.3
	18 1/2-19 1/2	14	8	7.4	6.9	6.8
	20 1/2-21 1/2	15	10	6.5	5.6	13.8
	22 1/2-23 1/2	15	11	6.9	6.3	9.2
	24 1/2-25 1/2	8	5	5.6	5.2	7.1
	26 1/2-27 1/2	13	12	6.8	6.0	11.1
	28 1/2-29 1/2	11	10	5.5	4.8	12.7
	30 1/2-31 1/2	9	8	6.4	5.6	11.8
	32 1/2-33 1/2	19	17	6.9	6.2	9.4
	34 1/2-35 1/2	15	12	6.4	5.7	11.7
	36 1/2-37 1/2	14	11	6.8	6.4	6.7
	38 1/2-41 1/2	39	20	6.2	5.7	8.9
Corn oil	1/2-1	13	10	7.5	7.4	1.3
	2 1/2-3 1/2	14	14	8.1	7.4	9.6
	4 1/2-5 1/2	14	14	7.2	6.5	9.9
	6 1/2-7 1/2	18	17	7.1	6.6	6.7
	8 1/2-9 1/2	9	9	7.2	6.6	9.2
	10 1/2-11 1/2	16	14	7.3	6.9	4.9
	12 1/2-13 1/2	6	6	8.0	7.5	6.3
	14 1/2-15 1/2	15	15	7.7	6.7	12.9
	16 1/2-17 1/2	10	9	6.7	6.2	6.7
	18 1/2-19 1/2	8	6	7.8	7.5	4.3
	20 1/2-21 1/2	15	10	6.9	6.4	7.2
	22 1/2-23 1/2	0	7	6.9	6.0	12.5
	24 1/2-25 1/2	10	7	6.7	5.7	14.9
	26 1/2-27 1/2	16	16	6.4	5.6	12.7
	28 1/2-29 1/2	11	10	7.3	6.5	11.0
	30 1/2-31 1/2	6	5	6.8	6.0	0.0
	32 1/2-33 1/2	15	13	6.44	5.6	12.0
	34 1/2-35 1/2	17	13	6.4	5.5	13.3
	36 1/2-37 1/2	14	11	6.8	6.4	6.7
	38 1/2-41 1/2	39	20	6.2	5.7	8.9

Table 12.5 Dominant-lethal test in male mice with SRC-II 915

Treatment	Treatment to fertilization interval (days)	No. of mated ♀♀	No. of pregnant ♀♀	No. of implantations (per preg. ♀)	No. of living embryos (per preg. ♀)	% Dead implants
SRC-II 915	1/2-1	10	9	8.8	8.0	8.9
	2 1/2-3 1/2	21	19	8.6	8.0	6.7
	4 1/2-5 1/2	16	16	7.5	6.9	7.5
	6 1/2-7 1/2	16	14	7.7	6.6	13.9
	8 1/2-9 1/2	19	17	6.9	6.4	7.6
	10 1/2-11 1/2	15	15	7.5	7.3	2.7
	12 1/2-13 1/2	15	15	7.1	6.7	6.5
	14 1/2-15 1/2	21	20	7.5	7.1	4.7
	16 1/2-17 1/2	11	11	7.1	6.5	9.0
	18 1/2-19 1/2	12	11	7.7	7.2	7.1
	20 1/2-21 1/2	18	18	7.4	6.8	9.0
	22 1/2-23 1/2	15	15	7.6	7.0	7.9
	24 1/2-25 1/2	16	16	7.0	6.6	5.4
	26 1/2-27 1/2	21	20	6.6	6.0	8.4
	28 1/2-29 1/2	19	16	6.6	6.2	5.7
	30 1/2-31 1/2	7	5	8.0	7.6	5.0
	32 1/2-33 1/2	4	4	7.5	7.0	6.7
	34 1/2-35 1/2	11	10	8.4	6.9	6.8
	36 1/2-37 1/2	5	5	7.2	6.4	11.1
	38 1/2-39 1/2	4	4	8.8	8.3	5.7
Corn oil	1/2-1	13	13	9.2	8.2	11.7
	2 1/2-3 1/2	17	17	8.9	7.9	10.6
	4 1/2-5 1/2	9	9	9.1	7.7	15.9
	6 1/2-7 1/2	15	15	8.2	7.5	8.1
	8 1/2-9 1/2	15	15	8.3	7.8	6.4
	10 1/2-11 1/2	15	15	7.7	7.3	5.2
	12 1/2-13 1/2	13	13	7.5	6.9	7.2
	14 1/2-15 1/2	18	18	7.4	6.2	16.4
	16 1/2-17 1/2	12	12	7.3	6.5	11.4
	18 1/2-19 1/2	13	12	7.7	6.6	14.1
	20 1/2-21 1/2	21	18	7.4	6.8	9.0
	22 1/2-23 1/2	14	14	7.2	6.7	6.9
	24 1/2-25 1/2	14	14	7.5	7.1	5.7
	26 1/2-27 1/2	23	21	7.2	6.7	7.3
	28 1/2-29 1/2	7	7	7.4	7.0	5.8
	30 1/2-31 1/2	6	6	7.5	7.0	6.7
	32 1/2-33 1/2	17	16	7.4	6.3	14.4
	34 1/2-35 1/2	8	6	6.8	6.0	12.2
	36 1/2-37 1/2	8	8	7.5	7.1	5.0
	38 1/2-39 1/2	7	6	8.3	6.7	20.0

posttreatment. Results to date indicate a similarity in the effects of SRC-II and H-Coal samples. In both cases litter size reductions were observed only in first litters and, although litter sizes for both pre- and posthydrotreated samples appear lower than those for controls, a more clear-cut reduction can be seen for the prehydrotreatment samples (Table 12.6)

12.2.2.4 Dominant-lethal test in females - The first litter effects observed in the total reproductive capacity studies may be due to dominant-lethal mutations, cell killing, or to nongenetic effects associated with alterations in female physiology. We attempted to study the first litter reproductive effect further by conducting a dominant-lethal experiment with SRC-II 915 sample using the same dose and strain of mice as those used in the total reproductive capacity study.

Results in Table 12.7 show the average number of living embryos is clearly lower in the experimental group than in the control group, as expected. It is also clear that the number of implants per female is lower in the experimental group than in the control group while no difference was observed with regard to the incidence of dead implantations. These data indicate that SRC-II 915 affected the rate of ovulation presumably via maternal physiological effect.

12.2.3 Ecological Test Results (J. M. Ciddings, S. E. Herbes, J. Fair, and C. P. Allen)²

Data on concentrations of water-soluble phenolic compound in raw and upgraded coal liquids, and oil-water partition coefficients for these compounds are required to estimate any potential environmental impacts associated with these materials. To complete this task a Dura-bond DB-5 capillary column has been installed and tested in a Varian VISTA 4600 gas chromatograph. Three suites of raw and hydrotreated coal liquids (H-Coal, ACD Repository Nos. 930, 933, 935, and 935; SRC-II, Nos. 915-919; and Exxon Donor Solvent, Nos. 923 and 923) are being extracted exhaustively with NaOH to permit isolation of phenolics, which are then concentrated by solvent extraction before GC analysis. Parallel oil samples are equilibrated with water (1:8 oil:water ratio) and aqueous phenolics are isolated by solvent extraction and analyzed similarly to determine oil-water partition coefficients. The high resolution of capillary column GC with complementary qualitative GC with

Table 12.6 First Litters in Total Reproductive Capacity Tests

Treatment	Litter size* (ave)
SRC-II 915	6.7
SRC-II 919	8.1
Control	8.9
H-Coal 931	7.8
H-Coal 935	8.2
Control	9.0

*All litters were born 18-24 days posttreatment.

Table 12.7 Dominant-Lethal Study in Female Mice with SRC-II 915

Treatment	Number of mated females*	Number of pregnant females	Number of implantations (per female)	Number of living embryos (per female)	Dead implantations (%)
SRC-II	39	20	6.6	4.7	29
Corn oil	47	31	11.8	8.8	25

*Females were mated during the first four days after treatment.

complementary qualitative GC/MS analysis (M. Buchanan and G. Olerich, Analytical Chemistry Division) permits quantification of all 9 C₂-phenol isomers, 10 C₃-isomers, 6 C₄-isomers, in addition to phenol, cresols, and more than 10 C₀-C₂ indanol and tetralol constituents. Completion of data collection is expected by August 1983.

REFERENCE

- ¹ L. E. McNeese, Fossil Energy Program Quarterly Progress Report for the Period Ending December 31, 1982, ORNL-5944 (March 1983).

13. FBC PROGRAM PLANNING AND ANALYSIS

R. S. Holcomb and R. L. Graves

13.1 Objective

The scope of this effort is to provide analysis and planning support to DOE in the area of advanced fluidized bed combustion.

Three specific tasks have been authorized by DOE: (1) PFBC Component Development, (2) Control Methodology, and (3) Industrial Applications.

The objectives of the PFBC Component Development task are to perform an assessment of the state of technology for the major components of the PFBC system, identify deficiencies in performance capabilities, propose improved designs for components, and prepare a development program plan for each component that requires additional development.

The Control Methodology task has as its objectives to define the potential control problems that are unique for PFBC, study control schemes for both the air cycle and steam cycle plants and propose possible improvements, and develop a control methodology for advanced PFBC concepts.

The objective of the Industrial Applications task is to conduct an assessment study for PFBC systems for industrial applications and its potential market as compared to conventional coal-fired systems.

13.2 Status Summary

13.2.1 Component Development Plan - R. L. Graves

The final report on this task is being drafted.

13.2.2 FBC Power Plant Control Methodology - J. F. Thomas

Work was resumed on this task in April after a temporary hold on the effort.

A computer code was developed to examine turndown characteristics of an air-cooled PFB power plant. Most of the design specifications in the code are similar to the Curtiss-Wright commercial plant conceptual design.

Preliminary calculations show no indication of difficulty in turn-down of the air-cooled PFB to about 50% of full load. However, turndown significantly below 50% load will result in improper fluidization of the bed (depending on distributor design) or unacceptably low bed temperatures which cause poor combustion and poor sulfur capture.

Investigation was begun to compare turndown characteristics of fixed and variable geometry turbine-compressor systems. It appears that a variable geometry turbine-compressor system may allow somewhat greater turndown and keep part-load efficiencies higher (by controlling excess air) than a fixed geometry unit. However, this portion of the work has not been completed.

Development of a turndown model for a hybrid PFB power plant was begun in late June.

13.2.3 PFB Industrial Applications - R. L. Graves

Work on this task has been completed and a draft of the final report is being typed.

14. COAL PREPARATION AND WASTE UTILIZATION

J. C. Moyers

This project was initiated to demonstrate the feasibility and develop to commercial use a process for the magnetic separation of the inorganic contaminants of pyritic sulfur and ash-forming minerals from fine coal. The ability to perform this separation by either wet or dry high gradient magnetic separation (HGMS) has been demonstrated in laboratory-scale bench tests. Work in this area continues under the sponsorship of the Tennessee Valley Authority (TVA). A small (approximately one ton per hour capacity) wet HGMS pilot plant is planned for initial operation during the summer of 1983 at TVA's Paradise coal preparation plant in western Kentucky.

Laboratory-scale beneficiation of dry fine coal has also been accomplished with open gradient magnetic separation (OGMS) devices. The OGMS process appears to be a feasible means of concentrating a wide variety of mineral ores and of decontaminating industrial process materials; scouting tests on several materials have been conducted for various parties.

Since its inception, however, and due in large part to the influence of TVA as a sponsor, this project has expanded its domain to include areas of research other than magnetic beneficiation. The development of a computer model for coal preparation plants to improve plant performance is one example. This program is not funded at present, but a working model has been developed. Further refinements and field testing will be done when funds are again available.

Another major undertaking has been the development of a dense medium sample separator (DMSS) to perform float-sink analyses on raw coal. This device uses a recirculating suspension of magnetite in water to effect separation at a selected specific gravity. Non-toxicity of the materials and low cost per unit weight of raw coal tested give the DMSS decided advantages over conventional float-sink methods with zinc chloride or organic liquids. The DMSS has performed satisfactory separations on +3/8 in. coal and has been delivered to TVA for use at the Paradise preparation plant.

Short-term projects are also undertaken from time to time. These may be initiated by a specific request from TVA or may develop from some larger project. Most of these are either related to magnetic separation or coal beneficiation in general.

14.1 Pilot Plant Demonstration of Wet High-Gradient Magnetic Separation

V. R. Brantley, J. C. Moyers and M. T. McFee

Representatives from TVA's ED&T Division visited ORNL on April 18 to review the pilot plant design and to discuss testing procedures. The trailer-mounted pilot plant had been moved to the Paradise preparation plant and connections to the plant were under way.

ORNL personnel joined TVA engineers at Paradise for shakedown of the pilot plant on April 26-29. Members of the pilot plant group at Muscle Shoals were also at Paradise the first two days to correct deficiencies and explain the workings of the pilot plant. Except for the normally expected minor problems, the shakedown went very smoothly.

Two features of the pilot plant that are somewhat different from pre-conceived understanding required consideration in establishing the test procedures and conditions. First, contrary to information given in the Sala manual for the HGMS carousel, the matrix boxes are not drained following the magnetics flush station but, instead, reach the prefill station full of flush water. This will make the use of classifying cyclone overflow material for flushing impractical, since the material would be carried into the magnetic separation region. It also drastically changes the amount of material required (either feed slurry or clear water) for introduction at the prefill station. If slurry from the underflow of the first feed slot is used for prefill, the slurry velocity through the matrix as it passes that slot probably will be quite low and not measurable. A better arrangement was to use clarified water for prefill and to route the underflow of the first feed slot similarly to the underflow of the other feed slots, so that it could be regulated and measured.

The second feature that limited the range of testing was the difficulty in changing the location of the moveable partition between the feed and

rinse portions of the magnet feed tank. The location of this partition establishes the allocation of the available slots between feed and rinse functions. A definite relationship exists between slot allocation, feed slurry flow rate, solids concentration, matrix loading, and rinse factor.

Procedures were established for wet seiving and dewatering samples that will be obtained during operation of the pilot plant. The Gilson Wet-Vac and the pressure-dewatering equipment in the Paradise laboratory will be used.

Two 55-gallon tanks, one for the non-magnetic product (non-mag tank) and one for the magnetic refuse (mag tank), receive slurry from the HGMS. Other streams also flow into these tanks. Rinse water goes to the non-mag tank and flush water goes to the mag tank. Both of these streams are monitored by rotameters. Desliming cyclone overflow also goes to the mag tank. Capacitance level probes are used to control the pumps which empty these tanks, so a convenient way to measure total flow rate into a tank is by measuring the level rise rate while the pump is off.

The magnet feed tank was removed and a section of false ceiling was taken down. The roof was then raised somewhat with 2x6's and wooden wedges to provide more head room; as a result, two people can now manage the tank installation or removal reasonably well. Another pressure gauge for measuring cyclone pressure drop was installed inside the trailer, supplementing the gauge on the trailer roof.

Removing the feed tank provided an opportunity to measure and photograph the seven slots in the upper magnetic pole piece. These slots are radially oriented and are $3/4$ in. wide by $4-3/4$ in. long. The land between slots is trapezoidal, measuring $2-1/6$ in. across the short parallel side and $2-5/8$ in. across the long parallel side.

The apex orifices in two of the cyclones were changed out to facilitate initial characterization testing of the cyclones. Slurry was fed to the cyclone header and various combinations of the three cyclones were run to check out all the lines and pumps. A total of five cyclone tests then were successfully run.

The magnet feed tank and the cyclone underflow launder cover were brought to ORNL for modification. PVC sight glasses were installed to indicate liquid levels in the feed and rinse sections for the feed tank, and the launder cover was sectionalized to allow easy removal for test purposes.

ORNL and TVA representatives met in Chattanooga on May 13 to discuss the HGMS test plan. Several areas of concern were successfully resolved, and a general outline of a plan agreeable to all parties was produced.

During a visit to the pilot plant on May 16, the modified magnet feed tank, the modified cyclone underflow launder cover, and two level indicators for flow rate measurements in the mag and non-mag tanks were delivered. These level indicators, fabricated from PVC pipe and fittings, are essentially guided floats that carry metering stems. The indicators are an improvement over the previously used fixed metering rod in that

- a. successive flow rate measurements showed much better repeatability than had been possible with the previous level indicator, and
- b. it is much easier for one person to perform flow rate measurements, thus reducing the number of people required for test work.

A total of twelve tests were run during May to constitute Phase I of the cyclone test program which characterized the material split and cyclone capacity with various combinations of cyclone inlet area, apex diameter, and vortex orifice diameter. All of the overflow and underflow samples were dewatered and the filter cakes were oven-dried prior to weighing. Results of these tests are presented in Tables 14.1 through 14.5.

Table 14.1 HGMS pilot plant phase I cyclone tests

Results of Cyclone Test No. 1-2 (I=0.56; A=.88; V=1.0)*

	<u>Overflow</u>	<u>Underflow</u>	<u>Total</u>
Slurry flow, gpm	22.6	25.3	47.9
Flow split, pct.	47.2	52.8	
Solids content, wt. pct.	2.96	7.76	
Solids flow, lbs/hr	336.3	1012.3	1348.5
Feed solids content, wt. pct.			5.51

Results of Cyclone Test No. 1-3 (I=0.56; A=.63; V=1.0)*

Slurry flow, gpm	33.6	9.9	43.5
Flow split, pct.	77.2	22.8	
Solids content, wt. pct.	3.40	13.5	
Solids flow, lbs/hr	574.8	718.5	1293.3
Feed solids content, wt. pct.			5.81

* I = inlet head area, in.²

A = apex inside diameter, in.

V = vortex finder inside diameter, in.

Table 14.2 HGMS pilot plant phase I cyclone tests

Results of Cyclone Test No. 2-1 (I=0.56; A=1.06; V=1.25)*

	<u>Overflow</u>	<u>Underflow</u>	<u>Total</u>
Slurry flow, gpm	30.5	26.7	57.2
Flow split, pct.	53.3	46.7	
Solids content, wt. pct.	4.24	7.62	
Solids flow, lbs/hr	657.8	1089.7	1747.4
Feed solids content, wt. pct.			5.97

Results of Cyclone Test No. 2-2 (I=0.56; A=.88; V=1.25)*

Slurry flow, gpm	38.5	14.9	53.4
Flow split, pct.	72.1	27.9	
Solids content, wt. pct.	3.08	11.3	
Solids flow, lbs/hr	600.4	872.5	1472.9
Feed solids content, wt. pct.			5.40

Results of Cyclone Test No. 2-3 (I=0.56; A=.63; V=1.25)*

Slurry flow, gpm	30.6	25.3	55.9
Flow split, pct.	54.7	45.3	
Solids content, wt. pct.	3.94	9.39	
Solids flow, lbs/hr	641.4	1212.7	1854.1
Feed solids content, wt. pct.			6.7

* I = inlet head area, in.²
 A = apex inside diameter, in.
 V = vortex finder inside diameter, in.

Table 14.3 HGMS pilot plant phase I cyclone tests

Results of Cyclone Test No. 3-2 (I=0.56; A=.38; V=.75)*

	<u>Overflow</u>	<u>Underflow</u>	<u>Total</u>
Slurry flow, gpm	29.7	4.1	33.8
Flow split, pct.	87.9	12.1	
Solids content, wt. pct.	2.56	15.2	
Solids flow, lbs/hr.	381.3	325.3	706.5
Feed solids content, wt. pct.			4.11

Results of Cyclone Test No. 3-3 (I=0.56; A=.63; V=.75)*

Slurry flow, gpm	20.8	16.8	37.6
Flow split, pct.	55.3	44.7	
Solids content, wt. pct.	2.54	7.59	
Solids flow, lbs/hr	264.6	648.2	912.8
Feed solids content, wt. pct.			4.76

* I = inlet head area, in.²

A = apex inside diameter, in.

V = vortex finder inside diameter, in.

Table 14.4 HGMS pilot plant phase I cyclone tests

Results of Cyclone Test No. 4-2 (I=0.56; A=1.06; V=1.25)*

	<u>Overflow</u>	<u>Underflow</u>	<u>Total</u>
Slurry flow, gpm	29.6	26.8	56.4
Flow split, pct.	52.5	47.5	
Solids content, wt. pct.	1.95	6.44	
Solids flow, lbs/hr	287.8	874.5	1162.3
Feed solids content, wt. pct.			4.06

Results of Cyclone Test No. 4-3 (I=0.56; A=.63; V=1.25)*

Slurry flow, gpm	47.5	3.5	51
Flow split, pct.	93.1	6.9	
Solids content, wt. pct.	3.0	26.3	
Solids flow, lbs/hr	712.5	501.2	1213.7
Feed solids content, wt. pct.			4.67

* I = inlet head area, in.²

A = apex inside diameter, in.

V = vortex finder inside diameter, in.

Table 14.5 HGMS pilot plant phase I cyclone tests

Results of Cyclone Test No. 5-1 (I=1.2; A=.88; V=1.0)*

	<u>Overflow</u>	<u>Underflow</u>	<u>Total</u>
Slurry flow, gpm	28.3	30.9	59.2
Flow split, pct.	47.8	52.2	
Solids content, wt. pct.	2.04	3.63	
Solids flow, lbs/hr	287.2	560.0	847.3
Feed solids content, wt. pct.			2.83

Results of Cyclone Test No. 5-2 (I=1.2; A=1.06; V=1.25)*

Slurry flow, gpm	37.9	35.2	73.1
Flow split, pct.	51.8	48.2	
Solids content, wt. pct.	2.59	5.43	
Solids flow, lbs/hr.	489.7	969.5	1459.3
Feed solids content, wt. pct.			3.93

Results of Cyclone Test No. 5-3 (I=0.56; A=.63; V=1.25)*

Slurry flow, gpm	47.3	5.5	52.8
Flow split, pct.	89.6	10.4	
Solids content, wt. pct.	3.05	11.7	
Solids flow, lbs/hr	719.9	329.4	1049.3
Feed solids content, wt. pct.			3.91

*
2I = inlet head area, in.²

A = apex inside diameter, in.

V = vortex finder inside diameter, in.

A series of tests comprising Phase II of the cyclone test program was initiated during June. This series, covering appropriate cyclone settings as identified during Phase I testing, will provide detailed knowledge of the size distribution and chemistry of the overflow and underflow materials.

Because removing the magnet feed tank was an awkward and time-consuming approach to changing the number of feed and rinse slots by rearranging the partition(s) in the tank, a hole was cut in the trailer roof to allow access without removing the tank. The desliming cyclone underflow launder can be easily shifted to permit the partition adjustments from on top of the trailer.

14.2 Development of the Dense Medium Sample Separator

V. R. Brantley and M. T. McFee

ORNL personnel visited the Paradise preparation plant on April 11 and 12 to set up and demonstrate the operation of the Dense Medium Sample Separator (DMSS). The DMSS was charged with a magnetite-water suspension at 1.45 sp gr, corresponding to the operating gravity of the dense medium vessels at the time of the visit. Samples of plant raw coal and dense medium vessel product and refuse were obtained for demonstration separations.

Separation of the +3/8 in. fraction of the plant raw coal produced 14.7% sinks. In separations of the dense medium vessel product and refuse materials, approximately 1.5% of the product reported as sinks while only a trace of the refuse floated. The large coal cleaning circuit in the main plant was, therefore, performing a sharp separation on the day of the demonstration.

The DMSS appeared to be well-received by Paradise plant personnel. The laboratory supervisor felt that separations are more easily carried out with the DMSS than in the presently used zinc chloride equipment. The wash plant operations supervisor was interested in obtaining two additional separators to permit separations at three gravities without the need for changing suspension densities.

Copies of the original DMSS design drawings were provided to the TVA Power Service Shop in Muscle Shoals for estimating the cost of fabricating the additional separators. Modification of the drawings to incorporate changes that evolved during developmental testing was initiated.

The cost of building two more DMSS units was estimated to be \$7200. ORNL provided TVA with information on toxicity and cost of several chemicals commonly used in float-sink analyses to facilitate comparative evaluation of a DMSS facility and a conventional float-sink facility. On the basis of this evaluation, TVA has decided to build a DMSS float-sink facility at Paradise.

15. BASIC CHEMICAL ENGINEERING STUDIES

J. S. Watson

This chapter summarizes results from a series of research studies funded by DOE/Basic Energy Sciences but related, at least in part, to Fossil Energy. In this quarter, we describe progress in experimental measurements of physical properties of fluids and fluid mixtures at high temperatures and pressures.

15.1 Physical Properties of Fluids at Extreme Conditions

D. F. Williams, C. H. Byers, and R. R. Brunson

This program involves fundamental studies of the role of materials and material properties in chemical engineering operations in the energy industry. More detailed background information can be found in previous progress reports.^{1,2,3} The development of a laser light-scattering technique for investigation of high-temperature transport properties of coal-fluid model compounds has been a central effort.

Progress has been made in both the experimental and development areas. The early assembly and testing of an inexpensive low-power (5 mW), low-temperature (0-90°C) spectrometer allowed us to validate the experimental method and to perform some scoping tests. A high-power (2W), high-temperature (to 500°C) spectrometer has been designed, constructed, and successfully tested. Pressures up to 1000 psi are possible with available cells. Preliminary experiments using this more powerful apparatus are in progress.

Experiments using the low-power spectrometer have helped to:

- (a) develop a precise experimental method, and (b) investigate candidate microparticles for high-temperature research. Validation of the new method included comparison of experimentally predicted properties with accepted literature values. Experimental predictions have normally been accurate to within 2% of the literature standards. Numerous microparticles have also been tested for use in organic fluids at high temperatures. An ideal light scattering "seed" (i.e., microparticle) would

provide for a relatively simple, strong, and stable signal over a broad temperature range. Low molecular weight polymers and inorganic oxide microparticles have been used successfully for seeding model coal fluids at moderate temperatures (0-200°C). Experiments at more extreme conditions are proceeding.

The apparatus that has been constructed for use in high-temperature investigations is illustrated in Fig. 15.1. A high-resolution spectrometer is coupled to a high-temperature enclosure and sample cell. The principles of operation of this apparatus were described in a previous report.² Construction and testing of a high-pressure seal is proceeding. Preliminary measurements indicate that excellent resolution and precision can be obtained with this instrument.

15.2 References for Section 15

1. L. E. McNeese, Fossil Energy Program Quarterly Progress Report for the Period Ending December 31, 1981, ORNL-5861 (April 1982).
2. L. E. McNeese, Fossil Energy Program Quarterly Progress Report for the Period Ending June 30, 1982, ORNL-5903 (September 1982).
3. L. E. McNeese, Fossil Energy Program Quarterly Progress Report for the Period Ending December 31, 1982, ORNL-5944 (March 1983).

Fig. 15.1. High-power, high-temperature laser-light scattering apparatus.

16. FOSSIL ENERGY INFORMATION CENTER

Carol Oen

16.1 Introduction

The Fossil Energy Information Center (FEIC) works closely with the many aspects of the Fossil Energy Program to (1) assure awareness of current developments reported in the literature, (2) identify, compile, organize, and analyze information of specific relevance, (3) construct specialized, computerized databases, (4) prepare literature reviews and critical reviews, (5) identify technical experts, and (6) identify information resources relevant to our projects.

16.2 Publications

The manuscript, "Health Effects of Diesel Exhaust," by Curtis Travis and Nancy Munro, was accepted for publication in Risk Analysis. This work originated as a request for a review of this topic for the ORNL Program Planning and Analysis group. Munro is the coauthor of a paper with Peter Witschi of the Biology Division, "The Problems of Toxicological Testing of Complex Mixtures," which is to be presented at the 3rd International Congress on Toxicology in San Diego in August. Munro is working with investigators in the Biology Division to produce a final report on the research results from studies using samples from the H-coal pilot plant at Catlettsburg, Kentucky. This work is under the direction of Ken Cowser of the Life Sciences Synthetic Fuels Program. Material continues to be selected by Joy Huffstetler for the current awareness newsletter for DOE/FE on legislative and regulatory matters.

16.3 Projects

The information component of the Fossil Energy Technology and Environmental Program is involved in designing an information system and a set of technical databases in support of the program. Joy Huffstetler has spearheaded the database design work and N. B. Gove of the Computer Sciences Division has led the system development efforts.

An initial survey of program participants provided information on user's perceived needs and expectations. Huffstetler has implemented a pilot-scale database of material from the Ft. Lewis project that is relevant to environment, health, and safety issues.

The inventory of federally funded acid precipitation under the leadership of Gloria Caton, has been used to answer requests from the Program Coordination Office. The SAS/GRAPH software has been used to provide a variety of bar graphs relating funding levels to the different task groups. Approximately 700 responses to requests were made during the quarter.

16.4 Meetings

Gloria Caton attended the American Society of Information Science (ASIS) mid-year meeting in Lexington, Kentucky, May 21-25 where she conducted a session, "Improving Online Access to Energy and Environmental Information," and discussed coal and acid precipitation issues with Susan Emerson, Information Design and Delivery.

Joy Huffstetler participated in the Special Libraries Association Annual Meeting in New Orleans, June 5-8. Nancy Munro attended the April 5-8 conference, "Reproduction: The New Frontier in Occupational and Environmental Health," in Park City, Utah.

17. GENERALIZED EQUILIBRIUM MODELS OF LIQUID AND GASEOUS FUEL SUPPLIES

J. R. Einstein

17.1 Background

A strategic goal of highest priority for the Fossil Energy (FE) Research and Development program is to reduce U.S. energy supply vulnerability to the economic and security implications of reliance upon scarce and increasingly expensive conventional petroleum resources. The objective is to develop a knowledge base for alternative supply technologies, to provide new sources of liquid and gaseous fuels including coal-derived liquids and gas. In support of this objective, Oak Ridge National Laboratory, together with its subcontractors Decision Focus, Inc. and Lewin and Associates, Inc., is conducting a research program, the principal elements of which are as follows:

1. Develop computerized models for U.S. liquid (LFS) and gaseous (GFS) fuels supply to enable quantitative assessment of competitive supply technologies, and provide DOE/FE with operational support in their use.
2. Develop an automated capability for LFS/GFS sensitivity and uncertainty analyses.
3. Develop a decision making methodology based on sensitivity theory to critically examine the potential benefits of various R&D programs.
4. Plan for contingencies in the event of supply interruptions (supply vulnerability analysis).
5. Provide DOE/FE with a "public sector home" for computer models and analyses.

Particular attention is being focused on representing mechanisms by which new technologies penetrate the oil market, and assuring reliable comparison of the relative economics of enhanced oil recovery,

unconventional gas, shale oil, synthetics, conventional onshore and offshore production, in meeting United States needs for liquid and gaseous fuels as functions of time.

17.2 Status Summary

17.2.1. Further Development of ORION: Improved Model of Onshore Conventional Oil Recovery

The REPCO code, developed by Lewin and Associates, Inc. (L&A) for a replacement-cost study,¹ incorporated an improvement in the modeling of drilling costs for oil fields. The dry-hole costs associated with exploratory and developmental drilling were treated separately, and the year-by-year timing of field development, and consequently of production and revenues, were modeled. An improved and extended version of this portion of the REPCO code has been incorporated into ORION, ORNL's code for projection of marginal costs of liquid and gaseous resource recovery. Among ORNL's additions to the model were: inclusion of the associated-dissolved gas (ADG) component in the finding-rate analysis; variation of the ADG/oil ratio with field size and depth class; different production rates of ADG and oil; increase of exploratory dry-hole rate and average well depth with cumulative drilling effort. Currently, the model is being extended to include secondary-recovery field development and secondary-recovery production profiles.

Marginal-cost vs. supply curves, calculated with ORION as modified, were used as input to the LFS calculations described in 17.2.3.

17.2.2. Studies of the Sensitivity of Marginal Cost for Onshore Conventional Oil Recovery to Three Geologic Parameters

The variation of the marginal cost of conventional crude-oil recovery with several of the fundamental geologic parameters has been investigated, in order to provide guidance in further development of the model embodied in the ORION code. The sensitivities of the marginal cost to

¹Ivello Kuuskraa and Frank Morra, Jr., "Replacement Costs of Domestic Crude Oil," Lewin and Associates, Inc., 1090 Vermont Ave., Washington, D.C. 20005, unpublished.

well depth, field size, and exploratory dry-hole rate can be determined over the entire ranges of these parameters through use of a modified version of the ORION code. Initial results indicate the importance of including in the model the changes in both average field size and average exploratory dry-hole rate, as factors in the decrease of exploratory finding rate with drilling effort. (In the model embodied in the REPCO code,¹ the dry-hole rate remained constant.) The suitability of the present model for the variation of the dry-hole rate with drilling effort is being studied.

17.2.3. Calculations with the Liquid Fuels Supply (LFS) Model

As part of the investigation of replacement costs for oil performed for D. J. Beecy's policy analysis needs, a series of calculations was carried out with the LFS model. The purpose of the calculations was to obtain the price of crude oil in the U.S. as a function of time, for comparisons with the "replacement costs" obtained by Lewin and Associates, Incorporated (L&A).¹ The L&A results were obtained using methods quite different from those used in the LFS model. Input data to the LFS calculations were obtained with program ORION, modified as described in the preceding section.

In order that the comparisons be as meaningful as possible, the demanded quantity of oil in the U.S. used in the LFS model was taken to be the same as that used in the L&A studies. Three LFS cases were considered:

Case 1 - The total U.S. demand for crude oil, including imports, was taken to be constant at 13.7 MMBBL/D, and the price track for imported oil was assumed to be equal to the base-case replacement-cost track in the L&A studies.

Case 2 - The same as Case 1, but the quantity of imported oil was assumed to be constant at 5.5 MMBBL/D. (Since the quantity of imported oil is fixed in this case, no imported oil price track is needed.) The demand for domestic oil was then constant at 8.3 MMBBL/D, the same as in the L&A studies.

Case 3 - The same as Case 2, but it was also assumed that no synthetic oil and no oil from shale and tar sands was produced.

The price of oil as a function of time, as given by the LFS model in the three cases, is compared with the L&A base-case results in Table 17.1. Case 2 should most nearly correspond to the L&A base case. The LFS prices in Case 2 are comparable to the L&A prices in the early years, but are considerably less than the L&A prices in the later years shown in the Table.

Table 17.1. Price of Crude Oil vs. Time

Year	Replacement Cost of Lewin & Associates, Inc.* 1982\$/BBL	Price of Crude Oil from Liquid Fuels Supply Model		
		Case 1** 1982\$/BBL	Case 2** 1982\$/BBL	Case 3** 1982\$/BBL
1980		36	38	41
1985		37	39	42
1990	30-40	38	44	48
1995	40-50	46	48	54
2000	50-60	54	52	59
2005	60-80	61	56	65
2010	80-100	66	59	70

*Base case results as of March 1983.

**The various cases are defined in the text.

17.2.4. Adjoint Sensitivity Studies

A paper ("The Application of Adjoint Sensitivity Theory to a Liquid Fuels Supply Model," R. G. Alsmiller, Jr., J. Barhen, J. E. Horwedel, J. L. Lucius, and J. D. Drischler) describing the methods used in the sensitivity methodology, as incorporated in the code system AUTO, and showing the results of applying this methodology to the Liquid Fuels Supply Model has been written and is undergoing internal review.

17.2.5. Task Performance

Responsibility for the various tasks performed during the April-June 1983 period was as follows:

Further Development of ORION: J. Barhen, J. R. Einstein, F. Morra, Jr.

Sensitivity of Marginal Cost to Three Geological Parameters:

J. R. Einstein, S. Smith

Calculations with the LFS Model: R. G. Alsmiller, Jr., J. E. Horwedel

Adjoint Sensitivity Studies: R. G. Alsmiller, Jr., J. Barhen,

J. E. Horwedel, J. L. Lucius, J. D. Drischler

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