ORNL/TM-5321

MASTER

Coal Technology Program Progress Report for February 1976

OAK RIDGE NATIONAL LABORATORY

OPERATED BY UNION CARBIDE CORPORATION FOR THE ENERGY RESEARCH AND DEVELOPMENT ADMINISTRATION

DISCLAIMER

Printed in the United States of America. Available from
the Energy Research and Development Administration,
Technical Information Center
P.O. Box 62, Oak Ridge, Tennessee 37830
Price: Printed Copy $4.00 ; Microfiche $2.25

ORNL/TM-5321

Contract No. W-7405-eng-26

COAL TECHNOLOGY PROGRAM

PROGRESS REPORT FOR FEBRUARY 1976

APRIL 1976

NOTICE This document contains information of a preliminary nature and was prepared primarily for internal use at the Oak Ridge National Laboratory. It is subject to revision or correction and therefore does not represent a final report.

OAK RIDGE NATIONAL LABORATORY
Oak Ridge, Tennessee 37830
operated by
UNION CARBIDE CORPORATION
for the
ENERGY RESEARCH AND DEVELOPMENT ADMINISTRATION

PREVIOUS REPORTS IN THIS SERIES

ORNL/TM-5044, Progress Report for August 1974
ORNL/TM-5045, Progress Report for September 1974
ORNL/TM-5046, Progress Report for October 1974
ORNL/TM-4787, Progress Report for November 1974
ORNL/TM-4796, Progress Report for December 1974
ORNL/TM-4850, Progress Report for January 1975
ORNL/TM-4873, Progress Report for February 1975
ORNL/TM-4892, Progress Report for March 1975
ORNL/TM-4946, Progress Report for April 1975
ORNL/TM-4966, Progress Report for May 1975
ORNL/TM-5010, Progress Report for June 1975
ORNL/TM-5037, Progress Report for July 1975
ORNL/TM-5092, Progress Report for August 1975
ORNL/TM-5124, Progress Report for September 1975
ORNL/TM-5186, Progress Report for October 1975
ORNL/TM-5214, Progress Report for November 1975
ORNL/TM-5246, Progress Report for December 1975
ORNL/TM-5301, Progress Report for January 1976

CONTENTS

COAL TECHNOLOGY PROGRAM PROGRESS REPORT FOR FEBRUARY 1976

ABSTRACT

This report — the nineteenth of a series — is a compendium of monthly progress reports for the ORNL research and development projects that are in support of the increased utilization of coal as a source of clean energy. The projects reported this month include those for hydrocarbonization research, solid-liquid separations, in situ gasification, analytical chemistry, engineering evaluations of nuclear process heat for coal conversion, coal-fueled MIUS, materials, and engineering evaluations of the Synthoil and Hydrocarbonization processes.

---

1. SUMMARY

J. P. Nichols

Highlights of our progress in February are summarized below:

° In hydrocarbonization research, final testing of the 20-atm bench-scale system is underway in preparation for experiments with hydrogen. Design modifications to raise the pressure from 20 to 80 atm for the bench-scale system are progressing satisfactorily.

° Results this month in supporting research and development in separations technology include laboratory-scale testing of a number of inexpensive pure compounds to improve the settling rate of solids in Solvent Refined Coal (SRC) unfiltered oil (UFO), bench-scale testing of the effect of the Tretolite additive on settling, and characterization tests on a new sample of UFO from the PAMCO-SRC process. The bench-scale settling of SRC-UFO mixed with Tretolite additive required longer periods of time at all concentrations to obtain a clarity equal to the laboratory-scale results.

° Laboratory results in experimental engineering support of an in situ gasification process include low-temperature pyrolyses at exceptionally low heating rates (0.3 C°/min). Highly pyrophoric chars were consistently produced by these experiments.

° In analytical chemistry, aqueous by-products from coal conversion technologies and oil shale retorting are analyzed directly to determine major organic components. Data are reported for an aqueous condensate from the Synthane gasification process, a scrubber liquor from the COED liquefaction process, and product water from simulated in situ retorting of oil shale.

° In the engineering evaluations of nuclear process heat for coal conversion, a report is being prepared discussing various aspects of the program. Also, a review of an ORNL report dealing with coal conversion and other GCR applications and a proposal from General Atomic for a bench-scale test program on thermochemical water splitting for hydrogen production has begun.

° In the coal-fueled MIUS program, preparations for procurement of tubing for the matrix in the fluidized-bed furnace and for fabrication of the furnace continued. Analyses of the AiResearch gas turbine and recuperator under coal-fueled MIUS operating conditions were near completion. Injected coal mixing rate tests in the cold flow model and performance tests of coal metering and feed systems continued.

° The assessment effort in the materials program on the Pressure Vessel and Piping Technology Program was accelerated. Initial specimens for evaluation on the inspection of wear and process-resistant coatings were received. Ultrasonic and x-ray fluorescence tests were completed on these specimens. The literature survey on formation of iron and nickel carbonyl is in progress. Experimental equipment is being assembled for the initial tests. A pressure let-down valve from PERC was examined after its removal from service. Severe erosion was identified.

° In the engineering evaluations work for Synthoil, process flow diagrams and heat and material balances were completed for most of the process units. Overall utilities requirements were calculated and the coal preparation flowsheets were finalized. For Hydrocarbonization, the flowsheet was revised to include additional coal data. Flowsheets were finalized for the acid gas separation and recycle, and the oil-solids separation.

2. HYDROCARBONIZATION RESEARCH

H. D. Cochran, Jr.

Summary

Yield data and carbon balances from earlier atmospheric-pressure experiments are reported. Further effort in experimental development has been curtailed. Successful shakedown testing of the 20-atm bench-scale system continued, and experiments with hydrogen will be performed early next month.

2.1 Review and Evaluation

(Completed)

2.2 Experimental Development

P. R. Westmoreland, J. B. Gibson, R. L. Andrews, and J. C. Rose

Ambient mock-ups

Occasional tests with the ambient mock-ups will be reported periodically, but no results are available from work during February. An effort is underway to reduce available data from the ambient mock-ups to a form useful for prediction and extrapolation, and results will be reported later. Analysis of solid recirculation performance data will be continued on a time-available basis.

High-temperature studies

No experiments were attempted in February, but the carbon balance for Run AHC-9 was completed, showing 11.2% liquid yield, and preliminary yields of char and liquid were determined for Run AHC-11. Liquid yield in Run AHC-9 was slightly less than in Run AHC-8, probably reflecting a lower hydrocarbonization temperature (1000°F vs 1050°F). The 9.1 wt % of carbon not recovered in Run AHC-9 was apparently char as suggested by an ash balance and by comparison to Run AHC-8. Liquid and solid analyses from Run AHC-11 permitted preliminary evaluation of the experiment. In AHC-11, smooth operation of recirculating fluidized-bed hydrocarbonization (to 1020°F) was achieved; however, approximately half the remaining char was found below the gas distributor plate, having sifted between the distributor plate and the reactor wall because of improper assembly. Coal in the plenum would not have reached 1020°F, so the high char yield probably resulted from incomplete hydrocarbonization.

No experiments are planned since this apparatus is now being used for residua carbonization. Yield data and a carbon balance for Run AHC-11 will be reported when completed.

2.3 Bench-Scale System

H. D. Cochran, Jr., and G. L. Yoder

Design and review

The final draft Safety Analysis Report for the bench-scale hydrocarbonization experiment has been issued as ORNL/CF-76/38. The experiment has been reviewed and approved for safety by representatives of ERDA-ORO following approvals from ORNL safety officers.

Design for modifications to the bench-scale system to raise its pressure capability from 20 to 80 atm is progressing satisfactorily.

The integral 80-atm reactor-preheater design will be prepared as an engineering drawing and should be available for inclusion in the March progress report. Bids for the hydrogen booster compressor should be received in April.

Fabrication and installation

There was no effort to report in this area during February. No effort is planned except maintenance as required.

Operation

Shakedown operation continued during February with successful feeding of -20 by +50 mesh coal to the reactor at 20 atm and 1200°F with nitrogen. Samples were taken for analysis. In the next test, approximately 5 lb of -50 by +150 mesh coal was fed to the reactor successfully with nitrogen. So, we are confident that our difficulties with coal feeding have been overcome. (The 1-ton batch of coal to be ground to -50 by +150 mesh at MERC has not yet been received.)

Several safety-related shakedown tests were required for safety approval and were completed successfully. The system was pressurized and leak checked at design temperature and at 1.15 times design pressure. The performances of the ventilation system and the back-up roof vent were checked first with smoke generators and then with helium and found to be acceptable. All instrument and controls components of the safety system and automatic shutdown system were tested and/or recalibrated individually, and the performance of the integrated system was tested successfully.

Introduction of hydrogen to the system will be initiated during the first week of March. The first 20-atm experiment with hydrogen will be performed using the -50 by +150 mesh coal expected from MERC.

2.4 Residua Carbonization

H. D. Cochran, Jr., and J. B. Gibson

System modifications to convert the batch-operated atmospheric hydrocarbonizer to a continuous feed residua carbonizer were completed during the previous month. The feed vessel, char receiver, and associated piping were installed and tested. A shakedown of the feeding system, reactor and char receiver was completed successfully using an inert ceramic material as the feed. The ceramic material, which will be used as a bed starter for the reactor during residua runs, had a particle size range of -45 to +140 mesh. A total of 8.4 lb of ceramic was fed to the reactor at a rate of 9.9 lb/hr. A fluidized-bed height of 21.4 in. was maintained in the reactor during the shakedown test.

The review and evaluation of the CSF carbonizer has been completed. The report is in the process of being distributed for comments.

Experimental runs with H-Coal vacuum tower bottoms will begin this month.

3. SUPPORTING RESEARCH AND DEVELOPMENT IN SEPARATIONS TECHNOLOGY

B. R. Rodgers

Summary

Results this month include laboratory-scale testing of a number of inexpensive pure compounds to improve the settling rate of solids in Solvent Refined Coal (SRC) unfiltered oil (UFO), bench-scale testing of the effect of the Tretolite additive on settling, and characterization tests on a new sample of UFO from the PAMCO-SRC process. Some inexpensive and readily available pure compounds were found which significantly improved settling rates in the laboratory-scale apparatus.

The bench-scale settling of SRC-UFO mixed with Tretolite additive required longer periods of time at all concentrations to obtain a clarity equal to the laboratory-scale results. A number of changes in operating procedures were tried to determine the differences, but none provided a satisfactory explanation.

Data supporting the results discussed this month will be included in the quarterly report for January-March.

3.1 Additive Agglomeration Studies: Laboratory Scale

S. Katz and B. R. Rodgers

Tests of additives to improve settling continued using the system previously described.[1] It was concluded that Tretolite additive significantly improved particle settling; optimum temperature appears the same as that previously found for simple thermal agglomeration and settling, 300 to 350°C, with the best results at the highest concentration tested (4000 ppm). Scouting tests with pure compounds suggest that a number of inexpensive materials may improve settling. The manner and conditions for dispersal of solid and liquid additives which are not readily soluble or miscible with the UFO appear important.

Agglomeration, which has been established by a large number of observations as an important mechanism leading to better settling, may not be the exclusive mechanism. Particle enlargement during the process as a result of recrystallization and chemical change is indicated as likely. Different additives appear to promote the settling through different overall mechanisms.

Additives of useful effectiveness showed a dependence upon concentration up to a given value, above which very little improvement occurred. For most additives, settling rates increased with temperature.

3.2 Additive Agglomeration Studies: Bench Scale

B. R. Rodgers, S. Katz, and D. A. McWhirter

Bench-scale results continue to indicate that longer settling times than previously indicated may be required to obtain a sufficient quantity of clarified SRC product. Eleven runs were made this month using a Tretolite additive at concentrations from 500 to 2500 ppm and 530°F. In most cases, 90 to 150 min were required to obtain 30 to 50% clarified product.

The standard operating procedure for the above runs consisted of injecting the additive into a stirred autoclave, bringing the autoclave to temperature, and transferring the mixture to the settler, which was maintained at the same temperature. This procedure is closer to field conditions than the laboratory-scale experiments, where the additive is mixed in a sealed tube and inserted into a heated silicone bath. However, the latter experiments obtained clarified product in shorter times for a given set of conditions, as reported previously.[1,2] A number of changes in bench-scale operation procedures were tried to determine the cause of this disparity of results:

(1) Heating the mixtures in the settler without stirring, instead of using the stirred autoclave.

(2) Mixing the additive in the feed pot, instead of injecting directly into the stirred autoclave.

The settling rates were similar for all procedures.

3.3 Characterization Studies

B. R. Rodgers and D. A. McWhirter

Samples of filtered and unfiltered oil from the PAMCO-SRC plant were received and analyzed. The material had a higher oxygen (6.7 wt %), nitrogen (1.12 wt %), ash (4.0 wt %), and cresol solids content (6.0 wt %) than the Wilsonville SRC material (3.3, 1.01, 3.2, and 4.0 wt %, respectively). Other data on the PAMCO material will be reported in the next quarterly report.

3.4 References for Sect. 3

1. J. P. Nichols (Program Director), Coal Technology Program Quarterly Progress Report for the Period Ending September 30, 1975, ORNL-5093 (December 1975).

2. J. P. Nichols (Program Director), Coal Technology Program Quarterly Progress Report for the Period Ending December 31, 1975, ORNL-5120 (in publication).

4. EXPERIMENTAL ENGINEERING SUPPORT OF AN IN SITU GASIFICATION PROCESS

R. C. Forrester, III

Summary

Laboratory results for the past month include low-temperature pyrolyses at exceptionally low heating rates (0.3 C°/min). Highly pyrophoric chars were consistently produced by these experiments, the results of which were presented to Dr. P. R. Wieber, ERDA program coordinator for Underground Coal Gasification, during his visit on the 24th.

4.1 Large-Block Pyrolysis Studies

R. C. Forrester, III, P. R. Westmoreland, F. H. Wilson, and G. D. Owen

Experiments conducted during February (and the latter part of January) have included pyrolyses at conditions shown in Table 4.1.

Table 4.1. Block pyrolysis: Recent test conditions

Sample Description	Heating rate (C°/min)	Maximum Temperature (°C)
1. Wyodak (Roland seam)	3	900
2. Wyodak (Roland seam)	3	1000
3. Wyodak (Roland seam)	3	500
4. Wyodak (Roland seam)	0.3	500
5. LERC test site (Hanna No. 1 seam)	3	500

The most interesting aspect of this work is that all of the low-temperature tests produced a pyrophoric char. As described in ORNL/TM-5291, the char produced by one experiment early in the program exhibited marked pyrophoricity, a phenomenon not previously observed by other researchers. Several subsequent tests were unable to reproduce this behavior, and the observed pyrophoricity was thought to have been anomalous. These latest experiments, however, have consistently produced highly pyrophoric chars, and preliminary indications suggest that the maximum pyrolysis temperature plays an important role in this phenomenon. (The pyrophoric materials are produced only at the lower temperatures.)

A brief survey of the literature describing pyrophoricity of various substances (coal, lignites, heavy-metal powders, etc.) was unable to uncover a reference to pyrophoric chars, but did provide many detailed theories concerned with the mechanism of self-ignition and ways to prevent this behavior. A bibliography containing more than 300 literature references to pyrophoricity and related problems has been compiled.

As indicated by Table 4.1, the programmable furnace system has recently been altered to provide PID control of heating rate between the limits of 0.1 and 10 Centigrade degrees per minute. (Heating rates are referenced to the surface of the coal block being pyrolyzed.) The effects of this order-of-magnitude reduction in heating rate will be examined in the course of the next few months' experiments.

4.2 ERDA's UCG Program

R. C. Forrester, III

Dr. Paul R. Wieber, Chief of In Situ Conversions for ERDA, has activated five working groups within ERDA's Underground Coal Gasification program whose purpose is to promote and facilitate rapid exchange of information and technical criticism among the various participants. These groups, with the names of their corresponding chairmen, are presented in Table 4.2.

Table 4.2. Technical working groups within the ERDA Underground Coal Gasification Program

Working group	Chairman (Affiliation)
Field Operations	Dr. C. F. Brandenburg (LERC)
Geology and Site Preparation	Dr. C. F. Brandenburg (LERC)
Laboratory Research	Dr. L. Z. Shuck (MERC)
Instrumentation	Dr. D. A. Northrop (Sandia)
Modeling	Dr. R. B. Rozsa (LLL)

Dr. Wieber has also expressed interest in creating a sixth group, which would explore Environmental Data Needs.

Although a formal presentation is not required, an ORNL observer is included at meetings of the Modeling group in order to keep abreast of computational data needs. The last meeting of that group was held at LLL on September 25, 1975. Code developments at LERC, MERC, and LLL were presented, as well as some comments about Russian models and an NSF-funded program at the University of Texas (Austin). The next meeting of this group is planned for the last week of April, and recent communications with LLL staff members confirm plans to present the results of kinetic code calculations based upon data generated by ORNL pyrolysis studies.

5. ANALYTICAL CHEMISTRY

W. D. Shults

Summary

Aqueous by-products from coal conversion technologies and oil shale retorting are analyzed directly to determine major organic components. Data are reported for an aqueous condensate from the Synthane gasification process, a scrubber liquor from the COED liquefaction process, and product water from simulated in situ retorting of oil shale.

5.1 Analysis of Aqueous By-Products from Coal Conversion Technologies and Oil Shale Retorting

B. R. Clark, C. H. Ho, and M. R. Guerin

Condensate water from the Synthane coal gasification process (Pittsburgh Energy Research Center) and scrubber water from the first stage in the COED process (FMC Corporation) have been analyzed directly for some of the major organic components. Whole samples were injected directly into a gas chromatograph equipped with a packed Tenax column as described in Sect. 5.2 concerning oil shale retorting by-product water. It is interesting to compare these results with the oil shale by-product water. Acetic acid concentrations are nearly identical, but other acids are much lower or not detectable. Phenol and cresols are present in large quantities at levels in agreement with previously reported values. These data are summarized in Table 5.1.

5.2 Analysis of the Aqueous By-Product from Oil Shale Retorting

B. R. Clark, C. H. Ho, and M. R. Guerin

Whole water samples are injected directly into a gas chromatograph equipped with a packed Tenax column. Polar compounds are separated with good resolution under the temperature programming conditions employed. Chemical identifications are made by co-chromatographic comparisons with pure compounds, and quantification is achieved using standard solutions. The by-product water from oil shale retorting contains carboxylic acids in a series ranging from acetic to decanoic acid. Various amides, cresols, and phenols are present in trace amounts. These are listed in order of abundance (ppm): acetic acid (605), heptanoic acid (263), hexanoic acid (252), octanoic acid (250), acetamide (232), valeric acid (210), propionic acid (208), butyric acid (132), nonanoic acid (105), propionamide (48), decanoic acid (45), o-cresol (27), m- and p-cresol (14), phenol (13), and butyramide (8).

Table 5.1. Major organic compounds in coal conversion by-product water

	Synthane condensate water (untreated) (ppm)	COED scrubber water (ppm)
Phenol	2070	2060
m+p-cresol	1830	1830
o-cresol	670	650
Acetic acid	619	602
2,5-dimethylphenol	248	217
3,5-dimethylphenol	225	240
3,4-dimethylphenol	94	873
2,6-dimethylphenol	44	30
o-ethylphenol	33	34
2,3-dimethylphenol	32	26
Proprionic acid	63	94
Butyric acid	18	40
Valeric acid	10	30
Hexanoic acid	16	32
α-naphthol	10	
β-naphthol	32	

5.3 Analytical Services

W. R. Laing and L. J. Brady

There was more than a threefold increase in the number of samples submitted for analyses this month as compared to the previous month. Of the total of 576 samples submitted, 527 were derived from solids-liquid separation tests.

Twenty-five coal samples were tested for heat value (Btu/lb), total sulfur, carbon, and hydrogen.

The gas chromatograph was used to determine nitrogen, carbon monoxide, and methane on two sets of samples in addition to the determination of the simulated boiling range of five liquid samples. Proximate and ultimate analyses were completed on one set of coal and char samples from a hydrocarbonization run.

A SPF-125S spectrophotofluorometer has been received and is being checked. This instrument will be used as an aid in the characterization of some of the components of coal-derived liquid samples.

6. ENGINEERING EVALUATIONS OF NUCLEAR PROCESS HEAT FOR COAL CONVERSION

W. R. Gambill

The various sections of the report to Fossil Energy titled "A Critical Evaluation of the Application of Gas-Cooled Reactors to Coal Conversion" were assembled, reviewed, and edited. This report, which will be issued in March after retyping, addresses the following topics:

- discussion of rationale for developing nuclear process heat for coal conversion,
- application of external hydrogen from a thermochemical water splitting unit to fuels synthesis,
- evaluation of a coal liquefaction process using either a nuclear or a fossil heat source for reforming,
- a conceptual design of a coal-steam gasification process heated by a gas-cooled reactor,
- a review of candidate materials for process heat exchangers (for reformers, steam gasifiers, and the Westinghouse thermochemical H_2 process).

The writer reviewed in detail a more comprehensive ORNL report to ERDA which includes the coal conversion evaluations and also treats other potential GCR applications, including petroleum refining, steelmaking, oil shale and tar sands processing, and peaking power generation.

A review was begun of General Atomic's proposal to ERDA for a bench-scale test program on thermochemical water splitting for hydrogen production.

It appears that Fossil Energy funding for further GCR/Coal Conversion Evaluations has been terminated and that any additional work will be conducted under the NRA program.

7. COAL-FUELED MIUS

A. P. Fraas and W. R. Mixon

This project for analysis, design, and demonstration of a concept utilizing a fluidized-bed coal combustion system as a heat source for a gas turbine generator suitable for applications in Modular Integrated Utility Systems (MIUS) is carried out under the ORNL-HUD-MIUS Program within the Energy Division. Work is supported by the U.S. Department of Housing and Urban Development under HUD Interagency Agreement No. 1AA-H-40-72 and by the Energy Research and Development Administration, Office of Fossil Energy (formerly Office of Coal Research, Department of the Interior), under ERDA contract No. E(49-18)-1742. The project consists of four phases: I — Conceptual Preliminary Evaluation; II — Conceptual Design; III — Detailed Design and Construction; and IV — Shakedown, Performance, and Endurance Tests.

Summary

Preparations for procurement of tubing for the matrix in the fluidized-bed furnace and for fabrication of the furnace continued. Analyses of the AiResearch gas turbine and recuperator under coal-fueled MIUS operating conditions were near completion. Injected coal mixing rate tests in the cold flow model and performance tests of coal metering and feed systems continued.

Furnace Procurement

Bids for the longest-term procurement item, the Incoloy 800 tubing for the matrix within the furnace, were received, a vendor was selected, and contractural arrangements were nearly completed during this period.

Negotiations with potential vendors for furnace fabrication continued. The preliminary furnace layout and fabrication problems of the fluidized-bed furnace were discussed with Foster-Wheeler personnel during a visit to their plant. They showed definite interest in bidding on the job and prefer to prepare the detailed shop drawings.

Preparation of layout drawings and specifications for a furnace fabrication bid package was in progress.

Turbine-Generator Unit

A meeting was held at AiResearch to review their progress on the evaluation of ways to adapt the Model 831-200 gas turbine to the MIUS application. Disassembled engines selected for MIUS use were inspected; results of the performance, mechanical, and control studies were presented; and the open- and closed-cycle test plans were discussed. Results were also presented of the performance analysis of AiResearch recuperators over a range of MIUS parameters, and materials of construction were recommended. The AiResearch study was near completion, and a published report of complete results is expected in March 1976.

Cold Flow Tests of a Fluidized Bed

A second test on the mixing rate of coal injected through feed ports into the 4-ft-square cold flow model of the fluidized bed was completed, and samples taken from the bed are being analyzed. The fluidizing velocity for the test was a little higher than the velocity chosen for minimum flow conditions for the operating system. Initial results indicated that the mixing rate was good in both the vertical and horizontal directions, a much more favorable situation than that found at the flow rate in the first test, which was a little below the full-scale design point for minimum flow.

Coal Metering and Feed System

Tests of the flow splitter type of system for dividing the coal feed stream into four equal parts indicate that each of the four streams can be kept within plus or minus 5% of the mean coal flow rate over the entire operating range, and that the results are repeatable from day to day and week to week. Thus, this system appears to be satisfactory for the full-scale MIUS system.

The vibrator-eductor type of coal feed system was tested using four eductors with adjustable stainless steel outlets. The vibratory mass was optimized to achieve a reproducible amplitude capable of delivering about 520 lb/hr of coal at a maximum setting of the voltage controller. With a fixed air flow through the feed system, coal delivery rate could then be varied by varying the vibratory amplitude. The system could be adjusted to give equal coal flow through each of the four feed tubes at a given amplitude setting, but equal flow in the four tubes was not maintained at other amplitude settings. The total feed rate is fairly predictable, but additional development will be necessary before equal feed rates can be obtained from all four eductors for all settings of vibratory amplitude.

8. MATERIALS

W. R. Martin and D. A. Canonico

The materials engineering and supporting technology reported herein are in support of activities directed by Materials and Power Generation, Division of Fossil Energy Research. Other related work not funded directly by this division of ERDA/FE is included also.

Summary

The assessment effort on the Pressure Vessel and Piping Technology Program was accelerated in February. Visits to Fluor, R. M. Parsons, and Bechtel were productive. Interim reports are being prepared, and additional visits to additional A-E's are being arranged.

Initial specimens for evaluation on the inspection of wear- and process-resistant coatings were received. Ultrasonic and x-ray fluorescence tests were completed on these specimens.

The literature survey on formation of iron and nickel carbonyl is in progress. Experimental equipment is being assembled for the initial tests.

A pressure let-down valve from PERC was examined after its removal from service. Severe erosion was identified.

8.1 Pressure Vessel and Piping Technology Assessment

D. A. Canonico, R. H. Cooper, R. K. Nanstad, and G. C. Robinson

A review of the piping and pressure vessel needs for coal conversion systems is in progress. The program will identify those areas where additional material property data needs are required in order to assure that the pressure boundary components in conversion systems can be designed, fabricated, and operated in a safe and reliable manner.

During February, work on this project was initiated. An outline of the report was prepared and responsibility for the various chapters was assigned. Initial work has included a review of the various ASME Code approved steels for pressure vessel application. This review identified the steels, their plate thickness limitations (if they exist), chemical analysis and minimum property requirements.

Concurrent with this effort, three major architectural engineering (AE) firms have been visited by members of the project staff. (Trip reports will be forwarded to the Materials and Power Generation Division of Fossil Energy - ERDA.) The aim of these visits was to obtain information on design philosophy and plant designs employed by the various AE's. We were particularly interested in the materials currently being considered for pressure boundary components.

The AE's visited were Fluor, Ralph M. Parsons, and Bechtel. We also visited Atomics International and discussed their molten-salt gasification process. They have designed and are planning to build a PDU in the near future.

Discussions with Fluor involved two major projects: (1) the coal liquefaction pilot plant at Cresap, West Virginia, and (2) the WESCO commercial gasification project. The Cresap facility is a pre-existing facility which Fluor is redesigning and rebuilding. They have had to remove most of the piping and many other components to upgrade the facility and plan to start up before Labor Day of this year. The WESCO project is a multi-train plant using the Lurgi gasification process. It will be commercial size, 20,000 tons/day coal input, but is currently pending financial arrangements.

The Bechtel Company discussed their design of a HYGAS gasifier for commercial operation. Design procedures and materials were discussed. Bechtel indicated that the material property needs for commercialization of their coal conversion systems are minimal.

The Ralph M. Parsons Company has two basic ERDA projects: (1) preliminary design services for various coal conversion processes, mainly liquefaction, and (2) technical evaluation services to help monitor liquefaction processes. They have 50-75 people working on coal programs and were very helpful with regard to specific information regarding their work.

8.2 Inspection Techniques for Wear- and Process-Resistant Coatings

R. W. McClung and G. W. Scott

This is the first report for this section. This work was authorized to commence in January 1976. Our first objective was to obtain specimens. We investigated three sources: (1) previously used or excess specimens from Argonne National Laboratory; new specimens, manufactured by (2) UCC-ND Y-12 Plant, or (3) ORNL Welding and Brazing Laboratory. Based on economics and capability, ORNL seems to be the best current choice, and preparations are underway to manufacture specimens here.

We received one specimen, No. C5, from Argonne. Preliminary ultrasonic and x-ray fluorescence spectrographic tests were performed on this specimen. The ultrasonic results were inconclusive. The spectrographic results indicate some unexpected phenomena which require further investigation.

Preliminary literature searches have produced some information for scoping the experimental efforts.

Review and Evaluation

Communications with ERDA (Fossil Energy Research Division) and management at Argonne National Laboratory to open communication channels at the working level occupied the first few weeks of project time. On February 19, we received ANL Specimen C5 (95% Co mix, 5% TiC, on Incoloy-800 substrate). On February 20, we received detailed information (via telephone) from Dr. R. Swaroop (of ANL) on the preparation of his specimen.

While setting up communications with ANL, we investigated the UCC-ND Y-12 Plant and the ORNL Welding and Brazing Laboratory as potential sources of coating specimens. The ORNL facility has a rectilinear motion capability suitable for the work anticipated. We are setting up the equipment and procuring specimen materials now.

Scientific and engineering literature was searched briefly for information on NDT of ceramic and cermet materials, mechanical and electrical properties of pure-phase coating materials, and high-temperature chemistry of ceramics and cermets. The chemistry data indicate that significant changes in the coating composition can be expected after prolonged use. Therefore, it is likely that multiple NDT tests will be required to evaluate aged coatings: one (or more) to characterize the material itself, e.g., conductivity; and others to determine desired condition of the material, e.g., cracks, nonbond, or other flaws. One case of coating composition change may have been found experimentally (see Section 8.2.2).

Penetrating Radiation Testing

Preliminary studies were performed on ANL specimen C5 with a Norelco Portaspec (portable x-ray fluorescence spectrometer). This instrument illuminates the specimen with 40-keV x-rays and measures the relative intensities of characteristic emission lines for elements above Z-23 (vanadium). The coated and metal-substrate sides of the specimen were analyzed independently. The substrate yielded lines for Fe, Cr, and Ni with intensities approximately equal to their nominal proportions in the alloy. The coating side produced a strong Co line and reduced Fe, Cr, Ni, and Mn lines, as expected. However, the Fe line now had the lowest intensity and was no longer proportional to its concentration in the alloy. This will be further studied; e.g., one possible explanation of the line structure is that Ni and Cr may selectively migrate from the substrate into the coating during aging.

Ultrasonic Testing

Estimates of acoustic velocities in pure-phase coating materials, computed from elastic moduli and densities, indicate that the velocities will be high enough to make thickness gaging by conventional pulse-echo technique very difficult.

The ANL-C5 specimen was examined for reflection and transmission properties in a simple through-transmission goniometer and in a Schlieren optical set-up. Coarse measurements of critical reflection angles and angles for generation of Lamb waves in the plate substantially agreed between the two devices. There appeared to be slight differences in the response, depending on whether the sound beam entered from the coating side or substrate side. Further work will determine whether the difference was due to the specimen or to uncertainties in the measurement systems.

8.3 Iron and Nickel Carbonyl Formation and Prevention

J. Brynestad and J. H. DeVan

We have completed our collection of literature pertinent to iron and nickel carbonyl formation and prevention. This information is being evaluated and organized into a report. Three autoclaves, 5 in. ID x 24 in. (net) long, for pressures up to 3000 psi and temperatures up to 650°F have been ordered. Equipment has also been assembled for the preliminary evaluation of chemical methods for the analysis of small amounts of iron and nickel carbonyl.

8.4 Failure Analysis of Materials and Components

D. A. Canonico and D. P. Edmonds

This project is devoted to the examination and evaluation of components that have been employed in liquefaction processes. Currently, we are examining a pressure let down valve trim set from the 1/2-ton-per-day Synthoil PDU at the Pittsburgh Energy Research Center. The primary purpose of the valve is to regulate the pressure differential in the operating unit. The average operating life of these trim sets is about 1000 hr. The valve delivered to ORNL was removed from service after operating at a pressure differential of 4000 psig for 915 hr at 125°C. The total weight of liquid, which contained 5-6% residual solids, let down through the valve was 22,875 pounds.

The trim set is made up of a valve seat and plug, both of which were cast (and machine ground) from Kennametal grade 701 (a proprietary alloy consisting of tungsten carbide in a chromium-containing cobalt-rich matrix). The plug stem and valve body are fabricated from type 316 stainless steel.

The valve seat and plug have both undergone severe erosion. Erosion of the trim set (stem, valve seat, and plug) is localized and is the reason for the short life of these let-down valves. The valve is a standard Masoneilan Wee-Willie Control Valve with the Kennametal grade 701 modifications. The plug and seat are brazed into position. Braze metal cracking is evident in the stem-to-plug braze. Measurements have been made of the trim set, and we found some ovality of the valve plug toward its tip and also found that a concentricity variation of 0.0033 cm (0.0013 in.) exists between the plug and the stem. We are investigating the possibility that the cracked braze could have caused the concentricity variation and that this lack of concentricity is responsible for the preferential erosion.

We are also investigating the material properties of the trim set. Scanning electron microscopy (SEM) studies are being conducted on the eroded surfaces. Our SEM observations to date do not indicate any difference between the severely eroded surfaces and the more uniformly worn surfaces.

8.5 Prestressed-Concrete Pressure Vessel Studies

W. L. Greenstreet

Nothing to report.

8.6 Other Related Work

R. H. Cooper, Jr. and J. H. DeVan

Fluidized-Bed Material Support Activities

Contracts for the purchase of Incoloy 800 tubing were reviewed.

GCR/Coal Conversion

We have completed a critical assessment of the materials problems associated with the coupling of an HTGR nuclear heat source to endothermic chemical processes of interest to fossil energy development. The study examined the materials requirements for high-temperature heat exchangers relating to three different processes: steam/coal gasification, steam/methane reforming, and thermochemical H_2 production. Candidate materials for these processes were listed, and their chemical and mechanical properties were rated against the process requirements. This review will appear in a report to Fossil Energy entitled, "A Critical Evaluation of the Application of Gas-Cooled Reactors to Coal Conversion."

9. ENGINEERING EVALUATIONS OF THE SYNTHOIL AND HYDROCARBONIZATION PROCESSES

J. M. Holmes, R. Salmon, and E. G. St. Clair

Summary

Synthoil. Process flow diagrams and heat and material balances were completed for all process units except the Claus sulfur plant, the Stretford unit, the ammonia plant, and the oxygen plant. The overall utilities requirements were calculated. The coal preparation flowsheet was finalized.

Hydrocarbonization. The flowsheet was revised to include additional raw coal needed for the fluid-bed combustion system. A contract was signed with Fluid Bed Combustion Company for the design and cost estimate of the fluid-bed combustor. Flowsheets were finalized for Unit 13, acid gas separation and recycle, and Unit 19, oil-solids separation.

9.1 Synthoil Process

R. Salmon, E. G. St. Clair, M. S. Edwards,
W. C. Ulrich, and D. A. Dyslin

Process flow diagrams and heat and material balances were completed for all process units with the exception of the Claus sulfur plant, the Stretford unit, the ammonia plant, and the oxygen plant. These are all proprietary units for which simplified flow diagrams will be presented. Some minor changes remain to be made in the gasification unit due to revisions in the low-temperature carbonizer unit.

The overall utilities requirements were calculated. A utilities system balance was reached for steam, water, electricity, and fuel gas. Utilities systems flow diagrams are now being prepared.

Work was started on cost collection for a preliminary cost estimate.

Other areas of the Synthoil flowsheet progressed as follows:

(1) Coal handling and preparation: The Synthoil coal preparation flowsheet was finalized; the pulverizers are located separately from those for feeding the gasifiers. Seven pulverizers, each having a capacity of 230 tons/hr, will feed the slurry system. Each pulverizer will be driven by a 2000-HP steam turbine, and the drying air for each pulverizer will be supplied by two 750-HP fans driven by steam turbines. The pulverized coal will be mixed with recycle oil directly beneath the cyclone separators and pumped at low pressure to a holding tank. The slurry will be agitated in the holding tank to maintain homogeneity.

(2) Gasification: Contacts were made and meetings were held with vendor representatives to obtain cost information on various equipment items (e.g., pumps, compressors, and heat exchangers) for the gasification unit.

(3) Low-temperature carbonization: The revised low-temperature carbonizer unit material balance was incorporated into the Synthoil flowsheet overall material balance. Efforts to obtain equipment cost information for this unit were initiated.

9.2 Hydrocarbonization Process

J. M. Holmes, D. S. Joy, G. R. Peterson, M. S. Edwards, C. B. Smith, and D. A. Dyslin

The design and cost estimation of a hydrocarbonization facility for the production of clean fuel equivalent to 100,000 bbl/day of fuel oil continued. The various units of the plant progressed as follows:

(1) Coal beneficiation: The flowsheet was revised to include additional raw coal needed for the fluid-bed combustion system. This coal will not have to be beneficiated but must be properly sized for consumption in the fluid-bed combustor.

(2) Hydrocarbonization: Cost estimation of the vessels for the hydrocarbonization unit continued. Consideration of construction materials for the Stage II carbonizer and the char burner led to a decision to use a 1/4-in.-thick inlay of Monel instead of the Incoloy 800 inlay originally proposed. Computer codes were written for the design of the carbonizer cyclones based on the American Petroleum Institute Cyclone Separator procedure (API Publication 931, Chapter 11). A computer code was prepared for estimating the purchased cost of the carbonizer vessels.

The hydrocarbonization char handling system is being studied. The char must be removed from a vessel at 125 psia and 600°F, then mixed with water and stored in a holding tank before being pumped through a slurry pipeline to a power plant. Some information has been obtained from vendors, but more information is needed.

(3) Fluid-bed combustor: Estimation of the high-pressure steam requirements for the plant showed that the raw coal requirements for the fluid-bed combustor would have to be increased. The increase amounted to 3100 tons/day, which is about 8% of the total coal feed to the plant. High-pressure steam (600 psia, 825°F) produced by the fluid-bed combustor is currently specified at 4.3 million lb/hr. A contract was signed with Fluid Bed Combustion Company for the design and cost estimate of the fluid-bed combustor. This work will be completed in about three months.

(4) Acid gas removal: The hydrocarbonizer make-gas treating plant (Unit 14) was sized, and equipment lists and utilities requirements were prepared. The methanator reactors in Units 14 and 21 were sized by Girdler Chemical, Inc. Catalyst volume and cost, exit temperatures, and pressure drops were also provided.

(5) Ammonia recovery: Chevron Research provided conceptual cost, design, and utilities requirements for two modes of sour water treating: one recovers anhydrous ammonia, and the other aqueous ammonia (25%). Investment cost was estimated at $7.60 million for the anhydrous ammonia process, and $5.65 million for the aqueous ammonia process.

(6) Flowsheets: Finalized flowsheets were prepared with equipment callouts and material balances for Unit 13, acid gas separation and recycle, and Unit 19, oil-solids separation.

THIS PAGE

WAS INTENTIONALLY

LEFT BLANK

INTERNAL DISTRIBUTION ORNL/TM-5321

1. R. G. Affel
2. T. D. Anderson
3. S. I. Auerbach
4. J. K. Baird
5. R. E. Barker
6. H. C. Beeson
7. M. Bender
8. B. G. Blaylock
9. N. E. Bolton
10. R. E. Brooksbank
11. W. A. Bush
12. D. A. Canonico
13. J. A. Carter
14. H. D. Cochran, Jr.
15. E. Copenhaver
16. L. T. Corbin
17. D. A. Creasia
18. W. K. Crowley
19. O. L. Culberson
20. F. L. Culler
21. J. E. Cunningham
22. V. A. DeCarlo
23. D. G. Doherty
24. A. S. Dworkin
25. M. S. Edwards
26. F. J. Endelman
27. G. G. Fee
28. D. E. Ferguson
29. L. M. Ferris
30. R. C. Forrester III
31. A. P. Fraas
32. W. Fulkerson
33. W. R. Gambill
34. D. A. Gardiner
35. C. W. Gehrs
36. J. B. Gibson
37. W. L. Greenstreet
38. M. R. Guerin
39. C. W. Hancher
40. L. A. Harris
41. S. E. Herbes
42. S. G. Hildebrand
43. R. M. Hill
44. R. S. Holcomb
45. J. M. Holmes
46. R. B. Honea
47. J. K. Huffstetler
48. C. L. Hunt
49. F. J. Hurst
50. G. R. Jasny, Y-12
51. W. F. Johnson
52. L. L. Johnston
53. R. L. Jolley
54. J. E. Jones
55. D. S. Joy
56. S. Katz
57. O. L. Keller
58. R. F. Kimball
59. W. R. Laing
60. R. S. Livingston
61. A. P. Malinauskas
62. G. B. Marrow, Y-12
63. W. R. Martin
64. W. J. McDowell
65. C. J. McHargue
66. J. R. McWherter
67-69. W. R. Mixon
70. G. E. Moore
71. J. E. Mrochek
72. P. Nettesheim
73-81. J. P. Nichols
82. L. C. Oakes
83. G. R. Peterson
84-85. T. W. Pickel
86. W. W. Pitt
87. H. Postma
88. J. J. Prislinger
89. W. T. Rainey
90. D. E. Reichle
91. C. R. Richmond
92. B. R. Rodgers
93-94. M. W. Rosenthal
95. T. H. Row
96. W. L. Russell
97. Royes Salmon
98. R. W. Schede, Y-12
99. C. D. Scott
100. A. J. Shor
101. D. S. Shriner
102. W. D. Shults
103. C. B. Smith
104. G. P. Smith
105. I. Spiewak
106. R. L. Spore
107. E. G. St. Clair
108. J. B. Storer
109. R. A. Strehlow
110. O. K. Tallent

111. A. J. Thompson
112. D. B. Trauger
113. W. C. Ulrich
114. P. R. Vanstrum, Y-12
115. J. S. Watson
116. J. R. Weir
117. P. R. Westmoreland
118. M. E. Whatley
119. J. C. White
120. M. K. Wilkinson
121. L. V. Wilson
122. R. G. Wymer
123. G. L. Yoder
124. C. S. Yust
125. Patent Office
126-130. Lab. Records
131. Lab. Records-RC
132-134. Central Research Library
135. Document Reference Section

EXTERNAL DISTRIBUTION

ERDA, Oak Ridge Operations

136. Research and Technical Support Division

ERDA, Washington

137. D. Ballantine, DBER
138. J. D. Batchelor, FE (Fossil Energy)
139. T. Beresovski, DRRD
140. E. L. Clark, FE
141. N. P. Cochran, FE
142. C. W. Edington, DBER
143. R. Franklin, DBER
144. S. W. Gouse, FE
145. W. S. Harmon, FE
146. G. E. Larson, FE
147. T. K. Lau, FE
148. R. W. A. LeGassie, AA/PA
149. J. L. Liverman, AA/ES
150. C. Miller, FE
151. G. A. Mills, FE
152. W. E. Mott, DBER
153. M. B. Neuworth, FE
154. E. S. Pierce, DPR
155. H. E. Podall, FE
156. J. L. Powell, FE
157. Robert Rabin, DBER
158. E. Schmetz, FE
159. G. Stapleton, DBER
160. R. E. Vener, FE
161. H. Wasson, DBER
162. P. C. White, AA/FE
163. R. L. Zahradnik

Department of Housing and Urban Development, 451 7th Street, S.W., Washington, D.C. 20410

164. G. S. Leighton
165. J. H. Rothenberg

National Science Foundation, 1800 G Street, N.W., Washington, D.C. 20550

166. R. S. Goor
167. Charles Johnson

Resource Planning Associates, Inc., 44 Brattle St., Cambridge, Mass. 02138

168. Robert Rea

U.S. Environmental Protection Agency, ETRL, 1055 Laidlaw, Cincinnati, Ohio 45237

169. William E. Pepelko

U.S. Environmental Protection Agency, Research Triangle Park, N.C. 27711

170. Charles B. Sedman

U.S. Steel Corp. Applied Research Laboratory, 125 Jamison Lane, Monroeville, Pa. 15146

171. N. S. Boodman, Section Supervisor

University of Kentucky, Institute for Mining and Materials Research, 213 Bradley Hall, Lexington, Kentucky 40506

172. Theresa Wiley, Institute Librarian
173. O. J. Haun
174. J. K. Shou

175-186. ERDA Pittsburgh Energy Research Center, U.S. Energy Research and Development Administration, Attention: Director for J. P. Barreca, 4800 Forbes Ave., Pittsburgh, Pa. 15213

187-192. The Director, Morgantown Energy Research Center, P.O. Box 800, Morgantown, West Virginia 26506

193. A. K. Ingberman, 1 Penn Plaza, Union Carbide Corporation, New York, New York 10001

194. D. E. Eissenberg, Union Carbide Corp., 270 Park Ave., New York, New York 10017

195. R. E. Davis, Kerr-McGee Technical Center, P.O. Box 25861, Oklahoma City, Oklahoma 73125

196. H. Beuther, Gulf Research and Development Company, P.O. Drawer 2038, Pittsburgh, Pa. 15230

197. Robert Hangebrauck, National Environmental Research Center, Research Triangle Park, North Carolina 27711

198. P. H. Given, Pennsylvania State University, College of Earth and Mineral Sciences, University Park, Pa. 16802

199. John W. Larson, Department of Chemistry, University of Tennessee, Knoxville, Tenn. 37916

200. Wendall H. Wiser, University of Utah, Department of Mineral Engineering, Salt Lake City, Utah 84112

201. William A. Peters, Massachusetts Institute of Technology, Department of Chemical Engineering, Cambridge, Mass. 02139

202. Donald Hanson, University of California, Department of Chemical Engineering, Berkeley, California 94720

203. S. G. Wellborn, Manager, Feedstocks Development, E. I. du Pont de Nemours & Company, Inc., Wilmington, Delaware 19898

204. Tetra Tech, Inc., 1911 N. Ft. Myer Drive, Suite 601, Arlington, Virginia 22209, Attention: Walter McGough, Jr.

205-206. Jack Gillespie, UCCND, P.O. Box 1410, Paducah, Ky. 42001

207. Jerry D. Kennedy, Sandia Laboratories, P.O. Box 5800, Albuquerque, New Mexico 87115

208. Prof. S. K. Chakrabartty, University of Alberta, Edmonton, Alberta, Canada

209-235. Technical Information Center, ERDA-ORO.