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Fossil Energy Program

**FOSSIL ENERGY PROGRAM SEMIANNUAL PROGRESS REPORT
FOR APRIL 1992 THROUGH SEPTEMBER 1992**

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Program Manager**

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FOSSIL ENERGY PROGRAM SEMIANNUAL PROGRESS REPORT FOR APRIL 1992 THROUGH SEPTEMBER 1992¹

R. R. Judkins, Program Manager

ABSTRACT

This report covers progress made during the period April 1, 1992, through September 30, 1992, for research and development projects that contribute to the advancement of various fossil energy technologies. Projects on the Fossil Energy Program are supported by the DOE Office of Fossil Energy, the DOE Morgantown Energy Technology Center, the DOE Pittsburgh Energy Technology Center, the DOE Fossil Energy Clean Coal Technology Program, the DOE Office of Basic Energy Sciences, the DOE Fossil Energy Office of Petroleum Reserves, the DOE Fossil Energy Office of Naval Petroleum and Oil Shale Reserves, and the U.S. Agency for International Development.

1. INTRODUCTION

P. T. Carlson

The Oak Ridge National Laboratory (ORNL) Fossil Energy Program research and development activities, performed for the Department of Energy (DOE) Assistant Secretary for Fossil Energy, cover the areas of coal, clean coal technology, support to the Strategic Petroleum Reserve, and support to the Naval Petroleum and Oil Shale Reserves. The principal focus of ORNL's fossil energy activities is coal, with emphasis on materials research and development; environmental, health, and safety activities; and bioprocessing of coal to produce liquid or gaseous fuels.

The Fossil Energy Program has projects in seven ORNL divisions (see Figure 1). Included as part of the Fossil Energy Program is the technical management of all activities on the DOE Fossil Energy Advanced Research and Technology Development (AR&TD)

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Materials Program. The AR&TD Materials Program includes research at six other DOE laboratories, at universities, and at industrial organizations. This Fossil Energy Program progress report, however, covers only those activities performed at Oak Ridge National Laboratory. Reports of work on the AR&TD Materials Program performed at other organizations may be found in the series of progress reports issued by the Fossil Energy AR&TD Materials Program.¹

1.1 MATERIALS RESEARCH AND DEVELOPMENT

Materials research and development activities at Oak Ridge National Laboratory consist of: ceramics development for high temperature applications, new metal alloys with unique mechanical properties, and corrosion research to understand the behavior of materials in coal combustion and conversion environments. The transfer of technology developed on this program is enhanced through interactions with industry and joint research programs with those interested in using the technology.

Fiber-reinforced ceramic composites with improved strength and toughness are being produced by the forced chemical vapor infiltration and deposition (CVID) process developed at ORNL. Ceramic composites have a variety of applications in fossil energy systems such as high-temperature heat exchangers and hot-gas cleanup filters. The ability to control the porosity of these ceramic composites through the CVID process means that both highly dense (for purely structural purposes) as well as porous composites (for filter applications) can be fabricated. Current work also has the goal of understanding the nature of the fiber/matrix interface with the objective of improving the mechanical properties of composites. Ceramic membranes for the separation of gases in high-temperature and hostile environments are being developed and tested. Other work is devoted to the microwave sintering of ceramics. ORNL has developed the ability to microwave sinter ceramics to high densities at temperatures several hundreds of degrees below those required with conventional radiant heating. This technology will be important in the fabrication of electrode and electrolyte materials with improved electrical properties for solid oxide fuel cells.

ORNL is developing advanced austenitic alloys for use in fluidized-bed and pulverized-coal combustion power plants. The objective of this work is to modify existing alloys to satisfy the strength and corrosion-resistance requirements of high-temperature and

high-pressure, second-generation power plants. Intermetallic alloys based on Fe_3Al are being developed for applications in which superior oxidation and sulfidation resistance and exceptional strength are required. Improved room-temperature ductility and resistance to hydrogen embrittlement are also being investigated. Materials and designs for tubesheets and manifolds for hot-gas filter systems are being examined, with the objective of recommending a tubesheet material suitable for long-term operation of these filter systems.

Corrosion research at ORNL centers on studies of the formation and breakdown of protective oxide scales, particularly in sulfur-containing atmospheres and on the effect of environment on corrosion of iron aluminides. With a specially-designed mechanical properties microprobe, an understanding of the properties of oxide scales is evolving.

Assessments of materials problems related to a variety of fossil energy technologies and identification of the research needed to solve those problems is an important part of ORNL's materials effort. One such activity is the assessment of structural ceramic materials proposed for use in the High Temperature Advanced Furnace (HITAF). In addition, ORNL has a commitment to transfer technology developed on the Fossil Energy Materials Program to others in the fossil energy community. Cooperative Research and Development Agreements (CRADAs) are utilized to transfer the technology developed at ORNL to industry. As another vehicle for information exchange, the Fossil Energy Materials Program provides materials testing and failure analysis support to operating coal conversion and utilization plants.

1.2 ENVIRONMENTAL ANALYSIS SUPPORT

Environmental analysis support activities include assistance to the Morgantown (METC) and Pittsburgh Energy Technology Centers (PETC) in reviewing and preparing site-specific documentation required by the National Environmental Policy Act (NEPA) for projects selected for participation in the DOE Clean Coal Program (CCP). The CCP is an important activity which is jointly funded by DOE and industrial organizations. ORNL staff have assisted in the preparation of a Programmatic Environmental Impact Analysis for the second solicitation of the CCP and a Programmatic Environmental Impact Statement that evaluates the impacts of the widespread use of new clean coal technologies being developed under the CCP. The latter document is the first comprehensive and detailed analysis that

shows the full potential of new coal technologies in reducing emissions of sulfur and nitrogen oxides, as well as of carbon dioxide gases. It also analyzes the quantities of solid wastes that would be produced using the new technologies. A key activity was the preparation for PETC of a draft Environmental Impact Statement (EIS) for the Healy Clean Coal Project in Healy, Alaska. This work is notable because it is the first site-specific EIS prepared for the Clean Coal Program. Assistance was also provided to the DOE Office of Fossil Energy in evaluating the environmental aspects of projects proposed for cost-shared funding under the fourth round of the Clean Coal Program.

Technical and analytical support is being provided to METC in the evaluation of environmental concerns related to METC-sponsored coal research and development projects, and by preparing NEPA assessments of the projects.

Technical and analytical support is also being provided to DOE for the Oil Research Program. The goal of the Oil Research Program is to maximize the economic producibility of domestic oil resources by implementing a research, development, and demonstration plan in collaboration with state governments, industry, and academia. A component of ORNL's involvement is the preparation of a programmatic NEPA assessment of the program.

The Fossil Energy Program provides assistance to PETC in satisfying the NEPA requirements for the retirement and dismantling of the Advanced Coal Liquefaction Research and Development Facility in Wilsonville, Alabama. Hydrogeologic, hazardous waste, and related investigations are being conducted to meet NEPA requirements. Another effort involves the preparation of a Preliminary Assessment for DOE Casper and the DOE Office of Naval Petroleum and Oil Shale Reserves of the shale pile and drums in the West Sharrad Gulch, Colorado, area and surrounding areas, with regard to potential hazardous waste pathways and target populations/sensitive environments, to satisfy Comprehensive Environmental Response Compensation Liability Act (CERCLA) requirements.

1.3 COAL CONVERSION DEVELOPMENT

Coal conversion development work on the Fossil Energy Program includes studies of the bioprocessing of coal, renewable hydrogen production for fossil fuel processing, and the evaluation of coal-derived liquids produced from mild gasification processes.

The bioprocessing of coal is being explored through the use of microorganisms to convert coal into useful liquid products. Bioreactor concepts that maximize coal solubilization and product yields are being examined. While most enzymes can not be dissolved in nonpolar media, a new technique has been developed for enhancement of the enzyme solubilization of coal in a nonpolar solvent. The resulting solution can then be used for coal solubilization in a nonaqueous environment. For the first time, a bacteria has been shown to interact with a bituminous coal in a hydrogen environment for the biological solubilization of coal. The study of renewable hydrogen production builds on promising new work at ORNL on the utilization of intact microalgae for photosynthetic water splitting. In this process, specially-adapted algae are used to perform the light-activated cleavage of water into its elemental constituents, molecular hydrogen and oxygen.

The evaluation of products from mild gasification processes provides data which can be used in systems studies of the relationships between process conditions, product yields, and product quality. The data not only assist industry in process development, but further demonstrate the potential usage of mild gasification products. Extensive characterization of char samples from two mild gasification processes has shown that the char from one process approaches the reactivity of high-volatile bituminous coal, while the other char has a reactivity similar to petroleum coke.

1.4 COAL COMBUSTION RESEARCH

It is known that fossil energy combustion devices, such as fluidized beds and pulsed combustors, can exhibit characteristic features of deterministic chaos. The ability to measure and describe chaotic components will contribute to greatly improved methods for characterizing, modeling, designing, and controlling commercial fossil energy processes such as combustion, coal gasification, hot-gas cleanup, and oil retorting. For these reasons, the Fossil Energy Program provides analytical support to METC in the evaluation of chaotic components in data from fluidized beds and other coal combustion processes.

In response to a request from the PETC, ORNL is providing technical assistance in the implementation of collaborative coal projects under the U.S. Agency for International Development (USAID)/Government of India Phase II, Alternative Energy Resources Development (AERD) Project.

1.5 FOSSIL FUEL SUPPLIES MODELING AND RESEARCH

ORNL is assisting the DOE Strategic Petroleum Reserve (SPR) Program through the assessment of alternative methods of financing oil acquisition and in the development of models for planning the capacity and management of the SPR.

1.6 COAL STRUCTURE AND CHEMISTRY

Research is also being conducted on the structure and chemistry of coal surfaces and interfaces to understand the complex processes and reactions occurring during the combustion of coal. Results have revealed that the hydrogen bonding structures of coal and the surface area of finely divided coal contribute significantly to the understanding of the properties of coal.

1.7 REFERENCE

1. Fossil Energy Advanced Research and Technology Development Materials Program Semiannual Progress Report for the Period Ending September 30, 1992, ORNL/FMP-92/2, December 1992.

Fig. 1. Organization of the Oak Ridge National Laboratory Fossil Energy Program

2. MATERIALS RESEARCH AND DEVELOPMENT

N. C. Cole

This section describes research and development activities performed for the Fossil Energy Materials Program. Work on the Fossil Energy Materials Program includes the fabrication and characterization of fiber-reinforced ceramic composites, development of ceramic fiber-ceramic matrix hot-gas filters, development and testing of ceramic membranes for separation of gases, microwave sintering of materials for fuel cells, development of iron aluminides, studies of environmental effects on iron aluminides, development and evaluation of advanced austenitic alloys, evaluation of materials for hot-gas filter support systems, fundamental corrosion and oxidation studies and materials testing and failure analysis support to coal conversion and utilization plants.

2.1 FABRICATION OF FIBER-REINFORCED COMPOSITES

D. P. Stinton, J. C. McLaughlin, and T. M. Besmann

INTRODUCTION

The purpose of this 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. Ceramic fiber-ceramic matrix composites are being fabricated by infiltrating fibrous structures with vapors that deposit on and between the fibers to form the matrix of the composites.

Fiber composites are in the limelight as a result of exceptionally high toughness values recently achieved for glass ceramics reinforced with silicon carbide fibers. Because use of ceramics is frequently restricted by inadequate toughness, any progress toward toughening ceramics will greatly expand their potential market. However, a generic problem that must be overcome is that normal ceramic fabrication processes tend to damage fibers mechanically and chemically when the fibers 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. The vapor consolidation technique has been used to prepare fiber composites with matrices of carbon and/or such ceramics as SiC, Si₃N₄, B₄C, BN, and TiB₂. Our goal is to demonstrate a rapid process for fabricating, via chemical vapor infiltration, a ceramic fiber-ceramic matrix composite consisting of materials of high interest to the fossil energy community. An initial assessment identified SiC fibers and matrices of Si₃N₄ and SiC as being promising. An infiltrating process utilizing a thermal gradient combined with forced flow of the reactants is being pursued.

DISCUSSION OF CURRENT ACTIVITIES

Fiber-reinforced SiC matrix composites of thick-walled tubular geometry (2.5 cm ID by 0.6 cm wall thickness by ~15 cm long) were fabricated by forced chemical vapor infiltration for nondestructive evaluation and mechanical property testing. Fibrous preforms of different fiber architectures (filament wound, cloth wrapped, or 3-dimensionally braided) were investigated to accommodate components with different mechanical property requirements. Nondestructive evaluation (radiography and computed tomography) was performed at ORNL prior to sending the tubes to Virginia Polytechnic Institute for mechanical property testing. Composite tubes will be mechanically evaluated in tension as well as torsion during the first quarter of FY 1993. The mechanical properties of the composite tubes will then be correlated with the results of the nondestructive evaluation.

A CRADA was signed with The 3M Company to establish a base line for oxide fiber-SiC matrix composites. Using the forced CVI process developed at ORNL, composites were fabricated using four different 3M fibers; Nextel 312 and 440 (aluminaboriasilica), Nextel 550 (aluminasilica), and Nextel 610 (alumina). Different interface treatments (CVD carbon and organic based carbon) were incorporated into the composites of each type. In addition, experiments were performed on the reactor configuration. Because the oxide fibers are much more insulating than Nicalon fibers, the bottom temperature was much cooler than desired. The goal of these experiments was to manipulate the temperature gradient (raise the bottom temperature) that the composite experiences during infiltration. The ability to control this bottom temperature is important in achieving dense composites of various fibers and shapes.

Because fiber-reinforced SiC-matrix composites are susceptible to sodium and potassium corrosion at high temperatures, a chemical vapor deposition process was developed during the past year to apply coatings that reduce or eliminate corrosion. Statistically designed experiments were used to identify deposition conditions that produce dense continuous Ta₂O₅ coatings. Coated composite samples have been corrosion tested this period. These tests consisted of applying 10 to 20 mg/cm² of sodium sulfate to the surface of a Ta₂O₅ coated composite. Materials were then annealed at 1000°C for 100 hours and examined by optical microscopy, scanning electron microscopy, and x-ray diffraction. Observation of the annealed samples by optical and scanning electron microscopy revealed no visible reaction between the sodium sulfate and the Ta₂O₅. Examination of the materials by x-ray diffraction showed that the Ta₂O₅ was unaffected by the exposure to sodium sulfate.

2.2 INTERFACES AND MECHANICAL PROPERTIES OF CONTINUOUS FIBER-REINFORCED CERAMIC COMPOSITES

R. A. Lowden, K. L. More, and O. J. Schwarz

INTRODUCTION

The purpose of this task is to examine fiber-matrix interfaces and optimize the mechanical behavior of continuous fiber-reinforced ceramic composites fabricated utilizing a forced-flow, thermal-gradient chemical vapor infiltration technique. The strength and toughness of fiber-reinforced ceramic composites are controlled by the properties of the interface between the fiber and the matrix, thus emphasis is to be placed on developing methods to characterize the fiber-matrix interface and measure interfacial stresses in fiber-reinforced ceramic composite systems. Coating or pretreatment processes can then be utilized to tailor the fiber-matrix interface within various composite systems and to optimize the strength and toughness of the composite.

It is well known that although the fibers and matrix play major roles in determining the final properties of a composite, the fiber-matrix interface has a significant influence on the fracture behavior and mechanical properties of reinforced ceramics. Typically, coatings are used to protect ceramic fibers from chemical attack during processing and to control interfacial forces. Carbon, whether intentionally deposited on the fibers prior to consolidation¹⁻³ or formed serendipitously during processing,⁴ is the most commonly used interlayer in ceramic composites today. Carbon coatings have performed well in a variety of systems; however, the poor oxidation resistance of carbonaceous materials has prompted intense scrutiny of their usefulness at elevated temperatures in oxidizing environments.

Carbon begins to oxidize at temperatures around 700 K and oxidation is rapid in air at temperatures above 1173 K. It has been shown that the oxidation of Nicalon®/SiC composites begins by attack of the carbon interface coating at exposed fiber ends.^{5,6} Once the carbon is removed along the entire fiber length, the matrix and fiber oxidize to form a silica layer that eventually bonds the components together. The strong bond at the fiber-matrix interface does not permit debonding and sliding, resulting in brittle behavior. Also, oxidation degrades the properties of the fiber, enhancing the embrittlement of the composite.

The poor oxidation resistance of carbon has lead to the examination of alternate coating materials or new concepts for controlling the force at the fiber-matrix interface in ceramic-ceramic composites. Hexagonal boron nitride possesses a structure and mechanical properties similar to those of graphitic carbon, however, BN offers a distinct improvement in oxidation resistance.^{7,8} Due to these attributes, it is expected BN could be used as a direct replacement for carbon. Earlier in this program, favorable results were achieved using a limited supply of CVD-coated fabric.⁹ This and the repeated success of others in employing BN as an interlayer in ceramic composites,¹⁰⁻¹² prompted the re-evaluation of BN as an interface layer for Nicalon® fiber-reinforced SiC composites.

DISCUSSION OF CURRENT ACTIVITIES

Summary

Boron nitride was examined as an interface coating for Nicalon®/SiC composites. Boron nitride coatings were deposited on fibrous preforms from gas mixtures containing boron trichloride (BCl_3), ammonia (NH_3), and hydrogen (H_2) prior to densification with silicon carbide employing chemical vapor infiltration. Interlayer deposition conditions were controlled to produce a polycrystalline hexagonal BN with a microstructure comparable to that of graphitic carbon. Room-temperature flexure strengths of as-fabricated composites, and specimens exposed in air at 1273 K, were measured to assess the effectiveness of the interface layer. As for composites with graphitic carbon interlayers, the properties of the composites were influenced by the thickness of the BN coating. The composites with BN interface coatings demonstrated significantly improved strength retention after short-term (24 h) oxidation, however, the toughness of the composites was degraded. The composition and microstructure of the fiber coating and the composite interfaces, prior to and after elevated-temperature exposure, were characterized using electron microscopy. No interaction between the BN interlayer and the fibers and matrix was observed for as-fabricated composites, however, a distinct change was noted at the Nicalon® fiber-BN coating boundary after oxidation. The embrittlement of the composites was attributed to changes at this interface and decomposition of the Nicalon® reinforcement that was accelerated by oxygen contamination in the as-deposited BN layers.

Composite Fabrication

Fibrous preforms were fabricated by stacking multiple layers of ceramic-grade Nicalon[®] plain-weave fabric rotated in a $0 \pm 30^\circ$ sequence within the cavity of a graphite holder. The layers were hand compressed to produce a preform with a nominal fiber loading of 40 vol. % and were held in place by a perforated graphite lid pinned to the holder. The polyvinylacetate cloth sizing was removed through multiple washings with acetone. The nominal size of the fibrous preforms was 45 mm in diameter and 12.5 mm thick.

Preforms were next coated with the boron nitride interface layers. The coatings were deposited using a forced-flow, isothermal chemical vapor infiltration approach from gas mixtures containing boron trichloride (BCl_3), ammonia (NH_3), and hydrogen (H_2), a preform temperature of 1373 K, and a reactor pressure of ≈ 5 kPa. The ratio of boron to nitrogen in the reactant gas mixture was held constant at unity. Reactant flows and concentrations were modified to produce: (i) deposition rates similar to those for the standard graphitic carbon layer, (ii) microstructures comparable to those of graphitic carbon, and (iii) a uniform layer throughout the preform. Layer deposition times were then varied to control coating thickness. The final thicknesses of the interface layers were calculated from preform weight gains.

The preforms were densified with silicon carbide using the forced-flow, thermal-gradient chemical vapor infiltration (FCVI) process.^{2,23} The SiC matrix was produced by the decomposition of methyltrichlorosilane (CH_3SiCl_3 , or MTS) in hydrogen at a hot-surface temperature of 1473 K and atmospheric pressure. The preforms were infiltrated with SiC to a maximum of 85 to 90 % of theoretical density in ≈ 20 h.

Characterization and Testing

Test bars were cut from the composite samples parallel to the 0° orientation of the top layer of cloth using a diamond saw, and tensile and compression surfaces were ground parallel to the long axis of the specimen. The average dimensions of the specimens were 2.5 x 3 x 40 mm and all specimens were measured and weighed to determine densities. Half of the specimens were oxidized in static air at 1273 K for 24 hours. Flexure bars were placed on an alumina plate in the cavity of an atmospheric box furnace and heated to temperature at a rate of $300^\circ/\text{h}$. Once the furnace achieved equilibrium, the final temperature was measured and set using a hand-held

optical pyrometer, and then maintained using a thermocouple-controlled programmer. At the specified time, the furnace was shut off and allowed to cool unassisted.

Room-temperature flexure strengths for as-fabricated and heat-treated composites were measured in four-point bending. A support span of 25 mm and a loading span of 6 mm were used with a crosshead speed of 0.50 mm/min. The load was applied perpendicular to the layers of cloth. Load-displacement curves were recorded to examine the fracture process and determine the loads for ultimate strength calculations. The fracture surfaces of the specimens were examined using a scanning electron microscope (SEM).

The composition and microstructure of the BN interlayers were examined using transmission electron microscopy. Specimens were prepared such that the area for analysis contained a quantity of fibers oriented perpendicular to the surface. The specimens were mechanically ground, polished, dimpled, and ion-milled to perforation using standard techniques. Microstructural characterization was conducted on a high resolution transmission electron microscope (HRTEM) operated at 400 kV. The BN layers were also analyzed by parallel electron loss spectroscopy (PEELS), conducted at 100 kV using a transmission electron microscope with a field emission gun in the diffraction mode (image coupled).

Mechanical Properties

Typical flexure load-displacement curves for the Nicalon®/SiC composites with boron nitride interface coatings are shown in Figure 1. The composites exhibited good strength and composite behavior, ie. failed gradually with fiber pull-out. The strength and toughness of the composites was influenced by coatings thickness (Table 1). Thicker coatings produced greater strain to failure, but also reduced strength beyond a given maximum.

Exposure to 1273 K in air for 24 h produced a slight discoloration of all specimens suggesting some degree of surface oxidation. As given in Table 1, control specimens with a carbon interface coating experienced a significant loss in flexure strength after the 24 h exposure. The composites with the BN interface coatings exhibited improved strength retention, with one sample experiencing virtually no loss in flexure strength after oxidation. The oxidized specimens, however, displayed lower toughness than for comparable untreated specimens. The loss in toughness, as defined as a decrease in strain to failure, was noted as a more rapid drop in the load-deflection curve beyond maximum load (Figure 2).

Figure 1. Representative load-deflection curves for composites with boron nitride interface coatings of varying thickness. [Curves are offset horizontally for clarity.]

Figure 2. Representative load-deflection curves for as fabricated and oxidized composites with boron nitride interface coatings. [Curves are offset horizontally for clarity.]

Table 1. Mechanical Properties of Nicalon®/SiC Composites with BN and Carbon Interfaces, Prior To and After Oxidation.

Deposition Time (h)	Thickness (μm)	As-Fabricated Strength (MPa)	Post-Exposure Strength (MPa)
<i>Boron Nitride</i>			
1.0	0.20	417 ± 68	284 ± 63
2.0	0.47	406 ± 72	345 ± 36
2.0	0.42	419 ± 67	409 ± 76
4.0	0.63	389 ± 59	282 ± 62
<i>Carbon[†]</i>			
1.0	0.13	421 ± 27	----
2.0	0.39	404 ± 67	108 ± 14
4.0	0.61	304 ± 30	----

[Values are average of 9 test specimens.]

[†] graphitic carbon coating deposited from propylene^{1,10}

Characterization

Characterization of the fracture surfaces employing scanning electron microscopy revealed more information regarding the failure process. Fiber pull-out was observed for the as-fabricated specimens, which was anticipated due to the extended strain to failure observed during flexure testing. The level of pull-out was dependent upon coating thickness. Thicker coatings produced more pull-out and longer protruding fiber lengths. Debonding was observed at the BN layer-Nicalon® fiber interface in all characterized specimens. Fiber surfaces were relatively clean and the BN coating remained bonded to the matrix. Decreased levels of fiber pull-out were found for the oxidized specimens, however, debonding was evident and, as in the as-fabricated composites, occurred at the BN layer-Nicalon® fiber interface.

Transmission electron microscopic analysis of the fiber coating for the as-fabricated composites with a BN deposition time of 2 h found the layer to be uniform throughout the

preform and $\approx 0.45 \mu\text{m}$ thick (Figure 3). This thickness measurement was in good agreement with the thickness calculated from weight gain (Table 1). The BN layer was turbostratic, composed of small, randomly-oriented hexagonal grains with the c-axis = 0.333 nm. High-resolution TEM characterization of the BN layer-fiber and the BN layer-SiC matrix interfaces in the as-fabricated state was conducted to examine chemical interactions that may have occurred during processing. No interaction was observed at the BN-fiber interface as shown by the clean transition from the featureless structure of the fiber to the turbostratic nature of the BN coating. A thin amorphous region ($\approx 5 \text{ nm}$) was found between the SiC matrix and the BN interlayer.

Figure 3. TEM image of the BN coating on Nicalon® in the as-fabricated composite. The coatings were uniform in thickness at $\approx 0.45 \mu\text{m}$.

PEELS analysis of several BN interlayers in as-fabricated composites revealed a significant amount of oxygen in the as-fabricated coating. The oxygen content was uniform across the thickness of the coating. Elemental analysis of the BN coating after oxidation using PEELS showed no discernable difference in composition. Electron microscopic characterization of the composites after oxidation did reveal significant changes at the boundary between the Nicalon[®] fiber and the BN interface layer (Figure 4). High resolution electron microscopy revealed a series of thin layers, beginning with a parallel alignment of the BN microstructure close to the fiber surface. Beyond this layer was an amorphous film, most likely composed of SiO₂, followed by a graphitic carbon layer. PEELS analysis of the two layers nearest the fiber surface found carbon and oxygen but no boron. In addition to the formation of the SiO₂/C sequence, there appeared to be a higher density of silicon carbide crystallites close to the surface of the Nicalon[®] fiber. This region is designated by the arrows in Figure 4.

Figure 4. Low-magnification TEM image of the BN/Nicalon[®] interface following oxidation of the composite for 24 h at 1273 K. The nature of this interface changed significantly compared to that observed prior to oxidation and consisted of a layered structure, as labelled on the micrograph.

Conclusions

A boron nitride interlayer proved to be an effective method for improving the short-term oxidation resistance of the Nicalon®/SiC composites. Polycrystalline hexagonal BN fiber coatings with a turbostratic structure were deposited on fibrous preforms which were densified with a SiC matrix employing the FCVI technique. Strengths and toughnesses of comparable to composites with graphitic carbon interlayers were observed, and mechanical properties and fracture behavior were influenced by the thickness of the BN coating. Although strength loss after exposure in air at 1273 K for 24 h was minimal, toughness was diminished. This decrease appears to be in part due to the decomposition of the fiber. A SiO₂/C dual layer was found at the BN layer-fiber interface in the heat-treated specimens. This layer is formed from interaction of the BN fiber coating and the fiber. Oxygen contamination in the as-deposited layers and diffusing into the coating during oxidation, caused the amorphous Si-C-O phase of the fiber to decompose and subsequently react to produce the SiO₂/C sequence. The deterioration lead to a decrease in reinforcement strength and a loss of toughness.

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2.3 MATERIALS SUPPORT FOR HITAF

V. J. Tennery and K. Breder

INTRODUCTION

The purpose of this project is to compare structural ceramic materials proposed for use in the air heater of a coal fired high temperature advanced furnace (HITAF) for power generation. The work will provide necessary initial structural ceramics parameters for design of a prototype system. A power generating system using United Technologies Corporation (UTC)/Siemens V84.4 gas turbine with clean air as the working fluid which is heated by a coal fired high temperature advanced furnace is being developed by a team consisting of: United Technologies Research Corporation, UTC Turbo power and Marine Division, Bechtel, Oak Ridge National Laboratory (ORNL) and a Joint Venture of Physical Sciences Inc. (PSI) Technologies, Reaction Engineering International (REI) and University of North Dakota Energy & Environmental Research Center (UNDEERC).

DISCUSSION OF CURRENT ACTIVITIES

The present reporting period is the first period for this project. There have been three meetings at which representatives for the entire team have been present. The design concept of the overall system has been developed further from the original proposal and through this the temperature and environments that the air heater materials will see has been better defined. The initial work that was performed on the selection of suitable ceramic materials has been confirmed and efforts will concentrate on SiC ceramics. Thorough literature surveys have been performed regarding the corrosion behavior of SiC and the high temperature mechanical properties of SiC. Further, a literature search regarding the DOE and EPRI sponsored ceramic heat exchanger work that was performed in the late seventies and early eighties has been performed.

Two ceramic materials have been selected for initial tests at ORNL, and two additional materials have been selected for a corrosion screening test. NT 230 from Norton Company is a siliconized silicon carbide with a very low amount of free Si. This has been ordered, machined into flexure test bars and is scheduled to be delivered the first week in October. Sintered α -SiC from Carborundum is the second material selected

at this point. Ceramic properties which will be needed for initial preliminary design have been selected, and the test matrix as described below has been determined. This follows the general outline in the ORNL task (FEAA291) with specific experimental details chosen to fit the need for materials data within the project. It is imperative that the materials properties be determined on flexure bars from the exact same type of material as will be used in the heat exchanger. Later data from tensile specimens will probably be required. Given the variability in the processing of structural ceramics along with the variability of the mechanical properties, it is necessary to establish as broad a database as possible for the selected materials. It is therefore necessary to do extensive testing on-state-of the art material and not rely on properties from similar tests which were done on previous similar material.

Test Matrix

FAST FRACTURE

RT, 1100°C and 1425°C at 40MPa/s 30 specimens at each condition.
(90 specimens)

DYNAMIC FATIGUE

Four stressing rates over approximately five orders of magnitude;
10MPa/s, 1MPa/s, 10^{-2} MPa/s, 10^{-4} MPa/s (testing times 10s, 5min,
6h and 300h)

Two temperatures; 1100°C and 1425°C.

10 specimens at each condition.

(80 specimens)

INTERRUPTED STATIC FATIGUE

Two stress levels, one high 70 - 80% of fast fracture load,
and one low

20 - 30% of fast fracture load, hold for 300h, then fast fracture.

Two temperatures 1100°C and 1425°C, 10 specimens at
each condition. (40 specimens)

FRACTOGRAPHY AND WEIBULL ANALYSIS

At all steps necessary fractography and statistical analysis are performed.

Corrosion Screening

A corrosion screening of four candidate materials will be performed. The materials will be the two grades of SiC and two composites (Lanxide). Billets of these are exposed to two types of coal ash at two, possibly three temperatures (1100°C, 1260°C and 1425°C) in a muffle furnace at the University of North Dakota Energy And Environmental Research Center. After exposure for 300h the billets are machined into flexure bars and their retained room temperature flexure strength will be measured at ORNL. The tensile surface during loading and fracture is a surface exposed to hot coal ash. The strength results are compared to the manufacturers data for as received strength (due to limited number of specimens) and to each other. Necessary fractography will be done at ORNL and both ORNL and UNDEERC will perform microscopy to study and characterize the reaction layers on the exposed surfaces.

Mechanical Properties

All strength measurements are done in four point bending on 3x4x50mm bars with chamfered edges. The test configuration includes 20mm inner span and 40mm outer span. All tests are done in ambient air.

2.4 MICROWAVE SINTERING OF CERAMICS FOR FUEL CELLS

M. A. Janney, M. L. Jackson and H. D. Kimrey

INTRODUCTION

The study of microwave processing of ceramic materials at ORNL has shown that some materials exhibit a significant "microwave effect" but that others exhibit little or no "microwave effect." (The "microwave effect" is manifested as lower temperature sintering or faster kinetics at a given temperature.) The biggest difference between the two classes of ceramics is their electrical conductivity. Materials that exhibit a "microwave effect" are either non-conductors or ionic conductors; materials that do not exhibit a "microwave effect" are electronic conductors. The purpose of the current investigation is to investigate both of these classes of materials in a single materials system. The system chosen for study is the $\text{ZrO}_2\text{-CeO}_2\text{-Y}_2\text{O}_3$ system.

The $\text{ZrO}_2\text{-CeO}_2\text{-Y}_2\text{O}_3$ system is attractive for study for a number of reasons. Its total electrical conductivity can be varied over several orders of magnitude. Its conductivity can be altered from being predominantly ionic to predominantly electronic in nature. The addition of Y_2O_3 to the system provides a means to fix the level of ionic conductivity in the system by the creation of oxygen vacancies. Electronic conductivity can be adjusted by varying the partial pressure of oxygen in the processing furnace, which reduces Ce^{+4} to Ce^{+3} and establishes electron charge carriers in the material.

An investigation of the role that ionic and electronic conductivity play in determining the "microwave effect" has been initiated. Initial tests have been made with $\text{ZrO}_2\text{-12 mol\% CeO}_2$. Subsequent studies are being conducted using $\text{YO}_{1.5}$ levels between 0 and 4 mol% and a CeO_2 level of 16 mol%.

RESULTS AND DISCUSSION

Microwave Sintering of $\text{ZrO}_2\text{-12 mol\% CeO}_2$

The sintering results for both microwave and conventional firing in air and $\text{N}_2\text{-4\% H}_2$ atmospheres are shown in Figure 1. There are substantial differences between the air

Figure 1. Sintering curves for ZrO_2 - 12 mol% CeO_2 in air and N_2 - 4% H_2 under conventional and microwave conditions.

and N_2 - 4% H_2 firings and between the microwave and conventional firings. For both conventional and microwave sintering, the samples fired in air sintered to higher final densities than those fired in N_2 - 4% H_2 . For both air and N_2 - 4% H_2 sintering, the samples that were microwave fired sintered to higher densities than those conventionally fired. The differences among the four test conditions can be understood as follows.

The difference in final density between the air and N_2 - 4% H_2 samples is caused by differences in the phase composition of the samples. The samples fired in air are completely in the tetragonal zirconia phase, as determined by x-ray diffraction. The samples fired in N_2 - 4% H_2 exhibit no tetragonal phase; the phase that is present does not appear to be monoclinic either, which is the phase that one would expect to observe. Effort is continuing to determine what this phase is that is stabilized by the reducing atmosphere. Furthermore, the conversion of the tetragonal phase, which is present during sintering, to this other phase during cool-down leads to severe checking and cracking of the samples.

The differences in sintering temperatures required to achieve a particular density by microwave and conventional firing can be explained by the presence of a "microwave effect." For both the air and N_2 - 4% H_2 firings, the samples fired in the microwave furnace sintered at $\sim 50^\circ\text{C}$ lower than those fired in a conventional furnace. At temperatures up to 1300°C , the microwave sintering behavior of samples fired in air and N_2 - 4% H_2

were the same. The deviation of the two curves at temperatures above 1300°C can be explained in terms of their different phase compositions as outlined above. The "microwave effect" was of the same magnitude for the samples fired in air and those fired in $N_2 - 4\% H_2$.

Synthesis of ZrO_2 -16 mol% CeO_2 - $xYO_{1.5}$ Powders

A large effort was made during the past six months to synthesize the powders that are required to perform the electronic/ionic conductivity experiments. The particular compositions that were chosen were ZrO_2 -16 mol% CeO_2 -0.0, 2.0, & 4.0 mol% $YO_{1.5}$. These compositions were chosen in order to meet the following constraints. First, the materials must be single phase tetragonal ZrO_2 at the sintering temperature. This simplifies the interpretation of the sintering kinetics. Also, the dielectric properties should change continuously with composition since no phase boundaries are crossed. Second, the materials should have a large electronic component in their conductivity under reducing conditions. Figure 2 shows that there is a factor of five difference in conductivity between air and argon atmospheres at 16 mol% CeO_2 . The increase in conductivity at low pO_2 is totally due to electronic conduction. Third, the materials should have a substantial increase in ionic conductivity with increasing $YO_{1.5}$ concentration. Chiou, et al² have shown that the ionic conductivity of ZrO_2 - 10 mol% CeO_2 - Y_2O_3 alloys increases linearly by a factor of ~20 as the $YO_{1.5}$ concentration increases from 0 to 4 mol%. The behavior of the ZrO_2 - 16 mol% CeO_2 - $YO_{1.5}$ system should be similar.

The powders were synthesized using a coprecipitation route. Aqueous Zr, Ce, and Y acetate solutions were combined in appropriate molar ratios at their natural pH of ~pH 4. Concentrated NH_4OH solution was added slowly to raise the pH to ~pH 8 at which point a combined Zr, Ce, and Y hydroxide gel was precipitated from solution. The gel was dried at 150°C to remove the excess water. Then it was calcined at 550°C to burn off the acetate residue and to convert the hydroxide to an oxide phase. After calcining, the powder was milled in an attritor mill to reduce the powders to primary particles. ZrO_2 - 12 mol% CeO_2 milling media that had been fabricated at ORNL were used to prevent contaminating the ZrO_2 - 16 mol% CeO_2 - $xYO_{1.5}$ powders with other cations. The final powders had an average particle size around 0.7 μm .

Figure 2. Conductivity of ZrO_2 - CeO_2 alloys as a function of CeO_2 concentration in air ($p\text{O}_2 = 0.21$) and in argon ($p\text{O}_2 \sim 4 \times 10^{-5}$). The vertical line at 18 mol% CeO_2 represents the phase boundary of the tetragonal phase. Redrawn from the data of Millet and Guillou.¹

Summary and Conclusions

It has been shown that the sintering of ZrO_2 - 12 mol% CeO_2 is affected by the atmosphere that is used during sintering and by the method of heating that is used, conventional vs. microwave. The "microwave effect" that is observed consists of lowering the sintering temperature for both air and N_2 - 4% H_2 fired samples by $\sim 50^\circ\text{C}$. Samples fired in N_2 - 4% H_2 were transformed from the tetragonal phase to another phase that is at present unidentified.

Powders were synthesized in the ZrO_2 - 16 mol% CeO_2 - $\text{YO}_{1.5}$ system with 0.0, 2.0, & 4.0 mol% additions of $\text{YO}_{1.5}$. These samples will be sintered in conventional and microwave conditions in the coming months to determine the role of total ionic conductivity and electronic conductivity in the "microwave effect."

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2.5 DEVELOPMENT OF IRON ALUMINIDES*

V.K. Sikka

INTRODUCTION

Iron aluminides based on the ordered Fe_3Al composition have good oxidation resistance and excellent sulfidation resistance. Furthermore, they offer advantages over stainless steels, including lower density and reduced consumption of strategic elements including chromium. In the past, the major drawbacks to the use of these materials in structural applications have been low room-temperature (RT) ductility (<5%) and a rapid drop in strength at temperatures above 600°C (ref. 1). Recently, by a combination of thermomechanical processing and heat treatment, the RT ductility has been increased into the range of 15 to 20% (ref. 2), and the high-temperature tensile and creep strengths have been increased by the addition of 1% Nb (ref. 3). While there is a growing data base on the properties of sheet material,⁴ little data exists on the mechanical properties of plate products, and no fatigue data are available.

In this paper, the tensile, creep, and fatigue properties of ductile Fe_3Al plate in two thicknesses are investigated and, when possible, compared to sheet properties. In addition, the results of Charpy-impact toughness tests are reported for one plate. The alloy investigated is designated FA-129, which is an ordered Fe_3Al alloy with a composition tailored for high temperature strength.³ The results show differences in tensile and creep properties for plate and sheet products. The results of high cycle fatigue tests show that cyclic loading at stresses below the yield strength does not induce fatigue failure at temperatures of 25 and 454°C and that there is an effect of plate thickness at 600°C.

DISCUSSION OF CURRENT ACTIVITIES

The Fe_3Al alloy studied was vacuum-induction melted by Special Metals Corporation (New Hartford, New York) and cast into a 165-kg round ingot with dimensions of 102-mm diam by 203-mm long with a small hot top. The composition

*Data taken from a paper by B. G. Gieseke, D. J. Alexander, V. K. Sikka, and R. H. Baldwin entitled "Mechanical Properties of Ductile Fe_3Al -Based Plates."

of the alloy is given in Table 1. The ingot was homogenized at 1150°C for 64 h, followed by 1 h at 700°C then air cooling. Next, the material was heated in air at 1000°C for 2 h and extruded through a rectangular die of 25 mm by 76 mm. Each piece was rolled at 800°C from a thickness of 25 mm to 19 mm. Rolling passes were 15% each with reheating times of 600 s each. Finish rolling was conducted at 650°C and two plates were produced: one 12.7-mm thick and the other 16.5-mm thick. The 12.7-mm plate was stress relieved at 700°C for 1 h and oil quenched, and the 16.5-mm plate was stress relieved at 750°C for 1 h and oil quenched.

Table 1. Composition of FA-129 iron aluminide (wt %)

Fe	Al	Cr	Nb	C	B
Balance	16.30	5.31	1.00	0.054	<0.001

Specimens were machined from the plates as described below. In each case, specimens from the 12.7-mm plate were stress relieved at 700°C for 1 h and oil quenched. Specimens from the 16.5-mm plate were stress relieved at 750°C for 1 h and oil quenched.

Standard size tensile specimens with a nominal gage length diameter of 6.35 mm were fabricated from the 12.7-mm plate. In addition, miniature (3.18-mm diam) tensiles were fabricated from the ends of one fatigue specimen from the 16.5-mm plate. Duplicate tensile tests were conducted at 25, 454, and 600°C using an initial strain rate of 2.67 by 10^{-3} /s and a resistance-heated, clam-shell furnace.

Hourglass fatigue specimens with a nominal diameter of 5.08 mm were machined from both plates. Fatigue tests were conducted at 24, 454, and 600°C on a servohydraulic test frame using an R-ratio of 0.05. Prior to testing, the gage length of each fatigue specimen was hand polished using 6- μ m diamond paste to remove all surface oxidation from the stress-relief process and to provide defect-free surfaces. Specimens were heated using a radio frequency induction unit, and the temperature at the center of the gage lengths was maintained to within $\pm 2^\circ\text{C}$.

Charpy V-notch tests were conducted on specimens oriented in the T-L orientation so that crack growth was parallel to the rolling direction. Six full size (10 $\times$ 10 $\times$ 50 mm) Charpys were machined from the 16.5-mm plate. The specimens were tested on a

semiautomated Charpy machine at 200°C increments from -200 to 800°C, and the impact energies were fitted to a hyperbolic tangent function to determine the transition temperature.

Creep tests were conducted in air on 2.36-mm-diam specimens machined from plate materials. The small quantity of available plate required that the creep specimens be machined from the ends of fatigue specimens. A total of four specimens were machined. Testing was completed at 650°C and 34.5 MPa using dead weight loading to duplicate conditions for which creep data existed on the sheet material.

Results

Tensile properties obtained on the plates are listed in Table 2 along with those previously determined for the 0.75-mm sheet products. As Table 2 shows, the RT ductility of the 12.7-mm plate (no data exist for the 16.5-mm plate) is reduced by nearly 50% in reference to the sheet material, yet the yield strengths at RT are quite similar. Furthermore, the RT ultimate strength in the 12.7-mm plate is reduced by 28%. At 454°C, the yield strengths of the plate materials are lower than that in the sheet material by approximately 18%, while the ultimate strengths are not significantly different. At 600°C, both the yield and ultimate strengths are slightly higher for the plate products.

Table 2. Tensile properties of alloy FA-129 plates

Product form	Temperature (°C)	Elongation (%)	Strength (MPa)	
			0.2% Yield	Ultimate
0.75-mm Sheet	25	15.12	426.1	894.3
0.75-mm Sheet	454	24.45	415.1	732.9
0.75-mm Sheet	600	43.97	375.1	445.4
12.5-mm Plate	25	7.78	433.0	644.8
12.5-mm Plate	454	15.7	341.4	696.5
12.5-mm Plate	600	63.0	406.2	455.2
16.5-mm Plate	454	22.7	335.1	730.5
16.5-mm Plate	600	41.6	418.9	476.1

Results of the Charpy-impact tests are shown in Fig. 1. The transition temperature, as measured at an energy level midway between the upper and lower shelves, was 308°C. The upper shelf energy was 37 J and the lower shelf energy is less than 5 J. The fracture surfaces showed a layered structure with many splits perpendicular to the fracture surface. Visual examination with a stereo microscope suggests that the fracture mode is all cleavage fracture, at least up to 200°C, with a small amount of ductile fracture present at 400°C. At 600 and 800°C, the fracture mode is essentially fully ductile.

Fig. 1. Absorbed energy versus temperature for full-size T-L specimen of alloy FA-129.

The results of the high-cycle fatigue tests at 600°C are plotted in Fig. 2(a) and show a difference in the fatigue response for differing plate thicknesses at all stresses. At higher stresses, the 16.5-mm plate has better fatigue resistance. Insufficient data are available at lower stresses to determine whether the data are converging to the same trend, but this would be expected. Furthermore, insufficient data exist to determine if a fatigue limit exists.

Extrapolation of the data suggests that the fatigue strength at 10^8 cycles should be greater than 120 MPa, which compares favorably to an estimated 150 MPa for 304 stainless steel.⁵

Fatigue tests were also conducted at 24 and 454°C. At RT, two tests were conducted with the maximum stress, $\sigma_{\max}$, equal to $0.95 \sigma_{ys}$, and no failures were observed in 10^7 cycles. At 454°C, no failures occurred when $\sigma_{\max}$ was below the 0.2% yield stress. The only three failures observed occurred when $\sigma_{\max}$ equalled 448, 467, and 490 MPa, all of which greatly exceed the average yield stress of the plates (338.3 MPa). These data are plotted in Fig. 2(b).

Fracture surfaces from several fatigue specimens were examined in a scanning electron microscope (SEM). At a temperature of 600°C, initiation always occurred at specimen surfaces. In at least one instance, initiation occurred at a iron-niobium

particle on the surface that had oxidized. At 454°C, several cases of subsurface initiation at Fe-Cr-Al particles were noted. At both 454 and 600°C, crack propagation is initially very fine as is shown in Fig. 3(a), but the scale is too small to allow determination of the crack growth mode. There is a rapid switch to cyclic cleavage that becomes rougher with increasing crack length, as evidenced in Fig. 3(b).

Of the original four creep specimens, only two yielded useful information. The results of the creep tests are shown in Figs. 4 and 5 along with data from the 0.75-mm sheet material. As Fig. 4 shows, the plate materials have lower creep rates, lower strains at failure, but higher rupture times than the sheet material, suggested improved creep resistance. However, as Fig. 5 shows, when plotted on a Larson-Miller plot, the difference is not profound. Knibloe and Wright⁶ have tested rod material of the FAL composition and found the results are similar to that for sheet material.

Fig. 2. Fatigue life as a function of maximum applied stress for alloy FA-129 plates at: (a) 600°C and (b) 454°C.

Discussion

The low ductility commonly observed at RT is the result of moisture-induced environmental embrittlement.¹ The recent improvements in RT ductility by thermomechanical processing are the result of minimizing the number of transverse grain boundaries, which slows hydrogen diffusion into the specimen interior.^{7,8} The decreased RT ductility observed in the plate materials is attributed to less plastic

deformation of the microstructure during fabrication and, hence, the presence of more retained grain boundaries for rapid hydrogen diffusion into the material.

Fig. 3(a). Area of slow initial crack growth, and (b) region of cyclic cleavage associated with rapid crack growth.

The other differences in the tensile properties are less notable with exception of the reduction in yield stress at 454°C. These differences are attributed to varying levels of plastic deformation imparted to the microstructures during fabrication. With decreasing amounts of reduction in thickness, the yield strength is reduced.

The results of the high-cycle fatigue tests are more difficult to interpret. At 600°C, typical behavior was observed and this will be considered first. In view of the fact that both the yield strength is higher in the 16.5-mm plate, it is not surprising that the fatigue resistance of this plate is better than that of the 12.7-mm plate. Fatigue damage will only occur when cyclic plastic strains are present,⁹ and for a given material, larger plastic strains result in reduced fatigue lives. Higher yield strengths reduce the amount of plasticity, and hence, increase the resistance to fatigue.

Fig. 4. Creep strain versus time for alloy FA-129 plate and sheet materials at 650°C and a stress of 34.5 MPa.

Fig. 5. Larson-Miller plot comparing creep rupture strengths of alloy FA-129 plate and sheet.

There is little environmental attack at either 454 or 600°C, available to contribute to crack initiation. Only a very thin oxide film, on the order of Angstroms thick¹⁰ and oxidized inclusions are visible on the specimen surfaces at 600°C. Yet, the density of oxidized inclusions is identical in both plates and the presence of these for nucleation sites cannot be used to explain the differences in observed fatigue lives. Furthermore, no signs of ratcheting (resulting from creep deformation) were observed on the sides of specimens using either optical or SEM techniques. The lack of creep strains is attributed to the lack of time for thermal processes to occur. Hence, differing creep responses of the two plates also cannot be used to explain a difference in fatigue properties.

At both RT and 454°C, no fatigue failures were observed at stresses below the measured 0.2% yield strength. This may suggest that the yield stress is sensitive to strain rate. At the much higher strain rates in the fatigue tests, the yield stress is undoubtedly higher, though the magnitude of the difference is not known. The high resistance of FA-129 to cracking has been observed by Stoloff and co-workers¹¹ while conducting fatigue crack growth tests on various allotropes of FA-129. They measured threshold values between 20 to 30 MPa√m, which are very high considering how brittle this material is.

As the creep data show, the plate materials have a better resistance to creep deformation. It is well documented that, in general, a large-grain microstructure will resist

creep better than an equivalent fine-grain microstructure. Hence, it is no surprise that the plates with their larger grain sizes have better creep resistance.

The Charpy-impact data, both the low-absorbed energies (3.5 to 37 J) and the high ductile-to-brittle transition temperature (308°C) are still limiting factors in the use of FA-129 for certain structural applications. Work needs to continue to make improvements in these two areas.

Conclusions

Data on the tensile properties of ductile Fe₃Al-based plates indicate a complex effect of plate thickness. Most notably, at RT in the thicker material, the ductility is cut in half and the ultimate strength is also reduced. At 600°C, the ductility and both the yield and ultimate strengths in the plates are improved over those in the sheet material. The fatigue data at 600°C suggest that the fatigue strength at 10⁸ cycles is similar to that for 304 stainless steel. At temperatures of 25 and 454°C, fatigue failure could not be induced at stress levels below the yield stress.

However, while the tensile, creep, and high-cycle fatigue properties of the plates suggest this alloy is suitable for engineering applications, the Charpy-impact data indicate that research is still necessary in the area of improved toughness.

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2.6 MICROALLOYED IRON ALUMINIDES

C. G. McKamey

INTRODUCTION

Development efforts at this laboratory have indicated that by controlling alloy chemistry and thermomechanical processing, environmental embrittlement of Fe₃Al-based alloys can be minimized.¹⁻³ Ambient temperature tensile ductilities of 10-20% and tensile yield strengths as high as 500 MPa can be achieved in alloy FA-129 (Fe-28Al-5Cr-0.5Nb-0.2C, at.%).²⁻³ However, the tensile strength of Fe₃Al-based alloys decreases dramatically above 600°C and creep-rupture strengths of the FA-129 type iron aluminides at temperatures of 550°C and above remain unsatisfactory.⁴ Additions of elements such as Ti, Mo, Zr, Hf, and Nb can improve high temperature strength, but at the expense of room temperature ductility.^{1,5-7}

Welding is another major area of concern in the development of iron-aluminide alloys for structural applications. The welding processes used must be capable of producing high quality weldments under field and shop conditions which are free of defects and have mechanical properties comparable to the base metal. Initial work on the weldability of iron aluminides has identified a propensity for cold-cracking and a possible degradation of the mechanical properties of the weldment in comparison to the base metal.⁸⁻⁹ Weldability of alloy FA-129 has been greatly improved by optimizing the welding process and parameters (e.g., using pre- and post-weld heat treatments).⁹ Studies have also shown that the weldability of iron aluminides is very sensitive to minor changes in composition of the base metal.^{9,10}

The objective of this task is to use macro- and microalloying techniques on alloy FA-129 to produce an Fe₃Al-based alloy with improved creep-rupture resistance and tensile strength to temperatures as high as 700°C. At the same time, the alloy should have adequate room temperature tensile ductility (>10%), good weldability and fabricability, and maintain the excellent corrosion resistance identified with iron aluminides. The scope of this task will include studying alloying effects on creep-rupture strength, high-temperature tensile strength, and weldability, and identifying positive and negative synergisms, which appear to play very important roles in all properties of this alloy system. This work is being coordinated with related efforts sponsored by the AIC Materials Program.

DISCUSSION OF CURRENT ACTIVITIES

During the last reporting period, composition FA-170 (Fe-28Al-5Cr-0.5Nb-0.4Mo-0.025Zr-0.05C, at.%) was chosen for further study because the preliminary data had indicated a potential for a good combination of properties.¹¹ During that same period, it became evident that the control of boron and carbon levels was necessary to maximize weldability.¹⁰ Also, previous studies had suggested that too much carbon can greatly degrade the creep-rupture properties,⁴ and that large niobium-based precipitates in FA-129 were providing initiation sites for premature fracture during Charpy impact tests.¹²

During this reporting period, five new alloys were prepared with nominal compositions based on FA-129 and FA-170. The purpose of making these alloys was to determine the level of boron, carbon, and niobium necessary to maximize ductility, strength, and weldability. The compositions chosen are listed in Table I. All alloys were prepared as 500-g ingots by arc-melting and drop-casting into chilled copper molds. Fabrication to 0.76-mm-thick sheet was accomplished by first forging 50% in two steps at 1000°C (to 15 mm thickness), then hot rolling at 800°C to 2.5 mm thickness and warm rolling at 650°C to the final thickness. After a stress relief heat treatment of 1 h at 700°C, flat tensile specimens (0.76 × 3.18 × 12.7 mm) were mechanically punched from the rolled sheet and were further annealed for 1 h at 750°C. Tensile tests were conducted at room temperature and 600°C in air at a strain rate of $3.3 \times 10^{-3} \text{ s}^{-1}$. Creep-rupture tests were conducted in air at 593°C and 207 MPa.

Table I shows the compositions produced in this reporting period, designated as FA-174 through -178. All contain Fe-28Al-5Cr-0.4Mo-0.025Zr but with various combinations of Nb, C, and B. In order to guarantee, for comparison purposes, that the starting microstructures were similar, part of ingot FA-170R was also rolled to sheet along with FA-174 to -178. Tests of alloys FA-170R, -174, and -175 show the effect of reducing the niobium content, while alloys FA-176, -177, and -178 show the combined effect of adding boron and reducing niobium. In order to promote creep resistance, the carbon level was kept at 0.05 at.%, which is much lower than the 0.2% in FA-129. Two tests of each alloy were conducted; the data from each test are listed in the tables that follow. Except for the creep tests of FA-174, the data for each alloy tested in both tension and creep-rupture were very reproducible, indicating good quality sheet and punched specimens without fracture-initiating edge flaws.

Table I also shows the tensile properties at room temperature and at 600°C. Average data for alloy FA-129 has been included for comparison purposes. Reducing the amount of

Table I. Compositions and tensile properties of FA-170-based iron aluminides.

Alloy ^a FA-	Nominal Composition (at.%)	RT ^b			600° C ^b		
		YS (MPa)	UTS (MPa)	Elong. (%)	YS (MPa)	UTS (MPa)	Elong. (%)
FA-129	Fe-28Al-5Cr-0.5Nb-0.2C	385	930	16	415	515	38
170R	Fe-28Al-5Cr-0.4Mo- 0.025Zr + 0.5Nb-0.05C	423	707	6.2	450	472	48.8
		419	738	7.2	461	501	52.7
174	+ 0.2Nb-0.05C	334	583	4.5	387	427	43.5
		339	573	4.5	393	434	47.9
175	+ 0.05C	356	663	7.2	394	437	44.0
		353	681	8.1	372	407	54.6
176	+ 0.5Nb-0.05C-0.005B	531	793	7.4	490	500	36.1
		545	815	7.8	499	508	43.1
177	+ 0.2Nb-0.05C-0.005B	363	630	6.3	396	430	40.9
		365	635	6.4	410	445	52.1
178	+ 0.05C-0.005B	360	692	7.9	387	421	52.4
		355	681	7.7	383	414	48.0

^aAll alloys were heat treated 1h at 700° C before punching specimens, then specimen were annealed for 1 h at 750° C.

^bTested in air at a strain rate of 3.3 × 10⁻³/s.

niobium below 0.5% tended to reduce significantly the tensile yield strength at both room temperature and 600°C. Adding boron to the composition containing 0.5% Nb resulted in an increase in yield strength at both room temperature and 600°C. Room temperature tensile ductilities of 6-8% were noted for all the alloy compositions except for FA-174 containing 0.2% Nb and no boron. In general the addition of 0.005% B increased room temperature ductilities slightly. As expected, ductilities at 600°C were good.

The creep-rupture tests at 593°C and 207 MPa (Table II) indicate that reducing niobium below about 0.5 at.% greatly reduces the creep life and increases the minimum creep rate (MCR). Also, at the 0.5% level of niobium, adding 0.005% B increased the creep-rupture life slightly, while boron added to alloys with 0.2% or no niobium gave no added

Table II. Creep-rupture properties of FA-170-based iron aluminides.

Alloy ^a	Creep at 593°C, 207 MPa			
	Test #	Life (h)	Elong. (%)	MCR (%/h)
FA-129		15-25	65-80	1-3
FA-170R	330	37.8	72.5	0.7
	331	29.0	64.3	0.8
FA-174	320	35.5	76.2	0.8
	327	9.4	67.8	2.9
FA-175	321	4.4	68.7	6.6
	326	3.6	68.6	8.0
FA-176	322	49.9	67.2	0.5
	325	50.8	56.6	0.4
FA-177	323	13.0	68.0	2.2
	328	14.8	68.5	1.8
FA-178	324	5.0	70.8	6.0
	329	4.6	66.8	6.5
^a All alloys were heat treated 1 h at 700°C before punching specimens, then specimens were annealed for 1 h at 750°C.				

benefit. The alloy with the best creep strength was the same one which had the best tensile strength, FA-176.

We have begun to investigate the effect of heat treatment on the creep rupture life. Table III shows the data to date on single tests. The results indicate that, at least with alloy composition FA-176, some improvement in creep life can be obtained by optimizing the microstructure. In general, the results of room temperature and

Table III. Effect of heat treatment on creep-rupture properties of FA-170-based alloys.

Alloy FA-	Heat treatment ^a	Creep at 593°C, 207 MPa			
		Test #	Life (h)	Elong. (%)	MCR (%/h)
174	1h/750°C	320	35.5	76.2	0.8
	1h/750°C+70 min/950°C	333	11.8	53.2	1.8
	24h/900°C	336	8.6	66.1	3.6
176	1h/750°C	325	50.8	56.6	0.4
	1h/750°C+70 min/950°C	332	107.6	49.1	0.1
	24h/900°C	334	59.9	63.4	0.3
^a All alloys were given 1h/700°C before punching tensile specimens.					

600°C tensile tests, as well as the 593°C creep results, indicate that alloy FA-176 has improved strength properties compared to alloys FA-170 and FA-129. We are presently beginning metallographic characterization of the microstructures with regards to grain size and precipitate size and composition. Also, weldability tests, including Sigmajig tests to determine sensitivity to fusion zone cracking,¹³ will be performed in the next reporting period.

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2.7 ENVIRONMENTAL EFFECTS ON IRON ALUMINIDES

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INTRODUCTION

The purpose of this task is to evaluate the corrosion properties of Fe_3Al -based alloys as they relate to fossil energy applications. A primary objective is to investigate the resistance of the alloys to mixed-oxidant (oxygen-sulfur) environments that arise in the combustion or gasification of coal. This includes the determination of effects of sulfur on oxidation kinetics and oxide microstructures, the effects of rare earth additions on sulfidation and oxidation resistance, and the mechanical behavior of reaction product scales in mixed-gas environments. Of additional concern are corrosion processes encountered when equipment is shut down for maintenance purposes, which may lead to attack by sulfur- and chlorine-containing acids. Also included in this task are studies of environmental effects on alloy ductility, especially effects on crack growth kinetics.

Laboratory tests of iron aluminide alloys in $\text{H}_2\text{S-H}_2\text{-H}_2\text{O-Ar}$ at 800°C have shown very low corrosion rates for alloys based on Fe_3Al and FeAl^1 . In more recent tests of binary Fe-Al alloys with lower aluminum contents, the corrosion rate in $\text{H}_2\text{S-H}_2\text{-H}_2\text{O-Ar}$ showed little change from that of the Fe_3Al alloy (28 at. % Al) down to a level of 18% aluminum.² However, the rate increased significantly when the aluminum content was lowered to 16%. Nevertheless, the corrosion rate at the 16% Al level was still markedly lower than for the Fe-Cr-Al class of alloys, nominally containing 20% Cr and 10% Al. A 20 at.% Al level was found² to be critical for sustained oxidation resistance of binary Fe-Al alloys in air at 900°C and above, although the addition of 5 at.% Cr at the 16 at.% Al level reduced the oxidation rate in air to that of alloys containing $\geq 20\%$ Al.

Further corrosion studies have been conducted to evaluate the potential of alloys containing 16 at. % Al for service in high temperature air and combustion gases and to demonstrate the resistance of Fe_3Al -based alloys to both high temperature oxidizing and sulfidizing environments. The oxidation behavior of both classes of alloys has been examined in isothermal and thermal cycling tests in air at temperatures up to 1150°C . The thermal cycling tests focused on the effects of reactive metal (zirconium) and rare

earth (yttrium) additions on scale adherence at 900°C and above. Test results for Fe₃Al-based alloys being exposed in an operating coal gasifier were received from the Coal Research Establishment (British Coal).

DISCUSSION OF CURRENT ACTIVITIES

Iron-aluminum alloys containing 16 at. % aluminum exhibit relatively high ductilities at room temperature and can be cold-worked to produce small cross-section product forms such as wire and thin sheet.³ Exposures of these alloys to air at 900-1000°C indicated that the addition of 5 at. % chromium significantly improved the oxidation resistance under isothermal conditions, while the addition of 0.1 at. % zirconium was highly beneficial to spalling resistance under thermal transients.² Further modifications to improve the mechanical properties and aqueous corrosion properties of the alloys have led to a reference composition (alloy FAP) containing 16% aluminum, 5% chromium, 1% molybdenum, 0.1% zirconium, and 0.1% carbon. Thermogravimetric tests of this latter alloy have been conducted in air at 900°C to compare its oxidation properties with those of Fe₃Al-based alloys containing 28% aluminum and with Fe-Cr-Al alloys containing 20% chromium and 10% aluminum. As shown in Fig. 1, the oxidation rate of the FAP alloy is similar to that of the higher aluminum and higher chromium

Fig. 1 Isothermal weight gains of FAP alloy (Fe-16%Al-5%Cr-1%Mo-0.1%Zr-0.1%C) in air at 900°C relative to Fe₃Al-based alloy (Fe-28%Al-5%Cr-0.1%Zr-0.05%B) and FeCrAl (Fe-9.1%Al-20.3%Cr-0.07%C).

compositions. The molybdenum addition does not appear to affect the air oxidation properties at 900°C - Fig. 2 shows little difference between the oxidation rate of the FAP alloy and an alloy of similar composition but without molybdenum. As discussed below, yttrium additions to the FAP composition are being evaluated with respect to oxide spalling resistance. However, as shown in Fig. 3, yttrium does not measurably affect the oxidation kinetics of the alloy under isothermal conditions at 900°C.

Fig. 2 Comparative oxidation rates of FAP (Fe-16%Al-5%Cr-1%Mo-0.1%Zr-0.1%C and similar alloy without molybdenum. (Tests conducted in dry air at 900°C.)

Experiments to evaluate the cyclic oxidation behavior of iron aluminides have been

Fig. 3 Effect of yttrium additions on air oxidation behavior of FAP alloy(Fe-16%Al-5%Cr-1%Mo-.1%Zr-.1%C) in isothermal tests at 900°C.

initiated. Specimens were exposed to heated laboratory air at 900, 1000, or 1150°C for incremental exposures of 24-72 h. At the completion of each elevated temperature period, the specimens were air quenched by direct removal from the furnaces. Measured weight changes are shown in Figs. 4-6. As already reported for isothermal conditions², the presence of chromium in an alloy with 16% aluminum (FAP) appears to have a beneficial effect on cyclic oxidation resistance (Figs. 4 and 5). The zirconium present in FAP may also be exerting a positive influence on spallation behavior.² Additions of yttrium (FAP-0.1Y and FAP-0.5Y) had little effect on the cyclic oxidation results at 900 and 1000°C (Figs. 4 and 5), but there was a substantial increase in weight gains for the FAP-0.5Y composition at 1150°C (Fig. 6). This susceptibility of the higher Y-containing alloy can be attributed to the rapid formation of Y_2O_3 . Fig. 6 also shows that, at 1150°C, the cyclic oxidation resistance of FAP-0.1Y is essentially the same as that for a Fe_3Al alloy (FAL). Further testing under more severe thermal cycling conditions will be required before a definitive comparison of the relative corrosion rates of 16 and 28 at.% Al alloys can be made.

Fig. 4 Weight changes of binary and FAP alloys in air at 900°C under thermal cycling conditions. Yttrium concentrations are in at. %.

Fe_3Al -based alloys have been supplied to the Coal Research Establishment (CRE) of the British Coal Corporation for testing in a 0.5 tonne/h, pressurized, air-blown gasifier located at Stoke Orchard. (The alloy compositions are similar to those tested previously⁴ in a non-pressurized gasifier at Stoke Orchard.) Test results have been received covering alloy performance during two initial runs in the pressurized gasifier. Both runs were

Fig. 5 Weight changes of binary and FAP alloys in air at 1000°C under thermal cycling conditions. Yttrium concentrations are in at. %.

Fig. 6 Weight changes of a Fe_3Al (FAL) and FAP alloys in air at 1150°C under thermal cycling conditions. Yttrium concentrations are in at. %.

essential shake-down tests of the gasifier and involved extended periods when the specimens were exposed to the ambient atmosphere at room temperature. All of the ferritic iron-based samples exposed during these two runs, including Fe_3Al specimens, showed heavy pitting, while the more highly alloyed austenitic materials were relatively unaffected. This suggests that the main source of corrosion in these two runs was sulfur-containing acids formed when moist air was admitted during the downtime periods. (The susceptibility of iron aluminides to corrosion by strong sulfur-containing acids has been documented by Buchanan and Kim.)⁵ The design pressure of the gasifier was initially set at 20 bar; however this pressure was not attainable in the unit as presently designed, so the actual operating pressure has been in the range 12-13 bar. This lower pressure resulted in gas temperatures that were lower than initially projected, and the exposure temperature of the samples was correspondingly reduced. The three test sections containing the Fe_3Al specimens were originally expected to reach 900, 700, and 500°C, respectively, but the temperatures actually realized were 700, 600, and 500°C. These latter temperatures are still considered to the test objectives, since the highest metal temperatures projected even for advanced gasifier concepts are generally below 700°C. The extent of corrosion of the Fe_3Al -based samples, as well as the other ferritic iron-based specimens, appeared essentially the same in all three test sections, a result that again suggests that downtime corrosion was the dominant corrosion process. A new set of Fe_3Al -based alloys, together with the FAP composition (16% aluminum) discussed above, has been supplied to CRE for testing in upcoming runs.

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2.8 ULTRAHIGH TEMPERATURE INTERMETALLIC ALLOYS

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INTRODUCTION

The thermal efficiency of energy conversion systems and heat engines increases by increasing their operation temperatures. At present, many advanced engines and energy systems have to operate at reduced temperatures because of limitation by structural materials whose strength decreases sharply above 800°C. Nickel-base superalloys, the state-of-the-art materials, can possibly be used at temperatures up to 1000°C on a short-term basis. Hence, there is a pressing need to develop new materials (particularly metallic ones) for use at temperatures above 900°C.

The intermetallic alloy, Cr_2Nb , with a C-15 cubic structure is attractive for high-temperature structural applications because of its high melting point (1700°C), relatively low density (7.7 g/cm³), and some potential resistance to oxidation at 1000°C. In addition, this intermetallic alloy has a wide range of composition homogeneity, indicating the possibility of improving its mechanical and metallurgical properties by alloying additions.

The major concern of this intermetallic alloy is its poor ductility and fracture toughness at ambient temperatures. The single-phased Cr_2Nb is very hard (DPH-800) and brittle at room temperature. Previous studies indicated that the mechanical properties of Cr_2Nb could be improved by introducing chromium-rich ductile particles through a precipitation reaction. Some two-phase alloys exhibited a compressive ductility of 4% at room temperature and a yield strength of over 700 MPa (~100 ksi) at 1000°C. These intermetallic alloys are substantially stronger than existing nickel-base superalloys at temperatures at least to 1250°C and offer strengths equivalent to some structural ceramics at these temperatures. Limited alloy development effort indicated that the strength and ductility of $\text{Cr}_2\text{Nb}/\text{Cr}(\text{Nb})$ alloys were further improved by alloy additions and microstructural control.

In addition to the concern with brittleness, the corrosion resistance of Cr-Nb alloys at high temperatures can be problematical due to possible spallation of multilayer scales, formation of chromium sulfides, and volatilization of chromia above 1100°C. Careful design of alloys to form more protective scales and/or the use of coatings offer opportunities to ameliorate the corrosion problems.

The results obtained so far indicate that the Cr₂Nb/Cr(Nb) alloys have an excellent strength for structural use at ultra-high temperatures (e.g. 1000-1300°C). Potential applications include hot components in advanced fossil energy conversion systems, advanced heat engines, and high-temperature cutting and grinding tools. The alloys, on the other hand, exhibited no tensile ductility at ambient temperatures. They showed some oxidation resistance at 1000°C, but long-term exposures resulted in spalling oxide scales from surfaces at this temperature. In this task, the mechanical and metallurgical properties of Cr₂Nb/Cr(Nb) alloys will be improved by control of alloy composition, impurity level, precipitation reaction, and material processing.

DISCUSSION OF CURRENT ACTIVITIES

The alloy development effort was initiated by preparation of high-purity Cr₂Nb/Cr(Nb) two-phase alloys with minimum cast defects. During the last reporting period, several high-purity Cr₂Nb/Cr(Nb) alloys were successfully prepared in a high-vacuum arc-melt furnace and cast into a preheated copper mold¹. This resulted in reduction in cast porosities and microcracks in the alloys. Fine Nb₂Cr particles (1 μm) precipitated out of the chromium-rich solid solution when heat treated at temperatures between 900 and 1300°C for 3 to 5 days. The coarsening of the precipitates at 1200°C reduces the microhardness from 649 to 502 DPH. No microcracks were observed around indents made at a load of 500 g, suggesting that the alloy is able to take plastic deformation without cracking.

During this reporting period, chemical analyses were made on a Cr₂Nb-base alloy (CN-43) prepared in a high vacuum using high-purity charge materials. The results indicated that the total interstitial (oxygen and carbon) in this alloy is only 170 wt ppm.

In comparison, the same type of alloys prepared previously contained as much as 700 to 1000 wt ppm.² Thus, the interstitial content in Cr₂Nb alloys can be effectively reduced by control of melting and casting processes.

In order to explore the hot fabricability of Cr₂Nb-base alloys, the alloy ingot (CN-43) was clad in Mo sheets and hot forged at 1100-1200°C in air. The alloy cracked quite badly after a reduction of 25%. This result indicates that the alloy had a limited hot fabricability at temperatures to 1200°C.

Specimens of CN-43 were examined by transmission electron microscopy (TEM). The specimens were prepared by ion milling because the alloy could not be successfully electropolished. Figure 1a shows a micrograph of the as-cast material and Fig. 1b shows the same alloy after an anneal for 5 d at 900°C and then 3 d at 1200°C. The eutectic structure (the darker phase in the micrographs) and chromium-rich patches are clearly seen in both conditions. In the as-cast specimen no further precipitations was observed. The Cr₂Nb phase was extensively internally twinned. Dislocation pileups were observed in the chromium-rich phase impinging on the eutectic phase. (In the figures, the white areas are multiple holes and are a result of the ion milling). In the annealed material, Fig. 1b, extensive secondary precipitation of the Cr₂Nb phase has occurred. No dislocations were observed in this material. These secondary precipitates were also internally twinned. Further analysis of these alloys is in progress.

Tensile specimens with a gage section of 3.2 mm diam x 6.4 mm length were prepared from the alloys CN-43 and 40. The specimens were first annealed for 5 d at 1000°C plus 3 d at 1200°C and then tensile tested at room temperature in air. Both alloys showed no appreciable plastic deformation and fractured prior to macroscopic yielding. In comparison, the same alloys exhibited an elongation of 7% in compression. These results suggest that the tensile ductility cannot be simply obtained for these alloys by reduction of interstitial contents alone.

Further studies will emphasize optimization of alloy composition and microstructure in order to achieve tensile ductilities. Metallographic examination reveals cleavage fracture as the major fracture mode in these alloys.

Fig. 1a is a TEM micrograph of the as-cast CN-43 material.

Fig. 1b shows the same alloy (CN-43) after an anneal for 5 d at 900°C and then 3 d at 1200°C.

During this reporting period, three series of new alloys were prepared with cast conditions listed in Table 1. The first series of the alloys CN-46 to 48 contain different levels of the element designated as "X", and the second series of the alloys CN-49 to 51 contain different levels of the element "Z." The third series of the alloys CN-52 to 55 were prepared based on modification of the alloy CN-43. The alloying element X apparently embrittles $\text{Cr}_2\text{Nb/Cr(Nb)}$ alloys and introduces macroscopic cracks during drop casting.

Table 1. Cast conditions of $\text{Cr}_2\text{Nb/Cr(Nb)}$ alloys

Alloy number	Cast condition
CN-46	Good cast ingot with a major crack at the central region
CN-47	Good cast ingot with a major crack at the central region
CN-48	Several macroscopic cracks
CN-49	Rough ingot surface, no macroscopic cracks
CN-50	Rough ingot surface, no macroscopic cracks
CN-51	Rough ingot surface, no macroscopic cracks
CN-52	Good cast ingot, no macroscopic cracks
CN-53	Good cast ingot with a major crack near the ingot bottom
CN-54	Excellent ingot condition, no cast defects
CN-55	Excellent ingot condition, no cast defects

The alloy ingots were sectioned and then annealed for 5 d at 900°C plus 3 d at 1000 to 1200°C. Metallographic examination reveals a mixture of two-phase structure as shown in Fig. 2. The primary chromium-rich patches (light contrast) were surrounded by an eutectic network (dark contrast). Fine precipitation of the Cr_2Nb phase is clearly observed in chromium-rich patches when specimens were annealed at 1000°C or above. The preparation of tensile and compressive specimens are in progress.

Fig. 2. Optical micrograph of CN-46 annealed for 5 d at 900°C plus 3 d at 1200°C; 625x.

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2.9 CORROSION PROTECTION OF ULTRAHIGH TEMPERATURE INTERMETALLIC ALLOYS

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INTRODUCTION

At present, any advances in operating temperatures and, hence, thermal efficiencies, of heat engines and energy systems are limited by strength or corrosion considerations. There is thus a pressing need to develop new materials (particularly metallic ones) that can be used in hostile environments at elevated temperatures. Laves-phase alloys based on Cr_2Nb may offer a possible solution to the materials problems associated with such high temperature deployment. In compression, Cr- Cr_2Nb alloys have been shown to be substantially stronger than conventional nickel-based superalloys at high-temperature while exhibiting some ductility.¹ However, much more development is needed to overcome poor ambient temperature ductility and low fracture toughness. In addition, there is some concern regarding the corrosion resistance of Cr-Nb intermetallic alloys in the temperature range of interest due to possible spallation of the multilayer scales that form on such materials, the rapid formation of chromium sulfides, and volatilization of chromia above about 1100°C.

The effort to develop ultrahigh temperature Cr-base intermetallic alloys that will not seriously degrade in high temperature corrosive environments consists of two interrelated parts: (1) improvements in the protective ability of the naturally formed scales and (2) the evaluation of a coating, or set of coatings, that would offer better corrosion resistance than the native oxide product. It is anticipated that while both scale improvements and coatings may be effective at the initial target temperatures (1000-1100°C), coatings or other surface treatments would have to be used at higher temperatures. The scale subtask involves close collaboration with Task ORNL-2(D) in the examination of the effects of alloying elements and microstructure on basic oxidation resistance at elevated temperatures. For the various developmental compositions, evaluation of scale protectiveness in terms of oxidation kinetics, composition, mechanical properties and spallation tendencies are conducted. The second part of the task involves the evaluation of possible coatings for use with the Cr-Nb alloys. This effort involves interactions with Ohio State University (Task OSU-3[A]), which will prepare coated specimens using halide-activated pack cementation and conduct some characterization of the as-coated materials. The work on the high temperature

corrosion of the coated alloys will be closely linked to the other subtask, that is, maximizing the corrosion resistance of the alloys within the limits of other properties, because any improvement in this regard increases the margin of protection provided by the coating.

DISCUSSION OF CURRENT ACTIVITIES

High Temperature Oxidation of Cr-Cr₂Nb Alloys

It was previously reported that the oxidation of Cr - 6 and - 12 at. % Nb alloys in air resulted in the formation of multilayer scales with an outer layer of chromia and inner products containing niobium.² The Cr - 12 at.% Nb binary alloy had significantly better oxidation resistance, in terms of overall weight gain and resistance to spallation, than one containing 6 at.%. This was thought to be associated with its decreased volume fraction of the Cr-rich phase, which appeared to preferentially react to form a distinctly different inner corrosion product.¹ Detailed analysis of a polished cross section of oxidized Cr - 12 at.% Nb by scanning electron microscopy (SEM) and energy-dispersive x-ray analysis has now revealed that the scales were composed of chromia at the gas-solid interface, underlying products containing chromium and niobium, and a porous inner layer that only formed on the Cr-rich phase (Fig. 1). (Such porosity was not obvious when only optical imaging was used.²) An as-oxidized (950°C) Cr-12% Nb specimen was fractured by bending and examined in cross section by SEM. Preliminary results indicated the presence of some voids along parts of the matrix-scale interface. This would indicate that the porosity observed in the inner layer found on the Cr-rich phase (Fig. 1) most likely formed during oxidation rather than from the loss of a brittle product during metallographic preparation of the cross section. The apparent porosity (possibly due to an agglomeration of voids caused by the outward flow of chromium cations³ or to impurities⁴) could be the reason for the previously-reported² tendency of the Cr-6% Nb alloy to be more susceptible to spallation because it contains a greater volume fraction of the Cr-rich phase on which this layer grows.

Fig. 1. Scanning electron micrograph of a polished cross section of Cr -12 at. % Nb exposed to air at 900°C for 168 h.

The results from the study of the isothermal oxidation of the binary Cr-Nb alloys indicated that increasing the volume fraction of the eutectic phase at the expense of the Cr-rich region by using niobium concentrations of at least 12 at. % appears to reduce scaling and spallation. . It was therefore appropriate to examine the effects of macro- and microalloying on the oxidation resistance of Cr-Cr₂Nb alloys containing 12 at.% Nb. The results for several such compositions are all summarized in Fig. 2, which also contains the data for the Cr -12% Nb binary alloy. There were no dramatic effects of alloying additions on the rate of scaling. Indeed, the binary alloy showed better isothermal oxidation behavior than any of the more highly alloyed compositions. Approximate parabolic rate constants (for times greater than 40 h) ranged from $5 - 16 \times 10^{-5} \text{ mg}^2/\text{cm}^4\cdot\text{s}$ for the other alloys compared to 2×10^{-5} for the binary composition.. However, no gross spallation during cooling after the isothermal exposures (as previously reported for Cr - 6% Nb ²) was noted for any of the alloys. Furthermore, there are some indications from preliminary cyclic oxidation experiments that alloying of the binary composition may offer some benefit in certain cases. Detailed characterization of alloying effects on oxidation resistance is currently underway.

Fig. 2. Weight gain versus time for air oxidation of Cr-Nb alloys at 950-965°C

Coatings

An approach and plan for the coatings subtask supporting the development of Cr-Nb alloys was prepared. The plan called for preliminary work on coating development to be done as part of the Ohio State University subcontract using Cr-12 at.% Nb as the baseline material. A decision on more appropriate compositions for specific coatings development will then be made at the end of FY93 based on consideration of progress made in the alloy design, corrosion, and Ohio State subtasks. If warranted, evaluation of coatings performance will be initiated as part of the ORNL corrosion work in FY94.

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2.10 INVESTIGATION OF AUSTENITIC ALLOYS FOR ADVANCED HEAT RECOVERY AND HOT-GAS CLEANUP SYSTEMS

R. W. Swindeman

INTRODUCTION

The purpose of this task is to provide materials technology to aide in the design and construction of advanced components for use in the fossil fuels power industry in the United States. In the near term, life-extension with improved flexibility and reliability in existing plants is an issue of primary concern, and alloys to meet these performance requirements are being investigated. In the longer range, improved efficiency will be needed, and this will come about by the development of advanced steam cycle concepts and combined cycle power plants. Here, the performance requirements for structural materials vary significantly from one application to the next, and the limiting performance criterion may be corrosion resistance, fabricability, or strength. Generally, the materials performance requirements become more demanding with increased service temperature, so a range of materials are being examined.

DISCUSSION OF CURRENT ACTIVITIES

Alloys for Service to 600° C

Materials problems associated with the life-extension of existing pulverized coal power plants include erosion/corrosion of waterwall tubing, corrosion and stress-rupture of superheater tubing, fatigue and cracking in headers, stress-rupture and thermal stress-induced cracking of main steamline piping and reheat piping, similar and dissimilar metal weld failures, and cracking in turbine casings. An understanding of the problems in existing plants will provide guidance in the selection of materials for advanced plants, so that the "mistakes" will not be repeated.

For those plants that have had failures in type 304 or 316 stainless steel piping, there exist several options. One option is the replacement of austenitic alloys by high strength 9Cr martensitic steels. This has been the selection when significant power cycling is expected. Another option is the selection of improved grades of molybdenum-bearing stainless steels. These include types 316N, 316LN, and modifications of type 316L stainless steel that are of interest in Europe and Asia (Ref. 1 and 2). In cooperation with South Carolina Electric and Gas Company and Toronado Energy Consultants, type 316N stainless steel was examined (Ref. 3) and found to possess excellent strength and ductility properties after long exposure times. Joints in piping were found to be a problem, but the use of controlled residual element (CRE) 16-8-2 stainless steel filler metal was found to be a good match for type 316N stainless steel. Most of this work has been completed and only a few tests remain in progress. Many of the advanced steam cycle plants are expected to have Gr 91 components. Super heater tubing, headers, and main steamline piping are potential applications for the steel. Gr 91 was originally developed for service about 540°C and is performing quite well at this temperature. The use of Gr91 in advanced steam cycle components operating at 600°C, however, requires more information about the long-time strength. Work has been undertaken at ORNL in co-operation with The Metals Properties Council to clarify the issue. Stress-rupture testing included heats of various tensile strengths, nitrogen levels, and product sizes. Tests were performed at higher temperatures and lower stresses. Data produced in Europe and Japan were also collected and the final stress-rupture database now exceeds 1000 tests. These data were analyzed in several different ways, and it was determined that a small reduction (approximately 5%) in the allowable stresses around 600°C would be needed to assure that European steels would not cause problems when used for construction conforming ASME Code rules. Action on this issue will be taken by appropriate Code groups. Work on other problems related to the use of martensitic steels in cyclic service will continue. A key issue relates to methods by which one can calculate damage due to transients related to power cycling. Both aging and straining may produce softening in Gr 91 steel. Higher creep rates and shorter rupture lives result. To estimate remaining life, several approaches are being examined. These include life-fraction summation by use of parametric analyses, isostress testing, and utilization of the Monkman-Grant correlation. An example of the Monkman-Grant correlation for as-tempered specimens is shown in Fig. 1a. The trend line has been re-drawn in Fig. 1b, where

it may be compared to data produced on two heats of aged steel. The aged data fall on the same trend line as the unexposed material, indicating that life in service-exposed material may be estimated once the minimum creep rate of exposed material is determined.

Fig. 1. Monkman-Grant plots for Gr 91 steel (a) as tempered, (b) after long time aging.

Alloys for Service to 700°C

Advanced steam cycle plants will require superheater tubing to operate at temperatures approaching 700°C and at pressures in excess of 30 MPa. Currently, the prime candidate alloys include fine-grained type 347 stainless steel, clad Esshete 1250, and niobium-nitrogen modified type 310 stainless steel (310HCbN). A high-temperature, ultrafine precipitate strengthened (HT-UPS) steel developed by Maziasz (Ref. 4) was examined for this application, and the evaluation of the steel in the bare and clad conditions has been virtually completed. One test, still in progress after 60,000 h at 700°C demonstrates the remarkable stability of the steel. See Fig. 2a. A modified alloy 800 material was also developed by Maziasz for advanced steam cycle use (Ref. 4). Research on this material has been continued, but the application has changed from superheater tubing to bellows and support structures in the petrochemical process industry. Testing of this material has also reached long times, and ductilities have far exceeded those observed in alloy 800HT. A curve produced at 650°C is shown in Fig. 2b.

Fig. 2. Long time creep curves for HT-UPS steels (a) heat CE3 in test for 60,000 h at 700°C and 100 MPa (b) heat AX2 that ruptured after 48,654 h at 650°C and 170 MPa.

The weldability of all of the advanced alloys is of concern, and efforts were undertaken in conjunction with the University of Tennessee to evaluate available filler metals. The CRE 16-8-2 stainless steel filler metal, mentioned earlier in connection with its use for type 316N stainless steel, continues to be a good match for the HT-UPS steel. The stress-rupture testing of weldments is now approaching 30,000 h. For corrosion resistance and strength, alloy 556 is being investigated, and data on weldments has been gathered for times approaching 20,000 h.

Alloys for Service above 700°C

Components that may operate above 700°C include tubing for advanced steam topping cycles, tubing for heat recovery in fluidized bed combustion and gasifier combined cycles, and support plates and ducting in hot-gas cleanup vessels. Some components will be pressure bearing and will require Code approved materials. Others structures will not require Code-approved materials, although Code-approved materials are often preferred. A variety of old and new alloys are being considered (Ref. 6).

The possibility of extending the use temperature of the modified alloy 800 was considered, but a few exploratory tests above 760°C indicated that modified alloy 800 had no significant strength or ductility advantage over alloy 800HT. A possible exception is HR120® (registered trademark of Haynes Alloys), but testing has not begun on this material. Additional studies of alloy 800HT were performed at temperatures in the range 760 to 980°C to assist the Pressure Vessel Research Council to develop criteria for setting allowable stresses for temperatures above 816°C. This work has been completed. Other materials being evaluated include HR-160®, RA333®, and type 310HCbN stainless steel. Modified type 310 stainless steels, such as 310HCbN, appear to be an improvement over types 310S and 310Cb stainless steels, but have not achieved the strength capability of alloy 800HT. A comparison of typical creep curves is provided in Fig. 3 for data collected at

Fig. 3. Comparison of creep curves for modified 310 stainless steels with type 310 stainless steel at 871°C and 35 MPa.

871°C and 35 MPa. Here, it may be seen that creep rates are lower and lives are longer for the modified 310 stainless steels. It is expected that coarse grain steels will have better creep strength at 871°C, but some optimization of strength may be possible for alloys that will be used in the temperature range of 760 to 816°C. Testing is underway to extend rupture data to 10,000 h. A comparison of creep rate data is possible, however, as shown in Fig. 4. This is a plot of log stress for a minimum creep rate of 0.001%/h versus temperature. Comparisons are made between type 310H stainless steel (Ref. 7), alloy 800HT (Ref. 8) and modified 310 stainless steel. Based on a small data base, it appears that the modified 310 stainless steel has approximately twice the strength of type 310 stainless steel and is superior to alloy 800 for temperatures below 815°C.

Fig. 4. Comparison of the creep strength of modified 310 stainless steel with 310 stainless steel and alloy 800 HT.

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2.11 ELECTROSLAG CASTING TECHNOLOGY TRANSFER

V. K. Sikka

INTRODUCTION

The objective of this activity is to transfer the electroslag casting technology of iron aluminides to industry. The specific objectives include: (1) conduct survey of companies with electroslag casting and electroslag remelting equipment, (2) offer to transfer electroslag casting technology to three selected companies, (3) produce electroslag remelted slabs (5,000 to 10,000 lb) of iron aluminide at an industrial organization, (4) produce electroslag remelted rounds (5,000 lb each) of iron aluminide at an industrial organization, (5) process rounds and slabs into bar and plate at an industrial organization, (6) evaluate the electroslag cast and processed product of iron aluminide at ORNL, and (7) prepare a report of technology transfer and material performance activities.

DISCUSSION OF CURRENT ACTIVITIES

As a part of technology transfer, three pieces of 9-in.-thick plate of iron-aluminide alloy FA-129 were shipped to Allegheny Ludlum Corporation (Brackenridge, Pennsylvania) during the last reporting period. Allegheny plans to process the slab into plates and sheets of various thicknesses using well established commercial practices. Work is still under way, and the results will become available during the next reporting period.

2.12 COAL CONVERSION AND UTILIZATION PLANT SUPPORT SERVICES

James R. Keiser and Tommy J. Henson

INTRODUCTION

The purpose of this project is to provide support to the staffs of the DOE Energy Technology Centers and of operating coal conversion and utilization facilities in the areas of materials selection, evaluation, testing, on-site examinations, and analysis of failed components. In addition to providing a valuable service to operators of these facilities, this activity assures that the Fossil Energy Materials Program staff are kept abreast of the materials problems that are being encountered in actual operating experience and provides input to the ongoing assessment of materials research needs.

DISCUSSION OF CURRENT ACTIVITIES

A 1987 visit to Japan by Oak Ridge National Laboratory (ORNL) and Department of Energy (DOE) staff members was the first in a series of exchange meetings to share information on materials for coal liquefaction. During this visit, discussions were conducted that contributed to a formal agreement between the Japanese New Energy and Industrial Technology Development Organization (AIST/NEDO) and the United States Department of Energy. One feature of this agreement is a plan for an exchange of corrosion samples such that samples supplied by Japanese researchers would be exposed in a U.S. coal liquefaction plant and U.S.-supplied samples would be exposed in a Japanese liquefaction facility. Following the exposure of such samples, examination of each set of samples would be conducted by researchers in the host country.

The exchange of corrosion samples was first implemented in August and September 1991, and exposure of samples took place during the last few months of 1991 and the first months of 1992. The fourteen samples supplied by Japan and exposed in the U.S. liquefaction plant were examined at Oak Ridge National Laboratory.

Fourteen samples provided by Mitsui SRC Development Co., Ltd. were exposed for 2497 hours through nozzles near the top of the two liquefaction reactors at the Wilsonville,

Alabama, Coal Liquefaction R&D Facility. The samples were exposed during the entirety of run 263, which was the final run conducted at this facility. Examination of the samples provided the following information.

1. Both sets of samples with aluminum coatings had significantly greater weight losses than any of the other samples. The hot-dipped aluminum coating spalled in many areas leaving a layer rich in aluminum and iron.

2. The alumina plasma-sprayed sample had an inner chromium-nickel layer, and there was a significant accumulation of metal sulfides between this inner layer and the base metal.

3. The titanium nitride CVD-coated sample had an adherent, continuous coating and a very low corrosion rate. Chlorine, likely a result of the CVD process, was present in the coating.

4. The three uncoated metals, 2.25 Cr-1 Mo, 9 Cr-1 Mo, and the material labeled as 321 stainless steel, had low calculated corrosion rates and showed no evidence of significant corrosion in the microscopic or microprobe examinations.

2.13 CLEAN COAL PROGRAM MATERIALS SUPPORT

J. R. Keiser and J. R. Mayotte

During the last six months, assistance was requested by Southern Company Services to address a cracking problem in metallic injector nozzles at one of their coal-fired power plants. The particular problem was occurring in large, alloy steel nozzles used for injecting powdered coal and air into a low NO_x unit at the Plant Hammond facility near Rome, Georgia.

Two Oak Ridge National Laboratory (ORNL) staff members visited the facility the latter part of May during a time when the particular unit was out of service so that the ORNL staff members could see examples of this cracking and could see the steam generating unit in which the injectors are located. Of the 16 nozzles on each of two walls (arranged in 4 rows with 4 in each row), several were observed to have cracks. A typical low NO_x injector nozzle is approximately 75 cm across, and it is divided into several regions through which mixtures of air and coal are injected. The compositions of the mixtures are varied from one region to another in order to promote the lowered production of nitrogen oxides. An example of cracking of a nozzle that is still in service is shown in Figure 1.

Figure 1. Photograph of crack in injector nozzle of low NO_x coal-fired steam generating unit.

Subsequent to the visit by ORNL staff members to Plant Hammond, another injector failed. It was decided to ship this entire injector to ORNL for examination. The portion of the injector shipped to ORNL is shown in Figure 2, and one of the cracked regions can be seen in Figure 3. There were several areas where cracking had occurred in this nozzle, and all of them were removed for microstructural examination. At the conclusion of this reporting period, the examination was still in progress. Results will be reported when the examination has been completed.

Figure 2. Injector nozzle from the Plant Hammond low NO_x steam generating facility. The center portion of the nozzle has been removed, and damage caused by a fire is visible on the inner portion of the nozzle.

Figure 3. Inner ring of nozzle showing two intentionally cut notches on either side of the photograph, and a crack in the inner ring about midway between the two notches.

3. ENVIRONMENTAL ANALYSIS SUPPORT

C. R. Boston and R. L. Miller

Activities in environmental analysis support included assistance to the Morgantown and Pittsburgh Energy Technology Centers (METC and PETC) in reviewing and preparing documents required by the National Environmental Policy Act (NEPA) for several projects selected for the Clean Coal Technology Program. A key activity was the preparation for PETC of a draft Environmental Impact Statement (EIS) for the Healy Clean Coal Project in Healy, Alaska. This work is notable because it is the first site-specific EIS prepared for the Clean Coal Technology Program. In addition, work began for METC on the preparation of a preliminary draft EIS for the Des Moines Energy Center Repowering Project in Pleasant Hill, Iowa. Another important activity was the preparation of a preliminary draft Programmatic Environmental Assessment (PEA) for DOE's Oil Research Program. Finally, ORNL is assisting DOE/FE in the preparation of an Action Description Memorandum for the continued funding of the fossil research and development program directed by METC.

3.1 ENVIRONMENTAL SUPPORT TO THE CLEAN COAL PROGRAM

R. L. Miller

Work during this six-month period focused on the preparation for DOE's Pittsburgh Energy Technology Center (PETC) of a draft Environmental Impact Statement (EIS) for the Healy Clean Coal Project (HCCP). The project, proposed by the Alaska Industrial Development and Export Authority and selected by DOE in the third solicitation of the Clean Coal Technology Program, would be located in Healy, Alaska, about 4 miles north of the nearest border of Denali National Park and Preserve (DNPP). The proposed project is a new 50 megawatt coal-fired power generating facility that would be collocated with an existing 25 megawatt conventional pulverized-coal unit owned and operated by Golden Valley Electric Association. The new facility would feature integration of advanced combustion and flue gas cleanup technologies to reduce emissions of SO₂ and NO_x. The EIS is notable because it is the first site-specific EIS prepared for the Clean Coal Technology Program.

Impacts to air quality, surface water, groundwater, and ecological and socioeconomic resources from construction and operation of the HCCP were evaluated and preliminary results indicate that, for most resource areas, the impacts are not expected to be major. Tentative findings for areas of potential concern are summarized below. Of primary concern, as predicted by analyses based on computer models, is the degradation of air quality and visibility expected in portions of DNPP because of HCCP operation. Also, during the winter, the length of ice-free water in the Nenana River downstream of the HCCP is expected to increase because of the HCCP's thermal discharge of once-through cooling water. Consequently, ice bridge formation on the river at the village of Ferry, located about 10 miles downstream, may be affected (the ice bridge is used by residents to transport supplies across the river during winter). Finally, socioeconomic impacts are expected during construction and operation of the HCCP, particularly in the areas of housing, education, traffic, police and fire protection, and medical services.

Work also began on the preparation for DOE's Morgantown Energy Technology Center (METC) of a preliminary draft EIS for the Des Moines Energy Center (DMEC) Pressurized Circulating Fluidized Bed (PCFB) Repowering Project. The DMEC project

would power a new gas turbine and repower an existing steam turbine by replacing an existing boiler with a new PCFB combustor at the DMEC site in Pleasant Hill, Iowa, near Des Moines, Iowa. Proposed by Dairyland Power Cooperative and Midwest Power and selected by DOE in the third solicitation of the Clean Coal Technology Program, the project would generate approximately 80 megawatts of electricity. The project, the world's first large-scale demonstration of PCFB technology, is expected to produce valuable data to assess plant reliability and performance that could lead to widespread commercial application of PCFB technology. In June 1992, DOE published a Notice of Intent to prepare the EIS, and a public scoping meeting was held in July 1992. Subsequently, ORNL staff members have been preparing an Implementation Plan for the EIS and have started work on the preliminary draft EIS. Potential resource areas of concern associated with the project include air quality, water resources, wetlands, and ecological resources.

Additional activities included reviews of Environmental Information Volumes prepared by the project participants for Clean Coal projects. The final Environmental Information Volumes are used by ORNL as a resource in preparing environmental documentation such as EIS's or Environmental Assessments (EA's) for the projects.

3.2 ACTION DESCRIPTION MEMORANDUM FOR METC R&D PROGRAM

C. R. Boston

ORNL provided technical assistance to DOE/FE in the preparation of an Action Description Memorandum (ADM) for the continued funding of the fossil R&D program that is currently directed by METC. The METC R&D program consists of over 300 individual projects that fall into eight program areas. The ADM addressed the potential impacts of the overall R&D program rather than impacts of individual projects since the latter are addressed individually under DOE's NEPA Implementation Procedures (10 CFR 1021). In general, the individual projects are relatively small (median funding level of \$1 million), short-term (median duration of about three years), and widely dispersed geographically. The vast majority of projects are conducted in existing facilities and produce only minor changes in the environmental impacts of those facilities. Potential programmatic issues identified in the ADM included: (1) cumulative impacts resulting from multiple projects occurring in the same time frame and at the same or nearby locations; (2) impacts from and enhanced prospects for eventual commercialization of concepts developed under the R&D program; (3) stimulated interest in the use of fossil relative to non-fossil technologies; and (4) concerns regarding NEPA compliance. The ADM will be the basis for DOE's decision on the appropriate level (Categorical Exclusion, Environmental Assessment or Environmental Impact Statement) of NEPA documentation for the R&D program.

3.3 OIL RESEARCH PROGRAM ENVIRONMENTAL SUPPORT

R. L. Miller

Work during this six-month period resulted in the completion of a preliminary draft Programmatic Environmental Assessment (PEA) for DOE's Oil Research Program. The PEA focuses on evaluating the overall environmental consequences of widespread commercialization of advanced oil recovery (AOR) technologies by the petroleum industry in the year 2010, emanating from the successful demonstration of cost-shared projects resulting from DOE solicitations. Although regional differences in impacts frequently are difficult to evaluate because of large variations in the affected environmental resources within individual regions, many expected regional differences in impacts are characterized in the PEA.

Overall, the analyses found that the level of environmental impacts resulting from widespread commercialization of AOR technologies, in which U.S. oil production would increase by about 4% over present levels, would be very similar to the level of existing impacts. In comparison with the proposed action, impacts would generally be less at existing oil fields with abandoned wells under the no-action alternative, in which oil production would decrease by about 40% in the year 2010 compared with present levels. However, this decrease in impacts would be offset by an increase in impacts in other geographical areas resulting from additional ocean tanker traffic transporting imported oil. In general, the types of impacts associated with the proposed action also were found to be similar to existing impacts. Some chemicals used and wastes generated by AOR technologies, particularly chemical flood and biotechnology, differ from those of conventional and secondary oil recovery efforts. Regulatory experience developed for existing oil recovery operations can be used to assist in minimizing potential impacts.

3.4 SUPPORT TO THE WILSONVILLE COAL LIQUEFACTION R&D FACILITY

F.G. Gardner, P.M. Kearl, and N.E. Korte

INTRODUCTION

The purpose of this task is to support the Pittsburgh Energy Technology Center (PETC) and their prime contractor Southern Company Services, Inc. in satisfying National Environmental Policy Act (NEPA) requirements for the retirement and dismantling of the Advanced Coal Liquefaction Research and Development (ACLR&D) Facility in Wilsonville, Alabama. Oak Ridge National Laboratory (ORNL) is assisting PETC in obtaining a sufficient waste characterization and hydrogeologic assessment to satisfy the current requirements of NEPA.

The primary field tasks involve the establishment of a hydrogeologic monitoring system and a characterization of potential waste areas. Information from these activities will be incorporated into an Environmental Assessment (EA) that will describe the potential impacts resulting from the decommissioning of the site.

DISCUSSION OF CURRENT ACTIVITIES

The initial activities conducted during fiscal 1992 were the preparation of a draft request for a categorical exclusion for the proposed fieldwork. PETC submitted this document to DOE headquarters at which time permission to proceed with the fieldwork was granted.

The initial field activities included a small field program to determine whether environmental contamination existed at the site. This initial program determined that a "construction waste landfill" near the ACLR&D facility contained buried drums. The drums were filled with organic waste. It has subsequently been determined that these drums are not DOE responsibility having been buried by contractors prior to DOE's involvement with the site. Further work at this location, therefore, is not planned by CRNL at this time.

The initial field program also discovered soil and groundwater contamination beneath and downgradient of the ACLR&D facility. Contamination was not limited to petroleum wastes but included the chlorinated solvent tetrachloroethene.

The hydrogeology at the site is quite complex consisting of relatively impermeable surface material underlain in some locations by karst. Because there has been apparently numerous episodes of folding and faulting, more work is necessary to adequately describe the site hydrogeology. Moreover, the full extent of soil and groundwater contamination have not been delineated both because more wells are needed to assess the downgradient extent of contaminated groundwater and because of access limitations due to the presence of the equipment remaining on site.

A series of field activities are planned to complete the site characterization. More soil sampling will be performed as equipment removal provides access to additional areas requiring characterization. Additional downgradient monitoring wells are also planned.

Characterization of the hydrogeologic system will continue with the installation of additional coreholes and the performance of a seismic survey. These data are needed to determine the extent of the connection between the highly contaminated shallow groundwater and the limestone aquifer underlying the site. It should be noted that the contamination in the surface unit, of itself, is only a minor threat to the environment because the unit is not very permeable. Indeed, the water level does not recover in several of the wells for hours or days following purging. On the other hand, potential contamination in the limestone aquifer would be a serious concern because it is a productive formation. Fortunately, while there are water supply wells utilizing the deeper aquifers in this area, none of the supply wells are near the Wilsonville site. Hence, there is no immediate possibility of human or environmental exposure.

The additional fieldwork that is required is expected to be completed during the first half of fiscal 1993. Submittal of the draft EA to PETC will follow within several months of the completed fieldwork.

3.5 WEST SHARRARD GULCH SHALE PILE AND DRUMS

C.A. Muhr

INTRODUCTION

The purpose of this task was to support the Department of Energy's (DOE's) Office of Naval Petroleum and Oil Shale Reserves in the preparation of a Preliminary Assessment (PA) under CERCLA (Comprehensive Environmental Response Compensation and Liability Act). A request by the Environmental Protection Agency (EPA) under the auspices of CERCLA led to the need for the task. The project site is located near Rifle, Colorado. Oak Ridge National Laboratory - Grand Junction, Colorado (ORNL-GJ) had performed previous work in the area for the Department of the Navy and, therefore, had personnel familiar with the site.

DISCUSSION OF CURRENT ACTIVITIES

The primary tasks to be accomplished were the following:

- A reconnaissance of the shale pile and drums that remain in West Sharrard Gulch.
- A reconnaissance of the surrounding area (up to 15 miles) to determine receptors for contamination potentially found in West Sharrard Gulch.
- A review of previous field work, analytical data, and site reports.
- Preparation of the pathway scoresheets and a summary report sufficient to fulfill EPA's requirements as defined in "Guidance for Performing Preliminary Assessments Under CERCLA".

The above tasks were performed in May and June of 1992. Site reconnaissance indicated that probable human exposures from the site were slight -- the nearest residence being approximately five miles away. Moreover, the piles were stable and did not appear to be subject to significant wind erosion.

The review of recent sampling data demonstrated that the rate with which contaminants are leaching from the pile has either ceased or slowed significantly. Drainage from the site, either by surface or groundwater, will enter the Colorado River system.

However, the small size of the site in comparison to the much larger Colorado River Valley alluvium or the Colorado River itself suggest that there are no significant potential impacts to the surrounding environment. Finally, the study noted that the site is relatively open to intrusion, although the remoteness of the site and the lack of vegetation are likely to limit the exposure to both human and animal receptors. The final report was provided to DOE in June of 1992.

4. COAL CONVERSION DEVELOPMENT

C. D. Scott

Fundamental bioprocessing research has concentrated on the use of biocatalysts in organic media and on advanced bioreactor systems. Coal conversion research has continued on the biological solubilization of coal using chemically-modified enzymes in organic solvents. Activities are also continuing on the study of mild gasification of coal.

4.1 BIOLOGICAL CATALYST IN ORGANIC MEDIA

C. D. Scott

Several potential coal bioprocessing concepts may utilize an organic solvent and/or produce liquid organic products. In either case, it will be necessary for the biological catalyst to be active in contact with or within the organic media. The major technical challenge associated with the use of biocatalysts in organic solvents is the maintenance of catalyst integrity and, in the case of intact cells, the viability of the microbial structure. Microorganisms or active biological fractions (e.g., enzymes) cannot normally maintain activity in an organic media; however, it may be possible to use microorganisms in a controlled aqueous environment that can be dispersed into the organic. Extracted enzymes may even be chemically modified so that they will dissolve in the organic media while maintaining catalytic activity.

ORNL RESEARCH ON ENZYME SOLUBILIZATION IN ORGANIC MEDIA

Two chemical agents are being investigated to chemically modify enzymes and other proteinaceous material for enhancing solubilization in organic solvents.

Dinitrofluorobenzene

Work has continued on the use of 2,4 dinitrofluorobenzene (DNFB) as the reagent to add dinitrophenyl (DNP) groups to enzymes. As before, two model enzymes/proteins are being used, hydrogenase isolated from *Proteus vulgaris* with techniques previously described and cytochrome c obtained from Sigma Chemical Co. Additional tests have been made to determine optimum reaction conditions for this chemical modification with the aim of maximizing solubilization of the protein in organic solvents while maintaining maximum catalytic activity.

It was found that a relatively mild set of conditions are required for the hydrogenase to achieve both the above goals. That is, the reaction was carried out for 30 min at 30°C in a 50% water-ethanol mixture that contained 0.66 vol% DNFB buffered to a pH of 8.5 with a 7 mM phosphate buffer. Under these conditions, about 40% of the original enzyme activity was maintained while the solubilization in benzene was in excess of 2 mg/mL.

Since cytochrome c is primarily used as a reducing agent rather than a biocatalyst, it was found that a much more severe chemical conversion could be used without significantly affecting its reducing properties. For that proteinaceous material, similar reaction conditions were used except for 1.3% DNFB and an a reaction time of 1 h. Maximum solubilization in benzene was in excess of 3 mg/mL.

Fatty Acid Anhydrides

As suggested in earlier reports, it is know that some enzymes are bound to cell membranes by linkages to biochemicals such as lipids. This results in a relatively hydrophobic environment that may be useful for enhancing solubility in organic liquids. It was previously shown in this program that some of these membrane-bound materials could be directly dissolved in benzene without prior chemical treatment. However, the solubilities were relatively low.

The fatty acids are major constituents of lipids and the longer carbon chain members ($>C_6$) of this class are relatively hydrophobic. On this basis, it was decided to investigate the possibility of chemically attaching these acid residues to enzymes. Acetic anhydride is know to interact with amino groups in proteins resulting in the acylation of the protein by linking the acetate with the amine while producing acetic acid:¹

Unfortunately, the acetate group is not very hydrophobic, therefore, it is not expected to enhance solubilization in nonpolar organic solvents. Since the longer-chain fatty acids are progressively more hydrophobic as the chain length increases, it was decided to investigate

the attachment of such fatty acid residues to enzymes by using the appropriate acid aldehyde. First, acetic anhydride was used as the modifying reagent in order to gain experience with these types of interactions. A modification of the method of Smyth² was utilized. Cytochrome c (0.5 mg/mL) from Sigma Chemical Co. was dissolved in water and 5 mL of the solution was contacted with 2.5-, 10-, or 20-mL of acetic anhydride with stirring at 30°C. The reaction proceeded for 15 min and the pH was maintained at approximately 6 by the addition of small increments of 0.1N NaOH. During the chemical modification, the major spectrophotometric peak at ~410 nm was shifted to a lower wavelength, the peak at ~280 nm was significantly decreased, and a new peak at ~620 nm appeared. These effects were progressively more significant as the amount of the anhydride was increased, thus, potentially providing a means of following the course of the reaction. There was no indication that the resulting acylated protein had an increased solubilization in benzene.

Although this study is in the very preliminary phase, some results have also been obtained with the use of caproic anhydride and caprylic anhydride (C₆ and C₈ fatty acids respectively). These two acid anhydrides are sparingly soluble in water so two approaches are being studied for interaction with proteins: (1) a water-ethanol solution is used to increase the anhydride solubilization while maintaining the protein in solution (In some cases up to 75% ethanol can be used while maintaining the enzyme in solution.); and (2) an immiscible organic liquid such as benzene is used in which the anhydride is soluble but which must be dispersed into the aqueous phase containing the enzyme.

A 50% solution of 95% ethanol in water containing 2 mg/mL cytochrome c was contacted with caproic anhydride by the addition of 80mL of the anhydride to 5mL of the cytochrome solution. The reaction was carried out with stirring at 30°C for 30 min and the pH was maintained between 7.0 and 8.0 by periodic additions of 0.1N NaOH. The spectrophotometric analysis of the resulting product indicated the same types of changes noted with the acetic anhydride; therefore, it was concluded that acylation did occur. The solution was evaporated and the residue was air-dried and then contacted with benzene at 30°C for 30 min. Subsequent spectral analysis of the benzene solution indicated that approximately .04 mg/mL of the modified protein was dissolved in the benzene. Without

chemical modification, there is no detectable solubilization (less than .005 mg/mL) of this protein in benzene.

A test was also made with caprylic anhydride. In this case, a 75% solution of 95% ethanol in water was used with 1 mg/mL of cytochrome c to which 100 mL of the anhydride was added. The reaction was again carried out at 30°C for 30 min with the pH maintained in the range to 7.2-7.6. After air drying, the solid residue was again contacted with benzene at 30°C for 30 min, and there was approximately 0.03 mg/mL of the modified protein dissolved in the benzene.

Preliminary experiments with the reaction of fatty acid anhydrides with hydrogenase have also yielded some interesting results. Approximately 40 mL of caprylic anhydride was added to an 80% aqueous solution of 95% ethanol containing 1.3 units/mL of hydrogenase. The mixture was stirred and maintained at 30°C for 15 min with pH control at 7.4 to 7.8 by the periodic addition of 0.1 N NaOH. Enzyme activity after reaction was approximately 50% of the starting value.

Future Work

Research will continue on the investigation of the modification of enzymes by both DNFB and fatty acid anhydrides. In the latter case, additional fatty acids will be investigated, especially those with longer carbon chain lengths.

ORNL RESEARCH ON MICROBIAL BIOTRANSFORMATIONS IN ORGANIC MEDIA

The current work is designed to test the feasibility of microbial processing of coal-derived materials within biphasic systems, with emphasis on the transformation of polyaromatic compounds. Sulfur removal from dibenzothiophene (DBT), a heterocyclic coal model compound, is being used as a model system in this effort. *Paecilomyces* sp. TLi, a fungus isolated from coal and previously shown to modify DBT, is the focus of this work. This organism catalyzes a sulfur-specific attack on DBT, with formation of a dihydroxybiphenyl. A minor side reaction has also been detected that leads to unknown products, possibly including some formed by ring cleavage. The goal of this work is to demonstrate activity against DBT in the presence of organic media and to assess the specificity of the reaction under these conditions.

Preliminary effort has focused on the development of biphasic systems for use in subsequent tests. Benzene was chosen for use in this work due to DBT's enhanced solubility in this solvent. The aqueous phase consisted of culture medium typically used to grow the organism. DBT transformation had previously been demonstrated in this medium.

Experimental Results

Efforts to resolve the several technical challenges associated with the proposed test system have continued. In earlier work, no degradation of DBT was detected. Recent work has focused on identifying the basis for the inhibition of the desired activity. DBT degradation in wholly aqueous cultures proceeds via an oxidative pathway. The reaction characteristics suggest that the responsible enzyme is indeed an oxygenase, in which case molecular oxygen may be predicted to be essential to DBT breakdown. In prior work, cultures were agitated gently in order to achieve mixing. Cultures are now routinely sparged with oxygen prior to the exposure to the organic phase, in which DBT is dissolved. Moreover, the organic (benzene) is now equilibrated with oxygen prior to introduction into the culture. Although there still is no evidence that DBT is attacked in cultures, this approach has enhanced emulsion formation in cultures, thus increasing the contact area

between the cellular biocatalyst and the bulk organic phase. (The biomass had previously been shown to partition itself at the interface between the two phases.) A salting-out method for breaking the emulsion prior to analysis has been successfully developed.

The absence of cellular activity in the test system may also be ascribed to toxic effects of the organic solvent used. The current test system utilizes pregrown biomass, which need not be actively respiring in order to catalyze the initial breakdown reactions that are routinely monitored in this work. Yet one or more oxidative activities may be sensitive to the solvent. The effect of exposure to benzene on cell growth was monitored as the simplest, yet most sensitive, assay of toxicity. Cultures were inhibited at benzene concentrations greater than 0.25% (34.7 mM). Also, benzene appeared to react with the biomass to form an amorphous, nonvolatilizable material that, when heated, turned into a tar. This behavior was absent in cultures that had not been exposed to the benzene, or in neat benzene samples. The benzene used in this work was of chromatographic purity. These results suggested that benzene may be an inappropriate solvent for the proposed work. Indeed, the preliminary evidence suggests that the solvent dissolves membranes, perhaps disrupting the activity of membrane-associated enzymes. Efforts are currently underway to survey a variety of solvents that are potentially more compatible with cell activity.

OXIDOREDUCTIVE PROCESSES RELEVANT TO THE CONVERSION OF COAL CATALYZED BY ENZYMES IN ORGANIC SOLVENTS

During the period covered by the third progress report, in an effort to find optimal organic solvents, we studied the hemoglobin-catalyzed oxidation of dibenzothiophene (DBT) by hydrogen peroxide in various organic solvents at different water contents. A correlation between the maximal degree of DBT conversion and solvent acidity was revealed: the higher the acidity, the greater the extent of the substrate oxidation. Since among all the solvents used, water is the strongest acid, the efficiency the transformation of dibenzothiophene was almost three times higher in water (containing 25% of 1-propanol) than in the best organic solvent (1,2-propanediol containing 1% of water; 99 and 26%, respectively).

In the beginning of this reporting period, we decided to test whether the nature of the organic solvent constituting 25% of the reaction medium impacts the level of the maximal transformation of dibenzothiophene. Table 1 presents the data on the oxidation of dibenzothiophene catalyzed by different concentrations of hemoglobin in a range of organic cosolvents (25% in aqueous buffer). It is seen that the maximal degree of oxidation of dibenzothiophene with hydrogen peroxide depends on the nature of the cosolvent and the concentration of the protein. At 25 μM hemoglobin, in almost all the solvents nearly complete transformation of dibenzothiophene occurred. Compared to horseradish peroxidase where at 25 μM enzyme only 18% of DBT was oxidized (see progress report for Oct.-Dec. 1991), for hemoglobin the conversion required much less protein. Even at only 5 μM hemoglobin, nearly a 100% transformation of the substrate was attained. In this case, a simple calculation indicates that one molecule of the hemoprotein turns over more than 40 molecules of dibenzothiophene. The oxidation of dibenzothiophene catalyzed by hemoglobin occurs much faster than that by horseradish peroxidase. The specific catalytic activity (i.e., the initial reaction rate divided by the protein concentration) of hemoglobin is two orders of magnitude greater than that of horseradish peroxidase (1.7 and $1.5 \cdot 10^{-2} \text{ min}^{-1}$, respectively). Interestingly, the situation is the opposite for the classical substrate of peroxidase *ortho*-phenylenediamine ($1.4 \cdot 10^4$ and 1.4 min^{-1} for peroxidase and hemoglobin, respectively).

The data in the table show that at low concentrations of hemoglobin, the oxidation of dibenzothiophene is incomplete and its maximal level is quite distinct in different solvents: at 2.5 μM hemoglobin, the maximal conversion of dibenzothiophene varies from above 50% in 1-propanol, ethanol, and acetonitrile to below 30% in N,N-dimethylformamide, ethylene glycol, and tetrahydrofuran (all at 25%). As shown before (progress report Jan.-Mar. 1992) for the 25% 1-propanol, hemoglobin inactivation occurs during the oxidation of dibenzothiophene: addition of the fresh protein to the reaction mixture after the reaction ceased causes the oxidation of the substrate to start again. Elucidation of the mechanism of this hemoglobin inactivation was one of the main goals of the work covered by this reporting period.

Table 1. Oxidation of dibenzothiophene catalyzed by hemoglobin in water containing 25% (v/v) of an organic solvent

[Experimental conditions: 230 μ M dibenzothiophene, 10 mM hydrogen peroxide, 20 mM acetate-phosphate buffer (pH 5.2), 30°C]

Concentration of hemoglobin (μ M)	Solvent	Oxidation of dibenzothiophene (%)
25	1-propanol	99
5	1-propanol	96
2.5	1-propanol	56
0.25	1-propanol	5
25	methanol	98
25	ethanol	99
2.5	ethanol	53
25	2-propanol	93
25	<i>tert</i> -butanol	94
25	acetonitrile	100
2.5	acetonitrile	54
25	ethylene glycol	91
2.5	ethylene glycol	29
2.5	N,N-dimethylformamide	27
2.5	tetrahydrofuran	26
2.5	acetone	35

We established in an independent experiment that there was no inactivation of hemoglobin when present without the substrates in the reaction medium during the entire period of time allowed for the oxidation to proceed. We also made certain that the time course of the dibenzothiophene oxidation did not change if hemoglobin had been preincubated with dibenzothiophene for 1 h prior to the addition of hydrogen peroxide to the reaction mixture. On the other hand, when H_2O_2 was added first to the protein solution, then there was no subsequent transformation of dibenzothiophene at all even if the latter was added after only a 5-min incubation of hemoglobin and hydrogen peroxide (Fig. 1A). Hence the protein is inactivated by hydrogen peroxide.

In order to shed light on the mechanism of hemoglobin inactivation during its incubation with hydrogen peroxide, we examined the visible absorption spectrum of the protein. This spectrum is a characteristic feature of hemoproteins reflecting the heme structure; it is very sensitive even to minor changes in the microenvironment and structure of the heme. As seen in Fig. 1A, the absorbance at the Soret band dropped more than tenfold in the first 5 min of the incubation of hemoglobin with hydrogen peroxide in an aqueous acetate-phosphate buffer containing 25% of 1-propanol. Furthermore, the entire spectrum of hemoglobin changed drastically within 5 min after hydrogen peroxide addition (Fig. 1B). These spectral changes suggest that the oxidative degradation of the heme in hemoglobin occurred, probably through a Fe(III)-bile pigment-protein complex as an intermediate. Thus, a likely reason for the observed inactivation of the protein is the oxidation of methylene bridges of the heme by hydrogen peroxide leading to an irreversible destruction of the heme structure. As Fig. 1A illustrates, the rate of the hemoglobin inactivation depends on the concentration of hydrogen peroxide: the process markedly slows down when H_2O_2 is diluted twenty-fold. The fact that there is a clear correlation between the decay in absorbance of hemoglobin (Fig. 1A) and that in its catalytic activity (Fig. 1C) suggests a causal relationship between the two.

In order to establish whether the observed destruction of the heme moiety is general, we studied the spectral changes of horseradish peroxidase during the oxidation of

Fig. 1. Hemoglobin-catalyzed oxidation of dibenzothiophene and spectral characteristics of the protein. A, absorbance at the Soret band in the presence of 10 (▽) and 0.4 (▼) mM hydrogen peroxide. Solid circles correspond to the time course of the S-oxide formation when dibenzothiophene was added 5 min after hydrogen peroxide. B, spectrum of hemoglobin before (—) and 5 min after (---) addition of hydrogen peroxide. C, oxidation of dibenzothiophene in the presence of 10 (a) and 0.4 (b) mM hydrogen peroxide. Experimental conditions: 2.5 μ M hemoglobin, 0.23 mM dibenzothiophene, 20 mM acetate-phosphate buffer (pH 5.2) containing 25% (v/v) of 1-propanol, 30°C.

dibenzothiophene by hydrogen peroxide. It was found that the decay in the absorbance at the Soret band also occurred in this case, albeit slower than for hemoglobin. This absorbance change was accompanied by an appearance of a peak at 670 nm, reflecting an inactive form (presumably a verdohemoprotein) of peroxidase. By analogy with a kinetic scheme suggested in the literature for horseradish peroxidase, we propose the mechanism of hemoglobin-catalyzed oxidation of dibenzothiophene which includes a concomitant inactivation of the enzyme by H_2O_2 (Fig. 2). According to this mechanism, the second molecule of hydrogen peroxide can also react with the protein, in particular if present in excess. In other words, a competition for the compound I between dibenzothiophene and hydrogen peroxide can take place. In this case, we can have a situation when increasing the hydrogen peroxide concentrations leads to no appreciable increase in the maximal product concentration. Indeed, the dependence of the maximal degree of oxidation of dibenzothiophene on the hydrogen peroxide concentration, depicted in Fig. 3, shows that at $[\text{H}_2\text{O}_2] < [\text{DBT}]$ the degree of oxidation increases when the concentration of hydrogen peroxide is increased. However, at higher hydrogen peroxide concentration the maximal degree of DBT oxidation levels off and even begins to decline. The mechanism shown in Fig. 2 and the data in Fig. 1A explain this seemingly puzzling observation, because not only the hemoglobin-catalyzed reaction but also the hemoglobin inactivation will be faster at higher H_2O_2 concentrations. Hence hemoglobin, while working faster, will have a shorter lifetime.

The proposed scheme (Fig. 2) also indicates that the way to shift the ratio between the productive route (horizontal line) and the nonproductive route (vertical line) is to affect preferentially the pathways initiating at compound I. We experimentally tested this prediction. Lowering the temperature should reduce the rates of the competing steps of the reaction to a different extent. With this in mind, we carried out the dibenzothiophene oxidation catalyzed by hemoglobin at two different temperatures, 7 and 30°C. As seen in Fig. 4, when the temperature is reduced from 30 to 7°C, the maximal degree of dibenzothiophene oxidation increases threefold. The turnover number of the reaction is 140 at 7°C, as compared to 46 at 30°C.

It was also found that the pH of the reaction medium influenced the transformation of dibenzothiophene. For example, the maximal degree of oxidation at pH 5.2 was nearly

Fig. 2. Schematic representation of the mechanism of hemoglobin-catalyzed oxidation of dibenzothiophene by hydrogen peroxide.

Fig. 3. Hemoglobin-catalyzed oxidation of dibenzothiophene as a function of the hydrogen peroxide concentration. Experimental conditions: 2.5 μM hemoglobin, 0.23 mM dibenzothiophene, 20 mM acetate-phosphate buffer (pH 5.2) containing 25% (v/v) of 1-propanol, 30°C.

Fig. 4. Oxidation of dibenzothiophene catalyzed by hemoglobin at different temperatures: (●) 7°C, and (○) 30°C. Experimental conditions: 1.5 μ M hemoglobin, 0.23 mM dibenzothiophene, 10 mM hydrogen peroxide, 20 mM acetate-phosphate buffer (pH 5.2) containing 25% (v/v) of 1-propanol.

twice as high as at pH 4.1 or pH 7.0 but almost 40% of the product at the last pH was the sulfone (otherwise, experimental conditions were the same as in Fig. 1C).

According to recent publications, inactivation of horseradish peroxidase with hydrogen peroxide involves the participation of superoxide radicals. Consequently, we examined the effect of tetranitromethane, a scavenger of the latter, on the oxidation of dibenzothiophene catalyzed by hemoglobin. It was found that in the system depicted in Fig. 1C, curve a, addition of 0.02% of the scavenger indeed increased the maximal product yield from 56 to 92%. Likewise, in the peroxidase system, 0.02% tetranitromethane raised the yield of dibenzothiophene-S-oxide from 18 to 28%. In contrast, 0.1 M mannitol or formate (known scavengers of hydroxyl radicals) had no appreciable effect on the process.

We decided to test whether other organic compounds modeling different structural units of coal could affect the oxidation of dibenzothiophene. For the system depicted in Fig. 1C, curve a, the presence of 1 mM methyl p-toluate (a model of organic oxygen in coal) resulted in no significant effect on the maximal degree of DBT oxidation. In contrast, 1 mM indole (a model of organic nitrogen in coal) lowered the maximal yield of dibenzothiophene-S-oxide in 25% propanol from 56 to 7%. These observations suggest that coal components may affect (adversely or perhaps beneficially) the hemoglobin-catalyzed desulfurization.

In future work, it should be important to determine whether the hemoglobin-catalyzed oxidation with hydrogen peroxide will be effective in lowering the organic sulfur content of a real (swollen) coal and what the operational characteristics and limitations of such a system will be.

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4.2 ADVANCED BIOREACTOR SYSTEMS

T. C. Scott

Advanced bioprocessing concepts can play an important role in coal utilization and conversion. This R&D program is aimed at elucidating the fundamental mechanisms that are important in appropriate bioprocessing concepts or coal interactions, particularly those that have potential generic impacts. Further, the program will be a collaborative partnership of ORNL with academic and industrial researchers.

To obtain the high throughput and low inventory needed for large-scale bioprocessing of coal, a new family of advanced bioreactor systems will have to be developed. The focus of the research in this area will be on continuous columnar bioreactors which have the potential for carrying out three-phase operations. Although both fixed and fluidized bed bioreactors will be studied, the initial work will be on liquid-solid fluidized bed systems and aqueous-liquid-solid fluidized bed systems for direct biological interactions with extremely small coal particles.

ORNL RESEARCH

In order to effectively describe and predict column performance for polydisperse particle systems, experimental information is needed in four vital areas: (1) axial pressure drop, (2) particle size distribution as a function of axial position, (3) dispersion characteristics of the liquid phase, and (4) dispersion characteristics of the particles. During the last reporting period work has concentrated on the first three of these four items.

Efforts have concentrated on increasing the number of measurement points in pressure drop studies and extending the investigation to a binary-solid system with a wider particle size range (50 μm and 110 μm). An additional twelve-inch section of one-inch-diameter glass pipe was added to the column. This section contains three additional ports for pressure measurements. A system of eight toggle valves was installed between the column pressure ports and the six pressure transducers. This allows selective pressure drop

measurements over eleven different sections of the bed. The total volume of the bed for this phase of the study has been increased by a factor of approximately 2.9. The bed consisted of a binary mixture of large ($110\ \mu\text{m}$) particles and small ($50\ \mu\text{m}$) particles in a 2.4:1 volumetric ratio of large to small particles. The surfactant concentration in the bulk liquid phase was increased to 0.5% (from 0.1%) to further ensure elimination of particle agglomeration. Figure 1 contains a series of pressure-drop data taken on the aforementioned system. Data were obtained for four flow rates in the range of 0.0045 to 0.0156 cm/sec. The curvature observed in the pressure-drop data suggest significant particle segregation at the lowest flow rate (0.0045 cm/s); however, as the flow rate is increased the curvature appears to become less prominent.

The apparent increase in particle segregation at the lowest flow rate, relative to that previously reported for the $50\ \mu\text{m}/70\ \mu\text{m}$ binary solid mixture, was expected because the larger particles are barely fluidized at this flow and thus would congregate at the bottom of the column. The apparent lack of significant segregation at the higher rates is puzzling but should become more clear as the fluorescence techniques allow direct measurement of particle segregation profiles.

Several methods have been investigated for determination of the particle distribution along the bed. The approach has been to attempt to bind a fluorescent dye to one of the particle sizes and take a video image of a portion of the bed. Suitable optical filters could then be used on the camera so that only the fluorescent particles would show-up. This image could be digitized and scanned to determine the fraction of the two particle sizes at a given point in the bed. We have met with some success in recent efforts to apply a fluorescent coating to the coal particles. A sample of 50-100 mesh (average particle diameter approximately $220\ \mu\text{m}$) was coated with fluorescent orange paint and has been in continuous contact with a 0.5% Tween 80 solution for over 3 weeks with no noticeable loss of fluorescent coating. These particles were mixed with a sample of $60\ \mu\text{m}$ coal particles and fluidized in 0.5% Tween 80 solution. The coated coal fluoresces bright orange under long-wavelength ultraviolet excitation. There is a distinct interface between the two size fractions under low-flow conditions ($<0.02\ \text{cm/sec}$) although an appreciable number of the large particles can be seen throughout the length of the bed.

Pressure Drop as function of Vertical Position
Mixed Bed: -270+325(45-53um) and -120+170(90-125um)
at four different flow rates

Fig. 1

Impulse changes in the electrical conductivity of the liquid phase have been used to determine liquid-phase dispersion characteristics. Conductivity probes machined into the wall of special column inserts allow measurement of the transient signal. The electrical contacts are flush with the wall of the column so as to minimize effects on flow in the system. The signals from these probes were recorded on the computer data acquisition system along with the pressure-drop data to help more clearly determine behavior of the bed. The method of moments was used to determine the effective liquid-phase diffusivity from the transient conductivity plots.

The extent of liquid-phase dispersion was measured in a liquid-fluidized bed of coal containing the bimodal mixture of nominal 50 and 70 μm -diameter particles discussed in the previous report. Impulse tests were conducted by injecting a one milliliter volume of 5M NaCl solution into the liquid stream below the glass retaining frit and measuring the conductivity response at three points along the length of the bed. The conductivity response was acquired every few seconds through a computer data acquisition interface and the response curves plotted.

Using a method of moments analysis developed by Bischoff and Levenspiel, the effective liquid-phase Peclet numbers and dispersion coefficients for three liquid flow rates were determined. Table 1 contains a listing of the values of the Peclet numbers and dispersion coefficients obtained from the experiments.

Table 1. Liquid-Phase Dispersion Coefficients Determined from Impulse Tests

Superficial Velocity (cm/s)	Peclet Number ($u_o L / \epsilon D_e$) ^a	Effective Dispersion Coefficient, D_e (cm^2/s)
0.00534	10.4	0.034
0.00912	3.1	0.199
0.0159	1.9	0.283

^awhere u_o is the superficial velocity, L is characteristic column length, ϵ is the column void fraction, and D_e is the effective dispersion coefficient.

The flow rates span the same range as the pressure-drop data discussed in the previous report. These results indicate that a significant amount of axial mixing occurs in the liquid-phase of the fluidized-bed system and that the magnitude of mixing increases as the flow rate is increased. Of particular interest is that dispersion coefficients determined for the liquid-phase are nearly identical to those calculated by Asif and Petersen for the effective particle diffusivities. This indicates that at the low Reynolds numbers encountered in the bed, relative transport of the particles, which gives rise to particle segregation, is dominated by the motion of the bulk liquid phase. This type of behavior would tend to smear out particle concentration profiles and lead to less particle segregation than expected in the system.

Future Work

The primary focus of future work will be measurement of liquid-phase dispersion phenomenon for the larger bimodal size distribution. In addition, the use of a fluorescent marker for particle-size distribution measurements will be continued. As appropriate pressure-drop, dispersion, and particle distribution data are generated, they will be compared to predictions of the numerical model being developed at WSU.

WSU MODELING RESEARCH

Introduction

The major goal of the ongoing research at WSU is the development of new models which will appropriately describe the hydrodynamics of advanced bioreactors for coal processing. This is accomplished by examining existing models which are available in the literature and then proposing necessary modifications in these existing models to arrive at improved and physically realistic models with enhanced predictive capabilities.

During the two previous quarters of the project, a mathematical model was developed using the basic mass conservation equations which was found to describe satisfactorily the total particle concentration a binary-solids fluidized bed. Details of this model were presented

at the 14th Annual Symposium on Biotechnology for Fuels and Chemicals and submitted for publication to *Applied Biotechnol. Bioeng.* In an effort to obtain a more predictive models, our efforts during this quarter have concentrated on reviewing other existing models, examining their underlying assumptions, and ascertaining whether they will provide a satisfactory description of the advanced reactors that are being developed at ORNL.

In particular, two models have been examined. The first of these is the model described by Van der Meer *et al.*¹ and later adopted by Di Felice *et al.*². Thus, in this report, we will discussed their model and examine and its applicability to the coal fluidized bed. Additionally, an important modification in the classified bed approach³ is also under consideration to enhance its utility to account for particle dispersion effects in advanced reactors for coal processing. Thus, we will also describe this model.

Description of the Model of Van der Meer *et al.*

Since the dispersion flux, J_d , of particle species 'i' in a binary-solids fluidized bed is counter-balanced by its classification flux, J_c , one may write

$$J_{d_i} = J_{c_i} \quad (1)$$

or,

$$-D_i \frac{dC_i}{dz} = U_i C_i \quad (2)$$

where, D_i is the dispersion coefficient of particle species 'i' and U_i is its classification velocity.

Unlike other existing models, Van de Meer *et al.* proposed a concentration dependence of U_i . They argued that the classification velocity of particles of species 'i' goes to zero when it is in its pure component zone but attains the peak value when it is in the environment of other particle species. In other words,

$$U_i = 0 \text{ if } C_i = C_{ip}; \quad U_i = U_{i*} \text{ if } C_i = 0 \quad (3)$$

where, C_{ip} is the pure component zone concentration of C_i which can be, in most cases, calculated from the Richardson-Zaki correlation.

They suggested the following linear relationship of the classification velocity of the particle species 'i' on its concentration

$$U_i = U_{i*} \left(1 - \frac{C_i}{C_{ip}} \right) \quad (4)$$

It is, however, important to note here that the binary-solid fluidization, in the event of segregation behavior, shows a change in the bulk density in the transition or the mixing zone. The above set of equations will, therefore, not be appropriate if C_i is taken to be the volumetric concentration of species 'i' which is the case in the work of Di Felice *et al.*³

Martin⁴ observed segregation behavior in the fluidized bed of ion-exchange particles when the diameter ratio of the two particle species were as low as 1.07. The density of these ion-exchange particles are very close to that of the coal particles and therefore, expected to possess similar fluidization characteristics. Martin *et al.*⁵ also showed that the classification velocity of a sphere in a swarm of different spheres can not be correctly described by the Richardson-Zaki correlation.

In the following, we will discuss the appropriate mathematical treatment of the same problem outlining important steps to arrive at the correct mathematical model.

From continuity:

$$\frac{d}{dz}(n_i) = 0 \quad (5)$$

which implies the z-dependence of mass flux, n_i , to be constant *i.e.*,

$$n_i(z) = \text{constant} \quad (6)$$

A sustained semi-batch fluidization at steady-state would require,

$$n_i(z) = 0 \quad (7)$$

In the presence of the counter-balancing effects of dispersion and convection (due to the classification velocity) contributions to the mass flux, we can write

$$n_i = D_i \rho \frac{d\omega_i}{dz} - U_i \rho \omega_i = 0 \quad (8)$$

where, ρ is the bulk density, ω_i is the mass fraction of i . In this case, the classification velocity U_i can be defined as

$$U_i = U_{ip} \left(1 - \frac{\omega_i}{\omega_{ip}} \right) \quad (9)$$

where, ω_{ip} is the pure component zone mass fraction of i .

Introducing the following dimensionless variables,

$$x = \frac{z}{L}; \quad y_i = \frac{\omega_i}{\omega_{ip}}; \quad Pe_i = \frac{U_{ip} L}{D_i} \quad (10)$$

The above equation can be rewritten as

$$\frac{dy_i}{dx} - Pe_i(1-y_i)y_i = 0 \quad (11)$$

If $x = x_0$ is the point in the mixing zone where the concentration y_i becomes 0.5, the solution of the above equation can be given as

$$y_i = \left(\frac{1}{1 + \exp(-Pe_i(x-x_o))} \right) \quad (12)$$

It is important to note that if species 'i' is the larger particle species in the binary solid fluidized bed, it will have negative classification velocity *i.e.*, the larger particles will tend to come down. As a result, Pe_i will be negative. On the other hand, Pe_i will be positive for smaller particle due to their tendency to move up. It has been demonstrated by Di Felice *et al.* that the variation of the particle concentration is linear in most cases. This means that Pe_i for both the particle species in binary-solid fluidized bed will be the same. This reduces the number of unknown parameters to be evaluated from the experimental data to only two, namely, Pe_i and x_o . For systems where the assumption of the linear concentration profile does not hold true, the Pe_i for the two particle species will be different and therefore will have to be evaluated from the experimental data.

Therefore, for large particle 'a', we have

$$\omega_a = \left(\frac{\omega_{ap}}{1 + \exp(Pe_a(x-x_o))} \right) \quad (13)$$

and for small particles 'b', we can write

$$\omega_b = \left(\frac{\omega_{bp}}{1 + \exp(-Pe_b(x-x_o))} \right) \quad (14)$$

where,

$$Pe_a = \left(\frac{U_a \cdot L}{D_a} \right); \quad Pe_b = \left(\frac{U_b \cdot L}{D_b} \right) \quad (15)$$

Here, U_{ao} are the classification velocity of 'a' in the neighborhood of particles of species 'b'. Similarly, U_{bo} is the classification velocity of 'b' in the neighborhood of 'a'. And D_a and D_b are the dispersion coefficients of species 'a' and 'b', respectively.

Results and Discussion

The comparison of the model predictions with the Juma and Richardson data⁶ is excellent so far as the concentration profile of the total particles are concerned. As a next step, the experimental data for the individual particle species will also be compared. The present model appears to confirm the fact, as pointed out by the model that we proposed previously (1), that the dispersion is the governing mass transport mechanism in the bed. On the other hand, the value of the Peclet number and therefore, the segregation tendencies are greater for gas fluidized beds. Again, the model predictions are in good agreement with the experimental data for the total particle concentration profile of coal particles. Its applicability for predicting the individual particle profile is yet to tested. However, the trend shows that the large particles are present in substantial concentrations in the upper region of the bed. Similarly, small particles could be found in lower bed regions.

One fact, hitherto unnoticed, becomes very obvious from the present analysis that the governing parameter in this case is the Peclet number which should be defined in such a way to include the effects of particle dispersion coefficients, particle segregation velocities and the height of the transition zone. Specifying this parameter alone will describe the mixing and segregation behavior of binary-solids fluidized beds.

Note that we have assumed here that the peclet number is the same for both the particle species. This assumption appears to hold true in this case.

Classified Bed Model

This approach, proposed by Al-Dabouni and Garside,³ consists of making the mass balance based on the assumption that the size group between diameter D_p and $D_p - dD_p$ is contained between heights z and $z + dz$ only, with no dispersion of particles. If $m(D_p)$ is the differential mass distribution function, we can write

$$-m(D_p)dD_p = (1-\epsilon)\rho_s A dz \quad (16)$$

The void fraction, ϵ , in the above equation can be evaluated using the Richardson-Zaki correlation. Its substitution gives

$$\frac{dz}{dD_p} = - \frac{m(D_p)}{A\rho_s[1-(U_o/U_p)^{1/n}]} \quad (17)$$

where, U_p is the terminal velocity of the particle of diameter D_p .

In fact, a correct mass-balance in this case can be written as

$$-m(D_p)dD_p = d[(1-\epsilon)\rho_s A z] \quad (18)$$

or,

$$\frac{dz}{dD_p} = - \frac{m(D_p)}{A\rho_s(1-\epsilon)} + \left(\frac{z}{1-\epsilon}\right) \frac{d\epsilon}{dD_p} \quad (19)$$

A comparison of equations (16) and (19) points out to the fact that neglecting the term $d\epsilon/dD_p$ in the mass balance leads to the classified bed model. If the Richardson-Zaki correlation is used to evaluate the void fraction, ϵ , one may write

$$\frac{d\epsilon}{dD_p} = - \frac{2\epsilon}{n D_p} \quad (20)$$

where, n is the Richardson-Zaki correlation index. Here, the dependence of ϵ on D_p enters via the terminal velocity term which shows a quadratic dependence on the particle diameter D_p .

At this stage, it is important to correctly evaluate the value of $(1-\epsilon)$ i.e., the particle concentration when the term $d\epsilon/dD_p$ is also present in the equation. Probably, it will require the introduction of some other mass balance conditions. During the next quarter, additional attention will be paid to this question, and an attempt will be made to use this modified classified bed model to provide a totally predictive model.

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4.3 BIOCONVERSION OF COAL

C. D. Scott

This program has examined the feasibility of using biological catalysts for the conversion of coal to useful liquid fuels. Biological reagents potentially useful in this application include intact microorganisms in pure or mixed culture and isolated enzymes. The current emphasis is on the investigation of the use of chemically modified enzymes in organic media to enhance liquefaction/solubilization of coal.

COAL LIQUEFACTION/SOLUBILIZATION TESTS

The chemical modification of hydrogenase from *proteus vulgaris* and cytochrome c with dinitrofluorobenzene (DNFB) was reported in Section 4.1. These modified enzymes with dinitrophenyl (DNP) groups were used in benzene or pyridine to convert coal to liquids.

Tests were carried out in shake flasks or in a small fluidized-bed bioreactor.

Conversion Tests in Shake Flasks

Scouting tests on coal solubilization continue to be made in shake flasks. These tests were made in 25-mL glass flasks in a temperature-controlled bath at 30°C with the eccentric drive operating the shaking motion rotating at 100 rpm. A series of tests were made simultaneously using a single hydrogen gas stream progressing through the head space in each flask. In all tests, 10 mL of benzene solution was used in contact with 50 mg of Illinois No. 6 bituminous coal. In order to determine the effects of coal size, -325 mesh coal was used instead of the usual -270+325 mesh samples was used in one test. Approximately 10% of the coal was converted in an 8-h period when ~1 mg/mL each of the DNFB-modified hydrogenase and cytochrome c were used compared to approximately 5% converted with no protein present or when about 1 mg/mL of modified and noncatalytic albumin was included.

As in other recent experiments, an evaluation was made of the particle size distribution of the feed and the solid residue after reaction. As observed before, the very small particles (<5 μ m) disappeared and the size of the larger particles decreased. However,

the overall conversion of the coal was about the same at that determined for the larger-particle-size coal; therefore, it was concluded that extremely fine coal particles will have little effect on the process and, thus, will not be required.

Fluidized-bed Tests

Fluidized-bed tests were made in a recently-modified tapered fluidized-bed bioreactor fabricated from glass. The reaction chamber was a 15-cm-long column in the form of an inverse truncated cone with a diameter varying from 1.25 cm at entrance to 2.5 cm at the exit. The reactor was temperature-controlled by circulating fluid in a surrounding jacket. The 0.5 g sample of Illinois No. 6 bituminous coal particulates (-270 mesh +325 mesh) was fluidized by pumping the reaction fluid containing a mixture of DNFB-hydrogenase and DNFB-cytochrome c at the rate of 2 to 3 mL/min. The system operated with continuous liquid recycle, and there was a hydrogen gas sparge in the upper part of the column.

Several tests have been made but the most significant was an attempt to reproduce a previous run in which pyridine containing ~ 2 mg/mL each of the modified hydrogenase and cytochrome was the reaction medium and there were two successive replacements of the reaction medium with fresh solution at 4 and 8 h. In the first test of this type reported in the last progress report, over 35% of the coal was converted. In this test, the same conditions were used except the modified biocatalyst concentrations were about a factor of two greater. As before, there was an indication of more coal conversion with the addition of each fresh batch of reaction medium. There also appeared to be greater conversion requiring more extensive washing of the solid residues to remove soluble materials. A total of 300 mL of pyridine was used to initially wash the residue followed by 200 mL of water (all washings were carried out in the same test tube with, 20 to 25 mL of the solvent used in each cycle followed by high-speed centrifugation and careful removal of the supernatant). It has been demonstrated in the past that less than 2% of the total residual solids are lost in the washing process.

The introduction of each fresh biocatalytic charge maintained or enhanced the coal conversion rate as indicated by an increase in the absorbance of the reaction solution at 376 nm (see Figure 1). The total coal converted on a moisture and ash-free basis was 42.4%. This was somewhat higher than that previously experienced in the similar test and certainly

Fig. 1. Conversion of bituminous coal in the small fluidized-bed bioreactor in pyridine with three successive additions of fresh biocatalytic reaction solutions.

adds credence to those results. Perhaps the indicated increase in coal conversion was due to an increase in concentration of the modified biocatalysts that were dissolved in the organic solvent. In a reference test that was identical to the above test except there was no biocatalyst present, there was an apparent 20.8% coal conversion with a major portion of that being water soluble. Thus, the inclusion of the biocatalyst significantly increased the conversion of the coal to a level that is sufficiently high to warrant serious process consideration. The next obvious experiment will be to use even more charges of the biocatalytic reaction fluid to further increase the degree of conversion.

Product Characterization

It was previously shown that the liquid product from hydrogenase-enhanced conversion of bituminous coal utilizing a pyridine medium produced a product that was somewhat more polar than that utilizing benzene. That is, a larger fraction of the product was water-soluble. This was also found to be the case in the most recent fluidized-bed test for solubilization of bituminous coal in pyridine. The product after air drying to remove pyridine was contacted with equal quantities of water and benzene. Approximately 80% of the product was extracted into the benzene phase with the remainder in the water phase. Some water-soluble material was removed from the coal residue during the water washing step. This material was predominantly of biological origin (perhaps precipitated enzyme) but some of the material has the appearance of the water-soluble product from aerobic solubilization of coal by microorganisms. Thus, it is likely to be relatively large molecular fragments from the coal. Perhaps this indicates that enzyme-enhanced conversion of coal progresses through at least two stages. First, breakup of the coal structure into large molecular fragments and then subsequent further breakdown of these large compounds into smaller reduced constituents.

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4.4 RENEWABLE HYDROGEN PRODUCTION FOR FOSSIL FUEL PROCESSING

E. Greenbaum

INTRODUCTION

Although carbon dioxide is the terminal electron acceptor of normal photosynthesis, other electron acceptors are possible. In particular, in their pioneering work, Gaffron and Rubin showed that in a dinitrogen atmosphere the enzyme hydrogenase can catalyze the photoevolution of molecular hydrogen.¹ Anaerobiosis (e.g., atmospheres of nitrogen or helium) is, from a physiological point of view, an unusual condition. It can, however, be used to study the question of alternate fates of photosynthetic reductant, in particular, the branching ratios between hydrogen evolution and carbon dioxide assimilation using water as the source of reductant. The focus of this paper is an understanding of partitioning photosynthetic reductant in the context of absolute rates of photosynthetic electron transport.

Gaffron and Rubin first showed that green algae (such as Scenedesmus) could liberate hydrogen gas in light, provided the algae remained under CO₂-free anaerobic conditions.¹ Further investigations indicated that the simultaneous photoevolution of oxygen and hydrogen from water is qualitatively analogous to normal photosynthesis in that the bulk of reductant is provided by water splitting.^{2,3} When such algae are exposed to light, the water-splitting complex of Photosystem II (PS II) provides reducing equivalents for the photoproduction of molecular hydrogen (catalyzed by hydrogenase), instead of carbon fixation. Chlamydomonas reinhardtii is another algal species that possesses the ability to perform biophotolysis of water.^{4,5,6,7}

Previous studies have shown the importance of a bicarbonate effect on the rate of photosynthetic electron transport (PET) or oxygen-evolving ability.^{8,9} Warburg and Krippahl¹⁰ first observed this effect which was further studied by Stemler and Govindjee.¹¹ In general, normal rates of electron transport in plants require bicarbonate (or dissolved CO₂).^{12,13} At the same time, of course, CO₂ is the key reagent of the Calvin cycle as terminal electron acceptor and activator of crucial enzymes.¹⁴ Under anaerobiosis, the Calvin cycle competes with hydrogenase for electrons activated by Photosystem I (PS I) and PS II

and overwhelms it when high amounts (1% in helium) of CO₂ are present.⁶ By titrating the carbon dioxide concentration in an algal environment, a value was sought such that enough inorganic CO₂ would be present to maintain relatively high PET rates while restricting the Calvin cycle of its basic reagent. The key concept here is the relative affinity of carbon dioxide to the Calvin cycle and the PS II binding site. With the Calvin cycle suppressed, reductant from water should favor the H₂-forming pathway. Conditions were sought in which improved hydrogen yields could be obtained. This goal was successful for Chlamydomonas reinhardtii. It clearly illustrates that control of atmospheric carbon dioxide concentrations is a rational approach to solving the photosynthetic water splitting problem. It also points the way for further improvement in yields.

DISCUSSION OF CURRENT ACTIVITIES

Three different light intensity/CO₂ concentrations (58 ppm, 30 ppm, and 0.8 ppm) are presented in Fig. 1 as rates of hydrogen and oxygen evolution versus time. The onset of light-activated hydrogen and oxygen photoproduction is evident as is their decline when the light is turned off. Dark hydrogen evolution is subsequently observed.^{1,15} Using these data, one can obtain gas yields during light periods by integrating the peaks. For hydrogen profiles, the first half-life measures the time of decay from the maximum rate to half maximum. All yields were normalized to 1 mg of chlorophyll (Chl) by dividing by the amount of Chl present for each trial (usually 0.1 mg).

Lower CO₂ Concentrations Increase H₂ Yields

Figure 2 illustrates the result of 11 experiments at varying carbon dioxide levels and 130 W/m⁻² irradiance. This light level was chosen because it generated the highest oxygen yields at most of the CO₂ concentrations used without causing photoinhibition. Oxygen yields indicated the activity of water splitting, which supplied the bulk of reductant for hydrogen synthesis. The six other light intensities exhibited patterns similar to 130 W/m⁻². Fifty-eight ppm was the highest CO₂ concentration tested because 350 ppm CO₂, which is

SIMULTANEOUS PHOTOEVOLUTION OF
MOLECULAR HYDROGEN AND OXYGEN
AS A FUNCTION OF ATMOSPHERIC
CARBON DIOXIDE CONCENTRATION

Fig. 1 Representative results of hydrogen (solid line) and oxygen (dashed line) evolution by *C. reinhardtii* at 58, 30 and 0.8 ppm carbon dioxide. A two-hour calibration period preceded the actual light reactions, which started at the third hour. Seven cycles of 1.5-hour light and 1-hour dark were performed for each of the seven irradiances (in order, from left): 227, 130, 64, 25, 6.3, 2.4, and 0.1 W m^{-2} ($\uparrow$ =light on, $\downarrow$ =light off). The peak areas, after background subtraction, represent yields of H_2 or O_2 and first half-lives (the decay time from maximum rate to half-maximum) were compiled for hydrogen. Other experimental conditions are described in the text.

Fig. 2 Algal photoproduction of hydrogen (■, dashed line) and oxygen (●, solid line) at various carbon dioxide levels. Shown are the trends of the gas yields (integration of peaks as in Fig. 1) for 1.5-hour light periods (130 W m^{-2} irradiance). All yields are normalized to 1 mg Chl. Of the eleven CO_2 levels tested, hydrogen production is greatest near 1 ppm, but oxygen yield at this point has dropped to 30% of the value at 58 ppm CO_2 .

close to normal atmospheric levels, produced similar gas yields (data not shown). As the CO_2 levels for algae decreased, hydrogen yields climbed slowly, reaching a maximum at 0.8 ppm (11,360 nmol), where the Calvin cycle was impaired presumably because of insufficient CO_2 supply. At the other extreme, CO_2 levels greater than 30 ppm allowed the Calvin cycle to dominate so that only quick bursts of hydrogen formed. The noteworthy result is the highest yield of hydrogen at 0.8 ppm CO_2 , not at 0 ppm, where the Calvin cycle would be totally deprived of external inorganic carbon.

Lower CO₂ Concentrations Inhibit H₂ Decay

Hydrogen rates peaked and declined in most of the 1.5-h light periods (see shape of H₂ peaks in Fig. 1). The low light intensities are a notable exception. First half-lives ($t_{1/2}$) indicated the duration of hydrogenase activity at various CO₂ concentrations (Fig. 3). These are not implied to be the half-lives of exponential decay. They reflect the real-time loss of light-activated hydrogenase activity, due to competition with the Calvin cycle and/or depletion of alternate donor reductant pools. No permanent damage to hydrogen-forming capacity resulted from this decline, as indicated by resurgent rates of hydrogen evolution during subsequent light periods. As displayed in Fig. 3, the decay is slowest at the 0.8 ppm CO₂ level, indicating that hydrogen photoproduction had its slowest decay at this level. The general trend showed first half-lives rising with decreasing CO₂ and roughly following the behavior of hydrogen yields.

Fig. 3 First half-lives of decay for hydrogen rates. These measure the time it takes for the maximum H₂ rate to decay to half-maximum. Shown here are the first-half-lives (●) for the 130 W m⁻² light level, taken from the data for Fig. 3, with a solid line as the "smooth fit" through the data. Since all the hydrogen rates experienced a notable decay from an initial burst, this half-life describes how sustained the hydrogenase activity of the algae was during the 1.5 hours of light. The peak near 1 ppm CO₂ indicates that the most sustained hydrogen evolution occurred here.

O₂ Yields Decrease with CO₂ Deprivation

Returning to Fig. 1 one sees the decline in O₂ yields with decreasing CO₂ levels. The trend is downward with less carbon dioxide. The algae require CO₂ (*in vivo*) at some level to maintain high rates of electron-transport, as indicated by oxygen production. At 0 ppm (pure helium) oxygen activity was 12% that at 58 ppm. However, an addition of only 0.8 ppm CO₂, the value where H₂ was maximized, more than doubled the oxygen rate. As expected, oxygen rates did not decline appreciably during the 1.5-h light periods (Fig. 1). The significance of this result is discussed below in the Discussion section.

Hydrogen to Oxygen Ratios

Only below 10 ppm CO₂ did hydrogen/oxygen-yield ratios approach two (Fig. 4), in contrast to levels greater than 30 ppm, where the ratio remained less than two. These numbers approximately indicate activity of the hydrogen pathway versus the Calvin cycle. For levels >30 ppm, carbon dioxide assimilation receives the bulk of photoproduced reductant. A yield ratio of two or more does not necessarily mean that reductant from PS I and II goes exclusively to the hydrogen pathway because of the presence of transient alternate reductant pools.¹⁵

Significance of Results

These experiments indicate that atmospheric control of CO₂ concentration is a method of controlling the fate of photosynthetic reductant. In the present case, the amount of carbon dioxide in the algal environment was titrated such that the decreasing CO₂ concentration led to increasing hydrogen yields and greatest sustained rate at the 0.8 ppm level. This observation can be explained by a slowing of Calvin cycle activity. With this usual sink for light-generated reductant impaired, the hydrogen pathway (through hydrogenase) can take up an increasing share of electrons. Below 10 ppm CO₂ is where the hydrogen pathway begins to overtake the Calvin cycle, where the yield ratios (H₂/O₂) are ~2. Conversely, low hydrogen yields (compared to oxygen) combined with short first half-lives (Fig. 3) above

Fig. 4 Hydrogen: oxygen yield ratios. These ratios (●) are derived from the yields shown in Fig. 2 (1.5 hours of 130 W m^{-2} light). The trend (solid line) is toward ratios of ≥ 2 below 10 ppm CO_2 . As explained in the Discussion, the ratios do not necessarily reflect the stoichiometric proportions of water splitting (comparing to the ideal ratio of 2, from Eqn. 1). What one can infer is that for CO_2 levels greater than 30 ppm, the Calvin cycle overpowers the hydrogen-evolving mode, since hydrogenase manages to wrest only a minor fraction of the reductant from water splitting. This results in a small (<1) H_2/O_2 ratio.

30 ppm CO_2 indicate that the Calvin cycle is the predominant pathway for photogenerated reductant in that region.

On the other hand, from the oxygen yield of Fig. 2, we can clearly see the importance of carbon dioxide for high rates of electron transport. Carbon dioxide, or its dissolved form, bicarbonate (HCO_3^-), acts on the acceptor side of PS II as various investigators have confirmed.^{12,16,13,9} In addition to being the well-known substrate for and activator of the Calvin cycle, carbon dioxide (or HCO_3^-) helps to assure normal, rapid rates of electron flow

through PS II's primary (Q_A) and secondary quinone (Q_B) acceptors, and the plastoquinone (PQ) pool. When the concentration of CO_2 was decreased, reduced efficiency of electron flow occurred, prompting the oxygen-evolving complex to slow its activity accordingly. This "bicarbonate effect" on oxygen-evolving capability by depletion of CO_2 (or HCO_3^-) has been discussed by Jursinic and Stemler.¹³

In considering the extent to which photosynthetic reductant can be used to produce molecular hydrogen, it is useful to ask the following question: what is the rate-limiting aspect of this process? The limiting step is definitely not the kinetics associated with the chemistry of hydrogen formation which occur on a millisecond time scale.¹⁷ This can partially be seen in the rapid initial bursts of hydrogen observed in Fig. 1. The limiting step is the generally sluggish movement of electrons generated via photosynthetic water splitting and movement through the electron transport chain.

As discussed above, in a pure helium atmosphere the rate of electron transport is 12% that at 58 ppm CO_2 , whereas only 0.8 ppm CO_2 more than doubles it to 28%. Although hydrogenase is an oxygen sensitive enzyme, the oxygen evolved in this system is not inhibiting it. Prior experiments have demonstrated this by titrating in oxygen upstream from the algal cell and observing its effect on hydrogenase activity. The photosynthetically produced oxygen is below this threshold.

It is concluded from these experiments that the differential affinity of CO_2 to the Calvin cycle and the Photosystem II binding site is the key parameter in determining the extent to which CO_2 assimilation can be bypassed while simultaneously maintaining a fully functional electron transport chain as expressed by photosynthetic oxygen evolution.

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4.5 MILD GASIFICATION PRODUCT CHARACTERIZATION

C. S. Daw, R. L. Graves, and A. L. Compere

INTRODUCTION

Background

From previous studies it is known that mild gasification of coal produces liquids that are potentially useable as diesel fuel or diesel fuel diluents [1,2]. However, the yield and quality of these liquids as well as the degree of upgrading required can vary substantially with the process severity (i.e., the degree of devolatilization). Char is similar in that the degree of devolatilization directly affects its combustion properties. The economic viability of any mild-gasification process is thus determined by tradeoffs among product yield, upgrading costs, and end-use requirements.

Project Description

The purpose of this investigation is to develop basic characterization data for the liquid and char products of mild gasification. Such data are needed to evaluate key relationships among process conditions, product yield, and product end-use value. Of particular interest is the suitability of the liquid (with minimal upgrading) as diesel fuel and the suitability of the char as boiler fuel, although non-fuel uses of these products are also considered.

Representative samples of mild-gasification liquids and chars are being obtained from industrial groups involved in the development of candidate processes. These samples are subjected to a variety of characterization tests including:

- chemical and physical analyses of the char and liquids;
- combustion testing of the liquids in a diesel engine; and
- combustion testing of the chars in laboratory reactors.

In general, ORNL is tasked to carry out the more detailed, unconventional laboratory characterizations such as proton NMR (nuclear magnetic resonance), FTIR (Fourier

transform infrared) spectroscopy, and neutron activation. Standard laboratory assays are carried out either by ORNL or major mild gasification teams. The use of the liquids as engine fuels, with either blending or mild upgrading, is still of interest so those evaluations have been continued. Although there are several high-value products that can be derived from the char, its use as fuel remains a potentially large market. In addition, it is anticipated that char combustion will supply a major fraction of process heat in commercial mild-gasification processes. Hence a basic understanding of the char combustion properties is important.

DISCUSSION OF CURRENT ACTIVITIES

The collaboration between ORNL and B&W under Cooperative Research and Development Agreement (CRADA) No. ORNL91-0066 was initiated by beginning pressurized combustion characterization tests of char samples from the IGT, ENCOAL, and WRI/AMAX candidate mild-gasification processes. Preliminary combustion tests were conducted at three temperatures (approximately 950, 1050, and 1150 Kelvin) and at two pressures (10 and 16 atm). In addition, the B&W/EPRI fluidized combustor simulation model was modified to account for the effects of pressure on bed hydrodynamics and combustion rate. A series of sensitivity tests were conducted to determine the fuel characterization parameters that are most important in determining combustion split and overall combustion efficiency under pressurized conditions. A generic pressurized fluidized bed (PFB) design similar to the American Electric Power (AEP) Tidd unit has been used as a basis. The results of the sensitivity analyses will be used to target the mild gasification char measurements most relevant to PFB performance. Where possible, additional char characterizations will be made for the candidate char samples to improve the reliability of the performance predictions.

As of the end of this reporting period, the char characterization work as presently defined in the CRADA has been completed. High-pressure kinetic parameters have been determined for one UCC (CTC) and two IGT chars. These parameters have been input to the B&W pressurized fluidized bed combustor simulation code in order to make comparative performance estimates with conventional coals in a Tidd-type combustor. A final DOE report summarizing the results is being written.

Coal Technology Corporation (CTC) and the University of North Dakota supplied a new coal liquid/diesel fuels for evaluation during this reporting period. To date, more work has been carried out at ORNL on the CTC product. The CTC material is intended as a heavy duty diesel fuel or home heating oil. The diesel fuel was produced by mild gasification of coal followed by extracting the 500-650F boiling range and filtering. This cut represented about 35-40% of the total coal liquids from the gasification process. No additives were put in the fuel. The preliminary estimate of the cetane number of the fuel was 34 as derived from single cylinder engine ignition delay measurements. The fuel specific gravity was 0.853, placing it among the lightest coal liquids we have seen in this multi-year program. Other analyses of the CTC product is as follows in Table 1.

Table 1 Analysis of the CTC coal-derived diesel

Carbon, %	84.42
Hydrogen, %	11.28
Kjeldahl nitrogen, %	0.057
Sulfur, %	0.47
Oxygen, %	3.673 (by difference)
Btu/pound	18,950
Flashpoint, °F	159
Aliphatic to aromatic ratio	12.1

A method for derivatizing the aromatic fraction of WRI middle distillate fuels (acquired last year) was successfully scaled from 1 micromole to approximately 1/20 mole. This much material, added to conventional diesel fuel, will provide a basis for determining whether more should be synthesized or whether it has properties which make it difficult to use in an engine. Engine tests are planned to verify the combustion properties of this novel material.

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5.0 COAL COMBUSTION RESEARCH

5.1 ANALYSIS OF FBC DETERMINISTIC CHAOS

C. S. Daw

DISCUSSION OF CURRENT ACTIVITIES

Activity during this reporting period was directed primarily on continued analyses of experimental fluidized bed and pulsed combustor data. In conjunction with the data analyses, new and improved chaotic time series analysis algorithms were developed.

Fluidized Beds

Experimental measurement of voidage and pressure signals from laboratory fluidized beds at the University of Tennessee and Morgantown Energy Technology have continued. In addition, data have also been obtained for ambient- temperature tests at Foster Wheeler Development Corporation, "hot" (i.e., combustion) tests at the Babcock and Wilcox Alliance Research Center, and fluidized bed computer model simulations at Morgantown Energy Technology Center. Sufficient data have been accumulated to begin compiling general maps of chaotic behavior that appear to repeat with moderate variations over a wide range of solid properties and operating parameters. Such maps are expected to yield new insights into how flow transitions in fluidized beds are generically related to transition sequences in other dissipative dynamical systems. It is also expected that these maps will be useful in developing new fluidized bed monitoring and control strategies.

Experience with analysis of the above data has also lead to the development of new, more efficient algorithms for chaotic time series analysis. These algorithms include methods for determining mutual information, Kolmogorov entropy, and separation of the important and "noisy" components in experimental data.

Four papers on the above activities have been submitted for presentation; two at the AIChE National Meeting in November 1992 (1&2) and two at the International Fluidized Bed Combustion Conference in May 1993 (3&4).

Pulsed Combustion

Analyses of experimental pulsed combustor pressure and temperature data from Morgantown Energy Technology Center are now underway. Preliminary findings have confirmed a significant similarity between the actual combustor behavior and the computer model predictions. The experimental data also confirm the dominance of deterministic chaos in the combustor behavior. It appears that the actual combustor is, in fact, somewhat more chaotic than the model. We are now attempting to determine the causes for this.

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5.2 TECHNICAL SUPPORT TO PETC-USAID COLLABORATIVE COAL PROJECTS

R. P. Krishnan

INTRODUCTION

In response to the request from the Pittsburgh Energy Technical Center (PETC), the Oak Ridge National Laboratory (ORNL) is providing technical assistance in the implementation of collaborative coal projects under the U.S. Agency for International Development (USAID)/Government of India (GOI) Phase II, Alternative Energy Resources Development (AERD) Project.

In May 1983, the GOI and the USAID initiated the AERD project with a coal conversion component comprising of six collaborative coal projects.

- (1) Evaluation of freeboard performance in a fluidized bed combustor (FBC)
- (2) Scale-up of an atmospheric fluidized bed combustion boiler
- (3) Rheology, stability, and combustion of coal-water slurries
- (4) Beneficiation of fine coals in dense media cyclones
- (5) Hot gas cleanup and separation
- (6) Cold gas cleanup and separation

The PETC, USDOE under a Participation Agency Service Agreement (PASA) had the management responsibility for implementing the collaborative coal projects. In the FBC projects, ORNL and BHEL, Trichy, India, were designated as the lead institutions for the collaborative efforts.

The successful completion of the above coal projects in June 1987 led to a strong interest by the participants in the AERD coal conversion projects to continue the involvement of USAID and the USDOE in the following projects.

Project 1: Development of Pollution Control Strategies for Abatement of NO_x and SO₂ Emissions from Coal-Fired Power Plants

Nitrogen and sulfur oxide emissions from fossil-fired power plants are expected to increase significantly with the installation of additional coal-fired power plants in India. The composition and characteristics of Indian coals are different from U.S. coals and this will

impact the selection of pollution control strategy. The existing data base in India on NO_x/SO_2 emissions from coal-fired power plants is not adequate to quantitatively define the magnitude of the emissions, which is the first step in the evaluation of control options.

The objectives of this project are to establish the necessary data base on NO_x/SO_2 emissions by (1) baseline monitoring in selected power plants in India using the state-of-the-art techniques developed in the U.S.; (2) testing known in-furnace control strategies practiced in the U.S. in selected power plants, in India (3) bench-and pilot-scale testing of Indian coals to quantify NO_x/SO_2 emissions; and (4) simulation and modeling of the combustion and heat-transfer processes in the boiler for NO_x/SO_2 prediction.

The BHEL, Trichy, will carry out the projects in India as part of their ongoing research and development on NO_x/SO_2 control from coal-fired power plants. Technical assistance from the U.S. will include identification and procurement of state-of-the-art equipment for NO_x/SO_2 measurement, and training of the BHEL engineers in selected U.S. utilities (TVA and others) on NO_x/SO_2 monitoring and control technologies, and participation of U.S. experts in the existing bench-scale/pilot-scale testing activities at BHEL and in the baseline monitoring of Indian power plants.

Project 2: Slagging Combustor Development for High-Ash Indian Coals

Indian coals have ash content in the range of 35 to 50% and ash fusion temperature over 1482°C (2700°F). For coals of such high-ash content, it would be advantageous from the operational, reliability, and boiler life considerations if the ash can be successfully rejected as a molten slag rather than be allowed to carry over with the flue gas as in conventional pulverized fuel boilers. The slagging coal combustor (SCC) has been developed along these lines and is now in the demonstration stage in the United States.

Recognizing the potential for this technology in India, the BHEL has an active research and development program under way. A 3.0 MW(t) process development unit has been erected and is in operation at Trichy. However, there are several fundamental and engineering issues that are yet to be resolved with respect to Indian coals (slagging potential, slag rejection – quantity and slag properties, ash carry-over from the combustor, optimum air preheat system, operating flexibility – start-up, shut-down, and effect of design parameters on slag recovery and combustor operation, carbon utilization and NO_x/SO_2 emissions) before the slagging combustor can be recommended for commercial applications.

The objectives of this project are to (1) demonstrate whether the slagging combustor technology is suited for Indian coals, (2) identify the engineering problems associated with the design, operation and scale-up of the combustor, and (3) design modifications needed in the BHEL slagging combustor to conduct long duration test runs on a variety of Indian coals differing in ash content and slagging tendency.

U.S. technical assistance in the design review of the BHEL slagging combustor, screening and selection of Indian coals based on their slagging potential, and on-site participation in the testing and data analysis is envisaged.

Project 3: Characterization of Indian Coals for Combustion and Gasification

With the deteriorating quality of coal in India (highly erosive coal) coupled with fuel switching by utilities, there is a critical need to quantify the impact of coal quality on power plant performance. Pilot-scale combustion tests are mandatory to provide boiler performance data on combustion efficiency, fuel ignition characteristics, flame stabilization, slagging, fouling, erosion and corrosion of boiler components, and gaseous and particulate emissions. Pilot-scale tests are also necessary for the full-scale burning in commercial boilers. In India, there is no facility available to conduct screening tests on coal.

The objective of this project is to design, erect and commission a pilot-scale Fuels Evaluation Test Facility (FETF) at BHEL, Trichy, which will serve as a focal point for combustion research in India. The PETC combustion research division and the ORNL will be the lead U.S. institutions collaborating with BHEL, Trichy in this project.

Project 4: Residual Life Assessment and Life Extension of Coal-Fired Power Plants

The assessment of remaining life of coal-fired power plant components based on quantitative, nondestructive, real-time measurements of the extent of damage to these components is an area which is actively pursued in most advanced countries where the latest diagnostic tools are available. The methodologies and techniques are the key to a successful remaining life assessment program. In keeping with the need for steady and reliable electric supply, the Ministry of Power, Government of India has recently embarked on a multi-million dollar power plant life assessment and rehabilitation program.

This project will be a collaborative effort, initially between the BHEL and the Electric Power Research Institute (EPRI), in which the diagnostic techniques, design criteria,

methodologies, and implementation strategies developed by EPRI for the U.S. utilities will be tested in selected Indian utilities. The highly erosive nature of Indian coals will provide an opportunity to test the engineering correlations for prediction of erosion of boiler and auxiliary components, and possibly extended their range of applicability.

Project 5: Environmental and Natural Resource Analysis of Coal Cycle

The mining, conversion, and disposal of waste and byproducts from coal utilization have serious environmental repercussions in India. Although there are regulations stipulated for air and water quality pollutants, they are not strictly enforced except in urban areas. This policy is going to change in the near future, and several groups are working in the country on allowable limits, environmental considerations for power plant siting, and impact of air/water/soil quality in the vicinity of coal mines and coal burning facilities. In all these tasks, environmental system models and an environmental data base are vital. Air and water quality data are only now being collected in India, mainly around the large power plants in central India.

The goal of this project is to develop environmental system models for prediction of air and water quality near coal-based power plants. The present data base will only permit development of the overall structure of the model and the process/environmental data needed as inputs for the system model. It is expected that the model can be refined as more data becomes available. The methodology and the model inputs and outputs will be established in this project.

The project will be carried out by the Tata Energy Research Institute (TERI), New Delhi. Assistance to TERI will be provided by ORNL, PETC, EPA in the screening, selection and adaption of the air/water quality prediction models developed in the U.S. for local conditions.

The AERD project ended on June 30, 1992. Four out of the five coal projects under AERD were essentially completed at this time. The only unfinished project was the Fuels Evaluation Test Facility (Project 3) which is under erection at BHEL, Trichy.

During this reporting period, the activities and accomplishments in each of the five coal projects are summarized below.

Project 1. The draft report on the emissions monitoring activities which was conducted at the Vijayawada Thermal Power Station (VTPS) in Vijayawada, India, 600

km north of Madras. jointly by BHEL, the Central Power Research Institute (CPRI), Bangalore, the Tennessee Valley Authority (TVA), and ORNL in February 1992 has been submitted to PETC for review and comments. No further activity is planned since the project is essentially complete.

Project 2. There was no further activity in this project beyond what was reported in the previous Semi-Annual Report (October 1991 - March 1992). The modifications suggested by US experts during the design review of the BHEL slagging combustor (SCC) in the U.S. were implemented by BHEL. PETC was to arrange for two weeks of start-up assistance in June 1992. However, there was a conflict in scheduling the visit of the US expert and the AERD project ended on June 30, 1992. USAID, New Delhi, is looking at alternative funding arrangements to PETC to provide short-term, on-site, technical assistance for the remaining activity in this project. When this comes through, the consultant who was scheduled to go in June 1992 will visit Trichy to assist in the shakedown trials and testing in the SCC.

Project 3. Erection of the FETF is continuing at Trichy. PETC/ORNL is communicating with BHEL regularly and providing the necessary assistance through correspondence. The last batch of the USAID equipment was shipped in the latter part of June 1992 and has been received at the site.

Substantial progress has been made in the erection since June 1992. Except for the control room, all the structures and columns have been erected. Rerouting of the existing water and sewage lines has been completed. Out of the 96 tons of steel released for fabrication, 73 tons have been fabricated. Majority of the detailed engineering including the electrical and the control/instrumentation systems have been completed. The only remaining items are the compressed air piping and the Dowtherm heat transfer fluid piping which are in progress. More than 80% per cent of the indigenous equipment for the FETF have arrived at the site. The rest is expected by December 1992. The projected schedule for completing the erection work is now February 1993. Precommissioning trials will begin in March 1993. ORNL/PETC on-site assistance is expected to resume once USAID, New Delhi, provides the additional funds requested by PETC. Since the AERD grant agreement with GOI ended on June 30, 1992, USAID can only provide the funds if an alternate arrangement is worked out with the GOI. USAID staff and the PETC program manager visited the FETF site in

June 1992. Subsequent to their visit, it has been decided that technical assistance from ORNL/PETC should be continued till the facility is built and shakedown trials are satisfactorily completed.

Project 4. With the completion of the boiler condition assessment demonstration by U.S. experts and BHEL at the Nasik Thermal Power Station (NTPS) in India during February - March 1992, all the deliverables in this project have been met. A final report was prepared after the completion of the metallurgical evaluation of the boiler tube specimens of the Nasik plant at Trichy. The report has been submitted to PETC.

Project 5. There has been no further activity on the project beyond what was reported in the Semi-Annual Report for October 1990 - March 1991. USAID funding for this project terminated in December 1990.

During the next reporting period, the progress on the FETF will be reported. ORNL/PETC will continue to provide technical assistance to BHEL till the facility is fully commissioned. However, no travel to the site can be undertaken by ORNL/PETC until the additional funds are made available to PETC and the USAID/PETC PASA or many other type of agreement becomes effective.

6. FOSSIL FUELS SUPPLIES MODELING AND RESEARCH

6.1 STRATEGIC PETROLEUM RESERVE PLANNING AND MODELING

P.N. Leiby

INTRODUCTION

The Strategic Petroleum Reserve (SPR) is a government-owned stockpile of crude oil intended to serve as a buffer against possible oil market disruptions. The overall purpose of this project is to develop and apply improved models for SPR long-run planning. Much of our earlier effort addressed large-scale planning issues such as the appropriate size of the reserve, and whether the reserve should be composed of crude oil or refined petroleum products. These questions were examined in part through the use of moderately detailed simulation and dynamic programming models. Always, a critical issue has been the large uncertainty surrounding future oil market conditions, and the resulting uncertainty regarding SPR program benefits. Current project efforts emphasize developing new ways to explicitly and flexibly portray this uncertainty or risk. The goal is to provide a comparatively simple, graphically-oriented modeling system with which SPR planners may explore these matters directly.

DISCUSSION OF CURRENT ACTIVITIES

Recent efforts have focused on the design and construction of an SPR Risk Model (called SPR-Risk hereafter). The sequence of required tasks includes:

- I. Expressing the existing larger model(s) in "reduced-form" as a single spreadsheet for use by SPR-Risk system
- II. Establishing connections with the probabilistic risk software (@Risk) to specify uncertainties
- III. Planning user interactions, designing and verifying user interface
- IV. Model and user interface integration and testing (with Baler/ICE)

The motivation for the SPR-Risk model is to provide a simple summary of the SPR behavior and results obtained from some of the larger SPR models (DISSPR, ORNLTEIS, and Hogan-Leiby), embedded in a framework which highlights risk and uncertainty. The SPR-Risk model is a PC-based, interactive, and user-friendly system. The SPR-Risk model is basically a spreadsheet connected to a risk-analysis engine (@Risk), with a smooth front-end for user control and output. It is executable under modifiable assumptions by a general audience of DOE managers. It is anticipated that more extensive changes in model behavior or assumptions may be made by a few experienced users. It focuses on possible drawdown events and rates, but may also report other market results and benefits measures to the extent that they can be represented in the reduced-form model. A variety of SPR planning questions are closely related to the anticipated frequency and rate of SPR drawdowns. Planning may also benefit from considering SPR outcomes in a framework which displays risk and the range of possible outcomes.

Some examples of issues for which this SPR-Risk Model is potentially helpful are:

SPR Financing Mechanisms

There is interest in assessing alternative financing mechanisms for the SPR, which may establish private claims on SPR oil. The issue then arises regarding property rights to oil withdrawn under a partial drawdown. The SPR-Risk model may be used to examine partial drawdown events to assess the likelihood of these events and the financial implications of alternative ownership.

SPR Capacity-Size Issues

Quick rough cuts at the SPR size issue can be performed, provided the assumptions do not exceed the bounds of the market behavior mapped in the reduced-form model. The SPR-Risk model could address the question "What risk function suggests sufficient use that larger capacity is needed, and how much additional capacity is provided by cavern expansion during drawdowns?"

SPR Drawdown Capability Issues

A system which displays drawdown frequencies and rates will be helpful in evaluating drawdown capability enhancement alternatives.

SPR Facilities Maintenance and Design Issues

The planned replacement of a West Hackberry brine pipeline exemplifies the major facilities re-investment choices necessary to assure compliance with SPR performance

criteria. The utility of such investments hinges on the risk of fill/draw/refill events necessitating the use of those performance capabilities. What are the benefits of maintaining a certain level of system readiness?

It is important to be clear on what the SPR-Risk model will not do. SPR-Risk will be based on reduced-form versions of the 3 principal SPR models, in which the following features are currently unavailable:

- Regional bottlenecks, transport constraints
- Crude oil mix, budget process, non-U.S. stock refill
- Utilization delays
- Regional reserves, product storage.
- Issues of refinery availability and connections to crude mix.

8. COAL STRUCTURE AND CHEMISTRY

V. J. Tennery

8.1 ANALYTICAL CHARACTERIZATION OF COAL SURFACES AND INTERFACES

E. L. Fuller, V. J. Tennery, T. A. Nolan, L. F. Allard, and A. Choudhury

Diffuse reflectance infrared spectroscopy (DRIS) was used as a major instrumental technique for studying the spectral regions in all of the coals of the Argonne Premium Coal Sample (APCS) set to obtain information regarding the stretching and bending frequencies of the various bond types found in the coals represented by this highly standardized set of coal specimens. This technique clearly delineates the O-H stretching frequencies from about 3500 to 2500 wave numbers. It was also a good tool for studying the complex frequency regime from about 2000 to 500 wave numbers, representing a dense regime of bending modes. Fourier self deconvolution was used to distinguish details in the "hydrocarbon" spectral region around 3000 wave numbers. Pocahontas No. 3 coal was found to have a minimum of seven spectral peaks in this region. The "coalification" of the various materials in the APCS was clearly discernible from the details observed in the region near 3000 wave numbers. For example, Beulah Zap, a lignite, and Wyodak, a sub-bituminous, both presented relatively simple and weak spectral responses in the O-H stretching frequency range, whereas Upper Freeport, a medium volatiles bituminous, and Pocahontas No. 3, low volatile bituminous, both exhibited rich spectral detail in this region.

Studies of coal samples were carried out to determine the initial effects of oxidation upon the coal structures. These oxidations were often carried out at 300°C for periods up to 200 h. Large changes were observed in the spectra near 3000 wave numbers, indicating the oxidation of the coal surface from these exposures.

Additional work was done in studying the surface area and porosity in a number of these coals.

Transmission electron microscopy (TEM) techniques were developed for characterizing the interfaces between included minerals and the coal structure in a number of the coals, but most of the effort was focused on Pittsburgh No. 8, a high volatile

bituminous which was considered representative of many bituminous coals. Observations of pyrite microcrystals with framboid structures in bulk coal specimens revealed the surprising result that a significant fraction of individual crystallites were in fact polycrystalline rather than single crystal. Further studies of macro single crystals of pyrite also revealed that all "single crystals" studied actually consisted of a system of small microcrystals even though the object appeared as a pyrite single crystal. Oxidation of the pyrite resulted in the formation of a surface film of goethite that coats the pyrite. Pyrrhotite was also observed on large crystals.

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