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Advanced Research and Technology Development

Fossil Energy Materials Program Implementation Plan for Fiscal Years 1986 Through 1990

Fossil
Energy
Program

OPERATED BY
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FOSSIL ENERGY
ADVANCED RESEARCH AND TECHNOLOGY DEVELOPMENT

FOSSIL ENERGY MATERIALS PROGRAM IMPLEMENTATION PLAN FOR FISCAL YEARS 1986 THROUGH 1990

Compiled by
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NOTICE: This document contains information of a preliminary nature. It is subject to revision or correction and therefore does not represent a final report.

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PREVIOUS REPORTS IN THIS SERIES

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ORNL/TM-7964	*Advanced Research and Technology Development Fossil Energy Materials Program Plan for Fiscal Years 1982 Through 1986*, R. A. Bradley and R. R. Judkins, December 1982.
ORNL/TM-8737	*Advanced Research and Technology Development Fossil Energy Materials Program Plan for Fiscal Years 1983 Through 1987*, R. A. Bradley and P. T. Carlson, July 1984.
ORNL/TM-8954	*Advanced Research and Technology Development Fossil Energy Materials Program Implementation Plan for Fiscal Years 1984 Through 1988*, R. A. Bradley and P. T. Carlson, October 1984.
ORNL/TM-9328	*Advanced Research and Technology Development Fossil Energy Materials Program Implementation Plan for Fiscal Years 1985 Through 1989*, R. A. Bradley and P. T. Carlson, February 1985.

FOREWORD AND ACKNOWLEDGMENTS

The development of this program implementation plan is the result of considerable effort by several individuals. Chapter 3 of Part II on Coal Gasification was prepared primarily by the staff of the Materials Science Division of Argonne National Laboratory under the leadership of W. A. Ellingson. The remainder of the document was prepared by the staff of the Fossil Energy Materials Program, Metals and Ceramics Division, Oak Ridge National Laboratory. Guidance for the preparation of this plan was provided by E. E. Hoffman, Department of Energy Oak Ridge Operations, and S. J. Dapkunas, Department of Energy Fossil Energy Office of Technical Coordination.

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ADVANCED RESEARCH AND TECHNOLOGY DEVELOPMENT FOSSIL ENERGY MATERIALS PROGRAM IMPLEMENTATION PLAN FOR FISCAL YEARS 1986 THROUGH 1990*

Compiled by
R. A. Bradley and P. T. Carlson

ABSTRACT

This program implementation plan for the Department of Energy Advanced Research and Technology Development (AR&TD) Fossil Energy Materials Program reviews the technical issues and the materials research and development needs of fossil energy technologies. The status and plans for research and development activities in the AR&TD Fossil Energy Materials Program to meet those needs are presented. Detailed information about these plans is provided for FY 1986 through FY 1988, and long-range plans are described for FY 1989 and FY 1990.

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PART I

INTRODUCTION

1. INTRODUCTION

1.1 PROGRAM DESCRIPTION AND OBJECTIVES

This implementation plan for the Department of Energy Advanced Research and Technology Development (AR&TD) Fossil Energy Materials Program was prepared in cooperation with the U.S. Department of Energy (DOE) Oak Ridge Operations (ORO) Office and the DOE Fossil Energy Office of Technical Coordination. It describes the program objectives, organization, and responsibilities of the various participants of the program. In particular, details of planned activities for FY 1986, FY 1987, and FY 1988 and an indication of anticipated activities through FY 1990 are presented.

The overall objective of the AR&TD Fossil Energy Materials Program is to conduct long-range basic research and development that address generically the materials needs of fossil energy systems, including materials for coal preparation, coal liquefaction, coal gasification, heat engines and heat recovery, combustion systems, fuel cells, magnetohydrodynamics, and oil shale processing. In addition, the scope of the Program includes the development of advanced materials and processing techniques.

The materials research thrust areas of the Program are (1) Structural Ceramics, (2) Alloy Development and Mechanical Properties, (3) Corrosion and Erosion of Alloys and Refractories, and (4) Assessments and Technology Transfer.

Materials research and development for specific fossil energy technologies are funded by various DOE offices having specific materials requirements for those technologies. The intent is that this program be consistent with the emphasis of DOE on long-range generic research to address the needs of evolving fossil energy technologies. An indication of the relationship between the long-range generic research of the AR&TD Fossil Energy Materials Program and the needs of these fossil energy technologies is given in Table I.1. Designations of the research efforts of the AR&TD Fossil Energy Materials Program are listed vertically according to research thrust area, and the fossil energy technology areas are listed horizontally. The X-symbols indicate those technology areas affected by

Table I.1. Relationships among materials research thrust areas and technology areas of the Advanced Research and Technology Development (AR&TD) Fossil Energy Materials Program

Thrust areas	Technology areas							
	Coal preparation	Coal liquefaction	Coal gasification	Heat engines and heat recovery	Combustion systems	Fuel cells	Magnetohydrodynamics	Oil shale
Structural ceramics								
ANL-1(A)			X	X	X			
ANL-1(B)			X	X	X			
ANL-1(C)			X	X	X			
B&W/ORNL-1(B)			X	X				
GT-1			X	X				
GT-1(A)			X	X				
INEL-1(A)			X	X				
INEL-1(B)			X	X				
LANL-1			X	X				
NBS-1			X	X				
ORNL-1(A)			X	X				
ORNL-1(C)			X	X	X	X		
UKCRE-1			X	X	X	X		
SC(I)-1			X	X	X	X		
SC(I,U)-1			X	X	X			
SC(U)-1(A)			X	X	X			
SC(U)-1(B)			X	X	X			
PNL-1						X	X	
Alloy development and mechanical properties								
CU-2(A)			X	X	X			
PNST-2		X	X					
UCB-2		X	X					
UCSB-2		X	X					
UTN-2		X			X			
WEC-2(A)		X	X					
WEC-2(B)		X	X					
SC(U)-2(A)			X	X	X			
CE-2				X	X			
CU-2			X		X	X		
HEDL-2	X		X	X	X	X		
ORNL-2(B)				X	X	X		
ORNL-2(C)				X	X			
ORNL-2(D)				X	X			
UT-2				X	X			
SC(I)-2(A)				X	X			
SC(I)-2(B)				X	X			
SC(I)-2(C)				X	X			
SC(I)-2(D)				X	X			
SC(I,U)-2(B)				X	X			
SC(I,U)-2(C)				X	X			
SC(I,U)-2(D)				X	X			
CSM-2			X		X	X		
INEL-2(A)		X	X		X	X		
INEL-2(B)		X	X		X	X		
ORNL-2(A)		X	X		X	X		
SC(U)-2(B)			X	X	X	X		
RDA-2		X	X	X				

Table I.1 (continued)

Thrust areas	Technology areas							
	Coal preparation	Coal liquefaction	Coal gasification	Heat engines and heat recovery	Combustion systems	Fuel cells	Magnetohydro-dynamics	Oil shale
Corrosion and erosion of alloys and refractories								
ANL-3(A)			X	X	X	X		
ANL-3(B)				X	X	X		
ERE-3		X						
GE-3			X		X			
ORAU-3			X	X	X			
ORNL-3(A)		X	X					
ORNL-3(B)			X	X	X			
PITT-3			X		X			
SC(I,U)-3(A)				X	X			
SC(I,U)-3(D)				X	X			
SC(I,U)-3(E)				X	X			
BCL-3	X	X	X					
LBL-3	X	X	X		X			
NBS-3(A)	X	X			X			
ORNL-3(C)		X			X			
UCIN-3	X	X	X		X		X	
UND-3(A)		X	X	X				
UND-3	X	X	X		X			
SC(I,U)-3(B)				X	X			
SC(I,U)-3(F)				X	X			
SC(U)-3(A)				X	X			
SC(U)-3(B)				X	X			
SC(I,U)-3(C)								X
ORNL-3(D)		X			X	X		
SC(I)-3(A)						X		
SC(I)-3(B)						X		
ISU-3			X				X	
MIT-3			X				X	
NBS-3(B)			X	X				
PNST-3			X				X	
VPI-3			X				X	
Assessments and technology transfer								
ORNL-4(B)		X	X	X	X	X		
SC(I)-4				X	X			
BCL-4	X							
SC(I,U)-4			X					

research in the different thrust areas. In many areas, the generic research of the program contributes to the understanding of materials problems in several fossil energy technologies.

Management of the program has been decentralized to DOE-ORO, with the Oak Ridge National Laboratory (ORNL) as technical support contractor. A substantial portion of the work on the AR&TD Fossil Energy Materials Program is performed by participating subcontractor organizations. All subcontractor work is technically monitored by program staff members at ORNL and at Argonne National Laboratory (ANL).

The program is organized by a work breakdown structure (WBS) in which projects are organized according to the materials research thrust areas described above. A schematic summary of this organization is provided in Fig. I.1. In this Plan, relevant materials research and development needs are identified by fossil energy technology in Part II. Descriptions of ongoing and planned research to address these needs are presented according to research thrust areas in Part III.

Tables in each chapter of Part III, Current and Planned Projects in the AR&TD Fossil Energy Materials Program, present funding levels for each project. The funding distribution for FY 1986 reflects the activities planned for that year; for subsequent years, the distribution reflects our assessment of research and development needs for the DOE Fossil Energy Materials Program. These needs were identified by an assessment of fossil energy materials needs,[1] from research and development proposals, through discussions with individuals and organizations interested in fossil energy materials development, and by a series of technology base reviews conducted annually by the DOE Fossil Energy Office of Technical Coordination. In addition, the AR&TD Fossil Energy Materials Program interacts with other DOE research programs, such as the Materials Science Program of the Office of Basic Energy Sciences (BES), through participation in the activities of the Energy Materials Coordinating Committee (EMaCC). One activity of EMaCC of particular importance to close coordination among programs is the annual technical report, the most recent issue of which covers research activities during FY 1984 (ref. 2). Numerous other interactions occur between the Fossil Energy Materials Program and other DOE programs to ensure that the goals of the program are consistent with

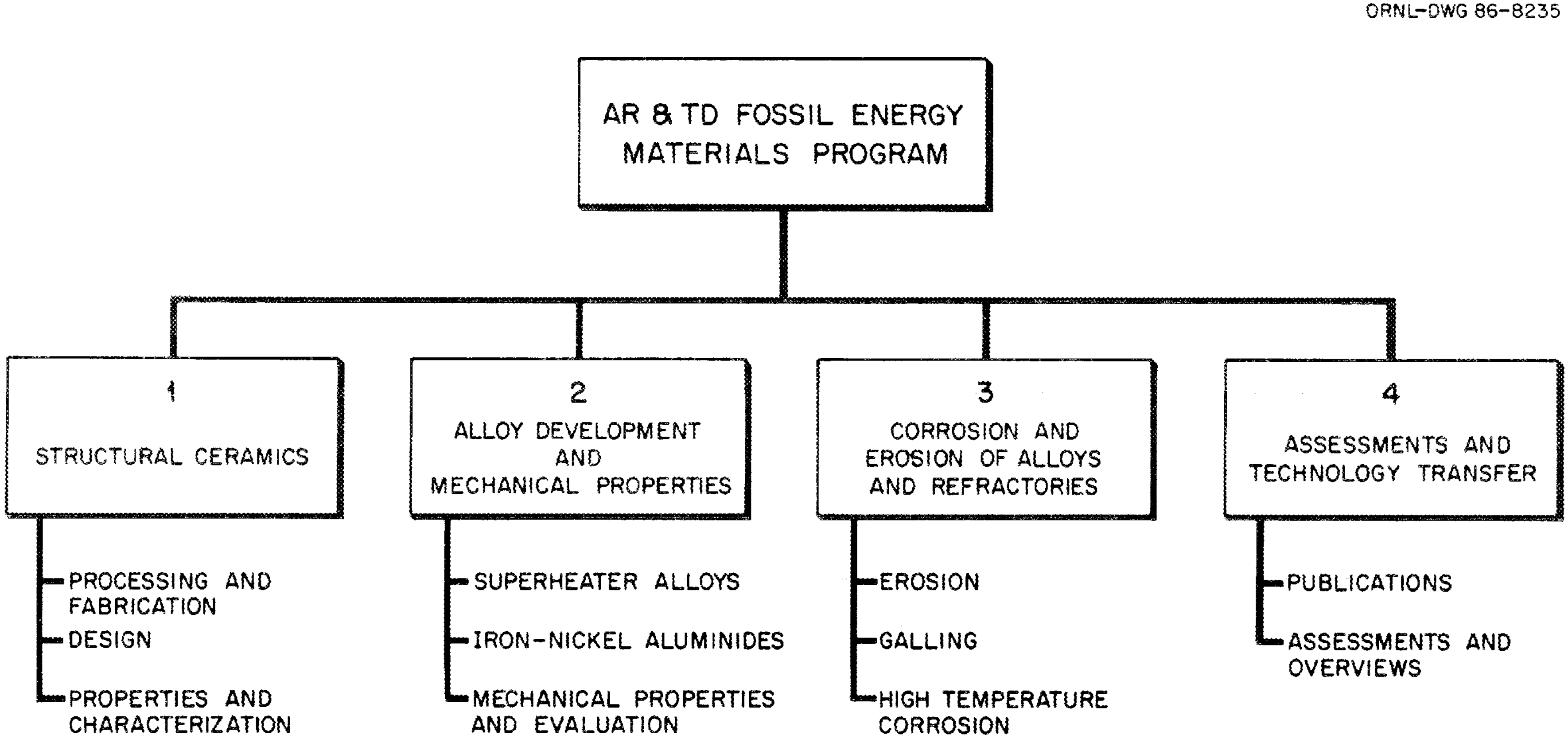

Fig. I.1. Work breakdown structure for the AR&TD Fossil Energy Materials Program.

the needs of fossil energy technologies. Finally, to maintain an awareness of current research needs, the program management and principal investigators in the AR&TD Fossil Energy Materials Program routinely receive news bulletins issued by the BES Materials Science Program on various subjects such as welding, erosion, structural ceramics, and sulfur attack. We expect this program implementation plan to be revised annually, and industrial and other research organizations are invited to contribute to future revisions.

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2. *U.S. DOE Energy Materials Coordinating Committee (EMaCC) Annual Technical Report, Fiscal Year 1984 with Fiscal Year 1985 Data*, DOE/ER-0241, July 1985.

PART II

MATERIALS RESEARCH AND DEVELOPMENT NEEDS OF FOSSIL ENERGY TECHNOLOGIES

1. COAL PREPARATION

1.1 TECHNOLOGY STATUS AND MATERIALS NEEDS

The recent increased emphasis on the efficient and cost-effective combustion of coal and on the retrofitting of oil- and gas-fired boilers to burn pulverized coal or coal-liquid slurries has increased the importance of proper cleaning and preparation of the feed coal. The performance and efficiency of the combustion facility depend strongly on coal quality. The inorganic mineral matter in the feed coal, which transforms and reacts during the combustion process, can be found in both the coal slag and fly ash waste products. The resultant slag and ash generally have highly deleterious erosive and corrosive effects on the components of a combustion facility. The particular problems of erosion, corrosion, slagging, and fouling during combustion are discussed in more detail in Chap. 5, Combustion Systems. The presence of mineral matter also results in erosion of coal-handling and coal preparation equipment. These problems are most economically addressed with adequate coal-cleaning techniques to reduce the ash and sulfur levels. In addition to pulverized coal, coal-water slurries are becoming economically attractive as replacement fuels for oil or natural gas in conventional combustors. The coal-water slurries typically contain 65 to 75% pulverized coal and 25 to 35% water. An important factor in the preparation of such slurries is the use of ultrafine, ultraclean coal, and this need has resulted in the development of advanced physicochemical cleaning methods for the removal of ash and sulfur. To produce coal-water slurries, the coal is ground 5 to 10 times finer than conventional pulverized coal and cleaned to 1 to 3% ash content and 0.5 to 1% sulfur content. Finally, public opinion on the question of acid rain, which may result from the combustion of high-sulfur coal, has increased the interest in advanced coal-cleaning techniques. The use of coal-water slurries may contribute to the reduction of sulfur oxides in the atmosphere in light of the requirement for ultraclean coals for the slurries. This may in turn reduce the amount of acid rain from coal combustion.

The principal objective of any coal preparation process is to remove the mineral impurities. The methods currently used commercially are derived largely from the separation of impurities based on the differences in specific gravity of the various coal constituents. These are generally referred to as gravity separation processes and typically use mechanical separators such as jigs, tables, and cyclones. Another commercial method used is froth flotation, which uses the differences in surface properties of the coal and its mineral matter to clean the coal physically. Physical cleaning or beneficiation extracts the coarser forms of mineral matter, including pyritic sulfur; however, none of the organic sulfur is removed. As the coal particle size decreases below 0.5 mm, gravity separation methods are ineffective in removing sufficient quantities of sulfur and mineral impurities. Techniques that can be employed for cleaning coal that has been pulverized to fine or ultrafine particle sizes are (1) selective coalescence, (2) heavy-liquid cycloning, and (3) froth flotation.[1]

The materials problems encountered with gravity separation processes are primarily due to erosion of pipes, chutes, cyclones, and screens. The problems of erosion and wear in physical coal preparation systems arise essentially from the constituents of the coal. A high-ash coal, for example, containing significant quantities of hard minerals (e.g., quartz and chert) and other inorganic matter will be more erosive than will a low-ash coal. Pipe erosion occurs primarily in elbow locations, and quite often the simplest approach to eliminating the problem is to design and build a facility on the basis of experience. Areas subject to excessive wear are identified in practice, and the faults are usually overcome by removing the eroded area and redesigning the elbow to include a blind tee. The blind tee initially catches the solids, which then become the impingement surface. Chute wear is minimized through the use of armor plate (hardened steel surfaces). Protective coatings could possibly be developed and plasma sprayed onto the critical surfaces of gravity separation cyclones to reduce erosive wear in these devices. Screen wear occurs at the site of product impingement, and operators minimize it by periodically rotating the screen locations. Screen wear can be dramatically reduced by use of rubber-coated screens; however, these screens cost considerably more than uncoated screens. In addition, rubber coating of screens reduces their capacity.

Theoretically, a high percentage of the ash and inorganic sulfur could be removed from the coal by physical cleaning methods; however, total sulfur reduction is limited by the concentration of organic sulfur in the coal. To reduce the organic sulfur and, thereby, the total sulfur content beyond the levels possible with physical cleaning, chemical coal cleaning methods are employed. The chemical coal cleaning methods developed by TRW (fused salt process) and the General Electric Company (microwave process) are based on alkali displacement and have demonstrated the ability to remove greater than 90% of the total sulfur from various coals. In addition, an acid wash, which follows desulfurization, has been shown to remove about 95 to 98% of the ash in the coal.[1] Removal of ash and sulfur to these levels represents a significant step in mitigating acid rain through the reduction of SO_x emissions from coal combustion. As a result of the increasing need for cleaner coals with the lowest possible ash and sulfur levels and their expanded use, more advanced chemical coal cleaning techniques are being developed. Because of the severity (corrosive fluids at high temperatures and pressures) of these advanced chemical cleaning techniques, materials selection is of utmost importance. We will follow the progress of research activities related to these advanced coal cleaning methods and will coordinate our research and development activities with the Coal Preparation Program in the DOE Fossil Energy Office of Coal Utilization, Advanced Conversion, and Gasification to address identified materials problems and to implement the appropriate efforts.

As discussed above, coal-water slurries are becoming attractive as replacement fuels for oil or natural gas. In fact, the ease of handling slurries in the same fashion as that for liquid fuels has resulted in slurries being considered as replacements for pulverized coal for combustion. Advanced cleaning techniques such as those mentioned above can produce ultrafine pulverized coals with about 1% ash. Ultrafine pulverized coals are extremely difficult to feed into the combustion zone in the dry state; consequently, the use of coal-water slurries (containing ultraclean coal) will result in more efficient combustion. The principal materials problems of both slurry production and slurry use arise from the often caustic nature of the chemical additives present in the slurries (to impede agglomeration) as well as from the erosive attack of the ash and other inorganic matter still present in the coal. Corrosion, erosion, and wear of slurry mixers, pumps, transport pipes, and feed systems for transport of the slurry, either during the production process or to the combustor, are materials problems that will continue to be addressed. The corrosive and erosive nature of the slurry due to entrained ash particles and hard minerals is accentuated by degradation processes within the slurry itself such as changes in viscosity, pH, and particle size. The latter problem arises when insufficient mixing allows the individual coal particles in the slurry to agglomerate. Research programs need to continue to address the problems of erosive-corrosive attack of key components of slurry production equipment if this technology is to remain economically competitive with pulverized-coal use.

A potential rival of conventional coal transportation is the proposed use of slurry pipelines.[2,3] Erosion and wear problems for this transportation system are expected to be similar to those experienced in slurry production processes. Pumps and mixing systems will be needed at various positions of the pipeline to maintain the flow of a uniform unagglomerated slurry. Erosion and corrosion will need to be reduced through the choice of proper materials or the application of coatings and claddings on conventional materials. Research activities on mechanisms of corrosion and erosion will greatly assist the ability to address these materials problems satisfactorily.

In addition to the effects that proper coal preparation will have on either pulverized-coal-fired or coal-slurry-fired combustion systems, the substantial reduction or the virtual elimination of ash, sulfur, and chlorine in the feedstock for coal conversion systems would dramatically temper the materials technology needs for these systems. These systems are discussed in Chap. 2, Coal Liquefaction, and in Chap. 3, Coal Gasification.

In summary, most of the materials problems of coal preparation are due to corrosion, erosion, and wear. These materials problems and needs will continue to be assessed by the AR&TD Fossil Energy Materials Program to understand better the corrosion and erosion problems and to identify the research needed to solve these problems. The results from a number of projects on the AR&TD Fossil Energy Materials Program, which address problems of erosion and corrosion in coal preparation [UND-3(A)], coal liquefaction [BCL-3, LBL-3, and NBS-3(A)], and coal combustion [ORNL-3(C), UCIN-3, and UND-3] environments, are expected to contribute significantly to understanding erosion and corrosion mechanisms that occur in coal preparation systems. Furthermore, we will coordinate our efforts with the research supported by the Coal Preparation Program of the DOE Fossil Energy Office of Coal Utilization, Advanced Conversion, and Gasification to ensure that the research projects initiated by the AR&TD Fossil Energy Materials Program are consistent with the current materials needs of this technology.

1.2 REFERENCES

1. *Coal Preparation Summary Program Plan*, Department of Energy Fossil Energy Office of Coal Utilization, Advanced Conversion, and Gasification, February 1984.

2. "Who Will Move the Coal," *Min. Eng. (N.Y.)* 29(10), 49–50 (October 1977).

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2. COAL LIQUEFACTION

2.1 TECHNOLOGY STATUS AND MATERIALS NEEDS

For several years direct coal liquefaction processes have been under development by private industry with support from DOE. These development activities have included the operation of four major pilot plants: the SRC-I plant in Wilsonville, Alabama (1974—present); the SRC-II/I plant in Fort Lewis, Washington (1974—1981); the Exxon Donor Solvent plant in Baytown, Texas (1980—1982); and the H-Coal plant in Catlettsburg, Kentucky (1980—1982). Only the Wilsonville plant remains in operation. The principal processes were described in a previous program plan.[1] Although the processes differ in detail, similar systems may be considered for identifying materials research and development needs. For this discussion, the direct liquefaction processes will be divided into the following major process areas: coal and slurry preparation, preheater and reactor system, pressure letdown and separation system, and fractionation system.

The research and development program described here is based almost entirely on the needs of direct coal liquefaction plants of the types mentioned above. Future activities should focus on the materials needs of advanced processes, which are currently at a bench-scale level of development. Many of our current projects and planned activities are appropriate for advanced processes. These include the areas of erosion, corrosion, and erosion-corrosion. Our present pressure vessel materials projects are being phased out and will be replaced, if needed, by projects addressing pressure vessels appropriate for advanced processes. Thus, as our plans suggest, research and development in these areas will be continued. The research and development activities for coal liquefaction that we have identified are discussed in Part III of this Plan.

2.1.1 Coal and Slurry Preparation System

The materials problems in the slurry preparation system of liquefaction process development units (PDUs) and pilot plants are fairly well understood: wear, erosion, and corrosion have been the main problems in the various components. In recent years, however, several changes have been introduced into component designs, materials selection, and process stream flow characteristics. It is not altogether certain that all the materials technology now maturing around pilot plant experience can be extended to larger scale plants without some degree of trial and error. Some materials substitutions can also be expected. Strong tough alloys are needed for coal-crushing equipment. Wear can be reduced by hardfacing critical areas. Selection of erosion-resistant piping materials in the slurry preparation system is not a significant problem if the design, sizing, and construction are adequate. Erosion-corrosion problems may increase with increasing slurry mixing temperatures. Pump and valve designs are critical, and new hardfacing alloys will be needed in these components to achieve satisfactory life. Piping and vessel materials that hold the recycle slurry must be selected to accommodate the erosive and corrosive species that will be present, such as coal ash, H_2S, and chlorides. Lining of critical vessels will be necessary in many cases.

Specific erosion areas needing attention include studies at lower particle velocities (0.9–6 m/s) on alternative materials and on liquid carriers typical of the slurries actually present. Chemical effects of coal liquids have scarcely been addressed. Effects of reaction products have been determined for only simple oxide films to date. Development of improved hardfacing materials and coatings and methods of applying these materials as liners are needed to extend slurry pump life. The use of inserts, liners, and coatings of erosion-resistant materials of compatible thermal expansion characteristics to slurry pump construction materials needs to be explored. Additional effort is required to characterize and understand the combined effects of mechanical wear and corrosion.

Nondestructive testing methods such as ultrasonic testing and eddy-current techniques for thickness determination and ultrasonic and infrared techniques to confirm bonding integrity should be investigated and developed for hardfacing in pumps, valves, and other components subjected to erosion.

2.1.2 Preheater and Reactor System

The high-pressure high-temperature hydrogenation section of coal liquefaction plants presents many problems from an economic and reliability point of view. The preheater coils, dissolver, and high-pressure separators will be designed to the rules of the *ASME Boiler and Pressure Vessel Code*, and the designs will incorporate sections of the American Petroleum Institute (API) codes where needed. Considerations that must be addressed in the design of these systems include pressure, temperature, fabrication techniques, welding procedures, steel composition, temperature cycling, and partial pressures of hydrogen and hydrogen sulfide. Potential failure modes that are addressed during materials selection include aging embrittlement, hydrogen attack, hydrogen embrittlement, sulfidation, erosion, stress rupture, creep-fatigue, chloride attack, polythionic acid attack, naphthenic acid attack, stress corrosion cracking, thermal fatigue, and dissimilar-metal weld cracking.

The technology for the design and fabrication of these vessels will be based on the demonstrated technologies used for fabrication of vessels for high-temperature high-pressure applications in hydrogen-hydrocarbon service in the petroleum refining and chemical industries. However, we expect the demonstration and commercial plants to require extensions of existing technology to larger vessels and possibly higher operating temperatures, and there may be problems with such extensions. For example, there is no existing design methodology in the public sector that provides for fatigue, creep-fatigue, crack growth, or thermal ratchetting at temperatures above 370°C. Logically, it will be the responsibility of the coal conversion projects to develop an adequate design methodology and data base. The recent de-emphasis of coal liquefaction projects has ended work in these areas. In the absence of such projects, approaches to design problems must be anticipated in order to structure meaningful research programs in the materials area.

The pressure vessels envisioned for the demonstration and near-term commercial coal liquefaction plants are large. Recent designs call for pressure vessels 3 to 4 m in diameter and 20 to 25 m in height, with a wall thickness of 0.3 to 0.4 m. The wall thickness will be the maximum for which the steelmaker can obtain the specified properties (usually measured at quarter thickness) in the selected steel. Vessel sizes would be the maximum that can be shop fabricated and transported to the plant site. Fabrication requirements hinge critically on the size of the reaction pressure vessel. Railroad transportation limits vessels to a diameter of 4.3 m, a mass of 725 Mg, and a maximum length of about 30 m. Vessels larger than the above sizes would require either plant siting near a navigable waterway or field fabrication.[2]

In addition to the problems inherent in thick-section heat-treated steels, processes are required to produce sound welds rapidly in any orientation on a vessel that cannot be moved. Conventional practice is submerged arc welding (SAW), which is highly automated and efficient but is generally usable only in the flat position. Processes that will give high deposition rates of high-quality welds in the field and that do not require the flat position are being developed by industry for heavy-wall vessels in the petroleum industry. Several different welding methods offer potential advantages. Examples are

1. narrow-groove variants of gas metal arc welding and hot wire-filler gas tungsten arc welding,
2. electron beam welding,
3. electroslag welding, and
4. adaptation of SAW to vertical and horizontal welds.

Any process used must have been qualified sufficiently to satisfy appropriate code and regulatory committees that the mechanical properties of fusion zone, heat-affected zone, and base metal will meet or exceed specific minimum values after all welding and heat treatment.

Satisfying code committees (in particular, the *ASME Boiler and Pressure Vessel Code*, Sects. VIII and IX) (ref. 3) will require more than a single set of tests on a single weld. The welding process with specified ranges of the welding parameters and heat treatment must be shown to give consistent mechanical properties at least as good as specified values. Ideally, these minimum properties should be those of the base metal being joined; if those for the weldment are lower, considerable administrative and technical complications can ensue in determining design rules for the weldment.[4]

Of the several possibilities for coal conversion vessel material, the most often selected is ASTM A 387, grade 22, class 2 (2.25Cr-1Mo steel),[5] which has better resistance to hydrogen attack than have lower alloy steels. In thick sections (about 0.2 m and greater) quenching and tempering are required to achieve class 2 mechanical properties. Where some hydrogen resistance can be sacrificed in favor of strength, ASTM A 543, type B, class 1 (3.5Ni-1.75Cr-0.5Mo), which is also quenched and tempered, is a possible alternative for vessels that operate at lower temperatures such as 371°C or less.

In any quenched and tempered alloy steel, tensile properties and toughness may vary through the thickness because of differences in cooling rate. If so, the properties of the steel will vary both with plate thickness and with the position in the plate from which the specimen is taken. The relationship between cooling rate (and, implicitly, position) and mechanical properties of each steel used must be determined as part of its characterization. Fracture toughness analysis must be part of the characterization of a candidate material for service, and fracture analysis must be part of the evaluation of any proposed pressure vessel design.

One of the more ubiquitous chemical species in any coal conversion system is hydrogen. In some systems it occurs at pressures of tens of megapascals and temperatures of several hundred degrees Celsius. Under these conditions hydrogen interacts strongly with ferritic steels to the detriment of their fitness for service at both high temperature (hydrogen attack) and low temperature (hydrogen embrittlement).

Hydrogen attack, a high-temperature process, occurs as carbon in the steel reacts with hydrogen to form methane. Near the surface, carbon diffuses to the surface, leading to decarburization and loss of strength. Internally, methane forms bubbles at nucleation sites; both decarburization and bubble growth by creep under methane pressure degrade mechanical properties. The petroleum industry has had to deal with the problem for several years. It uses Nelson curves, which show boundaries of hydrogen attack in temperature versus partial pressure of hydrogen coordinates, as its principal tool. For each steel composition, a Nelson curve shows combinations of temperature and hydrogen partial pressure below which hydrogen attack has not been found to occur. Although the Nelson curves have been very useful over the years, they have limitations. They are empirical, and a lack of fundamental understanding makes them difficult to modify for new situations. They are based on environments that occur in petroleum processing. The response of steels to equal hydrogen partial pressures when other species are present is unknown and may differ. The Nelson curves take no account of prior history such as forming, fabrication, welding, and heat treatment or service stress, which affect the distribution of carbon or stress in the steel. These curves should not be used for situations wherein stresses exceed the stress allowables in the Code.

Single-stage designs of direct coal liquefaction processes specify pressures of about 7 to 21 MPa and temperatures of about 425 to 455°C. Some process developers have indicated a need to go to even higher pressures and/or temperatures to improve product distribution, and other developments have focused on two-stage liquefaction, in which lower temperatures and pressures are employed. Rheinische Braunkohlenwerke AG in the Federal Republic of Germany is developing a direct liquefaction process to operate at 460°C and 31 MPa. Changes in materials requirements resulting from more severe operating conditions should be identified, and appropriate materials development work should be initiated. For example, a substitute for the current materials choice for dissolver vessels (2.25Cr-1Mo steel) would be needed to provide adequate resistance to hydrogen attack under these conditions. Substitutes being considered for these applications are a family of 3Cr-Mo alloys. A considerable amount of information on the 3Cr-Mo alloys has been developed on this program and on the DOE Fossil Energy Surface Gasification Materials Program.[6-9] The higher chromium content increases the hydrogen attack resistance, and a quench and temper heat treatment provides adequate strength for the steel. Several of these alloys offer promise for liquefaction, gasification, and petrochemical vessel applications.

In the domestic development of two-stage liquefaction processes, less severe conditions are likely to prevail than in current single-stage processes. Also, residence times may be decreased from 1 h or more to about 20 min. Thus, smaller dissolver vessels of available grades of steel would be appropriate.

At ambient temperatures a steel that has a critical hydrogen content or that is tested in a hydrogen environment displays a loss in toughness, called hydrogen embrittlement. Although this is a different phenomenon from hydrogen attack, it may be produced by the same environmental exposure. The greatest decrease in toughness is likely to occur in a steel that has been exposed to hydrogen at a high temperature and cooled too fast for the hydrogen to diffuse out. In addition, a steel held at an elevated temperature in any atmosphere for an extended period and then cooled to room temperature may display temper embrittlement, which is also a loss of toughness. Hydrogen embrittlement and temper embrittlement have separate causes but similar effects. Hydrogen embrittlement is more likely in high-yield-stress materials and is promoted by high stresses. Close coordination must be maintained between fabrication research and hydrogen interaction studies.

Fracture prevention in either monolithic or multilayered large pressure vessels for coal conversion may require more advanced experimental and analytical techniques than are in common use today. Such techniques either exist or are under development for nuclear reactor pressure vessel applications, but they are not generally used in pressure vessels designed to Sect. VIII, Div. 1 or 2, of the *ASME Boiler and Pressure Vessel Code*. The reason is primarily an economic one, and justification for undertaking design for fracture prevention requires examination. The design methodology requires characterization of the response to the stress state at a crack tip of a material and analysis of its structures and parts to predict that stress state. The materials tests, such as those of ASTM Standard Method E 399 and the precracked Charpy slow bend test, generally consist of loading a special precracked specimen and observing crack propagation by various means. Related fatigue tests are also useful. Data from these newer testing methods are more readily related to design and are more appro-priate to sections thicker than about 45 mm.

Although experience with smaller vessels has been excellent, the larger vessels planned for demonstration and commercial plants have no long-time service experience on which to develop reliable design criteria to supplement the rules in Sect. VIII, Div. 1 or 2, of the *ASME Boiler and Pressure Vessel Code*. It seems likely that design-by-analysis procedures will be needed to produce credible safety analyses for the large vessels. To implement these procedures, materials design data are needed from 370 to 540°C. Specific data include isochronous stress-strain curves, relaxation response, stress-rupture strength to 10^5 h, fatigue, and creep-fatigue design curves for the materials of construction.

Research on the relationships of mechanical properties to alloy composition and structure, environment, and stress state should initially address the classes of materials that are currently available and that will be used in first-generation plants. One type of task, for example, could use the most advanced microanalytical techniques to determine the reasons for variability from heat to heat and to develop the methods for optimizing mechanical properties and corrosion resistance by control of the microstructure. Further studies on constitutive relationships, environmental effects on crack initiation and propagation, and phase stability will give confidence in our ability to predict long-term service performance.

Basic studies on the mechanisms of attack by coal-derived liquids should form the framework for lifetime predictions and for designing improved cladding or structural materials. Topics include, for example, attack by typical organic liquids; the role of S, chloride, and N in such attack; the transport of Cl, S, Fe, Ni, and Cr in sulfide corrosion products at 200 to 300°C; and the complexing of Fe, Ni, and Cr in sulfonated hydrocarbons.

Welded chromium-molybdenum steels need postweld heat treatment procedures that do not lower mechanical properties below acceptable limits. Temperatures of some postweld heat treatments during fabrication could possibly be reduced without loss of integrity and produce steels with increased strengths. Programs such as those sponsored by The Metal Properties Council for API are aimed at improving the heat treatment procedure and will establish the influence of postweld heat treatment conditions on residual stresses and material properties. A determination of the permissible latitude of these conditions will follow from this.

Environmental interaction with weldments mainly means hydrogen attack and embrittlement. This concern could be put into the hydrogen attack category, but it critically needs to be addressed. All processes will require data in this field, and an experimental program to investigate the effects of hydrogen attack and embrittlement on weldments must be continued.

If demonstration or commercial plants are built, various types of dissimilar-metal joints will be required. Each design will probably have some critical dissimilar-metal joints. This ongoing problem should be dealt with by a continuing effort; nondestructive techniques such as ultrasonic testing are needed for inspection of dissimilar-metal joints.

Multilayer vessels may offer solutions to some of the materials problems with thick-wall vessels. Multilayer vessels offer several fabrication advantages and have been used in numerous petrochemical applications. However, the combination of pressures, temperatures, sizes, wall thicknesses, and nozzle penetrations needed for coal liquefaction dissolver vessels represents a technological extension well beyond current experience. If multilayer vessels are considered, design methodology, nondestructive testing (NDT) technology for fabrication examination, and in-service inspection procedures must be developed.

The necessity for field-fabricated vessels will raise an attendant need for field-applicable NDT; ultrasonic and field radiographic techniques should be investigated and developed as necessary. Nondestructive techniques should be developed for evaluation of weld overlay cladding. Eddy-current and ultrasonic methods for thickness determination and ultrasonic methods for bonding and undercracking inspection are likely candidates.

2.1.3 Pressure Letdown and Separation System

Materials problems in the pressure letdown and separation area include both erosion and corrosion. Erosion is especially a problem in the pressure letdown valves, for which selection of appropriate trim material has been difficult. To date, commercially available materials that have shown the best performance in letdown valves are cemented tungsten carbides with cobalt or cobalt-chromium binders. The PDUs and pilot plants have reported significant variations in the performance of a given grade or type from a given manufacturer. In addition to the basic materials limitations, the standard trim component designs for all available commercial letdown valves have proved inadequate for the extreme service conditions in processes for the direct liquefaction of coal. In general, design and component assembly process revisions have been made by each PDU and pilot plant to modify its sizes and types of valves to improve their reliability. To date, such specific modifications have been reasonably successful in that the pilot plants have been able to improve letdown valve performance to the point that process development could proceed. The maximum service life achieved for letdown valve trim has been several thousand hours at the Wilsonville Advanced Coal Liquefaction Research and Development Facility, but in most cases the service life was limited to 300 to 400 h. Of the two larger pilot plants that have operated, the H-Coal Pilot Plant at Catlettsburg, Kentucky, experienced serious valve problems, but the Exxon Coal Liquefaction Plant at Baytown, Texas, completed operations with no serious letdown valve failures. Desired life between required maintenance or replacement is about one year of operation, or 8000 to 10,000 h.

Corrosion observed in the separation system has consisted primarily of stress corrosion cracking, both chloride induced and polythionic acid caused. The cracking has often been observed in the heat-affected zone around welds but also was found in the cladding in separation vessels at the Fort Lewis, Washington, Solvent Refined Coal Pilot Plant.

Erosion due to the handling of coal upstream from the reactor and ash solids downstream was anticipated as a major materials problem in solvent refined coal (SRC) pilot plants, and experience in these plants has borne out the adverse effects of erosion on the operation of pumps and letdown valves in these processes. Projects to optimize materials selections for these applications are needed.

Letdown valve trim failures at the H-Coal Pilot Plant indicate a need for valve trim evaluation and fabrication programs. Erosion is a potential problem in the vacuum distillation units and in the initial atmospheric distillation units of the Exxon Donor Solvent and SRC-II systems. Specific materials problems in the separations systems involving both liquid-gas and solid-liquid separations are not well defined. Both corrosion and erosion-corrosion, as well as gas phase corrosion, have been observed in pilot plant liquid operations. Specific materials problems are being assessed against petroleum industry experience to determine if additional materials projects are needed.

2.1.4 Fractionation System

Materials considerations for the fractionation area of coal liquefaction systems are simplified by the absence of solids in most of the liquid streams, thus avoiding an erosion problem. Furthermore, process designers thought that the liquids being handled were similar enough to those in petroleum refineries that the technology associated with refinery operation would be sufficient to handle any problems encountered. Unfortunately, in the two SRC pilot plants, the H-Coal Pilot Plant and the Exxon Coal Liquefaction Pilot Plant, severe corrosion was observed, which was not explained by petroleum refinery technology. The most severe corrosion was found in the 220 to 260°C range in fractionation columns used to separate the filter wash solvent from a heavier liquid sometimes used as the recycle solvent. The corrosion is characterized by selective removal of iron from exposed alloys and formation of a sulfide scale. The severity of corrosion is proportional to the chlorine content of the coal feed, and mechanisms for chlorine transport, concentration in the columns, and corrosion of the columns have been developed. The formation of corrosive species and their transport as well as the corrosion process have been explained and duplicated in laboratory simulations. Methods for control of the fractionator corrosion were proposed and tested on a limited basis in pilot plant operation. This completed activity was highly successful. The ORNL activity was complemented greatly by activities at the Southwest Research Institute (an AR&TD project funded through The Metal Properties Council, Inc.), the Institute of Mining and Minerals Research of the University of Kentucky, the International Coal Refining Company, and the coal liquefaction pilot plants. On the basis of the results of these activities, plant designers should now be able to incorporate and test various control measures in plant systems.

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3. COAL GASIFICATION

3.1 TECHNOLOGY STATUS AND MATERIALS NEEDS

The several coal gasification processes currently under development for use in the United States were described in the program plan for FY 1981 (ref. 1). Although these processes differ considerably in detail and mode of operation, many features or process areas are common. Throughout this section, reference is made to low-, medium-, and high-Btu gas. Low-Btu (3–5 MJ/m^3) gas is made by gasifying coal with air and steam. To produce medium-Btu gas (10–20 MJ/m^3), coal is gasified with oxygen and steam. High-Btu (40 MJ/m^3) gas is produced by the catalytic methanation of the CO and H_2 in medium-Btu gas. In the discussions that follow, the gasification systems are divided into several common process areas, namely, coal preparation and feed systems, gasification pressure vessels, refractories for gasifiers, metal gasifier internals, gasifier heat exchangers, and gas cleanup and shift converter.

3.1.1 Coal Preparation and Feed Systems

Coal is fed into gasifiers as either a dry solid or a slurry with water or other liquid. Depending on the coal conversion process, several stages may be necessary to prepare the coal for injection. The equipment used in these stages includes storage hoppers; transport lines; pretreatment vessels; lock-hopper systems; and coal slurry feed systems, including slurry pumps, slurry feed lines, and slurry driers. Most of these components are exposed to fairly low temperatures (<100°C) and to benign environments typically consisting of slurries mixed with water, oil, or inert gases at pressures up to 10 MPa. However, some components encounter severe service conditions. For example, mild oxidation of coal to destroy its caking qualities is carried out in vessels heated to as high as 425°C in an oxygen atmosphere, and parts of the lock-hopper valve system that are close to the gasification reactors may be subjected to temperatures up to 425°C and pressures up to 11 MPa. The pretreatment unit generally consists of a vessel with a thermocouple assembly. The normal operating conditions for the unit are temperature, 400 to 425°C; pressure, atmospheric;

reactants, coal, steam, and either air or O_2; and environment, gas containing C_nH_{2n+2}, H_2, CO, N_2, H_2O, and CO_2, with some H_2S. Even at these more severe conditions, materials-related problems are not expected under normal operating conditions. Materials now in use in pilot plants appear to be adequate; refractory-lined carbon steel shells should be suitable for commercial application up to 425°C. In the Hygas Pilot Plant, a type 304 stainless steel (ASTM A 312) pretreatment vessel was in use at up to 650°C.

In some gasifiers, particularly high-pressure entrained-flow gasifiers, the char feed burner nozzle is exposed to high-temperature, high-velocity, erosive, and corrosive environments and is subject to thermal fatigue, which can be critical to performance.

The major materials-related problems with lock-hopper valves are abrasion and erosion of the balls and seats, which result in the inability to seal against the pressurized feed. Erosion is caused by impingement of solids passing through the open valve and by leakage across the sealing elements after the valve has been closed and a pressure differential created.[2-4] Materials research programs need to be strengthened for development of valves having satisfactory lifetimes at temperatures above 427°C under conditions of erosive and abrasive wear.

Hoppers made of carbon steel appear to be quite adequate. Hardfaced stainless steels may be used to line carbon steel construction to improve wear resistance. The use of materials such as Stellite 3, Stellite 6B (a Cr-Ni-B-Co alloy), and high-chromium white irons for ball and seat applications has improved component lives considerably. At present, high-chromium white iron alloys such as ASTM white cast iron with 28% chromium and 2.8% carbon (which showed more than 40 times the abrasion resistance of mild steel in bench-scale wear tests), type 440C stainless steel with a plasma coating of chromium oxide or tungsten carbide, and Graph-Air tool steels appear to be the most promising for this application.[5] These alloys could prove to be more economical than cobalt-base alloys such as Stellites 3 and 6B, which are much more expensive.

In a slurry feed system, the components of interest include coal slurry storage vessels, slurry tanks, mixing and feed discharge pumps, driers and preheaters, and feed lines. Temperatures and pressures are fairly low in most parts of the system; however, components between the discharge pump and gasifier may encounter temperatures and pressures as high as 425°C and 7 MPa, respectively. Slurry flow rates in the system normally range between 3 and 9 m/s. The environment in the system is usually not corrosive except when effluent gas is circulated to preheat the slurry before it is pumped into the gasifier. This gas may be corrosive because of such constituents as residual sulfur compounds and trace elements from coal. High pressure and temperature in some parts of the system, together with corrosive flue gas and, possibly, moisture associated with chemicals leached from the feedstock, tend to accelerate materials degradation through a combined action of erosion and corrosion.

The high-pressure slurry feed system brings coal up from atmospheric pressure to slightly above gasifier pressure. This allows the coal to be fed into the gasifier by gravity flow. Centrifugal pumps are generally used for low-pressure (≤4-MPa) applications, whereas for higher pressure operations positive-displacement reciprocating pumps are required.[6-9]

Slurry pumps are subject to erosion from coal particles moving at high velocities. The discharge velocities across the valves of high-pressure pumps range from 3 to 9 m/s. The vanes of impeller pumps move through the slurry at a high velocity and are subject to a spectrum of velocities and effective angles of particle incidence, but the surfaces of the surrounding pump housing constrain and direct the flow. In addition to erosion and corrosion, the pumps may have to withstand impact, shock loading, fatigue stress, and so forth. Several cases of erosion failures in pump components ranging from impellers to casings have been reported in pilot plant operations.[10]

Abrasion or wear of pump parts is governed by the size of the solid particles, slurry concentration, velocity of flow, impingement angles, and so forth. If the impact is direct, more elastic pump materials are selected; if the impact angle is relatively small with flow almost parallel to the surface, harder materials are selected. Parts of cast iron with Stellite hardfacing should perform satisfactorily under conditions of solid-particle impact.[11] Pumps with carbon or low-alloy casings, erosion-resistant impellers, and internal linings of 27% chromium high-carbon cast iron (HC-250) should also perform adequately. Materials suitable for high-pressure pumps include forged 12% chromium stainless steel for casings, type 440C stainless steel for impeller blades, and tungsten carbide for balls and seats of associated valves. In addition to use of the best available materials for slurry feed pump parts, one should consider the use of disposable parts and liners and localized application of multilayered metallic and ceramic coatings, where possible, in high-wear areas.

Coal slurry feed lines are subject to both erosion and corrosion. The fluid flow in a typical slurry feed line is turbulent to maintain the particulates in suspension. This turbulent motion, however, causes severe erosion at the pipe joints, elbows, valves, and other locations where the flow is perturbed. Misalignments at joints and other manufacturing defects also contribute to increased erosion in the feed lines. The slurry feed line should be designed for an optimum velocity high enough to prevent particle drag but low enough to prevent excessive friction and damaging particle impingement.

Carbon steel for low-temperature (<100°C) feed lines and austenitic stainless steels, such as types 347 and 316, for higher-temperature (up to 540°C) applications should perform satisfactorily. Hardfaced inserts must be considered where the flow changes direction. Erosion in 90° elbows has been reduced by replacing the elbow with a tee containing a blocked branch. Abrasive particles collect in the blocked branch and provide an abrasion-resistant layer over the most critical area of the line. The use of a blocked tee also permits the line to be opened periodically for inspection and maintenance. As with slurry pumps, slurry lines need to be examined closely, and materials programs to address erosion need to be initiated.

Unwelded alloy 800 appears to be a suitable material for the preheater coils under normal operation; types 304 and 316 stainless steel should perform equally well. Because the first few coils of the heater remain much cooler than those near the fired end, consideration should be given to the use of low-alloy 2.25Cr-1Mo steel for the low-temperature section of the coil, followed by types 304 and 316 coil segments as the temperature increases.[12,13]

3.1.2 Gasification Pressure Vessels

The specific pressure, temperature, and train capacity needed to make a given gasification process economical have a major influence on the selection of the pressure vessel material and construction methods, and there are literally a hundred or more gasification schemes.[14] These range in operating pressure from near atmospheric to more than 9.3 MPa. Gas temperatures vary from 650 to 1650°C, and coal input train capacities for current designs range from 725 to 2500 tons/d (ref. 15), although the capacity will probably center around 900 to 1000 tons/d. As a result of the wide diversity in the operating parameters, it is virtually impossible to pinpoint a set of operating parameters that can be used to develop a conceptual gasifier pressure vessel design for materials selection and performance evaluation. Without such a design, it is difficult to quantify the economic impact of alternative pressure vessel alloys and construction methods.

In his description of the construction of coal conversion vessels, Hicklen[16] narrows the choice of gasifier pressure vessel materials to five alloys identified in Table II.1. The A 516-70 is often described as a carbon-manganese (C-Mn) or carbon-silicon (C-Si) steel and would be selected when wall thickness did not exceed 75 mm (3 in.). The SA-302-C and SA-533-B steels, on the other hand, are identified as prime candidates for vessels that see service to 370°C or in vessels whose wall thicknesses would range from 50 to 250 mm (2–10 in.). Both steels contain 0.5% Ni for hardenability and 0.5% Mo for strength and resistance to hydrogen attack. These steels are often mentioned in connection with gasifier pressure vessel service.[15] Both have excellent strength to 371°C. The fourth and fifth steels listed in Table II.1 are the low-alloy SA-387, grade 22, class 2, and SA-387, grade 21, class 2, chromium-molybdenum steels: 2.25Cr-1Mo and 3Cr-1Mo. These are popular pressure vessel steels in the petrochemical and petroleum industries because of their good strength properties from 370 to 480°C. The chromium imparts resistance to oxidation and hydrogen attack, and the molybdenum imparts high-temperature strength. For gasifier applications, these steels as currently approved in the Code for pressure vessel application are of less interest than are the A 302-C and A 533-B, class 1, steels because of the lower allowable

Table II.1. Candidate plate steels for pressure vessels with wall thickness requirements of greater than 0.1 m

Steel identification[a]	Grade (class)	Chemical requirements (wt %)								Maximum thickness[c]		Tensile requirements					
		C[b]	Mn	P	S	Si	Mo	Ni	Cr	(mm)	(in.)	Ultimate strength		Yield point		Elongation in 51 mm (2 in.) (%)	Reduction of area (%)
												(MPa)	(ksi)	(MPa)	(ksi)		
SA-516	70	0.31	0.80–1.25	0.035	0.04	0.13–0.33				203[d]	8[d]	485–620	70–90	260	38	21	
SA-302	C	0.25	1.10–1.55	0.035	0.040	0.13–0.32	0.41–0.64	0.37–0.73				550–690	80–100	345	50	20	
SA-533	B(1)	0.25	1.10–1.55	0.035	0.040	0.13–0.32	0.41–0.64	0.37–0.73		305[d]	12[d]	550–690	80–100	345	50	18	
SA-387	21(2)	0.17	0.27–0.63	0.035	0.035	0.50	0.85–1.15		2.63–3.37			515–690	75–100	310	45	18	45
SA-387	22(2)	0.17	0.27–0.63	0.035	0.035	0.50	0.85–1.15		1.88–2.62			515–690	75–100	310	45	18	45

[a] Specifications designated SA have been taken from the *ASME Boiler and Pressure Vessel Code*, Sect. II, Part A.

[b] Maximum carbon content based on requirements for thickest plates.

[c] Maximum available plate thickness is limited only by the capacity of the chemical composition to meet specified minimum mechanical properties.

[d] Current practice normally limits the specification to this thickness.

stresses at temperatures up to 370°C. However, both of these low-alloy steels can be heat treated to produce much higher strength.[17,18] For example, the quenched and tempered A 542 version of 2.25Cr-1Mo has four higher strength classes.

The economic savings that would accrue from the use of an advanced steel would be many times the cost to the government for the development and code qualification of such a material. This conclusion is drawn from a study of assessment reports written from 1975 to 1982, which include requirements for high-Btu gasification processes. These reports reflect the opinions and technical judgments of people representing material producers, vessel fabricators, architect engineers, vessel users, code bodies, and research funding agencies.[17-26]

The need for a high-strength low-alloy steel for hydrogen service from 316 to 538°C is recognized by the technical community, and several approaches have been taken to meet this need. One approach, supported by the American Petroleum Institute (API) and The Metal Properties Council, Inc. (MPC), is to upgrade the 2.25Cr-1Mo steel by restricting the composition and introducing heat treatments (accelerated cooling, lower tempering temperatures) to improve short-time properties.[27] Another approach, taken by several industrial laboratories such as U.S. Steel,[28] Climax Molybdenum,[29] and Japan Steel Works,[30] is to include microalloying additions (V, Ti, and B) in a restricted-chemistry version of 2.25Cr-1Mo steel or 3Cr-1Mo steel to improve the heat-treating response and long-time strength properties. The first approach represents a near-term minimum-expense solution to the problem and has been formulated into a program by Subcommittee 1 of MPC. Clearly, DOE has little or no justification for developing a similar program. Action on the second approach has been deferred by industry on the basis that it will take a longer time and require more money to reach the ultimate objective of a code-qualified alloy with higher allowable design stresses and improved corrosion resistance. The development program on the microalloyed steel fits well within the mission of DOE in advancing the technology of coal conversion. Such a program has higher potential, in terms of applicability, than does the MPC program. The microalloyed steel development has a somewhat higher risk, so near-term returns are unlikely.

Development by DOE of a 3Cr-1.5Mo-0.1V alloy to the point that a Code case for low-temperature applications could be made should provide the needed confidence by industry to ensure the continued development, incorporation into the ASME Code, and use of the alloy for its broad range of applications. Quite importantly, the steel developed would offer a domestic alternative to foreign-produced alloys.

3.1.3 Refractories for Gasifiers

Gasifier refractories can be divided into low- and high-temperature applications. Low-temperature applications are those below about 1100°C, in which coal ash is still in solid form and does not react with the refractory. Degradation mechanisms are mainly gaseous corrosion and erosion by particulates. In addition to application in dry-ash and agglomerating ash gasifiers, such refractories are useful in pressurized fluidized-bed combustors, process heaters, cyclones, and associated piping. With cooling, low-temperature refractories can be substituted for refractories normally used in high-temperature applications (e.g., water-cooled refractory liners in high-temperature entrained gasifiers). High-temperature applications generally involve temperatures above about 1250°C, at which coal ash is molten and reacts with the refractory liner. The main degradation mechanisms here are (1) corrosion-erosion by molten slag and (2) damage caused by thermally induced mechanical stress. Typical applications are in slagging gasifiers and combustors. Refractories for molten-salt gasifiers may also be classified with this group, although temperatures are much lower (about 980°C), and no molten slag is present.

Refractories for low-temperature applications can generally be modeled after those used in the petrochemical industry.[31,32] Refractory concretes, both dense and insulating types, are standard materials in that industry. Results from extensive testing and evaluation programs to select the most suitable refractories for these applications have indicated that suitable low-cost materials are available commercially.[33]

Refractory service conditions in slagging gasifiers are much more severe than the conditions in dry-ash gasifiers because of the higher temperatures in slagging gasifiers and the corrosiveness of the slag. In the early 1970s slagging gasifier technology was severely limited by lack of suitable refractories. Therefore, a program was initiated at Argonne National Laboratory (ANL) to identify the refractory-bond systems best suitable for slagging gasifier applications.

Refractory experience in blast furnaces[34] served as a guide for refractory applications in slagging gasifiers. However, the atmosphere in a gasifier contains considerable sulfur and, most important, is more oxidizing. Consequently, the slag generally does not contain metallic iron, but may contain appreciable quantities (as high as 25%) of iron oxide. Therefore, successful performance in a blast furnace does not guarantee adequate performance in a gasifier. Thermodynamically, none of the currently available refractories are stable in the presence of typical coal slags. Therefore, the approach to ensure satisfactory operation is to modify refractory composition and structure, slag composition (through the addition of fluxing agents to the coal), and/or operating conditions to promote the formation of protective layers and/or to alter the kinetics of the refractory slag corrosion reactions.

One approach, and still the only viable method for operating at temperatures above 1600°C, is to cool extensively by using water walls coated with a thin, sacrificial refractory lining. This approach has limited practical application because the large heat loss drastically reduces the overall efficiency of the gasification system. For gasifiers operating at lower temperatures (1400–1600°C), the laboratory corrosion tests at Argonne indicated that thick refractory linings (with or without water cooling) of chromium-base refractories should be satisfactory in many applications.[35–42]

In particular, a fused cast picrochromite (a chromia-magnesia spinel containing 75–80 wt % Cr_2O_3) was quite resistant to slag attack in laboratory tests. More recently, a number of refractory suppliers, at least some of whom were encouraged by these laboratory results, developed sintered bricks of similar composition. Subsequent work at Argonne seems to confirm the superiority of the picrochromite refractories, and the laboratory results are supported by actual gasifier service.

The early work on the fused cast material indicated that while the picrochromite had superior corrosion resistance, its resistance to thermal shock and/or thermal-stress-induced fracture was unsatisfactory. Thermal-shock damage testing undertaken in a separate program at ANL confirmed that many of the picrochromite bricks then commercially available were in fact lower in thermal-shock damage resistance than a number of alumina-based refractories. Further research at ANL showed that thermal-shock damage resistance could be improved by microstructural alterations that improved fracture toughness. One composition, which includes about 17% ZrO_2, was demonstrated to have about 5 times the fracture toughness of pure magnesium chromite.

In addition to the work on picrochromite, tests at ANL, which were again confirmed by limited plant data, indicate that (at least in acidic slags) solid solution refractories of the composition 75% Cr_2O_3–25% Al_2O_3 have slag corrosion resistance comparable to that of the picrochromites. Also, these materials appear to possess superior thermal-mechanical properties.

Because some types of slagging coal gasification systems can operate at rather low temperatures (1400–1500°C) without a significant loss in efficiency, and because the corrosion rates of the refractories generally decrease as temperature decreases, the limiting factor in operating at relatively low temperatures in these processes is often the plugging of the slag tap hole. Because plugging of this hole is directly related to the flow properties of the slag, the criterion of maintaining the viscosity of the slag at less than 25 Pa•s (generally accepted as the point at which slag starts to flow under its own weight) may govern the selection of the process temperature, particularly in first-generation gasifiers. Data developed at ANL have demonstrated that slag temperature is a much more important variable than slag viscosity in controlling refractory corrosion. Thus, the use of fluxes (e.g., CaO or dolomite) to produce adequately low slag viscosities at temperatures sufficiently low to assure satisfactory refractory operating life is a viable method of operation.

The environments found in dry-ash gasifiers (temperatures $< 1200°C$) are significantly less demanding of refractory materials than are those of slagging gasifiers. To date, no critical problems have been identified from pilot plant exposures. Laboratory tests have shown that existing low-cost intermediate alumina products may give satisfactory service;

however, some questions remain. Results of research at Babcock & Wilcox indicated that the use of metal-fiber-reinforced monolithic linings results in less cracking during heatup. However, laboratory tests at the Virginia Polytechnic Institute indicated that carbon monoxide disintegration can occur in metal-fiber-reinforced monolithics as well as in materials with as little as 0.1% metallic iron. Thus, further research may be needed to characterize CO disintegration, especially in metal-fiber-containing refractories. Also, the mechanical properties, in particular the high-temperature creep of metal-fiber monolithics, need to be characterized. Long-duration exposures of promising candidate concretes are needed to identify optimal materials and potential refractory problems caused by upset conditions.

Refractory linings for gasifier transfer lines need attention. Available refractories have undergone a limited number of tests under conditions of flow and entrained-particle content typical of gasifiers. Most testing was under more severe conditions, so present units may be overdesigned. A test program should be considered to identify a material with optimal insulating value and resistance to erosion.

3.1.4 Metal Gasifier Internals

In contrast to the design situation for vessels and piping, no code or standard exists for vessel internals and long-life external components, especially for service in corrosive-erosive environments at elevated temperatures.

Natesan[43] has published reviews of corrosion behavior of materials in high-Btu coal gasifier environments as well as in low- and medium-Btu environments.[44,45] These reviews clearly establish that sulfidation is the major mode of material attack in these systems and that a viable alloy should develop protective surface oxide scales during the service life of the component.

Results from a recently completed program administered by the MPC show that several commercially available alloys exhibit acceptable corrosion rates of about 0.6 mm/year (24 mils/year) based on 10,000-h exposures. However, the corrosion experiments were conducted at oxygen partial pressures about 10^3 times the threshold for oxide formation or higher. The available data have been analyzed in detail to establish a criterion in alloy composition for minimum corrosion rate.[46] On the basis of the combined criteria for Fe:Cr ratios in the range 1.6 to 2.0 and an Ni:Cr ratio of about 1.0, the following alloy compositions have acceptable metal loss rates: 25 to 28 wt % Cr, 25 to 28 wt % Ni, and 50 to 44 wt % Fe. Alloys such as Incoloy 800 and type 310 stainless steel fall on either side of this range. The analysis indicates that the calculated composition range for Fe, Cr, and Ni can be used as a base on which to develop optimized alloys with minor alloying additions to improve scale adhesion, self healing, resistance to thermal cycling, and so forth and thereby provide acceptable corrosion performance in coal gasification atmospheres.

Metallic materials for internal members in a gasification system must operate under environmental conditions that have strongly deleterious effects on mechanical properties. The rupture strength of the best of these materials is quite low in the temperature range (800–1000°C) that typifies most second-generation gasification processes. The gasification environment may result in even lower levels of stress-rupture strength. Wells and coworkers reported 27 to 86% losses in stress-rupture life as a consequence of testing various metallic materials in high-Btu gasification environments rather than in air.[47] Their test specimens failed in 100 to 300 h at 815°C at stresses from 36 to 90 MPa. These short rupture times conflict with the desired useful life of 20,000 h (2.3 years) for commercial applications.

The effects of mixed-gas environments on mechanical properties are primarily determined at a fixed oxygen and sulfur activity in the gas phase. Although the uniaxial tensile data for several alloys preexposed to complex gas mixtures showed a loss in strength and tensile ductility, the residual properties are generally adequate for the internal components.[48-50] However, the data are based on 1000-h preexposure times, and the effect of longer exposure times was not established. The results of uniaxial and biaxial stress-rupture tests showed a loss in the 1000-h rupture strength of the materials preexposed to mixed-gas environments. Recently, Natesan showed that, if the test environment is such that the alloy can develop a protective oxide scale (i.e., the oxygen partial pressure is above the threshold partial pressure needed for oxide formation), then the creep properties of the materials are not significantly affected.[51] This has been confirmed by experiments in air, low-p_{O_2}, and oxygen-sulfur atmospheres with p_{O_2} greater than p_{O_2}(threshold). On the other hand, if the test environment is such that p_{O_2} is less than p_{O_2}(threshold), then the alloy exhibits significant sulfidation and substantial degradation in the creep properties, with significantly lower rupture life and rupture strain. On the basis of the morphological features of creep-tested specimens, we concluded that the breakdown or cracking of the protective oxide scale (i.e., mechanical properties of the scales) may determine the degree to which the oxygen-sulfur environment degrades the creep properties of the material. The mechanical testing effort is expected to continue into low-chromium heat exchanger materials with and without surface coatings.

Coal gasification environments generally contain particulates such as char and ash, which can interact both chemically and physically with materials of construction of various components. Char, derived from coal, is a major ingredient in any gasification scheme. The reactivity of chars can vary widely, depending on the coal from which the char was derived and processing conditions. In general, chars have high carbon contents and may contain appreciable amounts of sulfur and mineral matter. The corrosion behavior of materials used in elevated-temperature regions of the gasifiers can be affected by (1) the deposition of char and ash particles on the components, which thereby prevents the development of continuous protective oxide scales, and (2) the gasification of sulfur in the char to H_2S, which alters the mixed-gas chemistry to higher sulfur potentials in the vicinity of the component materials.

Very limited work is being conducted to evaluate the role of particulates on the corrosion behavior of materials.[52,53] The meager data now available show that the presence of particulates such as char can alter the mode of attack from oxidation to sulfidation. Furthermore, the corrosion rates at elevated test pressures in particle-laden gases were significantly greater than those in atmospheric pressure tests. In the selection of an alloy for use in internal components of coal gasification systems, the available results dictate that the char effect be considered, especially when the sulfur content of the char is high. To reduce the corrosion rates to acceptable levels, the alloy selected should develop protective oxide scales even in the presence of one to two orders of magnitude higher sulfur potential (caused by sulfur in the char) than in the gas phase.

Sulfidation is the major type of corrosion in environments that prevail in coal gasification systems. Therefore, it is essential that the alloys develop a protective oxide scale during the service life of the component. It should also be recognized that various ongoing corrosion programs involve evaluation of commercial materials, but that very little work is being conducted to modify or tailor alloys for application in coal conversion systems. Research activities in the areas of alloy composition modification, alloy coatings, alloy claddings, and weld overlays should be conducted for development of materials that resist corrosion and erosion when exposed to coal gasifier environments.

Significant additional work is required to establish the mechanisms of scale formation, adhesion and plasticity of the scales, and transport properties of cations (such as Cr, Fe, and Ni) and anions (such as O, S, and C) in and across the scale. Most alloys tested in a mixed-gas environment exhibit breakaway or accelerated corrosion at some stage of exposure, depending on temperature and partial pressures of sulfur and oxygen in the environment. It is imperative that alloys selected for application in coal conversion systems not exhibit breakaway corrosion during the service life of the component. However, very little is known about the mechanisms that cause accelerated corrosion. Additional work is required in this area so that the contents of minor alloying additions can be optimized judiciously.

Most long-term kinetic work has been conducted with commercial alloys, primarily in environments with fixed oxygen and sulfur partial pressures. Without a substantial understanding of the corrosion processes that occur in these environments, it is difficult to extrapolate and predict the corrosion rate for a given alloy under various practical conditions from the kinetic information obtained at a fixed gas composition. Several investigators have observed breakaway corrosion of alloys exposed to multicomponent gas environments. It has been established that sulfur in the gas environment accelerates the outward migration of base metal elements such as iron and nickel through the oxide scale leading to sulfidation at the external gas-scale interface. Significant additional research is required to develop predictive capability for onset of breakaway processes so that alloy modification can be approached systematically. It is also essential to develop a fundamental understanding of the role of chlorine in the gas phase on the corrosion of metallic materials of interest in moderate- to high-temperature components for coal gasification systems.

Experimental programs are needed to determine the fundamental aspects of the corrosion of materials exposed to particle-laden gas environments. The corrosion rates of materials are substantially greater at higher pressures if the experiments are conducted in particle-laden mixed-gas environments. Therefore, it is necessary to establish the influence of high pressures on the erosion parameters, such as particle velocity, to develop a better understanding of material behavior under corrosive-erosive conditions.

The effects of mixed-gas environments on mechanical properties must be known to establish the design and performance requirements of various components in a coal gasification system. Substantial additional work is needed to determine the long-term creep properties and to develop creep correlations that are useful to component designers.

Programs should be supported to design alloys that resist corrosion in complex gas atmospheres. Previous and ongoing programs have shown that the usefulness of conventional off-the-shelf engineering materials as internal members of a gasification plant is limited. Greater emphasis must be placed on novel design approaches that minimize the number of internal components and on alternative materials to achieve the desired lifetimes for the internal components. Avenues that involve alloy modification (composition, second-phase particles, etc.) and surface modification (duplex tubes, coatings, and weld overlays) should be supported at reasonable funding levels over a long period of time. The results from such programs not only will have a large impact on component performance but may be the only approach that can make these gasification schemes viable.

Studies of surface modification to improve lifetimes of internal components should have attendant studies for nondestructive testing (ultrasonics and eddy current) of the initial and interim surface conditions.

3.1.5 Heat Exchangers

Heat exchangers and waste heat boilers are generally absent from pilot plant systems but are essential in larger demonstration- and commercial-size gasification units to increase the process efficiency and to reduce the plant operating cost. Heat exchangers are an integral part of both dry-ash and slagging gasification processes. The raw gas outlet temperatures can range from about 1000°C or below in the dry-ash process to as high as 1400°C in slagging concepts. The so-called second-generation processes will produce raw gas rich in carbon monoxide and hydrogen; as a result, the inlet gas to the heat exchangers and waste heat boilers will have fairly low oxygen partial pressures and moderate to high sulfur partial pressures, depending on the coal feedstock.

Very little design information is available for the heat exchangers and waste heat boilers considered for various processes. A 150-ton/d demonstration plant based on a Texaco gasification process has been in operation since 1978 at the Ruhrchemie petrochemical plant in Oberhausen, Federal Republic of Germany. A 150 ton/d plant for NH_3 production, also based on a Texaco process, is in operation at Muscle Shoals, Alabama. A Texaco gasifier is also used in Southern California Edison's 100-MW(e) combined-cycle generating plant near Barstow, California. All these have heat exchangers or waste heat boilers operating with metal temperatures as high as possible.

Another process of considerable interest is the Shell-Koppers, a high-pressure entrained-flow process that has its origin in the atmospheric-pressure Koppers-Totzek technology. This process has reached pilot plant stage with the construction of a 150-ton/d unit at Harburg, Federal Republic of Germany. The process schematic shows waste heat boilers upstream of the cyclones. On the other hand, the Saarberg-Otto entrained low-Btu gasifier scheme shows waste heat boilers downstream of the cyclones. It is clear that the particle loading of the inlet gas stream will largely depend on the process concept, the raw-gas outlet temperature, and the hot-gas cleanup technology available. Even with sophisticated hot-gas cleanup systems, slag and particulate carryovers to the extent of 10% with particle sizes of 5 μm or less are expected.

Only limited technical information is available to predict material performance (lifetime, corrosion rates) in these heat exchangers and waste heat boilers. A substantial amount of corrosion information in the range 400 to 700°C in simulated low- and medium-Btu gasification atmospheres is required for judicious materials selection in these applications. The results developed thus far show that the presence of heat flux can accelerate the corrosion scale development and thus lead to a significant increase in scale thicknesses, especially at high gas temperatures.[54] The information, once generated, will identify the roles of critical variables such as metal and gas temperatures and gas chemistry on corrosion rates and will establish the process variable envelopes for several commercial materials for use in heat exchangers and waste heat boilers.

As pointed out, only structural ceramic materials have the potential for use in a heat exchanger application at temperatures higher than about 650°C. The design, fabrication, and application of these ceramic components is described in greater detail in Chap. 4, Heat Engines and Heat Recovery.

3.1.6 Gas Cleanup System and Shift Converter

Coal-derived gaseous fuels leave most gasifiers at high temperature and pressure. These fuels are laden with chemical impurities (such as H_2S, NH_3, H_2S, COS, HCN, oil, tar acids, and chlorides) and entrained solids (such as char, ash, and unburned coal). The raw product gas must be purified for several reasons, the most important of which are (1) to prevent entrained solids from interfering with operations downstream of the gasifier that produce high-Btu gas, (2) to increase life expectancy of downstream equipment and reduce equipment downtime, (3) to protect sensitive downstream catalysts, (4) to minimize erosion of hot turbine parts, and (5) to comply with air-pollution standards and with purity standards for pipeline distribution. Gas cleanup may be accomplished through either low- or high-temperature methods; only the latter are discussed here.

A major problem encountered in hot purification processes is erosion when high-efficiency solids removal equipment (i.e., cyclones and filters) is employed. Materials problems in the hot-gas solids separation step include erosion, deposition, and corrosion in the gasifier overhead lines and cyclones.

In coal conversion processes, construction materials will be subjected to the synergistic effects of erosion and corrosion at both low and high temperatures and at high pressures. In the absence of corrosion, the material removal rate may be controlled by ductile or brittle erosion. With corrosion product development, erosion of this product rather than the substrate will occur, and the rate of erosion of the corrosion product can be greater or less than that of the substrate.

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4. HEAT ENGINES AND HEAT RECOVERY

4.1 TECHNOLOGY STATUS AND MATERIALS NEEDS

Structural ceramics are of interest in fossil energy systems, particularly for use in heat engines and heat recovery devices, because of their ability to withstand high temperatures and corrosive-erosive environments. The term *structural ceramic* as used in this text describes a ceramic material to be employed under conditions in which the maximum working stress is an appreciable fraction of the average measured fracture stress for the material under those conditions. We have therefore used this definition to designate the material as a structural ceramic in terms of its ability to maintain its mechanical, physical, and dimensional stability under stress and various environmental conditions rather than using a more arbitrary definition based on less relevant characteristics such as melting point of the materials. Interest in these ceramic materials for potential applications in fossil energy systems focuses primarily on high-temperature environments. Most anticipated fossil energy applications of this type of material involve temperatures above 1100°C.

4.1.1 Heat Engines

Stationary heat engines for the production of power are an important application for coal and coal-derived fuels, and they represent significant materials problems not always encountered in engines that use petroleum fuels or natural gas. In particular, corrosion of engine materials by ash particles (or, if the ash is molten, by slags) and gaseous combustion products and erosion of surfaces by ash particles are unique problems for heat engine materials when coal-derived fuels are used. Gas turbine and diesel engines are the primary engine types for use in fossil systems.

Gas turbines and materials for these turbines are of considerable importance in the effective and efficient use of coal and coal-derived gases and liquids. Heated air and combustion gases from coal burned in a pressurized fluidized-bed combustor, gases from intermediate- or low-Btu gasifiers, and coal-derived fuels (liquids and solids) may be used in gas turbine systems.

Potential improvements in the efficiency of gas turbine systems for producing electricity from coal or other fossil fuels by use of structural ceramics for selected turbine components have been known for some time. Efforts to use ceramics in gas turbines were first formalized in the United States by the National Advisory Committee for Aeronautics [now National Aeronautics and Space Administration (NASA)] in the 1950s and later in a program undertaken in the early 1970s and funded by the Defense Advanced Research Projects Agency (DARPA) of the Department of Defense (DOD). During the DARPA program it became obvious that the available structural ceramics of the 1971 period were not adequate for use in gas turbines, but great strides were made in developing the methodology for design with brittle materials.

Some potential benefits anticipated with the use of uncooled turbines having turbine-inlet temperatures above about 1370°C were reported in October 1976 by the Committee on the Use of Ceramics in Industrial Gas Turbines.[1] This committee concluded that use of ceramics in the hot-gas path at turbine-inlet temperatures of 1370°C and above could increase the efficiency of a combined-cycle power plant by 2 to 3% to a net efficiency of over 50%, because the conversion efficiency of a gas turbine is roughly proportional to the absolute turbine-inlet temperatures if the pressure ratio is held constant. This is a very significant increase, which could ultimately have a major national impact on fuel consumption. The conclusions of this committee were fairly similar to those reached in 1975 by the National Materials Advisory Board,[2] which are still relevant today. The high-temperature combustion and hot walls of the combustor are of particular importance for lower-rank coal fuels, which will burn more completely and with lower emissions in the high-temperature radiant combustor.

For example, both of the advanced ceramic gas turbine (AGT) efforts currently being funded within the DOE Conservation Program have high turbine inlet temperatures as a principal goal. This program includes two major ceramic gas turbine efforts identified as the AGT 101 and AGT 100 engines. The AGT 101 engine being developed for vehicular propulsion by the Garrett-Ford team has as its final configuration (Mod II) an all-ceramic structure capable of 1370°C turbine inlet temperature.

The AGT 100 engine, also being developed for vehicular propulsion by the Allison Gas Turbine—Pontiac team, has the major goal of demonstrating a final engine configuration capable of operating with a turbine inlet temperature of 1288°C. Alternative fuels capability is an important goal of the AGT programs. The potential advantages of high turbine inlet temperatures in providing higher turbine engine efficiencies and alternative fuels capability for the AGT type engines (~70 kW) also apply to larger turbines of interest for cogeneration and utility application (5—100 MW).

In Japan the Agency of Industrial Science and Technology (AIST) has been conducting a large-scale seven-year program to demonstrate a 100-MW AGT with a combined plant efficiency greater than 50%. This is part of the "Moonlight" project, which began in 1978. The AGT is a large stationary gas turbine that drives an electrical power generator and includes exhaust heat recovery to drive a steam turbine power generator. The turbine input temperature is 1300°C. This program has included a great deal of ceramic materials development. However, the available structural ceramics during the period of performance for this project were not adequate for large turbine components, and cooled superalloy components are being used in the demonstration. The AIST and the parent Ministry of International Trade and Industry consider structural ("fine") ceramics to be a very high-priority development task in Japan, and they continue to fund and to promote aggressively ceramic development for heat engine application.

Silicon carbide (SiC) and silicon nitride (Si_3N_4) are the primary candidates for use in the AGT because of their high-temperature strength and oxidation resistance. Corrosion and erosion by particulate and gaseous combustion products of coal represent a unique requirement for turbines fired directly with fossil fuels. The principal developmental requirement for these materials in gas turbine applications is mechanical reliability at 1300 to 1400°C in corrosive and erosive atmospheres. Development of the required mechanical reliability can be realized only by a balanced effort that addresses the undesirable creation of flaws in raw materials and component processing; characterization of the behavior of flaws as a function of stress, environment, temperature, and time; and the design of components by use of realistic statistical descriptions of flaw populations and strength behavior.

A variety of ceramic materials have been and are still being investigated in various DOE and DOD programs for application at high stress and high temperatures in both heat engines and heat exchangers. These include ceramics wherein the major phase is silicon carbide, silicon nitride, silicon-aluminum oxynitrides, and others, but most work on national programs has been performed on silicon-carbide and silicon nitride. To address the materials research problems adequately in the area of structural ceramics and to attain significant results within the next five years, the expected available AR&TD Fossil Energy Materials Program funds will initially be focused primarily on SiC-base ceramics for several reasons. In past work on employing structural ceramics in heat engines and heat exchangers, the data clearly show that both dense SiC and siliconized SiC ceramics have considerable potential as high-temperature engineering materials. In addition, several industrial firms manufacture these SiC-base ceramics, and it is reasonable to expect positive results from this program to be transferred to at least some of the firms and thereby to generate industrial sources of improved SiC ceramics for future fossil energy systems. Potentially competing materials are Si_3N_4-base ceramics and related ceramics, primarily because of desirable high-temperature properties of this material and the large amount of research conducted on it in previous DOD and in current DOE heat engine programs. Other structural ceramics such as the sialons (e.g., the Si-Al-O-N system), which are related to the Si_3N_4 ceramics, or toughened ceramics (e.g., SiC-fiber-reinforced ceramics and transformation-toughened systems) are also considered as candidate materials with excellent potential and will be factored into the program as it progresses.

A structural ceramic materials technology program should include the critical examination of ceramic-matrix composite systems to assess their potential for application in gas turbines.[3] A ceramic-matrix composite as discussed here is defined as a material having a continuous homogeneous ceramic phase, reinforced with at least one other phase, which may or may not be continuous. The added phases may be either particulate or fibrous and may be ceramic or possibly metallic. The major purpose for considering a ceramic-matrix composite is to overcome the single greatest disadvantage of structural ceramics (brittle fracture characteristics) while taking advantage of their excellent high-temperature properties, corrosion resistance, and hardness. Data available suggest that the dispersed phases in ceramic-matrix composites greatly increase the fracture energy (toughness) and effectively arrest catastrophic crack propagation in the brittle major phase when the secondary phase has the correct mechanical and geometric properties. Toughness must be improved without degrading the fracture strength for the improvements to be usable.

Diesel engines are the other heat engine alternative for combustion of fossil fuels. Coal slurries or coal gases can be burned in diesel engines for power generation. Erosion, corrosion, and wear of the cylinder, piston, rings, and valves by ash from coal represent significant materials problems. Ceramic coatings on cast-iron components or monolithic ceramics may be necessary for the wear resistance required in the combustion chamber. High-temperature (~1000°C) radiant uncooled combustion chamber components will be required to achieve acceptable ignition delay, combustion efficiency, and gaseous emissions when coal or coal-derived fuels are used. The requirement of uncooled high-temperature combustion chamber materials that are resistant to corrosion and erosion by ash particles and gaseous products restricts the materials of construction to ceramics. High-temperature "adiabatic" engines introduce other materials problems not otherwise encountered. High-temperature lubrication and tribology requirements are not well defined, but low friction is obviously important and also limits materials selection to ceramics. Cyclic fatigue of materials at elevated temperatures could possibly be a problem, but it is not well characterized or understood.

Adiabatic diesel engines for transportation are being developed by DOD and by DOE Conservation and Renewable Energy. The Army Tank Command is developing uncooled engines for tanks and other armored vehicles to eliminate vulnerable cooling systems. The DOE Office of Vehicles and Engines Research and Development is developing adiabatic diesel components in the Heavy Duty Transport Program for fuel conservation. The high-temperature exhaust is used for turbocharging and turbocompounding the engine. The latter refers to expanding the exhaust through a gas turbine geared to the diesel engine's crankshaft.

Zirconia is a promising material for the transportation applications of adiabatic diesels. Zirconia has a coefficient of thermal expansion (CTE) that matches the CTE of cast iron fairly closely. The compatibility of CTE makes substitution of zirconia into conventional engines attractive. Zirconia is a very good thermal insulator for a structural ceramic. Plasma-sprayed zirconia on cast iron makes an excellent thermal barrier. Partially stabilized zirconia (PSZ) is very strong and relatively tough. The critical question for PSZ is whether or not the time-dependent behavior at operating temperatures in the engine will be adequate.

A new program entitled Ceramic Technology for Advanced Heat Engines was initiated by the DOE Office of Transportation Systems under the Assistant Secretary for Conservation and Renewable Energy in FY 1983 as part of a major new DOE effort. In addition, a major program initiative in structural ceramic technology has been taken by NASA, and this program is the responsibility of the NASA Lewis Research Center. The DOE program, a generic structural ceramic materials program, has the purpose of developing the industrial technology base needed for the AGT and adiabatic diesel engines for transportation. The NASA program is limited to turbine applications for aeronautics and is also generic.

Many of the objectives of the structural ceramic work to be conducted in the DOE and NASA programs are common to the needs and objectives of the Fossil Energy Materials Program.

4.1.2 Heat Recovery

The technology for transferring heat from one working fluid to another, such as gases, through a metallic heat exchanger is well established. Materials for metallic heat exchangers in combustion systems are discussed in Chap. 5; structural ceramics in heat exchangers for heat recovery are addressed here. This application is of interest only at temperatures high enough and in environments hostile enough that available alloys are unsuitable because of their lack of the mechanical strength or the corrosion resistance required.

Potential applications for ceramic heat exchangers in fossil energy are in two possible areas. In one, the heat exchanger is used to transfer heat from a fossil-fuel-firing process to a high-pressure working fluid such as helium for use in a closed-cycle Brayton system or to air or nitrogen for use in an open-cycle Brayton or possibly some other similar system. The second application uses the heat exchanger (recuperator) to recover heat from hot waste gases by preheating combustion air, batch materials, or process reactants or for some similar purpose.

Materials research and development on the high-temperature high-pressure unit outside the AR&TD program has been sponsored primarily by the Electric Power Research Institute (EPRI) in a recent Coal-Fired Prototype High-Temperature Continuous Flow Heat Exchanger Program. Results of that program provided considerable understanding of structural ceramics technology relevant to advanced heat exchangers, including tube-to-tube and tube-to-header joining needs. The heat exchanger design consisted of tubular inlet and outlet headers joined by U-tubes, which are the heat transfer surfaces.[4,5] Results from this program clearly indicated significant potential for ceramic heat exchangers for high-temperature applications. The design in the EPRI program focused exclusively on a tube-and-header with folded cross flow because of the energy flux requirements and the need to ensure that the coal slag on the hot face did not adversely foul the heat exchanger during service. Availability of candidate structural ceramics in a limited number of shapes was also a significant factor in determining several aspects of these early designs.

The research and development on ceramic heat exchangers for the waste heat recovery application has been conducted under both government and private sponsorship. Two earlier demonstration programs on recuperative ceramic heat exchangers were funded by the Office of Industrial Applications and Commercialization of DOE (INDUS—DOE). Two program efforts on tubular ceramic recuperators, supported by the Industrial Conservation Program through the Idaho Operations Office of DOE, are under way with industrial contractors. Specifically, the Babcock & Wilcox and the Garrett-AiResearch program efforts are directed to heat recovery from steel soaking pits and aluminum remelt furnaces. Both programs will use ceramic recuperators in the high-temperature regions of the burner ducts. The design phase of the recuperators is complete, and they are currently under construction. In addition, substantial efforts are under way on ceramic recuperators, supported by the Gas Research Institute. A program on materials for waste heat utilization is also under way at ORNL, supported by the DOE Industrial Conservation Program. Two other programs, the Ceramic Heat Exchangers for High-Temperature Fossil Fuel Combustion Environments Program at ORNL and the Ceramic Joining Project at the Solar Division of International Harvester, were initiated by the DOE Office of

Fossil Fuel Utilization and were managed by Pittsburgh Energy Technology Center in the Heat Exchanger Technology Program. Both of these programs are complete.

The two programs supported by INDUS-DOE involved the demonstration of much smaller ceramic recuperators on process heat furnaces. The GTE Sylvania program had the objective of demonstrating extended-surface honeycomb ceramic heat exchangers on five different types of production furnaces. This program is complete. A major program objective was to demonstrate the viability of the honeycomb type made of magnesium aluminum silicate or other ceramic material operating in a cross-flow mode with waste gas inlet temperatures of 1300°C and above with an effectiveness exceeding 50%.

The second INDUS contractor, TerraTek, Inc., had the major objective of demonstrating a very high-temperature ceramic heat exchanger capable of operating on a commercial glass-melting furnace or similar relatively dirty industrial hot waste gas source. Materials screening tests and selection were a part of this program. Limited evaluations were completed under this contract.

Of the 14 programs previously active in the Heat Exchanger Technology Program (HETP) sponsored by DOE Fossil Energy as listed in the May 1978 *Heat Exchanger Technology Program Newsletter*,[6] five were directly oriented to ceramic heat exchanger technology, and a sixth was oriented to heat transfer enhancement.

The HETP and Industrial Conservation have been the only organized DOE programs oriented to technology development of ceramic heat exchangers, with the exception of work at the Solar Division of International Harvester funded by the AR&TD Fossil Energy Materials Program and two solar energy programs. The AR&TD project at Solar resulted in successful assembly of an SiC ceramic heat exchanger during FY 1980, followed by successful high-temperature and leakage tests. Work involving coal combustion studies continued with EPRI support.

The use of structural ceramics in heat exchangers is anticipated to be less demanding than that in gas turbines, because in general the stress levels in these components will be lower and because more design latitude may be available in a heat exchanger than in the rotors and stators of a turbine. However, practical ceramic heat exchangers for fossil energy systems will typically be very large. Specific research and development needs for structural ceramics are detailed in the following paragraphs.

An understanding of the mechanical behavior of silicon carbide and silicon nitride ceramics at elevated temperatures in the presence of stress and atmospheric exposure conditions appropriate to the end use (hot gas exposure from clean and dirty fuels) is required. A critical evaluation of the oxidation and corrosion properties of SiC and Si_3N_4 under high-temperature service conditions is also required, as is an orderly sequence of ceramic heat exchanger module testing in aggressive fossil-fuel-fired environments to identify structural ceramic limitations in corrosion and joint durability. This testing should include materials exposure from actual fossil fuel combustion, rather than from simulated conditions, and should also include tube-and-header and possibly honeycomb designs.

Relationships between the powder properties, impurities, fabrication processes, and so forth and the final mechanical properties of silicon nitride and silicon carbide ceramics are poorly understood. This poor understanding limits a realistic assessment of the application potential for silicon nitride and silicon carbide ceramics as fossil energy system components. Near-net-shape fabrication of these ceramics is critically important for economic reasons. An investigation is required to determine the potential for fabricating high-density high-strength silicon-base ceramics by cheaper or simpler novel techniques and from lower cost starting materials.

Unlike metals, ceramics generally cannot be procured in standard sizes and then cut, joined, and assembled by the end user. Frequently, the ceramic part must be fabricated to its final or near final shape. The inability to join silicon carbide and silicon nitride ceramic shapes reliably once the parts have been densified is a serious impediment to the design of large assemblies such as heat exchangers. Furthermore, results from the AGT and later DARPA programs indicate that undesirable bonding can occur at ceramic-ceramic or ceramic-metal joints in a structure designed for a free mechanical interface. Such unwanted joining results in high stress and fracture in the ceramics during system cooldown. Joining and sealing of structural ceramics for high-temperature service is particularly important for heat exchanger applications. Mechanical compression seals for tube-to-header joints may be a desirable design choice if leakage can be maintained sufficiently low under service conditions. Alternatively, solid material joints or brazed joints must withstand multiple thermal and stress cycles in aggressive environments. Joint repair capability in the field (and possibly field fabrication of large tube-and-header ceramic heat exchangers) is very desirable for maintenance.

Nondestructive test development is needed for structural ceramic materials to detect flaws, study fabrication variables (through rather complete green-state characterization), and measure physical and mechanical properties. Potential techniques include X- and gamma-ray tomography; contact and projection radiography (real-time and film with image processing); ultrasonic methods including through-transmission; pulse-echo, and surface acoustics with advanced signal processing; nuclear magnetic resonance (NMR) spectroscopy; NMR imaging; and low-kV radiography with digital image processing.

A general deficiency in the structural ceramics area is the lack of a data base of key material properties as a function of temperature and time in reactive environments. These data must be developed for a consistent set of well-defined specimens and materials. This deficiency has resulted in a void in property-material specifications for structural ceramic applications wherein moderate or high stresses are experienced at high temperature. The only substantial effort of this type has been supported at IIT Research Institute by the U.S. Air Force and others.

Work is needed to identify the potential and limitations of cellular ceramic heat exchangers for large fossil energy system needs. If fouling and leakage can be controlled adequately in highly contaminated combustion gas environments, this design offers great potential for providing relatively small low-cost high-performance heat exchangers. Several candidate materials should be evaluated for fabricability, acceptable properties, leakage, and durability by means of module firing tests with coal, synthetic fuels, and residual oils. Such heat exchangers may have particular promise if advanced indirectly fired gas turbine systems with isolative heat exchangers and multiple fuel burners are attractive for the system's performance or economics.

4.1.3 Nondestructive Testing

Nondestructive examination (NDE) techniques for materials characterization and flaw detection can have a large cost impact if applied to green-state ceramic bodies before densification. Correlation of NDE-detected flaw data (size, type, and location) and characterization (density distribution, porosity distribution, binder/plasticizer distribution, elastic modulus variation, etc.) should lead to better failure prediction models. Nondestructive examination methods may also be used to inspect raw powders before processing steps to identify which powder step is introducing flaws. Characterization of microstructure (grain size, porosity, free silicon content) can also be related to processing parameters as well as component performance and may lead to better predictions of lifetime. However, the NDE effort should be directed not only to green-state specimens but to densified specimens as well. Also, laboratory specimens and actual components used in heat engines and heat recovery systems (e.g., turbine blades, piston caps, valve covers, valve wear plates, and heat exchanger tubes) should be studied by NDE together with a rather comprehensive fracture behavior effort. The type of defects to be detected by NDE is dependent upon whether the ceramic material is a monolithic material or a composite material, whether surface or bulk body is the most important, and whether the material is in a green or densified state.

The allowable load on structural ceramics is controlled by the stress necessary to propagate a suitably oriented and sized flaw to critical size. This critical flaw size may be as small as 10 μm. This is about two orders of magnitude smaller than those for metals, and special techniques must be developed to detect such small flaws. Most ceramic materials are subject to slow crack growth. In principle, the probability of failure can be predicted if the temperature, stress, and atmosphere are known; if the material is adequately characterized; and if the type and size of existing flaws are known. If it can be established that flaws are smaller than a determined critical size and that the material properties and slow crack growth behavior are known, the component life can be assured. This could perhaps be established by NDE methods, but the resolution and speed of such measurements must be improved. Component reliability must ultimately be assured by developing controlled processes for fabricating components and by keeping the manufacturing process in control. Nondestructive examination is an integral element of such a quality program and is preferable in terms of efficiency, cost, and quality to a program that depends on mass inspection and rejection of significant numbers of components.

4.1.3.1 Densified Ceramics

Process-induced defects, such as inadequate binder distribution or lack of uniform green density, embody themselves in the final product. Other flaws to be detected typically include high- and low-density inclusions, cracks, and large voids. In composite ceramics made with random-length random-oriented fibers (whiskers), typical flaws to be detected include whisker clusters, whisker stratification, and inclusions. In both monolithic and composite ceramics, where big loads are carried, measurement of residual stress levels in densified parts would also be desirable.

The best technical NDE approach for the ceramic material greatly depends on whether the material is a composite or a monolithic, if surface or whole-body flaws are most important, and if the material is in the densified or green-body state. Application of ultrasonic techniques to densified ceramics allows higher frequencies (>200 MHz) than those allowable for green-state ceramics. Higher frequencies provide shorter wavelengths for improved spatial resolution, which is necessary for detecting critically sized flaws in the whole body.

Use of focused acoustic transducers with appropriate signal processing should allow complete through-the-body flaw detection (and characterization) such that only selected planes in a body could be interrogated.[7] Exactly what the spatial resolution capability will be is yet to be determined. Special highly focused transducers may allow very high spatial resolution in the 25-μm range for specific types of defects.

Radiographic techniques (X- and gamma-ray computed tomography, X- and gamma-ray contact and projection, real-time, and film with image processing) also hold potential for interrogating densified ceramic bodies. It has been known for some time that low-kV radiographic imaging techniques are best for low-density materials.[8] Ellingson[9] has shown that for green-state ceramics, X-ray heat voltages less that 50 kV (photon energies ~20 keV) can be used, but for densified, reasonable-sized specimens with high-atomic-number material, up to 1 MeV photon energies are necessary for penetration. Highly tailored radiographic techniques do appear to hold promise for inspecting ceramic materials.

Computed tomography (CT)[10–14] can detect low- and high-density inclusions and cracks in the 25- to 50-μm range in quite large bodies, and it can map density distributions. The energy levels needed for CT imaging depends on the composition of the ceramics, the thickness, and the state (green or densified). An important attribute of CT is that it provides a method to interrogate the entire ceramic body in a noncontacting way and provides almost immediate images on which to base decisions. A great deal of work remains to be done to define the limits of operation for flaw detection and characterization and to reduce the cost of implementation.

Contact or projection radiographic imaging has strong potential for application to ceramics. Its drawback is that no through-thickness spatial information is provided. Thus, a high-density inclusion may be detected, but the method does not allow the location in the body to be determined. For thin parts, location in the thickness may not be important, and thus the image may be immediately useful. Analysis of X-ray images by digital image processing techniques will allow isodensity maps to be obtained as well as enhancement of low-contrast defects such as silicon inclusions in silicon-based ceramics.

Surface acoustic waves may be useful for detection of surface flaws, such as machining-induced cracks, by looking at backscattering. Backscattering may also be useful for characterizing surface finish (i.e., machining-induced roughness).

Small-angle neutron scattering, a new NDE technique, may be used to detect micropores and/or residual stresses. In general, studies must be carried out to establish the correlation between results of the various NDE studies.

4.1.3.2 Green-State Ceramics

For green-state ceramics, it is desirable not only to detect flaws such as agglomerates, inclusions (Fe, Si, etc.), voids, and cracks, but to characterize the specimens for density distribution, binder content and distribution, and porosity distribution. The delicate nature of green-state bodies implies that noncontacting methods be used. In addition, full-volume interrogation is necessary because it is not sufficient to look only at surface flaws.

In contrast to densified materials, where all chemical additives (binders, plasticizers, and sintering aids) have been burned out, green-state ceramic bodies still contain these additives. Further, it is usually considered that the distribution of these additives affects the distribution of the mechanical properties within the ceramic part. Thus, in addition to acoustic and radiographic techniques discussed earlier for densified ceramics, chemically sensitive NDE methods such as nuclear magnetic resonance (NMR) may have potential for application. Full-body mapping of porosity, distribution of carbon-containing binders/plasticizers, and perhaps silicon distribution in siliconized Si_3N_4 may be possible.[15] For mapping of porosity, dopants that are compatible with the additives but that have nuclear spins (i.e., the nuclei are detectable by NMR) may allow mapping of porosity. Perhaps green-body characterization is where NDE could offer the highest payoff in ceramic processing.

Present techniques most widely employed by industry for NDE of ceramics are X-ray radiography and fluorescent dye penetrant testing. These techniques provide a relatively coarse resolution of discontinuities (density variations, pores, cracks, inclusions, etc.). However, as noted earlier, efforts are under way to advance NDE techniques for structural ceramics. The techniques under study include advanced acoustic methods (including focused transducers and signal processing), X- and gamma-ray tomography, X- and gamma-ray radiography with digital image processing, NMR imaging, surface acoustic wave testing, small-angle neutron scattering, and overload proof testing. No single technique is expected to serve as a universal flaw detection and characterization method. Several techniques will be required to assess ceramic components thoroughly and cost-effectively in the green and densified states. Most of these techniques are currently being evaluated by the AR&TD Fossil Energy Materials Program and have application to heat recovery systems as well as heat engines.

Future studies should focus on selected structural ceramic specimens (SiC, Si_3N_4, ZrO_2, Al_2O_3), including samples in the green state. Samples should have variations in shape as well as variations in microstructure (grain size, grain distribution) and flaws (seeded inclusions, cracks, and pores).

Work on ceramics should include establishing the ability to characterize green-state bodies. This ability would affect not only ceramic process development but flaw detection as well. Variations in ceramic specimen parameters relative to flaw detection should be used to predict fracture behavior in laboratory specimens (tensile and flexure stress modes), and the relationship between flaw detection and failure needs to be established.

Fracture mechanics analyses and microstructural evaluation should be carried out to identify flaws most likely to limit component life so the NDE effort can focus on the most important areas. Studies must be carried out to correlate NDE results with fracture behavior to establish the utility of the NDE techniques. Tests must be performed on samples with controlled flaw populations to determine the effect of flaws on failure probability distribution.

A significant effort should be developed to evaluate CT, acoustic, and NMR imaging for ceramics in the green and densified state, and to correlate the data with fracture behavior. Cracks, porosity, and density variations are all potentially detectable with these advanced sophisticated methods. In addition to CT scanning, advanced NMR imaging systems for materials should be evaluated.

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5. COMBUSTION SYSTEMS

5.1 TECHNOLOGY STATUS AND MATERIALS NEEDS

5.1.1 Fluidized-Bed Combustion

The combustion of coal in a fluidized bed of crushed limestone or other sulfur sorbent offers a more energy-efficient approach for sulfur capture than is currently attainable with other more conventional combustion processes. When coal is burned in a fluidized bed, the bed temperature must be kept below about 950°C to prevent ash agglomeration. In fact, efficient removal of sulfur will probably limit the bed temperature to below 900°C; these relatively low combustion temperatures also limit NO_x emissions. The heat of combustion may be transferred to in-bed and above-bed tubes carrying water, steam, or air, or it may be removed by increasing the air flow to greater than that required for stoichiometric combustion. In the latter application, the bed is normally pressurized, and the combustion gases are expanded through a gas turbine. Although the tube temperatures of the in-bed heat exchangers vary greatly with choice of coolant, the heat exchanger concepts are alike in their requirements for uncooled support members, coal ports, ash lines, and other components that can operate at temperatures approximately equal to the bed temperature.

Materials requirements for fluidized-bed combustors (FBCs) have been addressed in several design studies.[1–3] All components contacted by the fluidized bed — heat exchanger tubes and supports, air distributor plate, coal and limestone feed nozzles, side walls, bed-drain hardware, and instrumentation — must satisfy operating requirements that are unique in terms of past operating experience for coal combustion systems. Design parameters, such as location of coal feed ports and air fluidizing velocities, strongly affect materials performance, and the compromises that can ultimately be achieved between design and materials requirements will be a major factor in establishing the feasibility of FBC concepts. Additional challenges to the designer are problems of creep and fatigue arising from imposed loads and vibrations. Not unique, but also of concern, are problems with dissimilar-metal welds.

Fireside corrosion of superheaters in conventional pulverized-coal-fired boilers is due to the deposition of ash-containing alkali sulfates on the metal. Sulfate-containing coatings are also formed on heat-exchanger and other metallic surfaces immersed in limestone-scavenged fluidized-bed combustors above approximately 400°C. In this case, the coatings are predominantly $CaSO_4$, which remains solid even at the maximum bed temperature. Nevertheless, chemical interaction between these coatings and the underlying metal—metal oxide substrate is a major factor in the corrosion of FBC materials. Also of importance is the distribution of air, coal, and combustion gas within the bed. Determinations of the oxygen fugacity of the bed by solid electrolyte probes responsive to oxygen anion activities show rapidly fluctuating oxygen pressures at any given point in the bed, the pressures reaching apparent levels as low as 10^{-10} Pa. This implies that transient reducing conditions exist in the vicinity of burning coal particles.

In addition to corrosion, the in-bed and freeboard heat exchanger components may also be subject to erosion. In practice the local gas velocities in the freeboard (above-bed) area of an FBC are comparable to those in conventional coal-burning systems. Thus, although the particle density is much higher in the FBC, problems with erosion in the freeboard region appear to be more conventional than those in the bed. Erosion patterns in the in-bed regions of fluidized beds have been of two general types. In the first type, tube surfaces and water-walls operating at temperatures lower than approximately 300°C in some (but not all) fluidized beds have suffered rapid erosive wear, the wear patterns conforming to classic abrasion by hard particles. The eroded surfaces appear highly polished, exhibiting no oxide films, sulfate, or char coatings. The second type of erosion has been manifested at higher temperatures (400—600°C) where the under surfaces of heat exchanger tubes have sometimes exhibited much higher wall losses than the mating upper surfaces. The latter form of erosion appears to be associated with an erosive effect of the growth and spallation of $CaSO_4$ and/or underlying oxide films. Neither form of erosion has been observed for heat resisting (austenitic) alloys operating at 800°C or above, where relatively thick, wear-resistant oxide films are formed. Three factors that appear important in effecting in-bed erosion are (1) localized high-velocity jets, (2) the angle between the tube axis and direction of air flow, and (3) the downward movement of bed material along water-wall surfaces. Bed design parameters, particularly the nominal fluidizing velocity, the design of the air distributor and lower bed plenum, and bed depth are fundamentally important in controlling erosion. In general, combatting in-bed erosion through material upgrading and coating has not been as effective as have controlling local particle velocities and using spoilers for disrupting adverse air flow patterns.

Erosion problems of still another form are encountered when the combustion gases from the FBC are expanded through a gas turbine. A substantial amount of work has dealt with gas turbines ingesting dusty air and with the recovery of energy from fluidized-bed catalyst regeneration units by expanding the product gas through turbines. All this work indicates that even moderate concentrations of 5-μm particulates can be very damaging at the high velocities in the engine. Because these erosion problems cannot be solved by materials selection only, design solutions must also be sought. The magnitude of the erosion problem is strongly influenced by the degree of hot-gas cleanup that can be realized and by the detailed aerodynamics of the turbine. The former strongly influences the particulate concentration, and the latter controls particle velocities and temperatures in multistage gas turbines. Solution of the coupled hot-gas cleanup and gas turbine erosion problem is probably the most difficult technological problem facing the pressurized fluidized-bed combustion (PFBC) system.

Erosion and deposition (fouling) have generally limited the lives of coal-fired gas turbines. However, at longer times or higher temperatures, hot corrosion of gas turbine components appears to be a significant threat.[4] After entering the turbine, the PFBC gases are cooled by expansion in the turbine and by contact with cooled metal parts or with the boundary layer surrounding them. Alkali sulfates can then condense on the metal surfaces. Thus, the selection of the metal temperatures controls not only the rate of the corrosion reactions but also the rate of deposition of corrodent on the surface. Although the alkali vapor concentrations produced in a PFBC are in most cases lower than those encountered in pulverized-coal combustion systems, the flux of alkali salts in the gas turbine will be substantially greater than that regarded as acceptable for current engines using distillate fuels. Temperature is critically important, and there is now strong evidence that corrosion of PFBC turbine components will be even more severe in the range 600 to 750°C than at higher temperatures. However, some alloys and claddings are clearly less susceptible to this type of attack than are others, and the choice of an adequate turbine protection scheme (material and surface temperature) is not yet clear.

Given the complexity of materials degradation processes in fluidized beds (e.g., erosion, corrosion, and erosion/corrosion), it is not surprising that the wastage rates reported for specific heat exchanger materials have differed by orders of magnitude among the various in-bed materials studies conducted to date.[5-7] However, the pattern of materials behavior has become more predictable as specific degradation mechanisms have been better identified. For example, at service temperatures of 800°C and above, candidate materials have narrowed to austenitic stainless steels (including Incoloy 800), and the degradation of these materials is controlled by classic oxidation/sulfidation mechanisms. The major concern with these materials is breakaway oxidation, which is associated with a critical distribution of internal sulfides near the oxide-metal interface. Still to be determined is the role of $CaSO_4$ deposits in the corrosion processes and the transport mechanisms of sulfur through the oxide film. Under steam boiler conditions (600°C and below), degradation of candidate heat exchanger materials has been negligible except where erosion has accelerated the normal oxidation processes or abraded unoxidized tube surfaces.

Although laboratory corrosion and erosion tests are extremely useful in establishing the environmental and temperature conditions under which a given degradation mechanism can operate, it is still necessary to relate these laboratory test results to fluidized bed design parameters (excess air and SO_2 in the flue gas, bed temperature, superficial velocity, sorbent-fuel ratio, coal and sorbent feed size, etc.) This requires the exposure of materials in an FBC dedicated to materials testing, where the corrosion performance of heat exchanger and turbine materials can be correlated with bed design and operating parameters. During FY 1985 an \$8,000,000 in-bed materials test program was completed under the sponsorship of Energy, Mines, and Resources (EMR) Canada. The test was conducted for a total of 10,000 h in a 1- × 1-m atmospheric fluidized-bed combustor owned and operated by the Nova Scotia Power Corporation. Materials data from this test are being made available to the United States through the Physical Metallurgy Research Laboratories, a technical arm of EMR. In addition, the Morgantown Energy Technology Center has solicited proposals for an in-bed materials testing program to investigate the effects of operating and design parameters on tube metal wastage in FBCs. These programs constitute an important adjunct to the AR&TD Fossil Energy Materials Program and are reflected in the current and proposed test programs for FBC materials studies.

Laboratory experiments under carefully controlled conditions should also be continued to understand the mechanisms and microstructural conditions that lead to breakaway oxidation at 800°C and above. Tests at lower temperatures should be conducted to establish the conditions under which erosion will affect the mechanical integrity of oxide films and $CaSO_4$ deposits. Laboratory tests are also required to identify the mechanisms of low temperature hot corrosion of turbine alloys and coatings in simulated PFB flue gas environments.

The materials requirements for certain hot-gas cleanup systems, such as cyclones, do not seem particularly difficult to meet, although candidate materials should be subjected to long-term testing. However, more advanced hot-gas cleanup systems (e.g., ionic conducting materials) are under development; their materials requirements must be determined, and successful materials performance must be demonstrated.

A current problem in steam generators is that oxide scale spalls from reheater and superheater tube surfaces and partially obstructs passages or damages turbines. Conditions of high heat flux, such as in liquid-metal heat exchangers, increase the extent of spallation.[8] Because the heat fluxes of FBC in-bed steam generators will be higher than those in current fossil-fired generators, the problem of spallation could be accentuated. A program should be initiated to determine the effect of the heat fluxes in FBC steam generators on oxide spallation. If the effect is significant, the benefits of chromizing or substituting more oxidation-resistant materials should be evaluated.

Dissimilar-metal joints between ferritic and austenitic boiler tubes are currently made with high-nickel filler metal. Such joints may not be suitable for applications that locate the joints within the fluidized-bed region of atmospheric FBCs (AFBCs), because such high-nickel alloys are susceptible to catastrophic sulfidation corrosion. The performance of joints made by existing methods must be related to operating temperatures and local bed conditions in AFBCs, and, if necessary, alternative joining methods and materials must be explored.

Nondestructive techniques (ultrasonic and eddy current) for in-service inspection should be developed and applied for tubing, dissimilar-metal welds, and other components.

5.1.2 Conventional Combustion

Two central objectives of the DOE Office of Fossil Energy for the development of combustion systems are (1) substitution of coal (or coal-liquid mixtures) for oil and natural gas in utility and industrial boilers and (2) extension of the reserves of oil and gas by improving the reliability and efficiency of boilers and furnaces.

Replacement of oil and natural gas by pulverized coal or coal-liquid mixtures in industrial and utility boilers requires solutions to a number of technical problems. The principal problems are those of fly-ash fouling, slagging, corrosion, and erosion of boiler tubes and other components in conventional combustors. These problems are caused in part by the mineral matter present in the feed coal and the transformation and reactivity of the mineral matter during and following combustion. An adequate understanding of the mechanisms responsible for the chemical and physical reactions seen with the use of coal or coal-liquid mixtures is needed. Boiler tube wastage in conventional pulverized-coal boilers is caused primarily by the corrosive reactions that occur at high temperatures between the compounds formed from the elements contained in the coal and the metal tube surfaces. Low-temperature corrosion is due mainly to attack by sulfur-containing acids. In addition to the development of more corrosion-resistant materials for boiler components, better coal cleaning techniques (as discussed in Chap. 1) will result in the removal of a large amount of the ash and sulfur from the feed coal and, thereby, reduce the problems caused by these materials. In addition to providing a better quality coal for pulverized-coal combustion, improvement of feed coal quality is an important step in the preparation of coal-liquid slurries for combustion in retrofitted oil or gas combustors. The prime problems encountered when oil- or gas-fired boilers are retrofitted to burn coal or coal-liquid slurries are corrosion, erosion, and wear of the burner nozzle. Again, proper coal cleaning will reduce this problem somewhat; however, burners will need to be redesigned to atomize the injected slurries into the combustion zone properly. The coal-liquid mixtures most successful to date have been coal-water mixtures.[9,10] Coal-oil mixtures have not proved economically attractive in comparison with current oil prices, and recent studies showed that considerable loss of power-generating capacity could be expected when coal-oil mixtures are fired in oil-fired boilers.[9] Slurry production also requires the addition of chemicals that cause a different type of fouling problem, and this area will need to be addressed as well before coal-water mixtures will replace oil or gas. However, the use of slurries resulted in NO_x emissions 100 to 200 ppm lower than those occurring when pulverized coal of the same quality was burned.[10]

Among the current materials limitations that the Electric Power Research Institute (EPRI) has singled out as particularly significant to electrical utilities are the corrosion fatigue of steam turbine rotors and blades and the oxide spalling of superheater materials, which causes erosive impingement on turbine blades.[11] The attainment of higher efficiencies in the steam-Rankine power cycle demands materials with improved fireside and steam corrosion resistance at 600 to 700°C. This is achievable by the substitution of more highly alloyed metals for present-day boiler materials, although not without a significant increase in plant capital costs. The development of oxidation- and sulfidation-resistant coatings to upgrade existing boiler materials may be a more cost-effective means of achieving the needed temperature increases.

Failure of dissimilar-metal welded joints in steam generators has become a major factor affecting the reliability of utility steam boilers.[12] Superheaters and reheaters delivering steam at 540°C commonly employ austenitic stainless steels for higher temperature regions and ferritic steels for lower temperature regions. Although these tubes can be joined with a variety of welding approaches, cracks are characteristically encountered in the ferritic material adjacent to the weld interface. Of 54 utilities responding to a survey by the Steam Power Panel of the American Society for Testing and Materials, American Society of Mechanical Engineers, and The Metal Properties Council, 20 reported dissimilar-metal weld failures.[12] These failures involve 60 units of a total of 320 and were not attributable to poor welding techniques. Because none of the techniques now used for joining stainless steel and ferritic tubes has resolved the cracking problem, the development of an improved type of dissimilar-metal weld is a major requirement for increasing the reliability of steam power plants.

The effluent emission standards imposed by the Environmental Protection Agency on fossil-fueled power plants require the removal of SO_2 from the stack gases of plants burning high-sulfur coals and fuel oils. The most common method for SO_2 removal is wet scrubbing. Typically the stack gas is quenched by water immersion and is then passed upward through a spray tower in which a chemical reagent, such as limestone or MgO, is contacted with the gas to capture sulfur-bearing species. Wet scrubbers can use a variety of liquids, ranging from seawater to both acidic and alkaline chemicals. As these liquids contact the flue gas, the absorption of SO_2 and SO_3 lowers the pH and increases corrosion. Chloride ions introduced by the coal, scrubber water, or sorbent also exacerbate the corrosion problem, especially where closed-loop recirculating water systems are used. The relatively low temperature of the combustion gas as it leaves the scrubber also poses a serious dewpoint corrosion problem (condensation of acids) in stack and blower sections downstream from the scrubber.

Corrosion problems experienced to date in the operation of pollution control equipment have been sufficient to warrant upgrading to more corrosion-resistant alloys to reduce downtime and repair.[13] Corrosion testing and field surveillance will be required to verify that the performance improvement in the upgraded materials is cost beneficial.

As noted above, the EPRI has instituted a materials development program to improve the reliability of steam turbine rotors and blades.

The AR&TD Fossil Energy Materials Program should match any advances in turbine material performance with commensurate improvements in steam supply components. Duplex materials such as corrosion-resistant claddings on austenitic stainless steels, when retrofitted into existing steam generators, have proved very cost-effective in reducing fireside corrosion under current boiler operating conditions.[14] The claddings used in the latter application are generically similar to those being developed for gasifier applications. Accordingly, coating and cladding developments for gasifier applications should be extended to cover potential coal-fired boiler applications at temperatures of 600°C and higher. Nondestructive techniques, including eddy-current, ultrasonic, and infrared methods, are needed to accommodate the cladding developments.

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6. FUEL CELLS

6.1 TECHNOLOGY STATUS AND MATERIALS NEEDS

A fuel cell is an electrochemical device that converts the chemical energy of a fuel and oxidant into electrical energy in a highly efficient manner. Once in operation, a fuel cell will continue to operate to convert chemical energy to electrical energy as long as both fuel and oxidant are supplied to the electrodes. A typical fuel cell consists of two electrodes (each possessing high electronic conductivity) and an electrolyte (either solid or liquid), which is an ionic conductor in intimate contact with each electrode. The electrolyte is a nonporous barrier, which separates fuel and oxidant. The electrodes are porous to facilitate transport of the fuel and oxidant to the reaction surfaces. The fuel is generally hydrogen or natural gas and is introduced at one electrode, while the oxidant (typically oxygen or air) is supplied to the other electrode. The reaction surfaces are the interfaces between each of the electrodes and the electrolyte. The oxidation of the fuel at the one electrode provides electrons to the external circuit; the reduction of oxygen (or air) at the other electrode uses electrons from the external circuit. Through the above process, a fuel cell can produce dc electricity on the order of hundreds of amperes per square foot of electrode area and voltages of about 1 V. Voltage levels can be increased by connecting a number of individual fuel cells in series. This configuration is referred to as a fuel cell stack.

The five principal types of fuel cells, categorized according to the type of electrolyte used, are the phosphoric acid, molten carbonate, solid oxide, alkaline, and solid polymer electrolyte fuel cells. The phosphoric acid, molten carbonate, and solid oxide fuel cells have applications primarily in the commercial and industrial areas, while the alkaline and solid polymer electrolyte fuel cells are used mainly for space, military, and transportation applications. Consequently, the latter group falls outside the scope of the AR&TD Fossil Energy Materials Program. In addition, the technological advances for the phosphoric acid fuel cell over the past ten years have been significant and have brought this technology very near to commercialization. Materials research that addresses this technology would therefore be inappropriate for a long-range generic research program such as the AR&TD Fossil Energy Materials Program. Consequently, the following discussion addresses only materials research needs for molten carbonate and solid oxide fuel cells.

6.1.1 Molten Carbonate Fuel Cells

The molten carbonate fuel cell (MCFC) operates from 600 to 700°C. It consists of a porous nickel anode, a porous nickel oxide cathode, an electrolyte structure that separates the anode and cathode and conducts only ionic current between them, and anode and cathode current collectors that may also serve as bipolar cell-separator sheets for stacks of cells.[1] The individual cells within a stack are maintained in physical contact by mechanical loading. The anode and cathode gases are sealed in the stack by the capillary action of a wet seal at the edges of the stack at the junction of the current collector and electrolyte structure.

The nickel anode sheet is typically about 0.8 mm thick and contains an additive of from 2 to 10 at. % Cr_2O_3 or Al_2O_3. The additive oxide strengthens the anode and stabilizes the nickel against in-situ sintering (coarsening). The nickel oxide cathode is a 0.4-mm-thick sheet that contains about 3 at. % lithium. The presence of lithium increases the electronic conductivity of the nickel oxide. Both the anode and cathode are porous. The cathode is a dual-porosity structure in which the fine pores (<1 μm) become filled with electrolyte to provide catalytic surfaces and ionic conductance paths, and the large pores (10 μm) remain unfilled to provide access of the gas to the cathode. Likewise, the anode is fabricated with 5-μm pores to permit gas access.

The electrolyte structure (matrix), sandwiched between the electrodes, is a composite structure of about 40 wt % of inert particulate matrix material, currently $LiAlO_2$, and 60 wt % of a mixture of alkali carbonates. The binary alkali carbonate mixture commonly used is 62 mol % Li_2CO_3–38 mol % K_2CO_3, which becomes a molten ionic conductor above 490°C. The resistance of the electrolyte matrix is directly related to its thickness; therefore, the thinnest matrix possible is preferred. The thickness currently used is about 0.5 mm for matrices up to 0.1 m^2 in area.

The anode and cathode current collectors (common bipolar sheets in stacks) are generally constructed of type 316 stainless steel; however, this material corrodes in the anode environment and is therefore usually protected on the anode side with a nickel layer. A more corrosion-resistant bipolar sheet is needed.

The principal materials problems with the MCFC are dissolution of the nickel oxide cathode, interface corrosion, corrosion of the anode and cathode current collectors, electrolyte loss, and sulfur tolerance of materials.

Dissolution of the lithiated nickel oxide cathode material in the presence of the carbonate salt is a serious problem at the high pressures (up to 1 MPa) proposed for large MCFC plants. (The potential result is the loss of mechanical and electrical stability and subsequent failure of the fuel cell.) Nickel oxide dissolves as a result of concentration-driven mass transport involving a low concentration of nickel ions in equilibrium at the cathode diffusing toward the anode, where the reducing conditions precipitate them as metal. The solubility at the cathode is proportional to the CO_2 concentration and, therefore, is greater for pressurized cells. The reaction, $NiO + CO_2 \rightleftharpoons Ni^{2+} + CO_3^{2-}$, involves solid and gaseous reactants and a condensed (liquid) product. In accordance with thermodynamic principles, as the pressure is increased over the cell, the system compensates by reacting the gases present to form solids to decrease the pressure and approach equilibrum conditions. In this situation, additional nickel dissolves in the carbonate melt as Ni^{2+}, which subsequently diffuses toward the anode. Based on cell failures, due to cathode dissolution in accelerated tests, it is unlikely that the goal life of 40,000 h can be reached with cells operating at high pressures of CO_2. Observed failures occurred by cell shorting as a result of nickel deposition in the electrolyte matrix.

Interface corrosion was a problem in the wet seal area in which the metallic cell separator contacts the electrolyte tile to form sealed compartments for the fuel and oxidant gases of the MCFC. Depending on the blanket gas composition, electrical potential gradients within the wet seal can give rise to possible galvanic corrosion problems, especially at the anode. Aluminizing these surfaces has proved effective for controlling this problem. An inert insulating layer of $LiAlO_2$ forms on the separator sheet surface.

The separator sheet, also called a bipolar plate, both maintains the electrodes in intimate contact with the electrolyte structure and provides a path for the current to or from the electrodes. The terms "separator sheet" and "current collector" will be synonymous in the following discussion. Corrosion of these components in the active area of the cell might cause cell degradation through contamination of the electrodes and electrolyte by the corrosion products. Typically, a salt layer on the electrode and current collector initiates the corrosion process. In addition, the growth of a corrosion product scale on the current collectors could cause excessive cell resistance. The most significant corrosion problem for the current collectors, however, is the possibility of through-corrosion allowing parasitic mixing of fuel and oxidant. The successful operation of an MCFC depends on the formation of a protective oxide scale; however, the scale must be thin, electrically conducting, and mechanically stable. Alternative materials and cladding materials have been examined for use as current collectors, but economic considerations limit the choices. Finally, the material chosen for the current collectors must resist oxidation by the oxidant gases. The corrosion of current collectors is a problem that must be solved before long-term service with MCFCs is possible.

Electrolyte losses due to evaporation, seepage, or corrosion processes are life-limiting factors in MCFCs. These losses, which result in decreases in the electrolyte conductivity, increased electrolyte structure porosity, and diffusion of reactants across the cell, cause a decrease in cell voltage and efficiency.[2,3] A possible problem with electrolyte matrices is crystal growth of $LiAlO_2$ during cell operation, which might result in unacceptable changes in the distribution of interstice size in the matrix and, consequently, in a decrease in cell performance.[4,5]

6.1.2 Solid Oxide Fuel Cells

The solid oxide fuel cell (SOFC) operates between 900 and 1100°C. The MCFC configuration is that of planar electrode and electrolyte sheets held in mechanical contact, but the configuration of the SOFC is typically that of a laminated cylindrical tube. The laminates, from the inner to outer diameter of the tube, consist of (1) a porous support tube of calcia-stabilized zirconia, (2) an air electrode (cathode) of strontium-doped lanthanum manganite, (3) an electrolyte of yttria-stabilized zirconia, and (4) a fuel electrode (anode) consisting of a cermet of cobalt or nickel metal with stabilized zirconia. In addition, an interconnection contact consisting of magnesium-doped lanthanum chromite is laminated to the air electrode and provides the electrical path between individual cells in a stack. During operation, oxygen (or air) is passed through the SOFC cylinder, while the fuel gas, generally hydrogen, is passed over the outer surface.[6-13]

The materials in an SOFC must (1) be stable in an oxidizing and/or reducing environment, (2) be chemically compatible with other materials in the cell at both the operating temperatures and higher fabrication temperatures, (3) have high electrical conductivities, and (4) have similar coefficients of thermal expansion to avoid delamination of the layers comprising the cell. The last criterion is particularly important because the process conditions cannot be selected independently for the fabrication of each component of an SOFC. Because the fabrication of an SOFC consists of progressive lamination, the sintering temperature of each successive layer must be lower than that of the preceding porous layer to avoid altering the characteristics of the previously deposited layers.[9-11]

The principal materials needs of SOFCs are (1) the development of a higher conductivity cathode material and (2) improvement in the sulfidation resistance of the fuel electrode (anode). The relatively low conductivity of the cathode material coupled with the long current path in the plane of the cathode results in the cathode being the principal component responsible for voltage losses due to internal resistance in an SOFC. In addition, the low conductivity of the cathode results in a nonuniform distribution of current around the circumference of the cell and through the electrolyte. The alternative cathode material should have an electronic conductivity greater than 75 $(\Omega \cdot cm)^{-1}$ at 1000°C, which is the conductivity of the currently used cathode material, strontium-doped lanthanum chromite.[9] Cell performance can be significantly improved through the development of higher conductivity cathode materials; however, the alternative materials should at the same time satisfy the other three criteria mentioned above. First, the cathode materials must be stable in an oxidizing environment at temperatures of cell operation (900–1100°C) as well as of cell fabrication (1100–1500°C). Second, the alternative materials must be compatible with the other cell components so that interdiffusion and chemical interactions at the interfaces are kept to a minimum, both for operating and fabrication conditions. Third, the alternative cathode material should have a coefficient of thermal expansion of about $1.0 \times 10^{-5}\,°C^{-1}$ to avoid delamination of the ceramic layers during fabrication and thermal cycling during operation.[6]

The development of anodes with increased sulfidation resistance is also needed. Experimentally, solid oxide materials are much more tolerant of sulfur than are the materials in other fuel cells. For example, approximately 800 h of operation at 50 vppm hydrogen sulfide have been observed with a nickel anode. After an initial voltage drop of about 5%, no further deleterious effects were noted. Furthermore, the initial performance loss was recovered at the end of the test, when sulfur-free fuel was re-introduced. However, much more data on sulfur tolerance are needed. A fundamental understanding of the effect of sulfur on fuel cell performance is required. Anode materials with even higher tolerances for sulfur are desired for more efficient operation. Furthermore, an increase in the sulfidation resistance would reduce the already minimal gas cleanup requirements and allow the use of more energy efficient hot-gas cleanup methods in combined coal gasification–SOFC plants. In addition, improving the sulfur tolerance would allow the direct use of liquid fuels such as diesel fuel (0.5 wt % sulfur).

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7. MAGNETOHYDRODYNAMICS

7.1 TECHNOLOGY STATUS AND MATERIALS NEEDS

Magnetohydrodynamic (MHD) power generation is the direct conversion of heat to electricity by passage of a high-temperature high-velocity electrically conducting fluid through a magnetic field. The principle of MHD power generation is the interaction of a partially ionized coal combustion gas with a transverse (to the fluid flow direction) magnetic field to induce an electric field within the fluid. Potassium carbonate injected into the combustion region provides the needed electrical conductivity of the fluid. Electrodes collect the current, and electric power can be supplied through an inverter to a power grid.

The major government MHD test facilities in the United States are located at the University of Tennessee Space Institute (UTSI) near Tullahoma, Tennessee, and at the Component Development and Integration Facility (CDIF) in Butte, Montana. The UTSI Coal-Fired Flow Facility was constructed to provide development testing of components simulating the complete MHD steam system. The CDIF was established to evaluate the performance of MHD components and systems, to compare performance of different designs, and to provide a basis for scaleup of MHD system designs.

The materials research, development, and evaluation needs for MHD components are considerable. These needs include metals and ceramics for channel electrodes, ceramics for electrode insulators and channel side walls, ceramics for a regenerative air heater for preheating combustion air, high-temperature metal alloys for a recuperative air preheater, and metals and refractories for the steam bottoming plant. These needs are being addressed primarily by the MHD program in the DOE Fossil Energy Office of Advanced Energy Conversion Systems and managed by the Pittsburgh Energy Technology Center (PETC). Although no MHD materials research is presently in progress on the AR&TD Fossil Energy Materials Program, an MHD project[1] at the National Bureau of Standards (NBS) was funded by the AR&TD Fossil Energy Materials Program in FY 1981. The objective of the project was to determine the dimensional stability of refractory materials for

MHD regenerative heat exchangers by measurement of properties such as yield strength, creep strength, and microstructural instability under both cyclic and static exposures to elevated temperatures.

Several materials projects, supported by the MHD program in the DOE Fossil Energy Office of Advanced Energy Conversion Systems, have contributed to an improved understanding of materials behavior in MHD systems.

One such project[2] at the Westinghouse Electric Corporation on MHD electrode development, completed in September 1982, consisted of laboratory screening tests to provide data on electrochemical stability and anode arc erosion resistance for selected electrode material candidates, engineering tests of preferred electrode designs under simulated MHD operating conditions, and preparation and fabrication of electrode materials. The emphasis was to evaluate metal electrode materials suitable as alternatives to platinum as an anode material. Several materials including chromium, E-Brite 26-1, Inconel 601, and type 330 stainless steel showed favorable resistance to electrochemical corrosion by slags and were evaluated in engineering tests.

In another project[3] at Avco Everett Research Laboratory, various designs of metal electrodes were evaluated during MHD channel tests. Electrode wear was found to be caused by several corrosion and erosion mechanisms, with electrochemical attack and arcing being the more important. Electrodes made of copper capped with platinum in areas of high electrode stress and non-nickel-bearing stainless steels performed well throughout 1300 h of channel testing at Avco and are currently in use at CDIF.

The primary objective of a project[4] at FluiDyne Engineering Company was to evaluate and select materials for use in the directly fired high-temperature MHD air heaters for MHD power plants. Long-term tests with fusion-cast magnesia–35% alumina cored brick and a spinel castable hot liner indicated that those materials are suitable for this application. A calcium-aluminate-bonded fused-grain spinel with 4 wt % stainless steel fibers showed only minimal degradation in a test valve system. A high-chromia fused cast refractory also appears to have promise for some MHD refractory applications.

At the NBS, work[5] on MHD seed-slag interactions and effects addressed, among other things, the corrosion of alloys in downstream components of MHD systems. The corrosion portion of the program included the development of test methods for assessing relative corrosion resistance of alloys, screening of alloys under some simulated downstream conditions, and evaluation of screened alloys to determine the applicability of certain alloys to downstream components.

A second study[6] at the NBS on creep and other properties of refractories resulted in data on the high-temperature compressive creep of refractories for use in MHD air preheaters. In addition, the refractories were ranked for creep resistance at 1400 to 1600°C. Of several materials tested, an excess magnesia spinel refractory, X-317, had the lowest creep and was most stable under the test conditions.

The corrosion of a wide variety of commercial refractories was studied at Argonne National Laboratory (ANL) under reducing conditions at 1500°C in the presence of mixtures of coal-ash slag and potassium seed.[7] For several refractories, the results appeared quite promising with a fused-cast chromia-spinel refractory material exhibiting superior corrosion resistance.

A second project[8] at ANL was concerned with the evaluation of materials for the MHD steam bottoming plant and the corrosion behavior of selected ASME-coded boiler materials exposed to simulated MHD combustion atmospheres for about 500 h at gas temperatures in the range 825 to 875°C. The data, in general, indicated that high-chromium alloys such as type 310 stainless steel and Incoloy 800 are suitable for steam heaters with tube temperatures above 475°C. Low-chromium alloys appeared to be suitable for service below 425°C.

During FY 1984, the national MHD program was redirected to conduct only that testing necessary to obtain design data for a retrofit plant by the end of this decade. This plant would be assembled by integrating an MHD topping cycle into an existing coal-fired power plant.

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8. OIL SHALE

8.1 TECHNOLOGY STATUS AND MATERIALS NEEDS

Oil shale is one of the energy resources being developed to satisfy the U.S. midterm energy requirements. The western Green River shale formation in Utah, Colorado, and Wyoming is the primary source of oil shale in this country. Two major methods of production are being pursued, surface and in-situ retorting, and materials requirements for the two differ in significant ways.

We address here some of the materials research and development needs that may be appropriate for funding as part of the AR&TD Fossil Energy Materials Program. However, oil shale retorting processes are nearing commercialization, and some of the identified materials research and development needs are more appropriately addressed by the oil shale industry. The needed areas of research that are appropriate for AR&TD Materials Program sponsorship will, for the most part, be based on industry's experience and its identification of specific materials problems.

Because of the tremendous quantity of rock that must be mined, transported, and handled (each ton of rock contains only 91 to 182 L of recoverable product) in aboveground retorting, more abrasion-resistant low-alloy steels may be required in the future. The need for longer-life mining components, such as rock-cutting heads, may also require materials development. The refractories available for a variety of elevated-temperature processes appear to be satisfactory for lining aboveground crucibles. The ability of the refractories to withstand the abrasion or combined corrosion and abrasion of the shale may become a problem. The effects of heating and cooling cycles and severe climatic changes during inactive periods may also limit refractory life. Corrosion of metals in hot retorting environments is a problem that should be addressed. Tumbling abrasion tests are directly applicable to a rotating-kiln retort and could be extended to other equipment items. High-temperature erosion by shale particulates should also be investigated.

Because of the quantity of fairly large-diameter piping that will be needed in in-situ retorts for injection and recovery wells, economics dictates that the lowest-cost low-alloy steels be used. In some systems, these pipes may pass through the retort, and their ability to withstand the corrosive environments of the retort for the required times is a problem. Protective coatings such as aluminizing on carbon steels and on low-alloy steels may solve this problem. In some retort designs, these pipes will not encounter the hot corrosive environment.

In vertical retorts, the thermowells can be more than 300 m long and must pass through the combustion and burned-out zones to carry their critical temperature measurements to the surface. The corrosion of their metal sheaths, which occurs because of the presence of oxygen and sulfur at 1000°C and even higher, can severely limit thermowell life. Temperatures high enough to cause severe attack may be maintained for periods ranging from many hours near 1000°C to days at over 800°C. The creep strength of thermowell sheaths must be sufficient to protect the internal components from the forces of shifting rock during the retorting operation. The development and demonstration of successful indirect chemical methods of monitoring retort zones may have eliminated the need for thermowells and materials research associated with these thermowells.

Maintaining reliable functioning of sump pumps to drive the products from the bottom of retorts to the surface can be a problem. The corrosion potential of the liquids and gases being pumped has not been well defined and may adversely affect the recovery piping and its control valves as well as the pumps. The fluid temperatures in these components will be about 250°C. Shale dust entrained in the oil may result in accelerated wear of pump components.

The uncertainty of future development of oil shale retorting processes makes it difficult to identify positively those materials research and development programs that should be undertaken. Whether both aboveground and in-situ retorting will become commercial is not clear. Some unresolved materials requirements of aboveground retorting were identified. Research and development to support more generic energy-supply materials requirements, such as those in mining and coal conversion, may be applicable to some of these needs.

The additional requirements of in-situ retorts are difficult to predict this early in the development and utilization of the process. The one-time use of the piping and other components in underground retorts may permit the use of already available materials, primarily those that are used in the oil-drilling industry. The thermowell problem is currently definable, but even here it is expected that, after the retort development period is over, retorts could be operated according to procedures established during the development without the need to monitor combustion zones. At this time more experience appears to be necessary, particularly in actual underground operations, before additional specific materials research and development programs can be defined. However, as improved alloy coatings are developed to reduce corrosion losses in the retort, attendant nondestructive testing development including ultrasonic and eddy-current methods should be accomplished to ensure adequate integrity.

Considering the magnitude and near-term timing of commercial oil shale processing, it would appear appropriate to perform a materials review and/or a materials needs assessment for surface retorting. If generic materials needs are identified, support of research addressing these needs by the AR&TD Fossil Energy Materials Program would be indicated.

9. TECHNOLOGY ASSESSMENT AND TECHNOLOGY TRANSFER

9.1 TECHNOLOGY ASSESSMENT

One of the more important responsibilities of the AR&TD Fossil Energy Materials Program is to be aware of technical issues and research and development needs of both established and emerging fossil energy systems. The assessment of materials problems and needed research to solve those problems in a wide variety of fossil energy technologies is the foundation of an active and relevant research program. The AR&TD Fossil Energy Materials Program fulfills this responsibility by use of technology assessments of materials needs in fossil energy systems.

One such assessment was performed in FY 1980 to identify materials problems in a variety of fossil energy systems.[1] Background information relative to the various technologies is given, and materials research needed to improve the viability and economics of fossil energy processes is discussed. The assessment is presented on the basis of materials-related disciplines that affect fossil energy materials development. These disciplines include design-materials interface, materials fabrication technology, corrosion and materials compatibility, wear phenomena, ceramic materials, and nondestructive testing. The needs of these various disciplines are correlated with the emerging fossil energy technologies that require materials consideration.

A second assessment was completed in late FY 1982 to identify and quantify the critical (strategic) materials requirements for a generic direct coal liquefaction facility.[2] It was performed as an engineering estimate of materials requirements based on engineering and technical data for this type of synthetic fuel facility. This method may be characterized as a microanalysis approach (i.e., building the whole from its parts) as opposed to the macroanalysis approach by use of national economic input-output data that forms the basis of some investigations reported in the literature.[3]

A third assessment was completed in FY 1985 to determine the status of materials technology for advanced-steam-cycle pulverized-coal plants and to identify materials research and development that would permit the design, construction, and reliable operation of more efficient power plants.[4] A pulverized-coal power plant employing an advanced steam cycle to improve the overall plant efficiency was defined. The proposed system was analyzed with existing computer codes to determine the net efficiencies achievable with various steam conditions (e.g., at temperatures between 593 and 650°C and pressures between 28 and 34 MPa). Through consultation with boiler and turbine-generator manufacturers, the ability of existing materials to meet the requirements for advanced steam cycles was determined. Materials research and development needs and areas of research that will provide the greatest payback in terms of improved efficiency and plant availability were identified. A report[4] documenting the findings and recommendations resulting from the study has been published. Prior to publication, a draft of the report was sent to boiler manufacturers, turbine-generator manufacturers, and the Electric Power Research Institute (EPRI) for their review and comment.

9.2 TECHNOLOGY TRANSFER

The transfer of technology to interested parties is aided by a bimonthly newsletter, *Materials and Components in Fossil Energy Applications*. This project (WBS element BCL-4), conducted for the AR&TD Fossil Energy Materials Program by the Battelle Columbus Laboratories (BCL), provides for the collection, evaluation, and dissemination of information pertinent to the use of materials and components in fossil energy applications. The program at BCL has been very effective for information and technology transfer and is expected to continue.

To provide a more effective distribution of information gained on this AR&TD Fossil Energy Materials Program, consolidated quarterly reports on the progress of the program were initiated in FY 1981 and have continued.[5] The consolidated quarterly reports cover the progress of all activities conducted on the program. Each report is divided into sections and chapters, with each section describing projects related to a particular fossil energy technology.

An important consideration of the AR&TD Fossil Energy Materials Program is to ensure that others in the fossil energy community, as well as in the overall research community, are knowledgeable of the reports and publications that result from each of the research projects on the Program. To facilitate this awareness and to encourage transfer of the technology developed on the Program, the AR&TD Fossil Energy Materials Program will publish in early FY 1986 a bibliography of publications by past and current participants on the Program.

Ad hoc meetings on current materials problems related to corrosion and erosion have been sponsored jointly by the AR&TD Fossil Energy Materials Program, the Office of Coal Processing, and the SRC/H-Coal Projects Office. Meetings on the subject of corrosion in liquefaction plant fractionation columns were held at Oak Ridge, Tennessee; Baytown, Texas; Lexington, Kentucky; and Birmingham, Alabama. These meetings brought together those parties directly involved in materials problems for coal liquefaction in a forum specifically designed for the transfer of information.

The Department of Energy, Electric Power Research Institute, Gas Research Institute, and National Bureau of Standards sponsor conferences on Materials for Coal Conversion and Utilization.[6] Seven of these conferences have been held, and they have been very effective in the transfer and exchange of information from the sponsors' programs. Proceedings of these conferences are published, making this information readily available.

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PART III

CURRENT AND PLANNED PROJECTS IN THE AR&TD FOSSIL ENERGY MATERIALS PROGRAM

1. STRUCTURAL CERAMICS

1.1 RESEARCH OBJECTIVES

Structural ceramic materials such as SiC or Si_3N_4 offer the potential of higher strength, lower creep, and greater oxidation resistance above 1000°C than do available engineering alloys, but they have the disadvantage of having large variations in strength (low Weibull modulus) and relatively low fracture toughness compared with alloys. The mechanical behavior of structural ceramics is determined by flaw sensitivity and unforgiving brittle behavior. Flaws may be pores, inclusions, grain boundaries, large grains, or other microstructural irregularities. Flaws introduced from the starting materials or from material processing and fabrication cannot be mitigated by microplasticity as they would be in ductile materials. Thus, the characterization of the starting materials and the processing technology are critical. The populations of flaws within structural ceramics are statistical in nature and must be treated as such in the design of components. For example, the strength of components made from the same material depends on component volume (and the probability of a critical flaw). Subcritical flaws may grow under stress and, in aggressive environments, may become critical and thus cause failure. The time-dependent behavior of brittle materials must be understood and considered in design with structural ceramics. The objective of this research area is to study the relationships between the chemical composition, microstructure, and properties of structural ceramics and fiber-reinforced ceramics used in fossil energy systems. An understanding of the mechanisms responsible for strengthening and toughening will provide the basis for the development of whisker- or fiber-reinforced ceramic composites with improved properties for high-temperature fossil energy systems. This area also includes work on nondestructive examination of ceramics, and on electrochemical behavior and phase chemistry of oxides for solid oxide fuel cells.

Current and planned research projects in this thrust area are described in the following section and are listed in Table III.1 at the end of the section.

1.2 SUMMARIES OF CURRENT AND PLANNED RESEARCH

ANL-1(A), "Development of Nondestructive Evaluation Techniques for Structural Ceramics," Argonne National Laboratory. The purposes of this project are to (1) evaluate and develop effective nondestructive evaluation (NDE) techniques (mainly acoustic and radiographic techniques) for detecting flaws and characterizing structural ceramics (green state and densified); (2) establish the types and characteristics of flaws that can be found by such techniques; and (3) determine correlations between detecte flaws, characterizations, and fracture behavior of the ceramics. The NDE techniques will be applied primarily to monolithic ceramics to detect porosity, cracking (surface and internal), inclusions, and density variations. Green-state specimens are being emphasized at present, but densified samples are included in the experimental program. This task is correlated with WBS element ANL-1(B).

ANL-1(B), "Effect of Flaws on the Fracture Behavior of Structural Ceramics," Argonne National Laboratory. The purpose of this work is to (1) establish correlations between the composition, microstructure, and mechanical properties of structural ceramics (Si_3N_4 and SiC) with well-defined flaws, and (2) provide information that will be used to relate mechanical properties to nondestructure evaluation (NDE) results obtained in WBS element ANL-1(A). The work will include fabricating specimens of Si_3N_4 and SiC with controlled flaws and measuring their mechanical properties (fracture stress, fracture toughness, and elastic modulus). Subsequently, microstructures of the fracture surface will be evaluated in order to locate the critical flaws. The results of the evaluation of mechanical properties and microstructure will be used together with the results of WBS element ANL-1(A) in a joint effort to correlate fracture behavior with flaws. Information obtained from these studies will help control processing of structural ceramics to improve mechanical properties. Furthermore, correlation of mechanical properties with NDE results will provide additional information that will help verify the ability of NDE to detect failure-initiating flaws. Knowledge of failure-initiating flaws is needed to help better define the flaws to be detected by NDE in WBS element ANL-1(A).

ANL-1(C), "Study of Fracture Stress and Fracture Toughness Behavior of Fiber-Reinforced Ceramic Composites," Argonne National Laboratory. The goal of this project will be to establish acceptable mechanical property evaluation methods for fiber-reinforced composites, with particular emphasis on fracture stress and fracture toughness measurements. Fracture toughness is currently considered a property of major importance for monolithic materials, yet its significance with respect to composites where multiple phases exist has yet to be resolved. The influence of chemical composition, microstructure, and fiber-matrix interaction on these mechanical properties will be investigated.

B&W/ORNL-1(B), "Transfer of CVD Infiltration Technology to Industry," Babcock & Wilcox and Oak Ridge National Laboratory. The purpose of this task is to transfer to industry the technology developed in WBS element ORNL-1(A) for fabricating ceramic fiber—ceramic matrix composites by the chemical vapor deposition (CVD) infiltration process. An agreement has been reached between ORNL and the Babcock and Wilcox Company (B&W) to collaborate in the further development of this technology. Jointly with B&W, ORNL will develop and characterize fiber-reinforced ceramic composites having improved fracture toughness. The development of useful composite materials will require (1) the development of higher density ceramic fiber preforms and (2) rapid, low-cost methods of infiltrating the fibrous preforms with a ceramic matrix. Babcock and Wilcox will develop the higher density ceramic fiber preforms at its Lynchburg, Virginia, facility. With the assistance of a B&W researcher located here part-time, ORNL will infiltrate the preforms by using the CVD process. New CVD apparatus and tooling are developed as part of this joint effort and tested by the B&W assignee at ORNL. The materials investigated include silicon-carbide and aluminum-oxide fibers, and CVD infiltration matrices of silicon carbide and silicon nitride. Oak Ridge National Laboratory will evaluate composite microstructures by using optical microscopy, and B&W will perform additional characterization by measuring the mechanical properties.

GT-1, "Development of Advanced Fiber-Reinforced Ceramics," Georgia Institute of Technology. The purpose of this work is to conduct a theoretical and experimental program to identify new compositions and processing methods to improve the physical and mechanical properties of selected fiber-reinforced ceramics. The ceramic matrix material to be studied in the first year is amorphous "fused" silica or modified silica glass, and the focus will on be the development of fiber-reinforced silica. Parameters to be studied include (1) differences in elastic modulus between matrix and fiber, (2) differences in thermal expansion, (3) nature of interfacial bond, (4) densification of matrix, (5) nature of fiber fracture—pull-out, (6) fiber diameter and fiber length-to-diameter ratio, (7) fiber loading, and (8) fiber dispersion and orientation. In addition, a model based on the information generated in the experimental phase of the program will be developed. Work will also be directed to the improvement of the physical and mechanical properties of sintered and reaction-bonded fiber-reinforced silicon nitride.

GT-1(A), "Modeling of Fibrous Preforms for CVD Infiltration," Georgia Institute of Technology. The purpose of this project is to conduct a theoretical and experimental program to develop an analytical model for the fabrication and infiltration of fibrous preforms. Chemical vapor deposition (CVD) has demonstrated considerable promise as a technique for fabrication of fiber-reinforced ceramic composites. Unidirectional and cloth-reinforced composites of SiC fibers in a SiC matrix have shown good strength and exceptional strain tolerance. However, results have been inconsistent with the fabrication of randomly oriented short-fiber composites. A critical problem has been the inability to consistently fabricate fibrous preforms with both high fiber loading and a permeability suitable for infiltration. A better understanding of the fundamental parameters controlling preform fabrication and CVD infiltration of such preforms is needed to guide further development. The proposed analytical model will (1) predict preform structure (density, porosity, fiber orientation, etc.) based on fabrication technique and fundamental fiber parameters (diameter, aspect ratio, etc.) and (2) predict permeation and heat conduction through the preform structure and, thus, predict the CVD infiltration performance. Initially, the model will be developed for preforms containing only one type of fiber, but extension to mixed fiber and fiber-particle blends is planned.

INEL-1(A), "Nondestructive Evaluation of Advanced Ceramic Composite Materials," Idaho National Engineering Laboratory. The purpose of this project is to develop an effective capability for nondestructive evaluation of ceramic-fiber-reinforced ceramic composites. The response of selected samples of sintered composite materials consisting of SiC fibers in SiC and Si_3N_4 matrices to both ultrasonic and radiographic techniques will be investigated. Experimental techniques and signal processing algorithms will be developed for (1) characterizing acoustic properties and sample morphology, including fiber size and distribution and the degree of bonding of the fibers to the matrix, (2) detecting flaws including cracks, porosity, fiber clusters, and bonding anomalies, and (3) detecting flaws in joints. The NDE techniques developed in this project will result in more effective and extensive use of advanced ceramic composite materials in fossil energy applications.

INEL-1(B), "Joining of Silicon Carbide Reinforced Ceramics," Idaho National Engineering Laboratory. The purpose of this project is to identify and develop techniques for joining composite materials reinforced with silicon carbide fibers. Primary emphasis will be on composite materials with either a silicon nitride or a silicon carbide matrix; lesser emphasis will be placed on silica reinforced with silicon carbide fibers. The work will investigate oxynitride and oxide glass joining materials and joining techniques that promote the devitrification of these materials to produce glass-ceramics and joints that are both strong and tough. Joining of composite matrix materials will be studied, and the resulting information will be applied to the joining of the fiber-reinforced composites. The joining material, surface preparaton, heat treatments, methods of binder application, joining technique, and joint configuration will be considered during joint design and fabrication. Microstructural examination of the joints will be conducted to investigate wetting, microstructure, mass transfer, and process parameter effects. Limited mechanical testing of joints will be conducted. Thermal cycling and service environment scoping tests will be performed for selected composite joints. Practical joining techniques must be developed to fully realize the advantages of ceramic composite materials reinforced with silicon carbide fibers. Successful joining methods will permit the design and use of complex component shapes and the integration of component parts into larger structures.

LANL-1, "Short Fiber Reinforced Structural Ceramics," Los Alamos National Laboratory. The purpose of this project is to investigate the utility of whisker reinforcement technology for producing structural ceramic composites of improved strength and fracture toughness. The project consists of two technical tasks. The first is to optimize a whisker growth process to produce alpha-phase silicon nitride (α-Si_3N_4) whiskers and beta-phase silicon carbide (β-SiC) whiskers of uniform size and optimum strength and in quantities suitable for composite use. The second task will involve determining the contribution of the whiskers to fracture strength and toughness in selected ceramic-matrix composites.

NBS-1, "High-Temperature Applications of Structural Ceramics," National Bureau of Standards. The objective of this study is to characterize the high-temperature failure mechanisms and factors that influence their operation with an aim toward improving the mechanical properties of structural ceramics, especially materials based on silicon carbide and silicon nitride, for coal conversion applications. This project consists of four tasks: (1) High-Temperature Fracture of Structural Ceramics, (2) Crack Growth Mechanism Maps, (3) Microstructure and Phase Alteration, and (4) Microstructure and Fracture in Reactive Environments.

ORNL-1(A), "Fabrication of Fiber-Reinforced Composites by CVD Infiltration," Oak Ridge National Laboratory. The purpose of this task is to develop a ceramic composite having high fracture resistance and strength yet retaining the typical ceramic attributes of refractoriness and high resistance to abrasion and corrosion. The desired fracture toughness and strength are on the order of 20 $MPa \cdot m^{1/2}$ and 500 MPa, respectively. In addition, a practical process capable of fabricating simple or complex shapes is desired. The ceramic fiber—ceramic matrix composites are fabricated by infiltrating low-density fiber structures with gases, which deposit as solid phases on and between the fibers to form the matrix of the composite. The goal is to demonstrate that a ceramic composite can be prepared by using materials of high interest to the fossil energy community. Our earlier assessment identified SiC fibers and matrices of SiC and Si_3N_4 as being most promising. Fiber dimensions, geometry, packing density, binder type and concentrations, and other processing variables are evaluated experimentally.

Initial experimental efforts focused on the use of a vacuum-forming molding process to form a low-density fiber bed suitable for gas infiltration. Once the fiber bed was formed, dried, and heat treated, the matrix of the composite was formed by CVD in a high-temperature furnace. A novel scheme (patent applied for) of forcing the coating gases to flow *through* the fiber bed was tested in an attempt to increase the deposition rate over rates normally obtained when the deposition gases flow across the surface to be coated. In addition, depending on the deposition reaction, a vacuum may or may not be used to assist the flow of gases through the fibrous parts. Important variables of the CVD process, such as temperature, gas composition, flow rate, and pressure, are systematically altered to maximize matrix density and to obtain a microstructure consistent with the goal of fabrication of high-toughness, high-strength ceramic composites.

The room temperature flexure strength and the stress-strain curve are currently determined in four-point flexure. The notched beam technique is used to measure the fracture toughness of the composite. However, the strength and fracture toughness values determined by these techniques may not be valid for fibrous composites, and other measurement techniques are being explored. Direct tensile measurements are being evaluated for these composites.

ORNL-1(C), "Development of Ceramic Fiber—Ceramic Matrix Filters for Hot-Gas Cleanup in Fossil Energy Systems," Oak Ridge National Laboratory. The purpose of this project is to develop a ceramic fiber—ceramic matrix composite that will be suitable as a high-temperature particulate filter for use in hot-gas cleanup systems. The goal is to produce a composite that has the requisite strength and toughness, but that also has sufficient porosity to be permeable to the gas stream and has the required size and distribution of porosity to be an effective filter. A practical process for fabricating porous ceramic fiber—ceramic matrix filter materials in both disk and cylindrical shapes will be developed.

UKCRE-1, "Investigation of the Mechanisms of Failure of Ceramic Materials for Hot Gas Filtration," United Kingdom Coal Research Establishment. High-temperature ceramic filters used for removing particulates from gas streams have been under evaluation at the United Kingdom

Coal Research Establishment (UKCRE). These filters, also called "candles," have been tested at 950°C in gasification atmospheres. Cracks at the point of attachment to the manifold have not only been a drawback to the application of this specific ceramic design, they represent a phenomenon generic to most rigid ceramic filters. No detailed phenomenological explanation of the failure has been determined. This task is a cooperative project of the DOE AR&TD Fossil Energy Materials Program and the UKCRE to develop an understanding of the mechanisms of failure of ceramic hot-gas filtration materials and, thereby, provide a basis for material and system improvements.

SC(I)-1, "Assessment of the Causes of Failure of Ceramic Filters for Hot-Gas Cleanup in Fossil Energy Systems and Determination of Materials Research and Development Needs," contractor to be determined. The purpose of this project is to determine the principal causes of failure of ceramic filters used for removal of fine particulates from high-temperature, high-pressure gas streams in coal conversion and utilization systems such as fluidized-bed combustors, direct coal-fired gas turbines, and coal gasification systems. As part of this project, the current practice for design and engineering of ceramic filters will be researched, and the current use for such filters in industrial and utility applications similar to those in the fossil energy systems listed above will be described. Materials failure experience will be examined, and causes of failure of ceramic filters will be determined through conversations with manufacturers and users and through laboratory failure analyses. Materials research and development that would improve the reliability of these filters, and design features of current filters that contribute to materials failure, will be identified.

SC(I,U)-1, "Structural Ceramics Densification Study," contractor to be determined. This work, to commence in FY 1988, will focus on techniques to fabricate powders into dense monolithic ceramics and ceramic-matrix composites with controlled microstructure. The emphasis of the work will be on practical methods to produce reliable ceramics such as heat exchanger tubes.

SC(U)-1(A), "Investigation of the Mechanical Properties of CVD Infiltrated Ceramic Composite Tubular Components," contractor to be determined. The purpose of this project is to develop an understanding of the long-term performance of CVD infiltrated ceramic composite components with the use of comprehensive mechanical properties tests of composite components such as tubes, plates, shells, and beams subjected to static and cyclic multiaxial loading at elevated temperatures over various time periods.

SC(U)-1(B), "Advanced Concepts in Design with Brittle Materials," contractor to be determined. This new task, beginning in FY 1988, will apply a combination of finite-element stress analyses and statistical descriptions of fracture strength to the design of structural ceramic components for fossil energy systems, such as heat exchanger and heat engine components. Design methodologies for typical components will be developed and demonstrated.

PNL-1, "Oxide Electrodes for High-Temperature Fuel Cells," Pacific Northwest Laboratory. The objective of this research is to find and develop highly electronically conducting oxides for use as cathodes in solid oxide fuel cells (SOFCs). Specifically, the work involves determining the effects of rare earth (RE) and indium oxide additions on the electrical transport properties of $HfO_2(ZrO_2)$-RE_xO_y-In_2O_3. In addition, the study will develop an understanding of the crystallographic, microstructural, and phase equilibrium factors that influence the above properties. The compositions of the $HfO_2(ZrO_2)$-RE_xO_y-In_2O_3 are varied, and the electrical properties are measured relative to the phase equilibrium and crystallo-graphic structures to determine the RE and In_2O_3 combinations that provide the highest electronic conductivity. The electronic conductivity, transference numbers, and Seebeck coefficient are measured as functions of temperature and oxygen partial pressure. An important part of this investigation involves the study of the stability of a particular oxide in the environments and temperature ranges of SOFC fabrication and operation as well as the compatibility of the oxide electrode with the other cell components. This latter criterion includes both chemical compatibility and relative thermal expansion coefficients.

Table III.1. Research projects for structural ceramics

Research project	Performing organization	Funding (thousands of dollars)[a]				
		FY 1986	FY 1987	FY 1988	FY 1989	FY 1990
ANL-1(A) — Development of Nondestructive Evaluation Techniques for Structural Ceramics	Argonne National Laboratory (ANL)	205	205	205	205	205
ANL-1(B) — Effect of Flaws on the Fracture Behavior of Structural Ceramics	ANL	135	135	150	150	150
ANL-1(C) — Study of Fracture Stress and Fracture Toughness Behavior of Fiber-Reinforced Ceramic Composites	ANL	0	0	90	120	150
B&W/ORNL-1(B) — Transfer of CVD Infiltration Technology to Industry	Babcock & Wilcox/Oak Ridge National Laboratory (B&W/ORNL)	100	100	0	0	0
GT-1 — Development of Advanced Fiber-Reinforced Ceramics	Georgia Institute of Technology (GT)	160	160	150	100	100
GT-1(A) — Modeling of Fibrous Preforms for CVD Infiltration	GT	40	0	0	0	0
INEL-1(A) — Nondestructive Evaluation of Advanced Ceramic Composite Materials	Idaho National Engineering Laboratory (INEL)	[b]	246	255	255	255
INEL-1(B) — Joining of Silicon Carbide Reinforced Ceramics	INEL	[b]	245	255	255	255
LANL-1 — Short Fiber Reinforced Structural Ceramics	Los Alamos National Laboratory (LANL)	250	250	250	250	250

Table III.1. (continued)

Research project	Performing organization	Funding (thousands of dollars)[a]				
		FY 1986	FY 1987	FY 1988	FY 1989	FY 1990
NBS-1 — High-Temperature Applications of Structural Ceramics	National Bureau of Standards (NBS)	240	240	250	250	250
ORNL-1(A) — Fabrication of Fiber-Reinforced Composites by CVD Infiltration	Oak Ridge National Laboratory (ORNL)	324	200	200	200	200
ORNL-1(C) — Development of Ceramic Fiber-Ceramic Matrix Filters for Hot Gas Cleanup in Fossil Energy Systems	ORNL	0	125	225	225	225
UKCRE-1 — Investigation of the Mechanisms of Failure of Ceramic Materials for Hot Gas Filtration	United Kingdom Coal Research Establishment (UKCRE)	[c]	0	0	0	0
SC(I)-1 — Assessment of the Causes of Failure of Ceramic Filters for Hot Gas Cleanup in Fossil Energy Systems and Determination of Materials Research and Development Needs	To be determined (TBD)	56	0	0	0	0
SC(I,U)-1 — Structural Ceramics Densification Study	TBD	0	0	200	200	200
SC(U)-1(A) — Investigation of the Mechanical Properties of CVD Infiltrated Ceramic Composite Tubular Components	TBD	140	200	200	200	200

Table III.1. (continued)

Research project	Performing organization	Funding (thousands of dollars)[a]				
		FY 1986	FY 1987	FY 1988	FY 1989	FY 1990
SC(U)-1(B) — Advanced Concepts in Design with Brittle Materials	TBD	0	0	120	120	120
PNL-1 — Oxide Electrodes for High-Temperature Fuel Cells	Pacific Northwest Laboratory (PNL)	200	200	200	200	200

[a] Entries for FY 1987 through FY 1990 are perceived funding needs rather than program guidance.

[b] Prefunded in FY 1985.

[c] Carryover funds from FY 1985.

2. ALLOY DEVELOPMENT AND MECHANICAL PROPERTIES

2.1 RESEARCH OBJECTIVES

The objective of research in this thrust area is to understand the chemical and physical metallurgy that affects the high-temperature mechanical properties, as well as welding and joining, of high-temperature alloys used as structural materials in coal conversion and utilization systems. Work in this area will include studies of mechanical properties, weldability and fabricability of materials ranging from advanced austenitic steels to ordered intermetallic alloys. The research in this area will provide the needed background for the development of high-strength, structural alloys for high-temperature applications in coal gasification and coal combustion systems. This area also includes projects near completion on pressure vessel materials for coal liquefaction applications.

Research projects are described in the following section and are listed in Table III.2 at the end of the section. As was noted above, and as will be obvious from the following descriptions, the emphasis in previous years on pressure vessel materials will be replaced by emphasis on high-temperature structural alloys for wider applications.

2.2 SUMMARIES OF CURRENT AND PLANNED RESEARCH

2.2.1 Pressure Vessel Materials

CU-2(A), "Hydrogen Attack in Cr-Mo Steels at Elevated Temperatures," Cornell University. This was the only in-situ hydrogen attack work supported by the AR&TD Fossil Energy Materials Program. All other programs that address hydrogen attack involve autoclave exposure followed by an evaluation. This work on the effect of constant stress and pressure on the nucleation and growth of methane bubbles in low-alloy steels was completed in early FY 1986. Models based on experimental observations were developed to describe hydrogen attack in 2.25Cr-1Mo steel, and the important metallurgical parameters were identified. Experiments were conducted on modified low-alloy steels, including those steels developed by the University of California at Berkeley on an AR&TD Fossil Energy Materials Program project completed in FY 1985.

PNST-2, "Three-Dimensional Residual Stress Characterization of Thick Plate Weldments with Advanced Instrumentation and Methodologies," Pennsylvania State University. This project is designed (1) to continue and expand previous work at Pennsylvania State University, (2) to involve the characterization of the three-dimensional residual stress field in an approximately 30-cm-thick (12-in.) V-groove weldment of 2.25Cr-1Mo steel, and (3) to evaluate various postweld heat treatment techniques and schedules proposed for the fabrication of large pressure vessels. This study is expected to provide the most accurate and detailed experimental residual stress analysis of large weldments to date and the needed information for accurate fracture mechanical calculation and finite-element modeling for these weldments.

UCB-2, "Study of Damage Mechanisms in Coal Conversion Atmospheres Affecting the Fatigue and Creep Rupture Properties of Cr-Mo Steels," University of California, Berkeley. The purpose of this project is to evaluate the effects of high-temperature service in adverse environments on the metallurgical properties (particularly on fatigue crack propagation and creep rupture properties) of weld metal and heat-affected zone (HAZ) regions in thick-section weldments of 3Cr-Mo steels. The overall objective is to develop techniques for modifying the microstructures (in the HAZ and base plate) resulting from welding in order to provide adequate resistance to environmentally induced damage while at the same time maintaining other desired mechanical properties.

Microstructures in the base metal, HAZ, and weld will be fully characterized in terms of microconstituents and phases. Damage in the form of microcavities or methane bubbles, situated in areas expected to be high-damage areas resulting from extended environmental exposure (e.g., to high-pressure, high-temperature hydrogen) and from welding, will be introduced. Fatigue crack growth characterization studies of weldments will be carried out to determine the influence of metallurgical features and environment on the fatigue crack growth rate from near-threshold to near-instability. Creep rupture testing will be done in order to investigate the influence of damage mechanisms in weldments that are time dependent in their effect on microstructure/mechanical property relationships.

UCSB-2, "Analysis of Hydrogen Attack on Pressure Vessel Steels," University of California, Santa Barbara. The initial objectives of this program have been achieved, and physical models that describe the initiation and development of methane damage in carbon steel, C-Mn-Si steels, 2.25Cr-1Mo steel, and weldments have been developed. Nelson diagrams have been predicted and appear to be reasonably consistent with available data. Additional work is needed to refine the analyses and to confirm the adequacy of the basic thermodynamic information available in the literature. The model has been particularly useful in establishing the relative importance of microconstituents, deformation mechanisms, and fracture mechanisms to the hydrogen attack process. In this sense it will guide the development of modified low-alloy steels for optimum resistance to hydrogen attack. In FY 1985 significant progress was made in examining the role that stress and plastic strain transients play in the hydrogen attack phenomena. Such information is vital because the current design rules for hydrogen service restrict the use of Nelson curves to situations in which the stresses do not exceed the primary stress intensities provided in the *ASME Boiler and Pressure Vessel Code*.

UTN-2, "Transformation, Metallurgical Response, and Behavior of the Weld Fusion Zone and HAZ in Cr-Mo Steels," University of Tennessee. Continuous cooling transformation diagrams were developed for several chromium-molybdenum alloys. The heat-affected zone (HAZ) and autogenously welded fusion zone microstructures of gas tungsten arc (GTA) welds were metallurgically characterized. The cold cracking tendency of the weld and HAZ regions are being determined as well as the effect of postweld heat treatment on the HAZ properties, microstructure, and cracking tendencies. Some weldments will be creep-rupture tested. Materials include 2.25Cr-1Mo, 3Cr-1.5Mo-V, and 9Cr-1Mo-V-Nb steels.

WEC-2(A), "Evaluation of 3Cr-1.5Mo Steel in a Simulated Coal Conversion Environment," Westinghouse Electric Corporation. The purpose of this work is to develop a fracture mechanics characterization of candidate materials for coal gasification pressure vessels. The apparatus to be used for the fracture characterization has unique capabilities for in-situ testing of steels in high-pressure high-temperature H_2-H_2S environments. The study will be complemented by a physical metallurgical evaluation of the various degradation processes observed in the basic characterization. This effort will focus primarily on the simulated environmental properties of a candidate material (3Cr-1.5Mo-V steel) to be used in pressure vessel construction for coal gasification processes. The environments and conditions to which the steel will be exposed are (1) a mixture of gases including H_2 and about 1% max H_2S and (2) 10.4 MPa pressure at 315°C. This is a laboratory simulation of the coal gasification environment, which, in addition, includes $CO-CO_2$ and H_2-H_2O. Because the selected steel will ultimately be welded, the following metallurgical considerations must also be evaluated: (1) weldability of the base metal, (2) weld metal composition, and (3) heat-affected zone (HAZ). Thus, it will eventually be necessary to test both the weld metal and the HAZ, as well as the base metal, to ensure reliability. The current work includes the base plate metal only.

WEC-2(B), "Investigation of the Correlation of Carbide Size and Percentage with Mechanical Properties of High-Strength Low-Alloy Steels," Westinghouse Electric Corporation. The purpose of this project is to examine the correlation between the size and percentage of carbides in high-strength low-alloy steels with the mechanical properties. Carbides from a set of at least 20 high-strength Cr-Mo steels will be analyzed by scanning transmission electron microscopy to determine the size, percentage, and type of carbides as a function of composition and tempering parameter. A model developed for characterization of the carbides will be used to develop correlations of composition and heat treatment with the following properties: (1) shift in the 54-J Charpy-V transition temperature due to temper embrittlement, (2) room-temperature yield strength and ultimate strength, (3) room-temperature Charpy-V impact energy, and (4) crack arrest threshold stress intensity.

SC(U)-2(A), "Modeling of Residual Stresses in Thick-Section Steel and Weldments," contractor to be determined. This work, to begin in FY 1988, involves the development of techniques to measure residual stresses and to develop finite-element models to describe the residual stresses present in large weldments. Also, techniques will be developed to measure metallurgical changes in structures. The eventual goal will be to provide methods for evaluating the fitness of a vessel for continued service after inspection, repair, or modification.

2.2.2 Superheater and Reheater Materials

CE-2, "Production of Test Heats of Candidate Alloys for Superheaters and Reheaters for Advanced Steam Cycles," Combustion Engineering, Inc. This task will involve the production of test heats (up to 40 compositions) of alloys developed or selected by ORNL for evaluation as superheater and reheater materials. Standard melting practices or modifications thereof based on the requirements of the particular alloys will be used. The test ingots will be shipped to ORNL for evaluation.

CU-2, "Mechanical Properties and Microstructural Stability of Advanced Steam Cycle Materials," Cornell University. The purpose of this project is to rank the strengths and metallurgical stabilities of advanced steam cycle superheater alloys at temperatures ranging from 650 to 760°C. Mechanical testing of the steels consists of relaxation experiments (~24 h duration each) that cover stresses producing deformation rates from about 10^{-3} to 10^{-9}/sec. The precipitate or dislocation microstructure of the steels in the grain boundary and matrix regions is being studied to determine the role of strain-time history on the stability of the microstructure. The relaxation data will be correlated with constant-load creep data provided by Oak Ridge National Laboratory [ORNL-2(C)] and analyzed in terms of deformation mechanisms to determine relative contributions of grain boundary and matrix deformations. The most promising alloys from the screening test will be included in relaxation tests at 700°C to determine optimum heat treatments for strength and metallurgical stability.

HEDL-2, "Application of Coatings to Candidate Superheater Alloys by the Electrospark Deposition Coating Process," Hanford Engineering Development Laboratory. The purpose of this task is to examine the use of the electrospark deposition coating process for the application of corrosion-resistant coatings to candidate superheater alloys. As coating materials are identified [SC(I)-2(C)] and tested [SC(I,U)-2(B)], the use of electrospark deposition as an application technique for these coatings will be investigated.

ORNL-2(B), "Development and Microstructural Evaluation of Advanced Austenitic Alloys," Oak Ridge National Laboratory. Alloys based on modifications to four groups of alloys will be developed on the basis of attributes required for advanced steam cycle superheater service. The four alloy groups to be studied include modified type 316 stainless steel, modified type 310 stainless steel, modified high nickel (alloy 800H) steels, and aluminum-containing steels. The bases for the alloy design include long-term strength and stability. Strength will be developed by control of chemical composition, and stability will be assured by suppression of intermetallic and other embrittling phases by the addition of elements that promote austenitic stabilization. Added strength will be achieved through the precipitation of fine carbides, nitrides, or phosphides that stabilize dislocation networks, prevent grain boundary migration, and resist coarsening during long service under constant and varying load conditions. Metallurgical tools used in these studies will include optical microscopy, electron microscopy, and microhardness measurements.

ORNL-2(C), "Evaluation of Mechanical Properties of Advanced Austenitic Alloys," Oak Ridge National Laboratory. Creep-rupture data on alloys developed in ORNL-2(B) will be gathered in the temperature range 600 to 760°C for times from 10 to 10,000 h. The effects of mechanical and thermal cycles will be examined, and results from testing will be used to establish cumulative damage models. Multiaxial stress testing, notched-bar stress-rupture testing, and creep crack-growth testing will be undertaken for constant and variable load conditions to verify cumulative damage models.

ORNL-2(D), "Weldability Studies of Advanced Austenitic Alloys," Oak Ridge National Laboratory. Evaluation of the weldability of the alloys developed in ORNL-2(B) will include a specialized technique on a device called a Sigmajig, which evaluates the hot cracking tendency of the weldments. Ranking of alloys is by the extent of cracking as a function of applied load and plate thickness. Weldments in the alloys produced as tubing will be evaluated against requirements of the ASME BPV Code Sections I and IX, which involve bend testing, tensile testing, and metallography. Additional evaluation will be based on varestraint and circular groove tests. Other tests not required by the Code may be identified during the course of this work, and those tests will be included as appropriate. The development of a suitable filler metal is an important part of this work. ORNL will work with university and industrial subcontractors [SC(I,U)-2(D)] in this development.

UI-2, "Development of a Design Methodology for High-Temperature Cyclic Application of Materials which Experience Cyclic Softening," University of Illinois. The objective of this project is to develop a design methodology for high-temperature cyclic conditions, taking into account the effects of strain softening. Since the problem of cyclic softening is generic to a wide class of medium- to high-strength low alloy steels, it is not the main purpose of this investigation to examine specific characteristics of any one steel but to investigate the general behavior of components subject to the cyclic softening phenomenon.

The specific objectives of the project are: (1) the development of simplified methods of component analysis to evaluate overall and local effects of cyclic softening on time-dependent deformations, (2) the development of an improved understanding of the mechanisms of interaction between intermittent cyclic stresses and reduction of resistance to creep deformation, (3) an evaluation of the possible effects of cyclic softening on the initiation and propagation of defects, (4) an evaluation of the possible effects of cyclic softening on the procedure for determining allowable design stresses for high-temperature design, and (5) provision of input into the material effort to extend life in existing power plants by examining the relation between material damage parameters and component performance criteria, for possible use in remnant life assessment.

SC(I)-2(A), "Production of Small Heats of Tubing," contractor to be determined. Based on the production and evaluation of the initial candidate alloys in ORNL-2(B), -2(C), and -2(D), the number of compositions will be reduced to sixteen in the four alloy groups. These alloys will be produced as small heats and will be formed into tubular shapes for evaluation. These tubes will be submitted to ORNL and will be evaluated for mechanical properties and phase stability. Surface protection methods for fireside and steamside corrosion will also be investigated.

SC(I)-2(B), "Production of Full-Size Tubing of Candidate Alloys," contractor to be determined. On the basis of evaluation of the small heats of tubing in SC(I)-2(A), the number of candidate alloys will be reduced to four alloys in two alloy groups. An industrial subcontractor will be selected to produce tubing by current commercial techniques. This tubing will also be delivered to ORNL and evaluated for the advanced steam cycle application.

SC(I)-2(C), "Surface Treatments of Tubing for Fireside Corrosion Protection," contractor to be determined. Selected surface treatments, developed for the candidate alloys in this project, will be tested in the project SC(I,U)-2(B) to determine their ability to provide resistance to corrosion on the steamside and in the fireside environment of advanced steam cycle systems. Alternative techniques including coatings (e.g., chromizing), claddings, and coextrusions will be investigated and demonstrated.

SC(I)-2(D), "Effect of Microalloying Additions on High-Temperature Strength of Candidate Alloys for Advanced Steam Cycle Superheaters and Reheaters," contractor to be determined. This project will be directed to understanding the performance (and thus the effect of microalloying additions) of advanced austenitic alloys under temperature and load cycling conditions that could be experienced in advanced steam cycle superheaters and reheaters. This project will be complementary to ORNL-2(C), but it will extend the range of testing to conditions more representative of actual steam cycles. Multiaxial stress testing, bend testing, creep testing, and crack initiation and growth testing will be performed. Data from these tests will be used in project ORNL-2(C) to further verify the cumulative damage models.

SC(I,U)-2(B), "Fireside Corrosion Tests of Candidate Superheater Tube Alloys, Coatings, and Claddings," contractor to be determined. Molten coal ash corrosion is probably the most critical materials concern for superheaters and reheaters in the advanced steam cycle plants. Laboratory tests of candidate alloys (with coatings and claddings) in environments that simulate the fireside environment of superheater and reheater tubes will be conducted. Tests of the superior candidate alloys may also be conducted in operating units or test furnaces. Our approach will be to fund this activity as a supplemental part of the Electric Power Research Institute (EPRI) Phase 1 test program, which will be conducted at lower temperatures. We anticipate a usual metal temperature of about 700°C whereas the EPRI Phase 1 program would involve usual metal temperatures of about 590°C.

SC(I,U)-2(C), "Steamside Corrosion Tests of Candidate Superheater Tube Alloys," contractor to be determined. Steam corrosion of superheater tubes in the advanced steam cycle systems is a critical problem because of the more rapid formation of scale at the higher temperatures. Exfoliation of the scale is the principal concern because of the damage to turbines that can result due to erosion. This project will involve laboratory tests of the candidate alloys and coating materials in the steam environment. This project, as well as project SC(I,U)-2(B), will provide information for the investigation of surface treatment techniques [SC(I)-2(C)].

SC(I,U)-2(D), "Joining Techniques for Candidate Alloys for Superheaters and Reheaters for Advanced Steam Cycles," contractor to be determined. The complete development of alloys for advanced steam cycle superheaters and reheaters will include the development of reliable filler metals and welding techniques, as well as the establishment of appropriate welding parameters. We will initiate a collaborative industry-university project in FY 1987 to develop these joining techniques.

2.2.3 Aluminides

CSM-2, "Investigation of the Weldability of Ductile Aluminides," Colorado School of Mines. The purpose of this project is to study the weldability of nickel-iron aluminides. The major thrust of the project is to determine the role of microstructure in the intergranular cracking of aluminides, with special emphasis on weld cracking susceptibility. This project is a cooperative effort of Oak Ridge National Laboratory (ORNL) and Colorado School of Mines (CSM) and will be conducted as a PhD thesis project by a CSM student working at CSM and at ORNL.

INEL-2(A), "Consolidation of Rapidly Solidified Aluminide Metal Powders," Idaho National Engineering Laboratory. The purpose of this project is to determine the most effective means of, and associated parameters for, consolidating rapidly solidified nickel-iron aluminide powders. Three consolidation techniques will be explored for the rapid solidification process (RSP) powders: hot extrusion (baseline), hot isostatic pressing (HIP), and dynamic (i.e., explosive) methods. The investigation of these consolidation techniques will emphasize the influence of pressure, temperature, and time on RSP structures. Structure/property assessments will be performed on the consolidated materials. In particular, thermal stability, mechanical properties, and oxidation response will be determined. The RSP aluminide powders and extrusions will be obtained from outside sources. Limited atomization investigations will be performed at the

Idaho National Engineering Laboratory to assess RSP parameters for the aluminide powders. Compositions of the aluminide powders will be based on Oak Ridge National Laboratory's assessment and initially will involve Ni-80, Fe-10, Al-10, B-0.02 (all in wt %), with and without microalloying additions, e.g., hafnium.

INEL-2(B), "Joining of Advanced Aluminides," Idaho National Engineering Laboratory. The objective of this project is to investigate weldability problems limiting the use of aluminides in welded structures. This includes weldability effects of minor alloying elements, process and process variable effects, solidification mechanics, filler material development, and extension to heavier sections.

ORNL-2(A), "Development of Iron and Nickel Aluminides," Oak Ridge National Laboratory. New improved alloys are needed for high-temperature components in severe environments for applications such as coal-fired gas turbines or diesel engines, fluidized bed combustors, coal gasification systems, and fuel cells. The purpose of this task is to design and test materials that will possess good mechanical properties at elevated temperatures and that will develop protective Al_2O_3 layers to prevent sulfidation attack. Aluminides based on the pseudobinary systems Ni_3Al-Fe_3Al and NiAl-FeAl will form the basis for development of materials with the required properties. Success in development of iron and nickel aluminides as structural materials could substantially improve the performance and reliability of advanced fossil energy systems.

The development of iron and nickel aluminides for critical components in coal combustion and conversion systems is based on determining phase relationships and understanding the structure-property relationships that determine the oxidation-sulfidation behavior, the mechanical properties, and the fabricability and weldability of the alloys. This requires a knowledge of the physical metallurgy of the alloy systems involved as well as the source of the grain-boundary embrittlement and the oxide/sulfide formation. Compositional control by macro- and microalloying and microstructural control by processing treatments will be used to optimize the desirable properties.

The initial approach of this task is to develop aluminides based on the pseudobinary system Ni_3Al-Fe_3Al. Iron will be macroalloyed to Ni_3Al

for solid solution hardening at elevated temperatures and for corrosion resistance in sulfidizing environments. Boron and other elements will be employed for controlling the chemistry and cohesion of grain boundaries. The development of aluminides will also be extended to the FeAl-NiAl system, which contains 50 at. % Al for better oxidation and corrosion resistance.

Welding studies will concentrate in two areas: evaluating weldability and developing an understanding of the factors controlling weldability. Part of the goal of this project will be to assess the effects of alloy composition and welding process variables on weldability by using both the electron-beam and gas-tungsten-arc processes to make autogeneous welds. This work will be done mainly with thin sheet material (typically 0.7 mm thick), but thicker material will also be used when available.

The more basic work will be subdivided into microstructural characterization and high temperature mechanical testing. The microstructural work will be aimed at characterizing fusion zone microstructures in terms of phase identification, distribution, and composition as well as microsegregation behavior. The high temperature mechanical testing will be used to determine the ductility and strength of alloys as a function of temperature. This information will be used to help evaluate weldability and fabricability and to help identify factors controlling cracking phenomena in aluminides. An attempt will also be made to incorporate a computer model of thermal stress analysis into this work.

SC(U)-2(B), "Joining Techniques for Iron-Nickel Aluminides," contractor to be determined. This university project will be initiated in FY 1987 and will be directed to the development of reliable joining techniques for the iron-nickel aluminides. It will draw on the information developed in WBS element CSM-2, which is an investigation of the weldability of ductile aluminides. We expect this project to lead to reliable welding methods with specified welding parameters appropriate for selected iron-nickel aluminides.

2.2.4 New Techniques

RDA-2, "Evaluation of the Feasibility of Pressure Quenching to Produce Hard Metastable Materials," R&D Associates, Inc. The purpose of this work is to design, build, and test a novel high-pressure press system to explore the scientific possibilities of pressure quenching of materials, that is, the retention at ambient conditions of metastable material phases normally observed only under extremely high pressures. The device will be capable of exerting pressures up to 6 GPa on small specimens of solids at room temperature and of releasing the pressure so rapidly (about 10 μs or less) that the high-pressure phases will be retained. It is anticipated that new materials will result from specific experiments on selected materials undertaken to demonstrate the capability of producing such materials.

Table III.2. Research projects for alloy development and mechanical properties

Research project	Performing organization	Funding (thousands of dollars)[a]				
		FY 1986	FY 1987	FY 1988	FY 1989	FY 1990
	Pressure vessel materials					
CU-2(A) — Hydrogen Attack in Cr-Mo Steels at Elevated Temperatures	Cornell University (CU)	[b]	0	0	0	0
PNST-2 — Three-Dimensional Residual Stress Characterization of Thick Plate Weldments with Advanced Instrumentation and Methodologies	Pennsylvania State University (PNST)	[b]	0	0	0	0
UCB-2 — Study of Damage Mechanisms in Coal Conversion Atmospheres Affecting the Fatigue and Creep Rupture Properties of Cr-Mo Steels	University of California (UCB)	150	0	0	0	0
UCSB-2 — Analysis of Hydrogen Attack on Pressure Vessel Steels	University of California, Santa Barbara (UCSB)	95	0	0	0	0
UTN-2 — Transformation, Metallurgical Response, and Behavior of the Weld Fusion Zone and HAZ in Cr-Mo Steels	University of Tennessee (UTN)	100	0	0	0	0
WEC-2(A) — Evaluation of 3 Cr-1.5 Mo Steel in a Simulated Coal Conversion Environment	Westinghouse Electric Corporation (WEC)	[b]	0	0	0	0
WEC-2(B) — Investigation of the Correlation of Carbide Size and Percentage with Mechanical Properties of High-Strength Low-Alloy Steels		[b]	0	0	0	0

Table III.2. (continued)

Research project	Performing organization	Funding (thousands of dollars)[a]				
		FY 1986	FY 1987	FY 1988	FY 1989	FY 1990
SC(U)-2(A) — Modeling of Residual Stresses in Thick-Section Steel and Weldments	To be determined (TBD)	0	0	135	135	135
	Superheater and reheater materials					
CE-2 — Production of Test Heats of Candidate Alloys for Superheaters and Reheaters for Advanced Steam Cycles	Combustion Engineering (CE)	40	0	0	0	0
CU-2 — Mechanical Properties and Microstructural Stability of Advanced Steam Cycle Materials	CU	140	140	140	0	0
HEDL-2 — Application of Coatings to Candidate Superheater Alloys by the Electrospark Deposition Coating Process	Hanford Engineering Development Laboratory (HEDL)	50	0	0	0	0
ORNL-2(B) — Development and Microstructural Evaluation of Advanced Austenitic Alloys	ORNL	90	110	115	75	50
ORNL-2(C) — Evaluation of Mechanical Properties of Advanced Austenitic Alloys	ORNL	90	130	130	150	160
ORNL-2(D) — Weldability Studies of Advanced Austenitic Alloys	ORNL	60	110	130	150	160

Table III.2. (continued)

Research project	Performing organization	Funding (thousands of dollars)[a]				
		FY 1986	FY 1987	FY 1988	FY 1989	FY 1990
UI-2 — Development of a Design Methodology for High Temperature Cyclic Application of Materials which Experience Cyclic Softening	University of Illinois (UI)	100	100	125	125	100
SC(I)-2(A) — Production of Small Heats of Tubing	TBD	120	150	0	0	0
SC(I)-2(B) — Production of Full-Size Tubing of Candidate Alloys	TBD	0	150	150	150	150
SC(I)-2(C) — Surface Treatments of Tubing for Fireside Corrosion Protection	TBD	0	250	250	250	250
SC(I)-2(D) — Effect of Microalloying Additions on High-Temperature Strength of Candidate Alloys for Advanced Steam Cycle Superheaters and Reheaters	TBD	150	300	300	300	300
SC(I,U)-2(B) — Fireside Corrosion Tests of Candidate Superheater Tube Alloys, Coatings, and Claddings	TBD	90	200	250	275	275
SC(I,U)-2(C) — Steamside Corrosion Tests of Candidate Superheater Tube Alloys	TBD	0	200	200	200	200

Table III.2. (continued)

Research project	Performing organization	Funding (thousands of dollars)[a]				
		FY 1986	FY 1987	FY 1988	FY 1989	FY 1990
SC(I,U)-2(D) — Joining Techniques for Candidate Alloys for Superheater and Reheater Materials for Advanced Steam Cycle	TBD	0	150	200	200	200
	Aluminides					
CSM-2 — Investigation of the Weldability of Ductile Aluminides	Colorado School of Mines (CSM)	50	50	50	50	0
INEL-2(A) — Consolidation of Rapidly Solidified Aluminide Metal Powders	Idaho National Engineering Laboratory (INEL)	[c]	246	255	255	255
INEL-2(B) — Joining of Advanced Aluminides	INEL	[c]	246	255	255	255
ORNL-2(A) — Development of Iron and Nickel Aluminides	ORNL	140	170	195	200	200
SC(U)-2(B) — Joining Techniques for Iron-Nickel Aluminides	TBD	0	150	200	200	200
	New techniques					
RDA-2 — Evaluation of the Feasibility of Pressure Quenching to Produce Hard Metastable Materials	R&D Associates, Inc. (RDA)	[b]	0	0	0	0

[a] Entries for FY 1987 through FY 1990 are perceived funding needs rather than program guidance.

[b] Carryover funds from FY 1985.

[c] Prefunded in FY 1985.

3. CORROSION AND EROSION OF ALLOYS AND REFRACTORIES

3.1 RESEARCH OBJECTIVES

Because of the mineral ash, sulfur, and chlorine content of coal, the heat exchanger and heat recovery components in coal utilization and coal conversion systems are subject to severe corrosion. These components include syngas coolers in coal gasification systems, superheaters and reheaters in pulverized-coal boilers, superheaters in industrial coal-fired boilers, heat exchangers in fluidized-bed combustors, and heat exchangers in hot-gas cleanup systems or steam-bottoming cycles associated with direct coal-fired heat engines.

Since sulfide scales are not protective in the environments of interest, the alloys used in heat exchangers in coal utilization and coal conversion systems depend on the formation of oxide scales to provide protection against catastrophic corrosion by oxygen or sulfur-bearing gases. In the temperature range of interest, only Al_2O_3 and Cr_2O_3 scales provide significant protection. However, even in alloys that initially form protective Al_2O_3 or Cr_2O_3 scales, the scale eventually breaks down as a result of penetration of sulfur, chlorine, or cation species through the scale, cracking of the scale due to thermal or mechanical (including growth) stresses, loss of adhesion of the scale to the substrate, or a combination of those mechanisms.

The purpose of this thrust area is to provide a generic development plan to understand the key factors that affect nucleation and growth of protective oxide scales and the mechanisms by which the scales degrade in sulfur-bearing atmospheres. The primary objective is to identify alloy modifications and surface treatments that will improve the mechanical performance and chemical integrity of oxide scales in the environments characteristic of coal combustion and coal conversion processes.

Another objective of this research thrust area is to investigate the mechanisms of erosion and wear of alloys and cermets used in fossil energy systems. An improved understanding of erosion mechanisms will provide the basis for the development of alloys and cermets that possess significantly improved erosion resistance. The research in progress and that planned is designed to lead to this better understanding of erosion processes.

Research efforts include studies of erosion behavior of alloys and cermets in coal preparation, coal liquefaction, coal gasification, coal combustion, and coal-fired heat engines.

This thrust area also includes research and development activities on materials for molten carbonate fuel cell (MCFC) systems. An important part of the involvement of the AR&TD Fossil Energy Materials Program in this research area is coordination with independent but related fuel cell activities sponsored by the Fuel Cells Program in the DOE Fossil Energy Office of Advanced Energy Conversion Systems. Such awareness of other programs ensures that the long-range goals of the AR&TD Fossil Energy Materials Program fuel cells effort will be consistent with the needs of the technology and compatible with work elsewhere. The principal problems with MCFCs are dissolution of the nickel oxide cathode, interface corrosion, corrosion of the anode and cathode current collectors, and electrolyte loss. The AR&TD Fossil Energy Materials Program will address the problems of nickel oxide cathode dissolution, alternative cathode materials, and corrosion mechanisms of anode and cathode current collectors in MCFCs.

Finally, this thrust area includes work near completion on the mechanical behavior of refractories for coal gasification systems.

Research and development activities for this thrust area are described in the following section and are listed in Table III.3 at the end of the section.

3.2 SUMMARIES OF CURRENT AND PLANNED RESEARCH

3.2.1 Corrosion of Alloys

ANL-3(A), "Corrosion and Mechanical Properties of Alloys for Internals and Heat Exchangers in Mixed-Gas Environments," Argonne National Laboratory. The purposes of this task are to (1) develop corrosion information in the temperature range 400 to 750°C in mixed-gas atmospheres containing O, S, and Cl by use of internally cooled tube specimens of selected commercial materials; (2) evaluate mechanisms of the formation and breakaway behavior of protective scales on base metals and weldments exposed to atmospheres containing O, S, and Cl; (3) experimentally evaluate the uniaxial creep rupture behavior of selected high-chromium alloys and weldments exposed to complex gas mixtures; (4) establish the synergistic effects of stress and environment on the materials behavior; (5) develop corrosion rate expressions on the basis of experimental data for long-term extrapolation to component design lives; and (6) correlate the creep properties such as rupture life, rupture strain, and minimum creep rate with the chemistry of exposure environment, temperature, and alloy chemistry.

Work being conducted under this task provides a basic understanding of the corrosion behavior of commercial and model alloys after exposure to multicomponent gas mixtures. The information on scale thickness, intergranular penetration, and morphological changes developed in this task provides a rational basis for the extrapolation of corrosion rates as a function of temperature, alloy composition, and chemistry of the gas environment. The corrosion experiments by a thermogravimetric technique in mixed-gas atmospheres on selected commercial high-chromium alloys and on model alloys fabricated with compositional variations will establish the role of different alloying elements on the mechanisms of scale development and adhesion and on breakaway phenomena leading to scale failure. The project on heat exchanger materials involves development of corrosion information in the low- and medium-Btu gasification atmospheres. The experiments are conducted with internally cooled tube specimens of selected commercial materials and some commercial coatings. The critical variables, such as gas temperature and metal temperature, are independently controlled in the ranges of interest in practical systems. The gas temperatures will range from 850 to 1100°C, a range that encompasses the raw gas outlet temperatures of dry ash and slagging gasifier types. The results from this program will establish the process variable envelopes for various commercial materials for use in heat exchanger applications. Incoloy 800H plates welded with low-nickel filler metals have been fabricated, and they will be examined for their corrosion resistance in mixed-gas atmospheres. Nickel aluminides and iron-nickel aluminides developed at ORNL will be examined for their sulfur resistance by using thermal gravimetric analysis and post-exposure analysis of specimens.

ANL-3(B), "Corrosion of Alloys in FBC Systems," Argonne National Laboratory. This work involves laboratory testing of the formation mechanisms and corrosion effects of $CaSO_4$ coatings on in-bed heat exchanger surfaces. More specifically, the purposes of this task are (1) to study experimentally the high-temperature corrosion behavior of iron- and nickel-base alloys and weldments with low-nickel filler metals in simulated combustion gas environments with a wide range of oxygen and sulfur potentials; (2) to study deposit-induced corrosion behavior of coated and uncoated heat exchanger and gas turbine materials after exposure to multicomponent gas environments; (3) to evaluate the sulfidation and oxidation resistance of ORNL-developed nickel aluminides and iron-nickel aluminides in simulated FBC atmospheres with and without deposits; and (4) to develop corrosion rate expressions, based on experimental data, for long-term extrapolation to component design lives.

ERE-3, "Reference Book on Performance of Materials in Coal Liquefaction Environments," Exxon Research and Engineering Company. Through the auspices of The Metal Properties Council, Inc. (MPC), several government, industrial, and university organizations are contributing information and data on materials performance in coal liquefaction environments for inclusion in a reference book. Such a book is not only desirable but is sorely needed as an archival reference to the great body of information developed over the past several years. Exxon Research and Engineering Company will collect information (chapters of the book) from the various authors, edit the submitted information, and compile it into a single reference source for subsequent publication.

GE-3, "A Mechanistic Study of Low-Temperature Corrosion of Materials in the Coal Combustion Environment," General Electric Company. The purpose of this work is to develop a mechanistic understanding of the low-temperature corrosion phenomena of materials exposed to environments characteristic of coal combustion. Specific tasks include (1) studies of the corrosion morphology and interface chemistry on selected specimens after exposure to coal contaminants; (2) thermochemical calculations to establish the range of conditions for stability of the alloy phases, corrosion products, and chemical compounds formed; and (3) specific laboratory tests to correlate the experimental results with predictions from the thermochemical calculations. Specimens are characterized with scanning electron microscopy, electron microprobe analysis, and X-ray diffraction. Reference alloys include IN-738, FeCrAlY-coated IN-738, RT-22-coated

IN-738, and two different CoCrAlY coatings on IN-738. The thermochemical calculations include (1) the minimum partial pressure of SO_3 required to form a K_2SO_4-$CoSO_4$ liquid and an Na_2SO_4-K_2SO_4-$CoSO_4$ liquid, and (2) the thermochemistry of low-temperature attack in the coal combustion environment on iron- and aluminum-rich coatings. Laboratory test results will be correlated with thermochemical calculations and phase stability plots.

ORAU-3, "Investigation of the Elastic Properties of Oxide Films and Adhesion of Oxides to Metal Substrates," Oak Ridge Associated Universities. The purpose of this project is to study the elastic properties of oxide films on metal substrates and to examine their adhesion properties. A dynamic resonance device has been designed and built for the study of elastic and anelastic behavior of thin films on metals. The approach is to measure both the elastic properties of Al_2O_3 as it forms on Pt, Pt-Al, Ni-Al, and (Fe,Ni)-Al alloys and of Al_2O_3 deposited by chemical vapor deposition on platinum substrates and the adhesive strength of the film-substrate composites. The microstructure and modes of failure of the Al_2O_3 films as they are subjected to thermal cycling will be related to the ability of the film to deform plastically and the manner in which the elastic-plastic behavior is influenced by platinum solution in the scale. The data from this study can form the beginning of the ability to modify the mechanical properties of an oxide-substrate composite and, thus, develop a truly protective oxide film.

ORNL-3(A), "Pilot Plant Materials Testing and Failure Analysis," Oak Ridge National Laboratory. This task provides screening data on the susceptibility to corrosion and stress-corrosion cracking of potential materials of construction for coal liquefaction plants. It also provides failure analyses and on-site examinations for the Wilsonville, Alabama, Advanced Coal Liquefaction Research and Development Facility. Corrosion coupons and stress-corrosion cracking specimens of selected alloys will be exposed in selected areas of the Wilsonville coal liquefaction facility. Metallurgical examinations of failed and selected components from Wilsonville and other coal conversion plants will also be made. Extensive use of optical microscopy, scanning electron microscopy, nondestructive evaluations, and other metallurgical techniques will be used. On request of the plant engineers, on-site examinations of vessels and components will be made.

ORNL-3(B), "Investigation of Corrosion-Resistant Oxide Scales on Iron-Based Alloys in Mixed Gas Environments," Oak Ridge National Laboratory. The purpose of this task is to develop protective oxide scales on Cr_2O_3- and Al_2O_3-forming iron-based alloys in mixed oxidant (O_2, SO_2, H_2S, H_2O) environments for coal-related applications at 600 to 800°C. Specific objectives include (1) the development of protective oxide scales by modifying oxide chemistry and microstructure to reduce the transport of sulfur through the scale; (2) the formation of a sulfur-diffusion barrier (i.e., SiO_2 layer) under or above the protective oxide scale to minimize the sulfur attack; (3) the study of the effects of alloy chemistry, oxide morphology, and temperature on the breakdown of protective oxide scales; and (4) the examination of methods to limit internal sulfidation. The mechanical performance and adherence of oxide scales in mixed oxidant gases will be studied by impinging tungsten carbide particles on the oxide within a scanning electron microscope under controlled temperature and environmental conditions.

PITT-3,"Investigation of Corrosion Mechanisms of Coal Combustion Products on Alloys and Coatings," University of Pittsburgh. The objective of this research project is to investigate the formation and breakdown of protective oxide scales in mixed oxidant gases. The results of this research will support the development of improved heat exchanger materials for applications in (1) heat recovery systems for coal conversion plants (particularly gasification) and (2) coal-fired industrial and utility boilers. The materials used in this study will be model alloys selected for their ability to form single oxides of chromium, aluminum, and silicon. The temperature range of interest is 500°C to 700°C, and the test environments contain mixed oxidants (O_2, CO_2, SO_2, H_2S, and Cl_2). Specific objectives include determination of the effect of surface pretreatment and preoxidation on the structure and properties of oxide scales, and the correlation of these treatments and the resulting structures and properties with the breakdown of the scales in mixed oxidant gases. Loss of scale protection by mechanical means (cracking, spalling, etc.) and by transport of corroding species (S and Cl) will be considered.

SC(I,U)-3(A), "Investigation of the Effects of Microalloy Constituents, Surface Treatment, and Oxidation Conditions on the Development and Breakdown of Protective Oxide Scales in Mixed Oxidant Gases for Coal-Related Applications," contractors to be determined. A 36-month experimental research project will be initiated in FY 1986 to investigate the chemical and metallurgical factors that control the nucleation, growth, and eventual breakdown of protective oxide scales on Al_2O_3- and Cr_2O_3-forming alloys or coatings in coal-related environments. The objective is to improve the corrosion resistance of heat exchanger materials by enhancing the mechanical properties and chemical passivity of corrosion-product scales based on alumina or chromia. The project will address the following effects pertaining to the development and breakdown of protective oxide scales: (1) the effect of microalloy constituents, (2) the effect of method of incorporation of microalloy constituents, (3) the effect of surface pretreatment, and (4) the effect of oxidation conditions.

SC(I,U)-3(D), "Development of Dispersion-Toughened, Spalling-Resistant Oxide Corrosion Scales," contractor to be determined. This project will begin in FY 1988 with the aim to develop protective corrosion scales on materials used in coal combustion and conversion systems. The objective is to develop techniques for modifying the compositions of in-situ oxide films and to evaluate the effects of the modifications on the fracture toughness properties of the films. Modifications will be made in accordance with principles recently developed to ductilize oxide ceramics and with the results obtained under WBS element SC(I,U)-3(A).

SC(I,U)-3(E), "Investigation of Effects of Heat Flux on Exfoliation of Oxide Films in Steam and Air," contractor to be determined. A problem limiting the use of ferritic steels in superheaters and reheaters above 540°C is the spallation of oxide films with the attendant obstruction of steam passages or turbine damage. The higher heat fluxes attainable with the fluidized-bed concept are expected to accentuate the problem. Silicon, a minor alloying element in steels, appears to be extremely beneficial in reducing oxide spallation. A research project is planned for initiation in FY 1988 to determine the influence of silicon additions to 2.25Cr-1Mo and 9Cr-1Mo steels on oxide spallation in steam generators and air preheaters. The project may also involve the evaluation of benefits accruing from surface treatments (e.g., chromizing) and the use of more highly alloyed materials.

3.2.2 Erosion of Alloys

BCL-3, "Evaluation of Advanced Materials for Slurry Erosion Service," Battelle Columbus Laboratories. The purpose of this project is to obtain erosion data on several candidate valve trim materials under a range of slurry erosion conditions. These data are useful to valve and process engineers in materials selection and valve design. Reconstituted coal-derived slurries have been used to erode candidate materials under a range of slurry velocities and impingement angles. The erosive slurries have been characterized, and the erosive resistances of cemented tungsten carbides and various ceramics have been ranked. The results of a service trial of an experimental carbide valve stem have been studied.

As part of this project, a suitable substitute erodent and liquid carrier combination has been developed to reduce levels of health risks and handling problems in standardized laboratory materials evaluation and screening tests. This project, which will be concluded in FY 1986, is helping to develop an understanding of materials behavior in slurry erosion.

LBL-3, "Studies of Materials Erosion in Coal Conversion and Utilization Systems," Lawrence Berkeley Laboratory. The objective of this project is to determine the erosion-corrosion behavior of materials used in the flow passages for of liquid slurries under conditions representative of those in coal liquefaction systems. Current efforts are aimed at an understanding of the mechanism of erosion in coal liquefaction environments.

One phase of this project, initiated in FY 1984, involves the investigation of the mechanisms of erosion-corrosion attack. Since existing data had been empirical or had been derived by an analysis of operating experience, a reliable prediction of material loss due to erosion-corrosion had not been possible. The determination of erosion-corrosion mechanisms in this project will certainly aid the ability to predict material losses and will be invaluable in selecting materials for use where erosion-corrosion is a problem.

NBS-3(A), "Mechanisms of Galling and Abrasive Wear," National Bureau of Standards. This project began at the National Bureau of Standards in FY 1983; its purpose is to develop an understanding of the wear mechanisms of materials associated with valves in coal conversion systems. This work addresses the mechanical and chemical effects experienced in closure regions of valves in coal conversion systems. It includes theoretical considerations of chemical reactions and effects of the working media on valve closure materials. Measurements are being performed to determine the static and kinetic coefficients of friction of the various combinations of test materials.

ORNL-3(C), "Mechanisms of Erosion-Corrosion in Coal Combustion Environments," Oak Ridge National Laboratory. The purpose of this task is to perform a fundamental study of the erosion, corrosion, and erosion-corrosion of alloys in coal combustion environments by direct observation of a surface being subjected to erodent particles in a stream of corrosive gas. The goal is to improve our understanding of the fundamental nature of erosion, corrosion, and erosion-corrosion. The basic feature of this study is the impingement of erodent particles on alloy surfaces that may be exposed to corrosive gas environments. Degradation of the alloys will be monitored by a scanning electron microscope equipped with a hot-stage test chamber. Single or multiple particle effects will be determined as well as the effects of temperature, corrosive medium, and characteristics (size, mass, hardness, and angle of impingement) of eroding particles.

UCIN-3, "Study of Particle Rebound Characteristics and Material Erosion at High Temperature," University of Cincinnati. The purpose of this effort is to investigate the erosion processes and fluid mechanics phenomena that occur in fluidized-bed combustors, coal-fired boilers, cyclones, pumps, turbines, valves, and other coal conversion systems. The overall objective is to develop a quantitative model that will facilitate the prediction of erosion in systems operating in particle-laden environments. The experimental study of the impact and rebound characteristics are being performed with selected solid particles, including Al_2O_3 and

SiO_2, with sizes from 5 to 200 µm. The target materials are selected according to present and anticipated materials needs of coal conversion systems. Candidate materials include stainless steel, INCO 718, Ti 6-4, and 2024 Al.

UND-3(A), "Erosion in Dual-Phase Microstructures," University of Notre Dame. The purpose of this work is to study the effects of the microstructure of metallic alloys on their erosion behavior. Of particular interest are the differences in erosion rates of the alloy matrix and second-phase particles. The materials being investigated include a series of white cast irons high in chromium and molybdenum with compositions tailored to vary systematically carbide volume fraction with constant carbide and matrix compositions. The role of large hard second-phase particles in erosion resistance is being investigated. This project will be concluded in FY 1986.

UND-3, "Correlation of Materials Structure with Flow Characteristics of Erosive Particles," University of Notre Dame. Since FY 1982, a project [UND-3(A)] sponsored by the AR&TD Fossil Energy Materials Program at the University of Notre Dame (UND) has involved the study of the effects of the microstructure of alloys on their erosion behavior. This new project, to be initiated in FY 1986, will emphasize the correlation of materials structure with flow characteristics of erosive particles. The work to be performed will be closely related to, and coordinated with, the study of particle rebound characteristics and material erosion being performed at the University of Cincinnati (UCIN-3).

SC(I,U)-3(B), "Flow Characteristics of Particles in a Simulated Coal-Fired Gas Turbine System," contractor to be determined. This work is scheduled to begin in FY 1987 and will provide a determination of the flow characteristics of particles in simulated coal-fired gas turbines. The tests will examine the effects of particle sizes and loadings in gas streams at temperatures characteristic of coal-fired systems subjected to cleanup by cyclone separators. The purpose of these tests is to determine the manner in which particles behave in these gas streams and, thus, obtain insight into the likely erosion modes. The need for additional cleanup and the need for development of materials to withstand erosion in such systems should be indicated by these tests.

SC(I,U)-3(F), "Investigation of the Mechanisms of Erosion and Corrosion of Materials During Combustion of Coal-Liquid Slurries," contractor to be determined. An investigation of the mechanisms responsible for erosion and corrosion of boiler tubes and components in oil- or gas-fired boilers that have been retrofitted to burn coal slurries is proposed for initiation in FY 1988. A bench-scale experiment may be designed to measure the extent of fly-ash erosion and corrosion of materials that are the current choices for construction of boiler tubes and related components. The results of this effort will provide input to the selection of materials used in conventional fossil-fired systems as well as information regarding necessary design changes to reduce the effect of fly-ash corrosion-erosion. Furthermore, an increased understanding of the mechanisms responsible for the corrosion reactions in the combustion zone and the relation of such mechanisms to the coal slurry quality and characteristics will improve the ultimate effectiveness of the combustion of coal-liquid mixtures.

SC(U)-3(A), "Investigation of Fluid Dynamic Behavior of Erosive Particulates in Gas Streams," contractor to be determined. The purpose of this investigation is to improve the understanding of erosion processes in gas streams. To fully understand erosion processes caused by particles entrained in gas streams, the fluid dynamic behavior of the particulates must be understood. Laboratory experiments have generally focused on erosive particles interacting with materials under carefully controlled flow conditions (particle velocity and impact angle). This project should aid attempts to correlate the results of the carefully controlled laboratory experiments with the experience of plant systems.

SC(U)-3(B), "Effects of Particle Size and Velocity on Erosion-Corrosion in an Oxidizing Environment," contractor to be determined. The combined effects of erosion and corrosion in an oxidizing environment are dependent on many factors including oxide scale adhesion, the eroding medium, and properties of the bulk material being eroded. The effects of particle size and velocity have not been unequivocally established. This project, which will be initiated in FY 1987, will focus on a determination of the effects of particle size and velocity on erosion and corrosion of materials in an oxidizing environment.

SC(I,U)-3(C), "Abrasion of Refractory Liners in Oil Shale Retort Systems," contractor to be determined. This project will study the degradation of refractories as a result of abrasive wear by oil shale particulates.

3.2.3 Fuel Cells

ORNL-3(D), "Investigation of the Mechanisms of Molten Salt Corrosion of Candidate Materials for Molten Carbonate Fuel Cells," Oak Ridge National Laboratory. The purpose of this task is to define and study the mechanisms controlling the corrosion of anode and cathode current collector materials in molten carbonate fuel cells (MCFCs). Important objectives include (1) the identification of the reaction products formed between carbonate salt and iron, chromium, and nickel under oxidizing (cathode side) and reducing (anode side) conditions; and (2) the measurement of the solubilities of structural metal oxides in the carbonate salt under acidic (cathodic) and basic (anodic) conditions. Differential thermal analysis/thermogravimetric analysis (DTA/TGA) studies are conducted to evaluate reactions between selected structural metals (Fe, Cr, and Ni) and molten carbonate salts. Aliquots of finely divided metal are loaded in gold capsules containing granular Li_2CO_3-K_2CO_3, and DTA/TGA of the mixtures is performed up to 700°C under controlled gas atmospheres. Thermal analysis is used to establish the melting points and identity of any molten reaction products.

The relative solubilities of structural metal oxides (Cr_2O_3, Fe_3O_4, and NiO) are determined in carbonate salt under oxidizing (air + CO_2) and reducing (H_2 + CO) gas conditions. By using a reference electrode developed on this project, the oxidizing potential of the salt under a given gas atmosphere is measured in terms of the oxygen ion concentration (O^{-2}), and the saturation concentration of the structural metal oxide at that oxygen ion concentration is recorded by atomic absorption analysis of a melt sample. Potentiometric techniques are used to continuously measure the oxygen ion concentration (oxidizing potential) of the salt under the different gas atmospheres.

SC(I)-3(A), "Investigation of the Effect of Electrolyte Melt Chemistry on Corrosion of Components in Molten Carbonate Fuel Cells," contractor to be determined. The purpose of this project will be to develop an understanding of the effect of electrolyte melt chemistry on the corrosion of components in molten carbonate fuel cells (MCFCs). High-temperature corrosion of iron- and nickel-base alloys in the presence of molten electrolytes (sulfates, carbonates) is strongly influenced by melt chemistry. Accelerated corrosion due to changes in the acidity and basicity of the melt are known to cause oxide scale fluxing, porous nonprotective oxide formation, and cracking and spalling of the scale. Of particular interest will be the corrosion behavior of candidate current collector materials under the conditions of operating MCFCs. In this regard the work will be complementary to the work presently being conducted under WBS element ORNL-3(D). As part of this project, candidate current collector materials from ORNL-3(D) will be tested for long times in an optimum electrolyte composition in laboratory-scale MCFCs for examination of long-term MCFC behavior and stability.

SC(I)-3(B), "Phase Equilibria and Corrosion of Molten Carbonate Fuel Cell Current Collectors in Ternary $(Li,Na,K)_2CO_3$ Electrolytes," contractor to be determined. The purpose of this task will be to investigate the thermodynamics controlling, and the phase equilibria that result from, the reactions between the materials used for current collectors in molten carbonate fuel cells and the ternary electrolyte, $(Li,Na,K)_2CO_3$. In addition, this work will study the mechanisms and kinetics associated with the corrosion of current collector materials in the presence of ternary electrolytes. Primary objectives include (1) the identification of the reaction products formed between structural elements (Fe, Cr, and Ni) and carbonate mixtures, $(Li,Na,K)_2CO_3$, under fuel cell operating conditions; (2) the evaluation of rate limiting processes controlling the corrosion of candidate current collector materials in $(Li,Na,K)_2CO_3$; and (3) the measurement of the equilibrium solubilities of Fe, Cr, and Ni (and their oxides) in ternary carbonate mixtures under fuel cell operating conditions.

3.2.4 Refractories

ISU-3, "High-Temperature Creep Behavior of Refractory Bricks," Iowa State University. This research effort is a continuation of the study of creep of refractories used to line fossil-fuel process vessels. The work will concentrate on those refractories intended for use at higher temperatures and under more severe conditions than can be tolerated by refractory concretes. Specifically, the research will focus on the creep behavior of high-chromia refractories suitable for lining the hot section of slagging gasifiers. Uniaxial creep experiments will be conducted in compression in air and mixed gases with very low oxygen partial pressures. The creep behavior of high-chromia refractories in uniaxial compression will be measured as a function of stress, oxygen partial pressure, and temperature. Oxygen partial pressures ranging from 21 kPa to 0.1 pPa will be used. Stress will be varied from 0.7 to 2 MPa. In addition, biaxial creep measurements will be made for selected refractories for which uniaxial creep measurements have been determined.

The creep data will be evaluated in cooperation with related work at the Massachusetts Institute of Technology (MIT-3) to correlate the creep behavior of these refractories with a mathematical model.

MIT-3, "Thermomechanical Modeling of Refractory Brick Linings for Slagging Gasifiers," Massachusetts Institute of Technology. The objective of this task is to study the failure mechanisms of refractory-brick-lined coal gasification vessels under transient temperature loadings. A thermomechanical model, which will include cyclic multiaxial nonlinear constitutive laws, temperature-dependent heat conduction, and temperature-dependent creep laws, is to be developed for refractory brick and mortar. The model will be implemented in a finite-element program for predicting the stress and strain distributions in brick-mortar linings during the heatup and cooldown cycles. Through simulation and parameter studies, design recommendations will be made for vessel configuration, material property combinations, and optimum heating schedules.

NBS-3(B), "Investigation of the Effect of Slag Penetration on the Mechanical Properties of Refractories," National Bureau of Standards. The purpose of this task is to determine the effect of slag penetration and microstructure on the fracture and deformation behavior of refractories. The fracture and deformation behavior of model refractories penetrated by slag will be characterized. The creep behavior of refractories will be determined as a function of applied load and temperature. Changes in density and microstructure will be determined for refractories that have been deformed in creep. Data will be evaluated on mechanisms developed to explain cavity formation, cavity coalescence, and crack growth in ceramic materials, and the models will be revised as appropriate. A model will be developed to predict the lifetimes of refractories in slagging gasifiers. In addition, a portion of the work will focus on a systematic compilation of data relating to slag properties and corrosion of refractories for advanced coal conversion systems.

PNST-3, "Thermodynamic Properties and Phase Relations for Refractory-Slag Reactions in Slagging Coal Gasifiers," Pennsylvania State University. The purpose of this project is to determine the chemical constraints affecting the performance of refractory materials under experimental conditions corresponding to those prevailing in slagging gasifiers. In particular, this project will concentrate on systems containing chromic oxide, because refractories containing significant amounts of this component have demonstrated excellent resistance to corrosion. Work on this project is divided among the following tasks: (1) determination of thermodynamic properties of various oxide components, especially chromium oxide and Al_2O_3, in silicate melts of compositions of interest in slagging coal gasifiers, (2) determination of kinetics and mechanisms of reactions between refractory phases and coal-ash slags, (3) delineation of phase relations in ZrO_2-containing systems, and (4) determination of thermodynamic parameters for reactions between FeO-containing slags and carbon.

VPI-3, "Alkali Attack of Coal Gasifier Refractory Linings," Virginia Polytechnic Institute. The purpose of this project is to investigate the physical and chemical characteristics of alkali attack of coal gasifier refractory linings under slagging and nonslagging conditions. Various refractories will be exposed to simulated coal gasification atmospheres containing alkali metals such as sodium and potassium. Following exposure, the phase changes and compound formation that occur in the refractories will be evaluated and compared with theoretical calculations. In addition, changes in selected physical and chemical properties of the refractories such as strength, thermal expansion, and solubility will be measured. The effect of sulfur in the formation of stable, nonreactive alkali compounds in coal gasification atmospheres containing alkali metals will be investigated.

Table III.3. Research projects for corrosion and erosion of alloys and refractories

Research project	Performing organization	Funding (thousands of dollars)[a]				
		FY 1986	FY 1987	FY 1988	FY 1989	FY 1990
Corrosion of alloys						
ANL-3(A) — Corrosion and Mechanical Properties of Alloys for Internals and Heat Exchangers in Mixed-Gas Environments	Argonne National Laboratory (ANL)	225	225	100	0	0
ANL-3(B) — Corrosion of Alloys in FBC Systems	ANL	110	110	250	375	375
ERE-3 — Reference Book on Performance of Materials in Coal Liquefaction Environments	Exxon Research and Engineering Company (ERE)	16	0	0	0	0
GE-3 — A Mechanistic Study of Low-Temperature Corrosion of Materials in the Coal Combustion Environment	General Electric Company (GE)	[b]	0	0	0	0
ORAU-3 — Investigation of the Elastic Properties of Oxide Films and Adhesion of Oxides to Metal Substrates	Oak Ridge Associated Universities (ORAU)	[c]	0	0	0	0
ORNL-3(A) — Pilot Plant Materials Testing and Failure Analysis	Oak Ridge National Laboratory (ORNL)	40	50	50	50	50
ORNL-3(B) — Investigation of Corrosion-Resistant Oxide Scales on Iron-Based Alloys in Mixed Gas Environments	ORNL	150	225	225	250	250
PITT-3 — Investigation of Corrosion Mechanisms of Coal Combustion Products on Alloys and Coatings	University of Pittsburgh (PITT)	80	80	0	0	0

Table III.3. (continued)

Research Project	Performing Organization	Funding (thousands of dollars)[a]				
		FY 1986	FY 1987	FY 1988	FY 1989	FY 1990
SC(I,U)-3(A) — Investigation of the Effects of Microalloy Constituents, Surface Treatment, and Oxidation Conditions on the Development and Breakdown of Protective Oxide Scales in Mixed Oxidant Gases for Coal-Related Applications	To be determined (TBD)	255	645	0	0	0
SC(I,U)-3(D) — Development of Dispersion-Toughened, Spalling-Resistant Oxide Corrosion Scales	TBD	0	0	500	600	600
SC(I,U)-3(E) — Investigation of Effects of Heat Flux on Exfoliation of Oxide Films in Steam and Air	TBD	0	0	200	200	100
	Erosion of alloys					
BCL-3 — Evaluation of Advanced Materials for Slurry Erosion Service	Battelle Columbus Laboratories (BCL)	[b]	0	0	0	0
LBL-3 — Studies of Materials Erosion in Coal Conversion and Utilization Systems	Lawrence Berkeley Laboratory (LBL)	300	300	350	350	350
NBS-3(A) — Mechanisms of Galling and Abrasive Wear	National Bureau of Standards (NBS)	75	75	100	100	100
ORNL-3(C) — Mechanisms of Erosion-Corrosion in Coal Combustion Environments	ORNL	180	200	200	200	0

Table III.3. (continued)

Research project	Performing organization	Funding (thousands of dollars)[a]				
		FY 1986	FY 1987	FY 1988	FY 1989	FY 1990
UCIN-3 — Study of Particle Rebound Characteristics and Material Erosion at High Temperature	University of Cincinnati (UCIN)	80	0	0	0	0
UND-3(A) — Erosion in Dual-Phase Microstructures	University of Notre Dame (UND)	[b]	0	0	0	0
UND-3 — Correlation of Materials Structure with Flow Characteristics of Erosive Particles	UND	50	100	100	100	0
SC(I,U)-3(B) — Flow Characteristics of Particles in a Simulated Coal-Fired Gas Turbine System	TBD	0	220	220	0	0
SC(I,U)-3(F) — Investigation of the Mechanisms of Erosion and Corrosion of Materials During Combustion of Coal-Liquid Slurries	TBD	0	0	200	200	100
SC(U)-3(A) — Investigation of the Fluid Dynamic Behavior of Erosive Particulates in Gas Streams	TBD	50	50	60	60	60
SC(U)-3(B) — Effects of Particle Size and Velocity on Erosion-Corrosion in an Oxidizing Environment	TBD	0	225	225	200	200
SC(I,U)-3(C) — Abrasion of Refractory Liners in Oil Shale Retort Systems	TBD	0	0	150	150	100

Table III.3. (continued)

Research project	Performing organization	Funding (thousands of dollars)[a]				
		FY 1986	FY 1987	FY 1988	FY 1989	FY 1990
	Fuel cells					
ORNL-3(D) — Investigation of the Mechanisms of Molten Salt Corrosion of Candidate Materials for Molten Carbonate Fuel Cells	ORNL	100	0	0	0	0
SC(I)-3(A) — Investigation of the Effect of Electrolyte Melt Chemistry on Corrosion of Components in Molten Carbonate Fuel Cells	TBD	75	200	200	0	0
SC(I)-3(B) — Phase Equilibria and Corrosion of Molten Carbonate Fuel Cell Current Collectors in Ternary $(Li,Na,K)_2CO_3$ Electrolytes	TBD	0	0	0	200	200
	Refractories					
ISU-3 — High-Temperature Creep Behavior of Refractory Bricks	Iowa State University (ISU)	60	0	0	0	0
MIT-3 — Thermomechanical Modeling of Refractory Brick Linings for Slagging Gasifiers	Massachusetts Institute of Technology (MIT)	[b]	0	0	0	0
NBS-3(B) — Investigation of the Effect of Slag Penetration on the Mechanical Properties of Refractories	NBS	[b]	0	0	0	0

Table III.3. (continued)

Research project	Performing organization	Funding (thousands of dollars)[a]				
		FY 1986	FY 1987	FY 1988	FY 1989	FY 1990
PNST-3 — Thermodynamic Properties and Phase Relations for Refractory-Slag Reactions in Slagging Coal Gasifiers	Pennsylvania State University (PNST)	40	0	0	0	0
VPI-3 — Alkali Attack of Coal Gasifier Refractory Linings	Virginia Polytechnic Institute (VPI)	*b*	0	0	0	0

[a] Entries for FY 1987 through FY 1990 are perceived funding needs rather than program guidance.

[b] Carryover funds from FY 1985.

[c] Prefunded in FY 1985.

4. ASSESSMENTS AND TECHNOLOGY TRANSFER

4.1 INTRODUCTION

The purpose of the technology assessment activity of the AR&TD Fossil Energy Materials Program is to maintain an awareness of the technical issues and research and development needs of established and emerging fossil energy technologies. Specifically, the performance of the assessments of materials problems and needed research to solve those problems in a wide variety of fossil energy technologies is an important part of the AR&TD Fossil Energy Materials Program.

In addition to technology assessments, the transfer of technology developed on the AR&TD Fossil Energy Materials Program to others in the fossil energy community is an important responsibility and serious commitment of the Program.

The activities associated with technology assessment and technology transfer are described in the following section and are listed in Table III.4 at the end of the section.

4.2 SUMMARIES OF CURRENT AND PLANNED ACTIVITIES

4.2.1 Technology Assessment

ORNL-4(B), "Membrane Separation of Gases from Coal Combustion and Coal Conversion Processes," Oak Ridge National Laboratory. The objective of this task is to assess the applications of membrane technology for separating and recovering gases (e.g., SO_2, H_2S, CO_2, NO, N_2, and O_2) encountered in coal combustion and coal conversion processes.

Commercial membranes will be selected and evaluated for use in separating gases such as SO_2, H_2S, CO_2, NO, N_2, and O_2, which occur in coal combustion and conversion processes. The permeability of pure gases through different types of membranes will be determined by measuring the flow rates of the gases through the membranes at different pressures. The most promising membranes will then be used to study the separation of gas mixtures such as H_2S and CO_2, N_2, and SO_2, as well as other gas mixtures of interest in coal combustion and conversion processes.

SC(I)-4, "Assessment of Materials Needs for Coal-Fired Heat Engines," contractor to be determined. The objective of this project is to review the materials requirements for coal-fired heat engines, to assess the state of technology for materials to meet those requirements, and to identify the primary areas in which materials research and development is required.

4.2.2 Technology Transfer

BCL-4, "*Materials and Components in Fossil Energy Applications* Newsletter," Battelle Columbus Laboratories. This newsletter communicates experience and test results related to fossil energy materials and components to those organizations involved in the development of fossil energy systems. The newsletter is issued by the DOE Oak Ridge Operations and is distributed bimonthly to about 2500 domestic and foreign subscribers.

SC(I,U)-4, "Transfer of Refractory Technology to Industry," contractors to be determined. This project will be initiated in FY 1986 and will be a collaborative effort of a university and an industrial organization. This activity will assure that the technology developed on projects in progress at Iowa State University (creep properties of refractory bricks), Massachusetts Institute of Technology (thermomechanical modeling of refractory brick linings), National Bureau of Standards (effects of slag penetration on mechanical properties of refractories), and Virginia Polytechnic Institute (alkali attack of refractories) will be transferred to appropriate industries in the fossil energy community.

Table III.4. Technology assessment and technology transfer activities

Activity	Performing organization	Funding (thousands of dollars)[a] FY 1986	FY 1987	FY 1988	FY 1989	FY 1990
ORNL-4(B) — Membrane Separation of Gases from Coal Combustion and Coal Conversion Processes	Oak Ridge National Laboratory (ORNL)	30	0	0	0	0
SC(I)-4 — Assessment of Materials Needs for Coal-Fired Heat Engines	To be determined (TBD)	65	0	0	0	0
BCL-4 — *Materials and Components in Fossil Energy Applications* Newsletter	Battelle Columbus Laboratories (BCL)	110	110	115	115	115
SC(I,U)-4 — Transfer of Refractory Technology to Industry	TBD	40	0	0	0	0

[a] Entries for FY 1987 through FY 1990 are perceived funding needs rather than program guidance.

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