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Period Ending September 30, 1981

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OAK RIDGE NATIONAL LABORATORY

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ORNL/FMP-81/4

**AR&TD FOSSIL ENERGY MATERIALS PROGRAM
QUARTERLY PROGRESS REPORT FOR THE PERIOD
ENDING SEPTEMBER 30, 1981**

**R. A. Bradley, Manager
Fossil Energy Materials Program**

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PART I — INTRODUCTION AND SUMMARY

ORNL-1.1(A) — MANAGEMENT OF THE AR&TD FOSSIL ENERGY MATERIALS PROGRAM

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Oak Ridge, Tennessee 37830

INTRODUCTION AND SUMMARY

This is the fourth combined quarterly progress report for those projects that are part of the Advanced Research and Technology Development (AR&TD) Fossil Energy Materials Program. The work described in this report covers the period from July 1, 1981 to September 30, 1981. The objective of the Program is to conduct a program of research and development on materials for fossil energy applications with a focus on the longer-term and generic needs of the various fossil fuel technologies.

The program includes research aimed toward a better understanding of materials behavior in fossil energy environments and the development of new materials capable of substantial enhancement of plant operations and reliability. Work performed on the program generally falls into the Applied Research and Exploratory Development categories as defined in the DOE Technology Base Review, although basic research and engineering development are also conducted.

This report covers those projects that are managed by Oak Ridge National Laboratory (ORNL) and DOE Oak Ridge Operations (ORO) plus one project that is managed by DOE Headquarters. The organizational relationship between DOE Headquarters, ORO, and ORNL is illustrated in Fig. 1.

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Task Leaders

Fig. 1. Organizational Relationships between DOE-HQ, DOE-ORO, and ORNL for the AR&TD Fossil Energy Materials Program.

A substantial portion of the work on the AR&TD Fossil Energy Materials Program is performed by participating contractor organizations. All subcontractor work is monitored by Program staff members at ORNL and Argonne National Laboratory (ANL). The technical monitors for each project are shown in Fig. 2.

The ORNL Fossil Energy Materials Program Office compiles and issues the report from camera-ready copies submitted by each of the participating contractor organizations. Distribution is as shown on pages 435-440. Future reports will be issued on a quarterly basis to a similar distribution.

This report of activities on the program is organized in accordance with a work breakdown structure defined in the AR&TD Fossil Energy Materials Program Plan for FY 1981 (Ref. 1) in which projects are organized according to fossil energy technologies. A graphic summary of this organization is provided in Fig. 3. This report is divided into parts and chapters with each part describing projects related to a particular fossil energy technology. Chapters within a part provide details of the various projects associated with that technology.

At present, no ORO/ORNL-managed projects are directed toward materials research and development for coal mining, cleaning, beneficiation, and handling; fuel cells; magnetohydrodynamics; or oil shale. Thus, these activities are not discussed in this report. As projects are initiated in these areas, the report will be expanded to include those activities.

We hope this series of AR&TD Fossil Energy Materials Program quarterly progress reports will aid in the dissemination of information developed on the program. Plans for the program will be issued annually. A draft of the program plan for FY 1982-86 has been prepared and is in the review process. This program plan (ORNL/TM-7964) will be issued in early FY 1982. The implementation of these plans will be reflected by these quarterly progress reports, and this dissemination of information will be augmented by topical or final reports as appropriate. Highlights of projects that are part of this program are provided in the bimonthly DOE newsletter, "Materials and Components in Fossil Energy Applications."

<u>Project Work Breakdown Structure Element and Title</u>	<u>Technical Monitor</u>
<u>Program Management; Task Leader: R. R. Judkins</u>	
ORNL-1.1(A), Management of the AR&TD Fossil Energy Materials Program	R. R. Judkins
ORNL-1.1(B), Critical Materials Requirements for Synthetic Fuel Facilities	D. L. Lennon
ANL-1.1, Technical Monitoring of Gasification Subcontracts	W. A. Ellingson
<u>Materials for Coal Liquefaction; Task Leader: R. R. Judkins</u>	
LBL-3.1.5, Coal Liquefaction Alloy Test Program	E. L. Long, Jr.
CE-3.2.1, Toughness Evaluation of Shielded Metal Arc and Submerged Arc Welds in Modified 9 Cr-1 Mo Steel	V. K. Sikka
UCB-3.2.1(A), A New Class of Steels for Thick Wall Pressure Vessels	R. W. Swindeman
UCB-3.2.1(B), Design of Low Alloy Steels for Thick Walled Pressure Vessels	R. W. Swindeman
UTN-3.2.1, Investigation of the Transformational Characteristics and Cold-Cracking Sensitivity of Modified 9 Cr-1 Mo Steel	V. K. Sikka
ORNL-3.2.2, Welding Support and Development	R. W. Swindeman
PNST-3.2.2, An X-ray Study of Residual Stresses in Narrow-Groove TIC Weldments	R. W. Swindeman
WEC-3.2.2, Development of Automated Welding Process for Field Fabrication of Thick Walled Pressure Vessels	R. W. Swindeman
CU-3.2.3, Hydrogen Attack in Cr-Mo Steels at Elevated Temperatures	R. W. Swindeman
ORNL-3.2.3, Evaluation of Fracture Toughness of Pressure Vessel Steels	R. W. Swindeman
UCSB-3.2.3, Analysis of Hydrogen Attack on Pressure Vessel Steels	R. W. Swindeman
WEC-3.2.3, Study to Optimize Cr-Mo Steels to Resist Hydrogen and Temper Embrittlement	R. W. Swindeman
MPC-3.2.4, -3.3.4, and -3.4.4, Corrosion in Coal Liquefaction Processes	R. R. Judkins
ORNL-3.2.4, -3.3.4, and -3.4.4, Liquefaction Corrosion	R. R. Judkins
ORNL-3.2.6, -3.3.6, and -3.4.6, Failure Prevention and Analysis in Coal Liquefaction Systems	R. W. Swindeman
BCL-3.3.5, Evaluation of Advanced Materials in Laboratory Tests and Pilot Plant Service for Use in Liquefaction Letdown Valves	E. L. Long, Jr.
<u>Materials for Coal Gasification; Task Leader: W. A. Ellingson</u>	
BOMA-4.1.1, Wear-Resistant Materials for Coal Conversion and Utilization	E. L. Long, Jr.
BOMT-4.2.4, Corrosion Resistance of Refractories for Coal Gasifiers	C. R. Kennedy
ANL-4.2.7(A), -4.2.7(B), and -4.3.7, Development and Application of Nondestructive Test Methods for Coal Conversion and Utilization Systems	R. W. McClung
ISU-4.2.8, Creep Behavior of Refractory Concretes	C. R. Kennedy
MIT-4.2.8, Thermomechanical Model for Refractory Concrete Liner Anchor Interaction	W. A. Ellingson
ANL-4.2.9, Determining the Resistance of Refractories to Corrosion-Erosion by Molten Slag	C. R. Kennedy
IITRI-4.2.9, Design, Engineering, and Evaluation of Refractory Liners for Slagging Gasifiers (Task B, Facility Design and Construction)	D. L. Lennon
IITRI-4.2.9, Design, Engineering, and Evaluation of Refractory Liners for Slagging Gasifiers (Tasks C through F, Refractories Testing)	C. R. Kennedy
PNST-4.2.9, Refractories in Slagging Gasifiers	C. R. Kennedy
UCC-ND-4.2.9, Engineering Evaluation and Review of IITRI Refractory Test Facility	D. L. Lennon
INEL-4.3.3, The Effect of Coal Gasification Atmospheres on Biaxial Creep of Alloys	K. Natesan
ANL-4.3.4 and -6.1.4, Corrosion and Mechanical Behavior of Materials for Application in Coal Conversion and Utilization	K. Natesan
INEL-4.3.4, Corrosion of Alloys for Tar Sands Systems and In Situ Gasification	K. Natesan
MPC-4.3.4(A), Corrosion of Metals and Refractories in Coal Gasification Plants	K. Natesan
MPC-4.3.4(B), Erosion/Corrosion of Materials in Coal Gasification Plants	K. Natesan
ANL-4.3.6, Failure Analysis of Components in Coal Gasification Systems	W. A. Ellingson
<u>Materials for Heat Engines and Heat Recovery; Task Leader: V. J. Tennery</u>	
NBS-5.1.10, High-Temperature Applications of Structural Ceramics	V. J. Tennery
ORNL-5.2.10, Materials for Ceramic Heat Exchangers	V. J. Tennery
<u>Materials for Combustion Systems; Task Leader: J. H. DeVan</u>	
ANL-6.1.4, High-Temperature Erosion Behavior of Materials	J. H. DeVan
GA-6.1.4, Materials Testing in an Atmospheric Fluidized Bed Combustor	J. H. DeVan
ORNL-6.1.4, Heat Exchanger and Internal Structural Materials for AFBC	J. H. DeVan

Fig. 2. Task Leaders and Technical Monitors of Projects of the AR&TD Fossil Energy Materials Program.

4/1/81

Fig. 3. Work Breakdown Structure for the AR&TD Fossil Energy Materials Program.

REFERENCE

1. Compiled by R. A. Bradley and R. R. Judkins, *AR&TD Fossil Energy Materials Program Plan for FY 1981*, ORNL/TM-7612 (May 1981).

PART II - MATERIALS FOR COAL LIQUEFACTION

LBL-3.1.5 - COAL LIQUEFACTION ALLOY TEST PROGRAM

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INTRODUCTION

The objective of the program is to determine the erosion/corrosion behavior of materials used in the flow passages of liquid slurries under conditions representative of those in coal liquefaction systems. From the understanding gained from testing a number of different materials over a range of controlled operating conditions within and beyond those of currently acceptable operating practice, slurry flow operating parameter guidelines and improved performance materials selection and design criteria will be developed.

The program is structured to investigate the major variables inherent in the design and operation of non-aqueous liquid-solid particle slurry systems. These are:

1. flow passage geometry
2. materials of construction
3. slurry composition and properties
4. operating conditions.

Program Plan Summary

1. state-of-the-art determination - completed
2. development and evaluation of test devices - completed
3. determination of the effects of flow passage geometry on erosion-corrosion of materials - in process
4. determination of the behavior of commercial and experimental materials - in process

5. development of an understanding of erosion-corrosion mechanisms
- in process

DISCUSSION OF CURRENT ACTIVITIES

Task 4 - Behavior of Materials

The initial elevated temperature tests in the slurry pot tester at 200 °F for a number of steel alloys resulted in a behavior pattern that has been observed at low elevated temperatures for aluminum in gas-solid particle erosion tests. In general, the erosion rate decreased with the increasing temperature. Fig. 1 shows the effect of temperature on six alloys tested. The A53 and 304SS alloys behaved in a similar manner as they have for all tests performed in the slurry pot. Their rates of erosion were markedly higher than those of the other four alloys tested, particularly at room temperature and 200°F.

The four, more erosion resistant alloys had lower erosion rates at 200°F than at 75°F. The A106 alloy is a finer grain size mild steel of the same nominal composition as the A53 pipe steel. Its lower erosion rate can probably be attributed to its finer grain size. The order of erosion rates with the 410SS having the lowest rate and the mild steel the highest rate has been consistent through the program. The significant increase for all alloys at 350°F is probably more the result of changes in the nature of the slurry than to changes in the erosion resistance of the alloys. A marked reduction in the viscosity of the slurry could cause the increase to occur. Elevated temperature viscosity tests in this temperature range are underway.

Fig. 2 plots seven alloys' erosion vs. time of exposure curves at 200°F for a slurry velocity of 20 fps. At the five hour test time, the spread in the amount of erosion ranged from 2 to 6 gm/cm² x 10⁻⁴, the highest eroding material having three times the erosion of the lowest. This is a considerably greater spread than occurs at room temperature. The reasons for the relative amounts of erosion of each alloy are being studied.

XBL 8110-7151A

Fig. 1 Erosion rate vs. Test Temperature

Fig. 2 Erosion of 7 alloys at 200°F, 20fps

Fig. 3 shows the erosion vs. time curves for six of the alloys at a higher velocity, 40 fps, at 200°F. It can be seen that the erosion rate markedly increases as the velocity of the slurry was increased, the A53 steel eroding five times more at 40fps than at 20fps after five hours of exposure. It is also interesting to note that the order of erosion rate changed among the alloys tested and that the A53 and 304 rates separated from those of the other alloys which were bunched together at a far lower erosion rate range. Fig. 4 shows the difference in the amount of erosion at the two test velocities more graphically.

The effect on the erosion of the test alloys at 350°F, the temperature at which slurries are prepared in the SRC coal liquefaction process is shown in Fig. 5 for a slurry velocity at 20fps. The same type of spread in performance as occurred at 200°F and at 75°F was observed. However, the order of the alloys was different. Again, the greatest amount of erosion occurred in the A53 mild steel. As the erosion time increases, the spread in the amount of erosion between the alloys increases significantly. At the higher temperature, the difference, in erosion between the A53 mild steel and the 304SS begins to reflect the higher strength of the stainless steel at elevated temperatures.

Increasing the erosion velocity to 40fps at 350°F test temperature, Fig. 6, has an interesting effect on the erosion behavior. The curves become straight, indicating that very little comminution of the eroding particles is occurring. Also, the amounts of erosion increase up to eight times greater at the higher velocity as can be seen in Fig. 7.

The jet impingement tester was used to determine the erosion behavior of additional alloys to those reported in the last quarterly report. Fig. 8 and 9 show the erosion of two Cr-Mo steels used in the chemical process industry as a function of impingement angle. As has been observed for other steels, an erosion peak is reached at an angle of 40° followed by a decrease and a subsequent increase toward 90° impingement angle. The 2½ Cr-1Mo and 5Cr-1Mo steels behave nearly the same at the lower velocity, but the higher Cr containing steel

XBL 8110-7157A

Fig. 3 Erosion of 6 alloys at 200°F, 40fps

XRI 8110-7155

Fig. 4 Erosion at 2 different velocities at 200°F

XBL 8110-7141A

Fig. 5 Erosion of 6 alloys at 350°F, 20fps

XBL 811C-7156 A

Fig. 6 Erosion of 6 alloys at 350°F, 40fps

XBL 8110-7152 A

Fig. 7 Erosion at 2 different velocities at 350°F

Fig. 8 Erosion of 2 1/4 Cr-1 Mo steel as a function of impingement angle

Fig. 9 Erosion of 5Cr-1Mc steel as a function of impingement angle

XBL 8110-7143A

erodes less at the 70fps velocity. The general trend is greater erosion at 90° impingement angle than at lower angles, as has been observed in previously tested steels. The 2½Cr-1Mo steel shows this effect most dramatically. The greater erosion resistance of the steel with the higher Cr content has also been observed in slurry pot testing.

It is currently postulated that the higher erosion that occurs at 90° impingement angle has some relation to the role that the lubricity of the liquid plays in impeding erosion. As the angle increases, the eroding particles can strike the surface with more effective vertical force, decreasing the role of lubricity. It is thought that lubricity decreases the effective kinetic energy of the particles striking the surface at more shallow impingement angles.

Task 5 - Erosion Mechanisms

The erosion capability of succeeding quantities of coal-kerosene slurry are shown in Fig. 10. Each 18 gallons of slurry caused the measured erosion plotted on the curve. It can be seen that after 18 gallons of slurry impinged on the 1020 spheroidized steel specimen, each succeeding 18 gallons resulted in the same amount of erosion. The shape of the curve is identical to that found in sequential erosion testing of ductile alloys in gas-solid particle streams, indicating that the erosion mechanism of ductile metals may be the same for both gas-solid particle and liquid-solid particle erosion.

Fig. 11 and 12 show the eroded surface of a 1018 steel and a 304SS specimen, respectively, exposed in the jet impingement tester. The amount and type of deformation that can be seen in the upper photo is typical of that seen on slurry eroded specimens. It is markedly less than the amount of surface deformation seen at much lower magnification on 1018 steel specimens exposed to a gas-solid particle eroding stream at similar test conditions. However, the basic mechanism of material loss appears to be the same, as can be seen in the lower photo in Fig. 11. A crater is formed and platelets of metal are extruded up from it. These platelets are subsequently knocked off the surface after they have been distressed sufficiently.

Fig. 10 Sequential erosion curve for spherical 1020 steel

XBL 8110-7142A

20 μm

5 μm

Fig. 11 Surface of eroded 1018 steel showing platelet formation

20 μ m

5 μ m

Fig. 12 Surface of eroded 304SS steel showing platelet formation

The large deformed area pictured was probably due to the impact of a large particle in a slurry of particles whose average size was less than 75 μ m. The very small craters covering the rest of the surface are typical of the size of plastic deformation caused by impinging particles in a liquid slurry erosion environment. The insulating nature of the viscosity and lubricity properties of the kerosene solvent also prevent impacting particles from making as large a plastically deformed area as they would in gas-solid particle erosion. The difference in the erosion rate between gas-solid particle and liquid-solid particle erosion is several orders of magnitude, the liquid slurries causing the lesser amount of erosion.

CE-3.2.1 -- TOUGHNESS EVALUATION OF SHIELDED METAL ARC AND
SUBMERGED ARC WELDS IN MODIFIED 9 Cr-1 Mo STEEL

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INTRODUCTION

Under subcontract to ORNL, C-E has pursued the development of an improved 9Cr-1Mo steel, modified with additions of V and Cb, to match the elevated temperature strength of austenitic steels while retaining the desirable properties of ferritic steels now used in energy systems. By procuring two 14 Mg (15 ton) steel mill heats, the Fossil Energy Program has expedited the commercialization effort for this material.

One technical objective has been the attainment of mechanical properties in the weld metal which equal those of the wrought base material. Included are the fracture toughness and the temperature range for ductile-brittle transition. Along with high creep strength, the base material exhibits CVN (Charpy V-Notch) impact properties which are consistent and acceptable for application as pressure parts in nuclear power systems. The 68J (50 ft.-lb.) transition temperature is generally less than 10°C (50°F) and upper shelf energy greater than 136J (100 ft.-lb.). An appropriate minimum requirement could be an upper shelf energy of 102J (75 ft.-lb.) and a 68J transition temperature at or below room temperature. Therefore the welding development work has focused on the effect of process and compositional variables on the resultant properties and microstructure of the weld metal.

RESULTS FROM PRIOR QUARTERS

As reported in References 1 through 5, more than 130 lots of filler metal have been made and evaluated. Ductile-brittle transition by Charpy V-Notch (CVN) testing was determined from 157 restrained butt-welds. Potential for achievement of desired weld metal properties was demonstrated¹ at an early stage when using the gas tungsten arc (GTA) welding process. Subsequently, excellent properties in GTA weld metal were also obtained without difficulty at ORNL.^{4,5} However from experience in weldability of alloy steels, the CVN impact properties were expected to be a potential problem when using the conventional slag shielded welding processes. Therefore the major effort has been on these processes, shielded metal arc (SMA) and submerged arc (SA).

Although control of high temperature strength has been demonstrated by alloying with V and Cb, the use of conventional welding slag systems has been an obstacle to achievement of consistent CVN impact properties. As with other high performance alloy steels, the use of modern welding slag systems with higher basicity now appears to be the most practical approach for the modified 9Cr-1Mo steel. Recently, these improved slag systems, now available from several commercial sources, have been used successfully in fabrication of large pressure vessels of 2 1/4Cr-1Mo steel, providing superior weld metal properties.

Over the past several years, 9 Cr-1Mo modified shielded metal arc (SMA) electrodes were used to weld 157 plates with 130 different electrode formulations. The compositions and mechanical properties of these welds have been reported previously.^{1,2,3,4,5} The 9Cr-1Mo welds modified with Cb and V were found to have good creep resistance, but often the toughness did not meet the desired standards. Effects of various weld chemistries have been studied. An electrode which had the necessary composition for creep resistance and which also had the best overall toughness properties was selected as the basis for follow-up work.

In addition to shielded metal arc welds, 2 submerged arc welds had been produced. One was tested for Charpy V-Notch (CVN) properties and found not to meet the desired toughness parameters. The flux was not of the high basicity, low oxygen type.

DISCUSSION OF CURRENT ACTIVITIES

Six SMA welds were completed of which one was a repeat of Lot 125 (M9107) which had the best overall properties from previous work. The core wire was mild steel and alloying of the weld was achieved through the coating. Sixteen submerged arc (SA) welds were made using Oerlikon OP76, a commercial, low oxygen potential, and very high basicity flux. Welds 9SAA3, 9SAA4 and 9SAA10 were made using modified 9Cr-1Mo filler wires. The weld compositions were adjusted, as required, by adding powders containing Cb and V. The CVN impact properties of 6 SMA welds and 10 SA welds are summarized in Table 1. The remaining 6 SA welds are presently being evaluated.

Two SMA welds and 3 SA welds meet the minimum toughness requirements set forth earlier. The toughness of the SMA welds are borderline after 1 hr. at 760°C (1400°F). Of the SA welds that achieve a 68J (50 ft.-lbs.) transition temperature below room temperature, one has low Cb and the other two have been heat treated at 760°C for 2 and 6 hrs. respectively. Three additional SA welds meet the upper shelf criteria, but they reach 68J energy at slightly above room temperature.

Oxygen has a direct effect on upper shelf energy as shown in Fig. 1. As the oxygen is decreased the upper shelf energy increases. The gas tungsten arc (GTA) welds often have low oxygen which appears to result in a high upper shelf energy. By using a high basicity, low oxygen, submerged arc flux, the SA weld oxygen can also be kept to a fairly low level. The SMA welds, in which the coating is highly deoxidizing, also show increased upper shelf energies when the weld oxygen is low.

From earlier results, alloying with Cb and V often appeared to impair weld metal toughness. Fig. 2 shows the 100% Shear FATT versus Columbium. The scatter above the minimum FATT for each level of Cb is

Fig. 1. Effect of oxygen content on CVN upper shelf energy of 9Cr-1Mo welds modified with 0.03 - 0.11 Cb and 0.18 - 0.24 V.

Table 1. Charpy V-Notch Properties of Recent Shielded Metal Arc and Submerged Arc Welds.

P.W.H.T.	Ident.	Hardness	Transition Temp., °F		Upper Shelf
		HRB	50 ft-lbs	100% Shear	Energy
		Avg.		FATT	ft-lbs
<u>SHIELDED METAL ARC</u>					
1400°F, 1 hr.	M9107	95.4	130	212	91
1400°F, 1 hr.	M9916	101.4	150	212	80
1400°F, 1 hr.	M9917	94.5	60	212	92
1400°F, 1 hr.	M9930	91.0	40	212	102
1400°F, 1 hr.	M9942	101.4	212	320	121
1400°F, 1 hr.	M9943	97.2	180	280	68
<u>SUBMERGED ARC</u>					
1400°F, 1 hr.	9SAA3	101.5	130	212	165
1400°F, 1 hr.	9SAA4	96.8	40	280	150
1400°F, 1 hr.	9SAA5	99.6	140	280	113
1400°F, 2 hr.	9SAA6	95.9	140	270	149
1450°F, 1 hr.	9SAA7	94.9	90	160	150
1400°F, 2 hr.	9SAA8	95.6	60	212	150
1400°F, 2 hr.	9SAA9	96.0	90	212	95
1400°F, 2 hr.	9SAA11	96.6	95	212	153
1400°F, 2 hr.	9SAA12	96.0	90	212	151
1400°F, 6 hr.	9SAA17A	93.6	55	212	150

great and can be caused by many factors. However note that the lower edge of the scatter band appears to be sharply defined, indicating that an increase in C_b causes an increase in the FATT. The rest of the scatter may be sorted sometime in the future as we learn the effects that the many variables have on one another.

Fig. 3 shows examples of welds made with three welding processes - GTA, SMA, SA. Their chemical compositions are shown in Table 2. The GTA weld was reported previously by ORNL⁶ and had an excellent transition temperature and upper shelf energy. The submerged arc weld also had excellent upper shelf energy but the transition temperature is slightly above room temperature. The shielded metal arc weld meets both criteria,

Fig. 3. CVN energy of welds having similar chemical composition deposited by different welding processes.

Table 2. Chemical Analysis of Weld Deposits.

Element	Gas Tungsten Arc Ht. No. 30394	Shielded Metal Arc M1917	Submerged Arc 9SAA7
C	0.10	0.065	0.076
Mn	0.46	0.94	0.49
P	0.014	0.003	0.009
S	0.005	0.018	0.009
Si	0.43	0.24	0.32
Ni	0.09	0.02	0.09
Cr	8.37	8.73	9.15
Mo	1.03	1.02	0.85
V	0.199	0.14	0.23
Cb	0.076	0.036	0.062
Ti	0.002	0.007	0.004
Co	0.056	0.013	0.023
Cu	0.04	0.03	0.03
Al ^a	0.013	<0.001	0.007
Al ^b	0.007	-	0.006
B	<0.001	<0.001	<0.001
W	0.05	0.12	0.01
As	<0.001	<0.001	0.002
Sn	0.002	0.001	<0.001
Zr	<0.001	<0.001	0.002
N ₂	0.052	0.034	0.037
O ₂	0.005	0.085	0.032

^a Total^b Soluble

barely. Because of inherent scatter in results from CVN impact tests, a repeat of the SMA test might result in lower toughness. One must realize that the type of flux which is covering the weld puddle can greatly affect the toughness of the weld. In addition, reactions between the various flux ingredients can result in differing microstructures. In the SMA weld, M9930, such a flux coating change resulted in a slight improvement in the transition temperature. Future work will concentrate on:

- (1) welding slag systems for additional improvement in toughness properties

- (2) effect of welding process variables on microstructure and properties.
- (3) clarification of the role of the major alloying elements, such as C, Mn, N, on microstructure and properties.

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UCB-3.2.1(A) - A NEW CLASS OF STEELS FOR THICK
WALL PRESSURE VESSELS

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INTRODUCTION

The objective of this program is to develop a new class of steels that can be field-fabricated into large diameter, thick wall pressure vessels for coal gasification/liquefaction systems. In previous work it was found that in some Fe-C-V-Ni alloys a good combination of strength and toughness could be obtained through an isothermal decomposition into ferrite and vanadium carbide.

The specific objective in the current program is to develop an Fe-C-V-Ni alloy which exhibits strength and toughness comparable to those of commercially available pressure vessel steels, such as A542 (A387) and A533, through a simple continuous cooling process. The program is divided into four tasks as follows:

1. Evaluation of Continuous Cooling Characteristics and Optimization of Composition
2. Vanadium Carbide Dissolution and Coarsening Kinetics
3. Hydrogen Attack Studies
4. Weldability Studies

The continuous cooling characteristics of six different Fe-C-V-Ni alloys will be determined in Task 1. The microstructure-mechanical property relationships in these alloys will be established for various austenitization conditions and cooling rates in order that optimal compositions and heat treatments may be assessed. In Task 2, vanadium carbide coarsening behavior during prolonged tempering at elevated temperatures will be investigated as will be the kinetics of dissolution into austenite when the alloy is heated to the very high temperatures often

encountered during welding. Hydrogen attack susceptibility will be investigated in Task 3 by measuring mechanical property degradation after exposing the alloys to high temperatures and high pressure hydrogen for sustained periods of time. Weldability of the Fe-C-V-Ni alloys will be studied in Task 4. The initial approach in this task is to characterize the microstructure and mechanical properties of the heat affected zone (HAZ) where rapid heating into the austenite range is followed by rapid cooling.

RESULTS FROM PRIOR QUARTERS

Evaluation of Continuous Cooling Characteristics
and Optimization of Composition

Continuous cooling transformation (CCT) curves have been presented in previous reports for the six alloys shown in Table 1 that constituted the initial system of alloys investigated. The start and finish temperatures for the decomposition of austenite appear nearly independent of vanadium and carbon content and seem to be fixed by the amount of nickel in the alloy. However, increasing the vanadium and carbon contents in the alloys has been shown to shift the transformation curves toward shorter times.

Mechanical properties evaluated (for the initial system of alloys) are summarized in Table 2. The best combination of tensile and impact properties for any of the alloys is obtained by austenitizing the material at 900°C. The 0.1C and 0.15C series alloys, after austenitization at 1000°C, were brittle at room temperature, but after austenitization at 900°C showed Charpy impact energies in the range of 170-225 ft-lbs at room temperature. The 0.2C alloys showed excellent impact properties at both 900°C and 1000°C austenitization temperatures while the tensile properties compared favorably with those for the 0.1C and 0.15C alloys. In this connection, from results so far, the 0.2C-1.0V-1.5Ni-0.5Mn alloy may be said to be the optimum composition for the initial system of alloys.

A second series of alloys, containing certain compositional modifications, has been obtained and will be investigated with the objectives of: (1) moving the nose of the pearlite and bainite curves further to the left (i.e., toward shorter times); and (2) raising the temperature (during the continuous cooling process) at which the transformation from austenite to vanadium carbide and ferrite takes place.

Transmission Electron Microscopy

TEM micrographs submitted in previous reports show the microstructures obtained for different compositions, austenitization temperatures, and cooling rates. For the initial series of alloys, the study of the microstructures in relation to the mechanical properties evaluated has shown that a random dispersion of vanadium carbide particles in a ferrite matrix is ideal while a bainite-like microstructure results in mechanical properties that are unsatisfactory. Investigation over the coming months will attempt to arrive at composition and austenitization temperature combinations that will produce the ideal microstructure at faster cooling rates such as might be associated with welding.

Vanadium Carbide Dissolution and Coarsening

Reporting on this task has been deferred in order to permit more time for study and interpretation of data.

Hydrogen Attack Studies

Samples have been prepared for the extended-time exposure of the Fe-C-V-Ni alloys to high pressure hydrogen at 550°C. The hydrogen attack apparatus is very tightly scheduled, however, and has not heretofore been available for use on this project.

Table 1: Chemical Compositions of Alloys

Alloy	Nominal (wt-pct)					
	C	V	Ni	Mn	Nb	Fe
A-1	0.1	0.5	1.5	0.5	0.025	bal
A-2	0.1	0.5	3.0	0.5	0.025	bal
B-1	0.15	0.75	1.5	0.5		bal
B-2	0.15	0.75	3.0	0.5		bal
C-1	0.2	1.0	1.5	0.5		bal
C-2	0.2	1.0	3.0	0.5		bal

Table 2: Mechanical Properties

Alloy	Aust. Temp. °C	Cooling Rate	Yield ksi	UTS ksi	El. %	RA %	CVN (ft-lb)	
							RT	Upper Shelf
A-1	900	1"	60	74	33	73	205	205
A-1	1000	1"	74	95	22	64	3	135
A-1	1000	slow	60	77	31	71	10	135
A-2	900	1"	76	90	31	70	160	165
A-2	1000	1"	113	131	22	60	3	35
A-2	900	fast	70	89	30	69	150	180
A-2	1000	slow	82	103	29	68	7	125
B-1	900	1"	61	75	37	78	225	225
B-1	1000	1"	93	116	24	64	16	152
B-2	900	1"	78	94	32	74	165	165
B-2	1000	1"	136	153	18	46	3	25
B-2	900	fast	85	97	31	72	185	185
C-1	900	1"	62	80	35	76	240	245
C-1	1000	1"	89	106	28	75	235	245
C-1	900	fast	64	75	34	75	-	-
C-1	1000	slow	73	86	34	75	235	240

DISCUSSION OF CURRENT ACTIVITIES

Evaluation of Continuous Cooling Characteristics
and Optimization of Composition

The continuous cooling transformation (CCT) curves for the first series of alloys indicated that undesirable microstructures/mechanical properties are obtained for very fast cooling such as would be expected to take place during welding. Therefore, three additional alloy modifications have been developed in the attempt to obtain desirable microstructures at the fastest cooling rates that might be experienced by an alloy during structural fabrication. The chemical compositions of these alloys are shown in Table 3. Although Alloy C-1 of the first series of alloys appears to have the most desirable mechanical properties, the base alloy selected for modification was Alloy C-2 since this alloy had slower decomposition kinetics and the effect of the alloy modifications could be determined more readily.

Because the effects of the alloying elements on transformation kinetics can best be seen on time, temperature, transformation (TTT) curves, such curves were obtained for the new series of alloys by use of dilatometry. An austenitizing temperature of 1200°C and a holding time of 15 minutes were used on all specimens to ensure that all vanadium and carbon had gone into solution. Figures 1 through 3 are the TTT curves for Alloys C-2, D-1, and D-2, respectively (the TTT curve for Alloy D-3 is not yet complete). From these curves, it is apparent that the 0.5Al addition and the 1.0Si addition move the austenite-to-ferrite starting curve to shorter times by over a factor of 10. The addition of aluminum had a greater effect on the growth kinetics as the completion curve to ferrite for Alloy D-1 is moved to much shorter times while the completion curve to ferrite for Alloy D-2 is hardly affected. Presently, it appears that the addition of 0.5Al has quickened the nucleation and growth kinetics by approximately a factor of 10.

The CCT's for Alloys D-1, D-2, and D-3 are figures 4 through 6, respectively. As indicated by the TTT curve, Alloy D-1 has had its

Table 3: Chemical Compositions of Alloys -
Second Series

Nominal (Wt-pct)								
<u>Alloy</u>	<u>C</u>	<u>V</u>	<u>Ni</u>	<u>Mn</u>	<u>Al</u>	<u>Si</u>	<u>Mo</u>	<u>Fe</u>
D-1	0.2	1.0	3.0	0.5	0.5	--	--	bal
D-2	0.2	1.0	3.0	0.5	--	1.0	--	bal
D-3	0.2	1.0	3.0	0.5	--	--	1.5	bal

Figure 1

Figure 2

Figure 3

Figure 4

Figure 5

Figure 6

CCT curve move dramatically to shorter times. The CCT curve for Alloy D-2 is improved over that for the base alloy but the improvement is not as marked as for Alloy D-1. Figure 6 shows that the addition of molybdenum has completely dominated the decomposition reaction. Alloy D-3 has the decomposition kinetics of a high Ni-Mo alloy. The molybdenum appears to have completely displaced the vanadium as the major carbide former.

UCB-3.2.1(B) -- DESIGN OF LOW ALLOY STEELS FOR
THICK WALLED PRESSURE VESSELS

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INTRODUCTION

The objective of this program is to modify existing commercial low-alloy steels or to develop new alloys which can be field-fabricated into large diameter, thick walled pressure vessels for coal gasification and liquefaction systems.

Emphasis will be placed on evaluating the effects of minor additions of Ni and Mn to 2.25Cr-1Mo steel, and Cr, Mn and Si to Mn-Mo-Ni steel.

Five areas of study have been defined:

- (1) Hydrogen Attack
- (2) Temper Embrittlement
- (3) Fracture Mechanics Testing
- (4) Weldability
- (5) Elevated Temperature Properties

The hydrogen attack study will investigate the metallurgical variables which control the attack susceptibility of low-alloy pressure vessel steels. The influence of microstructure, carbide stability, carbide morphology and alloying elements will be studied in detail. Comparisons will be made between commercial 2.25Cr-1Mo steel, SA533B and their alloy modifications, particularly those containing additional Cr which the Nelson curves predict to have improved hydrogen attack resistance.

Temper embrittlement studies will be continued on the modifications of 2.25Cr-1Mo to determine whether the minor additions of Ni and Mn enhance segregation of phosphorus to prior austenite grain boundaries. Both surface (quenched and tempered) and simulated cooled and tempered (12"-16" 1/4T location) microstructures will be examined. The effects of rare earth elements (mischmetal) in reducing the embrittlement

susceptibility of Cr-Mo and Ni-Cr-Mo steels will be assessed. The effects of impurity element segregation on the hydrogen attack susceptibility of these steels will also be studied.

The fracture mechanics program will obtain J_{Ic} and δ_{Ic} critical crack opening displacement values, using the unloading compliance test method, for the alloy modifications which show improved tensile strengths and charpy impact values. The relationship between these parameters and microstructural variables will be carefully studied.

The weldability study will investigate the nature of heat affected zone microstructures produced in plates of the base steels and their alloy modifications. Bead on plate tests will be used to determine the influence of heat input and preheat temperature on the heat affected zone microstructures. Mechanical property tests will evaluate the welds produced with the different alloy modifications.

Elevated temperature tests will determine whether the minor alloy additions have any major effect on creep rupture properties of these steels.

RESULTS FROM PRIOR QUARTERS

Hydrogen Attack of Model Alloy Systems

Samples of model alloy systems based on Fe-0.15C-0.5Mn with 2 atomic percent Cr, Mo or W have been exposed to hydrogen at 550°C and 1500 psi for 1000 hours. The tensile strength of the base steel was approximately the same as that of the sample exposed 500 hours while ductility in terms of reduction in area showed a 50% decrease in the sample exposed for 1000 hours. The tensile strength and ductility in both the Cr and Mo modifications remained the same for both 500 hour and 1000 hour exposures. The W modification showed a steady decrease in tensile strength, percent strain to fracture, and percent reduction in area as the exposure time increased. Fracture surfaces of all the alloy systems showed typical dimpled rupture failures. It was not possible to distinguish regions of voids attributable to hydrogen attack. However, the W modification showed a small region of intergranular failure with void

formation on the grain boundary facets which might have been a product of methane bubble formation. No sign of hydrogen attack could be detected with scanning electron microscopy in the Cr and Mo modifications.

Temper Embrittlement Study of A543

The effects of rare earth elements on the temper embrittlement susceptibility of A543 (3.5Ni-Cr-Mo) steel were investigated in three sample conditions: (1) A543; (2) Remelt A543; and (3) Remelt A543 plus rare earth elements. The results for base A543 steel have shown that 50 ft-lb impact transition energy shifted from -150°C to $+15^{\circ}\text{C}$ (165°C) for the oil quenched sample after embrittlement treatment and from -132°C to -14°C (118°C) for the simulated cooled samples after isothermal aging. Much larger shifts of the 50 ft-lb impact transition temperature resulted after isothermal aging. The remelt of A543 showed a drastic reduction of upper shelf energy probably due to a high inclusion content in the remelt condition. It thus was not possible to compare 50 ft-lb transition temperatures. However, 30 ft-lb impact energies showed a shift from -175°C to -5°C (180°C) for the oil quenched and tempered material after the isothermal aging treatment. The remelt also showed a comparable shift in transition temperature for the oil quenched and tempered base A543. Data for the remelt plus rare earth addition also showed low values of upper shelf energy when compared to the base steel. However, the 20 ft-lb transition impact energy increased only 20°C (-120°C to -100°C) for the oil quenched and tempered sample and 80°C (-150°C to -70°C) for the simulated cooled and tempered sample after isothermal aging. Although the shifts in 20 ft-lb transition temperatures are significantly lower for the rare earth treated samples, the benefits in terms of reduced susceptibility to temper embrittlement were overshadowed in this case by the high volume fraction of inclusions resulting from poor melting practice.

DISCUSSION OF CURRENT ACTIVITIES

Elevated Temperature Properties

The preliminary results of creep-rupture properties testing of A542 (2 1/4Cr-1Mo) and its modifications have been obtained this quarter. A broad range of creep behavior was closely observed in alloys containing minor compositional changes, mainly with Mn, Ni, Cr and their combinations. The most significant effect of alloy modifications on the creep properties was found to result from additions of Mn and Cr. For example, a 1%Mn addition to the base steel (A542) reduced creep strength as much as 35% at 600°C and 15% at 500°C. The increase in Cr content of about 0.75% combined with additions of 1.0%Ni and 0.5%Mn also decreased the creep strength of A542 but markedly improved long time creep ductility by about eighty to one hundred percent. However, the observed levels of creep strength in the Mn and Cr modified steel, when plotted on Larson-Miller parameters and compared with a conventional 2 1/4Cr-1Mo steel, were found to be within the scatter band for creep test results for various heat treatment conditions in the conventional 2 1/4Cr-1Mo steels¹. Detailed microstructural studies of the crept specimens in relation to the creep rupture mechanisms are currently underway.

Specimen preparation procedures and chemical compositions of the alloys tested have been reported previously² (See Table I). All test specimens were austenitized at 1000°C for 1 hour followed by a simulated cool at a rate corresponding to the quarter thickness location of 12 inch thick plates. Tempering was carried out at 650°C for 4 hours followed by water quench. Creep-rupture tests were conducted with smooth round bar specimens, having a 1 inch gauge length and a quarter inch diameter, in accordance with ASTM E-370 at three temperatures (600°C, 560°C, and 500°C) for durations of up to 1000 hours. The creep rates were closely monitored on the mounted-in dial gauge until specimens fractured.

Figure 1 (a,b, and c) presents the results of observed creep strengths plotted as a function of rupture time on a log-log scale at three different temperatures. The general effect of minor compositional changes on creep-rupture strength seems to be clearly visible although

Table I: Chemical Compositions of
A542 & Its Modifications

(wt/pct)

Steel Designation	C	Mn	Mo	Ni	Cr	Si	S	P	V	Al	Cu
A542 base*	0.15	0.42	0.91	0.10	2.18	0.30	0.009	0.015	-	0.019	0.08
543* (A542 + 1Mn)	0.15	1.50	0.96	0.13	2.25	0.33	0.007	0.009	-	0.021	0.09
547* (A542 + 0.5Mn + 0.5Ni)	0.15	0.92	1.03	0.51	2.27	0.28	0.008	0.013	-	0.021	0.09
548** (A542 + 0.5Mn + 0.5Ni)	0.16	0.92	1.03	0.51	2.25	0.28	0.008	0.013	0.022	0.035	0.09
550* (A542 + 0.5Mn + 1.0Ni)	0.16	0.95	1.02	1.02	2.29	0.29	0.007	0.014	-	0.014	0.10
551* (A542 + 0.75Cr + 0.5Mn+1.0Ni)	0.15	0.94	0.98	0.97	2.96	0.28	0.008	0.010	-	0.014	0.09

* 150-lb ingot cast by Lukens Steel Company

** Grain refined, 150-lb ingot cast by Lukens Steel Company

Figure 1

only a few data points for each alloy have been plotted. The increase in minor alloying composition for the A542 steel generally decreased creep strength throughout the temperature ranges investigated.

The creep-rupture strength of A542 and its modifications may be summarized as follows:

- a. Effect of Mn Additions. The 1% Mn modifications, when compared to the base steel (A542), caused a marked reduction in creep strength -- approximately 30% at 600°C and 15% at 500°C.
- b. Effects of Mn and Ni Additions. The 0.5%Mn + 0.5%Ni modifications, when compared to A542, also exhibited a reduction in creep strength but only about half of that observed in the 1%Mn modification.
- c. Effect of Ni Additions. The 0.5%Mn + 1.0% Ni modification, when compared to the 0.5%Mn + 0.5%Ni modification, did not change the level of creep strength thus indicating that the addition of extra Ni had not caused any significant changes in creep strength.
- d. Effect of V Additions. The 0.5%Mn + 0.5%Ni + 0.2%V modification has shown a small improvement in creep strength when compared to the 0.5%Mn + 0.5%Ni modification.
- e. Effect of Cr Additions. The addition of 0.75%Cr to the 0.5%Mn + 1.0%Ni modification resulted in reduction of creep strength by about 38% at 600°C and 18% at 500°C.

The present data on creep rupture strength have been compared with the currently published creep data by utilizing Larson-Miller's parameter method. Figure 2 plots A542 and its modifications in this manner together with the observed range of rupture strengths from conventional 2 1/4Cr-1Mo steel with various heat treatment procedures. It is clear from this comparison that the rupture strength of the present alloy systems lies within the upper side of the scatter band for slow cooled and tempered conditions of the reported data.

Figure 3 compares the present creep-rupture strength of A542 and 0.75%Cr + 0.5%Mn + 1.0%Ni modification to the strength level of 3Cr-1Mo steel developed by Lukens Steel Company³. It shows that the present 3Cr-1Mo steel is comparable to the low strength 2 1/4Cr-1Mo steel in the quenched and tempered condition while A542 exhibits only

Figure 2. Relationship Between Rupture Stress and Larson-Miller Parameter & Comparison with Conventional $2\frac{1}{4}$ Cr-1Mo Steel with Various Heat Treatments

Figure 3

slightly lower values of rupture strength than high strength quenched and tempered 2 1/4Cr-1Mo steel. This comparison seems to suggest that the creep strength of the present alloy compositions is not directly related to room temperature strength contrary to the results observed by Gulya and Marshall ³.

A comparison also has been made with 3Cr-1Mo steel developed by Climax Molybdenum Company as shown in Figure 4. It is shown that the creep strength of the present 3Cr-1Mo system lies at a much lower level than that for the alloy developed by Wada et al ⁴. It is noted, however, that their (Wada et al) 3Cr-1Mo steel contained much higher levels of Mo and V than the present 3Cr-1Mo steel.

A comparison of the present results of A542 and 3Cr-1Mo steels has also been made with the data of a conventional 2 1/4Cr-1Mo and vanadium modification developed by the Japan Steel Works. The present 3Cr-1Mo steel seems to be comparable to their conventional 2 1/4Cr-1Mo steel while A542 is comparable to their vanadium modified steel as shown in Figure 5. However, interpreting differences in creep strength in terms of minor alloying composition differences, when making comparisons with other industrial alloy systems, should be done with caution since a slight modification of heat treatment in itself may significantly alter creep strength. The detailed microstructural comparison with other laboratory materials is currently underway.

The variations of creep rupture ductility in terms of reduction in area in A542 and its modifications, plotted against rupture time, are shown in Figure 6 (a, b, and c). Notable features of this result were two distinctive curves of the reduced rupture ductility at the longer test times. In both the 1%Mn modification and the 0.5%Mn + 0.5%Ni modifications there has not been any improvement in creep ductility. It has been usually expected that a decrease in the level of rupture ductility is associated with an increase in high creep strength, as has been observed in A542. It is uncertain at the present time whether a reduction in ductility in Mn modified 2 1/4Cr-1Mo steel is related to the creep embrittlement phenomenon. In contrast to the Mn modification, the addition of 0.5%Ni to the 0.5%Mn + 0.5%Ni modification has improved the

Figure 4

Figure 5

Figure 6. Rupture Ductility in Terms of Reduction in Area (%)

creep rupture ductility without sacrificing creep strength. The modification with Cr has also improved rupture ductility although creep strength has been substantially lost when compared to the 1.0%Ni + 0.5%Mn modification. The preliminary examination of a few crept samples indicates that the development of low rupture ductility in A542, 543, and 547 steels seems to be associated with intergranular cracking along prior austenite grain boundaries. Further detailed microstructural examination, using TEM and SEM, will be needed and is currently in progress.

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UTN-3.2.1 - INVESTIGATION OF THE TRANSFORMATIONAL
CHARACTERISTICS AND COLD CRACKING SENSITIVITY
OF MODIFIED 9 Cr-1 Mo STEEL

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INTRODUCTION

A candidate replacement material for coal conversion reactor systems is a modified 9 Cr - 1 Mo ferritic alloy. An alloy with higher hardenability than 2 1/4 Cr - 1 Mo will be required in reactor vessels, since vessel wall thickness will be much greater in coal conversion systems and strength levels at mid-thickness regions can only be attained with higher alloy materials.

Use of a 9 Cr - 1 Mo material would allow the construction of larger vessels, since strength levels will be maintained to greater depths through the wall thickness. A further consideration in the selection of an alloy for use in coal conversion units is the ability to successfully fabricate a vessel which will give expected service. The most critical aspect of fabrication is the welding of the structure. The optimum preheat and post-weld heat treatments need to be determined so that fabrication problems are minimized. The specific tasks to be conducted for a definitive study of the weldability and HAZ reactions in 9 Cr - 1 Mo are delineated as

- (1) Determining the Ac_1 , Ac_3 , M_s and M_f temperatures at different heating and cooling rates.
- (2) Determining the location of the nose of the CCT diagram under appropriate cooling conditions.
- (3) Determining the stress relief cracking potential of standard and modified heats of 9 Cr - 1 Mo.
- (4) The conduct of Battelle underbead cracking tests on standard and modified heats of 9 Cr - 1 Mo.
- (5) The use of a hydrogen sensitivity test developed at the University of Tennessee to evaluate weldability of standard and modified heats of 9 Cr - 1 Mo.

RESULTS FROM PRIOR QUARTERS

Transformation Studies

The on heating transformation temperatures and the on cooling transformation temperatures were determined for a standard heat of 9 Cr and a modified heat of 9 Cr by the dilatometric technique employing the Gleeble apparatus. The heating rates, 10°F/second, 50°F/second and 100°F/second were used and the initial microstructure was varied to simulate a weld HAZ. The initial microstructure was varied by employing a series of subsequent thermal cycles. The initial condition of the material was normalized and tempered. Material in this condition was first subjected to a thermal cycle with a peak temperature of 1800°F, just above the Ac_3 producing a fine grain austenitic structure which subsequently transformed to martensite upon cooling. The Ac_1 and Ac_3 temperatures determined during the first cycle show the effect of the N & T starting microstructure. Ac_1 and Ac_3 temperatures determined during the second thermal cycle show the effect of an untempered grain refined martensitic structure, as would be seen in the grain refined regions of HAZ's in multipass welds. The peak temperature of the second thermal cycle was 2400°F, producing coarsening of the austenite grains, simulating the coarse grain region of the HAZ near the fusion line of a weld. The third thermal cycle was similar to the second, the peak temperature was again 2400°F. The effect of a martensitic microstructure transformed from coarse grained austenite was seen in this cycle.

Transformation studies thus far have shown that in the standard and modified 9 Cr, Ac_1 and Ac_3 temperatures are influenced by heating rate and starting microstructure. The modified 9 Cr showed lower Ac_1 and Ac_3 temperatures than did the standard 9 Cr, reflecting the difference in chemistry of the two materials. The M_s temperature for the two materials was approximately the same. Initial isothermal transformation studies indicate markedly different response in the modified 9 Cr materials wherein the austenite is stable for longer periods of time, indicating a shift in the ferrite nose. The

isothermal response of the modified 9 Cr materials requires further study to determine the influence of alloying elements if this heat treatment is to be used commercially.

Stress Relief Cracking Evaluation

The stress relief cracking potential of a standard 9 Cr and a modified 9 Cr was evaluated to determine if there is a potential for stress relief cracking in these materials. In order to establish a base line for PWHT response, tests were conducted on specimens in the as-received condition (N & T) to establish the stress required to produce a short time rupture (less than 2 hours) at 1350°F, the normal PWHT temperature. Tests were conducted by imposing a constant load (stress), then heating to 1350°F and maintaining the load and temperature constant until rupture. With the stress range for short time rupture established, stress relief cracking evaluations were conducted by imposing a controlled thermal cycle to produce the microstructure seen in the coarse grained HAZ, the region of the HAZ where stress relief cracking is observed. The thermal cycle employed represented a 50 kJ/in thermal cycle in 1 inch plate with a peak temperature of 2300°F. After the weld thermal cycle and cooling to room temperature, the specimen was stressed and heated at 200°F/sec. to 1350°F. This simulates a restrained weldment and PWHT. The specimens were held at the temperature and stress until rupture.

Initial stress relief cracking studies indicate that the modified 9 Cr alloy may not be susceptible to stress relief cracking. A decrease in ductility was observed in samples which underwent a weld thermal cycle as compared to samples which were tested without a weld thermal cycle. This ductility was high though in comparison to ductilities observed in test samples of steels with a susceptibility to stress relief cracking evaluated with similar techniques. Further work in this area is indicated to insure that these preliminary results hold true for other modified 9 Cr alloys and other weld thermal cycles.

Weldability Testing

Battelle Underbead Crack Tests

The standard test consists of depositing a weld bead with a 1/8 inch diameter E 6010 electrode using a current of 100 amperes at 24 to 26 volts and travel speed of 10 inches per minute (energy input 15,000 joules per inch). The specimens can be precooled or preheated to any desired temperature. After welding, the specimen is held at 60°F (room temperature) for 24 hours and then tempered at 1100°F for 1 hour. This tempering treatment is recommended to avoid any cracking that may occur during cutting and grinding. A longitudinal section through the weld is taken and the presence of underbead cracks is detected by either magnetic particle or metallographic techniques. As reported by researchers at Battelle, and also from work conducted at the University of Tennessee, the Battelle underbead cracking test has been found to be very useful in correlating underbead cracking susceptibilities of plain carbon and low alloy steels to their compositions (and hence hardenability). Preheat temperatures needed to avoid cracking can be established using the test and these agree well with those determined by practice.

The results of the testing until now with the underbead cracking test indicate that this test was not successful in evaluating the weldabilities of the 9 Cr and 12 Cr steels. Despite the fact that electrodes of matching composition which had been exposed to humidity were used, the HAZ's of either of steels remained unsusceptible to cracking. Autogenous welds with even 10% H₂ failed to cause HAZ cracking. The low restraint produced in the Battelle underbead cracking specimen is probably the reason why the test has failed to reveal the crack sensitivities of the 9 Cr and 12 Cr steels.

University of Tennessee Hydrogen Sensitivity Test

The Hydrogen cracking susceptibility samples are prepared by making autogenous GTA welds on the 1/8" thick coupons. During the deposition of the welds, H₂ is added to the shielding gas to saturate

the weld fusion zone with H_2 . Fig. 1 lists the welding parameters used. Five minutes after welding, the samples are strained in an apparatus shown in Figure 2. The augmented strain on the top surface of the weld in the longitudinal direction is given by:

$$\epsilon = \frac{t}{2R}$$

where: ϵ = augmented strain

t = specimen thickness

R = bending radius

By varying the bending radius, strain levels of 4%, 2% and 1% can be obtained. Cracking can be evaluated as a function of preheat temperature (70°F in this case) and test temperature (70° or 32°F). Cracking can also be evaluated as a function of heat input, and the amount of hydrogen in the shielding gas. Limited testing has been carried out on one heat of modified 9 Cr (No 176) and HT - 9. The modified 9 Cr and HT - 9 were welded at room temperature (70°F) and bent at room temperature (70°F). The modified 9 Cr did not crack whereas the 12 Cr did. The modified 9 Cr was then welded at 70°F and bent at 32°F. Cracking occurred 2 1/2 minutes after bending. This probably is due to the lowered ductility of the 9 Cr at 32°F. At this point of testing, it was becoming clear that the 9 Cr steel despite its high hardenability was showing very little susceptibility to cracking. Even in the hydrogen sensitivity test, where an external strain is applied to the sample, the 9 Cr steel had to be bent at a low temperature (32°F) to induce cracking. At the University of Tennessee, the hydrogen sensitivity test has been used with considerable success to rate plain carbon and low alloy steels with regard to their crack sensitivities. Since the amount of diffusible hydrogen also is an important factor, besides hardenability, which contributes to cold cracking, it was decided to conduct diffusible hydrogen studies on hydrogen sensitivity samples of 9 Cr and carbon steel. It was found that virtually no diffusible hydrogen evolved from the 9 Cr sample.

HYDROGEN SUSCEPTIBILITY TEST

Current	80 - 100 amps
Voltage	10 v
Travel Speed	5 ipm
Shielding gas	5% H ₂ , 95% A
Electrode	2% thoriated tungsten 1/16" dia.

Figure 1

**SCHEMATIC DIAGRAM OF
APPARATUS USED TO
STRAIN SPECIMEN**

Figure 2

When diffusible hydrogen measurements were conducted on the sample of plain carbon steel, 2.75 ml of hydrogen per 100 grams of weld metal was evolved. This preliminary test indicates that the solubility/diffusivity hydrogen in high Cr (9 Cr) is different from that in plain carbon steels.

DISCUSSION OF CURRENT ACTIVITIES

Hydrogen Sensitivity Tests

The susceptibility of one standard heat and four modified heats of 9 Cr - 1 Mo and one heat of 12 Cr - 1 Mo (HT-9) to cold cracking, are currently being evaluated using the UT Hydrogen Sensitivity Test. The compositions of these steels are given in Table 1. The samples were evaluated on a go no-go basis as cracked or not cracked. Cracking susceptibility was evaluated as a function of preheat, post weld weld, bending temperature and strain.

Results of Tests on 9 Cr - 1 Mo

Samples from one standard heat and four modified heats of 9 Cr - 1 Mo were welded at room temperature (85°F) and bent to 4% augmented strain at 32°F. 32°F was chosen because it is below the DBTT of the weld region of the 9 Cr - 1 Mo, and can be easily attained with an ice bath. Cracking occurred in all the samples within 2 - 5 minutes after bending. The delayed nature of the cracking became very apparent as testing progressed.

To confirm the fact that hydrogen was responsible for the delayed cracking, samples from the standard heat and modified heat 176 were welded at room temperature without any hydrogen in the shielding gas (100% Ar), and bent to 4% strain at 32°F. No cracking resulted even after a hold of 30 minutes. This result clearly demonstrated the role of hydrogen in promoting delayed cracking. Samples from the standard heat and modified heat 176 were then welded at 85°F and bent at 85°F to an augmented strain of 4%. No cracking was observed in these samples. The results summarized in Table 2 indicated that the

Table 1. Plate Chemistry - 9 Cr

Heat No.	30176-1	30383-1	30394	10148	K48603F	9-607
Type	Mod 9Cr	Mod 9Cr	Mod 9Cr	Mod 9Cr	STD - 9Cr	HT - 9
C	.081	.083	.084	0.089	0.065	0.20
Mn	.37	.46	.46	0.47	0.41	0.61
P	.010	.010	.010	0.021	0.025	0.016
S	.003	.004	.003	0.006	0.004	0.007
Si	.11	.41	.40	0.28	0.44	0.26
Ni	.09	.09	.09	0.16		0.54
Cr	8.61	8.46	8.57	9.24	9.12	11.65
Mo	.89	1.02	1.02	0.96	0.96	1.02
V	.209	.198	.198	0.21		0.29
Cb/Ta	.072	.072	.073	0.054		0.01
Ti	.004	.005	.005	0.002		<0.01
Co	0.10	.055	.055	0.019		0.09
Cu	.04	.03	.04	0.08		0.03
Al	.007	.002	.014	0.002		0.009
B	<.001	<.001	<.001	<0.001		0.001
W	<.01	.05	.05	0.01		0.61
As	.001	<.001	<.001	0.002		0.004
Sn	<.001	<.001	<.001	0.004		0.001
Zr	<.-01	<.001	<.001	0.001		0.002
Fe						
N	0.055	0.051	0.053	0.035		0.041
O				0.008		0.013

Table 2. Results of H₂ Sensitivity Tests on 9 Cr - 1 Mo

<u>Heat No.</u>	<u>Preheat temp (°F)</u>	<u>Postweld Hold</u>	<u>Bend temp. (°F)</u>	<u>Strain</u>	<u>Result</u>
<u>Tests Using 95% Ar+5% H₂</u>					
Std 9 Cr (K48603F)	85	-	32	4%	Cracked 4 mins. after bending
Mod. Ht. 176	85	-	32	4%	Cracked 2 1/2 min. after bending
Mod. Ht. 383	85	-	32	4%	Cracked 3 mins. after bending
Mod. Ht. 394	85	-	32	4%	Cracked 2 mins. after bending
Mod. Ht. 148	85	-	32	4%	Cracked 5 mins. after bending
Std. 9 Cr (K486303F)	85	-	85	4%	No cracking
Mod. Ht. 176	85	-	85	4%	No cracking
<u>Tests Using 100% Ar</u>					
Std. 9 Cr (K48603F)	85	-	32	4%	No cracking
Mod. Ht. 176	85	-	32	4%	No cracking

standard and modified 9 Cr behave basically in the same fashion as far as susceptibility to hydrogen/delayed cracking is concerned. Hardness measurements in the fused zone indicated a hardness of HRC 37 for the standard 9 Cr, whereas the modified heats showed a fused zone hardness of HRC 41. This difference is probably due to the lower carbon content of the standard 9 Cr when compared to that of the modified heats. Future work will include the study of the effect of strain level and post weld hold on all heats of 9 Cr - 1 Mo.

Results of Tests on 12% Cr - 1 Mo (HT-9)

Hydrogen sensitivity samples of HT-9 were initially welded at room temperature (85°F) and bent to a strain of 4% at room temperature (85°F). Cracking occurred immediately during bending. The same result was obtained where the strain was reduced to 2% and then 1%. Raising the preheat level to 200°F, 400°F and finally 600°F resulted in no change in the cracking sensitivity as shown in Table 3. The fused zone hardness remained the same at all the preheats (HRC 51-52). These results confirmed the fact that the air hardening nature of the steel gave rise to fully quenched martensite, having hardness much higher than that predicted by the carbon content, probably resulting from the contribution of Cr towards solution hardening. Specimen of HT-9 were then welded at 700°F. This temperature is above the M_s (570°F)¹ of 12% Cr-steel which has 0.1%C. Since the 12% Cr steel being studied contains 0.2%C, the M_s can be expected to be even lower. After welding, the specimens were immediately transferred to a furnace at 700°F and held at this temperature for two hours. At the end of the post weld hold period, the specimens were brought to room temperature by quenching in water and bent to augmented strains of 4%, 2% and 1%. The samples bent to 4% strain cracked during bending, whereas samples bent to 2% and 1% strains cracked 2 minutes and 4 minutes after bending respectively. Evidently the post-weld hold treatment (700°F/2hrs) was not sufficient to drive off all the hydrogen from the weld. To confirm the conclusion that hydrogen was responsible for the delayed nature of cracking, samples of HT-9 were welded using 100% Ar (without any H₂)

Table 3. Results of H₂ Sensitivity Tests on 12% Cr - 1% Mo (HT - 9)

<u>Heat No.</u>	<u>Preheat temp (°F)</u>	<u>Postweld Hold</u>	<u>Bend temp. (%)</u>	<u>Strain</u>	<u>Result</u>
<u>Tests Using 95% Ar+5%H₂</u>					
HT - 9	85	-	85	4%	Cracked during bending
"	85	-	85	2%	"
"	85	-	85	1%	"
"	200	-	85	4%	"
"	200	-	85	2%	"
"	400	-	85	4%	"
"	600	-	85	4%	"
"	600	-	85	2%	"
"	600	-	85	1%	"
"	700	700°F/2 hrs.	85	4%	"
"	700	700°F/2 hrs.	85	2%	Cracked 1 min. after bending
"	700	700°F/2 hrs.	85	1%	Cracked 2 min. after bending
<u>Tests Using 100% Ar</u>					
HT - 9	700	700°F/2 hrs.	85	4%	Cracked during bending
"	700	700°F/2 hrs.	85	2%	No Cracking
"	700	700°F/2 hrs.	85	1%	No Cracking

using the same preheat and postweld hold conditions (preheat 700°F, postweld hold 700°F/2hrs). After cooling the samples to room temperature, they were bent to augmented strains of 4%, 2% and 1%. The sample strained to 4% cracked during bending, whereas the samples strained to 2% and 1% did not crack on bending even after holding them in the bending device for 30 minutes. The results of these experiments clearly indicate the contribution of hydrogen towards the delayed nature of cracking. Future testing with HT-9 will include post weld holds at higher temperatures for longer times and post weld heat treatments below A_1 .

Conclusions

Results of hydrogen sensitivity tests with standard and modified heats of 9 Cr - 1 Mo indicate that the susceptibilities of the standard and modified heats towards hydrogen induced cracking are the same under the test conditions utilized. The necessity for the presence of hydrogen to cause cracking has been demonstrated. Further testing using various strain levels and post weld hold treatments will help to shed more light on any differences in susceptibilities, if they do exist.

Preliminary testing with the 12% Cr - 1 Mo (HT-9) has shown it to be highly susceptible to hydrogen induced cracking. The high hardenability of the steel coupled with its carbon content make it extremely susceptible to cracking. At the highest strain level employed (4%), HT-9 was found to crack without hydrogen. However, at lower strains (2% and 1%) cracking did not occur without hydrogen. Thus at lowered strain levels the susceptibility to cracking depends on whether hydrogen is present. Post weld holds at 700°F/2hrs did not eliminate cracking in the 12% Cr - 1 Mo steel. Future tests will include higher post weld hold temperatures and longer times. Post weld heat treatment below A_1 have also been included in the testing schedule.

Stress Relief Cracking Tests

Stress relief cracking tests were completed on the standard 9 Cr - 1 Mo and modified heat 176 to expand the results reported earlier. Stress relief cracking evaluations were made by imposing a controlled thermal cycle to produce the microstructure seen in the coarse grained HAZ, the region where stress relief cracking is observed. The thermal cycle simulated a 50KJ/in. heat input in a 1 inch plate, with a peak temperature of 2300°F. After the weld thermal cycle the specimen was stressed and heated at 200°F/sec to 1350°F. The thermal cycle and the application of stress are schematically shown in Fig. 3. This simulates a restrained weldment and PWHT. The specimens were held at the temperature and stress with rupture.

The results of the confirmatory tests as well as these reported in the earlier progress report are summarized in Table 4. The results show that the time to rupture for equivalent stress was greater for the thermal cycled samples than for the N and T samples. This is because the weld thermal cycle samples had untempered martensite resulting from the 2300°F peak thermal cycle. A lower ductility is seen in the modified 9 Cr samples which were first subjected to the weld thermal cycle as compared to the modified 9 Cr base line samples. The standard 9 Cr samples tested after the 2300°F peak thermal cycle did not exhibit a reduced ductility when compared to the standard 9 Cr base line samples. The confirming tests carried out showed the same trend as for values of stress and time to rupture are concerned. The results indicate that the modified 9 Cr may not be susceptible to stress relief cracking. A difference in ductility was observed in samples which underwent a weld thermal cycle as compared to samples which were tested without a weld thermal cycle. However, this ductility was high enough in comparison to ductilities observed in test samples of steel with a susceptibility to stress relief cracking evaluated with similar techniques.

The testing of all heats is continuing and the relative cracking tendencies of the standard vs. modified materials will be evident as the results are obtained.

STRESS RELIEF (REHEAT) CRACKING EVALUATION

STANDARD AND MODIFIED 9 Cr

Figure 3

Table 4. Stress Relief Cracking Evaluation

MATERIAL	THERMAL HISTORY	STRESS PSI	TIME TO RUPTURE	DUCTILITY (R.A.)
Std 9Cr (HT.K4860-3F)	N & T 200°F/s to 1350°F Hold to Rupture	22,000	1 min 30 sec	78%
Std 9Cr (HT.K4860-3F)	N & T 200°F/s to 1350°F Hold to Rupture	15,000	11 minutes	85%
Mod 9Cr HT. 176	N & T 200°F/s to 1350°F Hold to Rupture	21,400	10 min 30 sec	87%
*Std 9Cr (HT.K4860-3F)	50Kj/in - 2300°F Thermal Cycle Then 200°F/s to 1350°F Hold to Rupture	12,000	57 min 10 sec	78%
* "	"	15,000	10 minutes	82%
"	"	14,200	7 min 30 sec	81%
* "	"	18,000	4 min 20 sec	85%
"	"	20,200	1 min 30 sec	86%
Mod 9Cr (HT. 176)	"	20,400	48 minutes	56%
* "	"	24,000	46 min 55 sec	40%
* "	"	27,000	21 minutes	38%
"	"	31,600	13 minutes	35%
* "	"	30,000	8 min 55 sec	39%
"	"	35,700	8 minutes	35%
* "	"	33,000	7 min 45 sec	42%
* "	"	39,000	5 min 50 sec	39%
"	"	42,500	2 min 50 sec	49%

*confirming tests

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ORNL-3.2.2 - WELDING SUPPORT AND DEVELOPMENT

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INTRODUCTION

The purpose of this task is to investigate and develop economical techniques for welding and cladding critical components, to help evaluate and characterize heavy-section weldments, and to provide general consultation for welding of coal conversion systems.

RESULTS FROM PRIOR QUARTERS

During previous quarters, we have obtained a submerged-arc (SA) weldment from Chicago Bridge and Iron Company (CB&I) in 300-mm-thick 2 1/4 Cr-1 Mo steel plate. Evaluation of the weldment has included microstructural analysis, microhardness testing, Charpy impact testing, and postweld heat treatment (PWHT) studies. Charpy impact specimens from the chromium-molybdenum plate have also been exposed to simulated weld heat-affected zone (HAZ) thermal cycles for comparison to results from testing of the actual weldment HAZ. Finally, stainless steel weld overlay clads have been procured from a commercial manufacturer for evaluation. Present evaluation includes corrosion testing in SRC-I (sponsored by another program), fatigue testing (sponsored by another program), microstructural analysis, chemical analysis, microhardness testing, PWHT studies, and bend testing.

DISCUSSION OF CURRENT ACTIVITIES

During this reporting period we have evaluated room-temperature Charpy-impact properties of specimens exposed to thermal cycles to simulate multipass-weld heat-affected zones (HAZs). Specimens cut from a 300-mm-thick 2 1/4 Cr-1 Mo steel plate were reported in the previous

quarterly report.¹ Single-cycle specimens were previously evaluated. Specimens exposed to the two and three thermal cycles (Table 1) were tested in the as-welded and PWHT (690°C for 28 h) conditions. For as-welded specimens a second thermal cycle to temperatures above the A_{c1} (cycles K and L) does not significantly affect toughness. A second thermal cycle below the A_{c1} (cycles M, N, P, and R) significantly improves toughness, particularly for specimens heated to 1370°C on the first cycle. For the three-cycle specimens (cycles S and T), the intermediate cycles (955°C peak/17°C/s cooling rate) do not affect toughness significantly. As expected PWHT significantly improves the toughness of all simulated HAZ specimens except those exposed to a thermal cycle below the A_{c1} , where significant tempering has already occurred.

Table 1. Thermal cycles for simulated heat-affected zone study

Cycle	Thermal cycles, peak temperature (°C)/cooling rate (°C/s)		
	First	Second	Third
K	1370/44	955/17	
L	1370/22	955/17	
M	1370/44	730/11	
N	1370/22	730/11	
P	955/22	730/11	
R	955/17	730/11	
S	1370/44	955/17	730/11
T	1370/22	955/17	730/11

From metallographic examinations the following observations were made for fusion line Charpy-impact specimens.

1. For non-heat-treated specimens exposed to thermal cycles above the A_{c1} , most failures occurred in the coarse-grain HAZ.

2. For the non-heat-treated specimens exposed to thermal cycles below the Ac_1 , failures occurred in random locations.

3. For heat-treated specimens, failures occurred in random locations. One specimen failed in the weld metal along a plane of porosity and trapped slag. About 8% of the failure surface was covered with pores. Impact energy for this specimen was about 18% lower than that for the average but was still adequate (78 J upper shelf) for Code requirements. This level of porosity may seriously degrade fatigue properties of the weldment. A final report is in progress.

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PNST-3.2.2 - AN X-RAY STUDY OF RESIDUAL STRESSES
IN NARROW GROOVE TIG WELDMENTS

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INTRODUCTION

This study is to compare the residual stress field resulting from certain other types of welds to that of narrow gap hot wire gas tungsten arc (GTA) welds. It has been proposed that narrow gap (groove) welding could lead to the reduction of stress relief treatment in heavy 2.25 Cr - 1 Mo Steel sections. Furthermore, the low distortion resulting from the GTA process alone is indicative of lower residual stress inducement. As an integral part of this project, procedures for measuring three-dimensional residual stress contours in low alloy steel plate will be developed for application of a new type of x-ray stress analyzer developed by the principal investigator. Both x-ray and stress relief techniques will be applied to provide three-dimensional stress contours in the 2.25 Cr - 1 Mo Steel weldments.

RESULTS FROM PRIOR QUARTERS

In the first quarter ordering of components for the x-ray stress analyzer was initiated and the task I literature search begun and was completed in the second quarter. Also, in the second quarter, the design of the stress measurement carriage apparatus was completed and fabrication initiated and the major electronic equipment components were procured.

Assembly of the x-ray stress measurement instrument and computer controller was initiated in the third quarter as well as the search for an A387 plate source and weldment specimen fabricator.

In the fourth quarter initial software data refinement listings were written and x-ray stress data was synthesized to test the software. The search for suitable steel plate sources and weldment fabricators progressed as well as the survey of logistics problems in specimen machining, handling, and transportation. Two trips were made: one to review weldment characteristics and one to report to ORNL. Procurement and assembly of the x-ray stress instrument continued.

In the fifth quarter calibration and test fixtures for x-ray residual stress measurement were designed and fabricated. Design and fabrication of the stress head X-Y carriage continued, and procurement, assembly, and testing of the computer controller for the stress instrument progressed. Simultaneously, writing of software for data refinement continued. The most probable contour of the three-dimensional stress field which would be encountered in heavy steel plate weldments was determined from information supplied in an earlier literature search.

In the sixth quarter fabrication, assembly, and testing of the X-Y positioning stage and x-ray source was completed, and the frame for its mounting and positioning was designed. Incident x-ray beam collimators for the stress head were designed and fabricated as well as a special film holder for film camera work. Assembly of the x-ray stress analyzer computer controller was completed and found operational with the initial utility software. The software for K-alpha-two stripping and Lorentz-Polarization and Absorption correction was completed and tested on synthetic data. The experimental problems caused by increasing the specimen thickness from eight to twelve inches was studied, especially with respect to cutting and handling of the relatively massive specimens that would be needed.

In the seventh quarter, the x-ray stress instrument was completed and installed in the laboratory. Training in the operation and maintenance of the instrument was accomplished. Testing to characterize the operational parameters of the instrument as applied to x-ray stress measurement are in progress.

DISCUSSION OF CURRENT ACTIVITIES

Final assembly of the x-ray stress analyzer was completed and the data refinement and utility software were meshed and installed. Pre-delivery testing was performed at the manufacturer's site to insure that the instrument was operating as designed.

Two weeks of training on the operation and maintenance of the position sensitive detector and computer were obtained by PSU personnel at the manufacturer's facility. At the conclusion of this training, the instrument was disassembled and shipped to PSU. Upon reassembly and installation, characterization testing was initiated. This required that the detector be mounted on an x-ray tube source and the fiber optic detector surfaces positioned suitably for the required x-ray optics. Adjustments were made to the x-ray collimator and filters to provide suitable x-ray results. Testing and characterization are continuing in order to isolate hardware problems and develop optimum data refinement algorithms.

WEC-3.2.2 — DEVELOPMENT OF AUTOMATED WELDING PROCESS FOR
FIELD FABRICATION OF THICK WALLED PRESSURE VESSELS

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TASK I: (W R&D)

INTRODUCTION

A review of Currently Available Welding Processes and Project Planning.

RESULTS FROM PRIOR QUARTERS

A thorough Project Planning review of the entire program was made to incorporate new development and technological updates to enhance the program.

An extensive Process Review of technical literature as specifically applied to this program examined current state-of-the-art of all heavy section welding processes and the accompanying welding metallurgy. A review paper was written on an analysis that included all aspects of each welding process.

DISCUSSION OF CURRENT ACTIVITIES

This task is complete.

TASK II: (W R&D)

INTRODUCTION

The task's objective is the laboratory adaptation of the GTAW-HW narrow groove process to the vertical and horizontal welds of this program's materials. The process parameters developed in this adaptation also provide qualification data.

RESULTS FROM PRIOR QUARTERS

Sub-tasks such as R&D Facility Rearrangement, Materials Procurement, Torch and Shield Adaptation, Process Mechanical Control and NDT Evaluation are complete. These sub-tasks essentially verified prior conclusions.

Joint Design and Filler Wire Optimization, from the laboratory standpoint, are complete.

The recommended prep is a machined "U" groove of 60° included angle and 7/16 diameter bottom - the land thickness is dependent upon accessibility of the joint root backface for backchip and/or backweld or whether the joint requires guaranteed fusion without backchip.

Filler Wire Optimization has not been entirely satisfactory in that the physical properties of the deposit of commercial wire grades when used with this process appreciably overshoot the attainable physical properties of heavy section plate.

Special chemistry wire heats not only have long lead times but also long turnaround times for a chemical change. As a result, an acceptable but not ideal wire has been evaluated as the best commercial compromise. An idealistic wire heat delivered in July 1981 will be included in Task III (Full Section Process Refinement) work.

Sub-tasks Repair Techniques and Horizontal Parameters (4" qualification) will be completed under Task III for time expediency.

Although sub-task Vertical Parameters (down) has been completed and is now being tested, further work to evaluate Vertical (up) will be done under Task III.

Under Sub-Task Vertical Position Parameters/Non-Destructive Evaluation, the following has been reported:

"This test plate has been welded, UT'd, x-rayed, PWHT'd and destructive tested. The test results are recorded in this report attachment "TQ 339"--the Westinghouse Tampa format for the Section IX required PQR. This PQR documents all contract and Code required data for sub-task 2.12, 4" thick 3G-down procedure qualification.

DISCUSSION OF CURRENT ACTIVITIES

Final Task Report under Task II is attached. This completes all work on these sub-tasks.

TASK III: (WTP)

INTRODUCTION

Perform 8" thick field demonstration/qualification welds in the vertical and horizontal positions.

RESULTS FROM PRIOR QUARTERS

Sub-tasks Material Procurement and Plan for Demonstration Facility have been completed.

All program material was ordered and delivered to a detailed specification. This specification guaranteed compliance to all contract and code requirements.

Planning for the demonstration facility include development of equipment concept sketches and functional specifications. The equipment was designed to encompass essentially all components and functions of the demonstration weld.

Sub-tasks Demonstration Facility, PWHT Facility Proof Tests, and Filler Wire Procurement are complete.

Sub-tasks Demonstration Facility has had the welding equipment completed, proof tested at the vendor and was delivered to Tampa in July. Modifications required as a result of structural problems has delayed operation of the equipment. These equipment problems have been corrected and the equipment is operational.

The contract for sub-task PWHT Facility Proof Test has been awarded to a vendor. His PWHT specification has been written and approved. His equipment is on site for the demonstration welds.

Under sub-task Filler Wire Procurement, a new chemistry concept of filler wire design was ordered. Limited quantity was received in July 1981.

All required services of sub-task Field Site Preparation have been provided.

DISCUSSION OF CURRENT ACTIVITIES

The welding equipment of the sub-task Demonstration Facility is being modified, reassembled and checked out.

Destructive tests of the 4" 2G qualification plate is complete. The results will be reported in the next quarter as TQ-337.

A 3G-up 4" qualification plate has been welded PWHT'd, UT'd and x-rayed. Destructive testing is continuing the results will be reported the next quarter as TQ-338. 2G and 3G-up qualification tests in 8" test plates are in process of welding for tests.

TASK IV: (WTP) WELDING PROCEDURE HANDBOOK

INTRODUCTION

The handbook will include, for each of the weld positions, the final recommended procedure and parameters. Base material, weld

wire and gas specifications as well as PWHT and NDT procedures referenced in the weld procedure will be provided. There will also be included an equipment operating instruction and trouble shooting manual.

RESULTS FROM PRIOR QUARTERS

Base material weld wire, shield gas, and PWHT specifications, as well as NDT procedures (UT and RT) are complete.

DISCUSSION OF CURRENT ACTIVITIES

The Operator's Manual (including operating instructions and troubles shooting) is drafted and under review.

The Process Specification is complete.

CU-3.2.3 - HYDROGEN ATTACK IN Cr-Mo STEELS
AT ELEVATED TEMPERATURES

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INTRODUCTION

When a carbon or low alloy steel is exposed to high pressure hydrogen at elevated temperatures, it is well established that in addition to surface decarburization, internal damage or hydrogen attack will occur as a result of the formation of methane bubbles at the grain boundaries (1-6). It is also known that in the presence of an applied stress, the stress-rupture strength of these steels will be reduced with a loss in ductility at much lower hydrogen pressures whereas in the unstressed condition hydrogen attack would not be detected (1,2).

Current interests in coal conversion and other energy technology for which structural components are exposed to high temperature and high pressure hydrogen, has increased the need for more extensive materials performance data under these conditions (7). This type of data is required to establish various mechanical design criteria to insure the integrity of structural components.

Cr-Mo steels have been identified as potential structural materials for coal conversion plants. This project is designed to obtain micro-structure and mechanical property data of these steels under the simultaneous influence of high temperature and high pressure hydrogen and an applied stress. In particular the work will include an experimental determination of the kinetics of nucleation and growth of gas bubbles or cavities in 2½ Cr-1Mo steels at elevated temperatures under the influence of high pressure hydrogen and applied stress, and the development of kinetic equations for estimating the number density and size distribution of grain boundary bubbles or cavities as a function of time under conditions of interest to coal conversion plant operations (7).

The nucleation of methane bubbles at the grain boundaries, when low alloy steel is exposed to high pressure and high temperature hydrogen, has been found to be heterogeneous in nature and dependent upon the stability of the carbides present (8-10). Second phase particles at the grain boundary and grain boundary steps are favored high energy sites for nucleation. According to the current microscopic concepts of nucleation, the size of the critical nucleus and the magnitude of the free energy barrier of nucleation are roughly determined by the ratio of a surface tension term and the internal methane pressure (3). The time required to build up the internal methane pressure in a bubble of critical size can be expected to be a significant portion of the incubation time observed during hydrogen attack. For steels of high chromium content the stability of the carbides could be such that the equilibrium methane pressure may not be sufficient to cause the nucleation of methane bubbles.

In the presence of an applied stress, depending on the magnitude of the applied stress, grain boundary sliding will occur and cause deformation incompatibility at grain boundary steps and second phase particles. This deformation incompatibility can produce large tensile stresses at these sites which will enhance the rate of bubble or cavity nucleation (4,11). Under these circumstances, the size of the critical nucleus will be determined roughly by the ratio of a surface tension term and the sum of the internal methane pressure and the hydrostatic component of the tensile stresses. One can see that an applied stress can reduce significantly the size of the critical nucleus through the tensile stresses produced by deformation incompatibility and thus increase the probability of bubble or cavity nucleation.

The enhanced bubble or cavity nucleation caused by an applied stress can be responsible in part for the observed accelerated hydrogen attack (1,2,9,10). Theoretically, the presently available capabilities are not able to quantitatively predict the magnitude of this effect. One of the objectives of this work is, therefore, to determine experimentally the effect of applied stress enhanced bubble or cavity nucleation and to develop analytic correlations for data extrapolation based on experimental data.

If the equilibrium methane pressure resulting from CH_4 reaction is sufficient to cause bubble nucleation (as long as the internal methane pressure is greater than $2\gamma/R$ where γ is the surface tension of the bubble and R is the radius), the bubble will grow as a function of time in the absence of an applied stress. There can be different rate limiting mechanisms. First, the bubble growth can be controlled by the rate of supply of vacancies with the grain boundary being the source of vacancies (4). For this type of growth the internal methane pressure will always be greater than $2\gamma/R$. The bubble can grow by creep with internal pressure also greater than $2\gamma/R$ (12). If one removes the specimen from the hydrogen environment, the bubble will continue to grow at elevated temperatures until the magnitude of the internal pressure approaches that of $2\gamma/R$.

The bubble growth can also be controlled by the rate of formation of methane. For this rate limiting mechanism, the magnitude of internal methane pressure will be larger than, but close to that of, $2\gamma/R$ because there is a sufficient supply of vacancies or creep deformation to maintain the internal methane pressure near $2\gamma/R$. If one removes from the hydrogen environment a specimen containing bubbles whose growth is limited by methane formation, the bubble will not continue to grow when exposed to elevated temperatures.

It should be noted that for practical interests, a coal conversion plant will be operated under conditions (temperature and hydrogen pressure) where the rate of bubble growth under the influence of internal methane pressure would ordinarily be extremely small. However, the hydrogen environment could be sufficient with the aid of an applied stress, to nucleate grain boundary bubbles or cavities which could grow under the influence of this stress resulting in accumulated damage. In this work the growth kinetics under an applied stress will also, therefore, be investigated in detail. An important product of this work is the capability to estimate based on cavity nucleation and growth data, the number density and size distribution of grain boundary bubbles or cavities as a function of time under conditions of interest to coal conversion plant operations (7).

For thin wall components the design criteria for service at elevated temperatures are usually based on deformation limits due to creep, stress to rupture life and creep-fatigue interactions. These properties will be influenced by cavity formation especially the long term performance. For example, stress-rupture tests under high pressure hydrogen at high temperature have shown reduced life as compared to that in air or high pressure helium (2,6,13).

For thick wall components, design criteria are usually based on crack growth rate and fracture toughness. The existence of grain boundary bubbles or cavities is expected also to influence these properties.

RESULTS FROM PRIOR QUARTERS

For coal conversion technology a part of the materials requirement should represent an optimum combination of strength and resistance to hydrogen attack (7,14). In general, for a given Cr-Mo steel, a heat treatment procedure involving quenching and tempering at low temperatures and short durations, will produce high strength and carbides of low stability and thus, low resistance to hydrogen attack (15). On the other hand, a heat treatment procedure involving normalizing and tempering at high temperatures and long durations, will produce low strength and carbides of high stability and thus, high resistance to hydrogen attack. At the present the required heat treatment procedure is to be determined. An objective of this program is to, therefore, produce a part of the required information for materials selection.

We are fortunate in having received, through the courtesy of Drs. R.A. Swift and J.A. Gulya of Lukens Steel, both a normalized and tempered and a quenched and tempered piece of A387 steel which represent the two limiting heat treatment conditions of interest. These two materials will be the main sources of specimens for the present program.

In addition, some work will be done on an A542 steel obtained from Professor R.P. Wei at Lehigh University (properties are given in Table 1).

Specific conditions of heat treatment, properties and composition of the normalized and tempered A387 steel are given in Table 2. Similar data for the quenched and tempered material are also given in Table 2.

TABLE 1

PROPERTIES OF 2½ Cr-1 Mo (A542) STEEL PLATE

(Lukens Steel Heat C7158; A542, Class 2)

<u>Supplier's Analyses</u>	<u>C</u>	<u>Mn</u>	<u>P</u>	<u>S</u>	<u>Si</u>	<u>Ni</u>	<u>Cr</u>	<u>Mo</u>	<u>Al</u>
Ladle	0.11	0.43	0.007	0.016	0.24	ND*	2.33	0.93	ND
Check	0.10	0.45	0.012	0.018	0.23	ND	2.36	0.92	ND

*ND -- Not Determined

Heat Treatment

Austenitized 1650-1700°F, 1 hour per inch of thickness minimum, water quench + tempered 1180°F, 90 minutes per inch of thickness minimum, water quench.

Mechanical Properties

<u>Lehigh Data¹⁶</u>	<u>Yield Strength ksi(MN/m²)</u>	<u>Tensile Strength ksi(MN/m²)</u>	<u>Reduction of Area Percent</u>	<u>Elongation in 2 in. (5.08cm) Percent</u>
Longitudinal	108.8 (750)	118.3 (819)	62	20
	108.3 (746)	119.3 (822)	63	21
	<u>108.8 (750)</u>	<u>118.8 (819)</u>	<u>63</u>	<u>20</u>
(Av.)	108.6 (748)	118.8 (819)	63	21
Transverse	110.8 (763)	119.8 (825)	50	17
	<u>109.3 (753)</u>	<u>119.8 (825)</u>	<u>51</u>	<u>18</u>
(Av.)	110.1 (759)	119.8 (825)	51	17

TABLE 2

PROPERTIES OF 2½ Cr-1 Mo (A387) STEEL PLATE - 12 in. THICK

(Lukens Steel Heat B3085; A387 - Grade 22)

<u>Lukens Analysis</u> ¹⁷	<u>C</u>	<u>Mn</u>	<u>P</u>	<u>S</u>	<u>Si</u>	<u>Ni</u>	<u>Cr</u>	<u>Mo</u>	<u>Al</u>
Ladle	0.13	0.52	0.01	0.01	0.23	0.18	2.23	0.95	0.21

Normalized and Tempered Heat Treatment

Austenitized 1675°F, 12 hours, air cool + tempered 1275°F, 12 hours,
air cool

Mechanical Properties

<u>Lukens Data</u> ¹⁷	<u>Yield Strength ksi</u>	<u>Tensile Strength ksi</u>	<u>Reduction of Area Percent</u>	<u>Elongation Percent</u>
Transverse	42.4	77.4	64.3	24.3

Quenched and Tempered Heat Treatment

Austenitized 1675°F, 12 hours, Waterquenched + tempered 1275°F, 8 hours,
waterquench

Mechanical Properties

<u>Lukens Data</u> ¹⁷	<u>Yield Strength ksi</u>	<u>Tensile Strength ksi</u>	<u>Reduction of Area Percent</u>	<u>Elongation Percent</u>
Longitudinal	68.0	85.7	76.9	26.5

Both types of material are sections from the surface of a 12 inch (305mm) thick plate. The quenched and tempered steel shows a microstructure of tempered bainite with no proeutectoid ferrite, whereas the normalized material shows a microstructure of both bainite and proeutectoid ferrite (18).

During the first phase of this project (contract period September, 1978 - August, 1980) a major portion of the work was concentrated on the investigation of the normalized and tempered A387 steel. Information obtained on this material includes:

1. The incubation time and rate of methane bubble nucleation as a function of temperature and hydrogen pressure.
2. The effect of applied stress on the incubation time and rate of methane bubble nucleation.
3. The rate of stress induced cavity growth at the grain boundary.
4. Analytical equations for methane bubble nucleation.

A detailed description of the above results is given in a final report for the contract period September, 1978 - August, 1980.

At the end of the previous contract period the work on the quenched and tempered A387 began. This switch of emphasis was made upon the advice of Dr. Joe Long of ORNL, even though the planned test matrix for the normalized and tempered material had not been completely carried out. The quenched and tempered A387 is currently a favored candidate structural material because of its high strength. Based on current results, it might also be a better choice compared to the normalized and tempered material from the viewpoint of hydrogen attack. This is because a saturation methane bubble nucleation behavior was observed in the quenched and tempered steel. The saturation number of methane bubbles may not be significantly different in the quenched and tempered and normalized and tempered A387 steels. On the other hand, the rate of stress induced cavity growth was found to be significantly slower in the former material. As the work on the quenched and tempered material progresses, similar information as those listed above for the normalized and tempered material is being accumulated.

DISCUSSION OF CURRENT ACTIVITIES

In this quarter the investigation of hydrogen attack in a quenched and tempered $2\frac{1}{4}$ Cr-1 Mo steel was continued. Data on the nucleation of grain boundary methane bubbles as a function of hydrogen exposure time and temperature will be reported. Additional results were also obtained on the effect of stress on the rate of nucleation and time of incubation for the quenched and tempered steel.

Since an appreciable amount of nucleation data of quenched and tempered material has begun to become available, we have made a significant effort during the past few months to evaluate these data together with similar data obtained for normalized and tempered material from the viewpoint of the classical nucleation theory. A part of the result of this analysis will be reported in this quarterly report.

A. Nucleation Data

In the previous quarterly reports we presented grain boundary bubble number density data as a function of hydrogen exposure time at 600°C and 550°C (13.8 MPa hydrogen pressure) for a quenched and tempered $2\frac{1}{4}$ Cr-1 Mo steel. Additional data were obtained during this quarter for the quenched and tempered material with hydrogen exposure at 550°C and 500°C with the same hydrogen pressure (Figure 1). The number densities of methane bubbles were determined from SEM observations of polished and etched specimens after different times of hydrogen exposure followed by a creep growth treatment (19). The creep growth treatment was necessary to produce cavities of sufficient size for SEM examination. The base line value, in Figure 1, represents the number density of creep cavities introduced by the creep growth treatment alone. The actual number density of methane bubbles in each specimen is thus the difference between the observed number density and the base line value.

The number density of grain boundary cavities is seen to saturate for both the 600°C, and the 550°C data which probably reflects the exhaustion of available heterogeneous nucleation sites. Based on our

Fig. 1. Grain boundary cavity density versus hydrogen exposure time for the A-387 quenched and tempered steel. Data for hydrogen exposure at 600°C, 550°C, and 500°C are presented. The symbols are experimental data points and the lines are calculated.

previous electron microscopy work, these sites have been found to be on the surface of selected carbides (20). As reported in the previous quarterly, the apparent saturation level at 550°C appears to be less than the saturation level at 600°C.

B. The Effect of Applied Stress on Methane Bubble Nucleation

During this quarter experiments of hydrogen exposure of a quenched and tempered 2½ Cr-1 Mo steel at 600°C under a hydrogen pressure of 13.8 MPa and under an applied stress of 8 ksi were continued. Additional data are obtained for an applied stress level of 16 ksi with the same hydrogen exposure condition. As previously reported the severity of hydrogen attack increased significantly under an applied stress. Figure 2 shows a typical SEM photomicrograph of a polished and etched specimen of a quenched and tempered 2½ Cr-1 Mo steel which was hydrogen exposed under a 16 ksi applied stress. In Figure 3 the number density of grain boundary cavities as a result of hydrogen exposure under the above conditions is plotted versus hydrogen exposure time. Similar nucleation data without an applied stress are presented in Figure 1. The data obtained under an applied stress also shows an initial incubation period and after a period for nucleation, the approaching of a saturation level is shown. The most significant effects of an applied stress is the observed shorter time of incubation under a small applied stress. Otherwise, the general trends of the rate of nucleation and saturation level are similar with or without an applied stress.

Fig. 2. A SEM photomicrograph of a polished and etched specimen of hydrogen exposed A387, quenched and tempered 2 1/4 Cr-1 Mo steel. The hydrogen exposure conditions were 2000 psi and 600°C with a 16 ksi applied stress for 8 days. A large number of cavities are observed on the grain boundaries perpendicular to the stress axis (vertical in the picture).

Grain Boundary Cavity Density
vs
Hydrogen Exposure Time
A387 (Q+T) 2 $\frac{1}{4}$ Cr-1 Mo Steel

EXPOSURE CONDITIONS

Temp.	H ₂ Pressure	Applied stress	
600°C	2000 psi	0 ksi	Δ ———
600	2000	8	□ - - -
600	2000	16	○ - · - ·

Fig. 3. Grain boundary cavity density vs. hydrogen exposure time for the A387 quenched and tempered steel. Data for hydrogen exposure (600°C, 2000 psi) with an applied stress are presented. The symbols are experimental data points and the lines are calculated.

C. Analysis of Nucleation Data

In previous reports we have used the formulation of classical nucleation theory to develop correlations for our nucleation data. We have adjusted the required physical parameters from their literature values in order to fit the experimental data available at the time. Some of the adjustments produced, however, large deviations from the reported values of the physical parameters. For example, we had to change significantly the pre-exponential constant and the activation energy for grain boundary diffusion.

We have at the present available to us a broader data base resulting from our recent work on a quenched and tempered 2½ Cr-1 Mo steel. During the last two quarters we have analyzed our data by putting that of a normalized and tempered material and the quenched and tempered material together. In the present work we did not attempt to adjust the literature values of the physical parameters. We were interested in finding out primarily the validity of the classical nucleation theory in its present form. The important results of this exercise are

- i. The classical nucleation theory was found to be capable of predicting the temperature and the hydrogen pressure dependence of the rate of nucleation and the incubation time.
- ii. The same theory failed, however, to predict the value of the measured rate of nucleation and incubation time, and some of the calculated parameters were found to have nonphysical values.

The recent data analysis provided us additional physical insight as to the theoretical significance of our nucleation data. It should aid considerably in our effort for the development of correlations for data extrapolation.

C.1 Classical Nucleation Theory

The adaption of the classical nucleation theory (21,22) for the present interest has been reported in our previous quarterly reports (8,9). In the following we shall list only the key equations used in the data analysis described here.

The free energy associated with nucleation ΔG , is as given

$$\Delta G = -\alpha n + \beta n^{2/3} \quad (1)$$

where αn is the volume energy term and $\beta n^{2/3}$ is the surface energy term, n = number of vacancies per nucleus, $\alpha = \Omega P_{CH_4}$, with Ω , the atomic volume, P_{CH_4} , the internal methane pressure and $\beta = \sigma [9\Omega^2 \pi (2-3 \cos\theta + \cos^3 \theta)]^{1/3}$ with θ , the contact angle to the grain boundary and σ , the methane-iron surface free energy.

The rate of nucleation $\dot{N}$ has the form

$$\dot{N} = 3N_s [\pi/kT]^{1/2} \sigma \sin\theta \beta^{-1/2} \left(\frac{\alpha}{\beta}\right) D_{gb} e^{-G_{gb}/kT} e^{-\Delta G^*/kT} \quad (2)$$

where N_s is the saturation area density of methane bubbles, $D_{gb} e^{-G_{gb}/kT}$ is the grain boundary diffusivity and ΔG^* is the free energy barrier for nucleation.

The incubation time τ is expressed as

$$\tau = \frac{16}{9\pi} \frac{kT e^{G_{gb}/kT}}{\sigma \sin\theta D_{gb}} \left(\frac{\beta}{\alpha}\right)^3 \quad (3)$$

We can, therefore, write

$$\dot{N}_\tau = \frac{16}{3} N_s \left(\frac{kT}{\pi}\right)^{1/2} \left(\frac{\beta}{\alpha}\right)^2 \beta^{-1/2} e^{-\Delta G^*/kT} \quad (4)$$

The free energy barrier to nucleation ΔG^* is

$$\Delta G^* = \frac{4}{27} \left(\frac{\beta}{\alpha}\right)^2 \beta \quad (5)$$

and the critical nucleus size n^* is

$$n^* = \left(\frac{2\beta}{3\alpha}\right)^3 \quad (6)$$

These equations suggest that for the situation where $\Delta G^* \ll kT$

- i. The dominate temperature dependence in Equation 2 of $\dot{N}$ is through the temperature dependence of the grain boundary self diffusivity.
- ii. τ , through α , in Equation 3 is more sensitive than $\dot{N}$ to the methane pressure and is, therefore, a more sensitive function of temperature and hydrogen pressure.

In general:

- iii. The effects of variation in carbon activity can be expressed through changes in P_{CH_4} in α in Equations 2 and 3. We do not expect, therefore, a large change in the $\dot{N}$ and τ between the normalized and tempered and quenched and tempered materials.
- iv. We expect the temperature dependence of τ and $\dot{N}$ for the above two materials to be the same.
- v. The stress dependence of the τ and $\dot{N}$ can be estimated by replacing α by $(\alpha + \sigma_{conc.} \Omega)$ where $\sigma_{conc.}$ is a measure of the stress concentration at the nucleation site (10).

In the next subsection on experimental data we shall show that the available experimental information is consistent with the predictions listed above.

The available literature information on the physical parameters required by the equations given above will be described below.

From the work of James and Leak (23) we have

$$D_{gb} \delta e^{-G_{gb}/kT} = 11.2 \times 10^{-7} \exp(-41500/RT) \text{cm}^3/\text{sec} \quad (7)$$

where δ is the grain boundary thickness, which is approximately $4 a_0$ with $a_0 = 2.866\text{\AA}$. We shall assume the above expression to be applicable for the normalized and tempered material. Based on our data on stress induced growth of grain boundary cavities (24) we shall take D_{gb} to be a factor of 10 smaller for the quenched and tempered material.

The value of the contact angle θ is found to be small experimentally (20,24). We shall use a reference value of 6° for the data analysis. The value of surface tension σ is 0.8 J/m^2 (25). The atomic volume Ω is taken to be $3 \times 10^{-29} \text{ m}^3$. The estimated saturation levels N_s for both the quenched and tempered and normalized and tempered materials are on the order of $3 \mu\text{m}^{-2}$, this number reflecting the observed saturation density in the quenched and tempered material (26).

The relation between methane bubble fugacity f_{CH_4} and methane pressure P_{CH_4} is (27)

$$f_{\text{CH}_4} = P_{\text{CH}_4} \exp \left[P_{\text{CH}_4} \left(\frac{2.375}{T} \right) + 1.776 \times 10^{-3} \right] \quad (8)$$

where T is in $^\circ\text{K}$ and P_{CH_4} in MPa.

The methane fugacity and carbon activity a_c are related through

$$f_{\text{CH}_4} = (P_{\text{H}_2})^2 a_c K \quad (9)$$

where K is the equilibrium constant (3).

Based on the above relation, and taking the carbon activity for the quenched and tempered material to be $1/2$ that for a typical carbon steel at 600°C , this corresponds to about 50 wt. ppm (28). We can calculate the methane fugacity for the quenched and tempered material as

$$f_{\text{CH}_4} (\text{MPa}) = \left(\frac{P_{\text{H}_2} (\text{psi})}{14.7} \right)^2 1.0 \times 10^{-8} \exp \left(\frac{13925}{T} \right) \quad (10)$$

We have taken a_c for the normalized and tempered material to be a factor of two smaller, the corresponding methane fugacity will, therefore, be a factor two smaller compared to that calculated from Equation 10. These seemingly high activities are justifiable if one takes into account the presence of Fe_3C in both materials.

At 600°C and under a hydrogen pressure of 2000 psi Equations 8 and 10 will yield a methane pressure of 270 MPa and 370 MPa for the normalized and tempered material and the quenched and tempered material respectively.

Using the values of the physical parameters and the expressions for α and β given above, we can calculate the values for α and β to be 8×10^{-21} Joules and 1×10^{-20} Joules respectively.

C.2 Experimental Data

Figures 1,3,4,5 summarize the available experimental data on methane bubble nucleation for a normalized and tempered and a quenched and tempered $2\frac{1}{4}$ Cr-1Mo steel in the form of bubble area density vs. exposure time plots. Figures 3 and 4 show the effect of applied stress. From these data we can estimate the incubation time and the rate of nucleation. In the following we shall first examine the trend of the data shown.

Figures 6 and 7 show temperature dependence of the rate of nucleation and the incubation time of these two materials. It is seen from Figures 6 and 7 that the data trends for the two materials are similar as predicted by the classical nucleation theory. The temperature dependence of $\dot{N}$ is found to correspond to an activation energy close to G_{gb} given in the previous subsection. This result suggests that ΔG^* is small compared to kT in Equation 2. The temperature dependence of τ on the other hand corresponds to an activation energy which is different from that for grain boundary diffusivity reported by James and Leak (23).

The hydrogen pressure dependence of τ and $\dot{N}$ shown in Figure 5 is not strong. However, based on estimates of how the methane pressure should vary with temperature and hydrogen pressure, we would expect a stronger dependence according to the classical nucleation theory. This result suggests that the volume term in Equation 1 may have a weaker dependence on P_{CH_4} compared to that given by $\alpha = \Omega P_{CH_4}$.

In the following we shall use the classical nucleation theory to predict the temperature and hydrogen pressure dependence.

C.3 Hydrogen Pressure and Temperature Dependence of $\dot{N}$ and τ

We can choose a pair of experimentally measured τ and $\dot{N}$ values for a given hydrogen exposure condition as a reference. According to Equations

Fig. 4. Grain boundary cavity density vs. hydrogen exposure time for the A387 normalized and tempered steel. Data for hydrogen exposure (600°C, 2000 psi) with an applied stress are presented. The symbols are experimental data points and the lines are calculated.

Fig. 5. Grain boundary cavity density vs. hydrogen exposure time for the A387 normalized and tempered steel. Data for 2000 psi hydrogen exposure at 600°C, 580°C and 550°C are presented. Data for 1000 psi hydrogen exposure at 600°C are also presented. The symbols are experimental data points and the lines are calculated.

Fig. 6. A plot of the log of the rate of nucleation-vs.-reciprocal temperature for the A387 2 $\frac{1}{4}$ Cr-1 Mo steel in both the normalized and tempered and the quenched and tempered condition. This exhibits approximately the same temperature dependence for the rate of nucleation, invariant of the two different heat treatments and microstructure.

Fig. 7. A plot of the log of the incubation time-vs.-reciprocal temperature for the A387 2 $\frac{1}{4}$ Cr-1 Mo steel in both the normalized and tempered and the quenched and tempered condition. This material exhibits approximately the same temperature dependence also for the incubation time, invariant of the two different heat treatments and microstructure.

2 and 3 the incubation time and the rate of nucleation for other hydrogen exposure conditions can then be estimated for the case where $\Delta G^* \ll kT$ from

$$\dot{N}/\dot{N}_{\text{ref}} = [(1/T)^{1/2} \alpha e^{-G_{\text{gb}}/kT}] / [(1/T_{\text{ref}})^{1/2} \alpha_{\text{ref}} e^{-G_{\text{gb}}/kT}] \quad (11)$$

and

$$\tau/\tau_{\text{ref}} = [T e^{G_{\text{gb}}/kT} (\frac{1}{\alpha})^3] / [T_{\text{ref}} e^{G_{\text{gb}}/kT} (\frac{1}{\alpha_{\text{ref}}})^3] \quad (12)$$

We shall justify the assumption $\Delta G^* \ll kT$ in the next subsection. The above equations will produce a temperature dependence through the combined effect of $e^{G_{\text{gb}}/kT}$ and the temperature dependence of P_{CH_4} in α . The hydrogen pressure dependence is obtained through the dependence of P_{CH_4} on P_{H_2} .

For the calculated lines shown in Figures 1 and 5 we have assumed $\alpha \sim P_{\text{CH}_4}^{1/3}$ based on the argument given in the last subsection, and using the τ and $\dot{N}$ for $T=600^\circ\text{C}$ and $P_{\text{H}_2} = 2000$ psi as the reference. We have taken the carbon activities to be those given in the subsection on classical nucleation theory.

The solid line in Figures 1 and 5 represent the calculated τ 's and $\dot{N}$'s from Equations 11 and 12. It is seen from these figures that the classical nucleation theory, with appropriately chosen values for the carbon activity can be used to estimate the temperature and hydrogen pressure dependence of the incubation time and the rate of nucleation. The only required modification is to let $\alpha \sim P_{\text{CH}_4}^{1/3}$ instead of $\alpha = \Omega P_{\text{CH}_4}$ for Equation 1 in order to achieve the measured hydrogen pressure dependence. We note, however, that a range of carbon activities will generate similar temperature and hydrogen pressure dependence.

C.4 Numerical Calculations

In the numerical calculations we have attempted to use the values of the physical parameters as close to the literature and reference values given in subsection C.1 as possible. But staying with those parameters has necessitated our incorporating correction factors, defined as

$$\dot{N}(\text{calculated}) = \dot{N}(\text{experimental}) \times (\text{correction factor})_{\dot{N}} \quad (13)$$

$$\tau(\text{experimental}) = \tau(\text{calculated}) \times (\text{correction factor})_{\tau} \quad (14)$$

Using the values of parameters in Tables 3 and 4 we have found that the correction factors are of the order of 10^{11} to 10^{13} . This is not surprising because historically the classical nucleation theory has always suffered the same problem.

Table 3 lists also the value of ΔG^* calculated by using the literature and reference values of the physical parameters. It is seen that the assumption made throughout this analysis that $\Delta G^* \ll kT$ is justified.

In Table 5 we have listed the experimental and calculated τ 's and $\dot{N}$'s. The calculated value was based on the parameters in Tables 3 and 4. We note that the agreement between these two sets of values depends on the choice of the correction factors which have values of the order of 10^{11} to 10^{13} .

C.5 The Effects of Applied Stress

As discussed previously, the major effect of applied stress can be accounted for by the variation of α as a function of applied stress in Equations 2 and 3. We may write

$$\alpha = \alpha_{\sigma=0} + \sigma_{\text{conc.}} \Omega \quad (15)$$

where $\alpha_{\sigma=0}$ is the volume energy term in Equation 1 in the absence of an applied stress and $\sigma_{\text{conc.}}$ as defined previously, is a measure of stress concentration.

TABLE 3

PARAMETERS USED IN NUMERICAL CALCULATIONS(for the Normalized and Tempered Material at 600°C and $P_{H_2} + 2000$ psi)

<u>Literature and Reference Value</u>	<u>Value Used in Calculation</u>
$a_c = 25\text{ppm}$	
$P_{CH_4} = 270 \text{ MPa}$	
$\alpha = \Omega P_{CH_4} = 8 \times 10^{-21} \text{ Joules}$	$\alpha = 10^{-20} \text{ Joules}$
$\theta = 6^\circ$	$\theta = 6^\circ$
$\sigma = 0.8 \text{ Joules/m}^2$	$\sigma = 0.8 \text{ Joules/m}^2$
$\beta = 1.05 \times 10^{-20} \text{ Joules}$	$\beta = 10^{-20} \text{ Joules}$
$D_{gh} = 9 \times 10^{-4} \text{ m}^2/\text{sec}$	$D_{gb} = 9 \times 10^{-4} \text{ m}^2/\text{sec}$
$\Delta G_{gh} = 41500 \text{ cal/mole}$	$\Delta G_{gb} = 41500 \text{ cal/mole}$
	$N_s = 5.6 \text{ } \mu\text{m}^{-2}$
	$(\text{Correction Factor})_N = 1.6 \times 10^{13}$
	$(\text{Correction Factor})_\tau = 5.6 \times 10^{11}$
$\Delta G^* = 1.5 \times 10^{-21} \text{ Joules}$	
$= 1.2 \times 10^{-1} \text{ kT}$	
$n^* = 3 \times 10^{-1}$	

TABLE 4

PARAMETERS USED IN NUMERICAL CALCULATIONS(for the Quenched and Tempered Material at 600°C and $P_{H_2} = 2000$ psi)

<u>Literature and Reference Value</u>	<u>Value Used in Calculation</u>
$a_c = 50$ ppm	
$P_{CH_4} = 370$ MPa	
$\alpha = \Omega P_{CH_4} = 1.37 \times 10^{-20}$ Joules	$\alpha = 1.37 \times 10^{-20}$ Joules
$\theta = 6^\circ$	$\theta = 6^\circ$
$\sigma = 0.8$ Joules/m ²	$\sigma = 0.8$ Joules/m ²
$\beta = 1.05 \times 10^{-20}$ Joules	$\beta = 10^{-20}$ Joules
$D_{gb} = 9 \times 10^{-5}$ m ² /sec	$D_{gb} = 9 \times 10^{-5}$ m ² /sec
$\Delta G_{gb} = 41500$ cal/mole	$\Delta G_{gb} = 41500$ cal/mole
$N_s = 3 \mu m^{-2}$	$N_s = 3.3 \mu m^{-2}$
	$(\text{Correction Factor})_N = 7.3 \times 10^{10}$
	$(\text{Correction Factor})_\tau = 1.1 \times 10^{11}$

TABLE 5
INCUBATION TIMES AND RATES OF NUCLEATION
 "Experimental" versus "Theoretical"

Normalized and Tempered Material

<u>Exposure Conditions</u>		<u>Experimental</u>		<u>Theoretical</u>	
Temp. (°C)	P _{H₂} (psi)	$\dot{N}$ ($\mu\text{m}^{-2}\text{day}^{-1}$)	τ (days)	$\dot{N}$ ($\mu\text{m}^{-2}\text{day}^{-1}$)	τ (days)
600	2000	6.64×10^{-2}	16	5.16×10^{-2}	12
580	2000	3.24×10^{-2}	21	3.14×10^{-2}	17
550	2000	1.21×10^{-2}	30	1.44×10^{-2}	27
600	1000	7.0×10^{-2}	30*	3.95×10^{-2}	33

Quenched and Tempered Material

<u>Exposure Conditions</u>		<u>Experimental</u>		<u>Theoretical</u>	
Temp. (°C)	P _{H₂} (psi)	$\dot{N}$ ($\mu\text{m}^{-2}\text{day}^{-1}$)	τ (days)	$\dot{N}$ ($\mu\text{m}^{-2}\text{day}^{-1}$)	τ (days)
600	2000	2.0×10^{-1}	8.8	9.50×10^{-2}	8.8
550	2000	3.9×10^{-2}	15	2.67×10^{-3}	26
500	2000	-	90*	5.70×10^{-3}	92

*These experimental values may be modified as more data are available.

In the data analysis we have used the experimentally determined τ given in Figures 3 and 4 and Equation 3 to estimate the value of α , with all the other parameters independent of applied stress. The value of $\sigma_{\text{conc.}}$ can be estimated from Equation 14, using the assumption $\alpha_{\sigma=0}$ is of the order of ΩP_{CH_4} . The value of P_{CH_4} used is that given in Tables 3 and 4.

The results of the data analysis are listed in Table 6. It is seen from these results that $\sigma_{\text{conc.}}$ increases as expected with applied stress. We note, however, that the absolute value of $\sigma_{\text{conc.}}$ depends on the choice of the form of $\alpha_{\sigma=0}$, and the correction factors in Tables 3 and 4 are still required to achieve numerical agreement.

C.6 Discussion

Based on the present analysis we have found that:

- i. The classical nucleation theory is adequate in predicting the temperature and hydrogen pressure dependence of τ and $\dot{N}$ as well as their dependence on applied stress.
- ii. The same theory however, is far from adequate in estimating the numerical value of τ and $\dot{N}$ by using literature and experimentally determined values of the required physical parameters.

Several additional points should also be made:

- i. A range of carbon activity a_c apparently can be used to produce an adequate data fit. Since a 2½ Cr-1Mo steel is far from a homogeneous material, it will also be difficult to determine the effective value of a_c from an independent experiment.
- ii. The number of vacancies in a critical nucleus given in Table 3, calculated by using the reference values of the required physical parameters in the same table, has a value $n^* < 1$. This is a physically unreasonable situation reflecting also the inadequacy of the classical nucleation theory.
- iii. The volume energy term α in Equation 1 should also be discussed. The P_{CH_4} dependence of α used to fit the observed P_{H_2} dependence

TABLE 6
THE EFFECT OF APPLIED STRESS

Exposure Conditions: $T = 600^{\circ}\text{C}$, $P_{\text{H}_2} = 2000\text{psi}$

<u>Normalized and Tempered</u>					
Stress (MPa)	<u>Calculated</u>		<u>Experimental</u>		Calculated $\sigma_{\text{conc.}}$ (MPa)
	τ (days)	$\dot{N}$ ($\mu\text{m}^{-2}\text{day}^{-1}$)	τ (days)	$\dot{N}$ ($\mu\text{m}^{-2}\text{day}^{-1}$)	
None	12	5.16×10^{-2}	16	6.64×10^{-2}	0
55	5	6.5×10^{-2}	8.5	7.62×10^{-2}	70
110	.3	1.76×10^{-1}	2.5	3.0×10^{-1}	650

<u>Quenched and Tempered</u>					
Stress (MPa)	<u>Calculated</u>		<u>Experimental</u>		Calculated $\sigma_{\text{conc.}}$ (MPa)
	τ (days)	$\dot{N}$ ($\mu\text{m}^{-2}\text{day}^{-1}$)	τ (days)	$\dot{N}$ ($\mu\text{m}^{-2}\text{day}^{-1}$)	
None	8.8	9.5×10^{-2}	8.8	2.0×10^{-1}	0
55	5	1.1×10^{-1}	5	2.2×10^{-1}	77
110	.3	2.9×10^{-1}	.5	4.0×10^{-1}	770

is weaker than a linear P_{CH_4} dependence required by the classical nucleation theory. This situation is also physically unreasonable.

- iv. The values of P_{CH_4} and $\sigma_{conc.}$ based on the present analysis can be made to be of the same order. This result seems to be reasonable physically. Some independent confirmation will be desirable.

An important result of the present analysis is that we are now confident that we are able to develop without too much difficulty useful correlations for τ and $\dot{N}$ which will allow data extrapolation into the low temperature and low applied stress region. As more experimental data become available we should have better information on N_s and the P_{H_2} dependence of τ and $\dot{N}$. We are pursuing also additional theoretical analysis which will be useful in our future work.

C.7 Future Work

During the next quarter we should begin to obtain additional nucleation data at 500°C on the quenched and tempered material, the specimens of which are presently undergoing hydrogen exposure. These data will be obtained under hydrogen exposure conditions close to the operation conditions of a coal conversion plant.

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ORNL-3.2.3 — EVALUATION OF FRACTURE TOUGHNESS
OF PRESSURE VESSEL STEELS

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INTRODUCTION

This task is concerned with the influence of an operating environment on the in-service reliability and safety of large pressure vessels for use in second-generation coal conversion systems. The candidate steels from which these vessels will be constructed can be embrittled by exposure at the currently projected operating conditions of these units.

Several steels are candidates for the construction of large, second-generation commercial pressure vessels, including SA-516 grade 70, SA-204 grade B, SA-387 grade 22, class 2, SA-533 grade B, class 1, and A-543. The composition and strength requirements for these grades are given in Table 1. Mechanical properties data, including fracture toughness, are being obtained in this task.

RESULTS FROM PRIOR QUARTERS

In previous quarterly progress reports we discussed the effects of postweld heat treatment time on the tensile and fracture toughness properties of thick-section pressure vessel steels and weldments. The materials studied to date include those currently permitted for the fabrication of liquefaction and gasification vessels in accordance with the rules of Sect. VIII of the *ASME Boiler and Pressure Vessel Code* (ASME Code) and some that are experimental modifications of those steels. Table 1 contains information for the studied for which ASTM or ASME specifications exist. The experimental modifications include one from the Japan Steel Works which significantly increases the hardenability of 2 1/4 Cr-1 Mo steel through the use of V-Ti-B additions. In addition to thick-section

Table 1. Steels that may be considered for various components of coal conversion facilities

Specification ^a	Grade or type	Class or grade	Nominal composition, ^b wt %					Tensile properties, ^c MPa(ksi)	
			C	Mn	Cr	Mo	Ni	Yield strength	Ultimate strength
SA-516	70		0.31	0.85-1.20				260 (38)	485-620 (70-90)
SA-204	B		0.27	0.90		0.45-0.60		255 (37)	450-585 (65-85)
SA-533	B	1	0.25	1.15-1.50		0.45-0.60	0.40-0.70	345 (50)	550-690 (80-100)
SA-387	22	2	0.15	0.30-0.60	2.00-2.50	0.90-1.10		310 (45)	520-690 (75-100)
A 543	E	1	0.23	0.40	1.50-2.00	0.45-0.60	3.00-4.00	585 (85)	725-860 (105-125)

^aSA designates a steel specification approved by the *ASME Boiler and Pressure Vessel Code* and is included in Sect. II, Pt A. A designates a steel that is listed in the ASTM Standards but is not included in Sect. II of the *ASME Boiler and Pressure Vessel Code*.

^bSingle numbers are maximum values.

^cValues are room temperature tensile requirements for the specification. Single values are minimums.

commercial heats of candidate steels, we have investigated the influence of carbon contents near the limits permitted in SA-387 grade 22 on the mechanical properties of this grade of steel. The DATA TRAK was used to obtain microstructures in these steels representative of those obtained when quenching 152- to 305-mm-thick (6-12-in.) plates and forgings.

The tensile and Charpy-V impact properties of base and weld metal have been determined for welds made in thick sections of plate meeting ASME specifications SA-516 grade 70, SA-204 grade B, SA-387 grade 22 class 2, and base metal from the V-Ti-B modified 2 1/4 Cr-1 Mo steel.

Currently we have investigated the tensile and Charpy-V toughness properties of V-Ti-B modified 2 1/4 Cr-1 Mo steel plate when subjected to various heat treatments including the simulation of water quenching from the austenitizing temperature of 254- to 305-mm-thick plate. The tensile properties of Ni-V modified 2 1/4 Cr-1 Mo steel fabricated from three different deoxidizing processes were also determined after various heat treatments which simulated water quenching from the austenitizing temperature of the same thickness plates.

DISCUSSION OF CURRENT ACTIVITIES

V-Ti-B Modified 2 1/4 Cr-1 Mo Steel

We have continued to evaluate the mechanical properties of 29-mm-thick (1 1/8-in.) V-Ti-B modified 2 1/4 Cr-1 Mo steel plate supplied by the Japan Steel Works (JSW). During this period we have determined the effect of the "quality heat treatment" recommended by JSW. The as-received plate was normalized [1000°C (1830°F) for 4 h, air cooling] and tempered [650°C (1200°F) for 5 h, air cooling] at JSW before shipment to ORNL. At ORNL, the plate was given the additional quality heat treatment recommended by JSW: austenitized 5 h at 950°C (1745°F) and tempered 20 h at 690°C (1275°F), followed by air cooling after each treatment. The tensile properties and Charpy-V (C_v) impact toughness were determined for the plate after the quality heat treatment and were reported earlier.¹⁻³ The specimen orientation nomenclature has also been described.⁴

The C_v impact toughness results from specimens of the as-received plate are plotted in Fig. 1, and the toughness parameters are listed in Table 2. Results from the as-received plate after the additional quality heat treatment are also plotted in Fig. 1, and the toughness parameters are also listed in Table 2. The upper-shelf energy of the as-received plate is affected by orientation, but the transition regime is not. The upper-shelf energy level determined with RW-oriented specimens [136 J (100 ft-lb)] is superior to that of the upper shelf from WR-oriented specimens [109 J (80 ft-lb)]. The transition temperature from both orientations at the 68-J (50-ft-lb) energy level is near 116°C (240°F). The improvement in C_v toughness by the quality heat treatment is impressive (Fig. 1). The transition regime was decreased from 116 to -51°C (240 to -60°F) at the 68-J energy level, and the upper shelf increased a minimum of 136 J (100 ft-lb), from 136 to 272 J (100 to 200 ft-lb) for the RW orientation and from 109 to 245 J (80 to 180 ft-lb) for the WR orientation.

We also determined the ambient tensile properties and the C_v impact toughness of the V-Ti-B modified 2 1/4 Cr-1 Mo described previously from specimens machined from bars that were heat treated in the DATA TRAK heat treatment facility. The chemical composition, specimen preparation, and DATA TRAK facility were described in an earlier report.¹ The DATA TRAK facility was used to simulate the cooling rate at the quarter-thickness depth of 254 to 305-mm-thick (10-12-in.) plate when quenched in water from the austenitizing temperature. Austenitization was at 952°C (1745°F), followed by cooling at 0.3 K/s (0.6°R/s). Each bar produced two specimens. After the described heat treatment, the bars were subjected to additional treatments: (1) tempered at 663°C (1225°F) for 6 h followed by a postweld heat treatment (PWHT) of 28 h at 691°C (1275°F) or (2) the same PWHT with the temper omitted.

Tensile results from specimens receiving the heat treatments described are presented in Table 3. The results from W-oriented specimens indicate that a slight improvement in the yield and ultimate strengths would be obtained if the temper were omitted after the quench and before PWHT of the thick plate section. The minimum yield and tensile strengths to be expected appear to be 507 and 608 MPa (73.5 and 88.2 ksi), respectively.

HEAT TREATMENT

ORNL-DWG 81-12872

AS-RECEIVED

NORMALIZED: 1000°C (1830°F) FOR 4 h, AIR COOL

TEMPER: 650°C (1200°F) FOR 5 h, AIR COOL

QUALITY HEAT TREATMENT

AUSTENITIZED: 950°C (1745°F) FOR 5 h, AIR COOL

TEMPER: 690°C (1275°F) FOR 20 h, AIR COOL

Fig. 1. Effect of the "quality heat treatment" on the Charpy-V energy of 29-mm-thick (1 1/8-in.) V-Ti-B modified 2 1/4 Cr-1 Mo steel plate.

Table 2. Summary of Charpy V-notch impact properties of V-Ti-B modified 2 1/4 Cr-1 Mo steel plate^a after special heat treatment

Orientation	Temperature, °C (°F)				Upper-shelf energy	
	68 J (50-ft-lb) Transition	0.89-mm (35-mil) Lateral expansion	50% Shear	100% Shear	(J)	(ft-lb)
As-received ^b						
RW	113 (235)	127 (260)	129 (265)	182 (360)	136	100
WR	121 (250)	129 (265)	121 (250)	182 (360)	109	80
Quality heat treatment ^c						
RW	-57 (-70)	-54 (-65)	-37 (-35)	-23 (-10)	272	200 ^d
WR	-46 (-50)	-46 (-50)	-46 (-50)	10 (50)	245	180

^aPlate is 29 mm thick (1 1/8-in.).

^bNormalized 1000°C (1830°F) for 4 h; tempered 650°C (1200°F) for 5 h; air cooling after each treatment.

^cAustenitized 5 h at 950°C (1745°F); tempered 20 h at 690°C (1275°F); air cooling after each treatment.

^dExceeded machine capacity (326 J) between 93 and 149°C (200 and 300°F).

Table 3. Tensile properties^a of V-Ti-B modified 2 1/4 Cr-1 Mo steel at 25°C after austenitizing at 952°C for 1 h and simulating the quench rate at the quarter thickness depth in 254- to 305-mm-thick (10-12 in.) plate

Heat ^b treatment	Stresses, MPa (ksi)		Ductility, %		
	Yield ^c	Ultimate	Total elongation ^d		Reduction of area
			L/D = 7	L/D = 4	
Q + T + PWHT	507 (73.5)	608 (88.2)	16.4	24.3	78
Q + PWHT	510 (75.2)	610 (89.7)	16.2	24.1	78

^aAverage of two specimens, W orientation.

^bQ denotes 0.3 K/s (0.6°R/s) quench rate simulated by DATA TRAK; T denotes temper at 663°C (1225°F) for 6 h, followed by air cooling; and PWHT denotes a postweld heat treatment at 691°C (1275°F) for 28 h, followed by air cooling.

^cOffset yield, 0.2%.

^dRatio of gage length to gage diameter of 4 (L/D = 4) is calculated from the L/D = 7 data; strain rate is 0.016/min.

The C_y toughness results are plotted in Fig. 2, and the toughness parameters are listed in Table 4. The omission of the temper before the PWHT does not appear to affect the transition regime [-65°C (-85°F) at the 68-J energy level], but the upper-shelf energy seems to be increased by the temper before PWHT. At 10°C (50°F), the upper shelf after the quench, temper, and PWHT occurs at 265 J (195 ft-lb) and at 245 J (180 ft-lb) after the quench and PWHT. The upper-shelf energy after both heat treatments exceeded the machine capacity of 326 J near 93°C (200°F).

Ni-V Modified 2 1/4 Cr-1 Mo

We are also determining the tensile and C_y toughness of Ni-V modified 2 1/4 Cr-1 Mo steel. Six plates were supplied by U.S. Steel. The plates were fabricated from vacuum-induction-melted heats conforming to three deoxidation processes: (1) vacuum-carbon-deoxidized (VCD), (2) silicon-killed (Si-K), and (3) silicon-aluminum-killed (Si-Al-K). The initial heats weighed 91 kg (200 lb). Each heat was separated into two 45-kg

HEAT TREATMENTS

ORNL-DWG 81-12873

AUSTENITIZED: 1 h AT 952°C (1745°F)

COOLING RATE: 0.3 K/s (0.6°R/s)

CURVE A: TEMPERED 6 h AT 663°C (1225°F), AIR COOL

PWHT: 28 h AT 691°C (1275°F), AIR COOL

CURVE B: PWHT: 28 h AT 691°C, AIR COOL

Fig. 2. Variation of Charpy-V impact energy at the quarter-thickness depth in simulated 254- to 305-mm-thick (10 to 12-in.) V-Ti-B modified 2 1/4 Cr-1 Mo steel plate after various processing heat treatments.

Table 4. Effect of heat treatment on the Charpy V-notch impact properties^a of V-Ti-B modified 2 1/4 Cr-1 Mo steel plate after austenitizing at 952°C for 1 h and simulating the quench rate at the quarter-thickness depth in 254- to 305-mm-thick (10-12-in.) plate

Heat ^b treatment	Temperature, °C (°F)				Upper-shelf energy at 10°C (50°F)	
	68 J (50-ft-lb) Transition	0.89-mm (35-mil) Lateral expansion	50% Shear	100% Shear	(J)	(ft-lb)
Q + T + PWHT	-65 (-85)	-68 (-90)	-57 (-70)	-37 (-35)	265	195 ^c
Q + PWHT	-65 (-85)	-68 (-90)	-51 (-60)	-29 (-20)	245	180 ^c

^aWR-oriented specimens.

^bQ denotes 0.3 K/s (0.6°R/s) quench rate simulated by DATA TRAK; T denotes temper at 663°C (1225°F) for 6 h, followed by air cooling; and PWHT denotes a postweld heat treatment at 691°C (1275°F) for 28 h, followed by air cooling.

^cExceeded machine capacity (326 J) near 93°C (200°F).

(100-lb) melts, and the vanadium content of one was increased to between 0.34 to 0.37%. In addition, 1/2% Ni was added to all the 2 1/4 Cr-1 Mo heats.

Two heat treatment programs were performed. One program simulated the thermal cycle at the near surface of 254- to 305-mm-thick (10-12-in.) plate after austenitization, quench, temper, and PWHT. Specimen bars were held at 940°C (1725°F) for 1 h and cooled at 3 K/s (5°R/s) to simulate quenching in water from 940°C. The bars were then tempered for 6 h at 663°C (1225°F), followed by a PWHT of 28 h at 691°C (1275°F) with air cooling after each treatment. Specimen bars were removed after each step in the heat treatment to evaluate each phase of heat treatment.

The second heat treatment simulated the thermal cycle at the quarter-thickness depth in the 305-mm-thick plate under the same heat treatments except that the cooling rate at the quarter-thickness depth was 0.3 K/s (0.6°R/s). The quench simulation was also performed in the DATA TRAK facility.

Tensile results from tests at 24°C (75°F) with W-oriented specimens from bars subjected to the heat treatments described are listed in Table 5 and shown in Figs. 3 and 4. The mill chemical composition of the steels was reported earlier.¹ The following observations are made for the tensile strength behavior of the Ni-V modified 2 1/4 Cr-1 Mo steels at the simulated quarter-thickness depth in 305-mm-thick plate (cooled 0.3 K/s) when subjected to the quench-and-temper (Q + T) heat treatments described (Fig. 3).

1. The PWHT reduced the strength of Q + T steels in all cases examined.

2. The optimum tensile strength [739 MPa (108 ksi)] was obtained with the high-vanadium (0.037%) and the high-silicon (0.26%) Si-K steel.

3. Increasing the vanadium content increased the tensile strengths in the VCD and Si-K steels but had little or no effect on the Si-Al-K steel.

4. When the vanadium content was held constant, the Si-K steel with either the high- or low-vanadium content provided the higher tensile strength.

Table 5. Effect of cooling rate and heat treatment on the tensile properties^a of modified 2 1/4 Cr-1 Mo steel at 24°C after austenitizing at 941°C (1725°F) for 1 h

Metallurgical ^b condition	Cooling rate		Stresses, MPa (ksi)		Ductility, %		
	(K/s)	(°R/s)	Yield ^c	Ultimate	Total ^d elongation		Reduction of area
					L/D = 7	L/D = 4	
VCD ^{e,f} (US Steel heat 8116A)							
Q	0.3	0.6	816 (118)	1077 (156)	12.4	18.0	61
Q + T	0.3	0.6	570 (82.6)	684 (99.2)	16.0	23.2	77
Q + T + PWHT ₂₈	0.3	0.6	446 (64.8)	576 (83.4)	18.2	25.8	76
Q	3	5	922 (134)	1137 (164)	11.3	17.2	63
Q + T	3	5	585 (84.8)	699 (102)	16.4	24.1	77
Q + T + PWHT ₂₈	3	5	466 (67.7)	586 (84.8)	19.6	27.8	78
VCD ^{e,g} (US Steel heat 8116B)							
Q	0.3	0.6	836 (122)	1060 (158)	12.6	18.2	61
Q + T	0.3	0.6	627 (91.0)	722 (104)	13.6	20.2	74
Q + T + PWHT ₂₈	0.3	0.6	477 (69.2)	594 (86.1)	17.0	24.6	78
Q	3	5	942 (137)	1148 (166)	11.4	17.0	65
Q + T	3	5	649 (94.2)	742 (108)	14.5	21.4	75
Q + T + PWHT ₂₈	3	5	466 (67.7)	589 (85.4)	18.4	26.4	78
Si-K ^{e,f} (US Steel heat 8117A)							
Q	0.3	0.6	807 (117)	1108 (161)	12.1	17.3	59
Q + T	0.3	0.6	599 (86.9)	724 (105)	14.9	21.4	76
Q + T + PWHT ₂₈	0.3	0.6	462 (67.0)	600 (87.0)	19.0	26.8	75
Q	3	5	942 (136)	1164 (169)	12.5	18.6	62
Q + T	3	5	616 (89.4)	732 (106)	16.4	23.8	77
Q + T + PWHT ₂₈	3	5	478 (69.3)	603 (87.5)	17.6	24.8	77
Si-K ^{e,g} (US Steel heat 8117B)							
Q	0.3	0.6	828 (120)	1092 (158)	13.3	19.0	60
Q + T	0.3	0.6	628 (91.1)	739 (108)	15.2	22.1	73
Q + T + PWHT ₂₈	0.3	0.6	472 (68.4)	601 (87.2)	18.5	26.0	76
Q	3	5	934 (136)	1150 (167)	11.4	16.9	63
Q + T	3	5	660 (95.7)	761 (110)	14.7	21.6	76
Q + T + PWHT ₂₈	3	5	478 (69.4)	610 (88.4)	19.0	26.8	77
Si-Al-K ^{e,f} (US Steel heat 8118A)							
Q	0.3	0.6	842 (122)	1093 (158)	12.2	17.7	61
Q + T	0.3	0.6	562 (81.6)	693 (100)	15.9	22.8	76
Q + T + PWHT ₂₈	0.3	0.6	442 (64.1)	598 (86.6)	20.0	27.9	76
Q	3	5	942 (136)	1176 (170)	11.5	17.2	64
Q + T	3	5	594 (86.2)	712 (104)	14.6	21.3	77
Q + T + PWHT ₂₈	3	5	452 (65.4)	596 (86.4)	20.3	27.8	78
Si-Al-K ^{e,g} (US Steel heat 8118B)							
Q	0.3	0.6	822 (119)	1098 (159)	12.6	18.0	60
Q + T	0.3	0.6	562 (81.4)	694 (100)	16.1	23.2	76
Q + T + PWHT ₂₈	0.3	0.6	460 (66.6)	612 (88.7)	20.0	28.0	77
Q	3	5	925 (134)	1163 (169)	10.4	15.4	60
Q + T	3	5	598 (86.7)	715 (104)	15.4	22.4	77
Q + T + PWHT ₂₈	3	5	458 (66.4)	602 (87.3)	20.4	28.2	77

^aAverage of two specimens; W-orientation.

^bQ denotes quench rate simulated by DATA TRAK; T denotes temper at 663°C (1225°F) for 6 h, followed by air cooling; and PWHT₂₈ denotes postweld heat treatment at 691°C (1275°F) for 28 h, followed by air cooling.

^cOffset, 0.2%.

^dL/D = ratio of gage length to gage diameter. The values in the L/D = 4 column were calculated from L/D = 7 data; strain rate, 0.016/min.

^eVCD = vacuum-carbon-deoxidized, Si-K = silicon-killed, and Si-Al-K = silicon-aluminum-killed.

^fContent, <0.010% V plus 1/2 % Ni.

^gContent, 0.34 to 0.37% V plus 1/2 % Ni.

Fig. 3. Effect of cooling rate and heat treatment on the tensile properties of Ni-V modified 2 1/4 Cr-1 Mo steel plate at 24°C (75°F) after austenitizing at 941°C for 1 h.

Fig. 4. Effect of cooling rate and heat treatment on the ductility of Ni-V modified 2 1/4 Cr-1 Mo steel plate at 24°C (75°F) after austenitizing at 941°C for 1 h.

5. When the silicon content was held constant (0.26–0.27%), an increase in vanadium content resulted in increased tensile strength of the Q + T Si-K steel but had no effect on the Si-Al-K steel after the PWHT.

6. Increasing the silicon content of the high- or low-vanadium content steels increased the tensile strength of the Si-K steel but had little or no effect on the strength of the Si-Al-K steel.

The yield stresses generally followed the tensile stress trends with small exceptions. The yield and tensile stresses at the simulated surface (3 K/s cooling rate) were usually higher. Similar types of comparison can be deduced from the ductility results shown in Fig. 4.

In addition to the tensile results, we are in the process of obtaining Charpy V-notch toughness with specimens from the Ni-V modified 2 1/4 Cr-1 Mo steels subjected to the heat treatments described above.

Deformation-Induced Damage Mechanisms in Modified Low-Alloy Steels

Low-alloy steels modified by small additions of vanadium, titanium, and boron show exceptional promise as pressure boundary materials for heavy wall vessels that operate from 370 to 540°C. The lack of operating experience with these new materials will make it very difficult to obtain approval from the ASME Code for their use in the construction of coal conversion reaction vessels, even if large bodies of material design data exist. We believe that a basic understanding of the strengthening mechanisms and damage accumulation mechanisms in these alloys is needed to ensure that the design data and the design criteria developed for the Code Case are adequate.

We have initiated studies on a material provided to us by JSW.⁵ The alloy in question is claimed to have about 50% greater creep strength than SA-387, grade 22, class 2, and a 35% greater design stress intensity at 482°C. We wish to know how the alloy additions have improved the strength and whether or not exposure to deformation typical of secondary stress levels in pressure vessel service will degrade the strength and ductility.

We intend to develop a model to describe the accumulation of deformation-dependent damage by use of continuum mechanics concepts of the type proposed by Kachanov.⁶ We will then evaluate the adequacy of the

model from a material science viewpoint by approaches similar to those of Cane and Middleton.⁷⁻⁸

The starting point for our research was the evaluation of baseline mechanical properties such as tensile, creep rupture, fracture toughness, and fatigue. The material will be exposed to "damaging" conditions, and the subsequent change in microstructure and properties will be determined.

Some typical creep curves for the Japanese alloy at 482°C are shown in Fig. 5. It is apparent that the primary creep strains are very low, less than 0.5%, and that the strains at which tertiary creep starts are also low, less than 1%. These data indicate that degradation of the material starts very early in life and at very low accumulated strains. Even so, the material is much stronger than SA-387, grade 22, class 2. Our data confirm the finding of the Japanese in the sense that the creep strength of the modified alloy is at least 50% greater than that of 2 1/4 Cr-1 Mo steel at 482°C.

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UCSB-3.2.3 — ANALYSIS OF HYDROGEN ATTACK ON PRESSURE VESSEL STEELS

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INTRODUCTION

Steels used for fabrication of coal conversion vessels are exposed to hydrogen at high temperatures and pressure ($T \sim 450^\circ\text{C}$ and $P_{\text{H}_2} \sim 15 \text{ MPa}$).

Under these conditions hydrogen readily diffuses into the metal matrix and may react with carbon at internal surfaces to form methane. This phenomenon, known as hydrogen attack (HA), can result in internal decarburization and the nucleation, growth and eventual coalescence of grain boundary cavities. These microstructural changes, in turn, result in severe degradation of mechanical properties. Hence, HA may be a serious failure mechanism for thick-walled pressure vessels.

Selection of "safe" hydrogen pressure and temperature limits have been based on the empirical Nelson Curves; these curves have been developed for various broad alloy classes and qualitative failure criteria. However, because of extremely limited data and operating experience under the conditions pertinent to coal conversion technologies and probable requirements for fail-safe operation, Nelson curves may not be adequate for designing thick-walled pressure vessels.

The purpose of this research is to develop physical models of the HA process describing important mechanisms and containing pertinent environmental and metallurgical parameters. These models are then used to statistically correlate engineering and laboratory data and to extrapolate the data to predict HA behavior under actual vessel service conditions.

RESULTS FROM PRIOR QUARTERS

HA in Carbon Steels

An analysis of HA results in plain carbon steel has shown that the rate of nucleation of HA cavities is not consistent with the classical nucleation mechanisms. Hence, a nucleation model was developed based on pre-existing distribution of microvoids and/or gas bubbles. The instability criterion for growth is

$$r^* \geq \frac{M \gamma_s}{P_o} \quad (1)$$

where M is a numerical factor and has value of 0.77 for gas bubbles and of 2.0 for microvoids, γ_s is the surface energy and P_o is the equilibrium methane pressure. The model predicts cavity spacings of $\sim 1.0 \mu\text{m}$ at high hydrogen pressures and somewhat higher spacings at lower hydrogen pressures. These are qualitatively consistent with experimental observation of 1-5 μm cavity spacings.

It was also shown that the growth of HA cavities in carbon steel during incubation stage occurs by vacancy diffusion along the grain boundaries provided the methane pressure in the cavity exceeds a threshold pressure. In other words the cavity growth is constrained. The threshold pressure, measured experimentally, decreases with increase in temperature from $\sim 400 \text{ MPa}$ at 658 K to $\sim 200 \text{ MPa}$ at 723 K. It is well known that two-phase interfaces are not good sources or sinks for vacancies. For diffusional growth of voids to continue, the atoms removed from the voids should be plated uniformly along the grain boundary, otherwise internal stresses will be generated at the precipitates which oppose the void growth. However, the internal stresses can be relieved by local plastic deformation around the precipitates. A creep constrained cavity growth model was developed in which local plastic deformation around precipitates is achieved by the dislocation creep of matrix². The predictions of the model were in excellent agreement with McKimpson's³ data.

HA in 2½ Cr-1 Mo Steels

The diffusional growth model developed for carbon steels was extended to 2½ Cr-1 Mo steel by considering two carbide species M_3C tempered carbide and Cr_7C_3 carbide with higher stability. The model was calibrated with the limited dilatometry data of Sundarajan and Shewmon⁴ for temperatures around 500°C. The extrapolation of the model to lower temperatures (400-450°C) showed that HA may be a problem for vessels operating for the periods for 50,000 to 200,000 hours. This was in apparent contrast to the successful service of 2½ Cr-1 Mo steels in the chemical industry. Hence possibility that other factors such as availability of carbon and threshold pressure for cavity growth were considered. A carbon starvation model was developed in which rate of supply of carbon to cavities is limited by rate of dissolution of Cr_7C_3 carbide². The carbide dissolution rates were estimated from the isothermal transformation diagram for the quenched and tempered steel. The incubation times predicted by the model were much higher than those by diffusional growth model at lower temperatures (400-450°C) and suggest that vessels made of fully tempered i.e. 2½ Cr - 1 Mo steel with no unstable M_3C carbide, are relatively safe against HA. The Nelson curve derived from the model was consistent with the standard API decarburization curve when a modest threshold pressure was introduced in the model.

A creep fracture map for normalized and tempered 2½ Cr - 1 Mo steel was developed using simple models for high temperature fracture mechanism such as transgranular, triple point cracking and cavitation fracture. Both rupture times and fracture modes predicted for the alloy were in good agreement the experimental data. Further, the effects of HA on creep fracture in the alloy were considered. The cavity growth model by coupled diffusion-power law creep developed by Edward and Ashby⁵ was modified by including methane pressure within the cavities⁶. The creep fracture map under hydrogen exposure conditions indicates the dominance of regime of intergranular fracture and the reduction in rupture times.

DISCUSSION OF CURRENT ACTIVITIES

Constrained Diffusion Growth

Analysis of HA data suggests that cavity growth may be influenced by plastic deformation mechanisms or creep². Several factors may lead to creep controlled diffusion growth. However, three important and practical situations resulting in constrained growth are⁸

1. Particle Inhibition
2. Vacancy Source Control
3. Geometric Constraint

1. Particle Inhibition:

The presence of hard particles on grain boundary results in constraints for cavity growth. This is mainly due to the particle/matrix interfaces acting as poor sources or sinks for vacancies⁷. For diffusional growth of cavities the atoms removed from the cavities should be plated uniformly along the grain boundary otherwise internal stresses will develop which oppose further growth of cavities. The presence of particles makes uniform plating impossible, for cavity growth to continue the back stress has to be relieved by plastic deformation. Thus particle inhibition results in a threshold stress for cavity growth. A constrained growth model due to particle inhibition was developed for us for HA conditions in which local plastic deformation around particles is achieved by dislocation creep of matrix. The predictions of the model are in good agreement with McKimpson's data³ for carbon steel.

2. Vacancy Source Control:

The likely sources of vacancies for diffusional growth of cavities are grain boundary dislocations. If the density and the rate of climb of such dislocations is insufficient then the cavity growth is constrained. This model, called vacancy-source controlled cavity growth, was originally proposed by Ishida and McLean⁹ who suggested that dislocations arriving at grain boundaries from grain interiors provide

the necessary vacancy sources via their subsequent glide/climb motion in the grain boundary plane. Further, the presence of hard particles in the boundary can inhibit the glide/climb motion of grain boundary dislocations. Beere¹⁰ has recently shown that the cavity growth rate for the model is proportional to the creep rate in the material.

3. Geometric Constraint:

Experimental data indicates that HA cavities are generally observed on only a fraction of grain boundaries^{3,11}. Quite often cavities are very closely spaced on isolated grain facets surrounded by grains with uncavitated grain facets. This situation is illustrated in Figure 1. If the strain rate due to atom plating on the boundary between grains A and B is greater than the strain rate of surrounding material or cage then the cavity growth rate will be determined by the rate of deformation of cage and not by the diffusional kinetics.

A cavity growth model due to geometric constraints is presented here for HA conditions. It is assumed that the methane pressure within the cavities is constant and is equal to equilibrium methane pressure, P_o . In the absence of external applied stress, taking force balance

$$f_b \cdot \frac{\pi}{4} x^2 \cdot P_o = \sigma_1 \cdot f_b + \sigma_2 (1-f_b) \quad (2)$$

where f_b is the fraction of grain boundaries cavitated, σ_1 is the stress over the cavitated boundary facet, σ_2 is the stress in the cage surrounding the cavitated grain facet and $x = r/l$, r is the radius of the cavity and l is the cavity half spacing.

Further the strain rates in cavitated and uncavitated regions should be the same. Strain rate in the cavitated region is given by

$$\dot{\epsilon}_c = \frac{dv/dt}{\pi l^2 d} \quad (3)$$

where dv/dt is the cavity growth rate and d is the grain size. The cavity growth rate is given by¹⁰

Fig. 1. Schematic diagram showing geometric constraints due to cavities on isolated grain boundaries.

$$\frac{dv}{dt} = \frac{2\pi\Omega\delta_b D_b}{kT} (\sigma_1 + P_o) \cdot f(x) \quad (4)$$

where δ_b is the width of grain boundary, D_b is boundary diffusivity, Ω atomic volume, k is the Boltzmann's constant, T is temperature in degrees Kelvin and $f(x)$ is boundary ligament/stress term

$$f(x) = \frac{1 - x^2}{x^2 (1 - \frac{x^2}{4}) - \frac{3}{4} - \ln x} \quad (5)$$

Assuming that the deformation in cage occurs by power-law creep, the strain rate in the cage is given by

$$\dot{\epsilon}_g = B \cdot \sigma_2^n \quad (6)$$

where B and n are constants for the material.

The stresses σ_1 and σ_2 can be estimated by solving numerically equations (2) to (6). In the absence of external stress $\sigma_1 \ll \sigma_2$, and in fact σ_1 is compressive and σ_2 is tensile in nature. Thus cavity growth rate dv/dt , predicted by equation (4) is lower than that for unconstrained diffusion growth model¹². It will be shown later that the magnitudes σ_1 and σ_2 depend critically on f_b and are more or less independent of the cavity size (i.e. value of x).

Comparison of Experimental Data

The predictions of the model given in the previous section are compared with the recent HA kinetic data of Yu and Shewmon¹³ for quenched and tempered 2½Cr - 1 Mo steel. Using a sensitive dilatometer and following the procedure details of which are given elsewhere¹⁴, they measured specimen expansion rates, DLD, at various temperatures and hydrogen pressures. It was found that for $T > 550^\circ\text{C}$ steady state expansion rate was observed which was independent of time of exposure and the cycling history. However, for temperatures below 510°C the expansion rate observed initially was found to decrease continuously with time eventually reaching zero ($< 10^{-9} \text{ hr}^{-1}$).

Figure 2 shows the variation of the specimen expansion rate with reciprocal of temperature for hydrogen pressure of 20.3 MPa and over the temperature range of 550-580°C. The apparent activation energy is $\sim 206 \pm 38$ kJ mole⁻¹. Figure 3 shows the variation of the specimen expansion rate with hydrogen pressure for temperatures 550, 570 and 580°C. The hydrogen pressure exponent at 570 and 580°C are 1.7 ± 0.7 and 2.8 ± 1.2 respectively.

The steel used by Yu and Shewmon¹³ was quenched and tempered for 60 hours at 650°C which will produce Cr₇C₃ and Mo₂C. However, possibility of a small amount of remnant M₃C carbide can not be ruled out. Our analysis showed that the equilibrium pressures for the higher stability carbides Cr₇C₃ and Mo₂C are probably too low (less than 50 MPa) to cause the observed specimen expansion rates. Hence, the presence of M₃C carbide is assumed. The equilibrium constant, K_o, for methane reaction for M₃C carbide was taken from the work of Geiger and Angeles¹⁵ and is given by

$$K_o = 1.95 \times 10^{-6} \exp \left(\frac{12121}{T} \right) \text{ MPa}^{-1} \quad (7)$$

The details of estimation of equilibrium methane pressure are given elsewhere¹⁴.

Further, it was found that the power-law creep equation describing the deformation in the cage (equation (6)) depends on the magnitude of stress σ_2 . Cane¹⁶ has investigated creep deformation in a normalized and tempered 2½ Cr - 1 Mo steel at 565°C which is close to the temperature range used by Yu and Shewmon¹³. For stresses below 150 MPa stress exponent was ~ 4.0 and a somewhat higher value of ~ 12.0 was observed at higher stresses. The minimum creep rate is given by

$$\dot{\epsilon}_g = 7.8 \times 10^7 \sigma^4 \exp \left(- \frac{400000}{RT} \right) \text{ s}^{-1}, \text{ for } \sigma < 150 \text{ MPa} \quad (8)$$

$$\dot{\epsilon}_g = 5.1 \times 10^{-10} \sigma^{12} \exp \left(- \frac{400000}{RT} \right) \text{ s}^{-1}, \text{ for } \sigma > 150 \text{ MPa} \quad (9)$$

where σ is in MPa. The activation energy for creep of 400 kJ mole⁻¹ was taken from a previous report⁶ since creep data of Cane¹⁶ was at only one temperature (565°C).

Fig. 2. Variation of specimen expansion rate with reciprocal of temperature at hydrogen pressure of 20.3 MPa for 2 1/4 Cr-1 Mo steel¹³.

Fig. 3. Variation of specimen expansion rate with hydrogen pressure at 550, 570 and 580°C for 2 1/4 Cr-1 Mo Steel¹³.

Figure 4 shows the comparison between the model predictions and the temperature cycling data given in Figure 2. The parameters used in the correlation are given in Table I. The cavity growth rate, dv/dt , estimated using equation (4) was converted to DLDT using the relationship

$$DLDT = \frac{1}{3} \rho_c \frac{dv}{dt} \quad (10)$$

where ρ_c is the volume cavity density given by $\rho_c = \frac{3f_b N_c}{d}$, N_c is the local cavity density on the cavitated grain facet.

Two parameters of prime concern are cavity size (i.e. value of x) and the fraction of grain boundaries cavitated, f_b . As evident from Figure 4 the specimen expansion rates show large sensitivity to f_b and very small sensitivity to x . The large sensitivity of DLDT on f_b arises from two factors. A part of the higher DLDT at a higher f_b is due to increase in the volume cavity density, ρ_c . However, the increase in DLDT observed is considerably larger than the increment due to higher ρ_c . The major part is due to higher cavity growth rate (equation (4)) because the compressive stress σ_1 becomes smaller in magnitude. Physically this means there is less constraint for cavity growth at higher f_b .

For the parameters used in Figure 4, viz $f_b = 0.14 - 0.2$ and $x = 0.1 - 0.3$, the magnitude the stress σ_2 in the cage was less than 150 MPa and hence, power-law creep rate given by equation (8) was used. It is clear from Figure 4 that Yu and Shewmon's data is consistent with f_b value in the range 0.14 - 0.15. No detailed microstructural data on cavity distribution and their spacings was available. However, Yu and Shewmon¹³ observed cavities only in isolated areas. Hence, a value of $f_b \sim 0.15$ appears to be reasonable.

Taking values for $f_b = 0.15$ and $x = 0.1$, the specimen expansion rates predicted by the model are then compared in Figure 5 with the results given in Figure 3. The absolute magnitude of DLDT values are in the good agreement with the data even though the hydrogen pressure

Fig. 4. Comparison between the model predictions and the experimental data shown in Figure 2.

Table I

Parameters used for 2½ Cr - 1 Mo Steel in Comparison
Between the Model Predictions and Yu and Shewmon's Data¹³.

Parameter	Value	Reference
R	$8.314 \text{ J K}^{-1} \text{ mole}^{-1}$	
k	$1.38 \times 10^{-23} \text{ J K}^{-1}$	
Ω	$1.18 \times 10^{-29} \text{ m}^3$	
d	$5 \times 10^{-5} \text{ m}$	13
K_o	$1.95 \times 10^{-6} \exp \left(\frac{12121}{T} \right) \text{ MPa}^{-1}$	15
N_c^*	$4 \times 10^{10} \text{ m}^{-2}$	16
$N_c^{\S}$	$2.5 \times 10^{11} \text{ m}^{-2}$	17, 19
$\delta_b D_b$	$1.1 \times 10^{-12} \exp \left(- \frac{173700}{RT} \right) \text{ m}^3 \text{ s}^{-1}$	20

* for conditions with no hydrogen exposure

§ for conditions with hydrogen exposure

Fig. 5. Comparison between the model predictions and the experimental data shown in Figure 3.

exponent predicted by the model is somewhat higher. Yu and Shewmon¹³ reported values for exponent of 1.7 ± 0.7 and 2.8 ± 1.2 at 570 and 580°C respectively as compared to a value of 3.3 predicted by the model. Considering the amount of scatter in the data the agreement is quite good.

Hence, the limited dilatometry data of Yu and Shewmon on HA in 2½Cr - 1 Mo steels is consistent with the constrained diffusion model based on geometric constraints.

Effect of Applied Stress

It is fairly well established that external stress has a significant influence on HA in ferritic steels. The creep tests under hydrogen exposure conditions show considerable reduction in ductility and rupture times^{17,18}. The cavity density observed HA conditions is higher than the creep cavity density. Cane¹⁶ has reported creep cavity density of $\sim 4 \times 10^{10} \text{ m}^{-2}$ for tests in vacuum as compared to HA cavity densities of $2.5 \times 10^{11} - 10^{12} \text{ m}^{-2}$ reported by Li¹⁸, Sakai and Kaji¹⁹. Further, the decarburization due to HA may result in higher creep rates. Another factor which is of great importance is the orientation of HA cavities with respect to the applied stress. For example, under uniaxial loading conditions, cavities on grain boundaries oriented normal to the stress axis will experience maximum effect of applied stress where as cavities on boundaries parallel to stress axis will experience no effect. Hence the cavities on normal boundaries grow at faster rate as in case of creep cavities. This may result in lower f_b since cavities are randomly nucleated during HA. As already discussed previously the cavity growth rates are very sensitive to f_b and hence the effects of applied stress on cavity growth during HA may be quite complex.

The constrained growth model developed earlier is extended to include the effects of external stresses assuming that all cavitated boundaries are oriented normal to the stress axis. Equation (2) can be re-written as

$$\sigma + f_b \cdot \frac{\pi}{4} x^2 \cdot P_o = f_b \cdot \sigma_1 + (1-f_b) \sigma_2 \quad (11)$$

where σ is the applied stress. Rest of the analysis is the same as before except that for creep tests without hydrogen exposure the methane pressure, P_o , in equation (11) is equal to zero. Since all cavitated boundaries are oriented normal to the stress axis, the specimen expansion rate, DLDT is given by

$$DLDT = \rho_c \cdot \frac{dv}{dt} \quad (12)$$

Assuming rupture time as the time required to reach 0.2% swelling we get

$$t_r = \frac{0.002}{\rho_c \cdot \frac{dv}{dt}} \quad (13)$$

Figure 6 shows the comparison between the model predictions and the experimental creep rupture data for $2\frac{1}{2}\text{Cr} - 1\text{Mo}$ steel. The solid symbols indicate creep tests without hydrogen exposure and the open symbols indicate tests in hydrogen. The decrease in creep rupture strength under hydrogen exposure conditions is clearly evident. Also shown in Figure 5 is the scatter band of the creep rupture data for $2\frac{1}{2}\text{Cr} - 1\text{Mo}$ steel.

The stresses for rupture times of 10^5 hours were estimated from the model and the agreement between model predictions and experimental creep rupture data without hydrogen exposure is good for f_b value of 0.05. Further, the model predicts decrease in rupture strength under hydrogen exposure conditions. The magnitude of the decrease in the rupture strength is sensitive to f_b . From the analysis it appears that for laboratory short time tests ($t_f < 1000$ hours) in hydrogen f_b is not very much different from tests in vacuum or inert gas. Another reason for the low value of f_b for creep tests in hydrogen may be the orientation effect discussed earlier, viz., HA cavities on boundaries normal to stress axis will only contribute to increased swelling rate. However, situation may change under long time exposure and multi-axial loading

Fig. 6. Comparison between model predictions and the creep rupture data for 2 1/4 Cr-1 Mo steel

conditions typical of coal conversion pressure vessels. Higher f_b which may result under these conditions, will lower the creep rupture strength of the material.

Figure 7 shows the Nelson type curves predicted by the model based on a failure criteria of 0.1% swelling at 100,000 hours for $2\frac{1}{2}\text{Cr} - 1\text{Mo}$ steel. Also shown in Figure 7 is the standard API surface decarburization curve for the alloy. The Nelson curves predicted by the model in the absence of external stress for f_b values of 0.1 and 0.15 lie above the API decarburization curve. It is also seen that there is a threshold hydrogen pressure of 10 MPa for $f_b = 0.1$ which decreases with increase in f_b . The effect of external stress is to shift the Nelson curves to lower temperatures, and for hydrogen pressures greater than 15 MPa the amount of shift is $\sim 1^\circ\text{C}$ per MPa of external stress. Another effect of the external stress is the absence of threshold hydrogen pressure for HA.

SUMMARY AND CONCLUSIONS

A constrained diffusion growth model based on geometric constraints due to cavities on isolated grain boundaries has been developed for HA conditions. The cavity growth rates predicted by the model are consistent with the recent dilatometry data on a quenched and tempered $2\frac{1}{2}\text{Cr} - 1\text{Mo}$ steel. Further, the analysis indicates that $2\frac{1}{2}\text{Cr} - 1\text{Mo}$ steels containing unstable carbide M_3C are susceptible for HA whereas steels containing higher stability carbides such Cr_7C_3 and Mo_2C are unlikely to suffer HA. The Nelson curve predicted by the model lies above the standard API decarburization curve. It is also shown that in the presence of external stress the Nelson curve is shifted to lower temperatures and hydrogen pressures.

Fig. 7. Comparison between the Nelson type curves predicted by the model and the standard API decarburization curve for 2½ Cr-1 Mo steel.

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WEC-3.2.3 - STUDY TO OPTIMIZE Cr-Mo STEELS TO RESIST
HYDROGEN AND TEMPER EMBRITTLEMENT

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INTRODUCTION

The primary objective of this program is to evaluate a range of Cr-Mo steels in order to assess the role of compositional variables on the susceptibility to hydrogen and temper embrittlement. The program is divided into two phases. Phase I is designed to establish the hydrogen embrittlement susceptibility of commercial 2-1/4Cr-1Mo steels provided by the American Petroleum Industry. This phase consists of two parts. The first part is to assess the hydrogen embrittlement characteristics of the steels at conventional strength levels (Ultimate Tensile Strength, UTS, in the range 60-80 ksi or 400-550 MPa). The second part is to measure the hydrogen embrittlement susceptibility of the peak hardness zone (PHZ) in the heat affected zone (HAZ) adjacent to the weld. Since few large weld samples were available, tests were also to be conducted on plate material heat treated to a higher strength level corresponding to that of the PHZ. This corresponds to an UTS of the order 100-110 ksi or 690-760 MPa.

Phase II consists of an evaluation of 32 laboratory heats with compositions arranged according to a statistical design and tempered in a bainitic condition to two strength levels, corresponding to the ranges used in Phase I. The primary evaluations are for temper embrittlement and hydrogen embrittlement. Comparison of the data generated from the laboratory heats can be made with commercial samples from Phase I of the program for hydrogen embrittlement and with an independent API program for temper embrittlement. Based upon the data to be generated in Phase

II, it is anticipated that compositional areas with high or low susceptibility to either form of embrittlement may be identified.

The original intention was to use a simple rising load test on fatigue precracked Charpy specimens for the hydrogen embrittlement study. However, because the yield strength of this class of steel is so low, a study of the effect of specimen size on the validity of the data was included in Phase I. Consequently, tests were carried out on 1T, 2T and 3T Compact Tension (CT) specimens for comparison.

As a result of this study, it became clear that the inexpensive Charpy test would not yield reliable data. Moreover, the rising load test on a standard CT specimen would not necessarily give the value of the threshold stress intensity in the H_2S environment (K_{ISCC}). Two factors of considerable importance, i.e. the incubation time and plane-stress pinning of the crack, had to be considered in some detail. A review of the effects is given in Quarterly Report #4.

Since the revision of the test technique necessitated the use of larger specimens and a more complex test procedure, the scope of the program (but not the primary objectives) had to be revised. To date, it appears that the method for evaluating the hydrogen embrittlement susceptibility of the higher strength steels (690-760 MPa) is resolved.

The same technique that would satisfactorily produce cracking in the steels tempered to a higher strength level was totally unsuccessful for steels of a lower strength level. In order to obtain a screening test for the low strength steels, it was decided to introduce a more potent environment. The results of tests on both high and low strength steels subjected to the same (mechanical) test procedure using hydrogen sulfide gas saturated with water vapor for the environment appeared to be quite satisfactory in that steels over the entire strength level range were embrittled.

This report describes the initial and uncompleted analysis of the temper embrittlement data.

RESULTS FROM PRIOR QUARTERS

Combined Quarterly Report Nos. 1 and 2
May 7, 1979

This report gives

- i) The original structure and objectives of the program.
- ii) The formal statistical matrix to be used in Phase II of the program.
- iii) The levels of the alloying elements in the 32 steels of the statistical design compared with the ASTM A387 specification limits.
- iv) The experimental determination of the peak hardness in the heat affected zone (HAZ) via microhardness measurements.
- v) Considerations of the test requirements for hydrogen embrittlement measurements in low strength steels.

Quarterly Report No. 3
August 23, 1979

The report gives the data from one sample 2-1/4Cr - 1Mo steel which had been re-heat treated to a strength level comparable with that of the peak hardness zone of the HAZ. A standard 3T compact tension (CT) specimen tested in 50 psig (446 KPa) H₂S was compared with side grooved 2T and 1T CT specimens. It was shown that the plane stress zones inhibit crack advance in the 3T specimen and that estimates of the threshold stress intensity can be substantially lower if side grooves are incorporated. Incubation time effects were reduced by fatigue precracking the specimens in the environment.

Quarterly Report No. 4 (First Annual Report)
December 17, 1979

The first annual report gives a review of the status of the program and an outline of the most significant tests performed in H₂S to date.

A description of the new testing procedure developed to evaluate hydrogen embrittlement susceptibility is presented. The report lists estimates of the crack arrest stress intensities measured on commercial steels which have been re-heat treated to strength levels comparable with that of the peak hardness zone in the HAZ.

Quarterly Report No. 5
July 23, 1980

This report gives the results of tests designed to measure the threshold stress intensity in H_2S of the peak hardness zone in the HAZ of welds in 2-1/4Cr - 1Mo plate. Difficulty was encountered because of a variability in the location of the peak hardness zone relative to the weld-base interface. There are indications that the K_{arr} could be significantly below 80 ksi in.^{1/2} (88 MPa m^{1/2}) but the absolute values could not be determined from the current tests. Details of the forging process for heats produced for Phase II of the program are given.

Quarterly Report No. 6
July 28, 1980

Because of difficulties encountered in the testing of low strength steels in commercially pure H_2S , a modification to the program was incorporated to study the effect of strength level on hydrogen embrittlement susceptibility. The report presents the results of this study on one steel in which it was found that there appears to be a strength level limit, approximately 100 ksi (690 MPa) below which the 2-1/4Cr - 1Mo steel is immune to cracking in the H_2S environment provided by a tank of commercial high purity H_2S .

Quarterly Report No. 7
October 20, 1980

In phase II of the study, 32 heats with compositions based upon a statistical design have been cast and forged. The analytical chemistry

of the heats is reported and found to be very close to the original aim compositions. The initial stage of the heat treatment, transformation to a bainitic structure, is described. High percentages of ferrite were found in some of the samples. The occurrence of ferrite is discussed briefly in terms of the levels of alloying elements.

Quarterly Report No. 8
November 20, 1980

In the first annual report of this series (Report No. 4), the modified test method developed to assess the hydrogen embrittlement susceptibility in H_2S was described. It was found that the 2-1/4Cr - 1Mo and 1-1/4Cr - 1/2Mo steels with conventional post weld heat treated (PWHT) strength levels (UTS in the range 60-80 ksi or 400-550 MPa) were essentially immune to the test method using 50 psig (446 KPa) commercially pure H_2S as the environment. An evaluation of the effect of yield strength (Report No. 6) showed that, for one sample of 2-1/4Cr - 1Mo steel, there was a lower limit below which failure could not be induced. In this section a series of tests using a new environment of H_2S and water vapor is reported.

Quarterly Report No. 9
January 20, 1981

This was the second annual report of the program which reviewed the progress made in 1980. The report included (i) a discussion of H_2S environment tests on the heat affected zone in 2-1/4Cr - 1Mo steels. (ii) the effect of strength level on K_{Isc} in H_2S (iii) a set of tests designed to assess the experimental scatter in measurements of K_{Isc} in an environment of $H_2S + H_2O$ vapor.

Quarterly Report No. 10
April 10, 1981

The second phase of the program had been started. The initial results from H_2S + water vapor environment tests on higher strength Cr-Mo steels were discussed. All of the specimens tested exhibited a "reverse thumbnail" fracture mode.

Quarterly Report No. 11
July 20, 1981

The heat treatments and the resulting structures (bainite and percentage ferrite) are recorded along with the tempering conditions used to produce two strength levels in 32 steels with compositional variables Mo, Cr, Mn, Si, C and P.

DISCUSSION OF CURRENT ACTIVITIES

The second phase of the program has two components: i) the investigation of the effect of compositional variables (Mo, Cr, Mn, Si, C and P) on the susceptibility of the steels to temper embrittlement, and ii) the effect of the same variables on hydrogen embrittlement. The statistically designed set of 32 heats have been tempered to two strength levels. Unembrittled Charpy specimens and blanks to be temper embrittled have been machined and tested from both strength levels. Corresponding blanks were temper embrittled at 875°F (468°C) for 1000 hr. Tests on the temper embrittled steels are completed. The environmental tests on the high strength steels are also completed. Similar tests on the low strength steels have been started. The main emphasis in this quarter has been the regression analysis of the temper embrittlement data. This is proving to be more difficult than anticipated because percentage of ferrite and strength level have been included as additional variables.

Temper Embrittlement Study

The heat treatments, the resulting strength levels and percentage ferrite for each of the samples to be assessed were given in the last report, No. 11 of this series (reproduced in ORNL/FMP-81/3). Charpy impact energy curves have been generated for samples in the unembrittled condition and after isothermal embrittlement treatment at 468°C (875°F) for 3.6 Ms (1000 hr). The data derived from the experiments were the 40 ft lb transition temperature (40 ft lb TT), the fracture appearance transition temperature (FATT), the upper shelf impact energy and the shift in the transition temperatures due to the isothermal embrittlement, respectively, $\Delta T(40)$ and $\Delta FATT$. These data are the dependent variables in the temper embrittlement experiment. The independent variables are the composition (Mo, Cr, Mn, Si, C and P) and strength level (SL). A secondary dependent variable is the percentage ferrite (PF) formed in the austempering treatment. Ferrite was formed mainly in the low C - low Cr samples. This variable can be regarded as an independent variable in the analysis for temper embrittlement since it appears that the temper embrittlement characteristics of fully bainitic and fully ferrite-pearlite samples of the same steel are quite different.⁽¹⁾

The regression analyses, therefore, include eight independent variables, viz, Mo, Cr, Mn, Si, C, P, SL and PF. In the early regression analyses, it was found that the small variations in grain size were not important.

Since the original statistical design was intended for only the six compositional variables, the addition of two further independent variables has increased the complexity of the analyses, which are still in progress.

The regression analysis leads to a model or an expression relating the dependent variable (e.g., $\Delta FATT$) to terms which are independent variables or combinations of the independent variables. For example, a

quadratic model includes terms such as Mo , Cr^2 , CCr , MnP , etc. One measure of the quality of the model is the correlation coefficient between the observation and the model prediction, signified by r , which lies between 0 and 1. In general, r increases with the number of terms employed in the model. It is pointless, however, to include as many terms as experimental observations since this ensures that r approaches 1 and does not yield a meaningful model.

Our procedure then is to select a number of terms and obtain the best models based upon the selection of two of these terms, three terms, four terms and so on. An example of this approach is shown in Table 1. This process is repeated with a new set of terms, retaining the most significant terms of the previous runs. Thus by a process of elimination and iteration, the model is optimized.

The criterion for the selection of a model to represent the data will be based upon a number of considerations. First an attempt is made to find the combination of terms which will provide the highest value for r . Secondly and at the same time, the number of terms is reduced to a reasonable minimum. For example, there is little point in including an extra term in the model if r is increased only from .79 to .80. Thirdly, a preference is given to the model which has the most reasonable physical interpretation, based upon the current knowledge of the role of elements in temper embrittlement. Lastly, the model should make reasonable predictions for experimental data independently generated. Fortunately, data which can be used for an independent evaluation has recently been published by the API.⁽¹⁾ This check of the selected final models will be useful in the light of the two additional independent variables introduced in the main experiment.

Comparison with Current Models for Temper Embrittlement

There are three models (often referred to as embrittlement factors) in the literature which relate temper embrittlement to composition in 2 1/4 Cr - 1 Mo steels. The first by Bruscatto,⁽²⁾ primarily for weld

metal, delineated high and low embrittlement areas on a two dimensional plot of (Mn + Si) and $\bar{X} = (10 P + 5 Sb + 4 Sn + As)/100$. Recognizing that the iso-embrittlement curves in this plot are approximately hyperbolic, the embrittlement can be represented by a function of the form

$$\Delta TT = f_1[\bar{X} (Mn + Si)]$$

where ΔTT stands for the shift in the transition temperature.

The second model, by Murakami, et al,⁽³⁾ is primarily for plate material and is given by

$$\Delta TT = f_2 [(P + Sn) (Mn + Si) \times 10^4]$$

which is similar in form to that of Bruscatto.

The third, and most recent, by Berthet, et al⁽⁴⁾ is

$$\Delta FATT^{\circ}C = 99 - 125 Mn - 16760 P + 38000 MnP$$

where P = Mn are in wt %. In their study, Si was shown to be relatively unimportant. Their expression may be represented by $\Delta TT = f_3 [Mn, P, MnP]$. Since As, Sb and Sn are not present in the matrix of this DOE study, the first two functions (f_1 and f_2) may be represented by $\Delta TT = f_4 [MnP, SiP]$.

The best fitted equations of the form f_3 and f_4 to the data generated in this were

$$\Delta T(40) = -34 + 7720 MnP + 1552 SiP$$

and

$$\Delta T(40) = -27 + 52 Mn + 7897 MnP - 1920 P$$

with correlation coefficients of .54 and .58, respectively. It is

interesting to note that the coefficients of MnP and SiP are not equal in the first equation, thus implying that Si is not as deleterious as Mn.

For comparison, Table 1 gives the correlation coefficients for a range of terms included in the regression analysis for $\Delta T(40)$ of steels tempered to a low strength level, which is comparable with that of the post weld heat treated 2 1/4 Cr - 1 Mo steel. Clearly better correlations to the data are obtained with models different to those represented by functions with the terms used in f_3 and f_4 .

Two points should be made, however. First, the models represented by f_3 and f_4 are specifically for compositions close to 2 1/4 Cr - 1 Mo, whereas the model developed in this study applies to a slightly broader range in the compositional variables (Table 2). The broader range was introduced in the study specifically to enhance and thereby clarify the effect of composition. The second point, discussed above, is that the final model should be tested and possibly refined with independent data.

It is anticipated that the models for the various dependent variables ($\Delta FATT$, 40 ft lb TT, etc.) will be completed within the next quarter.

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TABLE 1. Initial Regression Analysis Models for $\Delta T(40)$ of Low Strength Steels Showing the Terms Included at Each Stage and the Corresponding Value of the Correlation Coefficient, r.

Number of Terms	2		3		4		5		6		7		8	
Terms*														
MnP		✓					✓	✓	✓	✓				✓
Mn	✓		✓	✓	✓	✓					✓	✓	✓	
MoCr	✓	✓			✓						✓		✓	
CrC			✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓
SL**														
Mo			✓		✓		✓				✓		✓	
MoP				✓			✓		✓	✓				✓
CrP													✓	
Cr											✓	✓	✓	✓
PF***					✓				✓	✓	✓	✓	✓	✓
SiP					✓	✓	✓	✓	✓	✓	✓	✓		✓
P							✓	✓	✓	✓				✓
C									✓		✓	✓	✓	✓
Si														
r	.69	.68	.74	.74	.78	.77	.80	.80	.81	.81	.85	.85	.86	.84

*In order of correlation.

**Strength level.

***Percentage ferrite.

TABLE 2. Actual Compositions of Heats of Cr-Mo-Steel
Compared with Aim Compositions in Wt %

Heat No.	Element					
	Mo	Cr	Mn	Si	C	P
1. Actual	1.30	2.72	.33	.65	.071	.020
Aim	1.25	2.80	.35	.65	.07	.021
2. Actual	1.27	2.78	.85	.24	.17	.009
Aim	1.25	2.80	.85	.25	.16	.009
3. Actual	0.62	2.73	.33	.26	.17	.022
Aim	0.60	2.80	.35	.25	.16	.021
4. Actual	0.63	1.53	.37	.26	.071	.009
Aim	0.60	1.50	.35	.25	.07	.009
5. Actual	0.62	1.55	.87	.64	.17	.020
Aim	0.60	1.50	.85	.65	.16	.021
6. Actual	0.61	2.84	.82	.66	.075	.007
Aim	0.60	2.80	.85	.65	.07	.009
7. Actual	1.25	1.47	.39	.65	.17	.011
Aim	1.25	1.50	.35	.65	.16	.009
8. Actual	1.29	1.46	.86	.24	.069	.020
Aim	1.25	1.50	.85	.25	.07	.021
9. Actual	1.25	2.74	.85	.62	.17	.019
Aim	1.25	2.80	.85	.65	.16	.021
10. Actual	0.61	1.49	.35	.62	.07	.020
Aim	0.60	1.50	.35	.65	.07	.021
11. Actual	1.29	2.69	.33	.25	.07	.010
Aim	1.25	2.80	.35	.25	.07	.009
12. Actual	1.32	2.71	.35	.65	.068	.023
Aim	1.25	2.80	.35	.65	.07	.021
13. Actual	1.27	1.50	.86	.65	.065	.010
Aim	1.25	1.50	.85	.65	.07	.009
14. Actual	1.25	1.46	.36	.26	.17	.021
Aim	1.25	1.50	.35	.25	.16	.021
15. Actual	0.63	2.78	.91	.28	.072	.021
Aim	0.60	2.80	.85	.25	.07	.021
16. Actual	0.62	2.11	.35	.64	.18	.009
Aim	0.60	2.80	.35	.64	.16	.009
17. Actual	0.32	2.19	.61	.45	.13	.014
Aim	0.30	2.25	.60	.45	.115	.015
18. Actual	1.63	2.22	.63	.45	.13	.018
Aim	1.60	2.25	.60	.45	.115	.015
19. Actual	0.95	0.78	.62	.44	.12	.016
Aim	0.90	0.80	.60	.45	.115	.015
20. Actual	0.95	3.48	.61	.44	.12	.014
Aim	0.90	3.50	.60	.45	.115	.015
21. Actual	0.95	2.25	.11	.46	.13	.016
Aim	0.90	2.25	.10	.45	.115	.015

TABLE 2. Actual Compositions of Heats of Cr-Mo-Steel
Compared with Aim Compositions in Wt %
(Continued)

Heat No.	Element					
	Mo	Cr	Mn	Si	C	P
22. Actual	0.93	2.13	1.15	.46	.13	.015
Aim	0.90	2.25	1.10	.45	.115	.015
23. Actual	0.96	2.25	.61	.06	.12	.016
Aim	0.90	2.25	.60	.05	.115	.015
24. Actual	0.93	2.24	.61	.89	.12	.022
Aim	0.90	2.25	.60	.90	.115	.015
25. Actual	0.90	2.23	.57	.43	.024	.014
Aim	0.90	2.25	.60	.45	.030	.015
26. Actual	0.92	2.20	.61	.47	.22	.014
Aim	0.90	2.25	.60	.45	.200	.015
27. Actual	0.92	2.15	.57	.47	.12	.002
Aim	0.90	2.25	.60	.45	.115	.025
28. Actual	0.94	2.20	.61	.44	.12	.028
Aim	0.90	2.25	.60	.45	.115	.027
29. Actual	0.94	2.08	.64	.45	.12	0.14
Aim	0.90	2.25	.60	.45	.115	0.15
30. Actual	0.91	2.14	.58	.45	.12	.014
Aim	0.90	2.25	.60	.45	.115	.015
31. Actual	1.22	2.77	.88	.65	.17	.018
Aim	1.25	2.80	.85	.65	.160	.021
32. Actual	0.62	1.45	.86	.27	.16	.009
Aim	0.6	1.50	.85	.25	.160	.009

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MPC-3.2.4 - CORROSION IN
COAL LIQUEFACTION PROCESSES

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INTRODUCTION

A research program to study the corrosiveness of various coal liquefaction process fluids is being conducted at Southwest Research Institute (SwRI) under the technical direction of The Metal Properties Council, Inc. (MPC). The program includes two major tasks: (1) corrosion tests utilizing representative coal liquids obtained from liquefaction pilot plants; and (2) quantitative chemical analyses of the coal liquids used in the corrosion tests.

The objectives of this program are to:

- o Determine the general susceptibility of carbon steels, stainless steels, and nickel-base alloys to corrosion in coal liquids.
- o Identify and measure concentrations of suspected corrosive species in coal liquids before and after corrosion tests.
- o Determine effects of temperature on the corrosion of metals and on the stability of corrosive species in coal liquids.
- o Relate extent, type of corrosion, and corrosion mechanism(s) to corrosive species present in coal liquids.
- o Provide background data for the interpretation of results of in-situ corrosion tests and failures in liquefaction plants.

As these objectives indicate, the major thrust of the program is directed toward determining the chemical species present in coal liquids which are responsible for corrosion, rather than toward the generation of corrosion-rate data suitable for use in plant design.

A detailed description of the program test matrix and test procedures may be found in the Fossil Energy Materials Program Quarterly Progress Report for the Period Ending December 31, 1980.

This report presents cumulative tabulations of the results of 100-hour corrosion coupon exposure tests, and chemical analyses, including results obtained during the current reporting period. Results of shorter interval coupon exposures designed to indicate changes in the corrosivity of the test fluids during the 100-hour tests are presented and discussed. A recently developed procedure for determining the relative concentrations of "weak base" and "strong base" amines is also presented. An updated accounting of coal liquids received by SwRI is shown in Table 1.

RESULTS FROM PRIOR QUARTERS

The two major program task areas are: (1) the performance of corrosion coupon exposure tests utilizing coal liquids obtained from liquefaction pilot plants; and (2) quantitative chemical analyses of the coal liquids used in the corrosion tests.

Autoclave test exposures and chemical analyses which have been completed in prior quarters include the following liquids:

- o Wilsonville/SRC-I, T105 Process Solvent without Na_2CO_3 ; designated A511, tested at 425, 500, and 575°F.
- o Wilsonville/SRC-I, T105 Process Solvent with Na_2CO_3 ; designated A521, tested at 425, 500, 575°F.
- o Wilsonville/SRC-I, T105 Overhead Process Liquid with Na_2CO_3 ; designated A411, tested at 350, 425, and 500°F.
- o Ft. Lewis/SRC-I, Wash Solvent Column Bottoms, Point 411; designated B312, tested at 500, 575, and 650°F.
- o Ft. Lewis/SRC-I, Wash Solvent Column Feed, Point 409; designated B112, tested at 425, 500, and 575°F.
- o Ft. Lewis/SRC-I, Wash Solvent Column Overhead, Point 410; designated B212, tested at 350, 425, and 500°F.
- o Ft. Lewis/SRC-II, Wash Solvent Column Feed, Point 409; designated C113, tested at 425, 500, and 575°F.

TABLE 1
COAL LIQUIDS RECEIVED BY SwRI

Plant Location/Process	Sample		Coal Description	Boiling Range (low, medium, high)	Sample Identification
	Description	Date			
Wilsonville, AL/SRC-I	V131B ⁽¹⁾ Process Solvent, no Na ₂ CO ₃	1-11-80	Kentucky No. 9 Dotiki Mine	Medium	A511
Wilsonville, AL/SRC-I	V105 Decanter Oil ⁽⁵⁾	4-25-80	Kentucky No. 9 Dotiki Mine	Medium	A211
Wilsonville, AL/SRC-I	T104 Overhead ⁽⁵⁾	4-25-80	Kentucky No. 9 Dotiki Mine	Low	A311
Wilsonville, AL/SRC-I	T105 Overhead ⁽⁵⁾	4-25-80	Kentucky No. 9 Dotiki Mine	Low	A411
Wilsonville, AL/SRC-I	T105 Bottoms ⁽⁵⁾	4-25-80	Kentucky No. 9 Dotiki Mine	Medium	A521
Wilsonville, AL/SRC-I	Deashed Product ⁽⁵⁾	4-25-80	Kentucky No. 9 Dotiki Mine	High	A611
Ft. Lewis, WA/SRC-I	WSC ⁽²⁾ Feed ⁽³⁾ Point 409	8-13-80	Kentucky 9 and Kentucky 11 Blend	Medium Medium	B112
Ft. Lewis, WA/SRC-I	WSC ⁽²⁾ Overhead Point 410	8-13-80	Kentucky 9 and Kentucky 11 Blend	Low	B212
Ft. Lewis, WA/SRC-I	WSC ⁽²⁾ Bottoms Point 411	8-13-80	Kentucky 9 and Kentucky 11 Blend	High	B312
Ft. Lewis, WA/SRC-II	WSC ⁽²⁾ Feed Point 409	9-18-80	Powhattan No. 6	Medium	C113
Ft. Lewis, WA/SRC-II	WSC ⁽²⁾ Overhead Point 410	9-18-80	Powhattan No. 6	Low	C213
Ft. Lewis, WA/SRC-II	WSC ⁽²⁾ Bottoms Point 411	9-18-80	Powhattan No. 6	High	C313
Ft. Lewis, WA/SRC-II	LEC ⁽⁴⁾ Feed Point 412	9-18-80	Powhattan No. 6	Medium	C413

(1) This material is recycled from T105 Bottoms and is identified by that sampling point.
The liquid was stored in a 55-gallon drum from 1-11-80 to 4-25-80.

(2) Wash Solvent Column.

(3) Same Light Ends Column Bottoms.

(4) Light Ends Column.

(5) With Na₂CO₃.

TABLE 1 (Continued)
COAL LIQUIDS RECEIVED BY SWRI

<u>Plant Location/Process</u>	<u>Sample</u>		<u>Coal Description</u>	<u>Boiling Range (low, medium, high)</u>	<u>Sample Identification</u>
	<u>Description</u>	<u>Date</u>			
Trenton, NJ/H-Coal	Vacuum Still Overhead	9/17/80	Wyodak (Lignite)	High	D114
Trenton, NJ/H-Coal	Vacuum Still Bottom	9/17/80	Wyodak (Lignite)	High	D214
Trenton, NJ/H-Coal	Atmospheric Still Overhead	9/17/80	Wyodak (Lignite)	Low	D314
Trenton, NJ/H-Coal	Atmospheric Still Bottom	9/17/80	Wyodak (Lignite)	High	D414
Trenton, NJ/H-Coal	Vacuum Still ⁽⁶⁾ Overhead	9/79	Kentucky #11	High	D125
Trenton, NJ/H-Coal	Vacuum Still ⁽⁶⁾ Bottom	9/79	Kentucky #11	High	D225
Trenton, NJ/H-Coal	Atmospheric Still ⁽⁶⁾ Overhead	9/79	Kentucky #11	Low	D325
Trenton, NJ/H-Coal	Atmospheric Still ⁽⁶⁾ Bottom	9/79	Kentucky #11	High	D425
Baytown, TX/EDS	Atmospheric Reflux Naptha	5/1/81	Illinois #6	Low	E116
Baytown, TX/EDS	Heavy Atmospheric Gas Oil	5/1/81	Illinois #6	High	E216
Baytown, TX/EDS	Light Atmospheric Gas Oil	5/1/81	Illinois #6	Medium	E361
Baytown, TX/EDS	Light Vacuum Gas Oil	5/1/81	Illinois #6	Medium	E416
Baytown, TX/EDS	Heavy Vacuum Gas Oil	5/1/81	Illinois #6	High	E516
Baytown, TX/EDS	Product Solvent	5/1/81	Illinois #6	High	E616

(6) This material was stored in a 55-gallon drum from 9/79 to 10/80.

TABLE 1 (Continued)
COAL LIQUIDS RECEIVED BY SwRI

<u>Plant Location/Process</u>	<u>Sample</u>		<u>Coal Description</u>	<u>Boiling Range (low, medium, high)</u>	<u>Sample Identification</u>
	<u>Description</u>	<u>Date</u>			
Baytown, TX/EDS	Light Atmospheric Gas Oil (Tray 23)	5/27/81	Illinois #6	Medium	E716
Baytown, TX/EDS	Solvent Hydrogenation Feed (CLPP)	8/81	Big Brown	High	E817
Ft. Lewis, WA/SRC-II	Middle Distillate (Composite Mixture)	9/81	(7)	Low	C218
Ft. Lewis, WA/SRC-II	Heavy Distillate (Composite Mixture)	9/81	(7)	High	C318

(7) Material removed from storage tanks could not be associated with a specific type of coal.

- o Ft. Lewis/SRC-II, Wash Solvent Column Overhead, Point 410; designated C213, tested at 350, 425, and 500°F.
- o Ft. Lewis/SRC-II, Wash Solvent Column Bottoms, Point 411; designated C313, tested at 500, 575, and 650°F.

Autoclave test exposures and chemical analyses which have been reported as partially completed in prior quarters include the following coal liquids:

- o Wilsonville/SRC-I, V-105 Decanter Oil; designated A211, tested at 425, 500, and 575°F.
- o Wilsonville/SRC-I, T104 Overhead Process Liquid; designated A311, tested at 350, 425, and 500°F.
- o Ft. Lewis/SRC-II, Light Ends Column Feed, Point 412; designated C413, tested at 575°F.
- o Trenton/H-Coal, Atmospheric Still Overhead, with Wyodak Coal; designated D314, tested at 500°F.
- o Trenton/H-Coal, Atmospheric Still Overhead, with Kentucky No. 11 Coal; designated D325, tested at 500°F.

Quantitative chemical analysis procedures applicable to the coal liquids were developed and reported in detail in the above noted Quarterly Technical Report for the project. The results of recent progress in the development of a method for determining the relative concentrations of "weak base" and "strong base" amines are presented in the discussion of current activities.

Results of autoclave coupon exposure tests in which the ratio of the volume of test fluid in the autoclave was varied relative to the coupon surface area were presented in the Fossil Energy Materials Program Quarterly Progress Report for the Period Ending June 30, 1981.

DISCUSSION OF CURRENT ACTIVITIES

Autoclave Corrosion Tests

Corrosion coupon exposures of six alloys are being performed in coal liquid samples selected from those listed in Table 1. The test alloys used in the coupon exposures are separated into two groups.

Group I is composed of ferritic alloys including carbon steel (A515, Gr. 70), 5Cr-1/2Mo steel (A387, Gr. 5), and Type 410 stainless steel. Group II consists of austenitic alloys which are expected to be less susceptible to corrosion. Included in Group II are Type 316 stainless, Hastelloy C-276, and Incoloy 825.

A cumulative list of results of 100-hour coupon exposures which have been completed on coal liquids received from the Wilsonville, Alabama SRC Plant; the Ft. Lewis, Washington, SRC Plant; the Trenton, New Jersey, H-Coal Plant; and the Baytown, Texas, EDS/ECLP Plant are presented in Tables 2 and 3.

In addition to the 100-hour coupon exposures described above several carbon steel coupon exposures were conducted in which the exposure test was periodically interrupted and pairs of coupons removed. These coupons were replaced with fresh coupons and the exposure test was then resumed following deaeration with inert gas. The purpose of these tests was to determine the effect of exposure time on the corrosivity of the fluids as measured by the weight loss of exposed carbon steel coupons. Several variations of this test have been made in order to determine the most effective test procedure. All exposures were made in glass-lined autoclaves with a solution volume to coupon surface area ratio greater than $20 \text{ cm}^3/\text{cm}^2$. The test procedures which were followed are presented below.

In the first test of this type (previously described in the Fossil Energy Materials Program Quarterly Progress Report for the Period Ending June 30, 1981), six carbon steel coupons were exposed to Exxon light vacuum gas oil at 575°F. After a five-hour exposure, the autoclave was cooled to room temperature. Two of the six original coupons were removed for cleaning and weighing. These two coupons were replaced with two fresh carbon steel coupons. The autoclave was deaerated with argon gas and reheated to 575°F. After an additional ten hours of exposure at 575°F, the autoclave was again cooled to room temperature. Two more of the original coupons and the two coupons inserted at the beginning of the ten hour exposure were removed for cleaning and weighing. These four coupons were replaced with four fresh carbon steel coupons and the high temperature exposure was resumed as before. After an additional 35 hours

TABLE 2
CORROSION RATE DATA FOR GROUP I ALLOYS IN COAL LIQUEFACTION PROCESS
FLUIDS(a)

Fluid Identification	Temperature (°F)	Corrosion Rate in Mils per Year		
		A515(b)	A387(c)	Type 410(d)
A211	425	9.1	5.9	1.2
A211	425	5.2	4.8	1.4
A211	500	15.1	13.0	4.1
A211	500	15.8	13.8	4.4
A211	575	14.4	24.0	1.5
A211	575	6.6	23.1	2.2
A311	425	4.5	8.1	5.4
A311	425	(e)	(e)	(c)
A311	500	18.6	16.9	8.4
A311	500	12.8	16.0	6.6
A411	425	17.9	(g)	<0.1
A411	425	15.7	1.3	(f)
A411	500	19.8	8.7	0.1
A411	500	25.6	(g)	0.1
A511	425	4.9	0.2	0.1
A511	425	4.7	<0.1	0.1
A511	500	5.4	0.7	0.1
A511	500	5.9	1.0	0.3
A511	575	9.4	6.0	0.7
A511	575	8.9	8.7	1.2
A521	425	3.7	2.3	<0.1
A521	425	3.6	2.8	0.2
A521	500	10.6	(g)	0.3
A521	500	10.8	2.6	0.3
A521	575	21.9	7.4	0.2
A521	575	22.0	9.8	0.1

(a) Partial results

(b) ASTM A515, Gr. 70

(c) ASTM A387, Gr. 5

(d) ASTM, Type 410 Stainless Steel

(e) Not complete

(f) No measurable weight loss

(g) Not determined

(h) Values not yet determined, coupons set aside for surface analysis

TABLE 2
CORROSION RATE DATA FOR GROUP I ALLOYS IN COAL LIQUEFACTION PROCESS
FLUIDS^(a) (Continued)

Fluid Identification	Temperature (°F)	Corrosion Rate in Mils per Year		
		A515(b)	A387(c)	Type 410(d)
B112	425	8.9	7.0	5.4
B112	425	8.9	7.0	5.8
B112	500	23.1	17.0	9.6
B112	500	22.4	16.2	9.7
B112	575	48.8	24.7	10.3
B112	575	48.6	24.9	10.5
B212	350	6.5	3.9	<0.1
B212	350	7.0	1.9	<0.1
B212	425	16.1	10.0	(f)
B212	425	15.1	10.2	<0.1
B212	500	20.1	21.4	1.8
B212	500	19.4	20.8	1.9
B312	500	27.8	18.3	3.1
B312	500	27.3	19.2	3.6
B312	575	51.7	22.5	0.7
B312	575	42.2	(g)	1.0
B312	650	130.8	20.5	9.2
B312	650	125.6	32.5	10.5
C113	425	5.3	5.9	3.8
C113	425	5.2	5.7	3.5
C113	500	9.3	8.4	5.4
C113	500	9.2	8.0	5.2
C113	575	17.7	9.8	4.1
C113	575	16.7	10.2	3.8

(a) Partial results

(b) ASTM A515, Gr. 70

(c) ASTM A387, Gr. 5

(d) ASTM, Type 410 Stainless Steel

(e) Not complete

(f) No measurable weight loss

(g) Not determined

(h) Values not yet determined, coupons set aside for surface analysis

TABLE 2
CORROSION RATE DATA FOR GROUP I ALLOYS IN COAL LIQUEFACTION PROCESS
FLUIDS^(a) (Continued)

Fluid Identification	Temperature (°F)	Corrosion Rate in Mils per Year		
		A515(b)	A387(c)	Type 410(d)
C213	350	5.1	2.8	12.2
C213	350	5.8	2.6	16.1
C213	425	9.6	10.3	13.1
C213	425	9.7	10.7	13.5
C213	500	22.5	21.5	3.7
C213	500	24.6	23.2	3.2
C313	500	5.0	3.9	1.1
C313	500	4.6	3.6	1.7
C313	575	27.3	36.8	17.0
C313	575	30.6	40.0	12.4
C313	650	14.8	2.9	0.9
C313	650	16.4	2.7	0.4
C413	425	8.6	7.4	1.7
C413	425	9.0	7.6	1.1
D114	500	0.7	0.7	0.3
D114	500	0.3	0.4	0.4
D114	650	7.8	3.6	0.5
D114	650	8.2	5.1	0.6
D125	500	3.4	3.4	0.8
D125	500	(h)	(h)	(h)
D125	650	25.1	7.5	3.5
D125	650	22.4	7.7	2.6
D314	350	1.7	(f)	(f)
D314	350	1.0	<0.1	<0.1
D314	500	5.4	2.9	1.1
D314	500	5.9	3.6	0.7

(a) Partial results

(b) ASTM A515, Gr. 70

(c) ASTM A387, Gr. 5

(d) ASTM, Type 410 Stainless Steel

(e) Not complete

(f) No measurable weight loss

(g) Not determined

(h) Values not yet determined, coupons set aside for surface analysis

TABLE 2
CORROSION RATE DATA FOR GROUP I ALLOYS IN COAL LIQUEFACTION PROCESS
FLUIDS^(a) (Continued)

Fluid Identification	Temperature (°F)	Corrosion Rate in Mils per Year		
		A515 ^(b)	A387 ^(c)	Type 410 ^(d)
D325	350	5.6	0.9	0.3
D325	350	5.8	1.0	0.3
D325	500	10.4	10.4	2.2
D325	500	10.0	10.4	1.7
D414	500	1.4	1.0	0.6
D414	500	1.3	1.0	0.6
D414	650	2.5	1.0	0.5
D414	650	2.4	0.6	0.3
D425	500	4.7	1.7	0.5
D425	500	4.3	1.7	0.5
D425	650	11.9	6.6	2.0
D425	650	14.8	8.4	2.5
E116	350	3.0	1.0	0.5
E116	350	1.4	1.5	0.5
E116	425	6.1	6.1	0.8
E116	425	6.2	7.2	1.1
E116	500	8.7	7.2	1.8
E116	500	9.8	7.9	2.9
E216	500	2.3	1.0	0.5
E216	500	2.8	1.1	0.5
E216	650	11.1	14.2	5.1
E216	650	10.4	10.4	5.1

(a) Partial results

(b) ASTM A515, Gr. 70

(c) ASTM A387, Gr. 5

(d) ASTM, Type 410 Stainless Steel

(e) Not complete

(f) No measurable weight loss

(g) Not determined

(h) Values not yet determined, coupons set aside for surface analysis

TABLE 2
CORROSION RATE DATA FOR GROUP I ALLOYS IN COAL LIQUEFACTION PROCESS
FLUIDS^(a) (Continued)

Fluid Identification	Temperature (°F)	Corrosion Rate in Mils per Year		
		A515(b)	A387(c)	Type 410(d)
E316	425	0.7	0.1	0.1
E316	425	0.7	0.1	(f)
E316	500	2.5	1.9	1.5
E316	500	(h)	(h)	(h)
E316	575	5.6	2.4	1.3
E316	575	5.1	1.8	0.9
E416	425	7.0	8.8	0.6
E416	425	7.4	7.9	1.3
E416	500	9.9	8.1	3.4
E416	500	(h)	(h)	(h)
E416	575	64.5	34.2	6.4
E416	575	71.6	33.8	9.9
E616	500	1.2	1.1	<0.1
E616	500	1.0	2.6	0.3
E616	650	2.2	1.5	0.4
E616	650	2.7	2.3	0.6
E716	500	4.8	3.9	1.1
E716	500	5.3	4.1	1.4
E716	575	14.5	10.5	3.1
E716	575	12.6	10.5	4.4
E817	500	4.7	2.4	0.8
E817	500	(h)	(h)	(h)
E817	650	14.1	8.5	1.0
E817	650	14.9	10.5	1.6

(a) Partial results

(b) ASTM A515, Gr. 70

(c) ASTM A387, Gr. 5

(d) ASTM, Type 410 Stainless Steel

(e) Not complete

(f) No measurable weight loss

(g) Not determined

(h) Values not yet determined, coupons set aside for surface analysis

TABLE 3
CORROSION RATE DATA FOR GROUP II ALLOYS IN COAL LIQUEFACTION
PROCESS FLUIDS^(a)

Fluid Identification	Temperature (F°)	Corrosion Rate in Mils Per Year		
		Type 316 SS ^(b)	Hastelloy C-276	Incoloy Alloy 825
A211	425	N11 ^(c)	N11	N11
A211	425	N11	(d)	(d)
A211	500	N11	N11	N11
A211	500	N11	(d)	(d)
A211	575	N11	N11	N11
A211	575	N11	(d)	(d)
A311	350	N11	N11	N11
A311	350	N11	(d)	(d)
A311	425	0.8	N11	N11
A311	425	(g)	(d)	(d)
A311	500	N11	N11	N11
A311	500	N11	(d)	(d)
A411	350	N11	N11	(e)
A411	350	N11	N11	(e)
A411	425	N11	0.2	(e)
A411	425	N11	N11	(e)
A411	500	0.2	0.3	(e)
A411	500	0.4	0.2	(e)
A511	425	<0.1	0.1	(e)
A511	425	0.2	<0.1	(e)
A511	500	<0.1	N11	(e)
A511	500	0.2	0.2	(e)
A511	575	0.2	0.1	(e)
A511	575	N11	<0.1	(e)

(a) Partial results

(b) ASTM A240, Type 316 Stainless Steel

(c) No measurable weight loss

(d) One Hastelloy C-276 and one Incoloy Alloy 825 coupon were exposed in this Group II Alloy Exposure Run

(e) Incoloy Alloy 825 was not included in Exposure Run

(f) Values not yet determined, coupons set aside for surface analysis

(g) Not determined

TABLE 3
CORROSION RATE DATA FOR GROUP II ALLOYS IN COAL LIQUEFACTION
PROCESS FLUIDS^(a) (Continued)

Fluid Identification	Temperature (F°)	Corrosion Rate in Mils Per Year		
		Type 316 SS ^(b)	Hastelloy C-276	Incoloy Alloy 825
A521	425	<0.1	N11	(e)
A521	425	0.2	0.2	(e)
A521	500	N11	N11	(e)
A521	500	N11	N11	(e)
A521	575	0.3	0.2	(e)
A521	575	0.1	0.3	(e)
B112	425	0.1	N11	0.1
B112	425	<0.1	(d)	(d)
B112	500	0.3	<0.1	0.3
B112	500	0.5	(d)	(d)
B112	575	1.8	0.2	<0.1
B112	575	1.7	(d)	(d)
B212	350	0.2	0.1	(e)
B212	500	0.2	0.1	(e)
B212	425	N11	N11	(e)
B212	425	N11	N11	(e)
B212	500	N11	N11	(e)
B212	500	N11	N11	(e)
B312	500	N11	N11	(e)
B312	500	N11	N11	(e)
B312	575	N11	N11	(e)
B312	575	N11	N11	(e)
B312	650	0.8	N11	(e)
B312	650	0.5	N11	(e)

(a) Partial results

(b) ASTM A240, Type 316 Stainless Steel

(c) No measurable weight loss

(d) One Hastelloy C-276 and one Incoloy Alloy 825 coupon were exposed in this Group II Alloy Exposure Run

(e) Incoloy Alloy 825 was not included in Exposure Run

(f) Values not yet determined, coupons set aside for surface analysis

(g) Not determined

TABLE 3
CORROSION RATE DATA FOR GROUP II ALLOYS IN COAL LIQUEFACTION
PROCESS FLUIDS^(a) (Continued)

Fluid Identification	Temperature (F°)	Corrosion Rate in Mils Per Year		
		Type 316 SS ^(b)	Hastelloy C-276	Incoloy Alloy 825
C113	425	1.1	0.2	0.1
C113	425	<0.1	(d)	(d)
C113	500	0.2	0.1	N11
C113	500	N11	(d)	(d)
C113	575	1.4	1.1	1.2
C113	575	1.4	(d)	(d)
C213	350	6.0	N11	N11
C213	350	2.0	(d)	(d)
C213	425	0.2	N11	N11
C213	425	N11	(d)	(d)
C213	500	0.3	0.2	0.1
C213	500	0.4	(d)	(d)
C313	500	0.6	0.5	0.4
C313	500	0.6	(d)	(d)
C313	575	0.8	0.5	0.6
C313	575	0.7	(d)	(d)
C313	650	<0.1	N11	N11
C313	650	N11	(d)	(d)
C413	425	0.1	0.1	0.1
C413	425	0.2	(d)	(d)
C413	575	0.2	N11	N11
C413	575	1.1	(d)	(d)

(a) Partial results

(b) ASTM A240, Type 316 Stainless Steel

(c) No measurable weight loss

(d) One Hastelloy C-276 and one Incoloy Alloy 825 coupon were exposed in this Group II Alloy Exposure Run

(e) Incoloy Alloy 825 was not included in Exposure Run

(f) Values not yet determined, coupons set aside for surface analysis

(g) Not determined

TABLE 3
CORROSION RATE DATA FOR GROUP II ALLOYS IN COAL LIQUEFACTION
PROCESS FLUIDS^(a) (Continued)

Fluid Identification	Temperature (F°)	Corrosion Rate in Mils Per Year		
		Type 316 SS ^(b)	Hastelloy C-276	Incoloy Alloy 825
D114	500	(f)	(d)	(d)
D114	500	0.2	<0.1	0.2
D114	650	0.5	0.4	0.7
D114	650	(f)	(d)	(d)
D125	500	0.5	0.3	0.4
D125	500	(f)	(d)	(d)
D125	650	0.3	<0.1	<0.1
D125	650	(f)	(d)	(d)
D314	350	N11	N11	N11
D314	350	(g)	(d)	(d)
D314	500	<0.1	(d)	(d)
D314	500	N11	<0.1	N11
D325	350	<0.1	0.1	0.1
D325	350	<0.1	(d)	(d)
D325	500	<0.1	0.2	0.2
D325	500	0.2	(d)	(d)
D414	500	0.2	0.2	0.2
D414	500	0.4	(d)	(d)
D414	650	N11	0.1	0.1
D414	650	<0.1	(d)	(d)

(a) Partial results

(b) ASTM A240, Type 316 Stainless Steel

(c) No measurable weight loss

(d) One Hastelloy C-276 and one Incoloy Alloy 825 coupon were exposed in this Group II Alloy Exposure Run

(e) Incoloy Alloy 825 was not included in Exposure Run

(f) Values not yet determined, coupons set aside for surface analysis

(g) Not determined

TABLE 3
CORROSION RATE DATA FOR GROUP II ALLOYS IN COAL LIQUEFACTION
PROCESS FLUIDS ^(a) (Continued)

Fluid Identification	Temperature (F°)	Corrosion Rate in Mils Per Year		
		Type 316 SS ^(b)	Hastelloy C-276	Incoloy Alloy 825
D425	500	<0.1	N11	N11
D425	500	<0.1	(d)	(d)
D425	650	0.1	N11	N11
D425	650	(f)	(d)	(d)
E116	350	0.3	0.3	0.3
E116	350	0.4	(d)	(d)
E116	425	0.1	N11	<0.1
E116	425	0.1	(d)	(d)
E116	500	<0.1	N11	N11
E116	500	N11	(d)	(d)
E216	500	0.2	<0.1	<0.1
E216	500	0.2	(d)	(d)
E216	650	1.7	<0.1	N11
E216	650	2.0	(d)	(d)
E316	425	<0.1	<0.1	<0.1
E316	425	0.1	(d)	(d)
E316	500	1.1	0.1	0.1
E316	500	(f)	(d)	(d)
E316	575	0.1	N11	N11
E316	575	0.2	(d)	(d)
E416	425	N11	N11	N11
E416	425	0.3	(d)	(d)
E416	500	0.2	0.1	<0.1
E416	500	(f)	(d)	(d)
E416	575	1.7	0.2	0.2
E416	575	1.5	(d)	(d)

(a) Partial results

(b) ASTM A240, Type 316 Stainless Steel

(c) No measurable weight loss

(d) One Hastelloy C-276 and one Incoloy Alloy 825 coupon were exposed in this Group II Alloy Exposure Run

(e) Incoloy Alloy 825 was not included in Exposure Run

(f) Values not yet determined, coupons set aside for surface analysis

(g) Not determined

TABLE 3
CORROSION RATE DATA FOR GROUP II ALLOYS IN COAL LIQUEFACTION
PROCESS FLUIDS^(a) (Continued)

Fluid Identification	Temperature (F°)	Corrosion Rate in Mils Per Year		
		Type 316 SS ^(b)	Hastelloy C-276	Incoloy Alloy 825
E616	500	0.1	0.1	0.1
E616	500	0.2	(d)	(d)
E616	650	0.5	Nil	0.2
E616	650	0.2	(d)	(d)
E716	500	<0.1	<0.1	<0.1
E716	500	0.4	(d)	(d)
E716	575	0.3	Nil	<0.1
E716	575	0.8	(d)	(d)
E817	500	1.0	0.5	0.5
E817	500	(f)	(d)	(d)
E817	650	0.2	0.2	0.1
E817	650	0.2	(d)	(d)

(a) Partial results

(b) ASTM A240, Type 316 Stainless Steel

(c) No measurable weight loss

(d) One Hastelloy C-276 and one Incoloy Alloy 825 coupon were exposed in this Group II Alloy Exposure Run

(e) Incoloy Alloy 825 was not included in Exposure Run

(f) Values not yet determined, coupons set aside for surface analysis

(g) Not determined

of exposure at 575°F, the autoclave was cooled a third time. The last two of the original coupons were removed with two of the four coupons which were added at the beginning of the 35-hour exposure. At this time, 50 percent of the solution was replaced with fresh solution. Four fresh coupons were placed in the autoclave in addition to the two remaining from the beginning of the 35-hour run. The autoclave was reheated to 575°F for five hours. Following this exposure, the autoclave was cooled and all of the remaining coupons were cleaned and weighed. The results of this test are shown in Figure 1.

The second test was also performed using Exxon light vacuum gas oil and carbon steel coupons at 575°F, (see Figure 2). Six carbon steel coupons were introduced at the beginning of the test. After a ten-hour exposure, two of the six original coupons were removed for evaluation. These two coupons were replaced with two fresh carbon steel coupons. The autoclave was deaerated with argon gas and reheated to 575°F. After an additional ten hours of exposure at 575°F, the test was again interrupted. Two more of the original coupons and the two replacement coupons inserted after the first ten hours of exposure were removed for evaluation. These four coupons were replaced with four fresh coupons and the exposure continued for an additional ten hours. The remaining two original coupons and four replacement coupons were then evaluated. This test was primarily intended to determine the reproducibility of the first test and to establish baseline data for the next test.

A third test was performed which differed from the previous test in that the carbon steel corrosion coupons were not introduced until after a ten-hour exposure of only the liquid in the glass-lined autoclave. This test was then continued in a manner similar to the previous test. The results of this test are shown in Figure 3.

Two additional tests of this type were performed following the same procedures outlined in the second test described above, but using fluid B212 (Ft. Lewis SRCI, Wash Solvent Column Overhead) at 500°F and fluid D325 (Trenton/H-Coal, Atmospheric Still Overhead) at 500°F. The results of these exposures are shown in Figures 4 and 5.

The weight loss data from corrosion coupons in the above interval tests predict the weight loss of the 100-hour exposures of carbon steel

FIGURE 1. WEIGHT LOSS OF CARBON STEEL COUPONS VS. TIME IN E416 FLUID AT 575°F.

- Indicates weight loss of coupons exposed from the beginning of the test.
- ◇ Indicates weight loss of coupons introduced after 5 hours.
- ▽ Indicates weight loss of coupons introduced after 15 hours.
- Indicates coupons introduced after 50 hours with the addition of 50% unexposed fluid.

Average weight loss of carbon steel coupons after 100-hour exposure in E416 fluid at 575°F is 371 mg.

FIGURE 2. WEIGHT LOSS OF CARBON STEEL COUPONS VS. TIME IN E416 FLUID AT 575°F.

- Indicates weight loss of coupons exposed from the beginning of the test.
- △ Indicates weight loss of coupons introduced after 10 hours.
- Indicates weight loss of coupons introduced after 20 hours.

Average weight loss of carbon steel coupons after 100-hour exposure in E416 fluid at 575°F is 371 mg.

FIGURE 3. WEIGHT LOSS OF CARBON STEEL COUPONS VS. TIME IN E416 FLUID AT 575°F AFTER A 10-HOUR BLANK EXPOSURE

△ Indicates weight loss of coupons introduced after 10 hours.

□ Indicates weight loss of coupons introduced after 20 hours.

Average weight loss of carbon steel coupons after 100-hour exposure in E416 fluid at 575°F is 371 mg.

FIGURE 4. WEIGHT LOSS OF CARBON STEEL COUPONS VS. TIME IN B212 FLUID AT 500°F

- Indicates weight loss of coupons exposed from the beginning of the test.
- △ Indicates weight loss of coupons introduced after 10 hours.
- Indicates weight loss of coupons introduced after 20 hours.

Average weight loss of carbon steel coupons after 100-hour exposure in B212 fluid at 500°F is 109 mg.

FIGURE 5. WEIGHT LOSS OF CARBON STEEL COUPONS VS. TIME IN D325 FLUID AT 500°F

- Indicates weight loss of coupons exposed from the beginning of the test.
- △ Indicates weight loss of coupons introduced after 10 hours.
- Indicates weight loss of coupons introduced after 20 hours.

Average weight loss of carbon steel coupons after 100-hour exposure in D325 fluid at 500°F is 55 mg.

in the same liquid at the same temperature. Trends in the data from exposures to the Exxon light vacuum gas oil (Figures 1 through 3) indicate a slight decrease in corrosivity of the fluid with time. However, the formation of a protective film on the coupons during the exposure had an equally notable effect on the decrease in corrosion rate as a function of time. As a consequence, it may be concluded that the 100-hour exposures in Exxon light vacuum gas oil have not been significantly affected by depletion of corrosive species.

The same conclusion may be drawn from the data in Figure 4 (carbon steel exposed in Ft. Lewis SRCI, Wash Solvent Column Overhead). It may be noted that there is very little decrease in the corrosion rate of freshly introduced coupons as a function of total fluid exposure time.

The weight loss data from coupons exposed in the Trenton/H-Coal, Atmospheric Still Overhead fluid (Figure 5), indicates significant decrease in corrosion rate with time. This decrease is apparently associated with the formation of a protective film on the coupon surface as well as with a decrease in the corrosivity of the fluid.

Chemical Analyses of Coal Liquids

Quantitative chemical analyses are performed on the as-received coal liquids and the post-test liquids from autoclave tests. Analyses are being made to determine concentrations of the following suspected corrosive species:

- o Total Nitrogen
- o Chlorine Compounds
 - Total Chlorine
 - Water Soluble Chlorides
- o Oxygen Compounds
 - Organic Acids
 - Phenols
 - Water
- o Sulfur Compounds
 - Total Sulfur
 - Hydrogen Sulfide

Elemental Sulfur, including reactive
polysulfidic sulfur

Mercaptans

Disulfides, including nonreactive polysulfidic
sulfur and disulfides formed by removal of
sulfur from reactive polysulfides

In addition to analyses of liquids, analyses for hydrogen sulfide and mercaptans are also being performed on gases present in autoclaves at the completion of autoclave tests.

A cumulative summary of analyses for fluids in the as-received condition is given in Table 4 for all fluids which have been tested up through the end of the current reporting period. Analyses for liquids after exposure in autoclaves are given in Tables 5 through 21.

The results of chemical analyses of as-received fluids versus the corrosion rate of carbon steel exposed to these liquids at 500°F are presented in Table 22. Similar data versus the corrosion rates of Type 410 stainless steel coupons exposed to the same process fluids at 500°F is presented in Table 23.

In addition to the chemical analyses originally incorporated in the test matrix, a method has been developed for determining the relative quantities of "weak base" amines and "strong base" amines. The method is described as follows.

The coal liquid sample is diluted with ether in a 1:1 ratio. Amines are extracted from this diluted sample with ten percent HCl. The extract is made alkaline with a saturated solution of NaOH. The amines are then extracted with ether. The ether extract is treated with a sodium acetate/acetic acid buffer (2N sodium acetate plus 0.4N acetic acid). This two-phase mixture is separated with the "strong base" amines being in the aqueous (buffered solution) phase and the "weak base" amines being in the ether phase. The amines from both phases are then recovered and weighed.

TABLE 4
AS RECEIVED FLUIDS

Species	Sample Identification											
	A211	A311	A411	A511	A521	B112	B212	B312	C113	C213	C313	C413
Total Sulfur wt.%	0.50	0.68	0.40	0.45	0.38	0.38	0.29	0.42	0.39	0.27	0.45	0.41
Elemental & Reactive Polysulfide Sulfur wt.%	0.0021	0.0017	0.0020	0.0022	0.0027	0.0021	0.0027	0.0018	0.0034	0.0016	0.0034	0.0035
Disulfide Sulfur wt.%	0.02	0.05	0.26	(a)	(a)	(a)	0.09	(a)	(a)	(a)	(a)	(a)
Hydrogen Sulfide Sulfur wt.%	0.090	0.01	(b)	(b)	(b)	(b)	(b)	(b)	(b)	(b)	(b)	(b)
Mercaptan Sulfur wt.%	0.070	0.410	0.006	0.026	0.039	0.044	0.021	0.034	0.026	0.063	0.015	0.044
Phenol % OH	1.51	0.31	4.96	1.11	1.27	2.82	5.01	1.06	1.50	3.86	0.63	1.40
Phenol % as P-Cresol	9.6	2.0	31.5	7.1	8.1	18.1	31.9	6.7	9.5	24.6	4.0	8.9
Acid Number mg KOH/g	(c)	(c)	0.3	0.1	(c)	0.3	0.1	0.1	(c)	0.3	(c)	(c)
Base Number mg KOH/g	0.1	2.6	(c)	(c)	0.05	(c)	(c)	(c)	(c)	(c)	(c)	(c)
Water ppm	1411	266	4700	310	1080	64	410	430	200	73	64	489
Total Chlorides ppm	<10	<10	<10	95	13	235	132	325	50	187	<10	36
Water Soluble Chlorides ppm	6	10	5	116	19	235	128	298	63	191	14	59
Total Nitrogen wt.%	0.91	1.29	0.51	0.76	0.84	1.02	0.63	1.01	1.26	1.24	1.16	1.07
Ash mg/l	0.3	1.7	(d)	16.0	0.8	0.3	4.0	3.6	0.2	1.7	1.4	1.4

(a) Less than 0.005 wt %
(b) Less than 0.0001 wt %
(c) Less than 0.05 mg KOH/g
(d) Less than 0.2 mg

TABLE 4 (Continued)
AS RECEIVED FLUIDS

Species	Sample Identification												
	D125	D314	D325	D114	D414	D425	E116	E216	E316	E416	E616	E716	E817
Total Sulfur wt. %	(e)	0.06	0.24	(e)	0.02	0.08	1.06	0.27	0.12	0.61	0.03	0.21	(e)
Elemental & Reactive Polysulfide Sulfur wt. %	0.0044	0.0029	0.0098	0.0034	0.0031	0.0038	0.0007	0.0061	0.0030	0.0083	0.0008	0.0038	0.0021
Disulfide Sulfur wt. %	(e)	0.013	0.068	(e)	(a)	0.007	0.005	(a)	(a)	(a)	(a)	(a)	(e)
Hydrogen Sulfide Sulfur wt. %	(e)	(b)	0.049	(e)	(b)	(b)	0.210	(b)	(b)	(b)	(b)	0.008	(e)
Mercaptan Sulfur wt. %	(e)	0.010	(a)	0.006	0.007	(a)	0.442	0.043	0.035	0.092	(a)	0.084	(a)
Phenol % OH ⁻	(e)	1.03	1.03	(e)	0.37	0.33	1.99	0.76	1.52	1.02	0.63	2.03	(e)
Phenol % as P-Cresol	(e)	6.5	6.6	(e)	2.4	2.1	12.6	4.8	8.4	6.5	4.0	12.9	(e)
Acid Number mg KOH/g	0.1	(c)	(c)	(e)	(c)	0.4	(c)	(c)	(c)	(c)	(c)	(c)	0.01
Base Number mg KOH/g	(c)	(c)	5.9	(e)	0.1	(c)	(c)	0.1	(c)	(c)	4.4	(c)	(c)
Water ppm	(e)	588	476	(e)	94	305	1012	507	490	133	382	739	(e)
Total Chlorides ppm	(e)	<10	10	(e)	<10	335	<10	<10	10	53	15	95	(e)
Water Soluble Chlorides ppm	(e)	5	8	(e)	8	290	7	7	7	73	16	91	(e)
Total Nitrogen wt. %	(e)	0.35	0.59	0.35	0.45	0.62	0.16	0.24	0.10	0.78	0.21	0.11	0.39
Ash mg/l	(e)	1.2	0.8	0.4	1.4	1.7	0.4	0.6	0.2	(d)	0.4	0.8	(e)

(a) Less than 0.005 wt. %
(b) Less than 0.0001 wt. %
(c) Less than 0.05 mg KOH/g
(d) Less than 0.2 mg
(e) Not complete

TABLE 5
RESULTS OF CHEMICAL ANALYSES OF SAMPLE A211
(Wilsonville, SRC-I, V-105 Decanter Oil)

<u>Species</u>	<u>As Received</u>	<u>Group I 425°F</u>	<u>Group II 425°F</u>	<u>Group II 500°F</u>	<u>Group I 575°F</u>	<u>Group II 575°F</u>	<u>Blank 575°F</u>
Total Sulfur wt.%	0.50	0.51	0.48	0.39	0.48	0.44	0.39
Elemental & Reactive Polysulfide Sulfur wt.%	0.0021	0.0018	0.0024	0.0031	0.0020	0.0018	0.0023
Disulfide Sulfur wt.%	0.02	0.02	0.01	0.005	0.03	0.03	0.02
Hydrogen Sulfide Sulfur wt.%	0.090	0.051	0.044	0.008	0.015	0.016	0.052
Hydrogen Sulfide Sulfur in Autoclave Gas Phase g/l	(a)	0.953	1.319	1.441	1.002	0.580	0.475
Mercaptan Sulfur wt.%	0.070	0.072	0.062	0.072	0.066	0.096	0.086
Mercaptan Sulfur in Autoclave Gas Phase g/l	(a)	0.013	(b)	0.020	0.024	0.018	0.007
Phenol % OH ⁻	1.51	1.61	1.55	1.57	1.56	1.49	1.50
Phenol % as P-Cresol	9.6	10.2	9.9	10.0	9.9	9.4	9.5
Acid Number mg KOH/g	(c)	0.05	(c)	(c)	(c)	(c)	(c)
Base Number mg KOH/g	0.1	(c)	(c)	0.3	(c)	0.1	(c)
Water ppm	1411	1147	1430	1295	889	1204	573
Total Chlorides ppm	<10	(d)	(d)	(d)	(d)	<10	(d)
Water Soluble Chlorides ppm	6	7	(e)	(e)	<10	5	(e)
Total Nitrogen wt.%	0.91	1.30	0.91	0.90	0.97	0.89	0.82
Ash mg/l	0.3	1.1	3.4	15.2	1.7	1.9	4.5

(a) Not applicable

(b) Less than 0.005 g/l

(c) Less than 0.05 mg KOH/g

(d) Total chloride concentration assumed to be less than 10 ppm

(e) Water soluble chloride concentration assumed to be less than 10 ppm

TABLE 6
RESULTS OF CHEMICAL ANALYSES OF SAMPLE A311
(Wilsonville, SRC-I, T-104 Overhead)

Species	As Received	Group II 350°F	Group II 425°F	Group I 500°F	Group II 500°F	Blank 500°F
Total Sulfur wt.%	0.68	0.79	1.08	0.66	0.61	1.40
Elemental & Reactive Polysulfide Sulfur wt.%	0.0017	0.0019	0.0024	0.0020	0.0026	0.0010
Disulfide Sulfur wt.%	0.05	0.05	0.07	0.02	0.03	0.07
Hydrogen Sulfide Sulfur wt.%	0.01	(a)	(a)	(a)	0.019	0.014
Hydrogen Sulfide Sulfur in Autoclave Gas Phase g/l	(b)	1.287	1.005	0.961	0.609	(c)
Mercaptan Sulfur wt.%	0.410	0.162	0.200	0.330	0.340	1.05
Mercaptan Sulfur in Autoclave Gas Phase g/l	(b)	0.020	0.039	0.070	0.030	(d)
Phenol % OH ⁻	0.31	0.33	0.49	0.35	0.31	0.29
Phenol % as P-Cresol	2.0	2.1	3.1	2.2	2.0	1.8
Acid Number mg KOH/g	(e)	(e)	(e)	(e)	(e)	(e)
Base Number mg KOH/g	2.6	0.1	0.2	0.1	0.3	(e)
Water ppm	166	140	156	164	174	158
Total Chlorides ppm	<10	(f)	(f)	(f)	<10	(f)
Water Soluble Chlorides ppm	10	(g)	(g)	9	8	(g)
Total Nitrogen wt.%	1.29	0.11	0.17	0.13	1.35	0.08
Ash mg/l	1.7	1.6	3.0	0.6	1.8	46.8

(a) Less than 0.0001 wt %

(b) Not applicable

(c) Not conducted

(d) Less than 0.005 g/l

(e) Less than 0.05 mg KOH/g

(f) Total chloride concentration assumed to be approximately 10 ppm

(g) Water soluble chloride concentration assumed to be approximately 10 ppm

TABLE 7
RESULTS OF CHEMICAL ANALYSES OF SAMPLE A411
(Wilsonville, AL/SRC-I T105 Overhead with Na₂CO₃)

Species	As Received	Group II 350°F	Group I 425°F	Group II 425°F	Group I 500°F	Group II 500°F	Blank 500°F
Total Sulfur wt.%	0.40	0.48	0.46	0.46	0.45	0.43	0.45
Elemental & Reactive Polysulfide Sulfur wt.%	0.0020	0.0030	0.0025	0.0024	0.0021	0.0020	0.0019
Disulfide Sulfur wt.%	0.26	0.22	0.24	0.22	0.24	0.23	0.22
Hydrogen Sulfide Sulfur wt.%	(a)	(a)	(a)	(a)	(a)	(a)	(a)
Hydrogen Sulfide Sulfur in Autoclave Gas Phase g/l	(b)	0.062	0.034	0.073	0.117	0.042	0.292
Mercaptan Sulfur wt.%	0.006	0.007	0.005	0.009	0.009	0.001	0.011
Mercaptan Sulfur in Autoclave Gas Phase g/l	(b)	(c)	(c)	0.006	0.005	(c)	0.013
Phenol % OH ⁻	4.96	5.02	5.02	5.02	5.06	5.11	4.97
Phenol % as P-Cresol	31.5	31.9	31.9	31.9	32.2	32.5	31.6
Acid Number mg KOH/g	0.3	0.2	0.1	0.1	(d)	(d)	(d)
Base Number mg KOH/g	(e)	0.2	0.2	0.2	0.3	(d)	0.2
Water ppm	4700	1200	1200	1120	1180	460	1340
Total Chlorides ppm	<10	(f)	(f)	(f)	<10	<10	(f)
Water Soluble Chlorides ppm	5	(g)	(g)	(g)	9	10	(g)
Total Nitrogen wt.%	0.51	0.55	0.53	0.54	0.54	0.55	0.54
Ash mg/l	(h)	0.8	(h)	0.9	0.9	1.4	8.7

(a) Less than 0.0001 wt %

(b) Not applicable

(c) Less than 0.005 g/L

(d) Less than 0.05 mg KOH/g

(e) Not conducted

(f) Total chloride concentration assumed to be approximately 10 ppm

(g) Water soluble chloride concentration assumed to be approximately 10 ppm

(h) Less than 0.2 mg

TABLE 8
RESULTS OF CHEMICAL ANALYSES OF SAMPLE A511
(Wilsonville, AL/SRC-I T105 Bottoms Without Na₂CO₃)

Species	As Received	Group I 425°F	Group II 425°F	Group I 500°F	Group II 500°F	Group I 575°F	Group II 575°F	Blank 575°F
Total Sulfur wt.%	0.45	0.44	0.46	0.44	0.44	0.44	0.45	0.43
Elemental & Reactive Polysulfide Sulfur wt.%	0.0022	0.0022	0.0027	0.0027	0.0026	0.0027	0.0026	0.0030
Disulfide Sulfur wt.%	(a)	(a)	(a)	(a)	(a)	(a)	(a)	(a)
Hydrogen Sulfide Sulfur wt.%	(b)	(b)	(b)	(b)	(b)	(b)	(b)	(b)
Hydrogen Sulfide Sulfur in Autoclave Gas Phase g/l	(c)	0.005	0.005	(d)	(d)	0.013	0.015	0.005
Mercaptan Sulfur wt.%	0.026	0.034	0.037	0.029	0.027	0.024	0.026	0.023
Mercaptan Sulfur in Autoclave Gas Phase g/l	(c)	(d)	(d)	(d)	(d)	(d)	(d)	(d)
Phenol % OH ⁻	1.11	1.08	1.08	1.07	1.08	1.04	1.04	1.07
Phenol % as P-Cresol	7.1	6.9	6.8	6.8	6.9	6.6	6.6	6.8
Acid Number mg KOH/g	0.1	(e)	(e)	0.4	0.4	0.5	0.4	(e)
Base Number mg KOH/g	(e)	(e)	(e)	(e)	(e)	(e)	(e)	(e)
Water ppm	310	1610	600	380	460	350	360	380
Total Chlorides ppm	95	(f)	(f)	(f)	(f)	82	97	(f)
Water Soluble Chlorides ppm	116	(g)	(g)	(g)	(g)	100	105	(g)
Total Nitrogen wt.%	0.76	0.76	0.78	0.80	0.78	0.74	0.80	0.76
Ash mg/l	16.0	4.1	4.6	1.6	2.4	1.0	2.6	9.5

(a) Less than 0.005 wt %

(b) Less than 0.0001 wt %

(c) Not applicable

(d) Less than 0.005 g/l

(e) Less than 0.05 mg KOH/g

(f) Total chloride concentration assumed to be approximately 100 ppm

(g) Water soluble chloride concentration assumed to be approximately 100 ppm

TABLE 9
RESULTS OF CHEMICAL ANALYSES OF SAMPLE A521
(Wilsonville, AL/SRC-I T105 Bottoms With Na₂CO₃)

Species	As Received	Group I 425°F	Group II 425°F	Group I 500°F	Group II 500°F	Group I 575°F	Group II 575°F	Blank 575°F
Total Sulfur wt.%	0.38	0.40	0.40	0.39	0.42	0.40	0.41	0.40
Elemental & Reactive Polysulfide Sulfur wt.%	0.0027	0.0026	0.0023	0.0028	0.0024	0.0022	0.0025	0.0023
Disulfide Sulfur wt.%	(a)	(a)	(a)	0.01	(a)	(b)	(a)	0.01
Hydrogen Sulfide Sulfur wt.%	(c)	(c)	(c)	(c)	(c)	(c)	0.003	(c)
Hydrogen Sulfide Sulfur in Autoclave Gas Phase g/l	(d)	(e)	0.006	(e)	0.013	0.006	0.022	0.017
Mercaptan Sulfur wt.%	0.039	0.035	0.040	0.020	0.044	0.036	0.033	0.014
Mercaptan Sulfur in Autoclave Gas Phase g/l	(d)	(e)	(e)	(e)	(e)	(e)	(e)	(e)
Phenol % OH ⁻	1.27	1.25	1.22	1.23	1.19	1.22	1.20	1.19
Phenol % as P-Cresol	8.1	7.9	7.8	7.8	7.5	7.7	7.6	7.5
Acid Number mg KOH/g	(f)	(f)	0.06	0.07	0.05	(f)	(f)	(f)
Base Number mg KOH/g	0.05	(f)	(f)	(f)	(f)	(f)	(f)	(f)
Water ppm	1080	678	360	1374	1190	360	320	935
Total Chlorides ppm	13	(g)	(g)	(g)	(g)	10	<10	(g)
Water Soluble Chlorides ppm	19	(h)	(h)	(h)	(h)	19	15	(h)
Total Nitrogen wt.%	0.84	0.99	0.92	0.83	0.95	0.92	1.10	0.95
Ash mg/l	0.8	5.0	4.0	15.0	8.0	14.0	6.0	4.0

(a) Less than 0.005 wt %

(b) Not conducted

(c) Less than 0.0001 wt %

(d) Not applicable

(e) Less than 0.005 g/l

(f) Less than 0.05 mg KOH/g

(g) Total chloride concentration assumed to be approximately 10 ppm

(h) Water soluble chloride concentration assumed to be approximately 10 ppm

TABLE 10

RESULTS OF CHEMICAL ANALYSES OF SAMPLE B112
(Ft. Lewis, WA/SRC-I, Wash Solvent Column Feed, Point 409)

Species	As Received	Group I 425°F	Group II 425°F	Group I 500°F	Group II 500°F	Group I 575°F	Group II 575°F	Blank 575°F
Total Sulfur wt.%	0.38	0.35	0.37	0.32	0.35	0.34	0.35	0.38
Elemental & Reactive Polysulfide Sulfur wt.%	0.0021	0.0018	0.0024	0.0015	0.0012	0.0014	0.0011	0.0013
Disulfide Sulfur wt.%	(a)	(a)	(a)	(a)	(a)	(a)	(a)	(a)
Hydrogen Sulfide Sulfur wt.%	(b)	0.001	(b)	(b)	(b)	(b)	0.002	(b)
Hydrogen Sulfide Sulfur in Autoclave Gas Phase g/l	(c)	0.010	(d)	(d)	(d)	(d)	0.056	0.016
Mercaptan Sulfur wt.%	0.044	0.069	0.042	0.068	0.071	0.057	0.056	0.040
Mercaptan Sulfur in Autoclave Gas Phase g/l	(c)	(d)	(d)	(d)	(d)	(d)	(d)	(d)
Phenol % OH ⁻	2.82	2.77	2.81	2.73	2.79	2.74	2.65	2.74
Phenol % as p-Cresol	18.1	17.6	17.9	17.4	17.7	17.4	16.9	17.4
Acid Number mg KOH/g	0.3	0.3	0.3	0.4	0.3	0.4	0.3	0.3
Base Number mg KOH/g	(e)	0.05	(e)	0.09	(e)	(e)	(e)	(e)
Water ppm	64	626	247	440	460	408	552	267
Total Chlorides ppm	235	235	245	225	230	232	172	(f)
Water Soluble Chlorides ppm	235	242	242	232	232	226	166	(f)
Total Nitrogen wt.%	1.01	0.94	1.06	0.90	0.87	0.90	0.93	1.05
Ash mg/l	0.3	1.4	2.5	3.7	4.6	7.5	29.7	9.3

- (a) Less than 0.005 wt %
 (b) Less than 0.0001 wt %
 (c) Not applicable
 (d) Less than 0.005 g/l
 (e) Less than 0.05 mg KOH/g
 (f) Not conducted

TABLE 11
RESULTS OF CHEMICAL ANALYSES OF SAMPLE B212
(Ft. Lewis, WA/SRC-I, Wash Solvent Column Overhead, Point 410)

Species	As Received	Group I 350°F	Group II 350°F	Group I 425°F	Group II 425°F	Group I 500°F	Group II 500°F	Blank 500°F
Total Sulfur wt.%	0.29	0.29	0.31	0.31	0.31	0.30	0.31	0.30
Elemental & Reactive Polysulfide Sulfur wt.%	0.0027	0.0025	0.0027	0.0018	0.0021	0.0013	0.0010	0.0011
Disulfide Sulfur wt.%	0.09	0.11	0.07	0.10	0.11	0.10	0.11	0.07
Hydrogen Sulfide Sulfur wt.%	(a)	(a)	(a)	(a)	(a)	(a)	(a)	(a)
Hydrogen Sulfide Sulfur in Autoclave Gas Phase g/l	(b)	0.021	0.008	(c)	0.008	(c)	(c)	0.021
Mercaptan Sulfur wt.%	.021	0.002	0.008	0.007	0.004	0.002	0.002	0.004
Mercaptan Sulfur in Autoclave Gas Phase g/l	(b)	(c)	(c)	(c)	(c)	(c)	(c)	(c)
Phenol % OH ⁻	5.01	5.01	4.95	4.85	4.83	4.80	4.77	4.77
Phenol % as P-Cresol	31.9	31.9	31.5	30.9	30.7	30.5	30.4	30.3
Acid Number mg KOH/g	0.1	0.2	0.1	0.3	0.3	0.2	0.2	0.1
Base Number mg KOH/g	(d)	(d)	(d)	(d)	(d)	(d)	(d)	(d)
Water ppm	410	430	132	480	320	430	410	183
Total Chlorides ppm	132	(e)	(e)	(e)	(e)	130	115	(e)
Water Soluble Chlorides ppm	128	(f)	(f)	(f)	(f)	138	117	(f)
Total Nitrogen wt.%	0.63	0.67	0.80	0.66	0.67	0.65	0.65	0.80
Ash mg/l	4.0	19.2	2.1	4.7	2.0	3.9	0.8	(g)

(a) Less than 0.0001 wt %

(b) Not applicable

(c) Less than 0.005 g/l

(d) Less than 0.05 mg KOH/g

(e) Total chloride concentration assumed to be approximately 125 ppm

(f) Water soluble chloride concentration assumed to be approximately 125 ppm

(g) Less than 0.2 mg

TABLE 12
RESULTS OF CHEMICAL ANALYSES OF SAMPLE B312
(Ft. Lewis, WA/SRC-I, Wash Solvent Column Bottoms, Point 411)

<u>Species</u>	<u>As Received</u>	<u>Group I 500°F</u>	<u>Group II 500°F</u>	<u>Group I 575°F</u>	<u>Group II 575°F</u>	<u>Group I 650°F</u>	<u>Group II 650°F</u>	<u>Blank 650°F</u>
Total Sulfur wt.%	0.42	0.42	0.43	0.42	0.41	0.37	0.38	0.39
Elemental & Reactive Polysulfide Sulfur wt.%	0.0018	0.0036	0.0032	0.0028	0.0025	0.0025	0.0032	0.0025
Disulfide Sulfur wt.%	(a)	(a)	(a)	(a)	(a)	(a)	(a)	(a)
Hydrogen Sulfide Sulfur wt.%	(b)	(b)	(b)	(b)	(b)	(b)	(b)	(b)
Hydrogen Sulfide Sulfur in Autoclave Gas Phase g/l	(c)	0.019	0.006	0.016	0.006	(d)	0.054	0.084
Mercaptan Sulfur wt.%	0.034	0.024	0.028	0.019	0.019	0.020	0.023	0.025
Mercaptan Sulfur in Autoclave Gas Phase g/l	(c)	(d)	(d)	(d)	(d)	(d)	(d)	(d)
Phenol % OH ⁻	1.06	1.04	1.05	1.00	1.00	0.86	0.86	0.89
Phenol % as P-Cresol	6.7	6.6	6.7	6.4	6.4	5.5	5.4	5.7
Acid Number mg KOH/g	0.1	0.4	0.2	0.1	(e)	0.1	0.1	0.1
Base Number mg KOH/g	(e)	(e)	(e)	(e)	(e)	(e)	(e)	(e)
Water ppm	430	240	200	230	220	380	420	410
Total Chlorides ppm	325	335	330	335	295	240	250	(f)
Water Soluble Chlorides ppm	298	276	277	278	244	185	185	(f)
Total Nitrogen wt.%	1.02	0.97	0.98	1.00	0.97	1.05	0.98	1.05
Ash mg/l	3.6	65.2	11.5	2.9	10.0	21.8	10.8	18.7

- (a) Less than 0.005 wt %
(b) Less than 0.0001 wt %
(c) Not applicable
(d) Less than 0.005 g/l
(e) Less than 0.05 mg KOH/g
(f) Not conducted

TABLE 13
RESULTS OF CHEMICAL ANALYSES OF SAMPLE C113
(Ft. Lewis, WA/SRC-II, Wash Solvent Column Feed, Point 409)

Species	As Received	Group I 425°F	Group II 425°F	Group I 500°F	Group II 500°F	Group I 575°F	Group II 575°F	Blank 575°F
Total Sulfur wt.%	0.39	0.38	0.38	0.37	0.35	0.36	0.39	0.39
Elemental & Reactive Polysulfide Sulfur wt.%	0.0034	0.0037	0.0031	0.0020	0.0021	0.0018	0.0022	0.0020
Disulfide Sulfur wt.%	(a)	(a)	(a)	(a)	(a)	(a)	(a)	(a)
Hydrogen Sulfide Sulfur wt.%	(b)	(b)	(b)	(b)	(b)	(b)	(b)	(b)
Hydrogen Sulfide Sulfur in Autoclave Gas Phase g/l	(c)	(d)	(d)	(d)	(d)	(d)	(d)	0.013
Mercaptan Sulfur wt.%	0.026	0.026	0.028	0.026	0.029	0.024	0.021	0.022
Mercaptan Sulfur in Autoclave Gas Phase g/l	(c)	(d)	(d)	(d)	(d)	(d)	(d)	(d)
Phenol % OH ⁻	1.50	1.42	1.39	1.37	1.38	1.35	1.44	1.38
Phenol % as P-Cresol	9.5	9.0	8.8	8.7	8.8	8.5	9.1	8.7
Acid Number mg KOH/g	(e)	(e)	(e)	0.05	0.05	(e)	0.06	(e)
Base Number mg KOH/g	(e)	(e)	(e)	(e)	(e)	(e)	(e)	(e)
Water ppm	200	95	145	180	174	357	403	311
Total Chlorides ppm	50	(f)	(f)	(f)	(f)	65	56	(f)
Water Soluble Chlorides ppm	63	(g)	(g)	(g)	(g)	67	61	(g)
Total Nitrogen wt.%	1.26	1.30	1.33	1.34	1.36	1.36	1.24	1.29
Ash mg/l	0.2	1.4	7.5	2.4	2.5	3.7	8.6	7.0

(a) Less than 0.005 wt %

(b) Less than 0.00001 wt %

(c) Not applicable

(d) Less than 0.005 g/l

(e) Less than 0.05 mg KOH/g

(f) Total chloride concentration assumed to be approximately 60 ppm

(g) Water soluble chlorides concentration assumed to be approximately 60 ppm

TABLE 14
RESULTS OF CHEMICAL ANALYSES OF SAMPLE C213
(Ft. Lewis, WA/SRC-II, Wash Solvent Column Overhead, Point 410)

Species	As Received	Group I 350°F	Group II 350°F	Group I 425°F	Group II 425°F	Group I 500°F	Group II 500°F	Blank 500°F
Total Sulfur wt.%	0.27	0.25	0.27	0.24	0.25	0.23	0.27	0.26
Elemental & Reactive Polysulfide Sulfur wt.%	0.0016	0.0025	0.0036	0.0027	0.0024	0.0024	0.0011	0.0008
Disulfide Sulfur wt.%	(a)	(a)	(a)	(a)	(a)	(a)	(a)	(a)
Hydrogen Sulfide Sulfur wt.%	(b)	(b)	0.001	(b)	(b)	(b)	(b)	(b)
Hydrogen Sulfide Sulfur in Autoclave Gas Phase g/l	(c)	(d)	(d)	(d)	(d)	(d)	(d)	(d)
Mercaptan Sulfur wt.%	0.063	0.063	0.063	0.058	0.066	0.062	0.063	0.067
Mercaptan Sulfur in Autoclave Gas Phase g/l	(c)	(d)	(d)	(d)	(d)	(d)	(d)	(d)
Phenol % OH ⁻	3.86	3.89	3.80	3.68	3.88	3.68	3.79	3.83
Phenol % as P-Cresol	24.6	24.7	24.1	23.4	24.6	23.4	24.1	24.3
Acid Number mg KOH/g	0.3	0.2	0.2	0.2	0.2	0.3	0.1	0.1
Base Number mg KOH/g	(e)	(e)	0.1	0.2	(e)	(e)	(e)	(e)
Water ppm	73	161	43	157	102	587	370	370
Total Chlorides ppm	187	190	(f)	(f)	(f)	180	140	(f)
Water Soluble Chlorides ppm	191	190	(g)	(g)	(g)	185	136	(g)
Total Nitrogen wt.%	1.24	1.38	1.26	1.28	1.37	1.18	1.29	1.26
Ash mg/l	1.7	0.8	1.7	1.6	2.2	1.3	5.9	7.8

(a) Less than 0.005 wt %

(b) Less than 0.00001 wt %

(c) Not applicable

(d) Less than 0.005 g/l

(e) Less than 0.05 mg KOH/g

(f) Total chloride concentration assumed to be in the range of 140-190 ppm

(g) Water soluble chloride concentration assumed to be in the range of 130-190 ppm

TABLE 15

RESULTS OF CHEMICAL ANALYSES OF SAMPLE C313
(Ft. Lewis, WA/SRC-II, Wash Solvent Column Bottoms, Point 411)

Species	As Received	Group I 500°F	Group II 500°F	Group I 575°F	Group II 575°F	Group I 650°F	Group II 650°F	Blank 650°F
Total Sulfur wt.%	0.45	0.40	0.42	0.40	0.41	0.40	0.45	0.44
Elemental & Reactive Polysulfide Sulfur wt.%	0.0034	0.0020	0.0042	0.0043	0.0044	0.0038	0.0041	0.0031
Disulfide Sulfur wt.%	(a)	(a)	(a)	(a)	(a)	(a)	(a)	(a)
Hydrogen Sulfide Sulfur wt.%	(b)	(b)	(b)	(b)	(b)	0.002	(b)	(b)
Hydrogen Sulfide Sulfur in Autoclave Gas Phase g/l	(e)	0.005	(d)	(d)	(d)	0.152	0.025	0.019
Mercaptan Sulfur wt.%	0.015	0.008	0.010	0.006	0.008	0.010	0.014	0.009
Mercaptan Sulfur in Autoclave Gas Phase g/l	(c)	(d)	(d)	(d)	(d)	0.017	(d)	(d)
Phenol % OH ⁻	0.63	0.52	0.57	0.49	0.59	0.49	0.61	0.61
Phenol % as P-Cresol	4.0	3.3	3.6	3.1	3.7	3.1	3.9	3.9
Acid Number mg KOH/g	(e)	(e)	(e)	(e)	(e)	0.1	(e)	(e)
Base Number mg KOH/g	(e)	(e)	(e)	0.1	(e)	0.2	(e)	(e)
Water ppm	64	367	79	398	88	485	465	549
Total Chlorides ppm	<10	(f)	(f)	(f)	(f)	<10	<10	(f)
Water Soluble Chlorides ppm	14	(g)	(g)	(g)	(g)	9	13	(g)
Total Nitrogen wt.%	1.16	1.29	1.33	1.30	1.30	0.93	1.14	1.12
Ash mg/l	1.4	2.4	3.8	2.8	4.6	10.7	8.5	16.6

(a) Less than 0.005 wt %

(b) Less than 0.0001 wt %

(c) Not applicable

(d) Less than 0.005 g/l

(e) Less than 0.05 mg KOH/g

(f) Total chloride concentration assumed to be approximately 10 ppm

(g) Water soluble chloride concentration assumed to be approximately 10 ppm

TABLE 16
Results of Chemical Analyses of Sample C413
(Ft. Lewis, WA/ SRC-II, Light Ends Column Feed, Pt. 412)

<u>Species</u>	<u>As Received</u>	<u>Group II 575°F</u>	<u>Blank 575°F</u>
Total Sulfur wt.%	0.41	0.38	0.38
Elemental & Reactive Polysulfide Sulfur wt.%	0.0035	0.0021	0.0023
Disulfide Sulfur wt.%	(a)	(a)	(a)
Hydrogen Sulfide Sulfur wt.%	(b)	(b)	(b)
Hydrogen Sulfide Sulfur in Autoclave Gas Phase g/l	(c)	(d)	0.173
Mercaptan Sulfur wt.%	0.044	0.045	(e)
Mercaptan Sulfur in Autoclave Gas Phase g/l	(c)	0.005	(f)
Phenol % OH ⁻	1.40	1.39	1.36
Phenol % as P-Cresol	8.9	8.85	8.6
Acid Number mg KOH/g	(g)	(g)	(g)
Base Number mg KOH/g	(g)	(g)	(g)
Water ppm	489	330	828
Total Chlorides ppm	36	15	(d)
Water Soluble Chlorides ppm	59	19	(d)
Total Nitrogen wt.%	1.07	1.08	1.08
Ash mg/l	1.4	12.4	11.1

- (a) Less than 0.005 wt %
(b) Less than 0.0001 wt %
(c) Not applicable
(d) Not conducted
(e) To be completed
(f) Less than 0.005 g/l
(g) Less than 0.05 mg KOH/g

TABLE 17
RESULTS OF CHEMICAL ANALYSES OF SAMPLE D314 and D325
(H-Coal Atmospheric Still Overhead)

Species	D314 As Received	D314 Group II 500°F	D314 Blank 500°F	D325 As Received	D325 Group I 500°F	D325 Group II 500°F
Total Sulfur wt.%	0.06	0.05	0.05	0.24	0.22	0.14
Elemental & Reactive Polysulfide Sulfur wt.%	0.0029	0.0039	0.0031	0.0098	0.0027	0.0022
Disulfide Sulfur wt.%	0.013	(a)	(a)	0.068	0.027	0.012
Hydrogen Sulfide Sulfur wt.%	(b)	(b)	(b)	0.049	0.011	0.001
Hydrogen Sulfide Sulfur in Autoclave Gas Phase g/l	(c)	0.067	0.052	(c)	0.169	0.174
Mercaptan Sulfur wt.%	0.010	0.017	0.021	(b)	0.032	0.042
Mercaptan Sulfur in Autoclave Gas Phase g/l	(c)	(d)	(d)	(c)	(d)	(d)
Phenol % OH ⁻	1.03	1.16	1.07	1.03	1.08	1.15
Phenol % as P-Cresol	6.52	7.37	6.81	6.58	6.87	7.27
Acid Number mg KOH/g	(e)	(f)	(f)	(f)	(f)	(f)
Base Number mg KOH/g	(e)	0.11	0.34	5.97	4.27	0.91
Water ppm	588	195	374	476	328	217
Total Chlorides ppm	<10	(g)	(g)	10	10	10
Water Soluble Chlorides ppm	5	5	(g)	8	7	6
Total Nitrogen wt.%	0.35	0.36	0.33	0.59	0.51	0.45
Ash mg/l	1.2	0.5	5.4	0.8	1.1	2.5

(a) Less than 0.005 wt %

(b) Less than 0.0001 wt %

(c) Not applicable

(d) Less than 0.005 g/l

(e) Not conducted

(f) Less than 0.05 mg KOH/g

(g) Chloride concentration assumed to be less than 10 ppm

TABLE 18
RESULTS OF CHEMICAL ANALYSES OF SAMPLES D414 and D425
(H-Coal Atmospheric Still Bottoms)

Species	D414 As Received	D414 Group I 650°F	D414 Group II 650°F	D425 As Received	D425 Group I 650°F
Total Sulfur wt. %	0.02	0.01	0.01	0.08	0.07
Elemental & Reactive Polysulfide Sulfur wt. %	0.0001	0.0037	0.0044	0.0038	0.0047
Disulfide Sulfur wt. %	(a)	(a)	(a)	0.007	(a)
Hydrogen Sulfide Sulfur wt. %	(b)	(b)	(b)	(b)	(b)
Hydrogen Sulfide Sulfur in Autoclave Gas Phase g/l	(c)	(d)	(d)	(c)	0.009
Mercaptan Sulfur wt. %	0.007	0.007	(a)	(a)	(a)
Mercaptan Sulfur in Autoclave Gas Phase g/l	(c)	(d)	(d)	(c)	(d)
Phenol % OH ⁻	0.37	0.33	0.35	0.33	0.30
Phenol % as P-Cresol	2.36	2.10	2.20	2.12	1.89
Acid Number mg KOH/g	(e)	(e)	(c)	0.43	(e)
Base Number mg KOH/g	0.13	(e)	0.20	(e)	0.18
Water ppm	94	100	226	305	320
Total Chlorides ppm	<10	10	<10	335	325
Water Soluble Chlorides ppm	8	7	7	290	25
Total Nitrogen wt. %	0.45	0.45	0.45	0.62	0.60
Ash mg/l	1.4	5.1	4.3	1.7	4.3

- (a) Less than 0.005 wt %
 (b) Less than 0.0001 wt %
 (c) Not applicable
 (d) Less than 0.005 g/l
 (e) Less than 0.05 mg KOH/g

TABLE 19
RESULTS OF CHEMICAL ANALYSES OF SAMPLES E116 and E216
(Exxon Reflux Naptha)
(Exxon Heavy Atmosphere Gas Oil)

Species	E116 As Received	E116 Group I 500°F	E116 Group II 500°F	E216 As Received	E216 Group I 650°F	E216 Group II 650°F
Total Sulfur wt.%	1.06	1.05	1.04	0.27	0.28	0.26
Elemental & Reactive Polysulfide Sulfur wt.%	0.0007	0.0008	0.0011	0.0061	0.0021	0.0026
Disulfide Sulfur wt.%	0.005	0.026	0.027	(a)	(a)	0.012
Hydrogen Sulfide Sulfur wt.%	0.210	0.014	0.013	(b)	0.006	0.004
Hydrogen Sulfide Sulfur in Autoclave Gas Phase g/l	(c)	0.452	0.669	(c)	0.406	0.482
Mercaptan Sulfur wt.%	0.442	0.339	0.330	0.043	0.019	0.018
Mercaptan Sulfur in Autoclave Gas Phase g/l	(c)	0.015	0.020	(c)	0.006	0.005
Phenol % OH ⁻	1.99	1.96	1.97	0.76	0.69	0.69
Phenol % as P-Cresol	12.6	12.5	12.5	4.8	4.4	4.4
Acid Number mg KOH/g	(d)	(d)	(d)	(d)	(d)	(d)
Base Number mg KOH/g	(d)	(d)	(d)	0.09	0.09	0.10
Water ppm	1012	1720	656	507	632	640
Total Chlorides ppm	<10	<10	<10	<10	10	<10
Water Soluble Chlorides ppm	7	5	5	7	18	7
Total Nitrogen wt.%	0.16	0.17	0.17	0.24	0.26	0.27
Ash mg/l	0.45	1.32	5.25	0.60	8.99	2.81

(a) Less than 0.005 wt %

(b) Less than 0.0001 wt %

(c) Not applicable

(d) Less than 0.05 mg KOH/g

TABLE 20
RESULTS OF CHEMICAL ANALYSES OF SAMPLES E316 and E416
(Exxon Light Atmosphere Gas Oil)
(Exxon Light Vacuum Gas Oil)

Species	E316 As Received	E316 Group I 575°F	E316 Group II 575°F	E416 As Received	E416 Group I 575°F	E416 Group II 575°F
Total Sulfur wt.%	0.12	0.11	0.11	0.61	0.62	0.65
Elemental & Reactive Polysulfide Sulfur wt.%	0.0030	0.0028	0.0026	0.0083	0.0058	0.0087
Disulfide Sulfur wt.%	(a)	0.026	0.026	(a)	(a)	(a)
Hydrogen Sulfide Sulfur wt.%	(b)	0.014	0.017	(b)	0.004	0.008
Hydrogen Sulfide Sulfur in Autoclave Gas Phase g/l	(c)	0.056	0.049	(c)	0.064	0.056
Mercaptan Sulfur wt.%	0.036	(a)	(a)	0.092	0.057	0.062
Mercaptan Sulfur in Autoclave Gas Phase g/l	(c)	(d)	(d)	(c)	(d)	(d)
Phenol % OH ⁻	1.32	1.31	1.28	1.02	1.10	1.08
Phenol % as P-Cresol	8.4	8.3	8.1	6.5	7.0	6.8
Acid Number mg KOH/g	(e)	(e)	(e)	(e)	(e)	(e)
Base Number mg KOH/g	(e)	(e)	(e)	(e)	(e)	(e)
Water ppm	490	299	473	133	922	756
Total Chlorides ppm	10	10	10	53	50	45
Water Soluble Chlorides ppm	7	6	6	73	59	63
Total Nitrogen wt.%	0.10	0.09	0.09	0.78	0.75	0.74
Ash mg/l	0.22	2.20	2.68	0.16	115.1	0.98

-
- (a) Less than 0.005 wt %
(b) Less than 0.0001 wt %
(c) Not applicable
(d) Less than 0.005 g/l
(e) Less than 0.05 mg KOH/g

TABLE 21
RESULTS OF CHEMICAL ANALYSES OF SAMPLES E616 and E716
(Exxon Product Solvent)
(Exxon T-201, Tray 23)

<u>Species</u>	<u>E616 As Received</u>	<u>E616 Group I 650°F</u>	<u>E616 Group II 650°F</u>	<u>E716 As Received</u>	<u>E716 Group I 500°F</u>	<u>E716 Group II 500°F</u>
Total Sulfur wt.%	0.03	0.03	0.03	0.21	0.18	0.20
Elemental & Reactive Polysulfide Sulfur wt.%	0.0008	0.0008	0.0008	0.0038	0.0001	0.0003
Disulfide Sulfur wt.%	(a)	(a)	(a)	(a)	(a)	(a)
Hydrogen Sulfide Sulfur wt.%	(b)	(b)	(b)	0.008	(b)	(b)
Hydrogen Sulfide Sulfur in Autoclave Gas Phase g/l	(c)	0.0018	0.0031	(c)	0.0211	0.0582
Mercaptan Sulfur wt.%	(a)	(a)	(a)	0.084	0.072	0.066
Mercaptan Sulfur in Autoclave Gas Phase g/l	(c)	(d)	(d)	(c)	(d)	0.006
Phenol % OH ⁻	0.63	0.62	0.61	2.03	1.97	1.97
Phenol % as P-Cresol	4.00	3.96	3.90	12.9	12.5	12.5
Acid Number mg KOH/g	(e)	(e)	(e)	(e)	(e)	(e)
Base Number mg KOH/g	4.38	0.47	0.56	(e)	(e)	(e)
Water ppm	382	315	191	739	291	415
Total Chlorides ppm	15	<10	<10	95	15	10
Water Soluble Chlorides ppm	16	7	4	91	8	16
Total Nitrogen wt.%	0.21	0.20	0.23	0.11	0.14	0.14
Ash mg/l	0.39	3.97	9.13	0.80	1.61	5.34

-
- (a) Less than 0.005 wt %
(b) Less than 0.0001 wt %
(c) Not applicable
(d) Less than 0.005 g/l
(e) Less than 0.05 mg KOH/g

TABLE 22

CORROSION RATES OF CARBON STEEL EXPOSED AT 500°F COMPARED WITH THE CONCENTRATION OF SELECTED CHEMICAL SPECIES

Corrosion Rate (mpy)	Total Sulfur (wt %)	Elem + React Polysulfide Sulfur (wt %)	Disulfide Sulfur (wt %)	Hydrogen Sulfide Sulfur (wt %)	Mercaptan Sulfur (wt %)	Phenol (% OH)	Acid No. mg KOH/g	Base No. mg KOH/g	Water (ppm)	Total Chlorides (ppm)	Water Soluble Chlorides (ppm)	Total Nitrogen (wt %)	Boiling Range	Fluid I.D.
1.1	0.03	0.001	(a)	(b)	(a)	0.63	(c)	4.38	382	15	16	0.21	High	E616
2.6	0.27	0.006	(a)	(b)	0.043	0.76	(c)	0.09	507	<10	7	0.24	High	E216
4.5	0.08	0.004	0.007	(b)	(a)	0.33	0.4	(c)	305	335	290	0.62	High	D425
4.8	0.45	0.003	(a)	(b)	0.015	0.63	(c)	(c)	64	<10	14	1.16	High	C313
5.1	0.21	0.004	(a)	0.008	0.084	2.03	(c)	(c)	739	95	91	0.11	Med	E716
5.7	0.06	0.003	0.013	(b)	0.010	1.03	(c)	(c)	588	<10	5	0.35	Low	D314
5.7	0.45	0.002	(a)	(b)	0.026	1.11	0.1	(c)	310	95	116	0.76	Med	A511
9.3	1.06	0.001	0.005	0.21	0.442	1.99	(c)	(c)	1012	<10	7	0.16	High	E116
9.3	0.39	0.003	(a)	(b)	0.026	1.50	(c)	(c)	200	50	63	1.26	Med	C113
10.2	0.24	0.010	0.068	0.049	(a)	1.03	(c)	5.97	476	10	8	0.59	Low	D325
10.7	0.38	0.003	(a)	(b)	0.035	1.27	(c)	0.05	1080	13	19	0.84	Med	A521
15.1	0.50	0.0020	0.02	0.090	0.070	1.51	(c)	0.11	1411	<10	6	0.91	Med	A211
15.7	0.68	0.002	0.050	0.01	0.410	0.31	(c)	2.6	166	<10	10	1.29	Low	A311
19.8	0.29	0.003	0.090	(b)	0.021	5.01	0.1	(c)	410	132	128	0.63	Low	B212
22.7	0.40	0.002	0.260	(b)	0.006	4.96	0.3	(d)	4700	<10	5	0.51	Low	A411
22.8	0.38	0.021	(a)	(b)	0.044	2.82	0.3	(c)	64	235	235	1.01	Med	B112
23.6	0.27	0.002	(a)	(b)	0.063	3.86	0.3	(c)	73	187	191	1.24	Low	C213
27.6	0.42	0.002	(a)	(b)	0.034	1.06	0.1	(c)	430	325	298	1.02	High	B312

(a) Less than 0.005 wt %
 (b) Less than 0.0001 wt %
 (c) Less than 0.05 mg KOH/g
 (d) Not conducted

TABLE 23

CORROSION RATES OF TYPE 410 STAINLESS STEEL EXPOSED AT 500°F COMPARED WITH THE CONCENTRATION OF SELECTED CHEMICAL SPECIES

Corrosion Rate (mpy)	Total Sulfur (wt %)	Elem + React Polysulfide Sulfur (wt %)	Disulfide Sulfur (wt %)	Hydrogen Sulfide Sulfur (wt %)	Mercaptan Sulfur (wt %)	Phenol (% OH)	Acid No. mg KOH/g	Base No. mg KOH/g	Water (ppm)	Total Chlorides (ppm)	Water Soluble Chlorides (ppm)	Total Nitrogen (wt %)	Boiling Range	Fluid I.D.
0.1	0.40	0.002	0.260	(a)	0.006	4.96	0.3	(b)	4700	<10	5	0.51	Low	A411
0.2	0.45	0.002	(d)	(a)	0.026	1.11	0.1	(e)	310	95	116	0.76	Med	A511
0.2	0.03	0.001	(d)	(a)	(d)	0.63	(e)	4.38	382	15	16	0.21	High	E616
0.3	0.38	0.003	(d)	(a)	0.039	1.27	(e)	0.05	1080	13	19	0.84	Med	A521
0.5	0.08	0.004	0.007	(a)	(d)	0.33	0.4	(e)	305	335	290	0.62	High	D425
0.9	0.06	0.003	0.013	(a)	0.010	1.03	(f)	(f)	588	<10	5	0.35	Low	D314
1.3	0.21	0.004	(d)	0.008	0.084	2.03	(e)	(e)	739	95	91	0.11	Med	E716
1.4	0.45	0.003	(d)	(a)	0.015	0.63	(e)	(e)	64	<10	14	1.16	High	C313
1.5	0.12	0.003	(d)	(a)	0.036	1.32	(f)	(e)	490	10	7	0.10	Med	E316
1.8	0.29	0.003	0.090	(a)	0.021	5.01	0.1	(e)	410	132	128	0.63	Low	B212
2.0	0.24	0.010	0.068	0.049	(d)	1.03	(e)	5.97	476	10	8	0.59	Low	D325
2.4	1.06	0.001	0.005	0.21	0.442	1.99	(e)	(e)	1012	<10	7	0.16	Med	E116
3.3	0.42	0.002	(d)	(a)	0.034	1.06	0.1	(e)	430	325	298	1.02	High	B312
3.4	0.27	0.002	(d)	(a)	0.063	3.86	0.3	(e)	73	187	191	1.24	Low	C213
3.4	0.61	0.008	(d)	(a)	0.092	1.02	(e)	(e)	133	53	73	0.78	Med	E416
4.1	0.50	0.002	0.020	0.090	0.070	1.51	(e)	0.11	1411	<10	6	0.91	Med	A211
5.1	0.27	0.006	(d)	(a)	0.043	0.76	(e)	0.09	507	<10	7	0.24	High	E216
5.3	0.39	0.003	(d)	(a)	0.026	1.50	(e)	(e)	200	50	63	1.26	Med	C113
7.5	0.68	0.002	0.050	0.01	0.410	0.31	(e)	2.6	166	<10	10	1.29	Med	A311
9.6	0.38	0.002	(d)	(a)	0.044	2.82	0.3	(e)	64	235	235	1.01	Med	B112

- (a) Less than 0.0001 wt %
(b) Not conducted
(c) Less than 0.2 mg
(d) Less than 0.005 wt %
(e) Less than 0.05 mg KOH/g
(f) To be completed

The results of this type of analysis for four liquids which have been analyzed are as follows.*

- o Ft. Lewis SRC-I Wash Solvent Column Feed:
 - Total Nitrogen - 1.01 weight percent
 - "Strong base" amines - 0.13 weight percent
 - "Weak base" amines - 4.35 weight percent
- o Ft. Lewis SRC-I Wash Solvent Column Bottoms:
 - Total nitrogen - 1.02 weight percent
 - "Strong base" amines - 0.11 weight percent
 - "Weak base" amines - 5.63 weight percent
- o Trenton H-Coal Atmospheric Still Overhead:
 - Total nitrogen - 0.59 weight percent
 - "Strong base" amines - 0.09 weight percent
 - "Weak base" amines - 3.41 weight percent
- o Baytown EDS Light Vacuum Gas Oil:
 - Total nitrogen - 0.78 weight percent
 - "Strong base" amines - 0.05 weight percent
 - "Weak base" amines - 2.40 weight percent

As a part of further study of this method, samples of the extracted amines are to be analyzed using mass spectrometry. An attempt will also be made to determine the nature of nitrogen compounds which are not extracted by this method; i.e., nitrogen compounds remaining in the coal liquid residue following the acid extraction.

* Concentrations of total nitrogen reflect the amount of elemental nitrogen only; concentrations of amines reflect the amount (weight) of amine compound present in solution.

ORNL-3.2.4, -3.3.4, AND -3.4.4 - LIQUEFACTION CORROSION

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A. STRESS-CORROSION CRACKING

J. R. Keiser, V. B. Baylor, J. F. Newsome, and M. Howell

INTRODUCTION

This work is being performed to assess the resistance of various materials to stress-corrosion cracking in coal liquefaction plants.

RESULTS FROM PRIOR QUARTERS

During prior quarters, several racks of U-bend specimens were exposed in the Wilsonville, Alabama, and Fort Lewis, Washington, solvent-refined coal (SRC) pilot plants; the Catlettsburg, Kentucky, H-Coal Pilot Plant; and the Baytown, Texas, Exxon Coal Liquefaction Plant (ECLP). Metallographic examinations of the exposed specimens have been performed.

Racks of U-bend specimens have been exposed at Fort Lewis since January 1979. Results from examinations through September 1980 are reported elsewhere.^{1,2} Results from U-bend exposures at ECLP were reported earlier.³ Specimens examined from the top of the dissolver at Wilsonville and specimens from H-Coal were examined and reported last quarter.⁴

DISCUSSION OF CURRENT ACTIVITIES

During this reporting period corrosion rates were calculated for U-bend specimens exposed in the bottom of the Wilsonville dissolver (R-101). They were in place from November 1980 through March 1981 for a total operating time of 1850 h. The corrosion rates given in Table 1 are high for the low-alloy steels (JO.8 mm/year) and low for the austenitic

Table 1. Corrosion rates of U-bend specimens exposed in bottom of Wilsonville dissolver (R-101) for 1850 h operating time above 425°C

Alloy ^a	Corrosion rate mm/year (mil/year)
7 Cr-1 Mo (HT8)	1.87 (74)
7 Cr-1 Mo (HT7)	1.79 (71)
9 Cr-1 Mo (modified)	1.31 (52)
9 Cr-1 Mo	1.14 (45)
HT9	0.84 (33)
Sancro 41X	0.24 (9.4)
410	0.23 (9.2)
321	0.10 (4.0)
304L	0.06 (2.3)
3RE14	0.05 (2.1)
304L-W	0.05 (2.1)
347-W	0.05 (1.9)
316L	0.05 (1.9)
316L-W	0.04 (1.5)
304-W	0.04 (1.4)
347	0.03 (1.2)
Sancro 28	<i>b</i>
321-W	<i>b</i>
332	<i>b</i>
332-W	<i>b</i>

^a_W = welded specimen.

^bSpecimen gained weight.

stainless steels (F0.1 mm/year). Visual examination indicated catastrophic cracks on the two 7 Cr-1 Mo and the two 9 Cr-1 Mo specimens.

Metallographic examination will be performed on other selected specimens to determine the presence of cracks.

Also during this quarter, racks of specimens were prepared for insertion into the H-Coal Pilot Plant. Specimens were also readied for the Exxon Coal Liquefaction Pilot Plant. Specimens to be tested in sulfur acids in the laboratory began long-term aging.

B. GENERAL CORROSION

J. R. Keiser, M. Howell, and J. F. Newsome

INTRODUCTION

The purpose of this work is to determine the potential for general corrosion in coal liquefaction plants. The corrosivity of the fluids is measured by exposing corrosion coupons in a number of vessels in the Fort Lewis and Wilsonville SRC Pilot Plants and the Catlettsburg H-Coal Pilot Plant.

RESULTS FROM PRIOR QUARTERS

Corrosion coupons have been exposed in a number of vessels in the Fort Lewis and Wilsonville SRC Pilot Plants, and results from examination of these samples have been reported in prior quarterlies. These studies have shown that sulfidation can be a serious problem in the reaction and separation areas, and a chloride-related mechanism causes serious corrosion problems in the fractionation area.

DISCUSSION OF CURRENT ACTIVITIES

During this quarter, examination was completed on four racks of coupons removed from the Catlettsburg H-Coal N-202 fractionator. Three racks of coupons were sent to Wilsonville, one for the hydrotreater and two for the T-102 vacuum column. Six samples from the Baytown plant were analyzed, and one of these was fractionated and the collected fractions analyzed.

Chemical analysis of six samples from the Baytown EDS plant were completed this quarter. The samples were collected while the plant was operating on Illinois No. 6 coal and while corrosion at tray 23 of the T-201 fractionator was thought to be fairly severe. Results of the chemical analyses (Table 2) show that the chlorine level and the neutralization number were highest for samples from the area where corrosion was most severe. The chemical analyses results indicate that the nitrogen content

Table 2. Results of chemical analysis of samples collected at the Baytown Exxon Donor Solvent Coal Liquefaction Plant

Exposure site	Chloride NAA ^a ($\mu\text{g/mL}$)	Neutralization number (mg KOH/g)	Nitrogen (%)	Sulfur (%)	Initial boiling point (°C)	Average boiling point (°C)	Final boiling point (°C)
T-201, overhead, No. 1	<16	0.48	<0.01				
T-201, overhead, No. 2	3.0	0.61	<0.01	0.96			
T-201, tray 23, No. 1	91.2	0.84			151	206	283
T-201, tray 23, No. 2	94.7	0.82			148	202	273
T-201, tray 23, No. 3	99.5 83.6	0.89	<0.01	0.26	152	199	251
T-202, bottoms	13.6	0.40			170	226	346

^aNAA = neutron activation analysis.

was unexpectedly low (<0.01 wt %) compared with 0.5 wt %, which is a typical value for Fort Lewis wash solvent column liquids. The average boiling point of liquid collected from the tray where corrosion is most severe at Baytown (tray 23) is 202°C, only 8° below the average for Fort Lewis tray 21 samples collected in September 1980. Additional samples collected at Baytown during two operating periods, one using high-chlorine-content Illinois No. 6 coal and one using low-chlorine-content Wyodak coal, are being sent to ORNL for analysis.

An atmospheric distillation was performed on a sample collected from tray 23 of the T-201 atmospheric fractionator at the Baytown, Texas, EDS pilot plant. The collected samples were analyzed for chlorine and neutralization number. The results (Table 3) show that the chlorine content was highest in the samples with boiling points above 195°C, and that, contrary to observations at Fort Lewis and Wilsonville, the neutralization number was inversely related to the chlorine content except for the highest boiling sample.

An atmospheric distillation was performed on a sample collected from tray 23 of the T-201 atmospheric fractionator at the Baytown, Texas, EDS pilot plant. The collected samples were analyzed for chlorine and neutralization number. The results (Table 3) show that the chlorine content was highest in the samples with boiling points above 195°C, and that, contrary to observations at Fort Lewis and Wilsonville, the neutralization number was inversely related to the chlorine content except for the highest boiling sample.

Table 3. Results of analyses of samples collected from distillation of oil from tray 23 of T-201 atmospheric fractionator at Baytown EDS pilot plant

Distillation temperature range (°C)	Amount of oil collected (g) ^a	Chlorine concentration (µg/mL) ^b	Neutralization number (mg KOH/g)
180 and below	22.5	26.4	1.09
180-190	14.5	86.7	0.80
190-195	36.2	97.4	0.88
195-200	34.0	120.4	0.71
200-204	43.3	120.7	0.67
204-206	48.9	106.7	0.57
206 and above	59.1	126.4	1.52

^aOriginal sample, 260 g.

^bBy neutron activation analysis.

REFERENCES

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BCL-3.3.5 - EVALUATION OF ADVANCED MATERIALS
FOR SLURRY EROSION SERVICE

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INTRODUCTION

This program is intended to address the needs of coal liquefaction pilot plants for erosion-resistant materials for trim, wear inserts or liners for letdown valves or pumps, through screening of candidate materials, characterization of the erosion behavior of generic materials, and investigation of routes to improving these materials.

RESULTS FROM PRIOR QUARTERS

This program was started in May, 1981. Consequently, the effort in the first quarter was devoted to procurement of test materials and setting up test procedures.

DISCUSSION OF CURRENT ACTIVITIES

The activities in this program have been grouped into three main tasks. Activities in each task are discussed separately.

Task I. Materials Screening Activities

A standardized test condition is being used to generate comparative erosion data for new materials intended for use in severe erosion service. The conditions are exposure to a jet of slurry of 8 percent by weight of solids (taken from the SRC-1 process at Wilsonville) in anthracene oil for 1 hour, at 100 m/s, 343°C (650 F) and an intended

impingement angle of 20° , in the Battelle slurry erosion rig. The surfaces of all materials are finished to 3.3×10^{-2} microns (arithmetic average) by grinding on a diamond wheel in the direction of slurry flow (where possible), to minimize the influence of surface roughness on erosion behavior. The parameter used to compare the erosion performance of all materials is maximum depth of the erosion crater, measured using a Talysurf Model 4 profilometer. A regular, partial rejuvenation procedure is used to maintain the erosivity of the recirculated slurry as uniform as possible. Specimens of the cemented tungsten carbide, Kennametal K701, which is used as a reference material, are run in the test at regular intervals as a further check on the test conditions.

The results of tests on cemented tungsten carbides are listed in Table 1, on novel cermet materials in Table 2, and on some metallic materials in Table 3. Of the cemented tungsten carbides, those with

TABLE 1. COMPARATIVE EROSION DATA FOR CEMENTED TUNGSTEN CARBIDES

Material	Specimen Designation	Source	Composition	Erosion Crater	
				Depth (μm)	Length (μm)
K701	Reference	Kennametal	WC-10% Co-4% Cr	3.4-5.6	$2.31-3.15 \times 10^3$
WC-Co	WA-41	GTE	WC-9.0% Co	9.6	2.72×10^3
WC-Co	WA-1	GTE	WC-6.0% Co	7.8	2.44×10^3
WC-Co	WA-2	GTE	WC-6.0% Co	6.7	2.29×10^3
WC-Co	WA-35	GTE	WC-6.0% Co	5.6	2.34×10^3
WC-Co	X-614	GTE	6% Co, total composition unknown	6.6	2.84×10^3
WC-Co	WA-3	GTE	WC-4.3% Co	6.6	2.59×10^3
WC-Co	WA-4	GTE	WC-3.0% Co	4.7	3.00×10^3
WC-Co	WA-107	GTE	composition unknown	5.1	2.49×10^3
WC-Co	WA-110	GTE	submicron carbide, composition unknown	6.6	3.00×10^3
WC-Co	WA-114	GTE	composition unknown	12.7	2.49×10^3
WC-Co	WA-119	GTE	composition unknown	15.2	2.39×10^3
WC-Co	WA-510	GTE	Non-magnetic carbide, composition unknown	86.4	2.64×10^3

TABLE 2. NOVEL CERMET MATERIALS

Material	Specimen Designation	Source	Composition	Erosion Crater	
				Depth (μm)	Length (μm)
K701	Reference	Kennametal	WC-10% Co-4% Cr	3.4-5.6	$2.31-3.15 \times 10^3$
TiB ₂ -Ni	NT 85 Q	ORNL	Bal TiB ₂ 0.4% Ni, 1% O ₂	17.0	
TiB ₂ -Ni	NT 85 R	ORNL	Bal TiB ₂ 0.4% Ni 1% O ₂	19.1	
TiB ₂ -Ni	NT 85 S	ORNL	Bal TiB ₂ 1.5% Ni 2.2% O ₂	22.5	
TiB ₂ -Ni	NT 85 T	ORNL	Bal TiB ₂ 1.0% Ni 2.0% O ₂	14.9	
TiB ₂ -Ni	NM T-85	ORNL	Bal TiB ₂ 8.6% Ni-90% Mo-10%	16.8	
Cr-cermets	C-HM-9	ORNL	56.7% wt. Al ₂ O ₃ 38.8% wt. B ₄ C 4.5% wt. Cr	19.1	2.93×10^3
Cr-cermets	C-HM-10	ORNL	38.9% wt. Al ₂ O ₃ 56.6% wt. CrB 4.5% wt. Cr	30.0	3.00×10^3
Cr-cermets	C-HM-12	ORNL	47.3% wt. Al ₂ O ₃ 48.2% wt. B ₄ C 4.5% wt. Cr	9.7	2.59×10^3
Cr-cermets	HM-7	ORNL	50.5% wt. CrB 49.5% at Colmonoy No. 6	35.1	2.27×10^3
CrB-cermets	100/CBC	ORNL	CrB-2% wt. Co	excessive erosion in 1 hr.	
CrB-cermets	101/CBF	ORNL	CrB-2% wt. Fe	excessive erosion in 35 min.	
CrB-cermets	102/CBN	ORNL	CrB-2% wt. Ni	not tested	
CrB-cermets	109/CBC	ORNL	CrB-12% wt. Co	not tested	
CrB-cermets	110/CBF	ORNL	CrB-12% wt. Fe	not tested	
CrB-cermets	111/CBN	ORNL	CrB-12% wt. Ni	not tested	

TABLE 2. (continued)

Material	Specimen Designation	Source	Composition	Erosion Crater	
				Depth (μm)	Length (μm)
CrB-cermets	112/CBC	ORNL	CrB-16% wt. Co	not tested	
CrB-cermets	114/CBN	ORNL	CrB-16% wt. Ni	not tested	
CrB-cermets	115/CBC	ORNL	CrB-20% wt. Co	not tested	
CrB-cermets	116/CBF	ORNL	CrB-20% wt. Fe	not tested	
Diamond	Stratapax/2538	GE	diamond compact	none*	
Diamond/Si-SiC	A	GE	low diamond, size 1*	135	2.95×10^3
Diamond/Si-SiC	B	GE	high diamond, size 1	~ 22.9	--
Diamond/Si-SiC	C	GE	low diamond, size 2	135	2.57×10^3
Diamond/Si-SiC	D	GE	high diamond, size 2	25-27	~ 150
Diamond/Si-SiC	E	GE	low diamond, size 3	187	2.94×10^3
Diamond/Si-SiC	F	GE	high diamond, size 3	7.7-10.2	--
Diamond/Si-SiC	CDC/3-G	GE	high diamond, size 6	~ 4.8	--
Diamond/Si-SiC	CDC/4-H	GE	high diamond, size 5	~ 6.9	--
Diamond/Si-SiC	CDC/5-I	GE	high diamond, size 4	~ 4.6	--
Diamond/Si-SiC	CDC/J	GE	high diamond, size 3	~ 7.9	--

* Size designations are 1 = coarse, 2 = fine.

TABLE 3. METALLIC MATERIALS

Material	Specimen Designation	Source	Composition	Erosion Crater	
				Depth (μm)	Length (μm)
Nitinol + B*	H-1	ORNL	53.1% wt. Ni 45.7% wt. Ti 1.1% wt. B	163	1.12×10^3
Nitinol + B*	H-2	ORNL	49.1% wt. Ni 47.5% wt. Ti 3.4% wt. B	130	1.36×10^3
Nitinol + B*	H-3	ORNL	46.55% wt. Ni 48.45% wt. Ti 5.0% wt. B	--	--

* alloy of 50-50 atomic percent Ni-Ti, + TiB₂.

3.0 to 6.0 percent Co binder eroded essentially at the same rate as K701, as did three others: X-614, WA-107, and WA-110, for which the compositions are not yet known.

The erosion depths measured on the Ni-cemented TiB_2 materials were considerably less than on previous compositions in this series. The reasons for the differences between the samples of current series have not been determined, and await detailed evaluation of the eroded surfaces and measurement of pertinent properties.

Of the Cr-bound $\text{Al}_2\text{O}_3/\text{B}_4\text{C}/\text{CrB}$ cermets, sample C-HM-12, which contained essentially equal proportions of Al_2O_3 and B_4C bound by 4.5 percent Cr, showed excellent promise. Only two of the CrB-Co/Fe/Ni cermets were tested since the versions containing 2 percent of Co or Fe eroded excessively under the standard test conditions. In view of the less rapid erosion of a CrB-49.5 percent Colmonoy No. 6 (Ni-13.5 Cr-4.25 Fe-4.25Si-3.00B-0.75C), specimen HM-7, the behavior of the lower binder content CrB cermets is surprising, and will be further discussed after structural and property determinations.

A commercial sintered diamond material, Stratapax 2538, was not measurably eroded under the standard test conditions; however, slight smoothing of the initially rough surface was visible at low magnification after the test. The developmental diamond-Si/SiC cermets have the potential for being produced in larger sizes and in shapes not possible with Stratapax. In the first series, A-F, the specimens with a high volume fraction of diamond eroded consistently slower than the low volume fraction versions, and of these the version with the smallest diamond particulate size (F) eroded slowest. The second series of these materials, G-J, were all high volume fraction, small diamond particle size varieties. Although accurate measurement of the depth of erosion on this latter series was difficult because of the inherent surface roughness, some trend to reduced erosion with reduced diamond particle size was suggested, all samples exhibiting erosion depths similar to that of K701.

The modified Nitinol materials produced the results shown in Table 3. These alloys showed considerably more erosion resistance in

this test than other metallics examined in previous programs (for example, 304 stainless steel was severely eroded in 5 minutes). Since the test conditions are exceptionally severe, the Nitinols will be re-tested under the lower velocity conditions to be adopted for future metallic candidate materials.

For all the specimens tested, examination of the erosion craters by scanning electron microscopy is in progress. In addition, measurements of hardness and fracture toughness are being made on selected materials.

Task II. Characterization of the Erosion Behavior of New Materials

The objective of this task is to investigate the mechanisms by which specific classes of advanced ceramics are degraded by erosive coal-derived slurries. Recent erosion damage studies, employing ceramic target materials, have established that the target response is influenced by the physical characteristics of the impacting particles (size, shape, hardness and elastic properties) and the variables of impingement such as velocity and angle. Careful control of these variables in the slurry jet impingement test should facilitate the evaluation of the microstructural response of the target materials. Initial efforts in this task were, therefore, concentrated on developing an artificial slurry with well defined erodent characteristics.

Energy-dispersive X-ray analysis (EDAX) of the undissolved solids separated from the coal slurries indicated a variety of compositions, but a preferential concentration of Si was noted in the majority of the particles. SiO_2 was, therefore, chosen as a suitable substitute erodent. A mean particle size comparable to the mean size of the insoluble particles in coal-derived slurries and a narrow size distribution about the mean were desired for the SiO_2 powder. A commercially available SiO_2 powder, fused silica grade GP 71 obtained from Harbison-Walker Refractories, was examined for this purpose. This is a 99.5 percent pure, amorphous grade powder, with Al_2O_3 as the major contaminant. The chemical and physical properties of this powder are given in Table 4.

TABLE 4. CHARACTERIZATION OF GP 71 FUSED SILICA POWDER

Composition, Percent	
SiO_2	99.5
Al_2O_3	0.2
Fe_2O_3	0.05
Na_2O	0.004
K_2O	0.004
Mean particle size, microns	7.0
Surface area, m^2/gm	1.377

The particle size distribution, determined by the centrifugal sedimentation technique (ASTM Standard Test Method C678-75), is shown in Figure 1.

FIGURE 1. PARTICLE SIZE DISTRIBUTION OF AS-RECEIVED HARBISON-WALKER'S GP 71 FUSED SILICA POWDER

The particle size ranges from 4 to 24 microns with a mean size of 7 microns. Figure 2 shows the particle shapes in the mean-size range. Particles are generally angular with sharp edges. Submicron particles appear to adhere to the larger particles. These were apparently not detected in the size-distribution analysis.

FIGURE 2. SCANNING ELECTRON MICROGRAPH OF FUSED SILICA POWDER, GRADE CP 71, OBTAINED FROM HARBISON-WALKER REFRACTORIES

The Harbison-Walker fused silica powder appears to be a candidate for the substitute erodent. The size range is well within the range of the insoluble particles in coal-derived slurries. A direct comparison of the two size distributions will be made after analyzing the size distribution of the silica powder by the laser particle size analysis technique. This latter technique was used in establishing the size distributions of the insoluble solids in the coal-derived slurries.

Following the selection of the erodent and the preparation of the artificial slurry, controlled jet impingement tests will be conducted on well characterized target materials. Materials tentatively selected for this study are hot-pressed, sintered and CVD forms of SiC, hot-pressed and CVD forms of B₄C, CVD form of TiB₂ and the reference material - Co-Cr bonded WC. Attempts will be made to understand the vast differences in the erosion responses of the same generic material

fabricated by different processes; for example, hot-pressed and CVD for forms of SiC. Short duration erosion tests will be conducted in an attempt to isolate individual particle damage sites. Examination of single-particle damage sites have been very valuable in providing information on the microstructural response in erosive wear. Finally, selected target materials will be evaluated more extensively in terms of their erosive wear kinetics, and dependence of the wear rates on the angle and velocity of the slurry jet.

Task III. Approaches to the Development of New Materials

Laser surface processing of hardfacing alloys is being considered as a means of modifying the surface microstructures to improve erosion resistance. The first experiments have concerned skin melting of three Stellite alloys to achieve grain refinement and thereby increase surface hardness. Subsequent work will seek to use material additions, along with the surface melting process, to further enhance erosive wear performance. These added components may participate either as alloying constituents or as separate hard-phase particles.

Figure 3 sketches the processing configuration for the initial surface-melting experiments. The BCL high power continuous wave CO₂ laser was employed. Laser output was shaped to a square cross section using overlap integration optics. The beam size was approximately 3 x 3 mm at the workpiece, and delivered power varied from 2 to 5 kilowatts.

Test specimens were placed on a graphite block which was translated under the laser beam at constant speeds of 1 - 10 cm/s. The interaction region was bathed in argon provided by a shielding nozzle. In some cases, the test pieces were preheated in a tube furnace at temperatures of 250° - 670°C (482 - 1184° F).

Specimens of Stellite 1 and Stellite 12 were made by sectioning a 2.5 cm-wide weld bead of each material. The specimen dimensions were ~ 25 x 10 x 5 mm (thick). The top surfaces were coated with flat black paint to increase laser absorption. Coupons of Stellite 6B alloy, some

FIGURE 3. PROCESS SCHEMATIC FOR LASER SURFACE MELTING OF STELLITE COUPONS

20 x 20 mm, were prepared from 1.5 mm-thick sheet stock. These coupons were given a mild grit-blasting treatment to create a matte surface finish.

(1) Stellite 1 - Smooth uniform melts were obtained in single passes. Cracking was present in all cases. At the highest preheat temperature investigated, 670 C, cracking was limited to three widely-spaced transverse cracks spanning the entire melt width.

(2) Stellite 12 - Uniform melts about 3 mm wide and 0.3 mm deep were produced as shown in Figure 4. A preheat temperature of 670 C was employed. No cracking occurred on these specimens. The melt zone exhibited a refined dendritic solidification microstructure. A direct comparison of the fusion zone microstructure and original grain size can be made from Figure 5, yielding an order of magnitude refinement in the laser-melted area. The grain size difference may be significant from the point of view of coal-slurry erosion. Note that the original

FIGURE 4. FUSION ZONE CROSS SECTION FOR SINGLE MELT PASS ON STELLITE 12 SPECIMEN
(a) 25X, (b) 250X (MORE HEAVILY ETCHED)

SUBSTRATE

LASER MELT ZONE

Fig. 5 Comparison of Fusion Zone Microstructure (right) with Original Substrate Microstructure (left)

grain size is larger than the average erosive particle size, while the laser-melted microstructure is considerably finer than the erosive particles.

Microhardness measurements in the laser-processed area averaged 710 KHN versus 522 KHN for the original material. This increase in hardness can be attributed at least partially to the refined microstructure. However, the presence of different carbide species in the processed region must also be considered. Two distinct carbide phases were detected in the original microstructure, but were not evident in optical micrographs of the laser-processed cross sections up to 1200X magnification.

(3) Stellite 6B - Smooth and thin melts were produced on these coupons at the higher powers and faster scan rates in the ranges previously reported. No specimen preheat was required, although in some melt passes there was evidence of localized interdendritic separation. Extended melt layers were produced by multiple laser passes with about 50 percent overlap from pass to pass.

A cross section taken perpendicular to the scan direction (Figure 6) revealed a thin dendritic surface layer of nearly uniform depth. There were no obvious heat-affected zone microstructural changes although a thin partial melt zone was detected. Overlapping melt passes produced no apparent differences in structure from single passes. In fact, the overlap zones are not even distinguishable in the cross section micrographs.

Figure 7 shows a high magnification view of a region in Figure 6. The dendritic grain size was comparable to that in the laser-melted Stellite 12. The layer thickness averaged 60 microns, which is extremely thin for a 10 cm/s scan rate. Hardnesses for this specimen were 600 KHN for the laser-melt region and 450 KHN in the original material. The percentage increase in hardness for Stellite 6 was the same as that for Stellite 12.

FIGURE 6. OVERLAPPING LASER MELT TRACKS ON STELLITE 6B SPECIMEN - FIELD OF VIEW EQUALS ABOUT TWO OVERLAP WIDTHS

FIGURE 7. LASER MELTED STELLITE 6B SPECIMEN CROSS SECTION AT HIGH MAGNIFICATION SHOWING REFINED DENDRITIC SOLIDIFICATION STRUCTURE

249-250

PART III — MATERIALS FOR COAL GASIFICATION

BOMA-4.1.1 — WEAR-RESISTANT MATERIALS FOR
COAL CONVERSION AND UTILIZATION

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INTRODUCTION

The purpose of this program is to evaluate the wear-resistance of valve materials and materials processing methods for improved wear in coal conversion and utilization components. This research is organized into four tasks: erosion testing of valve materials at several particle velocities and impingement angles, support to Morgantown Energy Technology Center (METC) valve development program, liaison and consultant to DOE contractors on materials for wear resistance, and testing of laser-processed valve seats in coal ash.

RESULTS FROM PRIOR QUARTER

Erosion Studies

Erosion studies at four particle velocities and six particle impingement angles were made on Stellite 6B, 316 stainless steel, and K-701 cemented tungsten carbide. These data will be published along with those for other valve materials in an erosion data bank.

Ball-Valve Tests

A 10,000 cycle test of HC-250 white cast iron ball and seats was completed in coal ash. Excessive scoring of the ball was noted, but no galling occurred. The valve seats were not damaged.

Laser Processed Valve Seats

A thermal-spray WC/Ni alloy coating, METCO¹ 36C, was tested on ball-valve seats in the ALRC ball-valve tester. The 12-mil coatings were fused to the two seats, one by flame and one by laser. After 10,000 open-close cycles in 450° F coal-ash, the ball (316-stainless steel coated with flame-fused METCO 19E) and seats were found to be in excellent condition. No galling was noted, and only very small abrasion scratches were seen. The laser-fused seat showed slightly less wear than the flame-fused seat.

Attempts to laser-fuse a METCO 19E coating on a ball-valve seat failed due to the use of excessive laser power density. Proper power setting and laser beam travel velocity has been determined for fusing the coating, and another attempt will be made.

¹ Specific brand names are used for identification and description only, and do not imply endorsement by the Bureau of Mines.

DISCUSSION OF CURRENT ACTIVITIES

Erosion Testing

Solid-particle erosion tests on valve materials have been completed on Stellite 6B, type 316 stainless steel, type 440-C stainless steel, HC-250 white cast iron, and K-701 and K-801 cemented tungsten carbides. The data, showing effects of particle velocity and impingement angle on wear, will be completed and tabulated in the next progress report, and a Topical Report on the erosion wear data will be prepared.

Laser Processed Valve Coatings

Laser-fused coatings of wear-resistant alloys were studied in FY 1980 for potential use as ball-valve seats. As a result of these studies, two coatings, METCO 19E Cr-Ni-B alloy and METCO 36C Ni-WC alloy,

were selected for application to ball-valve seats. During FY 1981, these two coatings have been applied to friction-wear specimens and 6-inch ball-valve seats for further study.

A. Friction and Rubbing Wear Study

A Falex-6 friction and wear machine was used to compare coefficients of friction and rubbing wear on lasered and non-lasered METCO 19E and 36C coatings on type 316 stainless steel thrust-washer samples. The thrust-washers were first flame-sprayed with about 12 mils of coating, then fused to densify and bond the coating.

For each coating composition, one pair of non-lasered (torch-fused) thrust washers was mated together for testing, as was one lasered pair. Laser-fusing was done on a 1.2 KW continuous wave CO₂ laser with a beam spot diameter of 0.1 inch and a beam velocity of 20 inches per minute. Before the thrust-washer specimens were tested, they were machine ground flat and smooth. Coefficient of friction and rubbing wear tests were conducted on the Falex-6 machine using a 100 pound axial load and a rotational speed of 120 cycles per minute for 3,000 cycles. Results of these tests, shown in Table 1, indicate very little difference in the wear or friction behavior of laser-processed METCO coatings and those fused by a conventional method.

TABLE 1. - Friction and Wear Behavior of METCO Coatings

Coating	Total wt. loss, grams in 3,000 cycles	Coefficient of friction
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METCO 19E	0.0179	0.723
METCO 19E, Lasered	0.0205	0.702
METCO 36C	0.0233	0.745
METCO 36C, Lasered	0.0223	0.766

B. Ball-Valve Seats With Lasered Coatings

The first attempt at laser-fusing a 0.012-inch thick coating of METCO 19E alloy on a 316 stainless steel ball-valve seat for a 6-inch ball-valve was not entirely successful. Insufficient power density to melt the coating into the substrate, and rapid cooling of the solidified coating are thought to have caused the poor bonding and cracked surface. These cracks appear to extend completely through the coating. Another attempt to laser fuse a METCO 19E coating on a ball-valve seat was successful. The seat has been ground and will be tested in hot coal ash soon. The laser-fusing setup is shown in Figure 1, and the as-lasered seat is shown in Figures 2 and 3.

Two ball-valve seats that were coated with 12 mils of METCO 36C were prepared for testing in the ALRC ball-valve test facility. The coating on one seat was laser-fused with a beam power of 1,200 watts and a spot diameter of 0.1 inch traveling at 18 inches per minute. Seven overlapping melt-passes were required to cover the entire seat surface. A second seat was heated by oxygen-acetylene flame to fuse the coating, a conventional method that sometimes causes warping on the part. The laser-fused valve seat is shown in Figure 4. Some porosity in the coating surface can be seen, but the cause of this porosity is not known.

The coatings on the two METCO 36C seats were machine ground prior to testing, and the two seats then mated against a ball with flame-fused METCO 19E coating. After 5,000 and 10,000 open-close cycles in the valve tester with 450° F coal ash, the ball valve was disassembled and the ball and seats visually examined and weighed. Prior to this test series, the METCO 19E coated ball had been run 10,000 cycles in another test with no weight loss or significant damage. Also, no weight losses were found on either the ball or the two seats after 5,000 cycles in coal ash. After 10,000 cycles, the METCO 19E ball coating and the lasered METCO 36C seat coating lost two grams. Although the visual inspection of the ball and seats after the test, and the very small weight losses indicate good wear resistance of the METCO coatings, the torque measured on the ball-stem was high, indicating probable high friction between METCO 36C and METCO 19E.

Fig. 1. Laser-fusing setup for processing ball valve seats.

Fig. 2. Ball-valve scat with laser-fused METCO 19E coating.

Fig. 3. Laser-fused METCO 193 coating on ball-valve seat; close view of as-lasered coating.

Fig. 4. Laser-fused METCO 36C coating on ball-valve seat.

BOMT-4.2.4 — GASEOUS CORROSION RESISTANCE OF REFRACTORIES
FOR COAL GASIFIERS

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INTRODUCTION

Coal gasification processes encompass a host of challenging materials problems. Although the technology and materials of construction of viable coal gasification complexes are available now, new areas of need to improve materials selection and reliability continue to arise. The objectives in this research program are to address some specific areas of refractory materials problems that have developed.

CO Disintegration

Results obtained from DOE-sponsored studies at Virginia Polytechnic Institute and State University indicate that carbon monoxide in typical coal gasifier atmospheres may have the potential to rapidly disintegrate iron-containing refractory lining materials under static conditions. An objective of this program is to substantiate this study of CO disintegration by evaluating results of exposure tests of refractories to high-pressure gasification atmospheres under dynamic conditions. Effects of iron, alkali, and stainless steel fiber reinforcement on refractory degradation in these conditions are included in the study.

CoGas Gasifier Refractories Screening Tests

Another objective in this research is to evaluate candidate refractory liner materials for the ICGG-CoGas coal gasifier. Exposure tests will be conducted in steam and CO/H₂O environments at 1,000° C and 105 psi. The refractory specimens to be exposed will be supplied by Dravo Corporation, design engineers for the gas demonstration plant. Characterization tests will include bulk density, apparent porosity, dimensional change, modulus of rupture and abrasion resistance.

Alkali Attack on Coal Gasifier Refractories

Refractory failure due to attack by alkalis which had been transported in the vapor phase to the refractory face occurred after 125 hr of operation at the slagging fixed-bed gasifier at Grand Forks Energy Technology Center. This gasifier processes lignite that has ash containing approximately 5 pct Na₂O. A thick buildup of condensed Na₂O in the devolatilization section of the gasifier was associated with the refractory failure. An additional objective of this program is to evaluate refractory liner materials for their resistance to Na₂O attack under conditions similar to those prevailing in the Grand Forks Gasifier.

RESULTS FROM PRIOR QUARTERS

CO Disintegration

In prior quarters, this program has concentrated on the gaseous corrosion of refractories in high-and low-Btu coal gasification atmospheres at lining hot-face temperatures of 730°-1,100° C and

pressures of 400-1,000 psi. At the temperatures encountered at the lining hot-face, steam appears to be the most aggressive gaseous component of the gasifier atmosphere. Calcium aluminate-bonded fireclay refractory concretes, in general, show significant improvements in strength as a result of exposure to steam or mixtures containing steam. Calcium aluminate-bonded high alumina refractory concretes, on the other hand, show a loss in strength in these environments. Refractory degradation associated with CO disintegration was not observed in the dynamic gasifier atmospheres containing appreciable carbon monoxide (18 pct) at the temperatures tested.

More recently, short-term (58 hours) exposures of refractories to lower temperature (500° C) CO-containing environments, characteristic of interior portions of the lining between the hot-face and metal shell, were conducted on dense, high and low alumina concretes. Visual inspection indicated that, with the exception of those containing stainless steel fiber reinforcement, these environments had little effect on the refractory concretes.

CoGas Gasifier Screening Tests

Results of screening tests of candidate dense alumina refractories for applications in the highly erosive zones of the ICGG-CoGas Gasifier also followed previous trends. Abrasion resistance and cold-crushing strengths of the fireclay castables showed significant improvements following exposures to steam and CO/steam mixtures at 1,000° C and 105 psi pressure. Little difference in results of the CO/H₂O = 3.5 and CO/H₂O = 7.0 exposure tests was noted. One high alumina concrete and one fireclay castable showed significantly better abrasion resistance

following exposure to environments in which $\text{CO}/\text{H}_2\text{O} = 7.0$ when compared to results of the $\text{CO}/\text{H}_2\text{O} = 3.5$ exposure test.

CoGas gasifier screening tests were concluded with exposures of 20 commercial refractories to the previously described conditions. The alumina refractories tested in this series included dense and insulating concretes, chemically-bonded plastics, and fired brick.

Following the exposures, most of the intermediate alumina dense concretes showed statistically significant improvements in flexural strength whereas two of the high alumina dense concretes showed significant strength decreases. All refractories registered significant reductions in apparent porosities following the steam exposure, whereas little change in porosities occurred following exposure to the $\text{CO}/\text{H}_2\text{O}$ mixture. Dimensional changes ranged from a shrinkage of 1.65 pct in an intermediate alumina insulating concrete exposed to steam to an expansion of 0.65 pct in a dense fireclay castable exposed to the $\text{CO}/\text{H}_2\text{O}$ mixture.

It appears from screening test results that lower alumina refractories perform as well or better than the higher alumina refractories in these test conditions and that commercial refractories are available to withstand the attack of high-velocity particles and gaseous species expected in the refractory lining hot-face zones of the ICGG-CoGas gasification demonstration plant.

Alkali Attack on Coal Gasifier Refractories

A mullite refractory cracked and spalled after 125 hours exposure to the gaseous atmosphere in the fixed-bed slagging gasifier at Grand Forks Energy Technology Center (GFETC). Hot-face temperature in this zone was about $1,000^\circ\text{C}$, and the pressure of the process was about 360

psi. The refractory failure analysis concluded that the transport of sodium from the high alkali lignite coal during processing caused formation of β -alumina and carnegieite and subsequent volume expansion (at least 30 pct) of the lining material.

A test simulating conditions prevailing in this zone of the GFETC gasifier has been established in which crystals of NaOH are packed into holes drilled in refractory test specimens and the refractories are subsequently subjected to a flowing high-Btu gas mixture* at 1,000° C and 360 psig for the test duration time. Following the exposure test, specimens are inspected for volume expansion, cracking, and mineralogical changes.

DISCUSSION OF CURRENT ACTIVITIES

CO Disintegration

In the investigation of refractory disintegration caused by carbon monoxide attack, a series of lightweight (insulating) and dense alumina concretes was exposed to a simulated high-Btu gasifier atmosphere* for 1,000 hours. Test temperature and pressure of the dynamic atmosphere were maintained at 500° C and 1,000 psig, respectively. During the exposure, the ratio of steam to dry test gas measured in the sample container gas exit line was lower than the ratio in the test gas fed to the sample container. Gas analyses also confirmed that the CO to CO₂ ratio in the exiting gas (0.5) was much lower than in the feed gas (1.5). When the sample container was opened at the completion of the

* High-btu feed gas composition (mole pct): 40 H₂O, 25 H₂, 18 CO, 12 CO₂, 5 CH₄

1,000 hour exposure, large deposits of carbon were found in the sample container, confirming carbon dioxide formation by the reaction:

Visual inspection of the exposed specimens, using ANSI/ASTM C-288 (Disintegration of Refractories in an Atmosphere of Carbon Monoxide) guidelines, revealed that almost all the refractories were affected by carbon monoxide in the gasifier atmosphere. A summary, including the refractories tested and results of the C-288 inspection, is given in table 1. Typical examples of the refractory deterioration observed are shown in figures 1 and 2. The presence of metallic iron caused increased damage in the 90 pct Al_2O_3 dense concrete (figure 3). This damage was very similar to damage caused by the addition of stainless steel reinforcement fibers to 50 pct Al_2O_3 dense concrete in a previously reported 58-hour simulated gasifier exposure test.

The changes in compressive strength and abrasion resistance of the refractories exposed to the gasifier environment at 500° C shown in table 2 are characteristic of results obtained following similar exposures conducted at 730°-1,100° C, when compared to air-fired specimens. These data may be misleading. To evaluate the extent of carbon monoxide in the gasifier environment, data are needed on refractories exposed to similar gaseous conditions without the presence of carbon monoxide.

Qualitatively, the refractory popouts and cracking, in addition to the accelerated damage occurring in the metallic iron-containing concrete exposed to a dynamic gasifier atmosphere at 500° C indicate refractory attack similar to that observed in static conditions at VPI and SU. However, it should be noted that the atmosphere used in this

Fig. 1. Lightweight alumina refractory concretes following 1,000-hour exposure to flowing high-Btu gas at 1,000 psig, 500°C. Circles indicate some of the surface popouts and cracks. .

Fig. 2. Dense alumina concretes following 1,000-hour exposure to flowing high-Btu gas at 1,000 psig, 500°C.

Fig. 3. Dense high alumina concrete containing 0.1 pct metallic iron following 1,000-hour exposure to flowing high-Btu gas at 1,000 psig, 500°C.

test did not contain NH_3 or H_2S , gases which are often present in a coal gasifier. To adequately assess the phenomenon of CO disintegration of refractories in coal gasifier environments, effects of these gaseous impurities need to be addressed.

TABLE 1. - Summary of visual inspection of refractory concretes after 1,000 hour exposure to simulated atmosphere*, 1,000 psig, 500° C

No.	Refractory concrete sample (pct Al_2O_3)	Post exposure refractory condition (ASTM C-288)
1	Lightweight (40)	Affected - small surface popouts and cracks
2	Lightweight (55)	Affected - small surface popouts
3	Lightweight (95)	Unaffected
4	Lightweight (40), rust added	Affected - small surface popouts
5	Lightweight (55), rust added	Affected - small surface popouts
6	Lightweight (95), rust added	Unaffected
7	Dense (50)	Affected - large surface popouts (1/4-inch) Many C spots
8	Dense (90),	Affected - small surface popouts
9	Dense (90), 0.1 pct Fe added	Destructive conditions - can be broken by hand pressure

* Test gas composition (mole pct): 18 CO, 40 H_2O , 25 H_2 , 12 CO_2 , 5 CH_4

TABLE 2. - Abrasion resistance and strength data on refractories heated to 500° C for 1,000 hours in air or steam-containing high-Btu gas atmosphere

Refractory concrete sample ID	Abrasion resistance, vol. refractory lost, cc		Cold-crushing strength, psi	
	Air, atm pressure	Gas, 1,000 psig	Air, atm pressure	Gas, 1,000 psig
DENSE:				
50 pct Al ₂ O ₃	1.09	1.34	6,970	↔ 9,283
90 pct Al ₂ O ₃	1.30	↔ 4.42	5,510	↔ 2,306
90 pct Al ₂ O ₃ + 0.1 pct Fe	1.26	↔ 16.36	5,781	↔ 1,120
INSULATING:				
40 pct Al ₂ O ₃	NA	NA	1,090	↔ 1,521
55 pct Al ₂ O ₃	NA	NA	1,260	↔ 1,688
95 pct Al ₂ O ₃	NA	NA	547	↔ 360
40 pct Al ₂ O ₃ + rust	NA	NA	814	↔ 1,582
55 pct Al ₂ O ₃ + rust	NA	NA	1,069	1,195
95 pct Al ₂ O ₃ + rust	NA	NA	534	418

↔ Denotes difference significant at 99 pct level of confidence (Student's t-test).

Alkali Attack on Coal Gasifier Refractories

After establishing the exposure mode best simulating the GFETC gasifier environment, a 100-hour test of the refractories presented in table 3 was conducted. When the test was interrupted for specimen inspection after 50 hours exposure time, the magnesia-alumina spinel (X13233) had failed catastrophically and was removed from further testing. Holes in the other specimens were refilled with NaOH, and the exposure test was continued for an additional 50 hours.

Post-exposure inspection of the remaining refractories revealed that, with the exception of a fused-cast chrome-spinel (MONOFRAX E), all the specimens suffered volume expansion, cracking or spalling. X-ray diffraction analyses revealed that either carnegieite, β -alumina or gibbsite, or a combination of these minerals had formed in the alumina-bearing refractories in this test series. (Refractory failure analysis determined that the volume expansion associated with the formation of carnegieite and β -alumina in the mullite refractory in the GFETC gasifier was also the cause of that refractory failure.)

The fused-cast chrome-spinel refractory (MONOFRAX E) was the only test specimen exhibiting no visual or mineralogical changes due to the 100-hour exposure test.

Additional testing of refractories in atmospheres simulating the devolatilization section of a fixed-bed slagging gasifier included the 12 commercial refractories listed in table 4. Again, refractories were exposed for 100 hours to a high-Btu gas atmosphere at 1,000° C temperature and 360 psig pressure; the test was interrupted after 50

TABLE 3. - Refractories exposed to GFETC gasifier conditions*

Refractory test material	Classification
LAVALOX B-135	Alumina-chrome ram mix, phosphate-bonded
X13233	Fused-cast magnesia-alumina spinel
MONOFRAX E	Fused-cast chrome-spinel
MONOFRAX K-3	Fused-cast alumina-chrome
50 pct Al_2O_3 castable	Fireclay castable
VALLE 623	Alumina-zircon ram mix
MULFRAX W	Rebonded fused-grain mullite
CORHART 317	Fused-cast magnesia spinel
90 pct Al_2O_3 castable	High alumina castable
UNICHROME	Fused-cast alumina-zirconia-chrome
SR-99	High alumina brick
RUBY	Alumina-chrome brick

* High-Btu gas (40 H_2O , 25 H_2 , 18 CO , 12 CO_2 , 5 CH_4), 1,000° C, 360 psig, 50-100 hour.

TABLE 4. - Refractories exposed to GFETC gasifier conditions

Refractory test material	Classification
MONOFRAX E	Fused-cast chrome-spinel
BISON	Super-duty fireclay brick
CORAL BP	High alumina brick, phosphate-bonded (burned)
MULFRAX W	Rebonded fused-grain mullite
HW 1-77	Super-duty fireclay brick
KX-99	Super-duty fireclay brick
KOACRETE D	Fireclay castable
VARNON BF	Super-duty fireclay brick
F 264	Magnesia ram mix, chromate-bonded
MAGNEL	Burned spinel-bonded periclase brick
GUNTAPITE 382	Magnesia ram mix, chromate-bonded
HW 23-75	Fireclay ram mix, phosphate-bonded

hours exposure for inspection, removal of damaged samples, and to refill holes with NaOH crystals.

As shown in figure 4, all three magnesia refractories (F-264, MAGNEL, GUNTAPITE 382) were severely damaged following 50 hours exposure and were removed from further testing. The mullite refractory (MULFRAX W) and the fireclay castable (HW 23-75) were beginning to crack, but were exposed for an additional 50 hours.

Following 100 hours of exposure, the four super-duty fireclay brick (BISON, HW 1-77, KX-99, and VARNON B-F) showed no signs of volume expansion or cracking, as shown in figure 5. With the exception of a trace amount of carnegieite formation in the BISON, X-ray analyses of these refractories indicated no mineralogical changes. Both exposed fireclay monoliths, KAOCRETE D and HW 23-75, indicated that some conversion of mullite to carnegieite had occurred. As in the previous test, the fused-cast chrome-spinel (MONOFRAX E) appeared unaffected by the exposure and no changes in mineralogy were detected.

Results of the screening tests of refractories for application in the gasification zone of the Grand Forks slagging gasifier indicate that a fused-cast chrome spinel and super-duty fireclay brick refractories exhibit superior resistance to sodium attack under these test conditions.

Fig. 4. Refractories exposed to 50-hour simulated GFETC gasifier conditions: 1000°C, 360 psig. The holes in the specimens were filled with NaOH crystals prior to exposure.

Fig. 5. Refractories exposed to 100-hour simulated GFETC gasifier conditions: 1000°C, 360 psig. The holes were refilled with NaOH crystals after the first 50 hours of exposure.
 *Exposed 150 hours to GFETC gasifier conditions.

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ANL-4.2.7(A,B) AND ANL-4.3.7 -- DEVELOPMENT AND APPLICATION OF NON-
DESTRUCTIVE TEST METHODS FOR COAL CONVERSION
AND UTILIZATION

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SUMMARY OF CURRENT ACTIVITIES

ANL-4.2.7(A): Development of an On-line Acoustic Valve Leak Detection System

The purpose of this program is to develop a nondestructive acoustic system to detect internal leakage past valves for lock-hopper and dry ash letdown service in coal gasification plants as well as block valves for liquefaction process plants.

During this reporting period, work on the fluid-acoustic test loop has been limited because of the necessity to prepare programmatic material for FY 1982 and FY 1983 fossil energy research planning.

ANL-4.2.7(B): Development of Acoustic Emission Nondestructive Testing to Detect Fracture of Concrete Linings

The purpose of this program is to develop techniques for the application of acoustic emission sensing to detect crack formation (or other mechanical degradation) in thick refractory concrete linings of the type envisioned for use in full-scale coal gasification processes. Plant operators need information on the pre- and in-service condition of refractory linings in vessels that are closed during the initial dryout period, when damaging thermomechanical degradation often occurs. A non-destructive acoustic emission sensing system is under development which holds potential for establishing the status (number and size of large cracks and presence of large spalls) of such linings. During the current quarter, work continued on preparation of a topical report on this subject.

ANL-4.3.7: Development and Application of a Nondestructive High-Temperature Erosive Monitoring System

The purpose of this program is to develop reliable on-line, high-temperature ultrasonic systems to measure erosive wear. As the result of an active program involving laboratory and field tests over the past six years, a first-generation, field-implementable system has been developed for real-time monitoring of erosive wear. During this quarter, field evaluations continued at the Solvent Refined Coal (SRC) Plant (Ft. Lewis, WA), the Exxon Donor Solvent Plant (Baytown, TX), the Morgantown Energy Technology Center (Morgantown, WV), and the BiGas Plant (Homer City, PA). During the past year, part of this development program has been funded by industry, with Exxon and Gult Oil (SRC Plant) cost-sharing in the current field tests.

a. Field Testing

During this reporting period, the pulser-receiver and automatic data acquisition system installed at Exxon's Coal Liquefaction Plant (ECLP) were repaired at ANL. Problems have arisen at ECLP relative to high-temperature monitoring of the wall thickness of cast stainless steel elbows. In addition, pressure-coupling techniques have been shown to be very sensitive to surface preparation and perpendicularity between the waveguide and the monitored pipe.

In Late July, the ANL-designed erosion scanner at the SRC Plant (which is to close down shortly) was removed and returned to ANL. The scanner and the automatic data acquisition system have given excellent performance. A joint SRC-ANL technical paper is being prepared to summarize the results of this work.

b. Electromagnetic Acoustic Transducer (EMAT)

Experiments with a prototype shear-wave EMAT continued. A Hall-effect gaussmeter was procured and calibrated. The magnitude of the static magnetic field under the rf coil was measured using aluminum, cold-rolled steel, and stainless steel as test samples.

At an input power of 400 W, the field strength for aluminum and stainless steel was 3000 gauss; cold-rolled steel showed a field strength of 8800 gauss. Rough calculations indicate that with the above static magnetic field, the shear-wave amplitudes in aluminum and cold-rolled steel should differ very little. Measurements reported earlier confirmed these calculations. However, the power input (static and rf field) must be increased by more than an order of magnitude in stainless steel to obtain the same shear-wave amplitude.

c. Ultrasonic Velocity Measurements

The results of ultrasonic velocity measurements as a function of temperature were reported previously.¹ Determination of grain size by the ASTM overlay method was completed and the results are shown in Table I.

No shear-wave velocity data were obtained from the Haynes 188 metal owing to the large diameter of the sample, which prevented wave conversion. Because of severe scattering and attenuation, longitudinal velocity measurements in the cast stainless steel sample could only be obtained by the direct-contact method at room temperature, using a lower-frequency (2.25-MHz) transducer. Micrographs from various regions of a cross section of the parent material (a cast stainless steel pipe) revealed different grain-structure zones, as shown in Fig. 1. Close to the inner and outer surfaces, the grains are more or less round (Fig. 1a); a band of radially oriented columnar grains is observed a short distance below each surface (Fig. 1b). Beyond these bands, in the middle part of the casting, the grains are columnar but oriented in all directions (Fig. 1c). This structure accounts for the severe scattering of stress waves.

A more detailed description of the work performed during the current quarter will be published elsewhere.²

¹Materials Technology for Coal-conversion Processes: Progress Report for April-June 1981, Argonne National Laboratory Report ANL/FE-81-53.

²Materials Technology for Coal-conversion Processes: Progress Report for July-September 1981, Argonne National Laboratory Report ANL/FE-82-1 (in preparation).

Table I. Grain Size and Ultrasonic Velocity of Selected Materials

Material	Grain Size ^a	Ultrasonic Velocity at Room Temperature (m/s)	
		Longitudinal Waves	Shear waves
304 SS	4-5	5.700×10^3	3.094×10^3
304L SS	7-8	5.732×10^3	3.085×10^3
316 SS	5	5.679×10^3	2.896×10^3
316L SS	5	5.682×10^3	3.072×10^3
347 SS	6-7	5.806×10^3	3.110×10^3
410 SS	8	5.955×10^3	3.288×10^3
2½Cr-1Mo Steel	8	5.939×10^3	3.245×10^3
Cold-rolled Steel	7	5.902×10^3	3.196×10^3
Haynes Metal 188	5-7	5.872×10^3	-
Stellite 6B	5-6	6.181×10^3	3.382×10^3
Cast SS (CF-3M)			
Cast 316 SS)	3-4	5.806×10^3	-

^aDetermined by ASTM overlay method.

(a)

(b)

(c)

Fig. 1. Micrographs of Cast Stainless Steel Pipe Revealing Distinct Grain-structure Zones.
(a) Adjacent to inner surface; (b) short distance below outer surface; (c) at center of casting.

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ISU-4.2.8 — CREEP BEHAVIOR OF REFRACTORY CONCRETES

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INTRODUCTION

The three main objectives of this work have been:

1. Evaluate the long term creep strain of high-alumina refractory concretes as functions of composition and microstructure.
2. Determine the creep mechanisms of these materials as functions of the composition, stress, strain and temperature.
3. Obtain creep strain data useful for mathematical modeling.

RESULTS FROM PRIOR QUARTERS

The activation energy and stress exponent for creep of a 90% alumina concrete, a 50% alumina concrete, and CA25 high purity cement were determined under various conditions. Creep of the cured concrete or cement on first heating had low activation energies, and stress exponents less than one. Creep after the initial heating exhibited much higher stress exponents and activation energies. They were much more resistant to creep. Prefiring specimens to 1200°C for five hours produced intermediate creep parameters for specimens tested at lower temperatures. After creep strain occurred at a given stress and temperature the creep strain at lower stresses or temperatures was much less than that which occurred for those conditions the first time stress

was applied. Processes such as crystallization, transformation, sintering, stress-aided sintering and steady state creep all are involved. There is a need to sort out these mechanisms to understand the creep process.

Refractory concretes after curing contain a number of hydrated calcium aluminate or alumina hydrates. When initially heated the hydrated compounds decompose and form various calcium aluminates, and alumina. The transformations and the sintering of the fine dehydration products are known to depend upon atmosphere¹. Initial experiments conducted on the concretes exposed to the DOE standard gasifier atmosphere for 1000 hours also exhibit less creep strain than concretes not pretreated, although the activation energy for creep appears unchanged. A comparison of the creep parameters obtained thus far is shown in Table I.

Because of the complexity of the creep structural changes much more research is needed on the microstructure of the concretes and the mechanisms of deformation associated with the microstructural changes. This has been one of the important activities this quarter, to be described in the next section.

Commercial concretes are not as simple as the DOE generic formula. A recent commercial development is a family of very low cement concretes - which are being considered for gasifier applications. Previous work has included experiments varying the cement content of the DOE generic formula to determine the effect of cement content on creep.

DISCUSSION OF CURRENT ACTIVITIES

During this quarter the specimens exposed to the DOE gasifier atmosphere at IITRI were analyzed further. Some of the specimens underwent dimensional changes, especially those with lower purity cement. When heated to 1000°C the high purity CA25 cement turned to a reddish brown color. From these changes it is apparent that more research is needed on the effect of atmosphere. Creep experiments on the neat cement specimens are being conducted. X-ray diffraction, SEM and weight loss experiments are being conducted.

During the quarter the experiments on the effect of cement content on the creep of the generic 90% alumina formula was completed. A paper based on that work is almost ready for publication.

During the quarter the creep experiments on the DOE generic 50% alumina formulation was also completed. A paper based on that work should also be ready for publication during the next quarter.

During the quarter Mr. Donald J. Bray completed his M.Sc. thesis on Creep of Refractory Concretes. A copy was provided for Dr. Oral Buyukozturk of MIT for his research on computer modeling of creep strain.

A report of this research was also provided to Dr. S. Schneider, N.B.S. for the Sixth Annual Conference on Materials for Coal Conversion and Utilization.

Table I. Analysis of Creep of 50+% and 90+% Al_2O_3 Refractory Concrete and CA-25C Cement.

Material	Conditions	ΔH_c	n
90+% Al_2O_3 Concrete	Initial heat-up	41 kcal/mol	0.5
	Cycled	149 kcal/mol	3.4
	Prefired (5 hrs. 1200 C)	63 kcal/mol	---
	IITRI (1000 hrs.)	46 kcal/mol	---
	IITRI (1000 hrs.) Cycled	155 kcal/mol	---
	Prefired (1000 hrs. 982 C)	42 kcal/mol	---
50+% Al_2O_3 Concrete	Initial heat-up	44 kcal/mol	0.7
	Cycled	151 kcal/mol	3.4
	IITRI (1000 hrs.)	83 kcal/mol	---
	Prefired (1000 hrs. 982 C)	56 kcal/mol	---
CA-25C Cement	Initial heat-up	33 kcal/mol	0.8
	Cycled	170 kcal/mol	2.9

REFERENCES

1. L. Y. Sadler III, N. S. Raymon, K. H. Ivey and H. Heystek, "Effects of High Pressure, High Temperature Steam-Containing Environments on Alumina Refractory Concretes," Bull. Am. Cer. Soc. 60, 7-3-708 (1981).

MIT-4.2.8 - THERMOMECHANICAL MODEL FOR REFRACTORY
CONCRETE LINER ANCHOR INTERACTION

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INTRODUCTION

The objective of this study are: (a) to develop a numerical capability model to predict the stress and strain distribution during the heat-up and cool-down cycles of refractory concrete lined coal gasification vessels, (b) to provide a behavioral understanding of the degradation process in concrete such as cracking and creep, and (c) through parameter studies to arrive at specific guidelines for an optimal design. The model includes nonlinear stress-strain relations under multiaxial cyclic stress states and temperature-dependent creep laws. The objective is also to recommend design criteria which include optimum heating schedule, material property combinations, and anchor configurations.

The approach taken to achieve these objectives includes both experimental and analytical studies. The experimental part of this work contains biaxial monotonic and cyclic compression tests on flat square refractory concrete specimens under different temperature environments. By using the test data, practical useful relationships between stress and strain and the failure criteria will be developed. The developed material model will then be utilized to perform simulation and parametric studies for a thorough understanding of the thermomechanical behavior of coal gasification vessels.

The technical work consists of the following tasks.

1. Organization of the Test Program: The test program is planned to achieve an efficient arrangement of testing equipment and selection of appropriate parameters so as to obtain most information out of a limited number of tests.

2. **Biaxial Compression Tests:** This task includes
 - (a) Design, construction, and installation of a biaxial loading frame for applying compressive stresses to flat square specimens in two perpendicular principal directions.
 - (b) Careful preparation, casting, placing, curing, and prefiring of refractory concrete specimens such that a close simulation of real situations will be obtained.
 - (c) Uniaxial monotonic compression tests under different temperatures to obtain stress-strain curve in full range of loading in both orthogonal directions.
 - (d) Uniaxial cyclic compression tests by monitoring strain increments under different temperatures to obtain full range of cyclic stress-strain curves.
 - (e) Biaxial monotonic compression tests under different temperatures to obtain biaxial stress-strain curves for the full range of loading from zero to failure.
 - (f) Special considerations to obtain the strain-softening characteristics.
3. **Mathematical Modeling of Refractory Concrete:**

Currently available material model for refractory concrete is based on the uniaxial compression tests with the assumption that its behavior is similar to that of ordinary concrete.¹ A more refined material model is needed to be used in predictive analysis to fully understand the behavior of coal gasification vessel linings.
4. **Development of Creep Model:** Creep plays an important role in the long-term behavior of coal gasification vessels under high temperature environment. Development of an improved creep model which takes into account the effect of temperature is warranted.
5. **Development of Heat Transfer Model:** Predictions obtained from previous analyses^{1,2} are not accurate since the response of the refractory materials to high temperature effects is highly dependent upon past temperature loading histories. Also, the critical condition of the vessel does not necessarily occur in the steady state. Development of a transient heat transfer model to predict

transient temperature distributions for subsequent stress analysis is required.

6. Numerical Simulation of Coal Gasification Vessel Tests: Due to the complex behavior of concrete and the liner anchor interaction, an accurate thermomechanical analysis is necessary to understand the behavior. Three-dimensional nonlinear finite element method together with the heat transfer model is utilized for the idealization of the structure and the response prediction.
7. Parameter Studies: The relative importance of each controlling parameter, such as the constitutive models, the material properties, anchor geometries, and heating rate, is assessed for economical and efficient design of the vessel structure.
8. Design Recommendations: Interpretation of the above parameter studies is made to provide specific guidelines for optimum design.

RESULTS FROM PREVIOUS QUARTERS

Experimental and analytical accomplishments from prior quarters are summarized below.

Experimental Work

During the last reporting period, details of the testing equipment, testing procedures, and the test results are presented. Results include mainly the stress-strain curves up to failure for 90% Al_2O_3 dense refractory concrete at room temperature, 1000°F, 1500°F, 2000°F and Litecast insulating refractory concrete at room temperature, 500°F, 1000°F, and 1500°F. At each temperature, proportional plane loading at four stress ratios (0., 0.153, 0.484, 1.0) are tested. Failure envelope plotted on biaxial plane shows significant biaxiality effect.

Analytical Work

General forms of the constitutive relations for refractory concrete were developed. Two types of material models were derived. The first one

pertains to the class of hypoelastic material but specifically with orthotropic formulation. In view of the inherent shortcomings of the orthotropic model, an alternative model with the combination of plastic and fracturing behavior was also developed for comparison.

A creep model for the ERDA 90 refractory concrete based on thermorheologically simple material behavior was developed using the tests performed at Iowa State University. Refinement of the model and extension to Litecast material are necessary.

DISCUSSION OF CURRENT ACTIVITIES

Development of Thermal Conductivity Model

Previous stress analyses for coal gasification vessels^{1,2} were based on steady-state temperature distributions. Predictions thus obtained cannot be expected to be accurate, since the response of the refractory materials to high temperature effects is highly path dependent. Knowing only the steady-state temperature distributions is not sufficient to accurately characterize the material behavior. Also, the critical condition of the vessel does not necessarily occur in the steady state.

In this quarter, a predictive model for transient heat flow through layered wall is developed. The model incorporates a practical effective conductivity concept for predicting thermal conductivity of refractory materials under operating conditions. A finite difference solution scheme is used for the one-dimensional parabolic differential equation.

Extensive verification of the program was made by comparing with analytical solutions, other numerical solutions, and experimental measurements. To show the application of the model to the coal gasification vessel, the predicted temperature histories across the vessel wall of Babcock and Wilcox (B&W) lining tests³ were treated as input for the three-dimensional finite element stress analysis program ARC.⁴ The results show good correlation with measurement.

Existing literature related to the field of effective conductivity of heterogeneous media and heat transfer through composite walls is voluminous. Herein, some representative ones only are indicated. The recent

work at Battelle Columbus Laboratories^{5,6,7} has provided an excellent review on the heat flow phenomenon. In this work an effective conductivity model has been developed which takes into account heat conduction in porous media, gas conduction, convection, and radiation through pores, and the effect of anchors, cracks, and gaps on the thermal conductivity. A computer program CONBEC was also developed which is capable of predicting steady-state heat flow and temperature distributions through multilayered gasifier vessel walls. Other works on numerical solution of transient heat transfer through composite media are those reported by Chung and Yeh^{8,9,10} on slabs, Thurston et al.¹¹ on box-girder bridge sections, and Tauchert¹² on pressure vessels.

The approach adopted in the present study is, first, to develop a simple, practical, effective conductivity model. A finite difference solution procedure with Crank-Nicholson time-marching scheme is then developed for the analysis of transient heat transfer through composite walls. Temperature-dependent material properties and boundary conditions are incorporated in the solution. The developed program is then verified in three stages:

- (1) by comparing the results with those from analytical solution for a particular case where material properties are independent of temperature;
- (2) by comparing with CONBEC program⁷ for steady-state temperature distributions;
- (3) by comparing with experimental measurement by B&W³ for their lining tests.

Finally, extensive parameter studies are performed and applications of the program indicated.

The first problem in the heat transfer analysis of porous media is to develop a temperature-dependent (equivalent) thermal conductivity model for the materials under the process environment. The thermal conductivity, in general, is different from those obtained from laboratory tests, mainly because either the gases in the process are different from those in the tests, or because materials may degrade (cracking, gap, etc.) during the process cycles. A predictive model which is able to estimate the thermal conductivity during the process from the provided laboratory test data is required.

The area of modeling heat flow through heterogeneous media is very broad and diverse. For example, in the modeling of heat flow through refractory concrete lining of the coal gasification vessel, one has to consider heat conduction through porous media, gas convection and radiation through pores, heat transfer in cracks and gaps, influence of metal anchors, moisture migration effect and influence of pressure, etc. An exhaustive treatment of all these effects is not intended in this paper. Instead, a simple effective conductivity model considering only the most important factors is developed in the following.

Consider a porous material of which the pores are filled with gas. The solid phase has a conductivity $k_s(T)$ and the gas has a conductivity $k_a(T)$; both are functions of temperature T . For concrete-type materials, the size and shape of pores are random. When the size and volume fraction of the pores are small, statistically, the overall effect can be approximated by randomly distributed small spheres with the same volume fraction. For this case, Maxwell¹³ derived from potential theory an equation for effective conductivity:

$$k = \frac{2k_s + k_a - 2V_a (k_s - k_a)}{2k_s + k_a + V_a (k_s - k_a)} k_s, \quad (1)$$

where k is the effective conductivity of the equivalent homogeneous media and V_a is the pore volume fraction. When the volume fraction is not small, the fields surrounding the pores begin to "interact." Severe mathematical difficulties arise. To deal with this situation one is required to fix the position of all pores; moreover, their position should be such that simple symmetry exists. Lord Rayleigh¹⁴ treated the case for the cubical array of spheres where the field is perpendicular to a side of a cube. The result, with the correction by Runge¹⁵ (cf. 5, 16), is given by

$$k = \left(1 - \frac{3 V_a}{\frac{2k_s + k_a}{k_s - k_a} + V_a - 0.525 \frac{k_s - k_a}{\frac{4}{3} k_s + k_a} V_a^{10/3}} \right) k_s \quad (2)$$

A variety of other models has been proposed in the past, e.g., analytical solution for pores with other shapes or other arrangements,^{14,17} approximate solutions,¹⁹ empirical equations, and statistical solutions.^{20,21,22}

Extensive surveys can be found in Refs. 5, 16, 22, 23, 24, 25. Several useful results are noteworthy. Eucken²⁶ generalized Maxwell's equation to multidispersed phases in a continuous media

$$k = \frac{1 - \sum_{i=1}^m 2 V_i \frac{k_s - k_i}{2k_s + k_i}}{1 - \sum_{i=1}^m V_i \frac{k_s - k_i}{2k_s + k_i}} k_s, \quad (3)$$

where there are m different dispersed phases and V_i , k_i are the volume fraction and conductivity of each dispersed phase. Fricke¹⁷ first introduced a generalized shape factor x derived from ellipsoid pores. Eq. 1 becomes

$$k = \frac{xk_s + k_a - xV_a (k_s - k_a)}{xk_s + k_a + V_a (k_s - k_a)} k_s \quad (4)$$

and accordingly, the numbers 2 in Eq. 3 can be substituted by x_i , the generalized shape factor of each phase. The shape factor x , in general, depends on the shape of the ellipsoid and the ratio of k_a to k_s .

In the CONBEC program, by applying results of Bruggeman,¹⁹ a mixture model was derived for effective thermal conductivity. The effective thermal conductivity with m continuous phases is the solution of the m th degree polynomial

$$\sum_{i=1}^m V_i (x_i + 1) \frac{k_i - k}{k_i + x_i k} = 0. \quad (5)$$

The equation applies to cases where all phases are continuous. When all the x_i s are equal to 2, it was shown that a unique positive root exists.

To show the applicability of the above models, consider typical process environment and materials in coal gasification. Thermal conductivities of coal gases and one refractory concrete are shown in Figure 1. It is seen that hydrogen has the highest conductivity among the gases. Crowley^{27,28} reported that for most insulating refractory concrete when the air or vapor in the pores is replaced with a process gas containing 60 to 80% hydrogen, the thermal conductivity usually doubles. This would easily result in more cracking in the lining and flow of hot gases directly to the

Figure 1 Thermal conductivities of B&W LI 2300 insulating refractory concrete and coal gasification process gases (Ref. 31)

shell. Comparison of the models is shown in Fig. 2 for $k_a/k_s = 0.1, 5$ and for V_a up to 0.5. The differences between the models, when one considers the uncertainty in measuring material properties, are insignificant for all engineering purposes. The simplest Maxwell's equation (Eq. 1) will be used in the following analysis. Eq. (2) is always close to Maxwell's. The mixture equation, although suggested in the CONBEC program, is not well founded theoretically. The determination of shape factor x requires professional guess rather than rigorous derivation; the solution of the polynomial is tedious and its root in some cases may not be unique. The tests by Austin²⁹ support the choice of Maxwell's equation.

Considering a porous material, we have the laboratory measured thermal conductivity $k_c(T)$. The pores are filled with gas (usually air or vapor) having thermal conductivity $k_a(T)$. The volume fraction of pores is V_a . When the material is exposed with process gas with conductivity $k_g(T)$, the effective conductivity can be found by applying Maxwell's equation,

$$k(T) = \frac{1 + 2 V_a r}{1 - V_a r} k_s(T) \quad (6)$$

$$r = \frac{k_g(T) - k_s(T)}{k_g(T) + 2k_s(T)} \quad (6a)$$

$$k_s(T) = P(T) + \sqrt{P^2(T) + Q(T)} \quad (6b)$$

$$P(T) = [(k_c(T) - k_a(T)/2) - V_a(k_a(T) - k_c(T)/2)]/2(1 - V_a) \quad (6c)$$

$$Q(T) = k_a(T)k_c(T)/2 \quad (6d)$$

where $k_s(T)$ may be called the pseudo-solid phase conductivity. The process gas environment usually comprises more than one gas. The thermal conductivity of the gas mixture has to be obtained first. The method of Brokaw for binary mixture or the approximation of Burgoyne and Weinberg for multicomponent mixtures as described in Refs. 30, 31 is suggested.

Figure 2 Comparison of effective conductivity models

The above procedure to estimate thermal conductivity in the process from test data automatically takes into account the important effect of gas radiation through pores. Gas convection and pressure have been shown to have little effect on effective conductivity (see Refs. 5, 7); they are neglected in the present study. To accommodate for the effect of cracks and gaps, it is recognized that cracks or gaps are usually either parallel or perpendicular to the heat flow direction. For example, in coal gasification, due to the axisymmetry of the vessels the principal axes of stresses remain in the axial, radial and hoop direction. Consequently gaps and radial cracks are parallel to the heat flow. Assume that one can estimate the volume fraction of gaps and radial cracks V_r and of hoop and axial cracks V_h . By applying Eucken's equation (Eq. 3) and Fricke's shape factor (Eq. 7), Eq. 6 is modified to be

$$k(T) = \frac{1 + 2V_a r + V_h \frac{k_h(T) - k_s(T)}{k_s(T)}}{1 - V_a r - V_r \frac{k_r(T) - k_s(T)}{k_r(T)}} k_s(T) \quad (7)$$

where $k_h(T)$ and $k_r(T)$ are thermal conductivities of the gas in V_h and V_r . They are obtained by adding radiation components to $k_g(T)$. Loeb's equation¹² as modified in use in Ref. 28 suffices for the purpose.

$$k_h(T) = k_g(T) + k_l(T) \quad (8)$$

or $k_r(T)$

$$k_l(T) = \text{radiation contribution to conductivity} \\ = 4\gamma de\sigma T^3 \quad (8a)$$

where γ = geometrical factor (=1 for present cases)

d = maximum dimension of cracks in direction of heat flow

e = emissivity of radiating surface

σ = Stefan-Boltzmann constant

T = average absolute temperature at the crack.

Note that for Eq. 7 in applying shape factor x , $x = 0$ is assumed for gaps and radial cracks (series model) and $x = \infty$ is assumed for hoop and axial cracks (parallel model).

Numerical Solution of the Heat Transfer Problem

The physical system considered is a long hollow cylinder with composite wall heated from centerline uniformly along the axis. The temperature distribution can thus be considered to vary in the radial direction only. The governing equation is

$$\frac{1}{r} \frac{\partial}{\partial r} (kr \frac{\partial T}{\partial r}) = \rho c \frac{\partial T}{\partial t} \quad (9)$$

where r = radial distance from centerline
 $k = k(T, r)$ = effective thermal conductivity
 ρ = density
 $c = c(T, r)$ = specific heat
 $T = T(r, t)$ = temperature.

Actual heat flow through coal gasification vessel walls is certainly more complex than the assumed one-dimensional flow. The gasification process is usually restricted on certain height of the vessel, so that the temperature distribution is not uniform along its whole height. The heat flow is also complicated by the presence of anchors and other asymmetrical structural components that result in locally three-dimensional heat flow. But it will be shown later that the effect of anchors on temperature distribution is insignificant. The solution is considered to be a good approximation to the most heated section along the height of the vessel.

The boundary conditions, whether subjected to prescribed temperature, natural or forced convection, or radiation can be written in terms of the heat transfer coefficient h ,

$$\left. \frac{\partial T}{\partial r} \right|_{r=r_b} = \pm h(T_b - T_w) \quad (10)$$

where $T_w = T|_{r=r_b}$ = wall temperature
 $T_b = T_b(t)$ = ambient temperature
 r_b = radial distance of boundary.

The negative sign applies when the boundary faces to the negative r direction and vice versa. For cases with prescribed temperature, take $k = \infty$. For cases with convection and radiation, h can be found from empirical formulas in standard texts or handbooks.

Finite Difference Discretization.

Figure 3 Finite difference grid

By central difference discretization in space and the Crank-Nicholson formula in time, Eq. 9 becomes

$$\frac{k_{i+\frac{1}{2}, n+\frac{1}{2}} r_{i+\frac{1}{2}} \delta_x (T_{i+\frac{1}{2}, n+1} + T_{i+\frac{1}{2}, n}) - k_{i-\frac{1}{2}, n+\frac{1}{2}} r_{i-\frac{1}{2}} \delta_x (T_{i-\frac{1}{2}, n+1} + T_{i-\frac{1}{2}, n})}{2r_i \Delta r_i} = \rho_i C_{i, n+\frac{1}{2}} \frac{T_{i, n+1} - T_{i, n}}{\Delta t_n} \quad (11)$$

$$k_{i+\frac{1}{2}, n+\frac{1}{2}} = k \left(\frac{T_{i+1, n+\frac{1}{2}} + T_{i, n+\frac{1}{2}}}{2} \right) \quad (11a)$$

$$k_{i-\frac{1}{2}, n+\frac{1}{2}} = k \left(\frac{T_{i-1, n+\frac{1}{2}} + T_{i, n+\frac{1}{2}}}{2} \right)$$

$$\delta_x(T_{i+\frac{1}{2},n}) = \frac{T_{i+1,n} - T_{i,n}}{r_{i+1} - r_i} \quad (11b)$$

$$\delta_x(T_{i-\frac{1}{2},n}) = \frac{T_{i,n} - T_{i-1,n}}{r_i - r_{i-1}}$$

$$\Delta r_i = \frac{r_{i+1} - r_{i-1}}{2} \quad (11c)$$

$$\Delta t_n = t_{n+1} - t_n \quad (11d)$$

Equation 11 is the central difference expansion of the governing equation at the half-time point $(i, n+\frac{1}{2})$; it results in second-order accuracy in both space and time. Since the physical system considered is multilayered, Eq. 11 has been made applicable for irregular grid spacings.

For each time increment Δt_n , Eq. 11 results in a system of $(m-2)$ equations for the $(m-2)$ internal nodes, where m is the total number of nodes. The two remaining equations are

$$\frac{T_{2,n} - T_{1,n}}{r_2 - r_1} = -h_1(T_{h,n} - T_{1,n}) \quad (12)$$

for interior hot face and

$$\frac{T_{m,n} - T_{m-1,n}}{r_m - r_{m-1}} = h_m(T_{a,n} - T_{m,n}) \quad (12a)$$

for exterior boundary. In Eqs. (12) (13),

h_1 = heat transfer coefficient for interior hot face

h_m = heat transfer coefficient for exterior boundary

$T_{h,n}$ = reaction hot temperature

$T_{a,n}$ = ambient temperature.

Nonlinear Solution Scheme

The discretization method used is an implicit method that involves solution of m simultaneous equations at each time increment. The system of equations is of tri-diagonal form that little effort is required to

solve. The result is unconditionally stable when material properties k and c do not vary radically with temperature. The only restriction on the size of time step is accuracy. When the time step is large, certain noise is introduced with the Crank-Nicholson method; the noise will vanish when the time step size is reduced to $2\rho c (\Delta r)^2 / \Delta t$, where the forward difference method converges.

In Eq. 11 one has to know k and c at time $n + \frac{1}{2}$ before the system of equations can be formulated. When the time step is small, one may proceed by a single forward difference to estimate the temperatures at time $n + \frac{1}{2}$,

$$T_{i,n+\frac{1}{2}} = T_{i,n} + \frac{\Delta t_n}{2} \frac{k(T_{i,n})}{\rho_i c(T_{i,n})} \left(\Delta_x^2(T_{i,n}) + \frac{1}{r_i} \delta_x(T_{i,n}) \right) \quad (13)$$

$$\Delta_x^2(T_{i,n}) = \frac{T_{i+1,n} - 2T_{i,n} + T_{i-1,n}}{(\Delta r_i)^2} \quad (13a)$$

$$\delta_x(T_{i,n}) = \frac{T_{i+1,n} - T_{i-1,n}}{2\Delta r_i} \quad (13b)$$

When the time step is large, however, the forward difference suffers from instability. The scheme used in this study is to predict the material properties at time $n + \frac{1}{2}$ from the past by direct extrapolation. When the solution is obtained at time $n+1$, the material properties at time $n + \frac{1}{2}$ is estimated again by interpolation and the equation is solved again. The procedure has been proved to be satisfactory.

Verification of the Program

A computer program has been written for the finite difference solution developed. The following sections describe the verification of the program by analytical solution.

In this section, transient heat transfer analysis through a typical coal gasification vessel wall with outer steel shell and two layers of refractory concrete lining is performed. The material properties are kept constant. Without increasing complication, the continuity of

temperatures at the interface of layers is relaxed through a heat transfer coefficient h , as defined in Eq. (16). This can be used to simulate gap problems by choosing suitable values for h . The geometry is shown in Fig. 4. The governing equation is given by

$$\frac{1}{r} \frac{\partial}{\partial r} \left(r \frac{\partial T_i(r,t)}{\partial r} \right) = \frac{1}{D_i^2} \frac{\partial T_i(r,t)}{\partial t} \quad \begin{array}{l} r_i \leq r \leq r_{i+1} \\ i = 1, 2, 3 \\ t \geq 0 \end{array} \quad (14)$$

where $D_i = k_i / \rho_i c_i$ = thermal diffusivity in the i th section.

Figure 4 Cross Section of the vessel considered in the analytical solution.

The vessel is subjected to the following external boundary and initial conditions:

$$k_1 \frac{\partial T_1(r_1, t)}{\partial r} = -h_1 [y_1(t) - T_1(r_1, t)] \quad (15)$$

$$k_3 \frac{\partial T_3(r_4, t)}{\partial r} = h_4 [y_2(t) - T_3(r_4, t)] \quad (15a)$$

$$T_i(r, 0) = V_i(r) \quad \begin{matrix} r_i \leq r \leq r_{i+1} \\ i = 1, 2, 3 \end{matrix} \quad (15b)$$

where $h_1, h_4 = h_m$ defined before

$y_1(t), y_2(t) = T_h(t), T_a(t)$ defined before.

At the internal boundaries, the following conditions are satisfied:

$$-k_i \frac{\partial T_i(r_{i+1}, t)}{\partial r} = k_{i+1} [T_i(r_{i+1}, t) - T_{i+1}(r_{i+1}, t)] \quad (16)$$

$$k_i \frac{\partial T_i(r_{i+1}, t)}{\partial r} = k_{i+1} \frac{\partial T_{i+1}(r_{i+1}, t)}{\partial r} \quad (16a)$$

for $i = 1, 2$.

The method of unique dependent variable substitution as suggested by Mulholland and Cobble³³ was used, which gives a new partial differential equation with homogeneous external boundary conditions. The solution is then obtained by series expansion and by using their orthogonality relationship. To obtain homogeneous external boundary conditions, let

$$T_i(r, t) = U_i(r, t) + \sum_{j=1}^2 L_{ij}(r) F_j(t) \quad (17)$$

$$r_i \leq r \leq r_{i+1}, \quad i = 1, 2, 3, \quad t \geq 0$$

where $F_1(t) = -y_1(t)$ and $F_2(t) = y_2(t)$ and further let

$$\frac{1}{r} \frac{\partial}{\partial r} \left(r \frac{\partial L_{ij}(r)}{\partial r} \right) = 0 \quad (18)$$

so that

$$L_{ij}(r) = A_{ij} \ln r + B_{ij} \quad (19)$$

$$r_i \leq r \leq r_{i+1}, \quad i = 1, 2, 3, \quad j = 1, 2$$

By substituting Eqs. 17 and 18 into Eq. 14, we obtain

$$\frac{D_i^2}{r} \frac{\partial}{\partial r} \left(r \frac{\partial^2 U_i(r, t)}{\partial r} \right) = \frac{\partial U_i(r, t)}{\partial t} + \sum_{j=1}^2 L_{ij}(r) \frac{dF_j(t)}{dt} \quad (20)$$

$$r_i \leq r \leq r_{i+1}, \quad i = 1, 2, 3, \quad t \geq 0$$

and initial conditions and boundary conditions can be written accordingly. It is seen that the external boundary conditions are homogeneous for $U_i(r, t)$. The solution then proceeds by applying the boundary conditions to Eq. 19. This results in 12 equations for A_{ij} and B_{ij} which can be solved analytically by some algebra. The solutions for A_{ij} and B_{ij} are given in the Appendix.

To solve for $U_i(r, t)$, the series form is assumed:

$$U_i(r, t) = \sum_{\ell=1}^{\infty} U_{\ell}(t) X_{i\ell}(r) \quad \begin{matrix} r_i \leq r \leq r_{i+1} \\ i = 1, 2, 3 \end{matrix} \quad (21)$$

When substituted into Eq. 20, the problem reduces to an eigenvalue problem for $X_{i\ell}(r)$ and an initial value problem for $u_{\ell}(t)$. The eigenvalue problem is

$$\frac{D_i^2}{r} \frac{d}{dr} \left(r \frac{d X_{i\ell}(r)}{dr} \right) + \gamma_{\ell}^2 X_{i\ell}(r) = 0 \quad \begin{matrix} r_i \leq r \leq r_{i+1} \\ i = 1, 2, 3 \end{matrix} \quad (22)$$

where γ_{ℓ} is an eigenvalue of the problem and $X_{i\ell}(r)$ an eigenvector. The solution of Eq. 22 is

$$X_{i\ell}(r) = G_{i\ell} J_0 \left(\frac{\gamma_{\ell}}{D_i} r \right) + H_{i\ell} Y_0 \left(\frac{\gamma_{\ell}}{D_i} r \right) \quad (23)$$

where $J_0(\cdot)$ and $Y_0(\cdot)$ are zeroth order Bessel function of the first and the second kind. The eigenvalues γ_{ℓ} are obtained by inserting Eq. 23

into the boundary conditions; the result is a system of 6 linear homogeneous equations from which the constants G_{il} and H_{il} can be determined. The matrix to determine γ_m and G_{il} , H_{il} is shown in the Appendix. The solution of the eigenvalue problem certainly will involve numerical work. The functions $X_{im}(r)$ and $X_{in}(r)$, $r_i \leq r \leq r_{i+1}$, $i = 1, 2, 3$, are orthogonal in the sense that

$$\sum_{i=1}^3 \rho_i c_i \int_{r_i}^{r_{i+1}} X_{im}(r) X_{in}(r) dr = \begin{cases} \text{const.}, & m = n \\ 0 & m \neq n \end{cases} \quad (24)$$

The initial problem for $u_\ell(t)$ is given by

$$\frac{d u_\ell(t)}{dt} + \gamma_\ell^2 u_\ell(t) = - \sum_{j=1}^2 \ell_{\ell j} \frac{dF_j(t)}{dt} \quad (25)$$

where $\ell_{\ell j}$ will be defined later.

The final solution of $U_i(r, t)$ is given by

$$U_i(r, t) = \sum_{\ell=1}^{\infty} \left\{ g_\ell e^{-\gamma_\ell^2 t} - \sum_{j=1}^2 \ell_{\ell j} \frac{dF_j(t)}{dt} * e^{-\gamma_\ell^2 t} \right\} X_{i\ell}(r) \quad (26)$$

where $*$ denotes convolution and

$$g_\ell = \frac{1}{N_\ell} \sum_{i=1}^3 \rho_i c_i \int_{r_i}^{r_{i+1}} r G_i(r) X_{i\ell}(r) dr \quad (26a)$$

$$\ell_{\ell j} = \frac{1}{N_\ell} \sum_{i=1}^3 \rho_i c_i \int_{r_i}^{r_{i+1}} r L_{ij}(r) X_{i\ell}(r) dr \quad (26a)$$

$$N_\ell = \sum_{i=1}^3 \rho_i c_i \int_{r_i}^{r_{i+1}} r X_{i\ell}^2(r) dr \quad (26c)$$

$$G_i(r) = V_i(r) - \sum_{j=1}^2 L_{ij}(r) F_j(0) \quad (26d)$$

A final solution for $T_i(r, t)$ can be obtained by applying Eq. 17.

An example with material properties shown in Table I is solved by both analytical methods and the finite difference program. The hot face temperature $y_1(t)$ is initially 70°F and heats up at a rate of 100°F/hr . The ambient temperature $y_2(t) = 70^\circ\text{F} = \text{const}$. The first 18 eigenvalues obtained is shown in Table II. The results converge quickly as the number of eigenvalues increases. For the present example, the difference is hardly noticeable if one uses only the first 10 eigenvalues.

Table I

i	1	2	3	4	unit
k_i	1.1	0.25	31.42	—	Btu/(hr ft $^\circ\text{F}$)
$\rho_i c_i$	30	9.96	53.88	—	Btu/(ft 3 $^\circ\text{F}$)
h_i	∞	∞	∞	1.5	Btu/(hr ft 2 $^\circ\text{F}$)
D_i	0.191	0.158	0.764	—	ft 2 /hr
r_i	1.5	1.875	25	2.594	ft

Table 2

ℓ	γ_ℓ	ℓ	γ_ℓ
1	0.56397	10	14.32000
2	1.52430	11	15.91321
3	3.15374	12	17.50862
4	4.75566	13	19.10127
5	6.35227	14	20.69755
6	7.94690	15	22.29845
7	9.54063	16	23.91801
8	11.13390	17	26.97825
9	12.72696	18	28.60375

The finite difference solution utilizes 9 nodes across the wall thickness with a time step of 0.5 hr. The temperature profiles from the two solutions at selected times are compared in Fig. 5. The results from the difference solution, with the coarse grid used, are almost identical to the analytical solution.

SUMMARY

In this quarter, an effective conductivity model for refractory concrete lining in coal gasification vessels is developed. Numerical solution of the transient heat transfer problem based on the finite difference method is implemented in a computer program. Verification of the program is made by comparing with analytical solution in a special case where material properties are constant.

NEXT QUARTER ACTIVITIES

A constitutive relationship for refractory concretes based on an orthotropic model will be finalized and reported in the next quarter. The creep model will be refined and extended for Litecast 75-28. Further verification of the heat transfer program will be made. Application of the heat transfer program with the stress analysis program ARC, in which new constitutive relationships will be implemented, will be initiated.

Figure 5. Comparison of the Transient Finite Difference Solution to the Analytical Solution

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APPENDIX

The solution for A_{ij} and B_{ij} are

$$A_{11} = A_{12} = 1/k_1 D$$

$$A_{21} = A_{22} = 1/k_2 D$$

$$A_{31} = A_{32} = 1/k_3 D$$

$$B_{11} = - \left(\frac{1}{h_2 r_2} + \frac{1}{h_3 r_3} + \frac{1}{h_4 r_4} + \frac{\ln r_2}{k_1} + \frac{\ln(r_3/r_2)}{k_2} + \frac{\ln(r_4/r_3)}{k_3} \right) / D$$

$$B_{21} = - \left(\frac{1}{h_3 r_3} + \frac{1}{h_4 r_4} + \frac{\ln r_3}{k_2} + \frac{\ln(r_4/r_3)}{k_3} \right) / D$$

$$B_{31} = - \left(\frac{1}{h_4 r_4} + \frac{\ln r_4}{k_3} \right) / D$$

$$B_{13} = \left(\frac{1}{h_1 r_1} - \frac{\ln r_1}{k_1} \right) / D$$

$$B_{22} = \left(\frac{1}{k_1 r_1} + \frac{1}{k_2 r_2} + \frac{\ln(r_2/r_1)}{k_1} - \frac{\ln r_2}{k_2} \right) / D$$

$$B_{32} = \left(\frac{1}{h_1 r_1} + \frac{1}{h_2 r_2} + \frac{1}{h_3 r_3} + \frac{\ln(r_3/r_2)}{k_2} + \frac{\ln(r_2/r_1)}{k_1} - \frac{\ln r_3}{k_3} \right) / D$$

$$D = \frac{1}{h_1 r_1} + \frac{1}{h_2 r_2} + \frac{1}{h_3 r_3} + \frac{1}{h_4 r_4} + \frac{\ln(r_2/r_1)}{k_1} + \frac{\ln(r_3/r_2)}{k_2} + \frac{\ln(r_4/r_3)}{k_3}$$

$$\begin{bmatrix}
 -\frac{\gamma_m}{D_1} J_1\left(\frac{\gamma_m}{D_1} r_1\right) & -\frac{\gamma_m}{D_1} \gamma_1\left(\frac{\gamma_m}{D_1} r_1\right) & 0 & 0 & 0 & 0 \\
 -\frac{h_1}{k_1} J_0\left(\frac{\gamma_m}{D_1} r_1\right) & -\frac{h_1}{k_1} \gamma_0\left(\frac{\gamma_m}{D_1} r_1\right) & 0 & 0 & 0 & 0 \\
 \frac{k_1}{h_2} \frac{\gamma_m}{D_1} J_1\left(\frac{\gamma_m}{D_1} r_2\right) & \frac{k_1}{h_2} \frac{\gamma_m}{D_1} \gamma_1\left(\frac{\gamma_m}{D_1} r_2\right) & J_0\left(\frac{\gamma_m}{D_2} r_2\right) & \gamma_0\left(\frac{\gamma_m}{D_2} r_2\right) & 0 & 0 \\
 -J_0\left(\frac{\gamma_m}{D_1} r_2\right) & -\gamma_0\left(\frac{\gamma_m}{D_1} r_2\right) & 0 & 0 & 0 & 0 \\
 k_1 \frac{\gamma_m}{D_1} J_1\left(\frac{\gamma_m}{D_1} r_2\right) & k_1 \frac{\gamma_m}{D_1} \gamma_1\left(\frac{\gamma_m}{D_1} r_2\right) & -k_2 \frac{\gamma_m}{D_2} J_1\left(\frac{\gamma_m}{D_2} r_2\right) & -k_2 \frac{\gamma_m}{D_2} \gamma_1\left(\frac{\gamma_m}{D_2} r_2\right) & 0 & 0 \\
 0 & 0 & \frac{k_2}{h_3} \frac{\gamma_m}{D_2} J_1\left(\frac{\gamma_m}{D_2} r_3\right) & \frac{k_2}{h_3} \frac{\gamma_m}{D_2} \gamma_1\left(\frac{\gamma_m}{D_2} r_3\right) & J_0\left(\frac{\gamma_m}{D_3} r_3\right) & \gamma_0\left(\frac{\gamma_m}{D_3} r_3\right) \\
 0 & 0 & -J_0\left(\frac{\gamma_m}{D_2} r_3\right) & -\gamma_0\left(\frac{\gamma_m}{D_2} r_3\right) & 0 & 0 \\
 0 & 0 & k_2 \frac{\gamma_m}{D_2} J_1\left(\frac{\gamma_m}{D_2} r_3\right) & k_2 \frac{\gamma_m}{D_2} \gamma_1\left(\frac{\gamma_m}{D_2} r_3\right) & -k_3 \frac{\gamma_m}{D_3} J_1\left(\frac{\gamma_m}{D_3} r_3\right) & -k_3 \frac{\gamma_m}{D_3} \gamma_1\left(\frac{\gamma_m}{D_3} r_3\right) \\
 0 & 0 & 0 & 0 & -\frac{\gamma_m}{D_3} J_1\left(\frac{\gamma_m}{D_3} r_4\right) & -\frac{\gamma_m}{D_3} \gamma_1\left(\frac{\gamma_m}{D_3} r_4\right) \\
 & & & & +\frac{h_4}{k_3} J_0\left(\frac{\gamma_m}{D_3} r_4\right) & +\frac{h_4}{k_3} \gamma_0\left(\frac{\gamma_m}{D_3} r_4\right)
 \end{bmatrix}
 \begin{Bmatrix}
 G_{1l} \\
 H_{1l} \\
 G_{2l} \\
 H_{2l} \\
 G_{3l} \\
 H_{3l}
 \end{Bmatrix}
 = \underline{0}$$

313-314

Matrix Equation for the Eigenvalue Problem in the Analytical Solution

ANL-4.2.9 -- EVALUATION OF REFRACTORIES FOR
SLAGGING GASIFIERS

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SUMMARY OF CURRENT ACTIVITIES

The purposes of this program are to (a) determine which commercial refractories are most likely to withstand environments encountered in slagging gasification processes, (b) identify grain bond systems that hold potential for improved refractory performance, (c) establish mechanisms of degradation at refractory-slag interfaces, and (d) characterize the viscosities of a variety of coal slags in reducing atmospheres. This laboratory program examines acidic and basic slags at temperatures up to 1600°C in contact with specially fabricated as well as commercially available refractory bricks to establish the corrosion-erosion behavior of the bricks.

During the current reporting period, work continued on the fabrication and assembly of the components for the gas-fired rotating-drum dynamic-slag corrosion test furnace. It is anticipated that shakedown runs of this furnace will commence in the next quarter.

A more detailed description of the work performed during the current quarter will be published elsewhere.¹

¹Materials Technology for Coal-conversion Processes: Progress Report for July-September 1981, Argonne National Laboratory Report ANL/FE-82-1 (in preparation).

IITRI 4.2.9 — DESIGN, ENGINEERING, AND EVALUATION
OF REFRACTORY LINERS FOR SLAGGING GASIFIERS

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INTRODUCTION

The objectives of this program under Department of Energy Contract No. De-AC05-78ET13410, "Design, Engineering, and Evaluation of Refractory Liners for Slagging Gasifiers," are to design, construct, and operate a Refractory Test Facility for the evaluation of refractory liners under slagging gasifier conditions.

The program is composed of six tasks which can be grouped into three parts. The first part includes only Task A, Conceptual Liner Designs, which summarizes the state-of-the-art of the design of refractory liners for slagging coal gasifiers. The second part includes Task B, Design and Construction of Test System; Task C, Refractory Liner Tests; and Task D, Liner Design Evaluation. The test system constructed in Task B is used to test refractories under simulated slagging gasifier operating conditions. In the third part, the results of Task A will be combined and modified with the results of Tasks B, C, and D to prepare refractory liner design models and develop recommended design practices, which can then be incorporated into a handbook for gasifier designers and refractory suppliers.

RESULTS FROM PRIOR QUARTERS

The contract for this program was awarded at the end of September 1978. Work was started on 1 October 1978, on Tasks A, B, and E. Task A, Conceptual Liner Design, has been completed; Task B, Test System Design and Construction, is in progress. Task C, Liner Tests, and Task D, Liner Design Evaluation, will begin upon completion of Task B. Task E, Liner

Model Development, is now inactive after an initial data compilation and theoretical model development effort. It will be activated as soon as data are available from Task D. Task F, Liner Design Handbook, was active along with Task A since the report of both tasks will use the same format. It is now inactive until the completion of Tasks D and E. The principal efforts on this program during all prior quarters have been to design and construct the test facility, Task B.

PROJECT STATUS

Construction of the test unit was essentially completed by July 31, 1981. A meeting of DOE, Oak Ridge National Laboratory, and IITRI personnel was held on July 31, 1981, to review the project and make plans for shakedown runs of the test vessel prior to making any test runs. Phase I of this work would consist of what remained of the subsystem tie-in and check-out from the construction work. This would consist of the following work as required to shake the entire system down.

- a) rework control circuits
- b) put in a remote start/stop switch for slag tap torch
- c) install piping and valves for gas analyzer
- d) install gas detector
- e) wire optical pyrometer
- f) wire generator gas detector
- g) extend thermocouple wiring to data logger
- h) install data logger operating cable.

Phase II was the integrated check-out and shakedown and familiarization of unit operation tasks. We have formulated a progressive check-out and shakedown approach which moves from a low probability of any system failure to an increased probability of a failure. This approach will also provide the operating team with time to familiarize themselves with the test unit operation.

The test plan is divided into tasks and was established as follows:

- Task 1) Run cold at atmospheric conditions (compressors, pumps, generator, and slag injection and removal system all run at same time to check entire system and familiarize ourselves with operation).
- Task 2) Run cold, but at a pressure of 100 psi.
- Task 3) Assemble auxiliary nozzle and equipment for low temperature heat-up of unit and dry out refractories.
- Task 4) Run through entire system with all burner systems to be fired at atmospheric conditions.
- Task 5) Go through complete start-up procedure with Davy McKee and burner people present.

This was considered to be a minimum shakedown schedule.

Task I was completed without any observable problems. While setting up for Task 2, cold pressure run, water was found in the test and slag tap vessels. Upon investigation, it was determined that the quick-disconnect hose fittings were leaking. This necessitated taking the test vessel apart, removing the top two sections, to fix the leaks and determine the cause of this problem. The leaks were caused by lowering the pressure differential between the high-pressure water liners and the pressure in the test vessel. When the differential is less than approximately 60 psi, the gaskets in the fitting deform causing leaks to occur. The manufacturing specifications indicated that at our operating conditions where 100 psi pressure differential was possible, no leakage should be anticipated. A pressure simulator was set up and several different types of gaskets were evaluated as well as using adhesives to maintain a seal. None of these fixes worked, and it was decided to never pressurize the vessel without first starting high-pressure water through the water hoses.

During the tests for checking the slag system, it was found that the Moyno pump had been damaged due to clogging during the original subsystem check-out test and system pressure could not be maintained. The Moyno pump barrel was replaced.

During further tests of the slag system, we found several valve assemblies that were put in wrong. The damaged valves had to be replaced and installed in the system.

We also determined that several of the automatic water control valves were not working properly. These were checked out and reset.

After these problems were attended to, a 24-hour high pressure cold run was successfully completed on September 10. Following this test, time was spent in correcting minor external piping leaks and correcting water flow specifications for maintaining cooling conditions in the test vessel.

It is anticipated that the shakedown tasks will be completed in the next quarter, and plans are being made for making the first refractory test run in the first quarter of calendar year 1982.

PNST-4.2.9 - REFRACTORIES IN SLAGGING GASIFIERS

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INTRODUCTION

This research is concerned with the high-temperature chemistry of oxide phases of importance as refractory materials in slagging coal gasifiers. Special attention is directed toward chromium oxide-containing phases (mainly Al_2O_3 - Cr_2O_3 solid solutions and various spinel phases involving Cr_2O_3 as a component). In order to provide the data base needed for an understanding of such reactions, equilibrium relations are being determined for a number of oxide combinations of simplified coal-ash slags, mainly in the system $\text{CaO-FeO-Al}_2\text{O}_3\text{-SiO}_2$, with refractory oxide components (MgO , Al_2O_3 , Cr_2O_3). Because iron and chromium occur in several valence states in oxide phases, the equilibrium relations in systems involving these elements are dependent on the oxygen potential under which the reactions take place. The present studies, therefore, are carried out under carefully controlled atmospheric conditions. Most of the runs are made under the relatively reducing conditions of a $\text{CO}_2\text{-H}_2$ atmosphere of ratio $\text{CO}_2/\text{H}_2 = 10/1$, while additional runs are being made in CO_2 or air.

RESULTS FROM PRIOR QUARTERS

Research done in previous quarters has established three important characteristics governing the behavior of chromium oxide in silicate systems of importance in slagging coal gasifiers, viz.: 1) The low solubility of Cr^{3+} in silicate melts, 2) The dissimilarity in crystal-chemical behavior of Cr^{3+} and Al^{3+} in solid phases of complex structures,

and 3) The drastic increase in solubility of chromium in silicate melts and attendant drastic lowering of liquidus and solidus temperatures in such systems at very low oxygen potentials. Phase relations in a number of systems formed by various combinations of the most abundant oxide components in typical coal ash and of the most promising refractory components have been studied and summarized in previous reports. Particular emphasis during recent quarters has been placed on additions of various amounts of iron oxide to selected parts of the system $\text{CaO-Al}_2\text{O}_3\text{-Cr}_2\text{O}_3\text{-SiO}_2$, and on the effects of oxygen potentials on such equilibria. Specifically, phase relations in the systems $\text{Ca}_2\text{Al}_2\text{SiO}_7\text{-CaAl}_2\text{Si}_2\text{O}_8\text{-FeAl}_2\text{O}_4$, $\text{Ca}_2\text{Al}_2\text{SiO}_7\text{-CaAl}_2\text{Si}_2\text{O}_8\text{-FeCr}_2\text{O}_4$ were determined in $\text{CO}_2\text{-H}_2$ atmospheres of ratios $\text{CO}_2/\text{H}_2 = 10/1$, and the effects of increasing the oxygen potentials to those of CO_2 and air atmospheres have been studied in the systems $\text{CaAl}_2\text{Si}_2\text{O}_8\text{-FeAl}_2\text{O}_4$ and $\text{Ca}_2\text{Al}_2\text{SiO}_7\text{-FeAl}_2\text{O}_4$. The present activities, as summarized in the subsequent section, represents a continuation and extension of these previous studies.

DISCUSSION OF CURRENT ACTIVITIES

One major effort during the past quarter was the delineation of phase relations in FeO-containing silicate systems of particular importance in slagging coal gasifiers, and comparisons of the role of this component with that of MgO in analogous MgO-containing systems. Examples of preliminary results obtained are shown in Figs. 1 and 2, illustrating liquidus phase relations in the systems $\text{CaAl}_2\text{Si}_2\text{O}_8\text{-FeO-Al}_2\text{O}_3$ and $\text{CaAl}_2\text{Si}_2\text{O}_8\text{-FeO-Cr}_2\text{O}_3$, respectively. As was the case in the analogous MgO-containing systems, anorthite occupies a relatively small primary phase area near the $\text{CaAl}_2\text{Si}_2\text{O}_8$ apex of the triangle, with the sesquioxide and spinel areas occupying the major parts of the composition triangle. The primary phase area of wüstite is much smaller in both systems than the periclase primary phase fields in the analogous MgO-containing systems. A second area of work was the determination of phase relations in systems of the type $\text{Ca}_2\text{Al}_2\text{SiO}_7\text{-FeO-X}_2\text{O}_3$, where X is either Al or Cr. Preliminary results showing the main features of the

phase relations are illustrated in Figs. 3 and 4. In the former system ($\text{Ca}_2\text{Al}_2\text{SiO}_7\text{-FeO-Al}_2\text{O}_3$) two calcium aluminate phases ($\text{CaAl}_{12}\text{O}_{19}$ and CaAl_2O_7) are present as stable phases on the liquidus surface, in addition to wüstite, spinel and sesquioxide (corundum). The spinel phase dominates the diagram whereas the sesquioxide phase occupies a relatively small area.

The approximate phase diagram for the system $\text{Ca}_2\text{Al}_2\text{SiO}_7\text{-MgO-Cr}_2\text{O}_3$, as illustrated in Fig. 4, shows the existence of wüstite, spinel and sesquioxide, in addition to gehlenite, on the liquidus surface. The diagram is similar to that observed for the system $\text{CaAl}_2\text{Si}_2\text{O}_8\text{-FeO-Cr}_2\text{O}_3$ except for the presence of gehlenite instead of anorthite as the primary silicate phase. In all cases, however, the most significant feature of the phase relations is the relatively low Cr_2O_3 content of the liquid phase in the silicate liquids at moderate temperatures ($\leq 1500^\circ\text{C}$), and the extreme partitioning of chromium into the sesquioxide and spinel phases.

Fig. 1 Approximate phase relations in the system $\text{CaAl}_2\text{Si}_2\text{O}_8\text{-FeO-Al}_2\text{O}_3$ in a $\text{CO}_2\text{-H}_2$ atmosphere of CO_2/H_2 ratio = 10:1. Abbreviations used have the following meanings: W = wüstite; SP = spinel ($\text{FeAl}_2\text{O}_4\text{-Fe}_3\text{O}_4$ solid solutions); SES = sesquioxide (corundum); AN = anorthite ($\text{CaAl}_2\text{Si}_2\text{O}_8$).

Fig. 2 Approximate phase relations in the system $\text{CaAl}_2\text{Si}_2\text{O}_8\text{-FeO-Cr}_2\text{O}_3$ in a $\text{CO}_2\text{-H}_2$ atmosphere of CO_2/H_2 ratio = 10:1. Abbreviations used have the following meanings: W = wüstite; SP = spinel ($\text{FeCr}_2\text{O}_4\text{-FeAl}_2\text{O}_4\text{-Fe}_3\text{O}_4$ solid solutions); SES = sesquioxide ($\text{Al}_2\text{O}_3\text{-Cr}_2\text{O}_3$ solid solutions); AN = anorthite ($\text{CaAl}_2\text{Si}_2\text{O}_8$).

Fig. 3 Approximate phase relations in the system $\text{Ca}_2\text{Al}_2\text{SiO}_7\text{-FeO-Al}_2\text{O}_3$ in a $\text{CO}_2\text{-H}_2$ atmosphere of CO_2/H_2 ratio = 10:1. Abbreviations used have the following meanings: PER = periclase; SP = spinel (MgAl_2O_4); SES = sesquioxide (corundum); CA = $\text{CaO}\cdot 6\text{Al}_2\text{O}_3$ ($\text{CaAl}_{12}\text{O}_{19}$); $\text{CA}_2 = \text{CaO}\cdot 2\text{Al}_2\text{O}_3$ (CaAl_4O_7); GEH = gehlenite ($\text{Ca}_2\text{Al}_2\text{SiO}_7$).

Fig. 4 Approximate phase relations in the system $\text{Ca}_2\text{Al}_2\text{SiO}_7\text{-FeO-Cr}_2\text{O}_3$ in a $\text{CO}_2\text{-H}_2$ atmosphere of CO_2/H_2 ratio = 10:1. Abbreviations used have the following meanings: PER = periclase; SP = spinel ($\text{MgAl}_2\text{O}_4\text{-MgCr}_2\text{O}_4$ solid solutions); SES = sesquioxide ($\text{Al}_2\text{O}_3\text{-Cr}_2\text{O}_3$ solid solutions); GEH = gehlenite ($\text{Ca}_2\text{Al}_2\text{SiO}_7$).

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VPI-4.2.9 — INVESTIGATION OF CARBON MONOXIDE DISINTEGRATION
OF REFRACTORIES IN COAL GASIFIERS

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INTRODUCTION

Refractories used in coal gasification vessels and piping are exposed to mixtures of hydrogen, steam, hydrogen sulfide, methane, carbon monoxide, and other gases over a wide range of temperatures and pressures. Many refractories are known to deteriorate when exposed for long periods of time to CO-containing atmospheres; especially if the temperature is below about 1300°F and if the refractory contains any iron containing compounds. It is, therefore, important to develop experience and engineering data on these refractories under simulated coal gasifying conditions and to attempt to determine the effect of each identifiable variable on the CO resistance of the refractories used in coal gasifiers.

OBJECTIVES

The objectives of this investigation are to determine 1) whether or not CO disintegration is likely to occur in the refractories used in coal gasifiers, and 2) to identify the conditions under which CO disintegration of the refractories can be expected to be a serious problem. It is also a goal of this investigation to develop information that will assist in the identification of refractory deterioration or failure that is caused by CO disintegration.

The objectives of this study include:

- 1) A systematic study of the effects of pressure, temperature, gaseous mixtures, and iron impurities in coal gasifier refractories.

- 2) Conduct an intensive study of the CO disintegration at high pressures (500-1000 psi) of fiber reinforced refractories in order to
 - a) evaluate the deterioration that can be expected from the various iron based fibers, and b) attempt to develop a fiber system that effectively resists disintegration.
- 3) Conduct a series of tests on insulating castables at high pressures to evaluate the extent of CO damage that can be expected in these back-up lining components.
- 4) Investigate the effect of alkali as an accelerator of CO disintegration.
- 5) Investigate the effect of early stages of CO disintegration of refractories on the abrasion (and possibly creep) resistance of the refractories.
- 6) Conduct a series of field examinations of gasifier linings to look for CO disintegration or related effects.
- 7) Prepare a comprehensive final report at the conclusion of this study that summarizes in reasonable detail the present knowledge of CO disintegration of gasifier refractories.

RESULTS FROM PRIOR QUARTERS

Based on the test data collected to date, the following observations have been made:

- 1) CO disintegration of high alumina castables is not likely to be a problem in coal gasifiers at atmospheric pressure. All gases added to CO tended to retard refractory disintegration compared with samples exposed to pure CO. A 1000 hr exposure to a simulated coal gasifier atmosphere did not produce any visual damage or strength loss in either castable examined.
- 2) CO disintegration of high alumina castables is a potential cause of refractory failure at high pressures. The time required for refractory deterioration rapidly decreases as pressure increases. The effect of even small amounts of iron impurities greatly accelerates the rate of disintegration.

- 3) In coal gasifiers, CO disintegration is likely to affect the abrasion resistance of the refractories long before any of the typical signs of CO disintegration are noted. The 50% Al_2O_3 castable is more susceptible to abrasion than the 90% Al_2O_3 castable.
- 4) The temperature range over which CO disintegration is active appears to be shifted to higher temperatures at high pressures.
- 5) Preliminary results suggest that alkali compounds, particularly K_2CO_3 , accelerate CO disintegration of high alumina castables.
- 6) The 50% Al_2O_3 castable disintegrates faster than the 90% Al_2O_3 castable, possibly a result of the higher iron content of the calcined kaolin used in the 50% Al_2O_3 refractory.
- 7) Stainless steel (AISI 316 and 446) reinforced castables possess very poor resistance to CO disintegration both at atmospheric and 1000 psi.

DISCUSSION OF CURRENT RESULTS

1. Initiation of Disintegration

The effect of H_2S additions to CO atmospheres were further investigated during this reporting period. The significant results are summarized in Table 1. It has been noted that the strength and abrasion resistance of a prefired, unexposed sample varies from batch to batch, so for each gas composition samples from the same casting batch were tested with and without exposure to the test gas. The "strength ratio" and "abrasion ratio" reported in Table 1 are the ratios of the measurements of exposed samples divided by the measurements of unexposed samples.

Last quarter it was found that H_2S reduced CO disintegration in undoped samples. By using shorter exposure times, it was found that the onset of damage in iron doped samples begins at about 3 hours and in undoped samples at 20-25 hours. The first degradation to appear is the formation of deep cracks. The degradation proceeds by further cracking of the center of each sample (see Figures 1 and 2). The strength of castables exposed to the $\text{CO}/\text{H}_2\text{S}$ mixture was affected before the abrasion resistance as the outer surface remain hard during the early stages of deep cracking.

TABLE 1. RESULTS OF EXPOSING A 90% Al_2O_3 CASTABLE
TO CO-CONTAINING ATMOSPHERES (1000 PSI/500°C)

<u>Dopant</u>	<u>Gas (Vol.%)</u>	<u>Time (Hours)</u>	<u>Compressive Strength (Psi±Std.Dev.)</u>	<u>Strength¹ Ratio</u>	<u>Abrasion Resist. (cm³ Removed)</u>	<u>Abrasion² Ratio</u>
-	99.2CO/.8H ₂ S	25	4929± 40	0.315	0.96	1.16
0.1 Fe	99.2CO/.8H ₂ S	25	COMPLETELY DISINTEGRATED			
-	99.2CO/.8H ₂ S	10	4302± 130	1.051	0.23	0.371
0.1 Fe	99.2CO/.8H ₂ S	10	COMPLETELY DISINTEGRATED			
-	99.2CO/.8H ₂ S	3	5516± 339	1.012	0.67	1.093
0.1 Fe	99.2CO/.8H ₂ S	3	5061± 349	0.945	0.544	1.209
0.1 Fe ³	CO	3	COMPLETELY DISINTEGRATED			
0.1 Fe ₂ O ₃ ³	CO	3	3097±2490	0.720 ⁴	0.181	0.5 ⁴

Notes:

1. $\text{Strength Ratio} = \frac{\text{Strength of Exposed Samples}^1}{\text{Strength of Prefired Samples}}$

2. $\text{Abrasion Ratio} = \frac{\text{Abrasion Resistance of Exposed Samples}}{\text{Abrasion Resistance of Prefired Samples}}$

3. Samples prefired at 500°C

4. Ratios calculated using samples prefired at 500°C instead of 1100°C.

2. Effect of Prefiring Castables

In service, a refractory castable lining will not be prefired across its entire thickness. In order to simulate this condition, samples doped with 0.1% Fe and 0.1% Fe_2O_3 were tested without prefiring at 1100°C. Instead, samples were heated in the test cell to 500°C and half were removed to compare exposed and unexposed strengths. The results indicate that prefiring may reduce the effectiveness of iron compounds as catalysts. Unprefired samples doped with 0.1% Fe completely disintegrated in 3 hours and 0.1 Fe_2O_3 doped samples exhibited considerable damage. Prefired samples have been found to take considerably longer to show signs of damage. More work is needed in this area because of the similarity to actual field conditions.

Figure 1. Appearance of 90% Al_2O_3 castable after 3 hours in $\text{CO}/.8\% \text{H}_2\text{S}$ at 1000 Psi and 500°C.

Figure 2. Appearance of 90% Al₂O₃ castable after 10 hours in CO/.8% H₂S at 1000 Psi and 500°C.

3. DOE Atmosphere

A series of lightweight (insulating) and dense high alumina castables was exposed to a high BTU atmosphere for 1000 hrs at 500°C and 1000 psig. The atmosphere did not contain H₂S or NH₃. All of the castables examined showed early signs of CO disintegration such as surface popouts, cracks and carbon deposition. Details of this work appear in the DOE quarterly report submitted by the U.S. Bureau of Mines, University, Alabama.

INEL-4.3.3 — THE EFFECT OF COAL GASIFICATION ATMOSPHERES
ON BIAxIAL CREEP OF ALLOYS

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INTRODUCTION

Several processes have been proposed for production of high-Btu coal gas, but none has been developed commercially. Concern exists regarding the integrity of possible construction materials under the relatively severe process conditions anticipated. No other industrial process is sufficiently similar to alleviate these concerns. A test program was, therefore, begun under the sponsorship of the American Gas Association to evaluate the behavior of various proposed construction materials in the coal gasification environments of greatest concern. This work has continued under the sponsorship of ERDA, DOE, and the Gas Research Institute. The Metals Properties Council (MPC) has been the prime contractor and has provided technical guidance.

Exposure of candidate materials, in both laboratory-simulated environments and pilot plants, has been used to evaluate such effects as corrosion, erosion-corrosion, and the possible effects of coal gasification atmospheres (CGAs) upon selected mechanical properties. Most of the corrosion and erosion-corrosion work has been done by the Illinois Institute of Technology Research Institute (IITRI). The mechanical properties work has been conducted primarily at the Southwest Research Institute (SwRI) on nine candidate alloys for gasifier internals. Impact, uniaxial stress rupture, tensile, and some fatigue properties have been measured there.

Many potential applications of these candidate alloys involve biaxial loading. A DOE-sponsored test program was, therefore, initiated by EG&G Idaho, Inc., at the Idaho National Engineering Laboratory (INEL) to measure the biaxial stress rupture strength, life, and ductility of four candidate alloys for gasifier internals under simulated CGA conditions. The data from the tests would be used to confirm any trends observed in the uniaxial stress rupture tests, demonstrate the differences caused by biaxial loading, and produce an empirical correlation between uniaxial and biaxial rupture strengths. Fatigue testing of these four alloys in CGA is planned for the future.

RESULTS FROM PRIOR QUARTERS

Two systems were designed and built to perform the described testing: one to test tubular specimens in air at atmospheric pressure, the other to test tubular specimens in various high-pressure simulated CGAs. The input compositions of these atmospheres are shown in Table 1.

TABLE 1. SIMULATED CGA COMPOSITIONS

	<u>MPC^a</u>	<u>Bigas</u>	<u>Synthane</u>	<u>Battelle</u>
H ₂	24	15	18	48
CO	18	12	10	26
CO ₂	12	13	18	5
CH ₄	5	7	16	6
H ₂ O vapor	40	52	37	14
NH ₃	1.0	1.06	0.6	0.6
H ₂ S	0.5	0.53	0.3	0.3

a. Composition used at IITRI, SwRI, and INEL (Reference).

Target 100-h biaxial stress rupture tests were then completed on the four selected alloys (Type 310 stainless steel, Incoloy 800H, Haynes 188, and IN-657). These alloys were shown by gaseous corrosion tests at IITRI to have comparatively good corrosion resistance to a simulated CGA. The rupture behavior was first determined in air at atmospheric pressure and then comparative tests were run at 1000 psi in air, an MPC reference CGA, and three widely differing simulated gasification pilot plant atmospheres. The temperature range used was 1200-1800°F. The results of these tests are presented in Figures 1-4. Two different heats of Type 310 stainless steel were tested.

These experiments have shown that the biaxial stress rupture behavior of these alloys is affected very little, if at all, by a nominal 100-h exposure to a simulated CGA except at 1800°F. The disagreement in values observed at 1800°F was postulated to be due to fatigue arising from the gas pressure control system (discussed in current activities). At lower temperatures, the biaxial stress rupture life/strength was usually close to the mean of the values of uniaxial stress rupture life/strength from several alloy heats reported in the literature. The biaxial ductility of a few percent at tube rupture was generally unchanged by exposure to CGA.

More recently, target 500-h tests were run at 1500°F in the MPC composition atmosphere, using the high-pressure system, to determine whether longer exposure to CGA will affect stress rupture behavior. No change in stress rupture behavior was detected in these longer-term tests.

The atmospheric pressure test system (APTS) was remodeled to permit the simultaneous testing of four specimens at atmospheric pressure in a simulated CGA. The partial pressures of oxygen and sulfur are controlled to achieve this simulation. Continuous gas flow is used to prevent depletion of the various chemical species and automatic flow control gives better control of gas composition than manual control.

Figure 1. Rupture parameter of biaxially loaded Type 310 SS in various atmospheres.

Figure 2. Rupture parameter of biaxially loaded Incoloy 800H in various atmospheres.

Figure 3. Rupture parameter of biaxially loaded Haynes 188 in various atmospheres.

Figure 4. Rupture parameter of biaxially loaded IN-657 in various atmospheres.

Tests in CGA at 1800°F with goal lifetimes of 500 h were not made for two reasons: first, extrapolation of corrosion observed in 100 h tests suggested that corrosion might cause premature rupture in the longer term tests; and second, interest in, and anticipated use of, these alloys at 1800°F has decreased greatly.

DISCUSSION OF CURRENT ACTIVITIES

Duplicate specimens of all four alloys were exposed in the remodeled APTS to a simulated medium-Btu CGA (simulating MPC composition) at 1650°F with a target life of 500 h. The calculated partial pressures at 1650°F of oxygen and sulfur were:

$$P_{O_2} = 6.4 \times 10^{-17} \text{ atm and } P_{S_2} = 3.2 \times 10^{-17} \text{ atm.}$$

The results of these tests are also shown in Figures 1-4. The trend of these data is consistent with previous results at and below 1650°F. This is also true for the values of strain at rupture. This consistency indicates that tests performed in the remodeled APTS are valid and also that a nominal 500-h exposure at and below 1650°F to a simulated medium-Btu gas has no adverse effect on the creep-rupture behavior.

An extra test of IN-657 was conducted in the high pressure system in an attempt to assess whether fatigue was the correct explanation for the reduced life of all four alloys when tested in this system at 1800°F. An additional valve was added to the system which reduced the fluctuation in the 1000 psi CGA pressure from a nominal value of 40 psi to 28 psi. This change increased the rupture life to approximately that observed when the environmental pressure was constant. This data point is labeled "reduced ΔP " in Figure 4. This increase in life supports the fatigue postulate.

Exposure of these four alloys to a simulated low-Btu gas in the remodeled APTS was begun during this quarter. Biaxial stress rupture tests of duplicate specimens at 1500 and 1650°F with a target life of 500-h are planned. The oxygen and sulfur partial pressures to be used for simulating low-Btu gas are given in Table 2.

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TABLE 2. SIMULATED LOW-BTU GAS COMPOSITION

Temperature (°F)	P_{O_2} (atm)	P_{S_2} (atm)
1650	3×10^{-18}	3.7×10^{-7}
1500	1×10^{-19}	1.3×10^{-7}

ANL-4.3.4 -- CORROSION OF ALLOYS FOR COAL GASIFICATION ENVIRONMENTS

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SUMMARY OF CURRENT ACTIVITIES

The purposes of this program are to (1) experimentally evaluate the high-temperature corrosion behavior of iron- and nickel-base alloys in gas environments with a wide range of oxygen, sulfur, and carbon potentials, (2) develop mechanical-property data on several Fe-Cr-Ni alloys exposed to complex gas mixtures typical of coal-conversion process environments, (3) develop corrosion information in the temperature range 400 to 750°C in simulated low- and intermediate-Btu gasification atmospheres using internally cooled specimens of selected commercial materials, (4) develop an approach that is based upon available thermodynamic and kinetic information for evaluating possible corrosion problems in coal-conversion systems, and (5) monitor technical aspects of gasification-materials programs funded by DOE/FE.

The corrosion behavior of structural metallic materials in complex multicomponent gas environments is of considerable interest for their effective utilization in coal-conversion schemes. Such research in low-Btu coal-gasification atmospheres has been insignificant relative to testing done in high-Btu gasification atmospheres; therefore, several low-Btu process environments have recently been characterized to define appropriate experimental conditions.¹ With lower oxygen potentials at sulfur potentials similar to those of high-Btu processes, low-Btu environments significantly degrade the structural integrity of commercial high-chromium stainless steels. Viable alternative alloys or coatings should develop continuous protective surface scales upon exposure to these aggressive environments. For this purpose, several nickel-base superalloys, solid-solution cobalt- and nickel-base alloys, and oxide dispersion-strengthened (ODS) alloys were exposed to simulated low-Btu

gasifier environments at 1144K for 120 h.² The alloys selected were C-276, 188, In-792, C-101, MA60000E, and MA956. The scale morphologies and compositions and the extent of subscale attack were analyzed as functions of exposure temperature, gas chemistry, and alloy composition. Thermogravimetric analyses were performed on the most resistant alloys in selected gas mixtures to determine scaling rates. Mechanistic regimes that depict various combinations of temperature and oxidation potential were established, based on morphological analyses of the corrosion products, and the best alloy type for each regime was identified from thermogravimetric results. A reaction model is presented for the corrosion of several alloy types in low-Btu simulation atmospheres.

The results, in general, showed that the alloys did not develop a continuous oxide scale at p_{O_2} values between the Cr_3S_4 - Cr_2O_3 thermodynamic boundary and the threshold kinetic boundary. This is primarily due to competition from sulfidation in the initial stages, coupled with slow nucleation and growth of chromium oxide to form a continuous external oxide scale. The presence of an oxide dispersion or high Al or Ti levels in the alloy increased the number of nucleation sites and enhanced growth rates; this resulted in greater oxide stability on the surface in the crucial initial stages. Thermogravimetric results revealed that pure Cr_2O_3 -formers oxidize at slow rates at p_{O_2} values greater than the kinetic threshold boundaries. However, upon crossing that boundary, alloys containing Al and Ti or an oxide dispersion are superior in terms of resistance to chromium sulfidation. At p_{O_2} values greater than the base-metal sulfidation boundary, only the ODS alloys exhibited protective scales while all the dispersion-free alloys showed accelerated rates of corrosion at 1144 K.

A more detailed description of the work performed during the current quarter will be published elsewhere.³

¹T. C. Tiearney, Jr. and K. Natesan, Journal of Materials for Energy Systems, Vol. 1, 1980, pp. 13-29.

²T. C. Tiearney, Jr. and K. Natesan, Sulfidation-Oxidation of Advanced Metallic Materials in Simulated Low-Btu Coal-Gasifier Environments, to be published in Oxidation of Metals.

³Materials Technology for Coal-conversion Processes: Progress Report for July-September 1981, Argonne National Laboratory Report ANL/FE-82-1 (in preparation).

INEL-4.3.4 — CORROSION OF ALLOYS FOR TAR SANDS SYSTEMS
AND IN SITU GASIFICATION

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INTRODUCTION

In Situ Gasification

In situ coal gasification has the potential for making available significant quantities of fossil energy resources which are currently either uneconomical or technologically unfeasible to mine, thus significantly increasing this country's recoverable energy reserves. In addition it provides the means of overcoming numerous health, safety and environmental obstacles to conventional mining, although it contains several potential obstacles of its own, such as ground subsidence and/or water table pollution.

Several potential materials problems are associated with in situ gasification. These include materials used for downhole piping (injection and production wells), instrumentation wells, and production lines and associated valves and elbows. The downhole piping and instrumentation wells both face a severe environment, being in or near the combustion zone. The production line piping, valves, and elbows face a potentially severe environment of corrosive gas, high-velocity gas flow with varying particulate content, and a relatively high temperature. For example, conditions have been reported where temperatures have reached 894 K (1150°F) near the wellhead, and production line velocities approached 90 m/s (295 ft/sec).¹ The particulate has consisted of varying amounts of coal char, ash, condensed hydrocarbons, and possibly hard mineral particles from the coal seam overburden. Similar conditions have resulted in

component failures from erosion or erosion/corrosion at in situ gasification sites, and severe erosion of specimens during a materials test run by the Idaho National Engineering Laboratory (INEL) at the Lawrence Livermore Laboratory experimental site near Hoe Creek, Wyoming.² All of these problems may limit site reliability if they are not mitigated.

This program was designed to expose a series of specimens to production line conditions at available in situ test sites involving various coal types and production conditions (including both oxygen/steam and air injection) for supporting coal seam combustion. Most specimens were selected from those materials undergoing evaluation for use in aboveground gasifiers in a program directed by the Metals Properties Council. The specimens were exposed at various angles to the product gas stream to allow a determination of whether any observed material degradation occurred as a result of corrosion, erosion, or a combination of erosion/corrosion under a variety of conditions.

In Situ Tar Sands

Tar sands deposits within the continental United States provide another potential domestic energy source. Most of these deposits exist in a form which requires in situ techniques to recover the entrapped tar or bitumen. These techniques include steam injection, in situ combustion, and chemical injection. The environment seen by the various downhole components and production line piping and components is dependent upon the extraction technique employed and the chemical composition of the particular deposit.

This portion of the program was developed to expose specimens to product streams at available in situ tar sands test sites. Specimens were selected from a range of materials representative of those currently used in, or potential candidates for, similar oil field operations. Specimen configurations were selected to assess the susceptibility of the candidate materials to various corrosion mechanisms.

RESULTS FROM PRIOR QUARTERS

In Situ Gasification

Specimens have been exposed in three separate in situ gasification field experiments under this program. These include the Hoe Creek-III test conducted by the Lawrence Livermore Laboratory at Hoe Creek, Wyoming and the Hanna IV-Phase I and Hanna IV-Phase II tests conducted by the Laramie Energy Technology Center (LETC) at Hanna, Wyoming.

A report detailing the results of the Hanna-IV and Hoe Creek III materials evaluations was published in March 1981.² This completed the planned work on this portion of the Materials and Components Task (INEL-4.3.4).

The report presented the following conclusions:

- a. There was no evidence of severe pitting corrosion, intergranular attack, or carburization or decarburization.
- b. Where corrosion did occur, oxidation appeared to be the principal mode with some evidence of sulfidation.
- c. Results of the evaluation of three downhole components, exposed to a much more severe environment than the product gas line specimens, again indicated that oxidation was the principal corrosion mechanism.
- d. The specimens which were flame-sprayed with 50 Cr-50 Ni showed mixed results. Those exposed at Hanna-IV Phase I showed little or no degradation while the specimen exposed at 45° to the gas flow at Hanna-IV Phase II had its coating completely removed, possibly due to high particulate content.

- e. The Alonized 316 stainless steel specimens exposed at Hoe Creek-III experienced preferential attack beneath the outer diffusion zone.

In Situ Tar Sands

Specimens were exposed at the LETC Vernal, Utah Tar Sands test site for a period of approximately 90 days. The materials evaluated and specimen types are listed in Table 1. A report detailing the results of

TABLE 1. TAR SANDS SPECIMENS

<u>Stress Corrosion Specimens</u>		
C-Ring:	P-105	Oil Country
	N-80	Tubular Goods
	C-75	
	304L	
	2 1/4 Cr - 1 Mo	
U-Bend:	Ferralium	
	Haynes 20 Modified	
	Hastelloy G	
	Hastelloy 276	

Corrosion Specimens

Ferralium

Haynes 20 Modified

Hastelloy G

Hastelloy 276

Samples tested in both the welded and nonwelded condition

this study was published in July 1981.³ This completed the planned work on this portion of the Materials and Components Task (INEL-4.3.4). The following are the principal findings and conclusions of this evaluation.

The materials examined in this test experienced no significant general corrosion, and showed no indication of severe pitting, intergranular corrosion, stress corrosion cracking, or erosion.

The specimens were located in the specimen chambers such that a part of each was covered by a stationary oil/water emulsion while the rest was exposed to a varying composition product stream flow. The fact that there was no difference between the two portions of the non-ferritic specimens indicates that no component of the emulsion or product stream to which those specimens were exposed played a significant role in the specimen material behavior.

The 2 1/4 Cr-Mo alloy specimens experienced some minor pitting. While the pitting was not severe, it may raise a question about the long-term suitability of this alloy. Also, a lack of knowledge about the specific environment as a function of time within the system precludes characterizing the actual source of the nonuniform general corrosion observed on the ferritic steel specimens, though the corrosion appears to be minimal.

It would be desirable to perform additional testing on the ferritic steel alloys to isolate the actual components of the environment which resulted in this corrosion.

This test program indicates that the steam injection technique for in situ tar sand liquefaction, as demonstrated at the Vernal, Utah test site, poses no significant materials problems during normal or nearnormal operating conditions. These results would, however, be expected to be dependent upon the bitumen chemistry at the individual tar sands sites (principally the presence of significant amounts of sulfur and/or

chlorine) and the quantity of sand or other mineral particles released into the system in conjunction with periods of high velocity steam resulting from steam breakthrough. Other in situ recovery techniques such as combustion and chemical injection may be expected to introduce unique problems.

DISCUSSION OF CURRENT ACTIVITIES

The currently planned work on this portion of the Materials and Components Task (INEL-4.3.4: Corrosion of Alloys for Tar Sands Systems and In Situ Gasification) has been completed.

REFERENCES

1. T. C. Bartke, L. Dockter, T. E. Sterner, I. E. Virgona and L. F. Wojdac, "Status Report on the Hanna III and Hanna IV Underground Coal Gasification Experiments," Proceedings of the 4th Underground Coal Conversion Symposium, Steamboat Springs CO, July 17-20, 1978.
2. R. B. Loop and D. M. LaRue, Materials Testing at the Hanna-IV and Hoe Creek-III In Situ Coal Gasification Sites, EG&G-FM-5396, March 1981.
3. R. B. Loop, Materials Testing at the Vernal, Utah Tar Sands Liquefaction Site, EG&G-FM-5517, July 1981.

MPC-4.3.4(A) - CORROSION OF METALS AND REFRACTORIES
IN COAL GASIFICATION PILOT PLANTS

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INTRODUCTION

This study, Phase II of the MPC coal gasification materials program, consists of coupon corrosion monitoring in operating coal gasification pilot plants. The data, together with those from the Phases I and III laboratory tests, permit increased confidence in materials selection and corrosion rate prediction for coal gasification plants. The program includes metals and refractories: metals have been exposed in both high-temperature gasifier locations and in lower temperature aqueous quench system locations; refractories have been exposed only in gasifier environments.

OUTLINE OF PREVIOUS WORK

The status of the program to date is summarized in Table 2-1. Coupons have been exposed in six pilot plants, and exposures are scheduled for 1981/1982 in two more pilot plants.

Short-term Phase I laboratory testing and Phase II pilot plant gasifier corrosion monitoring have shown a number of high-temperature alloys to be suitable for gasifier applications if operating temperatures are below 1600°F. In contrast, a number of alloys, including Monel 400 and IN-600, were consistently found to have unacceptable corrosion rates (>20 mpy) and are regarded as unsuitable for gasifier internals.

Of the alloys tested, those appropriate for use in the temperature range 1600°-1800°F appear to be limited to Fe-Cr-Ni types with greater than about 25% Cr, and the higher Cr cobalt-base alloys. In contrast to

TABLE 2-1. STATUS OF PHASE II PILOT PLANT
CORROSION MONITORING, SEPTEMBER 1981

Pilot Plant	Number of Test Locations		Exposure in Progress	Number of Exposures Completed	Completion of Test Program
	Metals	Refractories			
HYGAS	11	1	-	4	Yes
CONOCO COAL	4	2	-	3	Yes
Synthane	7	1	-	2	Yes
Battelle	5	2	-	1	Yes
BI-GAS	7 + 2 ^a	1	(2nd) ^b	1	No
U-Gas	3	1	(3rd) ^c	2	No
Westinghouse	7	1	1st	0	No
Peat Gas	7	0	1st	0	No
GEGAS Mountain Fuel ^d	Preliminary assessment of potential test location				

^aTwo new test racks were added (loc. 5 and loc. 6) in Lines 401 and 601 in the BI-GAS process.

^bSecond exposure to be completed during October.

^cThird exposure to begin in October 1981.

^dProposed 3000 lb/hr pilot plant near Salt Lake City, Utah.

their behavior in laboratory tests, aluminized coatings have generally detracted from the corrosion resistance of alloys in the pilot plant exposure.

Accumulated Phase II data for coal pretreatment and gasifier quench systems show that straight-run carbon steel and other iron-base alloys (2½Cr-1Mo, silicon iron, cast iron, Ni-Resist) corroded at unacceptable rates (>10 mpy) in almost all low-temperature pilot plant locations. Most austenitic stainless steels--especially 329, 18-8-2, 316--appear more acceptable than the ferritic and martensitic grades, the latter being susceptible to deep localized corrosion in some test locations.

To date, very limited degradation has been observed of dense refractories, exposed in six pilot plants under non-slagging conditions. In general, it appears that refractories with compositions of greater than

60% alumina and less than 30% porosity have experienced little degradation during exposure. Phosphate-bonded materials, originally thought to be unlikely to withstand the gasifier environments, have shown no significant attack.

There are exceptions to the generalized rule: Alfrax bubble alumina, with greater than 30% porosity, has shown no significant deterioration, whereas silicon nitride bonded silicon carbide with less than 30% porosity has deteriorated in atmospheres of high steam content.

CURRENT ACTIVITIES

Corrosion Data--Metals

During the reporting period, activities in the Phase II program included the following:

1. Completion of rack fabrication for BI-GAS (3rd exposure), U-Gas (3rd exposure), and Westinghouse (2nd exposure) pilot plants.
2. Completion of first draft of Synthane "topical" report.
3. Completion of CONOCO COAL "topical" report.
4. Continuation of exposures in BI-GAS (2nd exposure and Peat Gas (2nd exposure).
5. Initiated HYGAS "topical" report.
6. Completed physical property measurements of reference refractory specimens for BI-GAS (3rd exposure), U-Gas (2nd exposure), and Westinghouse (2nd exposure).
7. Corrosion monitoring discussion documents were forwarded to General Electric and Mountain Fuel Resources for review.
8. Completion of corrosion analysis of U-Gas gasifier second-exposure coupons.

Testing is in progress at Westinghouse (1st exposure), and Peat Gas (1st exposure); in BI-GAS, the second exposure is slated for completion in October. The third exposure in U-Gas will begin by the end of the year. Table 2-2 summarizes the nominal composition of alloys being exposed in pilot plant facilities.

TABLE 2-2. CHEMICAL COMPOSITION OF PHASE II TEST ALLOYS

Alloy	Composition, wt%									
	C	Mn	Si	Fe	Ni	Cr	Co	Al	Mo	Others
Carbon steel A515	0.22	0.62	0.2	Bal						
A515 (Al)										
Carbon-3 1/2 Mo	0.15	0.45	<0.03	Bal					0.5	
2 1/2 Cr-1 Mo	0.15	0.45	<0.3	Bal		2.25			1.0	
Cast iron	3.02	0.67	1.93	Bal	1.6				0.4	
Si-iron	1.1	1.5	14.5	Bal		0.5			0.5	0.5Cu
Ni-Resist	2.8	0.91	2.81	Bal	19.8	3.1				
Ni-Resist (Cu)	3.0	1.5	2.80	Bal	17.5	3.5				6.5Cu
405	0.08	1.0	1.0	Bal		13.0				0.2Al
410	0.13	0.35	0.54	Bal	0.5	12.0			0.1	
430	0.06	0.36	0.62	Bal	0.4	17.3				
446	0.10	0.45	0.38	74.6	0.4	24.0				
26-1	0.02	0.27	0.43	Bal	0.3	25.6			1.0	0.42Ti
329	0.05	0.5	0.4	Bal	4.3	27.1			1.4	
HC-250	3.03	0.5	0.7	68.1	0.1	27.5			0.01	
HK-40	0.4	2.0	2.0	Bal	20.0	28.0			0.5	
HL-40	0.47	0.6	1.4	47.1	19.4	30.9			0.01	
HL40-3Si	0.42	0.7	2.4	45.8	19.3	31.4			0.01	
304	0.05	1.45	0.54	70.0	9.1	18.8			0.34	
309	0.11	0.54	0.74	60.5	14.7	23.0				
310	0.06	1.71	0.68	52.2	20.2	25.0				
310(Al)										
314	0.06	1.90	2.21	51.6	20.0	24.0				
316	0.05	1.65	0.43	65.3	13.9	17.1			2.5	
321	0.04	1.61	0.40	Bal	10.0	17.7			0.4	0.35Cu, 0.2Ti
347	0.08	2.0	1.0	Bal	9-13	17-19				Cb+Ta, 10 X C min
Crutemp 25	0.07	1.5	0.6	47.2	24.8	25.4			0.4	
18-18-2	0.05	1.35	2.0	Bal	10.2	10.1				0.08Cu
20Cb3	0.03	0.56	0.50	Bal	33.0	19.4			2.1	3.1Cu, 0.91Cb+Ta
21-6-9	0.04	8.2	0.7	62.9	6.8	20.7			0.22	
22-13-5	0.05	5.3	0.5	Bal	13.5	21.1			2.25	0.14Cb, 0.2V, 0.3N
IN-800	0.03	0.80	0.33	47.1	30.8	20.6	0.10	0.32		0.42Ti
IN-800(Al)										
IN-793	0.03	0.72	0.40	43.2	32.2	21.4	0.02	1.76		
825	0.04	0.56	0.30	28.3	42.0	21.9		0.06	3.2	2.1Cu, 0.7Ti
RA-330	0.05	1.5	1.3	Bal	36.0	19.1				0.19Cu
RA-333	0.05	1.5	1.4	15.5	45.0	26.2	2.5		3.8	2.7W
30/50W	0.51	0.87	1.0	Bal	48.7	27.9				3.6W
IN-600	0.05	0.15	0.20	7.0	76.5	15.8	0.08			
IN-601	0.04	0.24	0.19	15.9	59.5	22.5	0.03	1.19		
Hastelloy X	0.09	0.69	0.44	19.5	44.6	21.9	2.5	0.21	9.1	0.5W
IN-671	0.06	0.06	0.39	1.1	47.8	50.2				0.24Ti
617	0.07				54.0	22.0	12.5	1.0	9.0	
N155	0.10	1.3	0.6	29.0	19.8	20.9	19.5		3.0	1.1Cb+Ta, 2.8W
T63WC	0.52	0.10	1.4	Bal	36.0	28.2	15.0			5W
188	0.09	0.6	0.4	1.2	22.9	22.0	Bal	0.22	0.6	0.07La, 14.5W
150	0.08	0.5	0.5	18.0	1.4	27.9	Bal		0.1	
6B	1.0	1.4	0.5	1.9	2.8	28.1	57.1		1.2	4.8W
Titanium 50A	0.02			0.14						0.14N, Bal Ti
Monel 400	0.14	1.06	0.14	1.9	63.6					33.2Cu
Al-Bronze				3.3	2.0			10.38		Bal Cu

Peat Gas Pilot Plant

First-exposure period corrosion testing is currently in progress in seven test locations. At present, corrosion coupons have been exposed to gasification conditions for only a short time (250 hr). After the installation of the new lock hopper feed system, gasification tests will be resumed toward the end of the year.

BI-GAS Pilot Plant

Nine third-exposure corrosion test racks are currently at the plant site (Homer City, Pennsylvania) awaiting installation. Included are two new test racks positioned in process piping as described in Table 2-3. To date, test specimens from the second exposure have accumulated an estimated 1400 hr of exposure under operating conditions with Montana Rosebud subbituminous coal as gasification feedstock.

TABLE 2-3. ADDED BI-GAS TEST LOCATIONS

IITRI Test Location No.	BI-GAS Piping Location	U-Bend Specimens (3/16 in. thick) for Both Racks
5	Raw product gas transfer line 401 (exit 10th floor) from V-301A (gasi- fier) to V-402 (char feed vessel)	Type 304 Type 304 ^a Type 321 stabilized Type 321 stabilized ^a
6	Product gas transfer line 601 from char feed vessel (V-402) at top floor level.	1½Cr-½Mo ^b 1½Cr-½Mo ^c

Average temperature and pressure: 800°F, 750 psig.
Racks to be mounted on blind flange in 8 in. tee.

^aSensitized at 1250°F for ½ hr.

^bWelded U-bend: E8018-B2 welding rod, 450°F preheat, 1250°F postheat
for ½ hr and furnace cooled.

^cWelded U-bend: E8018-B2 welding rod, 450°F preheat, no postheat.

Westinghouse Pilot Plant

Currently, first-exposure corrosion testing is in progress in eight test locations in the Westinghouse PDU. Test locations include the hot gas cycling and four recycle-char transfer lines to the gasifier. Eight corrosion test racks for the second-exposure period are being prepared for shipment to the plant site in Madison, Pennsylvania.

GEGAS Pilot Plant

Recent discussions identified potential materials test locations and preliminary rack designs. A discussion document outlining corrosion rack and coupon designs for corrosion monitoring in the GEGAS test facility has been forwarded to General Electric. Final recommendations on test locations are currently being assessed by General Electric personnel.

Mountain Fuel Resources

A discussion document outlining corrosion rack and coupon design for corrosion monitoring in the proposed 3000 lb/hr pilot plant was forwarded to Mountain Fuel Resources for review in July. Final recommendations are currently being assessed.

U-Gas Pilot Plant

During the reporting period, post-exposure metallographic analysis was completed for second-exposure period corrosion coupons from the U-Gas gasifier.

The second-exposure period encompassed U-Gas run 201 to VEGG-3. During the exposure the following coals were gasified:

<u>U-Gas Run No.</u>	<u>Coal Gasified</u>
157-160	Pittsburgh No. 8 Bituminous
201-206	Western Kentucky No. 6 Bituminous
VEGG-1	Australian Bituminous
VEGG-2	Wyoming Subbituminous
VEGG-3	Polish Bituminous

Bed temperatures ranged from 1835° to 1953°F at pressures of 14.8-58.8 psia.

Neg. No. 53138

Figure 2-1. Appearance of U-Gas gasifier metallic coupon test rack positioned below internal cyclone during second exposure.

The corrosion racks were situated in the gasifier freeboard section just below the internal cyclone as shown in Fig. 2-1. Temperatures at this test location are approximately 150°F below the bed temperature.

The corrosion data for test alloys from the U-Gas second gasifier exposure are presented in Table 2-4. In general, the cobalt-base and nickel-base alloys showed better corrosion performance than iron-base alloys.

Haynes 188, 6B, and Alloy X incurred the least corrosion losses which resulted in equivalent linear corrosion rates of <15 mpy during the 1581 hr exposure period. Marginal performance was obtained with N-155, IN-671, RA-333, IN-800(Al), and T63WC with linear rates of <31 mpy but >20 mpy. Higher corrosion losses (>5.5 mils) resulted from HL-40, HK-40, Type 310(Al) and Type 310; equivalent linear corrosion rates were >31 mpy.

TABLE 2-4. SECOND-EXPOSURE CORROSION DATA FOR U-GAS GASIFIER (FREEBOARD), LOCATION 1

Material	Scaling Loss, mils	Depth of Internal Penetration, mils	Total Sound Metal Loss, mils	Equivalent Linear Corrosion Rate, ^a mpy
IN-671	1.0	3.2	4.2	23.3
HL-40	0.2	6.3	6.5	36.0
HK-40	1.1	5.1	6.2	34.4
RA-333	0.2	5.3	5.5	30.5
N-155	2.2	1.8	4.0	22.2
Alloy X	0.2	2.2	2.4	13.3
310	0.2	9.1	9.3 ^b	51.5
310(A1)	3.0	5.7	8.7	48.2
6B	0.2	2.0	2.2	12.2
Haynes 188	0.2	1.6	1.8	10.0
T63WC	0.2	5.3	5.5	30.5
IN-800(A1)	0.6	4.1	4.7	26.0

^aBased on exposure of 1581 hr under operating conditions during U-Gas runs 157 to 160, 201 to 208, and VEGG-1 to VEGG-3.

Temperature range: 1835°-1953°F.

Pressure range: 14.8-58.3 psia.

^bLocalized grain boundary attack in one isolated area.

From a qualitative compositional standpoint, higher chromium content in the alloy was not a sufficient criterion for better corrosion resistance under the test conditions. This can be seen by comparing corrosion losses for T63WC, HK-40, and HL-40 to Haynes 188, Alloy X, and N-155. The first three alloys contain 20.9 to 22% Cr, while the latter three have 28.0 to 30.9 w/o Cr. Cobalt and nickel content compositions were also important. For alloys containing Ni, Cr, and Co (188, 6B, Alloy X, N-155, RA-333, T63WC) as major constituents, the higher the weight percent ratio of (Co + Ni)/Cr, the better performing the alloy.

For the coated alloys, IN-800(Al) experienced corrosion attack to an extent half that incurred by Type 310(Al). The corrosion attack was predominantly along cracks in the bulk coating for both coated alloys.

The corrosion performance of alloys in the quench system (2nd exposure) is currently being assessed. Preliminary observations have shown titanium 50A to be minimally affected by the aggressive environment. Type 329, although locally attacked in a few areas (~10% of surface area), is only surpassed by titanium 50A in corrosion performance. The remaining alloys show considerable attack as in the first exposure.

Corrosion Data--Refractories

During this quarter, specimens were prepared for the following coal gasification pilot plants: BI-GAS, 3rd exposure, location 1; U-Gas, 2nd exposure; and Westinghouse, 2nd exposure, off-gas location 1. In most cases, specimens were cut to design dimensions from samples of 9 in. straight bricks obtained from the refractory manufacturers. Two specimens were prepared, one for test and one for reference. If possible, the reference specimen was cut from the same brick immediately adjacent to the test specimen. Physical property measurements were made on all test specimens and on reference specimens for BI-GAS and U-Gas pilot plants.

TABLE 2-5. REFRACTORY SPECIMENS FOR BI-GAS THIRD EXPOSURE, LOCATION 1

Specimen No.	Specimen Type
2	Dense castable, calcium aluminate bond, 60% alumina
5	Dense castable, calcium aluminate bond, 54% alumina
6	Light castable, calcium aluminate bond, 54% alumina
8	Dense brick, phosphate bond, 85% alumina
29	Dense brick, phosphate bond, 85% alumina
18	Fused cast brick, alumina zirconia silica
21	Dense brick, clay bond, 40-50% alumina
25	Ramming mix, phosphate bond, 90% alumina
32	Dense castable, phosphate bond, 90+% alumina

Tables 2-5, 2-6, and 2-7 give the types of refractories to be exposed in each of the pilot plants. The U-Gas specimens are solid rectangular shapes, 4 x 2 x 3/4 in. The BI-GAS and Westinghouse specimens are smaller due to limited access; the test specimens' configurations and dimensions are shown in Figs. 2-2 and 2-3, respectively. The reference specimens for these are solid rectangular shapes of the same external dimensions.

The standard specimen preparation technique, which was used for all specimens but No. 20, was:

1. Specimens were rough cut from bricks with a diamond saw.
2. The surface of the specimens was ground with a 165 micron diamond disk until smooth.
3. Holes in the BI-GAS and Westinghouse specimens were diamond core drilled.
4. Code cuts to identify the refractory were made with a diamond saw, if feasible.
5. The specimens were brushed in running water and rinsed in distilled water to remove machining debris.
6. After drying overnight at 250°F (120°C), the specimens were fired for four hours at 1500°F (815°C).
7. The specimens were removed hot from the kiln and cooled in a desiccator to prevent hydration.

Specimen No. 20, a tar-impregnated dense 60% alumina brick, was gently dried from 24 hr under an infrared lamp instead of in a dryer and was not fired to avoid removing the tar-impregnation by oxidation.

Physical property measurements of P (apparent porosity), T (apparent specific gravity), and B (bulk density) were made by the liquid displacement method. Kerosene was used as the displacing medium to prevent possible rehydration of some types of refractories.

The formulas used were:

$$P \text{ (apparent porosity)} = \frac{W - D}{W - S} \times 100$$

$$T \text{ (apparent sp. gr.)} = \frac{D \times (\text{sp. gr. of kerosene})}{D - S}$$

$$B \text{ (bulk density)} = \frac{D \times (\text{sp. gr. of kerosene})}{W - S}$$

TABLE 2-6. REFRACTORY SPECIMENS FOR U-GAS COAL GASIFICATION PLANT,
SECOND EXPOSURE

Specimen No.	Specimen Type
1	Dense castable, calcium aluminate bond, 90+% alumina
2	Dense castable, calcium aluminate bond, 60% alumina
5	Dense castable, calcium aluminate bond, 54% alumina
8	Dense brick, phosphate bond, 85% alumina
14	Dense brick, nitride-bonded SiC, no alumina
20	Dense brick, vitreous bond, 60% alumina, tar impregnated
25	Ramming mix, phosphate bond, 90% alumina
32	Dense castable, phosphate bond, 90+% alumina

TABLE 2-7. REFRACTORY SPECIMENS FOR WESTINGHOUSE SECOND EXPOSURE,
LOCATION 1

Specimen No.	Specimen Type
2	Dense castable, calcium aluminate bond, 90+% alumina
5	Dense castable, calcium aluminate bond, 60% alumina
6	Light castable, calcium aluminate bond, 54% alumina
8	Dense brick, phosphate bond, 85% alumina
14	Dense brick, nitride-bonded SiC, no alumina
20	Dense brick, vitreous bond, 60% alumina, tar impregnated
21	Dense brick, clay bond, 40-50% alumina
25	Ramming mix, phosphate bond, 90% alumina
30	Dense brick, phosphate bond, 80+% alumina
32	Dense castable, phosphate bond, 90+% alumina
39	Dense brick, solid solution, 10% Cr ₂ O ₃ -90% alumina
40	Dense brick, solid solution, 16% Cr ₂ O ₃ -84% alumina

Figure 2-2. BI-GAS (location 1, 3rd exposure)
test specimen design and dimensions.

Figure 2-3. Westinghouse (location 1, 2nd exposure)
test specimen design and dimensions.

where D = dry weight
 W = saturated weight
 S = suspended weight.

The following procedure was used:

1. The dry specimens were placed in a desiccator and evacuated for $2\frac{1}{2}$ hr and left in the evacuated desiccator overnight.
2. Kerosene was admitted into the desiccator until the specimens were covered with at least 1 in. of kerosene. (Water was used for specimen 20 to avoid dissolving the tar impregnation.)
3. The desiccator was then evacuated for 6 hr.
4. Specimens were left in the evacuated chamber overnight.

5. After property measurements were taken, specimens were dried, refired at 1500°F (815°C) for 4 hr, cooled, and reweighed for a check on the dry weight, D. (The drying and refiring was omitted for specimen 20.)

The physical properties of the test and reference specimens for BI-GAS and U-Gas are compared in Tables 2-8 and 2-9, respectively. The property values of test and reference specimens are quite close, within 10%, for most refractories. The only exception is No. 18 in Table 2-8. This is a fused cast dense brick; the apparent porosity of the reference specimen is 71% more than for the test specimen due to a greater number of large pores in the former. However, the apparent specific gravity and bulk density are very similar so it is unlikely that the increased porosity will affect the performance of the refractory.

The physical properties for the test specimens for the Westinghouse pilot plant are listed in Table 2-10. Their values are quite close to the values of specimens for the other two pilot plants. The difference in apparent porosity between refractory No. 20 in Table 2-9 and in Table 2-10 is due to a difference in tar-impregnation.

PROJECTED WORK FOR THE NEXT QUARTER

Project activities for the next (fourth) quarter are as follows:

1. Complete U-Gas quench system second-exposure corrosion analysis.
2. Contribute to the second 1981 MPC Semiannual Meeting.
3. Amend Synthane Topical Report after receipt of reviewers' comments, and issue as a final report.
4. Forward HYGAS Topical Report to committee members for review, and then amend the report and issue as a final report.
5. Initiate corrosion analysis of BI-GAS second-exposure coupons.
6. Short topical reports will be issued on U-Gas and BI-GAS since the test programs have not been completed.
7. Physical property measurements will be completed on the Westinghouse reference samples.
8. Rotating rod abrasion tests will be begun on the BI-GAS, U-Gas, and Westinghouse reference samples.

TABLE 2-8. COMPARISON OF PHYSICAL PROPERTIES OF TEST SPECIMENS
AND REFERENCE BLANKS FOR BI-GAS COAL GASIFICATION PLANT,
THIRD EXPOSURE, LOCATION 1

No.	Refractory Description	Specimen	Apparent Porosity, %	Apparent Specific Gravity	Bulk Density, g/cm ³
2	Dense castable, calcium aluminate bond, 60% alumina	Test	28.6	3.06	2.19
		Ref.	28.0	3.04	2.19
5	Dense castable, calcium aluminate bond, 54% alumina	Test	27.9	2.91	2.10
		Ref.	27.4	2.90	2.11
6	Light castable, calcium aluminate bond, 54% alumina	Test	55.1	2.85	1.28
		Ref.	53.5	2.72	1.27
8	Dense brick, phosphate bond, 85% alumina	Test	19.7	3.38	2.71
		Ref.	20.0	3.34	2.71
29	Dense brick, phosphate bond, 85% alumina	Test	17.7	3.46	2.85
		Ref.	17.7	3.45	2.84
18	Fused cast brick, alumina- zirconia-silica	Test	2.1	3.88	3.80
		Ref.	3.6	3.95	3.81
21	Dense brick, clay bond, 40-50% alumina	Test	12.4	2.68	2.34
		Ref.	12.1	2.69	2.36
25	Ramming mix, phosphate bond, 90% alumina	Test	17.0	3.49	2.90
		Ref.	17.0	3.45	3.55
32	Dense castable, phosphate bond, 90+% alumina	Test	24.8	3.59	2.70
		Ref.	24.6	3.55	2.68

TABLE 2-9. COMPARISON OF PHYSICAL PROPERTIES OF TEST SPECIMENS
AND REFERENCE BLANKS FOR U-GAS COAL GASIFICATION PLANT,
SECOND EXPOSURE

No.	Refractory	Specimen	Apparent	Apparent	Bulk
	Description		Porosity, %	Specific Gravity	Density, g/cm ³
1	Dense castable, calcium aluminate bond, 90+% alumina	Test	26.1	3.57	2.64
		Ref.	26.1	3.57	2.64
2	Dense castable, calcium aluminate bond, 60% alumina	Test	25.3	2.97	2.22
		Ref.	22.7	2.59	2.00
5	Dense castable, calcium aluminate bond, 54% alumina	Test	27.6	2.86	2.07
		Ref.	27.3	2.87	2.09
8	Dense brick, phosphate bond, 85% alumina	Test	19.8	3.40	2.74
		Ref.	18.6	3.39	2.76
14	Dense brick, nitride-bonded SiC, no alumina	Test	18.9	3.18	2.58
		Ref.	17.9	3.16	2.60
20	Dense brick, vitreous bond, tar impregnated, 60% alumina	Test	1.06	2.69	2.66
		Ref.	1.23	2.72	2.68
25	Ramming mix, phosphate bond, 90% alumina	Test	18.2	3.48	2.85
		Ref.	18.1	3.48	2.85
32	Dense castable, phosphate bond, 90+% alumina	Test	25.5	3.58	2.67
		Ref.	25.7	3.58	2.66

TABLE 2-10. PHYSICAL PROPERTY MEASUREMENTS OF TEST SPECIMENS
FOR WESTINGHOUSE COAL GASIFICATION PLANT,
SECOND EXPOSURE, LOCATION 1

No.	Refractory Description	Apparent Porosity, %	Apparent Specific Gravity	Bulk Density, g/cm ³
2	Dense castable, calcium aluminate bond, 90+% alumina	28.5	3.04	2.17
5	Dense castable, calcium aluminate bond, 60% alumina	26.8	2.88	2.10
6	Light castable, calcium aluminate bond, 54% alumina	52.9	2.73	1.29
8	Dense brick, phosphate bond, 85% alumina	18.1	3.36	2.75
14	Dense brick, nitride bond SiC, no alumina	18.4	3.15	2.57
20 ^a	Dense brick, vitreous bond, 60% alumina, tar impregnated	1.50	2.73	2.69
21	Dense brick, clay bond, 40-50% alumina	11.5	2.66	2.36
25	Ramming mix, phosphate bond, 90% alumina	15.2	3.49	2.96
30	Dense brick, phosphate bond, 80+% alumina	15.9	3.32	2.79
32	Dense castable, phosphate bond, 90+% alumina	24.4	3.57	2.70
39	Dense brick, solid solution, 10% Cr ₂ O ₃ -90% alumina	15.9	3.83	3.22
40	Dense brick, solid solution, 16% Cr ₂ O ₃ -84% alumina	13.9	3.84	3.30

^aDistilled water was used for property measurements of No. 20.

MPC-4.3.4(B) - EROSION-CORROSION OF MATERIALS
IN COAL GASIFICATION PILOT PLANTS

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INTRODUCTION

The MPC program on materials for coal gasification is subdivided into several phases. The objective of the Phase IV testing program is to provide baseline data on the erosion-corrosion resistance of materials potentially useful for the construction of gasifier internals. The results provide information additional to that from the Phase I high-temperature gas corrosion program as a basis for materials selection decisions.

Two high-temperature test reactors have been constructed for the Phase IV erosion-corrosion testing program, one operating at atmospheric pressure and the other at pressures of up to 1000 psi.* Both reactors utilize as a test environment the simulated coal gasification atmosphere approved by MPC.

In the 1981 program, alloys will be evaluated under several combinations of test conditions encompassing temperatures of 1650° and 1800°F, erodent velocities of 25 to 150 fps, operating pressures of atmospheric to 1000 psi, erodents of low, medium, and high sulfur chars and inert Al_2O_3 , and times of 50 to 250 hr. A primary objective of the 1981 program is to provide information on the interrelation of metal loss, exposure time, and erodent velocity.

* All pressures are gauge values, i.e., psig.

OUTLINE OF PREVIOUS WORK

The Phase IV erosion-corrosion testing program has been in progress at IITRI since 1976. Atmospheric and high pressure test facilities were designed and constructed for the program, and testing in these facilities commenced in 1976 and late 1978, respectively.

By the end of 1980 a total of 3327 hr of atmospheric and 1710 hr of high pressure tests had been completed. These test programs have been planned to maximize output of design-oriented engineering data rather than as a study of erosion-corrosion mechanisms.

Prior to commencement of the 1981 program, the erosion-corrosion behavior of 22 alloys and 10 refractories in the range of simulated gasifier environments had been investigated. From the results, several general trends in the erosion-corrosion behavior of the alloys tested could be tentatively identified:

1. Good corrosion resistance was a necessary but not a sufficient requirement for good erosion-corrosion resistance.
2. Erosion-corrosion losses were generally higher at 1000 psi than at atmospheric pressure.
3. Erosion-corrosion losses increased with increasing temperature and H_2S level.
4. Erosion-corrosion losses appeared independent of char particle size, in the range -30 to +140 mesh.
5. Some of the erodents were considerably more aggressive than others.

These conclusions were regarded as highly tentative because, firstly, test times were short--maximums of 250 hr in the atmospheric and 100 hr in the high-pressure reactors--and, secondly, only a few data points were available from the broad matrix generated by the large number of variables acting in the system.

CURRENT ACTIVITIES

Test Equipment

Atmospheric Unit

The last quarter has seen one failure occurring in the atmospheric unit, resulting in downtime higher than that normally anticipated. This failure was the opening of a solder-bellows joint and cracks in the brass bellows. There are four of these assemblies, and this failure has occurred this year once before. To correct this repeated failure, a new type of bellows is being used and these are made of 347 stainless steel.

High Pressure Unit

The last quarter has seen no failures occurring in the high-pressure unit, resulting in downtime lower than that normally anticipated.

Post-Exposure Corrosion Analysis

Analysis of specimens from both atmospheric and high-pressure tests entailed gravimetric, micrometric, and selected metallographic evaluations. Scanning electron microscopy and EDX analysis of surface and subsurface corrosion products of a limited number of samples will be performed when appropriate.

Gravimetric analysis involved weighing the samples before exposure (W_a); after exposure (W_b); after cleaning the eroded surface (W_c); and after complete cleaning of the sample (W_d). Consequently, ($W_a - W_c$) gave an indication of the extent of metal loss from the eroded surface, and ($W_a - W_d$) represented the total weight loss of the sample due to erosion-corrosion of the top surface and corrosion of the remaining surfaces.

After complete cleaning of the samples, point micrometer measurements were taken to obtain the remaining thickness of the samples in the eroded regions. Thickness measurements were also taken in noneroded regions. Figure 4-1 illustrates the relationship of micrometer measurements to

t_a = Original thickness

t_b = Average thickness in non-eroded area

$\frac{t_a - t_b}{2}$ = Average thickness loss due to corrosion (one surface)

t_c = Minimum measured thickness in eroded area

t_x = Maximum thickness loss due to erosion-corrosion of eroded surface

$$= t_a - [t_c + (t_a - t_b)/2]$$

Figure 4-1. Schematic diagram of relationship of micrometer measurements to erosion-corrosion and corrosion.

erosion-corrosion thickness loss for the eroded surface and to corrosion thickness loss for the remaining surfaces of the samples.

Gravimetric analysis provided only a rough estimate of erosion-corrosion since molten corrosion products were often transmitted to the edges and back surfaces, causing localized corrosion. This contributed to greater apparent erosion-corrosion loss ($W_a - W_c$), since it is assumed that corrosion on the back surface was uniform and minor compared to erosion-corrosion. This was not always the case, however, because of the interactions of liquid corrosion products from the eroded surface.

Micrometric measurements after cleaning provided the most accurate measurements of maximum metal loss due to erosion-corrosion. These measurements could be normalized for localized back-surface corrosion, in most cases, by comparison with the sample thickness on the top surface where no erosion-corrosion occurred. Accordingly, gravimetric data were considered only supplemental in the analysis of test samples.

Test Schedules

The revised 1981 test schedules for the atmospheric and high-pressure units are shown in Table 4-1 (a number of alterations to the earlier proposed schedules are still awaiting final approval). These schedules present a total of 1500 hr for the atmospheric and 1000 hr for the high pressure, and were approved at the April 23, 1981, meeting of MPC Subcommittee 9, Phase IV. The Committee also approved the use of coke as the new standard erodent.

Test Alloys

Table 4-1 specifies three different alloy groups A, C, and D, and these are shown in Table 4-2 along with the previous groups used. Alloy groups A and C are the alloy groups which have been used over the past few years. The new group, D, will be made up of the best alloys from groups A and C when evaluated at the conditions of 1800°F-50 fps-250 hr-1.0 v/o H₂S-coarse FMC erodent in the atmospheric reactor. This test

TABLE 4-1. SUMMARY OF APPROVED 1981 EROSION-CORROSION TESTS

Test No.	Completed	Erodent ^a	Press., psig	Temp., °F	H ₂ S, v/o	Vel., fps	Time, hr	Alloy Series
<u>ATMOSPHERIC</u>								
44	X	Spent	1	1800	0.1	100	100	A
45	X	Spent	1	1800	0.5	100	100	A
46	X	FMC	1	1800	1.0	50	250	C
47	X	FMC	1	1650	1.0	50	250	A
49	X	Coke	1	1800	1.0	100	100	A
50	b	Coke	1	1800	1.0	25	200 ^c	A
51	b	Coke	1	1800	1.0	50	200 ^c	A
52		Coke	1	1800	1.0	100	200 ^c	A
53		Coke	1	1800	1.0	150	100 ^d	A
Total							1500	
<u>HIGH PRESSURE</u>								
HP29		FMC	1000	1650	1.0	50	250	A
HP30		Al ₂ O ₃	600	1800	1.0	100	50	A
HP31	X	Spent	1000	1650	1.0	100	50	A
HP32	X	Coke	1000	1800	1.0	100	100	A
HP33	e	Coke	500	1800	1.0	25	200 ^c	A
HP34	e	Coke	500	1800	1.0	50	200 ^c	A
HP35	f	Coke	500	1800	1.0	100	200 ^f	A
Total							1000	

^aErodent size: -30 +50 mesh.

^b50 hours of testing completed.

^cSpecimens to be inspected at 50, 100, and 200 hours.

^dSpecimens to be inspected at 50 and 100 hours.

^e100 hours of testing completed.

^f150 hours of testing completed.

TABLE 4-2. MATERIAL SELECTION FOR EROSION-CORROSION TEST GROUPS

Series A	Series B ^a	Series C	Series D	Series R
800 ^b	800 ^b	800 ^b	800 ^b	800 ^b
671 ^b	671 ^b	671 ^b	671 ^b	671 ^b
446	446	32X	The 10 best alloys from groups A & C	<u>Brick</u>
188	188	N155		90% alumina, self-bond (Kricor)
601	601	T63WC		85% alumina, phosphate bond (Chemal 85B)
310	310	150		70% alumina, mullite (Alumex)
310(A1)		6B		60% alumina, pitch impregnated (Ufala TI)
800(A1)		Alloy X		45% alumina, fire brick (KX-99)
Crutemp 25		HK-40		90% alumina-10% chromia (HW Ruby)
RA-333		30/50W		<u>Castable</u>
LM-1866		HL-40		90% alumina, calcium aluminate bond (Castolast G)
Co-Cr-W No. 1		<u>Alternates</u>		60% alumina, calcium aluminate bond (Superbrikcast A)
		Fe-36Cr-36Ni		<u>Insulating Refractory</u>
		Fe-31Cr-36Ni		54% alumina castable, calcium aluminate bond (Litecast 75-28)
		Fe-31Cr-28Ni		77% alumina brick, vitreous bond (Insulcor)
		Fe-31Cr-44Ni		
		329		

^aDuplicate samples.^bReference materials.

has been done for the A series in test 43, and the C series alloys are scheduled to be run this year as test 46. Group D will include the reference alloys 671 and 800.

Test Eroducts

The ultimate and ash analyses of erodents used currently are shown in Table 4-3. This table includes the new erodent, coke, which shows a sulfur level between that of the high-sulfur chars (FMC and Husky) and the low-sulfur char (BI-GAS), and an ash analysis of about the same composition as the FMC.

Test Results

Test 46 - Atmospheric

Test 46 was completed during this quarter and was to operate with series C alloys at 1800°F-50 fps-250 hr-1.0 v/o H₂S with coarse FMC erodent. The test could not be run for the full 250 hr but had to be stopped at 192 hr because of a change in the FMC erodent. This erodent has been used several times and now seems to be breaking up. The summary of the gravimetric, micrometric, and photographic data is given in Fig. 4-2, which also lists the test conditions for this run. The data for maximum erosion-corrosion metal loss fall into two groups. The least attacked group lost from 0.7 to 4.8 mils and consists of the alloys 671, HL-40, N155, 329, 150, Alloy X, 6B, 30/50W, and 32X. The most attacked alloys were 31Cr-36Ni, 800, and HK-40 which lost 9.0, 9.4, and 14.5 mils, respectively.

Test 50 - Atmospheric

This was the first interruption of test 50 after 50 hr of testing. This test operates with series A alloys under the conditions of 1800°F-25 fps-1.0 v/o H₂S and coarse coke erodent with a total time of 200 hr. A summary of gravimetric, micrometric, and photographic data is given in Fig. 4-3. The data from this first interruption give very low maximum erosion-corrosion losses running between 0.4 and 1.0 mil for 800 and aluminumized 310, respectively.

TABLE 4-3. ULTIMATE AND ASH ANALYSIS OF ERODENTS

Component	Analysis of Erodents, wt %				
	FMC ^a	Husky ^b	Coke ^c	Spent ^d	Al ₂ O ₃ ^e
<u>Ultimate</u>					
C	75.92	74.30	87.18	83.26	-
H	2.21	2.04	0.34	1.05	-
N	0.77	0.64	0.90	0.48	-
Cl	0.03	0.02	0.07	0.03	-
S	2.69	1.89	0.81	0.14	-
Ash	14.73	17.56	10.08	13.04	100
<u>Ash</u>					
SiO ₂	44.00	19.97	49.42	40.31	0.06
Al ₂ O ₃	24.31	10.94	24.72	24.38	+99.5
TiO	1.03	0.48	1.20	1.14	-
Fe ₂ O ₃	22.36	7.66	14.24	1.85	-
CaO	2.11	22.17	3.57	22.30	-
MgO	0.94	8.65	1.61	6.90	-
K ₂ O	2.53	0.60	1.89	0.50	-
Na ₂ O	0.27	2.41	1.24	0.57	0.21
SO ₃	1.65	25.71	1.00	0.27	-
P ₂ O ₅	0.27	0.15	0.33	0.08	-
SrO	-	0.50	0.01	-	-
BaO	0.01	0.10	0.08	-	-
Mn ₃ O ₄	-	0.11	0.23	-	-
Unknown	0.54	0.55	0.46	1.70	-

^aWestern Kentucky coal prepared by COED process.

^bWestern coal processed by the Husky Oil Company.

^cMetallurgical coke.

^dMontana rosebud coal which has been through the BI-GAS gasifier.

^eAlcoa Chemical tubular alumina, grade T61.

				Gravimetric ₂ Data, mg/cm ²		Micrometric Data, mils	
		Alloys	Alloy Code	Corro- sion	Erosion- Corrosion	Corro- sion	Erosion- Corrosion
Test No:	46	800	A	10.8	3.4	1.6	9.4
Reactor:	Atm	671	M	8.3	13.3	0.6	1.5
Erodent:	FMC	150	WW	15.4	21.2	0.6	4.8
Size:	Coarse	N155	VV	7.3	3.8	0.5	1.1
Pressure:	0.3 psig	32X	3K	17.2	39.0	0.2	1.2
Temp.:	1800°F	Alloy X	Y	30.9	-9.7	0.2	0.7
H ₂ S:	1.0 v/o	HK-40	3Q	6.9	40.8	<0.2	14.5
Velocity:	50 fps	30/50W	3H	14.9	23.2	0.9	1.9
Time:	250 hr	6B	3A	5.0	6.3	0.2	1.0
Alloy		HL-40	QQ	14.3	3.4	1.1	1.8
Series:	C	329	W	12.7	15.7	1.1	2.6
		31Cr-36Ni	4H	21.2	17.1	0.5	9.0

Neg. No. 53751

1X

Figure 4-2. Summary of gravimetric, micrometric, and photographic data from test 46.

				Gravimetric ₂ Data, mg/cm ²		Micrometric Data, mils	
				Corro-	Erosion-	Corro-	Erosion-
Alloys				sion	Corrosion	sion	Corrosion
Test No:	50	800	A	3.3	2.1	0.2	0.4
Reactor:	Atm	800(A1)	A	0.7	4.2	0.5	0.8
Erodent:	Coke	601	C	3.9	-1.9	0.1	0.4
Size:	Coarse	310	D	4.4	2.5	0.3	0.5
Pressure:	0.3 psig	310(A1)	D	2.7	8.0	0.6	1.0
Temp.:	1800°F	RA-333	DD	4.8	1.6	0.5	0.5
H ₂ S:	1.0 v/o	LM 1866	LM	2.3	1.8	0.2	0.5
Velocity:	25 fps	446	K	6.3	0.4	0.5	0.5
Time:	50 of	671	M	5.7	0	0.8	0.8
	200 hr	Crutemp 25	UU	3.5	0.2	0.4	0.4
Alloy		188	XX	0.9	1.3	0.4	0.4
Series:	A	Co-Cr-W No. 1	3Z	1.6	-0.1	0.2	0.5

Neg. No. 53742

1X

Figure 4-3. Summary of gravimetric, micrometric, and photographic data from test 50 at 50 hr.

Test 51 - Atmospheric

Test 51 is being run at 1800°F-50 fps-1.0 v/o H₂S with coarse coke erodent and series A alloys. This test completed 50 hr of testing, but analysis of this test is still in progress and will be reported in the annual report.

Test HP33 - 500 psi

Test HP33 has completed 100 hr of testing under the conditions of 1800°F-25 fps-1.0 v/o H₂S-series A alloys and coarse coke erodent. The results of the first 50 hr are given in Fig. 4-4 as a summary of gravimetric, micrometric, and photographic data. This summary shows maximum erosion-corrosion metal loss falling between 0.5 and 3.6 mils for alloys Co-Cr-W No. 1 and 310(A1), respectively. Analysis of the second 50 hr of testing is still in progress and will be reported in the next quarterly.

Test HP34 - 500 psi

The first 100 hr of testing on HP34 has been completed under the conditions of 1800°F-50 fps-1.0 v/o H₂S-coarse coke erodent on series A alloys. A summary of the gravimetric, micrometric, and photographic data for the first 50 hr of testing is given in Fig. 4-5, and Fig. 4-6 presents the 100 hr data. A detailed comparison of these data is still in progress, but alloy 188 exhibits the most resistance to erosion-corrosion attack and RA-333 the poorest in both the 50 and 100 hr tests. A complete analysis will be given in the annual report when the 200 hr data are available.

Test HP35 - 500 psi

Test HP35 has completed 150 hr of testing in this quarter and was run under the conditions of 1800°F-100 fps-1.0 v/o H₂S-coarse coke erodent and series A alloys. The summaries for the gravimetric, micrometric, and photographic data for the 50, 100, and 150 hr interruptions are given in Figs. 4-7, 4-8, and 4-9, respectively. Alloys 800 and 601 were removed from the test after 50 hr and Crutemp 25 was removed after 100 hr because of damage, and in all cases a 310 sample was used for a replacement. The complete analysis of this test is still under way and will not be completed until the 200 hr data are available, but initial analysis shows alloys 310(A1) and Co-Cr-W No. 1 losing the least metal of all the alloys--1.0

				Gravimetric Data, mg/cm ²		Micrometric Data, mils	
Alloys				Corro- sion	Erosion- Corrosion	Corro- sion	Erosion- Corrosion
Test No:	HP33	800	A	4.0	3.4	0.7	1.4
Reactor:	HP	800(A1)	A	2.7	31.5	1.4	2.4
Erodent:	Coke	601	C	2.6	0.2	0.6	1.2
Size:	Coarse	310	D	4.4	1.9	0.6	1.9
Pressure:	500 psig	310(A1)	D	2.8	30.8	1.0	3.6
Temp.:	1800°F	RA-333	DD	2.7	4.3	0.2	1.2
H ₂ S:	1.0 v/o	LM-1866	LM	2.5	0.2	0.3	1.1
Velocity:	25 fps	446	K	9.3	-2.0	0.3	0.7
Time:	50 of	671	M	4.2	0.8	0.9	1.3
	200 hr	Crutemp 25	UU	2.5	2.2	0.5	1.8
Alloy		188	XX	2.5	1.3	0.5	1.2
Series:	A	Co-Cr-W No. 1	3Z	1.5	-0.2	0.4	0.5

Neg. No. 53681

1X

Figure 4-4. Summary of gravimetric, micrometric, and photographic data from test HP33 at 50 hr.

				Gravimetric ₂ Data, mg/cm ²		Micrometric Data, mils	
Alloys				Corro- sion	Erosion- Corrosion	Corro- sion	Erosion- Corrosion
Test No:	HP34	800	A	21.1	40.6	2.0	10.0
Reactor:	HP	800(A1)	A	2.0	8.3	0.4	1.0
Erodent:	Coke	601	C	6.0	10.7	0.2	6.7
Size:	Coarse	310	D	20.8	53.7	1.2	4.1
Pressure:	500 psig	310(A1)	D	3.1	28.2	0.2	3.8
Temp.:	1800°F	RA-333	DD	10.3	75.8	2.7	18.1
H ₂ S:	1.0 v/o	LM 1866	LM	3.3	6.0	<0.2	1.5
Velocity:	50 fps	446	K	17.3	-1.5	0.6	1.1
Time:	50 of	671	M	12.3	28.6	<0.2	1.8
	200 hr	Crutemp 25	UU	16.9	34.3	1.5	10.6
Alloy		188	XX	6.7	1.6	0.5	1.0
Series:	A	Co-Cr-W No. 1	3Z	7.5	0.9	<0.2	1.7

Neg. 53593

1X

Figure 4-5. Summary of gravimetric, micrometric, and photographic data from test HP34 at 50 hr.

				Gravimetric ₂ Data, mg/cm		Micrometric Data, mils	
Alloys				Corro- sion	Erosion- Corrosion	Corro- sion	Erosion- Corrosion
Test No:	HP34	800	A	33.0	47.5	3.2	17.4
Reactor:	HP	800(A1)	A	3.4	10.2	<0.2	2.6
Erodent:	Coke	601	C	10.8	13.7	0.9	10.4
Size:	Coarse	310	D	25.8	64.5	2.1	20.6
Pressure:	500 psig	310(A1)	D	7.1	42.2	1.9	3.9
Temp.:	1800°F	RA-333	DD	14.7	94.3	4.5	21.0
H ₂ S:	1.0 v/o	LM-1866	LM	5.7	11.0	1.1	7.6
Velocity:	50 fps	446	K	72.6	96.4	6.3	8.3
Time:	100 of	671	M	17.7	32.9	1.3	3.5
	200 hr	Crutemp 25	UU	24.3	83.8	2.0	12.5
Alloy		188	XX	9.5	2.8	1.3	1.6
Series:	A	Co-Cr-W No. 1	3Z	9.2	4.4	0.4	1.9

Neg. No. 53743

1X

Figure 4-6. Summary of gravimetric, micrometric, and photographic data for test HP34 at 100 hr.

				Gravimetric ₂ Data, mg/cm		Micrometric Data, mils		
Alloys				Alloy Code	Corro- sion	Erosion- Corrosion	Corro- sion	Erosion- Corrosion
Test No:	HP35	800	A	33.5	195.9	2.7	74.2	
Reactor:	HP	800(A1)	A	2.2	3.9	1.2	2.5	
Erodent:	Coke	601	C	10.4	67.6	0.2	80.2	
Size:	Coarse	310	D	18.5	28.4	0.4	28.3	
Pressure:	500 psig	310(A1)	D	3.3	6.1	0.5	1.0	
Temp.:	1800°F	RA-333	DD	17.1	-2.8	0.6	8.7	
H ₂ S:	1.0 v/o	LM-1866	LM	4.5	4.9	0.2	1.4	
Velocity:	100 fps	446	K	21.1	-20.0	0.9	4.0	
Time:	50 of	671	M	20.2	0.9	1.0	2.2	
	200 hr	Crutemp 25	UU	20.6	54.7	1.1	30.8	
Alloy		188	XX	31.1	-22.3	0.5	15.3	
Series:	A	Co-Cr-W No. 1	3Z	14.8	-18.9	<0.2	0.4

Neg. No. 53553

1X

Figure 4-7. Summary of gravimetric, micrometric, and photographic data from test HP35 at 50 hr.

				Gravimetric Data, mg/cm ²		Micrometric Data, mils	
				Corro- sion	Erosion- Corrosion	Corro- sion	Erosion- Corrosion
Alloys		Alloy Code					
Test No:	HP35	800(Al)	A	4.5	8.4	0.6	9.6
Reactor:	HP	310	D	33.5	200.0	1.5	102.9
Erodent:	Coke	310(Al)	D	6.6	15.8	0.7	6.9
Size:	Coarse	RA-333	DD	26.8	9.1	0.7	15.6
Pressure:	500 psig	LM-1866	LM	7.3	76.7	0.9	78.0
Temp.:	1800°F	446	K	52.2	153.4	1.9	88.4
H ₂ S:	1.0 v/o	671	M	29.6	14.6	1.6	11.0
Velocity:	100 fps	Crutemp 25	UU	30.5	236.3	1.8	95.0
Time:	100 of	188	XX	43.6	42.3	1.0	27.6
	200 hr	Co-Cr-W No. 1	3Z	18.4	-13.5	<0.2	9.8
Alloy Series: A

Neg. No. 53647

1X

Figure 4-8. Summary of gravimetric, micrometric, and photographic data from test HP35 after 100 hr.

				Gravimetric Data, mg/cm ²		Micrometric Data, mils	
				Corro-	Erosion-	Corro-	Erosion-
				sion	Corrosion	sion	Corrosion
Test No:	HP35	Alloys	Alloy Code				
Reactor:	HP	800(A1)	A	6.9	8.0	1.2	11.1
Erodent:	Coke	310	D	43.7	240.4	1.7	105.9
Size:	Coarse	310(A1)	D	11.6	21.9	1.5	8.5
Pressure:	500 psig	RA-333	DD	34.2	17.2	2.2	15.3
Temp.:	1800°F	LM-1866	LM	11.6	88.1	1.9	79.9
H ₂ S:	1.0 v/o	446	K	86.6	211.7	9.2	88.2
Velocity:	100 fps	671	M	38.5	27.3	1.8	13.3
Time:	150 of	188	XX	54.3	81.9	3.7	26.7
	200 hr	Co-Cr-W No. 1	3Z	21.8	-11.8	0.6	10.3

Alloy
Series: A

Neg. No. 53750

1X

Figure 4-9. Summary of gravimetric, micrometric, and photographic data from test HP35 after 150 hr.

and 0.4 mil in 50 hr and 8.5 and 10.3 mils in 150 hr, respectively. The least resistant alloys, which are still in the test, are 310 and 446. These lost 28.3 and 4.0 mils after 50 hr and 105.9 and 88.2 mils after 150 hr.

PROJECTED WORK FOR NEXT QUARTER

The next quarter should see the completion of the 1981 test plan for both units barring any unforeseen equipment problems. Analysis of the data should also be completed and will be reported on in the annual report.

ANL-4.3.6 -- FAILURE ANALYSIS OF COMPONENTS IN COAL GASIFICATION SYSTEMS

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SUMMARY OF CURRENT ACTIVITIES

The analysis of a failed spent char transfer line assembly from the IGT HYGAS Pilot Plant is presently being completed. This line is used to transport spent char discharged from the bottom of the last stage of the gasifier. Under typical operating conditions, spent char at 820 to 980°C (1500 to 1800°F) falls down the vertical portion of the line through a char discharge control valve. This vertical line joins a horizontal line at a tee junction, and at this point the char is met by a stream of saturated steam at 288°C (550°F) and approximately 6.9 MPa (1000 psi) pressure, which transports the char downstream for disposal. The 7.6-cm (3-in.)-dia Schedule 80 pipe used to fabricate the vertical and horizontal lines in the assembly was originally made of Incoloy 800. However, after a previous failure of the line in 1976, most of the Incoloy 800 piping was replaced with RA330. At the time the present failure occurred, the only Incoloy 800 piping remaining in the assembly was a section approximately 32.5 cm (12.9 in.) long located immediately adjacent to the hub downstream from the tee. The hub, which is a standardized component supplied by a commercial vendor, is made of Type 316 stainless steel.

The present failures occurred at three locations in the horizontal line of the assembly downstream from the tee. The first of these locations was at the Type 316 stainless steel hub. A through-wall crack extending around approximately 65 to 70 percent of the circumference of the hub was present here at a region of apparent stress concentration. Also present were numerous shallower parallel circumferential cracks located upstream from the large through-wall crack. A through-wall crack about 4 cm long was also present at the second failure location, a

circumferential weld approximately midway between the tee and the hub on the downstream side of the horizontal line. The crack lies very near the weld fusion line. The final crack detected was located in the horizontal line at the point where the vertical line is slipped into it. The horizontal line contains a cutout at this location, and the crack was present near the bottom of the cutout. Deformation visible at the crack tip indicated that the fracture was ductile rather than brittle.

Although the analysis of this series of failures is not yet completed, sufficient evidence has been obtained from metallographic and scanning electron microprobe analyses to reach some tentative conclusions. Fatigue striations present over a portion of the fracture surface of the through-wall crack in the hub indicate that fatigue, probably associated with cyclic bending due to thermal stresses, contributed to the failure. However, extensive grain-boundary penetration by sulfur is observed in the hub, and sulfidation appears to have played the dominant role in the hub cracking. The cracks observed at the other two locations in the line are attributed to tensile thermal stresses. At the midpoint between the tee and the hub, the circumferential crack initiated at an undercut at the edge of the final weld pass, and the crack at the cutout at the tee was located at a point of stress concentration due to the geometry of the component.

A more detailed description of the work performed during the current quarter will be published elsewhere.¹

¹Materials Technology for Coal-conversion Processes, Progress Report for July-September 1981, Argonne National Laboratory Report ANL/FE-82-1 (in preparation).

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PART IV — MATERIALS FOR HEAT ENGINES AND HEAT RECOVERY

NBS-5.2.10 -- HIGH TEMPERATURE APPLICATIONS
OF STRUCTURAL CERAMICS

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INTRODUCTION

The achievement of higher efficiency thermochemical engines and heat recovery systems requires the availability of high temperature, high performance structural materials. Structural ceramics such as SiC, Si₃N₄ and certain Al₂O₃-Si₃N₄ combinations have received particular attention for these applications due to their basic characteristics of good strengths coupled with good corrosion and thermal shock resistances. Even with these positive attributes, improved reliabilities and extended lifetimes under service conditions are necessary for structural ceramics to gain industrial acceptance and use. The problems are mechanical and/or chemical in nature and are enhanced by the fact that these materials are subjected to high temperatures, reactive environments and extreme thermal gradients.

With an objective of improved performance for heat engine/heat recovery applications the NBS program on structural ceramics addresses these problems through the determination of the critical factors which influence mechanical and microstructural behavior. The activities of the program are grouped under four major subtasks with each designed to develop key data, associated test methods and companion predictive models. The status of the subtasks are detailed in the following sections.

NBS 5.2.10(A) - HIGH TEMPERATURE FRACTURE OF STRUCTURAL CERAMICS

RESULTS FROM PRIOR QUARTERS

Four-point bend tests on notched bars of Si_5AlON_7 were completed and the results compared with previous work on an yttria-doped SiC (NCX34) and with literature values for Si_3N_4 . Reduced scale testing rigs using SiC were manufactured to test small billets of experimental materials. Fifteen different compositions of Si_3N_4 + Y.A.G. materials obtained from Professor Tien of University of Michigan using these rigs were tested at 1300 °C in order to avoid oxidation. Further studies of Tien's Si_3N_4 were conducted to ascertain critical stress intensity factors and to clarify some inconsistencies in earlier results. A literature survey of available data on fracture toughness, crack growth behavior and creep properties of SiC, Si_3N_4 and sialon was completed. Four-point bending tests under constant displacement rate were performed on several SiC and sialon specimens. For α -SiC tested in air, the results showed little oxidation and high resistance to slow crack growth up to 1300 °C. For sialon specimens ($\text{Si}_{6-z}\text{Al}_z\text{O}_z\text{N}_{8-z}$), it was found that as z increases, the susceptibility to crack growth and oxidation decreases.

The asymptotic behavior of the stress intensity factor as a function of crack length for 4-point bending at small and large crack lengths was investigated in more detail. This work is useful for future numerical solution schemes. Also, an analysis of load-deflection curves which compute crack growth behavior (V-K) without requiring a knowledge of Young's modulus or machine compliance was completed.

High temperature four-point bending tests under constant displacement rate condition have been performed on notched reaction sintered SiC specimens. Several ways of initiating cracks were tried before a chevron notch was utilized. This produced a stable crack growth period and a sharp crack.

A paper entitled "Slow Crack Growth in Sialon" was presented at the International Symposium on Fracture Mechanics of Ceramics, University Park, Pennsylvania July 17, 1981. A paper entitled "Effects of Deformation on the Fracture Behavior of Si_3N_4 and Sialons" was presented at the 2nd NATO

Advanced Study Institute held at Falmer, England from the 27th of July to the 7th of August, 1981. Both of these papers presented work which came partly from this task.

DISCUSSION OF CURRENT ACTIVITIES

Further analyses of the four-point bend test were completed. One analysis allows the determination of the tensile creep behavior from flexural testing of trapezoidal cross-sections. A further analysis deducing tensile behavior from bending and compression tests will be finished shortly. These results will be written up and published. A sensitivity analysis just performed on four-point bending allows us to judge what type of crack growth behavior we may be able to measure properly in flexure. Materials not having these crack growth characteristics require a mechanically more stable test specimen such as the double-torsion specimen. This has proved to be the case for α -SiC and we are now fabricating these sorts of specimens from this material. We are still awaiting the delivery of β -SiC to complete work on this material. In the meanwhile, we are working ahead on the properties of the siliconized silicon carbide.

NBS 5.2.10(B) - CRACK GROWTH MECHANISM MAPS

RESULTS FROM PRIOR QUARTERS

Preliminary maps for Si_3N_4 have been drawn. A computer program for automatically drawing maps from K-V data has been written. Data for SiC has been collected with the aim of constructing a crack growth mechanism map. An evaluation of K_{IC} was made because its definition by ASTM E-399 conflicts with common usage in the ceramic community. A preliminary crack growth mechanism map for a commercial hot pressed SiC was constructed from published information. The literature survey of fracture and crack growth mechanisms was completed for SiC, Si_3N_4 and sialon.

A crack growth model based on diffusion mechanisms was developed. The model entails a grain-boundary crack growing in steady state due to applied stress by stress assisted surface and grain-boundary diffusion. By further assuming the grain on either side of the crack behaves elastically, the model predicts a unique K-V relationship and a threshold K below which no crack growth will take place. A comparison of this prediction to a set of creep crack growth data on sialon at 1400 °C showed good agreement.

The paper entitled "A diffusive crack growth model for creep fracture" (NBSIR 81-2255) was accepted for publication in J. Am. Ceram. Soc.

An investigation into the energy release rate of this crack growth model was included in this paper. The results show that J is the total amount of energy consumption rate which consists of a portion consumed in the creation of new crack surfaces and the remaining portion dissipated in the matter transport processes.

The theoretical prediction of V-K functional relationship based on diffusion-controlled crack growth was mapped into K-T space in order for the future data to fit in the diffusive crack growth area of the mechanism maps.

A paper entitled, "Crack Growth Mechanism Maps" was published in Advances in Fracture Research. This paper describes the concept of crack growth mechanism maps and details their construction.

DISCUSSION OF CURRENT ACTIVITIES

Data obtained in part A above is being analyzed here in order to construct a crack growth mechanism map for NCX34. Since this material (i.e., Y_2O_3 doped silicon carbide) is one of the most promising nitrogen ceramics, the map may prove very useful.

Due to the work performed in this DoE sponsored research project, the investigators were invited to participate in a recent NATO Advanced Study Institute on nitrogen ceramics. Also, we have been invited to present our work on time dependent failure mechanisms in silicon carbide to next summer's Gordon Conference on ceramics. Much of the work to be presented directly emanates from this DoE project. Our main emphasis in the review

and evaluation of crack growth theories has been in diffusive crack growth theories. We believe that this is the long term mechanism of failure and, hence, the one of technological importance.

NBS-5.2.10(C) - MICROSTRUCTURE AND PHASE ALTERATION

RESULTS FROM PRIOR QUARTERS

X-ray analyses were performed on various sialon and as-received silicon carbide samples. Also, preliminary x-ray data were obtained on alpha silicon carbide oxidized in the temperature range from 1200 to 1500 °C.

A literature survey was begun to collect references on the oxidation and the high-temperature thermal and mechanical properties of silicon carbide.

A concept for a high-temperature x-ray furnace was developed in which the sample serves as the heating element.

DISCUSSION OF CURRENT ACTIVITIES

Phase Analysis

The various SiC polytypes, including β -SiC, can be indexed on hexagonal unit cells which differ principally in the stacking in the c-axis direction. In considering the structural polytypes of SiC, it is convenient to focus on the placement of Si-atoms, since the C-tetrahedra can be referenced with respect to the Si-sublattice. The Si-atoms can assume either a cubic packing or a hexagonal packing in the c-axis direction. The SiC polytypes are a consequence of various combinations of these two types of packing [1].

In view of the number of potential structures, it appears advisable to use a structural analysis procedure which takes account of these structural variations in a fundamental manner. Such a procedure is one that assigns occupation probabilities to each lattice site in the (001) planes above the first two fiducial planes for which the site occupations are

defined, a priori. This procedure recognizes that the x-rays inherently average over many unit cells so that occupation probabilities are consistent with the method of measurement. The resulting theoretically calculated structure factors and predicted diffraction pattern will have diffraction maxima which correspond to the range of structural polytypes, but each maxima will have a weight, or composite probability, assigned to it. Among peaks characteristic of a given polytype, relationships between the composite probabilities are to be expected. Comparison of observed peaks and peak intensities with the predicted pattern will establish the set of polytypes which are consistent with the data and will indicate those peaks which are assignable to impurities. It is also expected that this analysis can be employed in oxidation studies to target groups of peaks for observation during the oxidation process. Such an approach may identify those polytypes which are most subject to oxidation.

Theoretical calculation of the structural factors and predicted x-ray diffraction pattern are now in progress.

Structural Ceramics Bibliography

A structural ceramics bibliography is attached. Although SiC and oxidation studies were emphasized in the literature search, references also were collected for Si_3N_4 and Si_3N_4 -oxide systems and for other properties.

High-Temperature X-ray Diffraction

Designs for a high-temperature x-ray diffraction furnace were prepared. These include drawings for the furnace housing (cover and endplate) and the ceramic insulation.

Oxidation Studies

SiC sample holders and setter plates were prepared and conditioned at 1500 °C. Currently, two furnaces for this study are being relocated to another laboratory, and work on this study is suspended until suitable

electrical power is installed.

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NBS-5.2.10(D) - MICROSTRUCTURE AND FRACTURE IN REACTIVE ENVIRONMENTS

RESULTS FROM PRIOR QUARTERS

An apparatus for mechanical testing structural ceramics in gaseous combustion products at temperatures up to 1400 °C has been designed, and the components required to construct the apparatus have been ordered from commercial suppliers. The apparatus includes a laboratory box furnace which is gas tight, a gas blending system which can control the flow and composition of a mixture of 5 gases (SO_2 , H_2O , CO_2 , O_2 , and N_2), and an existing, displacement rate controlled, loading machine. The furnace will provide a 6 inch cube cavity that is heated electrically by molybdenum disilicide elements. The gas mixture at nominally one atmosphere pressure will flow through the furnace cavity. The gas blending system controls the flow of each gas component by the thermal conductivity of its mass.

DISCUSSION OF CURRENT ACTIVITIES

The furnace system is under construction by its manufacturer. We have conferred with the manufacturer to have the furnace modified so that load bearing rods can be introduced through top and bottom ports of the furnace. Regular access to the furnace cavity for placement of a test specimen between the bearing rods is made through a sealed, water-cooled front door.

Gas tight fixtures were designed for attachment to the top and bottom furnace posts so that loading could be transferred from the test machine to a specimen in the furnace. Commercial flanges and bellows required for the fixtures were obtained. Accessory components are presently being machined to hold the bearing rods. All of these parts will then be welded together to make the fixtures.

The commercial gas blending system was delivered. The system includes separate controllers which maintain the flow of each gas individually over a specified flow range before blending. Unfortunately, the supplier inadvertently transposed the ranges requested for SO_2 and N_2 . The units for these two gases were returned for recalibration.

Alteration of the laboratory room facilities were initiated to provide power and cooling-water to the furnace and to exhaust the flow of gas from the furnace out of the room.

Although construction of the apparatus is not yet completed, we expect that its assembly will soon be underway and its operation will be verified on schedule by December 1981.

ORNL-5.2.10 - MATERIALS FOR CERAMIC HEAT EXCHANGERS

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INTRODUCTION

The use of structural ceramics in heat exchanger (HX) applications must consider not only the long-term stability of these materials in the severe environments of coal-fired systems but also the microstructural-compositional factors that influence their chemical and mechanical response under such conditions. To this end, mechanical properties of several commercial silicon nitride and carbide ceramics are being examined before and after exposure to the hot combustion product environment of various coal-oil mixtures (COM) having different coal ash compositions.

In Combustion Exposure Test 2 (CE 2), flexural specimens are being studied for microstructural-compositional and mechanical changes brought about by long-term exposure at about 1220°C to the slag from the combustion of a basic COM.

RESULTS FROM PRIOR QUARTERS

In previous quarters, the fracture strengths before and after exposure to acidic COM in CE 1 of several SiC and Si₃N₄ ceramics were characterized. At the same time, the microstructure of and the nature of second phases present in the as-received materials were analyzed, and mechanisms responsible for the strength degradation as a result of the CE-1 exposure have been sought by examining the changes in the second phases present in the as-exposed ceramics. In the last quarter, the effects of impurities on enhancing the surface oxidation of SiC and Si₃N₄ ceramics were discussed.

DISCUSSION OF CURRENT ACTIVITIES

During this quarter, the second combustion exposure test (CE-2) was completed. This test exposed Si_3N_4 and SiC ceramics (Table 1) in contact with the slag formed by the combustion of a mixture of 20 wt % basic coal in fuel oil (No. 6) for approximately 240 h at an average temperature of 1230°C . Specimens to be used for posttest measurement of flexure strengths were placed in the flue of the combustion chamber [Fig. 1(a)] and, thus, were exposed to the effects of the gas and particulate flow of the exit stream. During the first 60 h of CE-2, visual observations revealed a rapid corrosion rate and loss of some samples — some presumably by movement of the fixtures and the effects of the exit gas stream [Fig. 1(b)]. After 70 to 85 h of exposure at the maximum temperature, none of the samples were observed in the test fixtures [Fig. 1(c)]. At the conclusion of the test, analysis of recovered samples gave graphic evidence of the extreme rate of corrosion (Fig. 2). In fact, only about 6 samples of the original 32 appear to have been displaced from the fixtures either by the force of the exit gases or by motion of the fixture during heatup. The remainder were lost by thinning of the samples from the corrosive action of the basic slags.

Table 1. Four-point flexure strengths, MPa

Specimen	As-received	After CE-1	After CE-2
KT SiC ^a (siliconized SiC)	209.1 ± 39.6 ^b	195.7 ± 28.0	
NC-203 SiC ^c (hot-pressed SiC)	593.0 ± 86.5 ^b	440.5 ± 30.0	365.9 ± 120.5
Hexalloy ^a (sintered α -SiC)	367.9 ± 52.5 ^b	208.6 ± 40.0	277.7 ± 26.2
SNN 522 ^d (sintered Si_3N_4)	514.3 ± 65.3 ^b		
NC-132 Si_3N_4 ^c (hot-pressed Si_3N_4)	851.2 ± 54.9	298.1 ± 14.2	
NCX-32 Si_3N_4 ^c (hot-pressed Si_3N_4)	808.1 ± 69.1	320.6 ± 34.9	

^aProduct of Carborundum, Niagara Falls, N.Y.

^bTest specimen from new lot.

^cProduct of Norton Company, Worcester, Mass.

^dProduct of AirCasting Company, Torrance, Calif.

(a)

(b)

(c)

Fig. 1. View of test specimen from exit side of flue. (a) Before start of test. (b) After approximately 60 h of exposure, some samples still remain in test fixtures; these are primarily SiC materials; note the slag accumulation on the remaining specimen. (c) After completion of exposure to the slag formed by the combustion of the basic coal-oil mixture, all the specimens in the test fixtures were displaced.

Fig. 2. Test specimen fixture after CE-2 exposure. The remainder of the flexure bars are in the horizontal groove in the fixture. Two flexure bars, each having one extremely tapered end, are embedded in the slag just above the groove.

The samples that fell from the fixture in the initial stages and, thus, were exposed to the basic slag but not to the erosive effects of the exit gases were recovered from the combustion chamber. Initial measurements of the strengths of these as-exposed flexure bars are shown in Table 1. The corrosive effects of the basic slag led to strength losses of about 25% for the sintered α -SiC* and 38% for the hot-pressed NC-203† SiC. As seen in Table 1, the strengths retained after exposure to the basic slags at 1230°C are comparable to the values for the same silicon carbide ceramics after exposure to acidic slag at 1220°C in CE-1. However, the surface recession rates of the ceramics are much greater in the basic slag conditions than are those observed in the acidic slag conditions. This trend is expected because the silicate layer that forms on the surface of the SiC and Si₃N₄ ceramics in oxidizing conditions will be more reactive with the basic slag and hence offer less protection for the underlying ceramic.

Current efforts are focused on characterizing the corrosion products formed on the surface and within the interior of the ceramics exposed in CE-2. Laboratory furnace facilities are also being readied to expose these same materials to the basic slag under oxidizing conditions to characterize completely the degrading effects of the basic slag. In addition, long-term 2000- and 5000-h oxidation exposures have been initiated on these same ceramics to determine the microstructural and property changes that can occur and to relate these to the initial composition. Such data are needed because the stability of these materials during oxidation changes with time and because little or no data exist for exposures above 1000 h. Understanding the role of the initial densification additives and impurities in the SiC ceramics on the long-term mechanical reliability is required to achieve improvements in materials.

*Product of Carborundum Corporation, Niagara Falls, N.Y.

†Product of Norton Company, Worcester, Mass.

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PART V — MATERIALS FOR COMBUSTION SYSTEMS

ANL-6.1.4 - CORROSION OF ALLOYS IN FBC SYSTEMS

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SUMMARY OF CURRENT ACTIVITIES

The purposes of this program are to (1) experimentally evaluate the high-temperature corrosion behavior of iron- and nickel-base alloys in simulated combustion gas environments with a wide range of oxygen and sulfur potentials, and (2) evaluate deposit-induced hot-corrosion behavior of heat-exchanger and gas-turbine materials with and without coatings after exposure to multicomponent gas environments.

Deposit-induced hot-corrosion behavior of heat-exchanger and gas-turbine materials exposed to multicomponent gas environments is of considerable interest in advanced energy systems that utilize fossil fuels. For this purpose, characterization of environments in direct-combustion processes and evaluation of materials exposed to complex gas mixtures that simulate normal operating conditions and off-normal excursion situations are needed. In fluidized-bed combustion systems, the presence of sulfated limestone and the low oxygen partial pressure lead to deposition of CaSO_4 . The presence of locally reducing oxygen partial pressures in the vicinity of the deposit can lead to sulfidation/hot corrosion of the heat-exchanger tube surface.

During this reporting period, experiments have been conducted to evaluate the relative contribution of gas-phase interactions and that of sulfated limestone deposit on the corrosion behavior of potential candidate heat-exchanger materials. For this purpose, ring specimens of carbon steel, Fe-2½Cr-1Mo and Fe-9Cr-1Mo ferritic steels, Type 310 stainless steel, and Incoloy 800 with coatings of reagent grade CaSO_4 have been exposed to an argon environment for 500 h. The gas temperature was maintained at 1123 K while the metal temperatures were controlled at 977 and 866 K in two different specimen probes. Upon completion of the exposures,

cross sections of the tube specimens were examined using a scanning electron microscope (SEM) equipped with an energy dispersive x-ray analyzer and an electron microprobe to identify the type and location of different corrosion product phases in the scale layers.

Figure 1 shows the specimen images for Incoloy 800 and Type 310 stainless steel in the uncoated condition after exposure to an O_2 - SO_2 gas mixture in run 115. The alloys exhibited 3 to 4- μ m-thick chromium-rich oxide layers after exposure, with virtually no sulfur penetration. Figure 2 shows the specimen image and the elemental mapping for Type 310 stainless steel in the $CaSO_4$ -coated condition after a 500-h exposure in Run 125 to the same gas mixture as in run 115. In this experiment, the interaction of $CaSO_4$ deposit with the alloy results in a nonprotective Cr-rich oxide layer, with significant sulfur penetration. The scale thickness and the depth of sulfur penetration observed in the 500-h exposures are small, but there are indications that the mode of interaction in the presence of deposit under heat-flux conditions will be more degrading than in the absence of deposit. To establish the relative influence of the gas-phase environment and the deposit on the mode of interaction, experiments have been conducted on $CaSO_4$ -coated specimens in an argon environment. Figure 3 shows the specimen image and the elemental mapping for Type 310 stainless steel in the $CaSO_4$ -coated condition after exposure to an argon environment in run 130. The photographs indicate a duplex scale layer consisting of outer chromium oxide and inner chromium-rich sulfide. As the sulfur concentration decreased towards the base metal, chromium sulfides were observed, predominantly at the grain boundaries. The preliminary results presented thus far clearly show that the $CaSO_4$ deposits can have a profound effect on the type and morphology of scales developed in candidate heat-exchanger materials.

Similar experiments are being conducted with the above materials to establish the effects of multicomponent gas mixtures, metal and gas temperatures, heat flux, type of deposit, and deposit sequence on the oxidation/sulfidation behavior of heat-exchanger materials.

A more detailed description of the work performed during the current quarter will be published elsewhere.¹

Fig. 1. SEM Photographs of Incoloy 800 and Type 310 Stainless Steel Specimens after 500-h Exposure to an O_2 - SO_2 Gas Mixture in Run 115.

¹Materials Technology for Coal-conversion Processes: Progress Report for July-September 1981, Argonne National Laboratory Report ANL/FE-82-1 (in preparation).

Fig. 2. SEM and EDX Photomicrographs of $CaSO_4$ -coated Type 310 Stainless Steel Specimen after 500-h Exposure to O_2 - SO_2 Gas Mixture in Run 125.

Fig. 3. SEM and EDX Photomicrographs of CaSO_4 -coated Type 310 Stainless Steel Specimen after 500-h Exposure in an Argon Atmosphere in Run 130.

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GA-6.1.4 - MATERIALS TESTING IN AN ATMOSPHERIC
FLUIDIZED-BED COMBUSTOR

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INTRODUCTION

The objective of the Materials Test Program at General Atomic Company was to determine the mechanism of calcium sulfate film formation on cooled and uncooled heat transfer surfaces in an atmospheric fluidized-bed combustor. The tests included combinations of various fuels, sorbents, sulfur sources, and water sources to study their possible interactive effects.

RESULTS FROM PRIOR QUARTERS

None.

DISCUSSION OF CURRENT ACTIVITIES

The AFBC Materials Test Program at General Atomic Company was performed June 1 - September 30, 1981. Thirteen 8-hour tests were conducted in a 16-inch diameter fluidized-bed combustor. Table 1 shows the Test Matrix and the major process variables that were held constant in each test. Issuance of a topical report is in progress.

Test Description

The calcium sulfate film which formed on in-vessel heat transfer surfaces by burning Kentucky No. 9 coal with limestone served as a "base case" against which film produced in the other tests were compared. The films were categorized according to location in the burner vessel, type of heat transfer surface, and relative amount and consistency of deposited material. In-vessel heat transfer surfaces included water-cooled tubes both in-bed and in the freeboard, an air-cooled tube in-bed, and uncooled

Table 1
Test Matrix

Test No.	Fuel	Sorbent	Sulfur Source	Water Source	CaSO ₄ Film Deposit on In-Bed H ₂ O-Cooled Tube
1	Kentucky No. 9 Coal	Limestone	Fuel	Fuel	Thick Film
2	Propane	-	Gypsum	Fuel	Traces of Thick Film
3	Propane	Limestone	SC ₂ Gas	Fuel	Thick Film
4	Propane	Limestone	SC ₂ Gas	Steam/Fuel	Thick Film
5	Graphite	-	Gypsum	-	None
6	Graphite	Limestone	SO ₂ Gas	-	Thin Trace of Film
7	Graphite	Limestone	SO ₂ Gas	Steam	Thick Film
8	Coke/Graphite	Limestone	Fuel	-	None
9	Coke/Graphite	Limestone	Fuel	Steam	Thin Film
10	Coal Tailwashings	-	Gypsum	Fuel (low)	None
11	Coal Tailwashings	Limestone	SO ₂ Gas	Fuel (low)	Semi-Thin Film
12	Coal Tailwashings	Limestone	SO ₂ Gas	Steam/Fuel (low)	Thick Film
13	Kentucky No. 9 Coal	Dolomite	Fuel	Fuel	Thick Film

Process Conditions To Be Held Constant

Bed Temperature: 1600°F
 Superficial Velocity: 6 ft/sec
 Excess Air: 20%
 Bed Depth: 4 ft
 Recycle of Elutriated Fines: None

tubes in-bed, in the freeboard, and in the bed disengaging zone (splash zone).

Fuels for the tests included Kentucky No. 9 coal, propane, graphite, syncrude coke (high-sulfur), and coal tailwashings (low-sulfur, high-ash). Limestone and dolomite served as sorbents. The sulfur sources included fuel-sulfur, bottled SO_2 gas, and granular gypsum. The water sources consisted of fuel-hydrogen and steam injection to the bed.

Results

The test results strongly indicate that water plays an important role in the mechanism for calcium sulfate film deposition on heat transfer surfaces in a fluidized-bed combustor. Deposits formed on the water-cooled tubes in Test 2. This test was fueled by propane (water is a product of combustion). In a similar test (Test 5), graphite was burned (absence of water) and no film deposited on any of the in-vessel heat transfer surfaces. In both tests, the only source of sulfur was in the granular bed ash (gypsum), with the differences between the two being the presence/absence of water and gaseous/solid fuel.

Tests in which water (either fuel-H and/or steam) and sulfur (either fuel-S and/or SO_2 gas) were both added produced the greatest amounts of calcium sulfate deposit on water-cooled tubes in the burner--Tests 1, 3, 4, 7, 9, 12, 13. The results of each test are described in terms of the amount of calcium sulfate deposited on the in-bed water-cooled tubes, since these tubes accumulated the most significant amount of film over the duration of each test. Traces of calcium sulfate film were observed in tests where sulfur dioxide gas (little or no fuel-S) was added, with minimal amounts of water (low fuel-H, no steam)--Tests 6, 11. Test 8, in which fuel-sulfur (no SO_2 gas) was added with only a minimal amount of water (low fuel-H, no steam), no calcium sulfate film formed on any of the heat transfer surfaces. No calcium sulfate film deposited on the tubes in tests where no water (very low fuel-H, no steam) was added and the main source of sulfur was in the granular bed ash (gypsum)--Tests 5, 10. Test 2

was the only test in which the sole source of sulfur was the granular bed ash (gypsum), yet calcium sulfate film deposited on the heat transfer tubes. This is probably due to the large amount of water generated with the combustion of propane.

Little or no deposits formed on air-cooled or uncooled tubes in any of the tests. A thin crusty layer of material (ash, char, calcium sulfate, unreacted limestone) formed on the water-cooled tubes in the freeboard in all the tests.

The color of the calcium sulfate film deposits ranged from a dull, rust-red to a highly-polished black. No discernable metal wear or corrosion was apparent on any of the in-bed or freeboard heat transfer tubes over the duration of the test program.

ORNL-6.1.4 - HEAT EXCHANGER AND INTERNAL
STRUCTURAL MATERIALS FOR AFBC

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INTRODUCTION

The objective of this research has been to study the oxidation-sulfidation of atmospheric fluidized-bed combustor (AFBC) heat exchanger materials. A consistent observation derived from in-bed surveillance examinations has been the presence of well-developed, contiguous CaSO_4 coatings on all heat exchanger and associated hanger surfaces exposed to the fluidized-bed environment. These coatings are potentially important because they react with the normally protective oxides produced at the metal surface and may lead to increased oxygen and sulfur activities within the oxide compared to the nominal activities in the fluidized bed.

RESULTS FROM PRIOR QUARTERS

Two types of experiments have been performed. In the first, alloy specimens are exposed to a range of oxygen and sulfur gas pressures, which are representative of the gas conditions in an AFBC. After the exposure the alloys have been subjected to metallographic analysis. In the second the reactions between CaSO_4 and Fe, Ni, Co, Cr, 304 stainless steel, 2 1/4 Cr-1 Mo steel, 9 Cr-1 Mo steel, and alloy 800 were studied by differential thermal and thermogravimetric analyses. These reactions were studied because CaSO_4 is present as a coating on the heat exchangers in AFBCs which utilize limestone as a sulfur sorbent.

DISCUSSION OF CURRENT ACTIVITIES

Attempts to grow a CaSO_4 film by a gas transport process (by the transport of calcium as the gaseous hydroxide) were not successful. To

determine that the film in an atmospheric fluidized-bed combustor (AFBC) is formed by direct contact between CaSO_4 and heated components in the bed, a glass fluidized bed was constructed. In these experiments a type 308 stainless steel wire was suspended in the bed and heated resistively to 500 or 800°C. The bed material was either CaSO_4 or the CaO-CaSO_4 eutectic composition. After each experiment the wire was examined optically, and that part of the wire immersed in the bed was compared with a section of the wire at the same temperature but protected by an alumina sheath. The results of these experiments show that, in the absence of combustion, a CaSO_4 film can be formed on a heated substrate. The film does react with the substrate, and CaO added to the bed accelerates the attack. For example, when the substrate at 800°C was suspended in the CaO-CaSO_4 bed for 10 h, a thick film formed with sufficient metal thinning to cause a temperature increase of about 100°C.

The equipment to measure the rate of reaction when the P_{O_2} and/or P_{S_2} is rapidly changing is now complete and operational. The pulsing valves have been added, and preliminary tests show that the valves and the mounting gaskets are leakfree. With the entire system evacuated to about 13.3 mPa (10^{-10} torr), a valve pulse of about 1 m/s causes a pressure rise to 13.3 mPa (10^{-4} torr). The valve input was at about 133 kPa (10^3 torr). Because this pressure rise is close to the shutoff pressure of the mass spectrometer, a gas system has been built to reduce the input pressure. The gas system will use the liquid-gas equilibria to reduce the input pressure. For example, the vapor pressure of oxygen at liquid nitrogen temperature is about 1.3 kPa (10 torr). If a region of the gas system is held at liquid nitrogen temperature, the input oxygen pressure is about 1.3 kPa (10 torr). This gas system has been attached to the main system and is being tested.

The abstract of a completed paper on the reactions between nickel or cobalt with their sulfates follows.¹

A differential thermal-thermogravimetric analysis (DTA-TGA) study shows that both nickel and cobalt react with their respective sulfates to form oxide (NiO or CoO) and sulfide (s) (Ni_3S_2 or Co_9S_8 and Co_4S_3). In the case of the $\text{Ni} + \text{NiSO}_4$ reaction, it is clear that the reaction occurs at $T < 530^\circ\text{C}$ as a solid state process. A similar reaction

process is proposed for $\text{Co} + \text{CoSO}_4$. These reactions are briefly discussed with respect to studies of the oxidation-sulfidation of cobalt and nickel, and it is proposed that the rate-determining step in these studies is the formation of the sulfate.

REFERENCE

1. P. J. Ficalora, "Solid State Sulfidation of Nickel and Cobalt - Reactions Between the Metals and Their Sulfates," to be submitted for publication in the open literature.

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