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**MATERIALS SCIENCE DIVISION
COAL TECHNOLOGY
SEVENTH QUARTERLY REPORT,
APRIL-JUNE 1976**

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ARGONNE NATIONAL LABORATORY, ARGONNE, ILLINOIS

Prepared for the U. S. ENERGY RESEARCH

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Argonne, Illinois 60439

MATERIALS SCIENCE DIVISION
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APRIL-JUNE 1976

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HIGHLIGHTS

Task A -- Evaluation of Ceramic Refractories for Slagging Gasifiers
(D. Stahl)

The second run of the slag-abrasion-corrosion rig has been completed, and the analysis of the 15 refractory samples has begun. Preliminary analysis indicates that the magnesia-chrome, chrome-bonded alumina, and fusion-cast spinel bricks have substantially better abrasion-corrosion resistance than the other compositions.

Task B -- Evaluation of Ceramic Coatings for Coal-conversion Plants
(D. Stahl)

Thermal-shock testing has indicated that resistance to spalling can be improved with the use of graded alumina-chromia and magnesia-alumina multi-layer coatings. The first corrosion-erosion test run for a total of 100-h exposure has been completed by Solar, Inc. Of the ceramic coatings, only magnesium zirconate survived the exposure. The refractory specimens exposed simultaneously with the coated metal specimens exhibited moderate or no attack.

Task C -- Nondestructive Testing of Coal-plant Components
(W. A. Ellingson, G. C. Stanton, W. J. Shack, and N. P. Lapinski)

The in-situ erosion measuring system for the main coal feed line for the Synthane coal-gasification pilot plant has been installed and initial tests have been completed. Erosion measurements will be continuously obtained from the ultrasonic pulse-echo system to map the erosion pattern and establish erosion rate.

Various transducers have been evaluated to establish the frequency content of gas flows through simulated valve leak geometries. Spectral analysis has been used to establish resonant frequencies of the mounting fixtures and

open-end tube resonances and verify the resonant frequencies of the transducers. Quantitative analysis of the thermal profiles of erosion specimens has been enhanced by development of an isometric computer display of resultant thermal images. These image displays will be employed on studies of thermal-contact resistance. Gamma-radiography results have clearly established the application of this technique for refractory bore definition and refractory patching identification. Field results on both the Morgantown stirred-bed gasifier off-gas line and the Bi-Gas pilot plant have shown that gamma radiographs establish crack patterns in refractories and the wall thickness of water-coolant tubes.

Task D -- Corrosion Behavior of Materials in Coal-conversion Processes
(K. Natesan and O. K. Chopra)

A thermodynamic approach has been developed to characterize the gas environment in different pilot-plant coal-gasification processes. The analysis is used to examine the thermodynamic stability of iron- and nickel-base alloys in these process environments. The results show that the sulfur and oxygen potentials in all the processes are in a region where chromium oxide will be thermodynamically stable. In the absence of a continuous oxide layer, sulfidation of the alloys is expected, which can lead to severe corrosion rates, particularly when liquid nickel sulfides are formed. It is concluded that a protective Cr_2O_3 layer is essential for an effective application of these alloys in coal-conversion processes. An experimental program was initiated to evaluate the effect of multicomponent gas environments on the tensile behavior of selected commercial alloys.

Task E -- Erosion Behavior of Materials in Coal-conversion Processes
(M. M. Mamoun)

The analytical models formulated to determine the erosion rates for various materials used in coal-gasification processes account for the effects of several important variables such as the impact velocity, angle of impingement, size, shape, mass flux, and mass density of the eroding solid particles; mechanical and physical properties of the eroded surface and eroding particles; and operating temperatures.

Task F -- Component Performance and Failure Analysis
(S. Greenberg, C. W. Boquist, D. R. Diercks, J. E. Sanecki, and J. Y. N. Wang)

Failures of HYGAS pilot-plant components resulted from, or were aggravated by, operation under off-design conditions, which resulted in much more corrosive environments than would have occurred under design conditions. Type 310 stainless steel was recommended to provide improved performance of the dip leg in the ash-agglomerating gasifier. In the cases of the coal pretreatment vessel cooler and main gasifier transfer-line expansion joint, it is believed that present materials of construction would be suitable under design conditions.

MATERIALS SCIENCE DIVISION
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Abstract

This progress report summarizes the work performed by the Argonne National Laboratory Materials Science Division for the Advanced Research and Supporting Technology Office of the Fossil Energy Division of ERDA during the period April-June 1976.

Introduction

The present work is being performed by Argonne National Laboratory (ANL) for the Fossil Energy Division of ERDA. This is the seventh quarterly report, for the period from April through June 1976. Progress is reported on each of the six major tasks:

A. Evaluation of ceramic refractories to withstand abrasion-corrosion by coal slag that will be encountered in slagging gasifiers, particularly the Bituminous Coal Research (BCR) Bi-Gas coal-gasification pilot plant;

B. Evaluation of ceramic coatings and refractories for metal parts to increase their resistance to erosion and corrosion in coal-gasification pilot plants;

C. Development, evaluation, and application of nondestructive testing (NDT) methods for use in coal-plant fabrication, construction, and operation to ensure component integrity;

D. Development of computer models to predict the corrosion behavior of materials used in coal-gasification plants;

E. Development of computer models to predict the erosion behavior of materials used in coal-gasification plants; and

F. Analysis of pilot-plant components that have failed or are removed from service for other reasons.

Task A -- Evaluation of Ceramic Refractories for Slagging Gasifiers
 (Principal Investigator: D. Stahl)

During the last three months, run 2, of 500-h duration, was completed in the slag-abrasion-corrosion (SAC) rig. Table I summarizes the results obtained. Samples for slag chemistry changes have been sent out for analysis. Preliminary results on the refractories indicate that the magnesia-chromia brick, chrome-bonded alumina brick, and fusion-cast spinel brick are substantially superior to the other compositions. It would appear that a magnesia-chrome spinel, mixed iron-magnesia/chromia-alumina-iron spinel, or straight magnesia-alumina spinel might prove to be as resistant as the fusion-cast spinel, which showed negligible attack.

The SAC rig is being made ready for run 3. The center rotating holder has been eliminated because of its poor performance in previous testing. (The rotating holder in the center of the rig again broke, after ~150 h of run 2, and dissolved in the slag.) Since the furnace burners fire tangentially, it is thought that the slag motion will be adequate. To corroborate this, the slag velocity near the slag-brick interface will be measured.

The bricks chosen for run 3, all placed on the circumference, are listed below:

1. Magnesia-chrome-alumina	9. Magnesia-alumina spinel
2. Fused-cast chrome-magnesia	10. Magnesia-chrome-alumina
3. Chrome-bonded alumina	11. Chrome-Fe ₂ O ₃ -alumina-magnesia (RAM)
4. Silicon oxynitride	12. Fused-cast alumina
5. Magnesia-chrome-alumina	13. Fused-cast alumina-zirconia
6. Alumina-chrome	14. Alumina-zirconia-silica
7. Magnesia-chrome-alumina-Fe ₂ O ₃	15. Chrome-bonded alumina
8. Magnesia-chrome-Fe ₂ O ₃	

TABLE I. Refractories Exposed in Slag-abrasion-corrosion Rig Run 2^a

Identification Number	Composition	Bond	Location of Specimens	Normalized Material Lost, vol %	Maximum Depth of Penetration, mm	Maximum Depth of Abrasion, mm	Remarks
1	Al ₂ O ₃ (99%)	Sintered ↓	X,Q	28.9	64	57	-
24	Al ₂ O ₃ (97.6%)		X	4.5	~18	17	-
25	Al ₂ O ₃ (99.5%)		X,Q	9.4	76	~25	-
16	Al ₂ O ₃ (90%)-Cr ₂ O ₃ (10%)		X	8.2	~25	~10	-
19	MgO (53%)-Cr ₂ O ₃ (19%)		X	2.3	~10	~5	-
20	MgO (59%)-Cr ₂ O ₃ (19%)		X,Q	1.6	~10	~5	-
91	SiC (79%)-Si ₃ N ₄ (18.5%)		X,Q	~100	64	64	Reduced to metal
93	SiC (73%)-Al ₂ O ₃ /SiO ₂ (14/11)	Chemical ↓ (CA) (RAM) ↓	X,Q	~100	64	64	Reduced to metal
17	Al ₂ O ₃ (85%)-P ₂ O ₅ (3.6%)		X	40.3	76	64	-
28	Al ₂ O ₃ (93.3%)-P ₂ O ₅ (1.2%)		X	20.5	64	33	-
27	Al ₂ O ₃ /Cr ₂ O ₃ (81/10)-P ₂ O ₅ (6.7%)		X	5.9	43	18	-
202	Al ₂ O ₃ (Winnofos Bond)		X	45.5	76	56	-
2	Al ₂ O ₃ (99%)-Na ₂ O (0.4%)	Fusion Cast ↓	X	7.2	~0.5	19	-
4	Al ₂ O ₃ (99%)-B ₂ O ₃ (0.5%)		X,Q	8.3	<2.5	22	-
22	Spinel (65%)-R ₂ O ₃ (~30%)		X,Q	Neg	Neg	Neg	-

^aCA = castable, RAM = ramming mix, X = circumference, Q = rotating shaft, and Neg = negligible.

The question has been raised as to whether a significant temperature gradient exists across the brick during the runs. To determine this, holes will be drilled to the brick cold face and intermediate positions. Thermocouples will be installed to measure (a) cold-face temperatures on bricks of different thermal conductivities and (b) temperature profiles.

Task B -- Evaluation of Ceramic Coatings for Coal-conversion Plants
(Principal Investigator: D. Stahl)

The major activities during the reporting period involved: (1) preparation of various substrate-coating systems; (2) thermal-shock testing of substrate-coating systems; and (3) evaluation of coated specimens and refractories at Solar, Inc. Some corrosion testing was performed this quarter, but the results will be reported in the next quarterly report.

1. Preparation of Coatings

Plasma-spray coatings of various oxides (ZrO_2 , Al_2O_3 , $Al_2O_3-Cr_2O_3$, $MgO \cdot ZrO_2$, $MgO \cdot Al_2O_3$, $Al_2O_3-ZrO_2$, and Y_2O_3) with intermediate layers of either NiCrAl, T800, Co base, or Amdry 348 were prepared. The coatings are listed in Table II. In accordance with previous practice, substrates of Types 304 and 310 stainless steel and Incoloy 800 were employed. In many cases, the coatings were graded by mixing the ceramic and metal intermediate layers in increasing proportion of ceramic up to the fully ceramic top coat. The objective of these graded coatings is to provide a transition between the metal substrate and the poorer thermally expanding ceramic. Some success was achieved in this effort, as observed in the table and discussed in the following section.

TABLE II. Coating Structures and Thermal-shock Test Results

Identification Number	Substrate-coating Systems		Number of Cycles ^a
A30T13	304 SS	-NiCrAl-75% Al_2O_3 + 25% ZrO_2	6 ^b
C30T13	IN 800		6 ^b
E30T13	310 SS		6 ^b
A9T8	304 SS	-NiCrAl-70% NiCrAl + 30% Al_2O_3 -30% NiCrAl + 70% Al_2O_3 - Al_2O_3	3 ^c
C9T8	IN 800		4 ^c
E9T8	310 SS		4 ^c
A10T8	304 SS	-NiCrAl-50% NiCrAl + 50% (Al_2O_3 + Cr_2O_3)-30% NiCrAl + 70% (Al_2O_3 + Cr_2O_3)-50% Al_2O_3 + 50% Cr_2O_3	4 ^b
C10T8	IN 800		4 ^b
E10T8	310 SS		4 ^b
A13T8	304 SS	-NiCrAl-70% NiCrAl + 30% ($MgO \cdot Al_2O_3$)-30% NiCrAl + 70% ($MgO \cdot Al_2O_3$)- $MgO \cdot Al_2O_3$	1
C13T8	IN 800		4 ^b
E13T8	310 SS		4 ^b
A29T8	304 SS	-NiCrAl-70% NiCrAl + 30% (50% Al_2O_3 + 50% ZrO_2)-30% NiCrAl + 70% (50% Al_2O_3 + 50% ZrO_2)-50% Al_2O_3 + 50% ZrO_2	2 ^c
C29T8	IN 800		2 ^c
E29T8	310 SS		1
A9A12	304 SS	-Amdry 348- Al_2O_3	1
C9A12	IN 800		2 ^c
E9A12	310 SS		3 ^c
A12A12	304 SS	-Amdry 348- ZrO_2	1
C12A12	IN 800		2 ^c
E12A12	310 SS		2 ^c
A13A12	304 SS	-Amdry 348- $MgO \cdot Al_2O_3$	1
C13A12	IN 800		2 ^c
E13A12	310 SS		2 ^c
A14A12	304 SS	-Amdry 348- MgO + ZrO_2	1
C14A12	IN 800		4 ^b
E14A12	310 SS		4 ^b
A28A12	304 SS	-Amdry 348- ZrO_2	2 ^c
C28A12	IN 800		2 ^c
E28A12	310 SS		1
A9T28M	304 SS	-NiCrAl- ZrO_2 - Al_2O_3	5 ^c
C9T28M	IN 800		5 ^c
E9T28M	310 SS		5 ^c
A13T28M	304 SS	-NiCrAl- ZrO_2 - $MgO \cdot Al_2O_3$	5 ^c
C13T28M	IN 800		5 ^c
E13T28M	310 SS		5 ^c
A20T28M	304 SS	-NiCrAl- ZrO_2 - Cr_2O_3	1
C20T28M	IN 800		1
E20T28M	310 SS		1
A9VV5-6	304 SS	-Co base-50% Cobalt + 50% Al_2O_3 - Al_2O_3	1
C9VV5-6	IN 800		1
E9VV5-6	310 SS		1
A10VV5-6	304 SS	-Co base-50% Cobalt + 50% (50% Al_2O_3 + 50% Cr_2O_3)-50% Al_2O_3 + 50% Cr_2O_3	1
C10VV5-6	IN 800		2 ^c
E10VV5-6	310 SS		1

TABLE II. Coating Structures and Thermal-shock Test Results (Contd.)

Identi- fication Number	Substrate-coating Systems		Number of Cycles ^a
A13VV5-6	304 SS	-Co base-50% Cobalt + 50% (MgO·Al ₂ O ₃)-MgO·Al ₂ O ₃	1
C13VV5-6	IN 800		1
E13VV5-6	310 SS		1
A14VV5-6	304 SS	-Co base-50% Cobalt + 50% MgO·ZrO ₂ -MgO·ZrO ₂	1 ^c
C14VV5-6	IN 800		4 ^b
E14VV5-6	310 SS		4 ^b
A28VV5-6	304 SS	-Co base-50% Cobalt + 50% ZrO ₂ -ZrO ₂	1
C28VV5-6	IN 800		1
E28VV5-6	310 SS		1
A30VV5-6	304 SS	-Co base-50% Cobalt + 50% Al ₂ O ₃ -Al ₂ O ₃	1
C30VV5-6	IN 800		1
E30VV5-6	310 SS		1
A29TT5	304 SS	-NiCrAl-50% NiCrAl + 50% (50% ZrO ₂ + 50% Al ₂ O ₃)-50% ZrO ₂ + 50% Al ₂ O ₃	2
C29TT5	IN 800		2
E29TT5	310 SS		2
A9D19-7	304 SS	-T800-50% Al ₂ O ₃ + 50% T800-Al ₂ O ₃	1
C9D19-7	IN 800		1
E9D19-7	310 SS		1
A10D19-7	304 SS	-T800-50% (Al ₂ O ₃ + Cr ₂ O ₃) + 50% T800-50% Al ₂ O ₃ + 50% Cr ₂ O ₃	1
C10D19-7	IN 800		1
E10D19-7	310 SS		1
A13D19-7	304 SS	-T800-50% (MgO·Al ₂ O ₃) + 50% T800-MgO·Al ₂ O ₃	1
C13D19-7	IN 800		1
E13D19-7	310 SS		1
A14D19-7	304 SS	-T800-50% (MgO·ZrO ₂) + 50% T800-MgO·ZrO ₂	1
C14D19-7	IN 800		1
E14D19-7	310 SS		1
A28D19-7	304 SS	-T800-50% ZrO ₂ + 50% T800-ZrO ₂	1
C28D19-7	IN 800		1
E28D19-7	310 SS		1
A29D19-7	304 SS	-T800-50% (Al ₂ O ₃ + ZrO ₂) + 50% T800-50% Al ₂ O ₃ + 50% ZrO ₂	1
C29D19-7	IN 800		1
E29D19-7	310 SS		1
A8T10	304 SS	-NiCrAl-75% Cr ₃ C ₂ + 25% NiCr	4 ^c
C8T10	IN 800		4 ^c
E8T10	310 SS		4 ^c
A11T10	304 SS	-NiCrAl-Chromium Carbide-NiAl Blend	6 ^c
C11T10	IN 800		6 ^c
E11T10	310 SS		6 ^c
A12TT5	304 SS	-NiCrAl-50% NiCrAl + 50% ZrO ₂ -ZrO ₂	4 ^c
C12TT5	IN 800		4 ^c
E12TT5	310 SS		4 ^c
A28TT5	304 SS	-NiCrAl-50% NiCrAl + 50% ZrO ₂ -Y ₂ O ₃	4 ^c
C28TT5	IN 800		4 ^c
E28TT5	310 SS		4 ^c

^a Number of cycles survived before spalling.^b No sign of spalling after these cycles; testing was discontinued.^c Specimen developed spalling at edges; testing was discontinued.

2. Thermal-shock Testing

All of the coated specimens prepared during this quarter plus some others were tested for spalling resistance. For these tests, the specimens were cooled in air (~10 min) after furnace soaking at 980°C. The results of the tests are shown in Table II.

The use of Amdry 348, Co base, or T800 as intermediate layers offered no improvement over the NiCrAl previously used. As expected, only the $\text{MgO} \cdot \text{ZrO}_2$ top coats on Type 310 stainless steel and Incoloy 800 were satisfactory. Graded compositions using NiCrAl as an intermediate layer achieved improved results, e.g., alumina-chromia and magnesia-alumina (spinel) in a four-layer coating survived four cycles without spalling. In addition, a ceramic mix of alumina and zirconia on an NiCrAl intermediate layer exhibited excellent thermal-shock resistance by surviving six cycles without spalling. These promising coatings will be next evaluated for corrosion-erosion resistance.

3. Corrosion-erosion Testing at Solar, Inc.

The first corrosion-erosion test run has been completed by Solar, Inc., and a report that covers this portion of the effort has been issued.¹ The test included 15 ceramic-coated specimens, 15 refractory specimens, and a bare Type 310 stainless steel specimen as a reference. Specimen descriptions are shown in Tables III and IV. The total exposure time was 100 h, which consisted of 17-, 33-, and 50-h durations. The short runs were the result of two system failures: failure of O-ring seals on the heater power feedthroughs, which caused severe gas leaks and loss of chamber pressure, and failure of the slinger shaft bearing due to an overload caused by mismatched thermal expansion and a loose slinger. Other problems included excess water condensation and flowmeter blockage due to ammonia reaction products. In all

tests, the temperature was controlled at 980°C (1800°F) and the pressure was maintained at 240 kPa (35 psi). Char particle velocity averaged ~38 m/s (~125 ft/s), and the gas composition, except for steam and ammonia, was close to the ERDA-Metals Properties Council (MPC) composition.

TABLE III. Coating/Substrate Combinations of Metallic Specimens

Identi- fication Number ^a	Substrate	Coating
A9T	304 SS	Al ₂ O ₃
C9T	IN 800	
E9T	310 SS	
A10T	304 SS	50% Al ₂ O ₃ + 50% Cr ₂ O ₃
C10T	IN 800	
E10T	310 SS	
A12T	304 SS	ZrO ₂ cubic stabilized with CaO
C12T	IN 800	
E12T	310 SS	
A14T	304 SS	Magnesium zirconate (MgO·ZrO ₂)
C14T	IN 800	
E14T	310 SS	
A20T	304 SS	Cr ₂ O ₃
C20T	IN 800	
E20T	310 SS	

^aA typical specimen number was A9T-S1, where S1 indicates sample 1.

The results for the ceramic-coated specimens are shown in Table V. Only the specimens coated with MgO·ZrO₂ survived the run. Of these six coating specimens, five survived three thermal cycles and 100 h of erosion/corrosion without obvious spall or coating failure. The sixth specimen did experience a start of coating failure during its second 50 h of exposure. In general, Type 310 stainless steel and Incoloy 800 substrates were superior to Type 304 stainless steel, possibly as a result of their lower thermal expansion.

TABLE IV. Composition (wt%) of Ceramic Specimens

Refractory												Other Oxides
Identi- fication Number	Name	Al ₂ O ₃	SiO ₂	CaO	MgO	TiO ₂	ZrO ₂	Cr ₂ O ₃	P ₂ O ₅	K ₂ O + Na ₂ O	Fe ₂ O ₃	
104	Mono-A2	98.7	0.5	-	-	-	-	-	-	0.03	0.09	0.5 as B ₂ O ₃
102	Mono-A1	99.3	0.08	0.13	-	-	-	-	-	0.39	0.06	-
109	Castolast-G	93.7	0.1	5.6	0.1	0.1	-	-	-	0.1	0.3	-
116	CS 612	89.7	0.05	T	T	0.2	-	-	-	0.1	0.1	-
136	SION	Contains Si ₂ ON ₂ ~70; Si ₃ N ₄ ~20; and SiC ~10										
155	AA-22	89.6	0.7	-	3.4	-	-	-	6.2	0.1	0.05	-
153	Brick Ram 90	89.5	6.0	-	-	-	-	-	3.7	0.2	-	0.6
161	Alumex 70	72	23.21	0.32	0.17	2.02	-	-	-	0.97	1.34	-
162	AR 400	62	7.2	6.3	0.14	-	23.2	-	-	0.9	0.18	-
164	LoAtrade GR	55.5	35.5	4.0	0.35	1.5	-	-	-	1.0	1.25	-
165	Mono-R	51	14	-	-	0.05	34	-	-	1.1	0.12	0.15 as BeO
166	Fraxcast ES	57.7	33.8	6.3	0.2	1.0	-	-	-	0.2	0.7	-
171	Kaocrete HS	46	40	10.2	0.2	2	-	-	-	0.3	1.0	-
191	Refrax 20	0.3	1.3	0.3	Si ₃ N ₄ = 18.5; SiC = 79						0.3	-
193	Sil-tech	14.0	10.8	0.2	1.0	0.2	-	-	-	0.2	0.6	73.0 as SiC

TABLE V. Erosion/Corrosion Test Results--Metallic Specimens^a

Results of Tests 1(A) and 1(B)--Specimens Exposed to 50 h							
Specimen Number	Type	Total Exposure, h	Weight, g (± 0.0003 g)			Physical Description	
			Initial	Final	Change		
A9T-S2	Coated Metal	17	132.8574	132.6943	-0.162	Coating spalled from edges and back surface	
C9T-S2			133.1391	131.9385	-1.201		
E9T-S2			134.3148	133.1853	-1.129		
A10T-S2			137.5543	134.7110	-2.843	Coating spalled from front and back surface and edges	
C10T-S2			136.0418	133.6493	-2.392		
E10T-S2			133.5484	132.3798	-3.167		
A20T-S2			141.0624	135.2764	-4.786		
C20T-S2			138.5082	132.7282	-5.780		
E20T-S2			138.2484	132.8629	-5.383		
A9T-S1	Coated Metal	33	136.3926	136.0719	-0.321	Some coating spalled from front surface and edges	
C9T-S1			132.9919	132.5560	-0.436		
E9T-S1			132.5076	131.5773	-0.930		
A10T-S1			140.2884	137.4119	-2.876	Coating spalled from front and back surface and edges	
C10T-S1			135.6531	132.5551	-3.098		
E10T-S1			133.2851	130.1555	-3.129		
A20T-S1			138.4376	133.6509	-4.787		
C20T-S1			139.3122	133.1919	-6.120		
E20T-S1			140.3091	134.1164	-6.193		
A12T-S2	Coated Metal	50	140.0531	135.6402	-4.413	Coating spalled from front surface and edges. Partial spalling on back surface	
C12T-S2			141.1302	138.6060	-2.524		
E12T-S2			138.3660	135.9207	-2.445	Coating spalled from front surface only	
Results of Test 2--Specimens Exposed for 50 h							
A12T-S1	Coated Metal	50	142.4890	140.1007	-2.388	75% of coating spalled from front surface starting at bend	
C12T-S1			141.3496	140.3997	-0.950		
E12T-S1			140.9328	139.9873	-0.946		
A14T-S1			141.0876	141.3260	+0.238	No coating failure. Slight visible erosion. Uniform gray discoloration of impinged surface	
C14T-S1			140.2687	140.4804	+0.212		
E14T-S1			135.2933	135.4402	+0.147		
Results of Tests 1(A), 1(B), and 2--Specimens Exposed 100 h Total							
Specimen Number	Type	Total Exposure, h	Weight, g (± 0.0003 g)				Physical Description
			Initial	Change during First 50 h	Change during Second 50 h	Total Change for 100 h	
A14T-S2	Coated Metal	100	141.8209	+0.149	-0.069	+0.081	No coating failure after 50 h. Spalling started at nose of bend after 100 h. 8% of front surface spalled
C14T-S2			139.9400	+0.215	+0.040	+0.255	
E14T-S2			140.2760	+0.159	+0.026	+0.185	No coating failure. Slight visible erosion. Uniform gray discoloration of impinged surface
Type 310 SS (Reference)	Bare Metal		19.9654	+0.056	+0.009	+0.065	No erosion visible. Uniform gray discoloration with yellowish tint

^a Specimens were lightly brushed, air blown, and weighed after testing.

The results for the 15 ceramic specimens also included in the erosion test are listed in Table VI. All specimens survived the 100-h test with moderate or no attack. The weight loss decreased with increasing density, and material that exceeded 2.90 g/cm^3 exhibited negligible changes. The three specimens (SION, Refrax 20, and Siltech) that contain large amounts of oxidizable material, e.g., SiC and Si_3N_4 , all gained weight, which indicates that atmospheric conditions may have been too oxidizing.

Task C -- Nondestructive Testing of Coal-plant Components
(Principal Investigators: W. A. Ellingson, G. C. Stanton,
W. J. Shack, and N. P. Lapinski)

1. Infrared Imaging

To improve the quantitative value of using thermography to detect erosion or spalling of refractory linings in steel shells, the thermal contact resistance of the steel/refractory interface must be carefully controlled. Theoretical predictions of contact resistance are available in the literature^{2,3} for metal-to-metal contacts, but little information is available on thermal contact resistance between refractory and steel shells.

This quarter, emphasis has been placed on development of a facility to examine the thermal profiles of erosion-induced wall thinning with controlled thermal contact resistance and computer analysis of the thermal images. Figure 1 is a schematic of the facility. The 10 x 10 x 30-in. box-type furnace made by the Blue-M Company is capable of heating to 1250°C. Design cross sections up to 10 in. thick are capable of being accepted. The particle launcher is capable of launching projectiles of various shapes from 20 to 300 ft/s. The velocity is presently obtained by means of breaking thin foils and measuring the voltage drop across each foil, which yields a known time interval to traverse a known distance. The change in the thermal pattern on the refractory or refractory-lined steel shell is viewed by the Model 750 AGA infrared scanning camera.

TABLE VI. Erosion/Corrosion Test Results--Ceramic Specimens, Tests 1(A), 1(B), and 2^a

Number	Specimen		Weight Change, g (± 0.0005 g)				Physical Description after 100 h
	Name	Form ^b	Initial Weight, g	During First 50 h	During Second 50 h	Total Change for 100 h	
104	Mono-A2 (Reference)	B	86.7751	-0.003	+0.002	-0.001	No visible erosion. Gray/black deposit on impinged surface.
102	Mono-A1	B	92.8273	+0.023	+0.006	+0.029	No visible erosion. Gray/black deposit on impinged surface.
109	Castolast-G	C	91.5132	-0.414	-0.062	-0.476	No visible erosion. Gray/black deposit on impinged surface.
116	CS-612	B	102.0899	-0.062	-0.003	-0.065	No visible erosion. Gray/black deposit on impinged surface.
136	SION	B	68.6982	+2.721	+0.180	+2.901	No visible erosion. Light gray discoloration. Slight weight loss during first 50 h, which resulted from damage in handling.
153	Brick Ram 90	C	99.4256	-0.027	-0.012	-0.039	No visible erosion. Gray/black deposit on impinged surface.
155	AA-22	C	88.9209	-0.285	-0.085	-0.370	No visible erosion. Gray deposit with pink/yellow tint.
161	Alumex 70	B	73.6872	-0.406	-0.094	-0.500	Some binder erosion. Black deposit with yellowish tint.
162	AR 400	C	78.9711	-1.319	-0.160	-1.479	Corners, edges, and binder show some erosion. Slight damage during first 50 h. Partial black deposit.
164	LoAhrade GR	C	63.0424	-0.955	-0.120	-1.075	Some binder erosion. Partial black deposit. Slight damage during first 50 h.
165	Mono-R	B	125.0410	+0.042	+0.006	+0.048	No visible erosion. Black deposit with yellowish tint.
166	Fraxcast ES	C	73.7900	-4.590 ^c	-0.016	-4.606	No visible erosion. Black deposit with yellowish tint. Some weight loss during first 50 h, which resulted from damage in handling.
171	Kaocrete HS	C	57.9730	-1.963	-0.364	-2.327	Obvious erosion of binder over entire impinged surface. Partial black deposit.
191	Refrax 20	B	90.6470	+1.755	+0.097	+1.852	No visible erosion. Black deposit with yellowish tint.
193	Siltech	B	78.6791	+0.060	+0.018	+0.078	No visible erosion. Black deposit with yellowish tint.

^aTotal exposure time = 100 h. Specimens were lightly brushed, air blown, and weighed after testing.

^bB = brick and C = castable.

^cVisual examination did not indicate any erosion or other damage to account for the high measured weight loss. Experimental error is suspected.

Fig. 1. Experimental Arrangement for Studying Sensitivity of Thermography to Erosion of Refractory Structures. Neg. No. MSD-62856.

At the present stage, the thermal images on the electronic display are stored by taking photographs with a Minolta camera. The developed 35-mm film transparency is digitized using an image processor, and the resultant digitized data are plotted by means of an IBM 370/195 computer.

A sample data presentation photographed by the camera is shown in Fig. 2. Only data in the picture field are digitized and programmed for three-dimensional plotting as shown in Fig. 3. The capability of the three-dimensional picture to reveal temperature variation is obvious. But the data also reveal some undesirable noise effects, which can be ascribed to the following:

Fig. 2. Typical Photographic Image Obtained from the Infrared Monitor Electronic Display and Used for Digital Image Processing.

Fig. 3. Resultant Isometric Display of the Digitized Photographic Image. Neg. No. MSD-63048.

(a) The infrared image displayed contains a large number of scanning lines, which can be removed in the photographic negative by using slow-speed film coupled with a long exposure time. In the trial run shown, Kodak Tri-X film, which has an ASA speed rating of 400, was used. This film speed limits the shutter speed to $1/4$ s, which results in only 6.25 (infrared) images overlapped in each 35-mm frame.

(b) The filter for the photomultiplier tube in the image processor was not employed in the trial run. As a result, noise is introduced in the scanned data even if the original photographic negative is perfect.

A Kodak Panatomic-X film (ASA 32) has been chosen for the new experiments. With the use of filters in the image processor, the quality of data output is expected to improve.

The first series of thermal-pattern recognition tests will be with commercial refractories from Norton and A. P. Green, which are listed in Table VII. The specimens are $4\text{-}1/2 \times 9 \times 1\text{-}1/4$ in. thick, and initial results will be obtained from a monolithic layer so that the effect of thermal contact resistance can be assessed. The effect of using interstitial materials to reduce thermal contact resistance will be addressed in the next set of tests.

TABLE VII. Refractories for Initial Thermal-pattern Recognition Studies

Manufacturer	Refractory Identification
A. P. Green	G-20
A. P. Green	G-28
A. P. Green	G-32
Norton	Alundum

2. Ultrasonics

a. In-situ Erosion Study.

Installation of the fully instrumented Synthane coal-feed transfer line was completed. The instrumented section and associated electronics, described in previous reports,^{2,3} were installed in the Synthane coal-gasification system during May (Figs. 4 and 5).

After mechanical installation the electronic instrumentation was connected for initial tests. Preliminary data on pipe wall thickness and ultrasonic signal waveform (Fig. 6) for each of the transducer/waveguide systems were obtained.

To assess the effect of impedance of the necessary long lead cable, ultrasonic wall-thickness measurements and waveform photographs were obtained using all transducer/waveguide systems at two locations: (1) in the plant, by connecting the pulser-receiver directly to the sequential-switch circuit through a 1.83-m (6 ft) coaxial cable and (2) in the control room, by connecting through the 76.2-m (250 ft) coaxial lead cable. Thickness readings from each location agree within 0.076 mm (3 mils) at 13 of the 27 waveguides and within 0.61 mm (24 mils) at two additional waveguides. The remaining 12 waveguides provide signals wherein the backwall reflection is not clearly identifiable. However, the 15 waveguides that provide identifiable backwall reflections are expected to provide sufficient data to measure the amount, rate, and pattern of erosion. In addition, the waveform photographs from the other 12 waveguides may provide information about the inner-wall surface that results from erosion.

In related laboratory activities, experiments were conducted to determine the effect of microstructural changes (induced by prolonged exposure at elevated temperatures) upon ultrasonic response for Type 304 stainless

Fig. 4. Partial Flow Diagram of Synthane Coal-gasification Process Showing Installation Location of In-situ Erosion-measurement System. Neg. No. MSD-62436.

Fig. 5. Fully Instrumented Erosion-measurement System As Installed. Neg. No. MSD-62987.

Fig. 6. Typical Waveform of Ultrasonic Echo from Transducer/Waveguide System 9. Interface echo is on the left of the screen and backwall echo is on the right. Neg. No. MSD-63012.

steel, which is used for transfer lines. Eleven specimens 2.54 cm (1 in.) square were cut from a 1.27-cm (0.5 in.) thick bar of Type 304 stainless steel. One piece was retained as a control specimen, and the other 10 were heat treated in stainless steel foil envelopes at 538°C (1000°F) for various periods from 51 to 1000 h and cooled in still air. Each specimen was sectioned after heat treatment and examined for grain-size characteristics and grain-boundary width (Figs. 7-9).

The specimens were then examined for ultrasonic attenuation using a 5.0-MHz, 1.27-cm (0.5 in.) diam Acrotech Gamma series longitudinal-wave fingertip contact transducer and a Sonics Mark I pulser-receiver. Each specimen was examined in sequence. The difference in the calibrated gain control setting required to bring the first and the second echos to 50% of the cathode-ray tube (CRT) screen height was considered to be the attenuation

Fig. 7. Photomicrograph of Type 304 Stainless Steel Control Specimen in Non-heat-treated Condition. Mechanically polished and electrolytically etched with 10% oxalic acid in H_2O . Mag. 100X. Note absence of pronounced grain-boundary network. Neg. No. MSD-62988.

Fig. 8. Photomicrograph of Type 304 Stainless Steel Specimen Heat Treated 304 h at $537^{\circ}C$ ($1000^{\circ}F$). Mechanically polished and electrolytically etched with 10% oxalic acid in H_2O . ASTM grain size 5. Mag. 100X. Note pronounced grain-boundary network. Neg. No. MSD-62985.

Fig. 9. Same Specimen as in Fig. 8 but at Mag. 1000X. Neg. No. MSD-62984.

over the 2.54-cm (1 in.) acoustic path length. The test sequence was repeated a total of five times, and the average of the readings is shown in Fig. 10. These data indicate that the effect of the metallurgical changes on ultrasonic response is negligible.

Another laboratory experiment was conducted to determine the stability of the Branson 303-B pulser-receiver time-analog-gate digital thickness readout under simulated operating conditions over a 550-h period. A waveguide was made from 1.59-cm (0.625 in.) diam x 15.24-cm (6 in.) long AISI C-1020 carbon steel rod and fitted with brass cooling fins. One end of the waveguide was brazed to a 1.9-cm (0.750 in.) thick plate of Type 304 stainless steel. A Chromel/Alumel thermocouple was brazed to the plate near the waveguide/plate interface. An Aerotech Gamma series 5.0-MHz, 1.27-cm (0.5 in.) diam longitudinal-wave ultrasonic transducer was cemented to the other end of the waveguide using Eastman 910 cement.

Fig. 10. Effects of Heat-treatment Time at 538°C (1000°F) on Type 304 Stainless Steel. Upper curve depicts 5.0-MHz ultrasonic signal attenuation per inch of sound path length. Lower curve depicts grain-boundary width. Neg. No. MSD-62980.

The waveguide/plate assembly was secured across the opening of an electric box furnace and heated to 316°C (600°F) at the waveguide/plate interface (Fig. 11). The data shown in Fig. 12 indicate that the digital readout is quite stable, varying <0.08 mm (3 mils) over the 550-h period. Backwall signal amplitude was monitored during the test and found to decrease from its original 80% CRT height to 65% CRT height (<1 dB) with the gain control constant.

Since material thickness and ultrasonic wave velocity (and hence the ultrasonic thickness digital readout) are temperature dependent, another experiment was conducted to determine the effect of elevated pipe-wall temperatures on the digital thickness readout. The same waveguide/plate/furnace/instrumentation configuration as in Fig. 11 was used. The time-analog gate was calibrated at 1.9 cm (0.750 in.) with the waveguide/plate assembly at

Fig. 11. Block Diagram of Instrumentation System Used for Time-analog-gate Digital Thickness Readout Stability Test at High Temperature. Neg. No. MSD-62433.

Fig. 12. Ultrasonic Signal Amplitude Decay and Digital Thickness Readout Variation vs Time in 3/4-in.-thick (1.9 cm) Type 304 Stainless Steel at 600°F (316°C). Neg. No. MSD-62954.

room temperature. The waveguide/plate assembly was then heated to furnace temperatures of, for example, 93, 148, and 204 to 704°C (200, 300, and 400 to 1300°F). The temperature of the backwall (furnace) surface of the plate was assumed to correspond to the furnace temperature. The temperature of the outer surface of the plate (interface surface) was measured with the interface thermocouple, and the two temperatures were averaged. The digital thickness readout dimension and plate average temperature were recorded at each furnace temperature. These data were used to construct the temperature-compensation curve shown in Fig. 13.

Fig. 13. Temperature-compensation Curve for Ultrasonic Thickness Measurement in Type 304 Stainless Steel at Elevated Temperature. Neg. No. MSD-62955.

(1) Future Plans. Future plans include the following:

- (a) Finalize the Synthane in-situ erosion-measurement installation.
- (b) Accumulate a data base for the Synthane coal-feed transfer line.
- (c) Install a similar in-situ erosion-measurement instrumentation system at the Bi-Gas pilot plant on four product-gas transfer-line blocked tees and on the coal-feed sweep line to measure in-situ erosion rates and patterns.
- (d) Install wall-thickness instrumentation on the HYGAS pilot-plant high-pressure cyclone during the HYGAS annual shutdown in August to measure in-situ erosion as part of a continuation of a previous study.³
- (e) Begin examination of the effect of erosion patterns on backwall reflections.

3. Acoustic Emission

a. Acoustic Leak Detection.

Work on a quantitative method for acoustic leak detection has continued this quarter. Preliminary experiments have been performed to evaluate the usefulness and range of applicability of various types of commercially available transducers for acoustic leak detection. The optimum transducer should produce a signal that can be correlated with mean flow parameters such as the mass flow rate and mean velocity and should be relatively immune to the background noise generated in the coal-conversion process.

Three types of transducers have been examined: a low-g-level accelerometer (Endevco Model 2217E), a piezoelectric pressure transducer (Atlantic Research LC 71-1), and two acoustic-emission transducers [Acoustic Emission Technology Corporation (AET) FC-500-HD and FC-175]. The pressure transducer is not suitable for field work since it must have direct contact with the fluid. Drilling access ports through a pipe wall or valve body is unacceptable, and it would be difficult to keep the flow channel unobstructed. However, the pressure transducer provides the most direct measure of a flow quantity, and, thus, it is useful to compare its output with that of the other types of transducers.

The various transducers differ widely in their frequency response. The Endevco low-g-level accelerometer is flat from ~ 100 to 10,000 Hz; it has a resonance peak at ~ 50 kHz. No detailed information is presently available about the frequency response of the pressure transducer; examination of the spectra obtained using the pressure transducer indicates that a resonance peak exists at ~ 40 kHz. Assuming that the transducer response can be modeled as a single degree of freedom system, the response can be considered flat to $\omega_f/4 \sim 10,000$ Hz, where ω_f is the frequency at resonance. The acoustic-emission transducers operate at much higher frequency ranges. We have examined both resonant and broad-band acoustic-emission transducers.

Preliminary experiments were performed to determine the relative sensitivity of each type of transducer for detection of signals generated by gas flow through a 1.6-mm (1/16 in.) orifice under various pressure drops.

The gas flow noise is a broad-band signal that can be detected by the accelerometer and pressure transducer, which respond to the low-frequency portion of the noise spectrum, and the acoustic-emission transducers, which respond to the high-frequency portion.

The accelerometer and pressure transducer were coupled to an Endevco Model 2735 Charge Amplifier. The output of the amplifier was fed into a Tektronix Model 7L5 spectrum analyzer to obtain the power spectrum of the flow noise. To stabilize the signal, continuous data were recorded for 5 s, with the maximum amplitude at each frequency stored. Unfortunately, a severe impedance mismatch exists between the charge amplifier and the spectrum analyzer. This has not been a severe problem in our preliminary work, since the primary concern here has been whether a signal can be detected. A simple isolation amplifier has been built to remedy the problem, and it will be used in all subsequent experiments.

Typical power spectra for nitrogen obtained using the pressure transducer are shown in Fig. 14. The frequency distributions obtained with the pressure transducer (at least below the resonance of the transducer) are

Fig. 14. Power Spectra for Nitrogen Flow Obtained by Use of a Pressure Transducer. Neg. No. MSD-63020.

actually representative of the frequency distribution of the pressure fluctuations within the flow. The noise is almost "white," and the frequency content is insensitive to pressure, which is in agreement with the mathematical model proposed in the January-March 1976 Quarterly Report.³ The ordinate in Figs. 14a-c can be considered to be a measure only of relative amplitude since the signal was chopped. Typical power spectra for nitrogen obtained with the accelerometer are shown in Fig. 15. The peak at 2 kHz is probably associated with a resonance of the mounting system that acts as a lumped-mass single degree of freedom system.

Fig. 15. Power Spectra for Nitrogen Flow Obtained by Use of a Low-g-level Accelerometer. Neg. No. MSD-63019.

Since it is not our concern to measure the actual frequency content of the noise, the coloration of the frequency spectra by the resonances of the measuring system is not a problem. The resonances are easily detected and measured. If the noise signal is nearly "white" or the resonance peak is located in the dominant frequency range of the noise, then a single measurement, the height of the resonance peak, can characterize the noise level.

On the basis of this idea we explored the use of two types of acoustic-emission transducers produced by AET: a resonant-type transducer (Model FC-175) with a resonance at 175 kHz and a broad-band transducer (Model FC-500-HD), which is nominally flat from 125 kHz to 2 MHz. The transducer output was amplified using an AET Model 201 signal processor. The resultant output was then analyzed using the Tektronix 7L5. Typical spectra obtained with the resonant-type transducer are shown in Fig. 16 for air, nitrogen, and carbon dioxide, all with a driving pressure of 100 psi. The frequency distributions of these spectra can be compared with those shown in Fig. 17 for the broad-band transducer. The amplitudes have been altered by a change of scale on the 7L5 and, at present, can be used only to give relative amplitudes for different runs with the same transducer. The differences in the transducer characteristics are apparently being overwhelmed by the resonances associated with the mounting system, which acts as a waveguide.

b. Future Plans.

Having verified that the gas flow noise can be detected by transducers of widely differing frequency response, our future laboratory work will be concerned with developing quantitative relationships between the noise signal and mean flow parameters. Our initial field work will consist of scoping studies, similar to those conducted in the laboratory this quarter, designed to verify the detectability of signals and identify the types of transducer and frequency range most immune to extraneous background noise.

Fig. 16. Power Spectra Obtained by Use of a Resonant-type Acoustic-emission Transducer. Neg. No. MSD-63018.

Fig. 17. Power Spectra Obtained by Use of a Broad-band Acoustic-emission Transducer. Neg. No. MSD-63017.

4. Radiography

a. Gamma Radiography Testing of Full-scale Mock-ups.

Evaluation of the use of penetrating radiation (gamma radiography) to detect defects in various refractories has continued this quarter. After the full-scale cross section of the refractory/steel laminate mock-up of the Battelle-Columbus gasifier³ was fired and thermally cycled, a second set of radiographs was generated for comparison with pre-curing data. The results of this test revealed numerous cracks, both internal and surface, as shown in Figs. 18 and 19. Figure 18 shows one quadrant before curing and thermal cycling. Figure 19 shows the same area after curing. Note the clearly defined crack. Refractory moisture content did not prove to be a significant factor. The average photographic density difference between the radiographs taken shortly after the refractory was poured and those taken after curing was only ~ 0.41 .

Fig. 18. Gamma Radiographs of the Refractory/Steel Mock-up before Curing. Neg. No. MSD-62979.

Fig. 19. Gamma Radiographs of the Refractory/Steel Mock-up after Curing. Neg. No. MSD-62978.

b. Penetrameter Development.

Disk-type penetrameters developed in laboratory tests and fabricated from high-density refractory were successfully used in the field at the MERC stirred-bed gasification system in Morgantown, WV.

The penetrameters are 2.54 cm (1 in.) in diameter and 0.635 cm (0.250 in.) thick, with a 1.27-cm (0.500 in.) diam throughhole in the center. These penetrameters were constructed especially to be used when performing gamma radiography of (1) the refractory/steel laminate mock-up of the Battelle-Columbus gasifier, (2) the Bi-Gas gasifier vessel at Homer City, PA, and (3) the refractory-lined transfer lines at MERC.

c. Field Radiography.

Two field trips have been made this quarter. The first trip was made April 26-30 to MERC to gamma radiograph the refractory-lined transfer line downstream of the gas producer up to the cyclone. Figure 20 shows the transfer line and the locations that were gamma radiographed. Figure 21 is a cross-section elevation of the piping between the gas producer and cyclone.

The refractory in the transfer line is Johns Manville JM-2100 VLI, which is no longer manufactured. Consequently, no laboratory preparations were made to determine exposure parameters.

Fig. 20. Simplified Schematic of the Refractory-lined Transfer Line Showing Areas That Were Gamma Radiographed. Neg. No. MSD-63009.

Two sets of radiographs were taken on the transfer line using a 40-Ci ^{60}Co source. DuPont NDT 75 and Eastman Kodak Type AA film were employed with lead foil screens of 0.254 mm (0.010 in.) at the source and back side of the cassette and 0.137 mm (0.005 in.) between the film. This film combination was used because of the speed difference. DuPont NDT 75 is 2.3 times faster than Eastman Kodak AA film for ^{60}Co radiography. This difference was found to be ideal because the bore (which contains less material) was discernible on the slower speed film (AA) and the thicker sections were clearly visible on the faster (NDT 75) film. In addition, exposure times were reduced as a result of the introduction of the faster film. Exposure times ranged from 45 min for views A through G to 6 min for view H (Fig. 20).

A second set of radiographs was generated to examine the condition of the refractory. Exposure times ranged from 2 to 7 min.

Results of this field examination are shown in Table VIII. A typical crack observed is shown in Fig. 22, which was taken at position A. From the gamma radiographs, one can also observe the nonuniform bore contour (probably due to erosion) and a circumferential weld. Position E (Fig. 23) shows refractory inhomogeneity and a steel liner that was placed into the bore. The steel liner is visible in positions C through E. Position G shows an area where the refractory was repaired with a material less dense than the Johns Manville JM-2100 VLI used in the line (Fig. 24). A crack can also be observed coming from the repaired area and going into the refractory.

Since this was the initial visit to the MERC facility, the results obtained could not be compared with any base-line data. Future plans include a return visit to the MERC facility to gamma radiograph the same areas and discern whether any changes, such as erosion, have taken place.

A second field trip was made to the Bi-Gas coal-gasification pilot plant to gamma radiograph sections of the gasifier vessel. All of the data obtained from this field trip have not been compiled to date. A formal report will be forthcoming in the near future.

d. Future Plans.

Another refractory/steel laminate mock-up of the Battelle-Columbus gasifier will be poured and gamma radiographed prior to and after curing. Certain areas that may contain cracks will be sectioned and compared with the gamma radiographs to determine crack depth.

Mock-ups of areas examined at the Bi-Gas coal-gasification pilot plant will be constructed, radiographed, and compared with the data already on hand.

TABLE VIII. Cracks Detected in Refractory

Location	Number of Cracks Detected	Dimension of Cracks (length x width)	
		in.	cm
A	3	10 x 1/16	25.4 x 0.158
		3 x 1/32	7.62 x 0.079
		8 x 1/16	20.3 x 0.158
B	1	5 x 1/32	12.7 x 0.079
C	0	-	-
D	1	2 x 1/32	5.08 x 0.079
E	1	4 x 1/16	10.16 x 0.158
F	6	8 x 1/16	20.3 x 0.158
		6 x 1/16	15.24 x 0.158
		(2) 4 x 1/8	10.16 x 0.317
		3 x 1/8	7.62 x 0.317
		2 x 1/8	5.08 x 0.317
G	6	(2) 7 x 1/8	17.78 x 0.317
		(2) 4 x 1/16	10.16 x 0.158
		(2) 3 x 1/8	7.62 x 0.317
H	0	-	-
A1	1	8 x 1/16	20.32 x 0.158
B1	0	-	-
C1	0	-	-
D1	0	-	-
E1	0	-	-
F1	3	6 x 1/16	15.24 x 0.158
		(2) 5 x 1/16	12.70 x 0.158
G1	1	7 x 1/16	17.78 x 0.158

Fig. 22. Gamma Radiograph Taken at Position A Showing the Bore Contour and a Crack in the Refractory. Neg. No. MSD-62974.

Fig. 23. Gamma Radiograph Taken at Position E Showing Inhomogeneity of the Refractory. Neg. No. MSD-62975.

Fig. 24. Gamma Radiograph Taken at Position G Showing Refractory Repair and a Crack. Neg. No. MSD-62976.

Task D -- Corrosion Behavior of Materials in Coal-conversion Processes
(Principal Investigators: K. Natesan and O. K. Chopra)

The objective of this subtask is to apply thermodynamic data and concepts to the prediction of probable corrosion reactions that involve candidate materials over the range of temperatures and gas compositions anticipated in coal-gasification plants. This information, coupled with corrosion-rate data obtained under similar conditions, will be used to select candidate materials for evaluation of mechanical-property changes in simulated gasifier-plant conditions.

Much of our knowledge concerning the high-temperature corrosion behavior of commercial iron- and nickel-base alloys is derived from studies of high-purity metals and simple alloys in well-characterized binary and ternary gas mixtures. Although the results from these simple experiments aid in the

establishment of the relative corrosion behavior of different metals, the usefulness of such information in the prediction of the corrosion rates of multicomponent alloys in complex gas environments is quite limited. Studies on fundamental processes such as oxidation, carburization, sulfidation, and nitridation are generally conducted over a relatively short period, with the objective to identify the most stable phases formed and determine the mechanism and rate-limiting step for the process. Thermodynamic considerations have been used to rationalize the experimental observations in terms of the reaction potential of the gas species at the temperature and pressure of interest. Gulbransen and Jansson⁴ have reported a thermodynamic analysis of reaction-product phase stability for metals in two-component reactive gases, e.g., $\text{SO}_2 + \text{SO}_3$, $\text{H}_2 + \text{H}_2\text{S}$, $\text{CO} + \text{CO}_2$, and $\text{H}_2 + \text{H}_2\text{O}$, by means of what is commonly known as Ellingham diagrams. These diagrams depict the stability of the condensed phases for a given metal as a function of thermodynamic activities of the two reactive gaseous components. A similar approach for the evaluation of the corrosion behavior of metals in multicomponent gas mixtures is usually limited to the determination of a stable compound(s) that is formed as a result of exposure of the metal to the gas mixture.

The combustion-gas composition in coal-conversion processes generally depends on the type of process and feedstock analysis in addition to operating temperature and pressure. The gas mixtures usually consist of CO , CO_2 , H_2 , H_2O , CH_4 , H_2S , and NH_3 ; as a result, the simultaneous presence of reactive elements such as O, C, H, N, and S must be considered in the evaluation of the material behavior in the gas environment. The room-temperature compositions⁵ of the gas mixtures anticipated in different pilot-plant processes are listed in Table IX. These compositions are based on the use of low-sulfur coal in the processes. Also listed in the table is the composition selected

TABLE IX. Estimated Gas Compositions (vol%) in Various Coal-gasification Processes with Low-sulfur Coal Feedstock

	HYGAS	CO ₂ Acceptor	Synthane	Battelle- Union Carbide	Bi-Gas	MPC Selected
H ₂	17	52	19	48.8	15	24
CO	21	11	9	26	12	18
CO ₂	21	6	21	5	13	12
CH ₄	15	3	12	6	7	5
H ₂ O	25	28	36	14	52	39
H ₂ S	0.1	0.03	0.1	0.3	0.5	0-1.0
NH ₃	1	1	1	1	1	1
P(psi)	1200	300	1000	100	1000	-
T(°F)	1750	1600	1800	1800	1700	-

by MPC for use in the experimental research programs for corrosion evaluation.⁶ It is evident that the processes can have a wide variation in gas composition, and, therefore, materials performance in different processes is not expected to be the same, even for identical conditions of temperature and pressure. It is also evident that to cover the entire spectrum of gas-composition variation the experimental program will be time consuming and expensive, especially if long-term corrosion rates under high-pressure conditions are required.

A computer program has been developed to characterize the gas environments in terms of oxygen, sulfur, carbon, hydrogen, and nitrogen potential at various temperatures and pressures.⁷ This phase of the study is essential in the long run to (1) characterize the gas environment for a judicious interpretation of experimental data of different investigators, (2) perform

systems analyses for various coal-conversion processes, and (3) enable an effective alloy selection process for specific applications. The thermodynamic formalism, which led to a set of nonlinear equations, was used to examine the gas environments in the pilot-plant processes listed in Table IX. Table X lists the calculated values of oxygen and sulfur partial pressures P_{O_2} and P_{S_2} , respectively, and carbon activity a_C at 1000 and 700°C. The results show that at a temperature of 1000°C the oxygen partial pressures range from 7.2×10^{-17} to 4.5×10^{-15} atm and the sulfur pressures from 8.4×10^{-12} to 6.1×10^{-9} atm in these processes. The results also indicate that the MPC selected gas composition (with 0.1% H_2S) is approximately the same as that anticipated in the Synthane coal-conversion process.

The sulfur partial pressures calculated in these processes can be used to evaluate the sulfidation behavior of materials in the gas environment. In the absence of a protective oxide, the calculated sulfur pressure (or P_{H_2S}/P_{H_2}) for different processes can be superimposed on the isocorrosion-rate curves reported in the literature⁶ for austenitic stainless steels. Such a comparison is shown in Fig. 25. The values of P_{H_2S}/P_{H_2} for all processes except CO_2 -Acceptor are in the range 1.8×10^{-3} to 4.6×10^{-3} and are insensitive to temperature. Under these conditions, the steel should corrode at a rate of 20 to 100 mils per year at a temperature of 800°C. The P_{H_2S}/P_{H_2} ratio calculated for the CO_2 -Acceptor process is in the range 4×10^{-4} to 6×10^{-4} , which should result in negligible sulfidation attack of the steels. At a temperature of 980°C (≈1800°F), protection of the steel by the formation of a Cr_2O_3 layer on the surface is minimized as a result of formation and subsequent vaporization of CrO_3 . Under these conditions, the

TABLE X. Calculated Values for Oxygen, Sulfur, and Carbon Potentials for Gas Compositions in Different Coal-gasification Processes with Low-sulfur Feedstock

Process	T = 1000°C			T = 700°C		
	P_{O_2} , atm	P_{S_2} , atm	a_C	P_{O_2} , atm	P_{S_2} , atm	a_C
HYGAS	4.6×10^{-16}	1.2×10^{-10}	0.011	1.4×10^{-22}	3.2×10^{-15}	0.657
CO ₂ -Acceptor	6.3×10^{-16}	8.4×10^{-12}	0.004	2.8×10^{-22}	2.2×10^{-16}	0.168
Synthane	1.5×10^{-15}	1.8×10^{-10}	0.004	4.6×10^{-22}	4.1×10^{-15}	0.221
Battelle-UC	7.2×10^{-17}	7.0×10^{-10}	0.024	4.8×10^{-23}	2.4×10^{-13}	0.93
Bi-Gas	4.5×10^{-15}	6.1×10^{-9}	0.002	1.5×10^{-21}	1.3×10^{-13}	0.072
MPC Selected (0.1% H ₂ S)	2.3×10^{-15}	2.1×10^{-10}	0.003	7.2×10^{-22}	4.6×10^{-15}	0.147

Fig. 25. Superimposition of Sulfur Potentials in Pilot-plant Processes on Isocorrosion-rate Curves for Austenitic Stainless Steel.

results of the MPC program at the IIT Research Institute showed⁸ a sulfur corrosion rate of ~ 125 mils/1000 h for Types 304 and 316 stainless steel, which is in agreement with the values predicted from the present analysis.

The oxidation behavior of Fe-Cr and Ni-Cr alloys shows that Cr_2O_3 will be a thermodynamically stable oxide at all chromium concentrations in the alloy. Under the process conditions, the simultaneous presence of O_2 and S_2 should be considered when the alloy behavior is evaluated. Figures 26 and 27 show the Ellingham diagrams for Fe-Cr-O-S and Ni-Cr-O-S systems at 1200 K ($\sim 1700^\circ\text{F}$) along with the calculated partial pressures of oxygen and sulfur in different coal-conversion processes. The open symbols in these figures

Fig. 26: Thermochemistry of the Fe-Cr-O-S System at 1200 K. The gas environments in pilot-plant processes are indicated by different symbols.

Fig. 27. Thermochemistry of the Ni-Cr-O-S System at 1200 K. The gas environments in pilot-plant processes are indicated by different symbols.

are the calculated pressures for the gas compositions listed in Table IX, and the closed symbols are for an H_2S concentration of 1.0 vol% in the process gas environment. The analysis shows that chromium oxide is thermodynamically stable in Ni-base alloys and the oxides in Fe-base alloys will be a mixture of iron and chromium oxides. The effect of an increase in the sulfur concentration in the coal feedstock (Appalachian coal in contrast to Western coals) is to shift the process gas compositions in the direction of increasing P_{S_2} . Under such conditions, a distinct possibility for the formation of Fe and Ni sulfides exists. Since the sulfide layers are not protective in nature and the growth rates of sulfide layers are orders of magnitude larger than those of oxide layers, the corrosion rates of these alloys may become prohibitively large. Furthermore, in the case of Ni-Cr alloys, an increase in sulfur potential in the gas environment can lead to formation of Ni sulfides that are liquids at this temperature and can result in catastrophic corrosion rates. Therefore, an effective utilization of Fe-Cr and Ni-Cr alloys requires that a protective Cr_2O_3 layer be established upon exposure of the materials to a coal-gasification environment. Although Cr_2O_3 is thermodynamically stable at all chromium concentrations in Ni-Cr alloys, a large chromium content in the alloy is required for an external protective layer. The chromium concentration required for the external scale formation is a function of temperature and oxygen potential in the environment, and these functional relationships are yet to be established. It has been reported that a value of 20-25 wt% Cr in the alloy is necessary for the application of Ni-Cr alloy at 900°C and 0.1 atm oxygen pressure.⁹

The experimental program under this subtask involves evaluation of corrosion rates of commercial iron- and nickel-base alloys in multicomponent gas mixtures that include CO , CO_2 , H_2 , CH_4 , H_2O , and H_2S . A program has been initiated to evaluate the effect of multicomponent gas environments on the

tensile behavior of selected alloys. The alloys proposed for testing are Type 310 stainless steel, Incoloy 800, HL-40, and INCO-671. The alloys will be exposed for 1000 h in a given gas environment at a specified temperature before mechanical testing. It is proposed that at least three gas mixtures and three exposure temperatures be used in these experiments.

Task E -- Erosion Behavior of Materials in Coal-conversion Processes
(Principal Investigator: M. M. Mamoun)

The analytical studies on material loss in an erosive-corrosive environment have resulted in the formulation of analytical models that can be used to accurately determine the erosion rates of both ductile and brittle solid materials.

These models account for the effects of impact velocity, angle of impingement, size, shape, and mass density of the eroding solid particles on erosive wear rates. The models also consider the effects on erosion rates of factors such as the mechanical and physical properties of the eroded surface and eroding particles and operating temperatures.

Programs have been developed to determine the erosion rates of various metals, alloys, and refractory ceramics that are being considered for use in coal-gasification processes. Some of the numerical data on material loss by erosion were presented in previous quarterly reports.^{2,3} Additional numerical data on the erosion rates for various materials have been calculated. The validity of the calculated data has been established from the close agreement with available experimental data.

An experimental test apparatus designed to investigate the erosion behavior of materials has been assembled. Considerable effort was expended in the design and fabrication of some of the parts necessary for determining

parameters such as the average value of the impact velocity of the eroding particles, mass flux of the erosive media, and volumetric flow rate of the carrier fluid.

Task F -- Component Performance and Failure Analysis

(Principal Investigators: S. Greenberg, C. W. Boquist, D. R. Diercks, J. E. Sanecki, and J. Y. N. Wang)

The work during this quarter was devoted entirely to failed components from the HYGAS pilot plant.

1. HYGAS Pilot Plant

a. Coal Pretreatment Vessel Cooler.

Investigation of the failed thermocouple and failed thermocouple protection tube has been completed, and a report has been issued.¹⁰ Efforts to estimate temperature on the basis of precipitate identification were not successful, but the previous estimate that the maximum temperature was at least 900°C (1652°F) is still valid. Detailed discussions with HYGAS personnel revealed that the most severely corroded portion of the thermocouple protection tube was immersed in "clinker" with an estimated melting temperature of 927-982°C (1700-1800°F).^{*} A sample of the clinker was obtained for melting point determination, which yielded a result of 1125-1195°C (2057-2183°F) and confirmed the work of Wang.¹⁰

Subsequent to the failures discussed above and the failure of a cooler located in the center of the vessel (the result of thermally induced mechanical buckling), a second cooler failed. In contrast to the first failed cooler, which showed no indication of severe corrosion, the second cooler was severely corroded and suffered tube rupture in at least one area. It was learned from discussions with HYGAS personnel that this cooler came from

^{*}HYGAS estimate.

the same area of the vessel as the failed thermocouple and was also in contact with clinker. Detailed destructive examination of the cooler (to determine, if possible, the relative corrosion on inside and outside tube surfaces) is being delayed pending nondestructive examination to determine tube wall thickness as a function of location.

Design operating temperature of the coal pretreatment vessel is $\sim 427^{\circ}\text{C}$ (800°F), and no evidence exists that the carbon steel (SA106 Grade 2) cooler would be unsatisfactory at this temperature. Thus, these failures are evidence of process control problems rather than material problems.

b. Main Gasifier Transfer-line Expansion Joint.

(1) Incoloy 800 Bellows. The bellows failed as a result of perforations in an isolated area of one convolution. At present it is not known whether the perforations are widespread or restricted to the one convolution. (We have received only two convolutions for examination, including the perforated convolution.)

In addition to the perforations, both surfaces of the bellows are covered with a sulfur-containing film and sulfides have been identified. The outside of the bellows is exposed to a nominally inert ("pure" nitrogen) environment, but leakage of various sulfur-containing substances satisfactorily explains the presence of sulfide on the exterior surface.

Metallographic examination demonstrated that the perforations originated on the inside surface. Considerable pitting occurred in the vicinity of the perforations. Although it is possible that the bellows was defective as fabricated, it is believed the most likely cause of failure was chloride pitting. The bellows contained a large quantity of coal product

as received from HYGAS, and the operating conditions of the gasifier are such that moist coal product can be in contact with the bellows. This coal product contains ~0.2% water-soluble chloride, and the leach solution has a pH of ~6. Incoloy 800 is susceptible to pitting attack in such an environment.

If the cause of failure has been correctly diagnosed, the material selection problem presented is difficult. Incoloy 800 is a reasonable choice for design conditions, i.e., sulfur-containing gases at a temperature of 649°C (1200°F), but is not a good choice for an acid chloride environment. Molybdenum-containing alloys, e.g., Type 316 or 317 stainless steel, Inconel 625, or Hastelloy C, have superior pitting resistance but would not be as satisfactory as Incoloy 800 in high-temperature sulfur-containing gaseous environments. If gasifier operating conditions cannot be modified so as to eliminate (or at least greatly reduce) the accumulation of periodically wetted chloride-containing deposits in contact with the bellows, it may be that no commercially available metal will provide long-term service.

(2) Type 330 Stainless Steel Piping. Massive intergranular cracking was observed in the heat-affected zone (and to a lesser extent in the weld deposit) of welded joints (Type 330 stainless steel welded to Type 316 stainless steel and Incoloy 800). The relatively high silicon content of Type 330 stainless steel and the cyclic operation of the gasifier may have contributed to the cracking, but it is believed the more likely explanation is corrosion (in an environment similar to that discussed in Section B.1) of sensitized material. Metallographic examination of crack surfaces has produced no evidence to support mechanical failure.

Failure of this piping poses no threat to personnel (because of its location). However, it is obvious that other welded components of Type 330 stainless steel exposed to a similar environment are also

vulnerable. As in the case of the bellows, the material selection based on design conditions is reasonable. No obviously better material choice for the present actual operating conditions exists. (The fact that a Type 316 stainless steel flange was used in this assembly indicates that perhaps Type 316 stainless steel piping would also be satisfactory. If so, Type 316L stainless steel would be more resistant to intergranular corrosion in the heat-affected zone of the welds.)

c. Ash-agglomerating Gasifier.

(1) Incoloy 800 Pressure Taps and Thermocouple Protection Tubes. These tubes failed as a result of excessive corrosion. Plant operating schedules necessitated that we make recommendations for improved materials prior to initiation of the detailed failure analysis. On the basis of operating conditions, sulfidation was assumed to be the cause of failure, and, in consultation with HYGAS personnel, Types 310 and 446 stainless steel were recommended as likely to provide improved performance. Subsequent chemical and energy-dispersive X-ray analysis confirmed that sulfidation had occurred.

Both types of stainless steel were used in the next gasifier run. Type 446 stainless steel performed satisfactorily, but Type 310 stainless steel failed. HYGAS personnel reported that some evidence exists that the Type 310 stainless steel tube may have melted rather than corroded, but we have not yet received samples for examination.

(2) Incoloy 800 Internal Cyclone Dip Leg. This pipe failed as a result of severe corrosion, particularly at the bottom end (closest to the fluidized bed), where the temperature is $\sim 1038^{\circ}\text{C}$ (1900°F). At the bottom end, the metal appeared to have been completely converted to corrosion

product and a simple flapper valve had broken off. The top end (close to the cyclone) was in much better condition, but even here regions of severe attack occurred, i.e., as much as one-third of the wall thickness had been corroded.

Chemical analysis and initial metallographic examination indicate that appreciable carburization and sulfidation have occurred at the top end of the pipe. In addition, material that had been molten was observed on the inside surface at the top end of the pipe. This is evidence of off-design operating conditions and may indicate that at least part of the damage is the result of hot corrosion.

It was suggested that Type 310 stainless steel would provide improved performance when compared with Incoloy 800, particularly in the relatively cool (upper) portions of the pipe. The operator plans to use Type 310 stainless steel and Alonize the flapper valve, a plan with which we agree.

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ERRATUM

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Page 25, Fig. 13:

Figure 13 in ANL-76-22 is a flow diagram of a low-pressure Ash Agglomeration Process used in the HYGAS Process. The correct Fig. 13 is shown below:

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Fig. 13. Flow Diagram of IGT HYGAS Process. (From "HYGAS: 1972 to 1974," Interim Report No. 1, July 1975.)