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Environmental Protection Technology Series

PILOT PLANT STUDY OF CONVERSION OF COAL TO LOW SULFUR FUEL

Industrial Environmental Research Laboratory
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PILOT PLANT STUDY OF CONVERSION OF COAL TO LOW SULFUR FUEL

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EXECUTIVE SUMMARY

The purpose of this program is to develop, on a bench and pilot scale, the operating conditions for the key step in the IGT process to desulfurize coal by thermal and chemical treatment. This process, to date, uses the "sulfur-getter" concept. A sulfur-getter is defined as a material that has a greater chemical affinity for sulfur than the coal has. Lime has been selected as the sulfur-getter for this program.

The program reported here was divided into two phases. In Phase I, the problem was directly attacked on a pilot-unit scale. The results of this work indicated that the program should be redirected (Phase II) to smaller-scale test apparatus so that more basic data could be obtained for eventual scale-up to pilot scale.

In the initial project phase, a coal-lime mixture was experimentally treated at atmospheric pressure with a reducing gas in a heated, fluidized-bed reactor. This reactor could treat up to 200 lb/hr* of mixture to temperatures of 1200°F. The coal used in the initial tests was from the Illinois No. 6 seam and contained about 3% sulfur.

Work in the initial program phase resulted in the discovery that less sulfur was removed than expected at these conditions. Two factors were believed responsible:

1. The coal heat-up rate in the fluidized bed was nearly instantaneous, which appeared to cause organic sulfur fixation.

2. The coal showed signs of weathering; therefore, the total sulfur content was not readily available for hydrogen treatment.

At this point, the program was redirected (Phase II) to the operation of smaller-scale test units that featured controlled heat-up rates. The smaller-scale units also permitted an increased number of tests over a broader range of conditions, with savings in time and manpower. Coal samples from several mines throughout the country were obtained for tests in this equipment.

A coal-lime mixture was treated with hydrogen, in batch-type reactors, to temperatures of 1500°F. Heat-up rate, terminal temperature, residence time, and particle size were the variables tested.

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* English units are commonly used in this document in areas of engineering development; SI units are used in more basic research areas. Refer to Conversion Table page xi.

Preliminary tests eliminated the Western coals (i.e., subbituminous and lignite) because the sulfur content of the raw coal was low and not readily amenable to treatment. Also, the preliminary tests indicated that the coals from the Midwestern and Eastern United States required pretreatment to prevent caking during hydrotreating. This is accomplished by heating the fluidized coal at atmospheric pressure to 750°F in the presence of oxygen.

On the basis of the preliminary tests with several coals and the relative abundance of the types of coal, a coal from the Western Kentucky No. 9 seam was chosen for complete characterization. This coal is from the Illinois basin and contains over 3% sulfur. Tests were run covering a wide range of the parameters listed. These tests prove that acceptable sulfur levels were attained at treatment temperatures of 1500°F. The higher temperatures result in significant tar removal and some gasification of the coal. These effects necessitate further research into quantity, chemical makeup, and handling of gas and liquid streams.

The testing resulted in the discovery that treatment with lime does not capture all the sulfur that is released from the coal. A more thorough examination of the effectiveness and benefits of lime is required in future work.

A conceptual process design, based on laboratory and bench-scale data, is presented. That process will produce a solid fuel that can be burned directly in conformance with Federal EPA New Source Performance Standards (NSPS).

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CONVERSION FACTORS

Non SI Units	Operation	SI Unit
atmosphere	x 101325	N/m^2
Btu	x 1055.87	J
Btu/lb	x 2327.794888	J/kg
cal	x 4.19002	J
^oC	+ 273.15	K
^oF	$(5/9)(T_F + 459.67)$	K
^oF/min	x .0092592	K/s
foot	x 0.3048	m
inch	x 0.0254	m
in H_2O	x 249.082	N/m^2
in H_2O/ft	x 2988.98	N/m^3
pound	x 0.45359237	kg
psi(a)	x 6894.7572	N/m^2
SCF/hr	x 0.000007865790722	m^3/s

Mesh — An Empirical Measure of Particle Size:

U.S. Mesh	Opening Size mm
10	2.00
12	1.68
14	1.41
20	0.84
30	0.59
40	0.42
60	0.25
80	0.177
100	0.149

SYMBOLS

Symbol	Meaning
Cp	Heat capacity
K	Equilibrium constant (when not preceded by a numeral)
N	Solution normality

OBJECTIVE

The objective of the program is to determine experimentally, on a bench- and pilot-unit scale, the operating conditions for the key step in the IGT process to desulfurize coal by thermal and chemical means. The current NSPS for solid fossil-fuel combustion has largely been observed by switching to low-sulfur fuels. Achieving the goals of this program will increase the supply of low-sulfur fuels.

INTRODUCTION

Researchers at the Institute of Gas Technology (IGT) have conceived a process for the removal of sulfur from coal by thermal and chemical means. A patent has been granted on this process and assigned to IGT. The objective of the current work in this program has been to develop the key step of that process.

The process incorporates low-pressure treatment of the coal in a reducing atmosphere, forming hydrogen sulfide (H_2S). The equilibrium partial pressure of H_2S over coal is not high, even at elevated temperatures. In this process, therefore, a "sulfur-acceptor" ("sulfur-getter") is added to the coal-reductant system. The sulfur-getter is defined here as a material that has a greater chemical affinity for sulfur than coal has, thus overcoming the equilibrium limitations. One example of a sulfur-getter is lime. Hydrogen sulfide has a much lower equilibrium partial pressure over lime than it has over coal; therefore, the reducing gas will react with the sulfur in the coal, forming H_2S. The H_2S, however, will react almost immediately with the lime. In this system, the sulfur is transferred from the coal to the lime with an H_2S intermediate.

The first step in the overall chemical reaction is to release the sulfur from the coal as H_2S. However, the sulfur in the coal is not a distinct chemical species, but exists in many forms that react with hydrogen at varying temperatures. The H_2S can also back-react with the coal, forming stable coal-sulfur complexes. The program is designed to test the removal of sulfur from the coal at varying temperatures, to determine the severity of treatment required for manufacturing an environmentally satisfactory solid-fuel product. The sulfur-getter was included in the system to enhance the sulfur-removal rate and minimize the back-reaction.

MATERIALS

COAL

The coals used in the project, their proximate and ultimate analyses, and sulfur-by-type analyses are presented in Tables 1 and 2. Two coals from the Illinois No. 6 seam are listed. The first of the Illinois coals was originally used in the project because it was readily available. However, this coal was severely weathered, and sulfur removal proved difficult. The second coal sample was therefore obtained for additional testing. These coals provided a wide range of sulfur content. Their rank ranged from the low-sulfur Western coals to the higher-sulfur-bearing Midwestern and Eastern coals.

Fluidization characteristics were evaluated on a sample of Illinois No. 6 coal scalped at —10 mesh. These fluidization tests were made in a 1.5-inch-diameter Lucite apparatus, utilizing air at ambient temperatures. The resulting fluidization curve is shown in Figure 1. The apparent minimum fluidization velocity of 0.03 ft/s is lower than expected and is probably caused by the wide range of particle sizes. The velocity required for suspending the larger particles was about 1 ft/s, but they do not greatly influence the pressure drop across the bed or the apparent minimum fluidization velocity. Better fluidization and mixing were expected in the pilot unit because of the distribution-plate design and the continuous flow of material.

In the second phase of the program, after extensive screening by small-scale thermobalance tests of all the coals listed, Western Kentucky No. 9 coal was selected as a good sample for complete testing. Later, a coal from West Virginia was also examined. Most Western coals could be eliminated from testing because their initial sulfur content was low; also, the high oxygen content of the Western coals was attacked by the reductant, causing process inefficiency. Preliminary treatment was discovered to be necessary to prevent agglomeration of the selected coals at the operating conditions of the proposed system. The pretreatment conditions were determined for these coals, as discussed starting on page 80.

ACCEPTOR

Limestone ($CaCO_3$) was the original acceptor considered for this program. The laboratory analysis of Tymochtee limestone, obtained from Huntsville, Ohio, is presented in Table 3. This material was relatively coarse, and fluidization characteristics (Figure 2) of both —14 and +14 mesh were evaluated. The —14 mesh exhibited characteristics similar to the —10 mesh coal, but at slightly higher velocities. The +14 mesh material could not be fluidized at gas velocities less than 1 ft/s.

TABLE 1. RAW COAL ANALYSIS

	Ill. No. 6*	W. Ky. No. 9	Ind. No. 5	Pittsburgh Seam Pa.	Pittsburgh Seam W. Va.	Mont. Subbituminous	N. D. Lignite	Ill. No. 6 †
Proximate Analysis	wt %							
Moisture	3.72	5.9	9.0	1.5	7.7	17.6	24.5	5.8
Volatile Matter	36.1	33.4	34.5	27.6	33.8	35.7	32.0	24.8
Ash	9.8	14.8	11.9	30.8	10.8	3.6	6.3	35.7
Fixed Carbon	50.38	45.9	44.6	40.1	47.7	43.1	37.2	33.7
Total	100.00	100.0	100.0	100.0	100.0	100.0	100.0	100.0
Ultimate Analysis, (Dry)								
Ash	10.20	15.68	13.10	31.29	10.91	4.38	8.30	37.88
Carbon	69.32	67.47	68.60	56.67	73.43	72.42	64.67	49.08
Hydrogen	4.76	4.66	4.63	3.81	4.89	5.01	4.17	3.38
Sulfur	2.62	4.06	3.92	1.45	3.01	0.84	0.64	1.20
Oxygen	11.89	6.75	8.32	5.63	6.45	16.36	21.22	7.31
Nitrogen	1.21	1.38	1.43	1.15	1.31	0.99	1.00	1.15
Total	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00

* Weathered coal.
† New sample.

TABLE 2. SULFUR IN COAL BY TYPE

Sulfur, By Type	Ill. No. 6*	W. Ky. No. 9	Ind. No. 5	Pittsburgh Seam		Mont. Sub-bituminous	N.D. Lignite	Ill. No. 6†
				Pa.	W. Va.			
	wt %							
Sulfide	0.00	0.00	0.07	0.04	0.05	0.00	0.04	0.00
Sulfate	0.32	0.07	0.00	0.00	0.00	0.00	0.00	0.00
Pyritic	0.89	2.30	2.02	1.08	1.49	0.29	0.21	1.14
Organic	1.79	0.97	1.24	0.26	1.37	0.37	0.28	0.04
Total	3.00	3.34	3.33	1.38	2.91	0.66	0.53	1.18

Note: The total sulfur presented here does not agree with the values presented in Table 1. The analysis of sulfur-by-type uses different laboratory procedures that are more accurate. Therefore, the total sulfur values from this table were used for data analysis.

* Weathered coal.
† New sample.

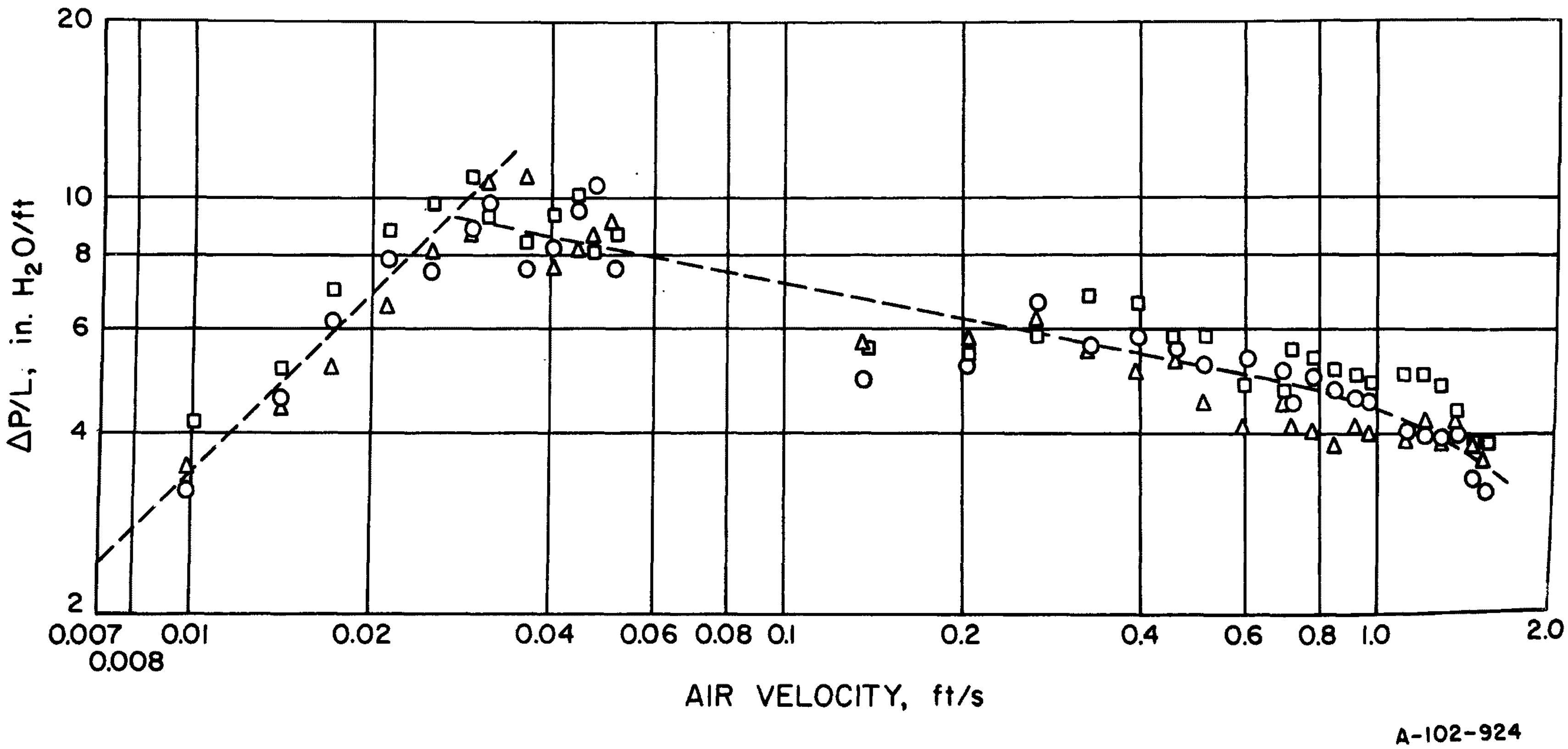

Figure 1. Fluidization characteristics of Illinois No. 6 coal, −10 mesh.

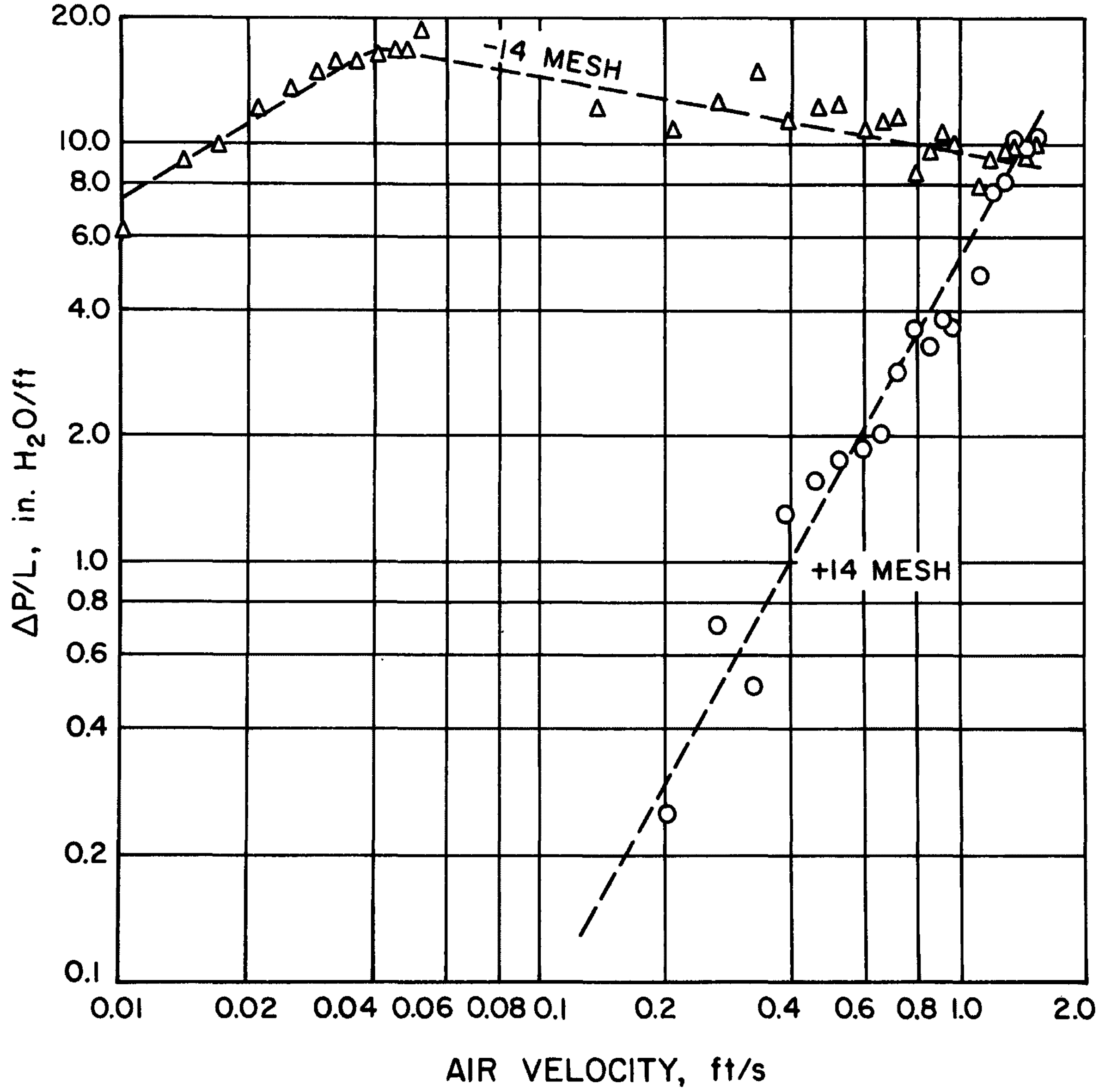

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Figure 2. Fluidization characteristics of Tymochtee limestone.

TABLE 3. LIMESTONE ANALYSIS

Proximate Analysis, wt %	
Moisture	3.3
Ultimate Analysis, wt %	
CaO	30.5
MgO	18.6
CO_2	42.93
S	0.26
Acid Insoluble	7.7
Screens, % retained on	
10	29.5
14	16.0
20	16.8
30	6.9
40	5.4
60	5.8
80	3.3
100	1.5
200	4.8
325	3.1
Pan	6.9
Bulk Density, lb/cu ft	106.0
True Density, g/ml at 25°C	2.717

The original process concept suggested that a coarse-sized limestone and finer coal would be desirable because this type of mixture would provide easier separation after treatment. A mixture of 3 parts −10 mesh coal and 1 part +14 mesh limestone was fluidized, with the results shown in Figure 3. Nearly quantitative segregation occurred in this test, indicating that separation was feasible, but that co-fluidization, required for the pilot unit, was poor. A smaller size consist was required for the limestone. As a result, ease of separation was sacrificed for the better mixing required in the pilot unit, and other separation techniques would require evaluation.

Later thermodynamic studies indicated that quicklime (CaO) would be a better acceptor than limestone, because lower temperatures and energy inputs are theoretically required for both the initial desulfurization reaction and

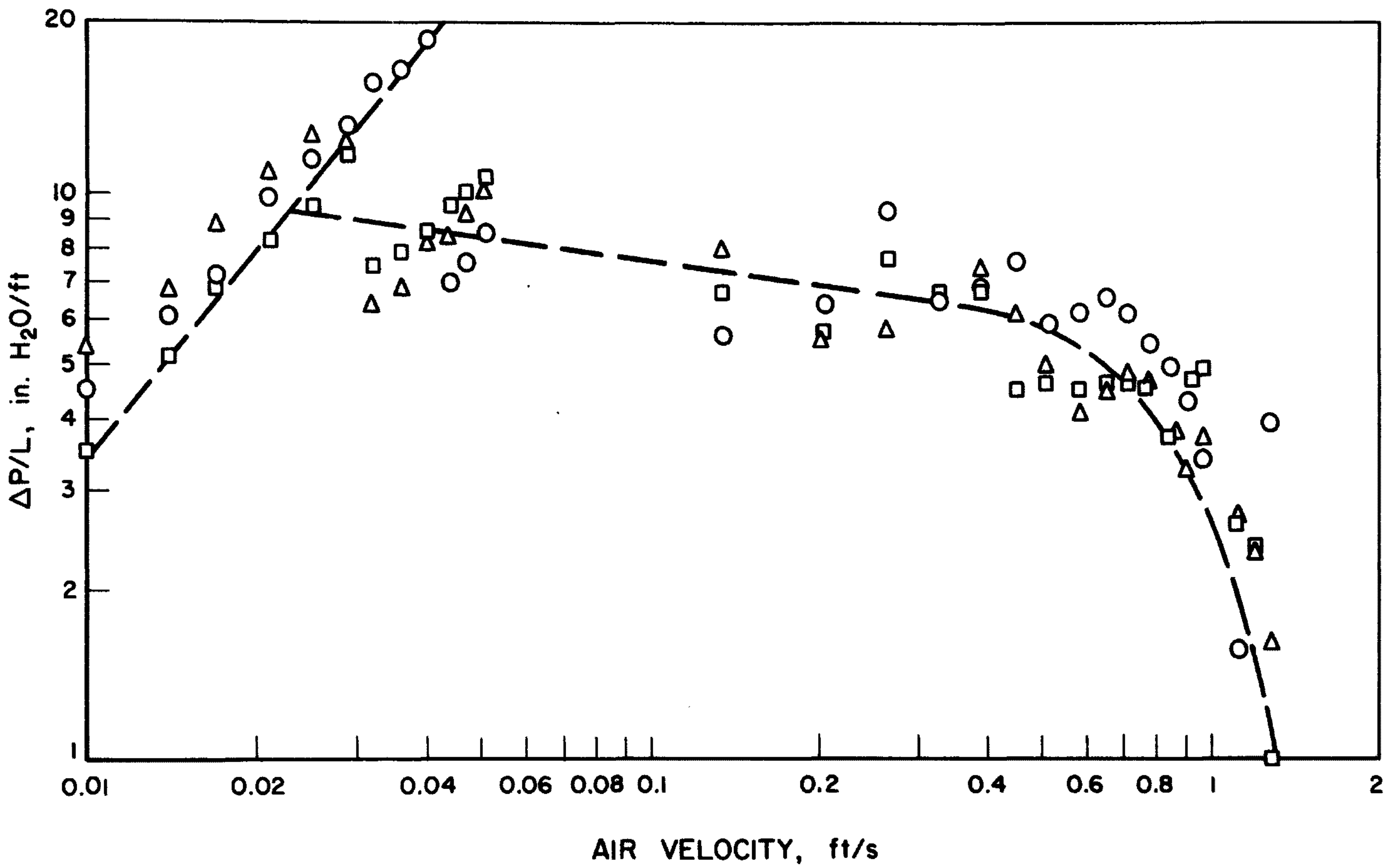

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Figure 3. Fluidization curve for mixed coal-limestone (25% +14 mesh limestone and 75% —10 mesh coal).

the acceptor regeneration. The program was therefore redirected to use quicklime as the acceptor. Since limestone and quicklime are physically similar, smaller particle lime must be used for adequate mixing.

MIXTURE

In the first tests, a mixture of 4 parts coal and 1 part lime by weight was used for the feed. This ratio was chosen to provide several (approximately 4 to 5) times the stoichiometric lime-sulfur requirement. Laboratory results from the first test runs indicated that the lime had hydrated and carbonated from the coal moisture and handling. The ratio was changed to 2 parts coal and 1 part lime for subsequent tests to allow sufficient lime for these experimental side effects and still have excess lime for desulfurization.

The size consist chosen for the two constituents was based on the fluidization tests discussed above. Coal was screened at −10+80 mesh and the lime at −20+60 mesh. The fines were removed to prevent excess dust loading of the exit gas system.

THERMODYNAMIC STUDY

A thermodynamic study of the C-H-S-O-Ca-Fe system was made to a) indicate the theoretical limitations of the possible reactions, b) aid in selecting sulfur-getter material and getter/coal ratio, and c) provide an input for the later kinetic studies.

Graphs showing the log of the equilibrium constant, K, as a function of temperature for various system reactions are shown in Figures 4 to 7. The data for these graphs were calculated independently by two individuals using different data sources and calculation techniques. The results agreed closely and differed only because of variations of material properties given in different references. The accuracy of the calculations is determined by comparison of the calculated equilibrium constant with literature values.

Equilibrium data are not available for the coal-sulfur system as it exists naturally. Sulfur exists in coal in many forms (pyrite, sulfide, sulfate, organic), and the organic coal-sulfur chemistry is complex.

However, the literature indicates that much of the organic sulfur in the coal is eliminated more readily than the pyritic sulfur. An even more difficult sulfur-removal problem is the final decomposition of the ferrous sulfide that is formed when iron pyrite is desulfurized. The decomposition of the ferrous sulfide, therefore, was selected as the basis for the thermodynamic study.

Figure 4 presents the free energy calculation for the reaction —

$$FeS + H_2 \rightleftarrows Fe + H_2S$$

This calculated graph agrees well with the experimental data obtained by Rosenquist (3). His data, over the range of 932° to 1410°F, may be represented by —

$$\log K = \log \frac{P_{H_2S}}{P_{H_2}} = \frac{-3100}{T} + 0.179$$

where T is the temperature expressed as °F. However, significant variations in the value of the calculated equilibrium constants can occur, depending on the literature source for the thermodynamic constants of FeS. For example, Rosenquist determined a ΔF for the formation of FeS at 298 K as −22,700 cal/g-mol. Other published values are —

Kubaschewski and Evans (2)	−24,500
Rossini, et al. (4)	−23,200
Clark (1)	−24,311

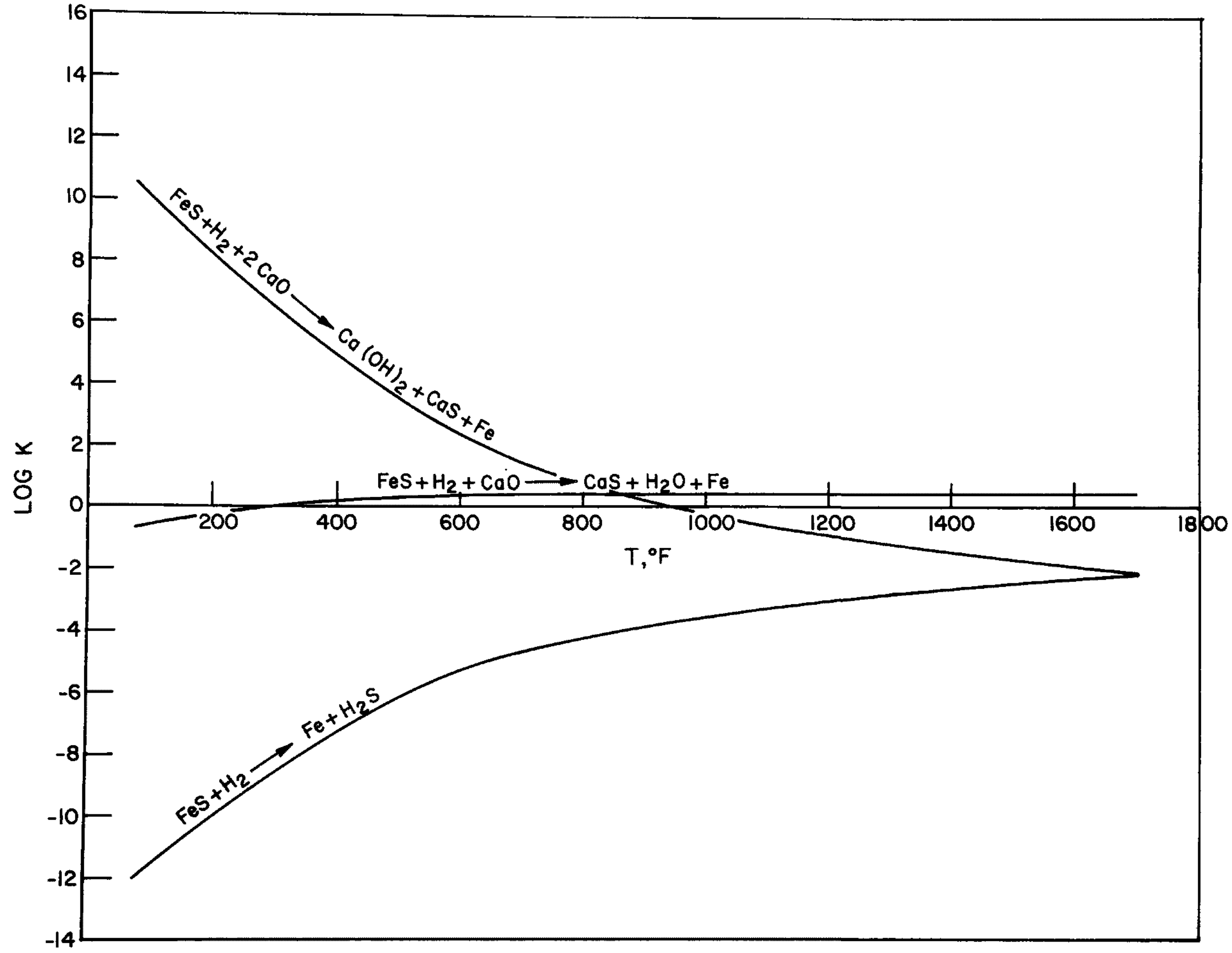

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Figure 4. Thermodynamic equilibrium in coal-getter process for FeS + CaO and FeS + H_2 reactions.

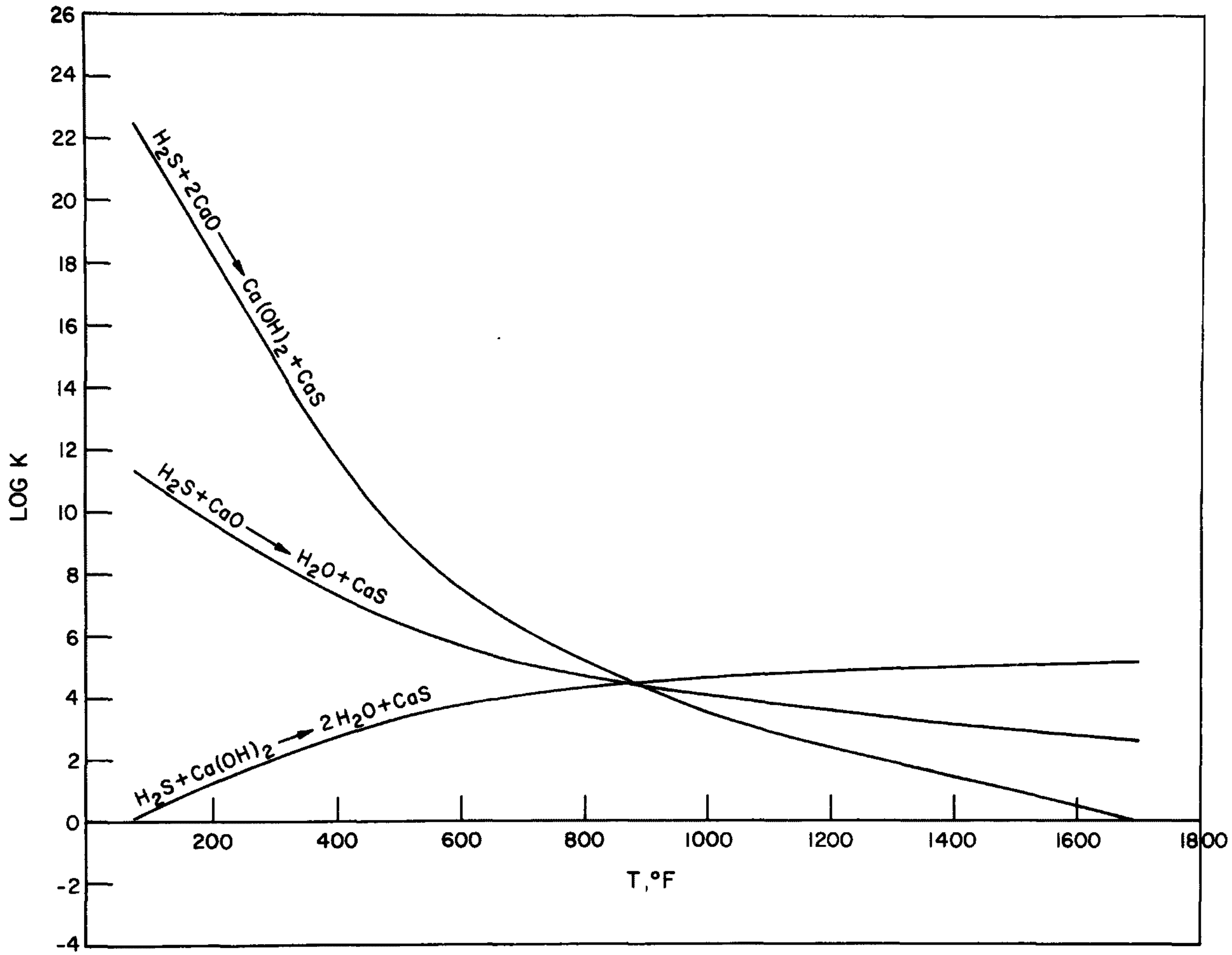

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Figure 5. Thermodynamic equilibrium in coal-getter process for H_2S + CaO reactions.

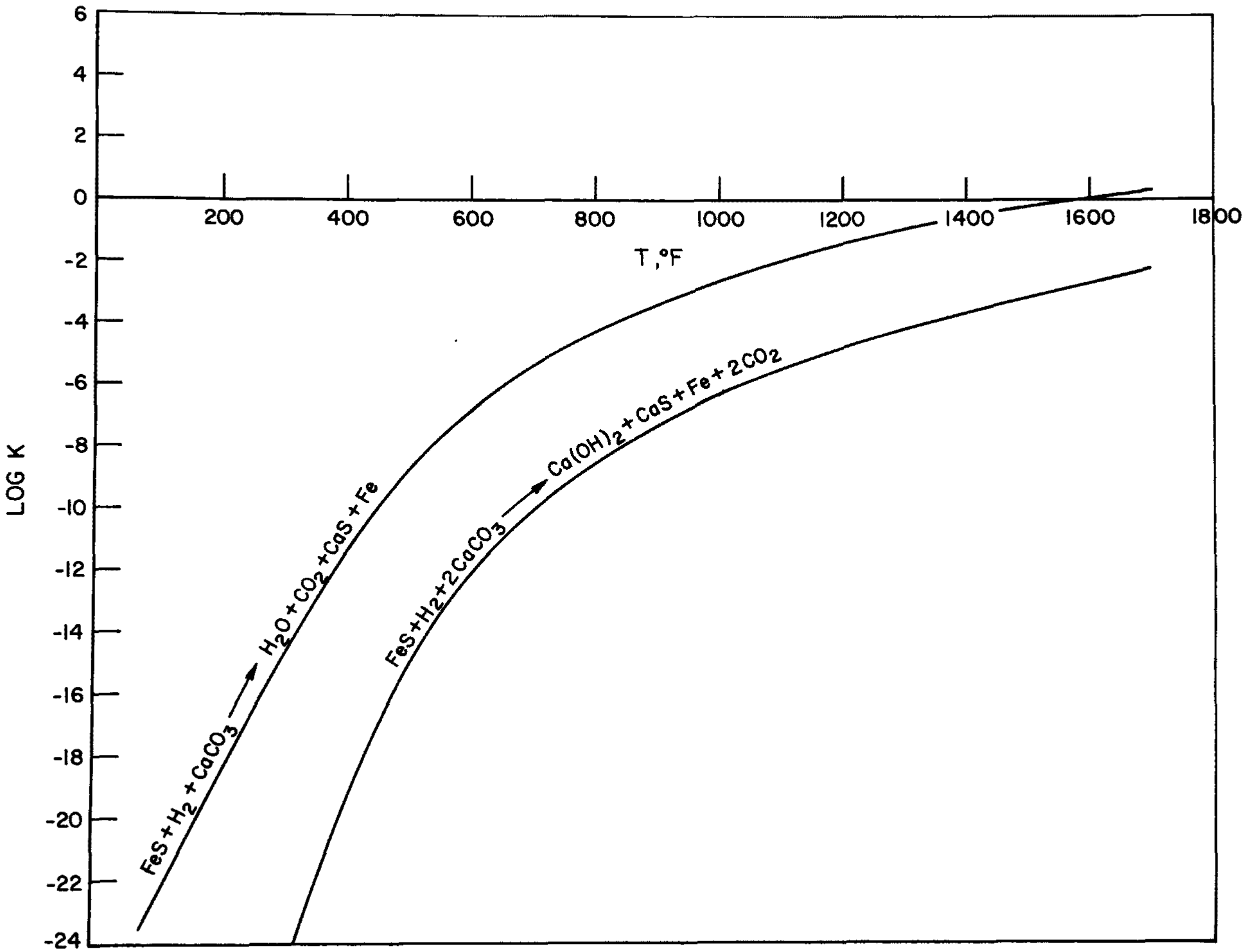

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Figure 6. Thermodynamic equilibrium in coal-getter process for FeS + $CaCO_3$ reaction.

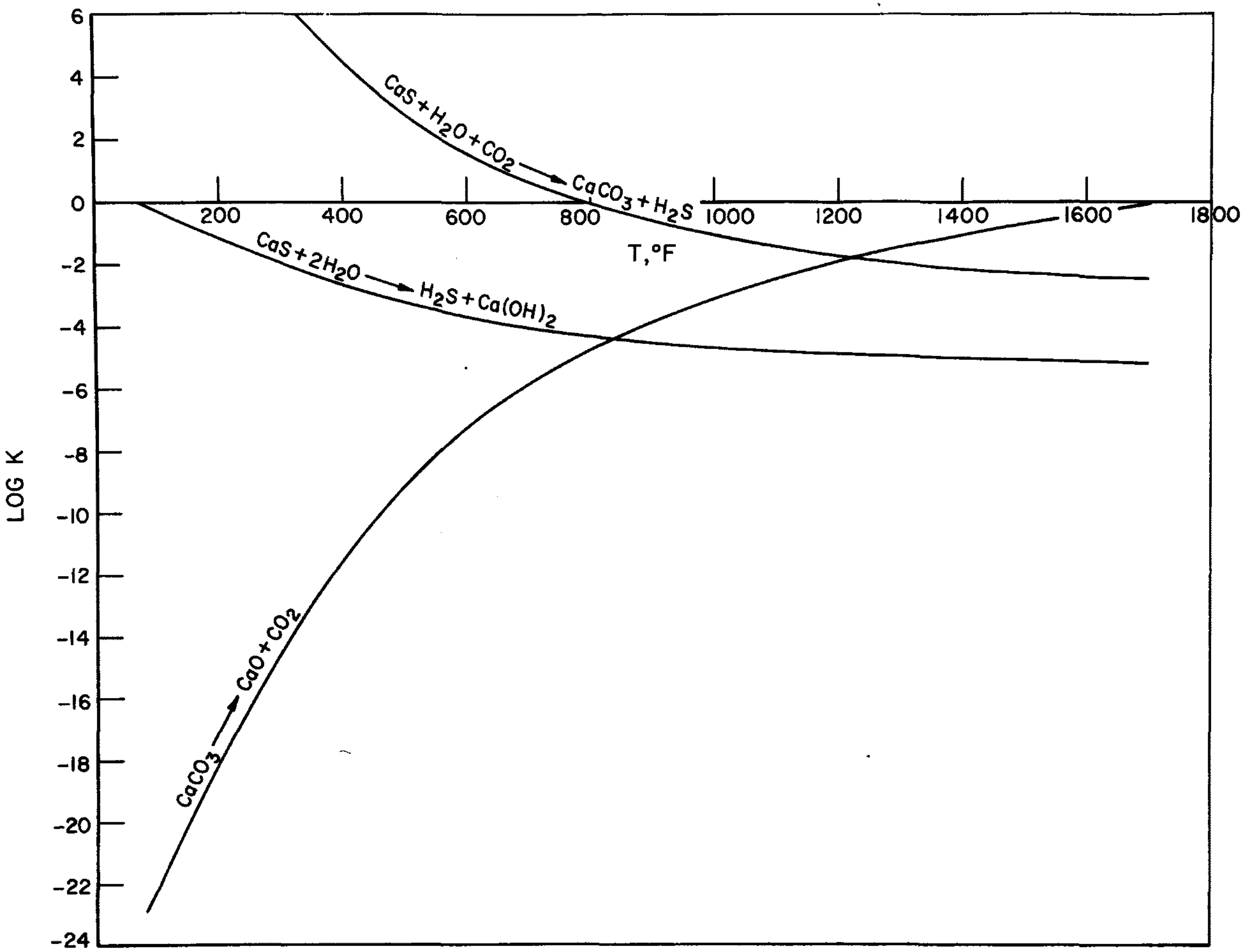

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Figure 7. Thermodynamic equilibrium in coal-getter process for $CaCO_3$ and CaS + H_2O reactions.

These differences alone can cause log K to vary by 0.5 at 900°F. In addition, heat capacity (C_p) data differ from various sources, and this effect can cause additional changes of 0.6 in the value of log K.

Another thermodynamic problem is the differing choice of standard states for sulfur in the literature. Care must be exercised in the thermodynamic calculations of sulfur compounds because of this problem.

The graph (Figure 4) for the hydrotreatment of FeS indicates that the equilibrium partial pressure of H_2S is very low, even at elevated temperatures. The equilibrium constant, K, for the reaction is equivalent to the ratio of the partial pressure of H_2S to H_2. Even at elevated temperatures, the equilibrium constant is less than about 10^{-2}; therefore, the equilibrium partial pressure of H_2S is low. Excessive hydrogen recycle rates would be required to completely desulfurize even small quantities of pyritic coal if the hydrotreating process alone were employed.

The sulfur-getter concept was based on the results presented in the previous paragraph. The coal could not be economically desulfurized by hydrogen alone. However, if a "sulfur-getter" — a material with a greater thermodynamic affinity for sulfur — were introduced into the system, the back pressure of the H_2S would be reduced and the iron would desulfurize. Limestone is an example of this getter:

$$H_2S + CaCO_3 \rightleftarrows CaS + H_2O + CO_2$$

As graphed in Figure 7, the reaction should proceed to the right at temperatures in excess of 800°F. However, when the generation of H_2S is included —

$$FeS + H_2 \rightleftarrows H_2S + Fe$$

gives

$$FeS + H_2 + CaCO_3 \rightleftarrows H_2O + CO_2 + CaS + Fe$$

and

$$FeS + H_2 + 2CaCO_3 \rightleftarrows Ca(OH)_2 + CaS + Fe + 2CO_2$$

log K values of −2.6 and −6.4 result at 1000°F and are lower at reduced temperatures (Figure 6).

Reactions with $Ca(OH)_2$ are more favorable, but those with quicklime —

$$FeS + H_2 + CaO \rightleftarrows CaS + H_2O + Fe$$

and

$$FeS + H_2 + 2CaO \rightleftarrows Ca(OH)_2 + CaS + Fe$$

are both favorable in the temperature range to be studied (Figure 4). The second reaction is favored at temperatures lower than 875°F, indicating that the required lime addition is double that expected for simple conversion to CaS. Quicklime is therefore a better acceptor than limestone, so quicklime was used in the test program.

Regeneration of the CaS was also studied. Several cases were analyzed thermodynamically and are shown in Tables 4 through 8 and Figures 8 and 9.

Case I is regeneration of the CaO and CaS solid mixture with H_2O. At temperatures of 300 to 500 K, all the CaO is converted to $Ca(OH)_2$. Conversion of CaS to $Ca(OH)_2$ decreases with the increased temperature. Table 4 shows the equilibrium composition of the $1CaO:0.3CaS:3H_2O$ system. At 300 K (80°F) the operation must be in a vacuum if the water is to remain in the vapor phase; the maximum total pressure at which water can be in the gaseous phase is 0.5320 psia. Only 30% of the CaS is converted to $Ca(OH)_2$ at this condition. Complete CaS conversion to $Ca(OH)_2$ is possible at these temperatures if the operation is done at higher pressure. For complete reaction at 212°F, the pressure should be 15.95 psia, and at 440°F the pressure required is 2584 psia.

Case II treats the CaO-CaS mix with both H_2O and CO_2. In this system, all the CaO goes to $CaCO_3$ between 700 and 1110 K. At 1300 K, the partial pressure of CO_2 must be above 5.0505 atmospheres, to prevent the decomposition of the $CaCO_3$. The conversion of CaS decreases with the temperature. The CO + S_2 formation does not start until the temperature reaches 1100 K. At 1300 K the reaction —

$$CaS + CO_2 \rightarrow CaO + CO + 1/2S_2$$

is more favorable, and the conversion of CaS is increased. The results are shown in Table 5 and Figure 8.

Case III, treatment of the CaO and CaS with CO_2 only, results in conversion of all the CaO to $CaCO_3$ between 700 and 1100 K. The conversion of CaS to $CaCO_3$ decreases as the temperature increases from 700 to 1100 K. The presence of CO and S_2 is not possible in the resulting gaseous phase up to 1100 K. However, at 1300 K, the reaction —

$$CaS + CO_2 \rightarrow CaO + 1/2S_2 + CO$$

takes place, with the decomposition of CaS to CO and $1/2S_2$. This increases the relative conversion of CaS as the temperature increases from 1100 to 1300 K. Figure 9 and Table 6 tabulate the data.

Cases IV and V, treatment with O_2 and SO_2, respectively, were not desirable because of the formation of $CaSO_4$. These results are shown in Tables 7 and 8. Considering these studies, the most favorable one is the first, i.e., regeneration with H_2O only, because $Ca(OH)_2$ requires lower heat and temperature to regenerate to CaO than the $CaCO_3$ does.

TABLE 4. CASE I(0.3 MOLE CaS, 1 MOLE CaO, 3 MOLES H_2O)

Temperature	300 K (80°F)		373 K (212°F)			500 K (440°F)			
Reaction K Values									
$CaO + H_2O \rightarrow Ca(OH)_2$	Very large		1.0016×10^4			8.03×10^3			
$CaS + 2H_2O \rightarrow Ca(OH)_2 + H_2S$	1.469		0.23982			1.48×10^{-3}			
Pressure, psia	14.7	0.5320*	14.7	15.95†	147.0	14.7	147	1470	2584
Composition, mole									
Solid Phase									
$Ca(OH)_2$	1.3	1.092	1.28559	1.30	1.30	1.00295	1.0592	1.20745	1.3
CaS	--	0.208	0.01441	--	--	0.29705	0.2408	0.09255	--
Liquid Phase									
H_2O	1.38929	--	--	--	--	--	--	--	--
Gas Phase									
H_2O, mole	0.01071	1.816	1.4288	1.40	1.40	1.9941	1.8816	1.5851	1.4
H_2O, %	3.452	95.18	83.34	82.35	82.35	99.85	96.95	88.43	82.35
H_2S, mole	3.00	0.092	0.28559	0.30	0.30	0.00295	0.0592	0.20745	0.3
H_2S, %	96.554	4.82	16.66	17.65	17.65	0.15	3.05	11.57	17.65
CaS Conversion, %	100.00	30.7	95.20	100.00	100.00	0.98	19.73	69.15	100.00

* Pressure at which all water can remain in vapor phase.

† Pressure above which all CaS can be converted into $Ca(OH)_2$.

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TABLE 5. CASE II (0.3 MOLE CaS, 3 MOLES H_2O, 3 MOLES CO_2, 1 MOLE CaO)

Temperature	700 K (800°F)	900 K (1160°F)			1100 K (1520°F)		
Reaction K Values							
$CaO + CO_2 \rightarrow CaCO_3$	1.10×10^{5}	107.24			3.020		
$CaS + 2CO_2 \rightarrow CaCO_3 + COS$	4.90×10^{-3}	3.015×10^{-4}			5.6×10^{-5}		
$CaS + 2CO_2 \rightarrow CaCO_3 + CO + 1/2\ S_2$	9.80×10^{-6}	1.982×10^{-5}			3.336×10^{-5}		
$CaS + 2CO_2 \rightarrow CaCO_3 + CO + 1/8\ S_8$	5.86×10^{-5}	1.763×10^{-5}			1.563×10^{-5}		
$CaS + H_2O + CO_2 \rightarrow CaCO_3 + H_2S$	1.3214	2.161×10^{-2}			1.748×10^{-3}		
$CaS + H_2O \rightarrow CaO + H_2S$	1.64×10^{-5}	2.015×10^{-4}			9.96×10^{-4}		
$CaS + CO_2 \rightarrow CaO + CO + 1/2\ S_2$	--	--			--		
Pressure, atm	≥1	1	10	100	1	10	100
Composition, mole							
Solid Phase							
$CaCO_3$	1.3	1.02574	1.225834	1.3	1.002148	1.02112	1.18835
CaO	--	--		--			
CaS	--	0.27426	0.074166	--	0.297852	0.27888	0.11165
Gas Phase, mole							
CO_2	1.7	1.97402	1.77321	1.700	1.997804	1.97843	1.8078
COS	--	0.00024	0.003014	0.0080	0.000048	0.00045	0.00385
H_2S	0.3	0.0255	0.22282	0.2920	0.002100	0.2067	0.18450
S_2	--						
H_2O	2.7	2.9745	2.77718	2.7080	2.9979	2.97933	2.8155
CO							
Gas Phase, %							
CO_2	36.17	39.6847	37.1258	36.1088	39.9732	39.7364	37.5713
COS		0.0048	0.0631	0.1699	0.0010	0.0090	0.0800
H_2S	6.38	0.5126	4.6652	6.2022	0.0420	0.4152	3.8344
S_2							
H_2O	57.45	59.7979	58.1459	57.191	59.9838	59.8394	58.5143
CO							
CaS Conversion, %	100.00	8.582	75.278	100.00	0.716	7.040	62.783

TABLE 5. CASE II (0.3 MOLE CaS, 3 MOLES H_2O, 3 MOLES CO_2, 1 MOLE CaO) (Continued)

Temperature		1300 K (1880°F)	
Reaction K Values			
$CaO + CO_2 \rightarrow CaCO_3$		1.98×10^{-1}	
$CaS + 2CO_2 \rightarrow CaCO_3 + COS$		4.357×10^{-5}	
$CaS + 2CO_2 \rightarrow CaCO_3 + CO + 1/2\ S_2$		1.165×10^{-4}	
$CaS + 2CO_2 \rightarrow CaCO_3 + CO + 1/8\ S_8$		1.2406×10^{-5}	
$CaS + H_2O + CO_2 \rightarrow CaCO_3 + H_2S$		7.664×10^{-4}	
$CaS + H_2O \rightarrow CaO + H_2S$		7.36×10^{-3}	
$CaS + CO_2 \rightarrow CaO + CO + 1/2\ S_2$		1.1181×10^{-3}	
Pressure, atm	1	10	100
Composition, mole			
Solid Phase			
$CaCO_3$	--	--	1.104462
CaO	1.073074	1.045474	
CaS	0.0226926	0.254526	0.195538
Gas Phase, mole			
CO_2	2.948845	2.976445	1.876596
COS			
H_2S	0.021919	0.021919	0.08552
S_2	0.025578	0.011778	0.009471
H_2O	2.978081	2.978081	2.914480
CO	0.051155	0.023555	0.018942
Gas Phase, %			
CO_2	48.9388	49.5102	38.2588
COS	--		--
H_2S	0.3638	0.3646	1.7435
S_2	0.4245	0.1959	0.1931
H_2O	49.4240	49.5374	59.4184
CO	0.8489	0.3918	0.3862
CaS Conversion, %	24.358	15.158	34.821

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TABLE 6. CASE III (1 MOLE CaO, 0.3 MOLE CaS, 3 MOLES CO_2)

Temperature	700 K (800°F)			900 K (1160°F)		
Reaction K Value						
$CaO + CO_2 \rightarrow CaCO_3$		1.13×10^{5}			107.24	
$CaS + 2CO_2 \rightarrow CaCO_3 + COS$		4.927×10^{-3}			3.0155×10^{-4}	
$CaS + 2CO_2 \rightarrow CaCO_3 + CO + 1/2S_2$		9.786×10^{-6}			1.982×10^{-5}	
$CO + 1/2\ S_2 \rightarrow COS$		503.6			15.212	
Pressure, atm	1	10	100	1	10	100
Composition						
Solid Phase, mole						
$CaCO_3$	1.009714	1.086016	1.30	1.0006	1.01192	1.055350
CaS	0.290286	0.213984		0.2994	0.28808	0.24465
CaO						
Gas Phase, mole						
CO_2	1.980572	1.827968	1.4	1.9988	1.976164	1.88930
COS	0.009714	0.086016	0.3	0.0006	0.011918	0.05535
CO						
S_2						
Gas Phase, %						
CO_2	99.5119	95.5059	82.3529	99.9700	99.4005	97.1537
COS	0.4881	4.4941	17.6471	0.0300	0.5995	2.8463
CO						
S_2						
CaS Conversion, %	3.238	28.672	100.00	0.200	3.973	18.45
Minimum Pressure for 100% Conversion of CaS, atm		52.81			>>100	

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TABLE 6. CASE III (1 MOLE CaO, 0.3 MOLE CaS, 3 MOLES CO_2) (Continued)

Temperature	1100 K (1520°F)			1300 K (1880°F)		
Reaction K Value						
$CaO + CO_2 \rightarrow CaCO_3$	3.049			0.198		
$CaS + 2CO_2 \rightarrow CaCO_3 + COS$	5.626×10^{-5}			4.357×10^{-5}		
$CaS + 2CO_2 \rightarrow CaCO_3 + CO + 1/2S_2$	3.3356×10^{-5}			1.165×10^{-4}		
$CO + 1/2\ S_2 \rightarrow COS$	1.6867			0.374		
Pressure, atm	1	10	100	1	10	100
Composition						
Solid Phase, mole						
$CaCO_3$	1.000113	1.001123	1.011066		1.0126	1.0058
CaS	0.299774	0.298877	0.288934	0.2595	0.2874	0.2942
CaO				1.0405		
Gas Phase, mole						
CO_2	1.999774	1.997754	1.977868	2.9595	1.9275	1.9884
COS	0.000113	0.001123	0.011066			
CO				0.0405	0.0126	0.0058
S_2				0.0202	0.0063	0.0029
Gas Phase, %						
CO_2	99.9943	99.9438	99.4436	97.9902	99.0280	99.5644
COS	0.0057	0.0562	0.5564			
CO				1.3410	0.6473	0.2904
S_2				0.6688	0.3237	0.1452
CaS Conversion, %	0.038	0.370	3.689	13.5	4.20	1.93
Minimum Pressure for 100% Conversion of CaS, atm		>>>100			>>>>100	

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TABLE 7. CASE IV (0.3 MOLE CaS, 1 MOLE CaO, 3 MOLES SO_2)

Temperature		900 K (1160°F)	
Reaction K Values			
$CaO + SO_2 \rightarrow CaSO_3$		2.533×10^{-3}	
$CaS + 2SO_2 \rightarrow CaSO_4 + S_2$		64.021	
$CaS + 2SO_2 \rightarrow CaSO_4 + 1/2\ S_4$		60.4395	
$CaS + 2SO_2 \rightarrow CaSO_4 + 1/3\ S_6$		90.4383	
$CaS + 2SO_2 \rightarrow CaSO_4 + 1/4\ S_8$		55.5027	
$CaS + 3/2\ SO_2 \rightarrow CaSO_3 + 3/4\ S_2$		8.5918×10^{-1}	
$CaS + 3/2\ SO_2 \rightarrow CaSO_4 + 3/8\ S_4$		7.6865×10^{-1}	
$CaS + 3/2\ SO_2 \rightarrow CaSO_3 + 1/4\ S_6$		10.3993×10^{-1}	
$CaS + 3/2\ SO_2 \rightarrow CaSO_3 + 3/16\ S_8$		7.2106×10^{-1}	
$CaO + 3/2\ SO_2 \rightarrow CaSO_4 + 1/4\ S_2$		2.99×10^{5}	
$CaS + 1/2\ SO_2 \rightarrow CaO + 3/4\ S_2$		0.003395	
Pressure, atm	1	10	100
Composition			
Solid Phase, mole			
CaO			
CaS			
$CaSO_4$	1.3	1.3	1.3
Gas Phase, mole*			
S_2	0.320266 (24.2640)	0.089127 (7.6395)	0.019105 (1.729)
S_4	0.057574 (4.3614)	0.05054 (4.3394)	0.024518 (2.219)
S_6	0.040295 (3.0528)	0.111436 (9.5517)	0.122436 (11.082)
S_8	0.001787 (0.1354)	0.015574 (1.3349)	0.038739 (3.5061)
SO_2	0.9000 (68.1859)	0.9000 (77.1435)	0.9000 (81.463)
CaS Conversion, %	100	100	100

* Values in parentheses indicate percent.

B-103-1603

TABLE 7. CASE IV (0.3 MOLE CaS, 1 MOLE CaO, 3 MOLES SO_2) (Continued)

Temperature	1100 K (1520°F)		
Reaction K Values			
$CaO + SO_2 \rightarrow CaSO_3$		15.28316	
$CaS + 2SO_2 \rightarrow CaSO_4 + S_2$		0.36134	
$CaS + 2SO_2 \rightarrow CaSO_4 + 1/2\ S_4$		0.07903	
$CaS + 2SO_2 \rightarrow CaSO_4 + 1/3\ S_6$		0.05384	
$CaS + 2SO_2 \rightarrow CaSO_4 + 1/4\ S_8$		0.02627	
$CaS + 3/2\ SO_2 \rightarrow CaSO_3 + 3/4\ S_2$		0.04526	
$CaS + 3/2\ SO_2 \rightarrow CaSO_4 + 3/8\ S_4$		0.014477	
$CaS + 3/2\ SO_2 \rightarrow CaSO_3 + 1/4\ S_6$		0.010855	
$CaS + 3/2\ SO_2 \rightarrow CaSO_3 + 3/16\ S_8$		0.006337	
$CaO + 3/2\ SO_2 \rightarrow CaSO_4 + 1/4\ S_2$		122.0	
$CaS + 1/2\ SO_2 \rightarrow CaO + 3/4\ S_2$		0.00296	
Pressure, atm	1	10	100
Composition			
Solid Phase, mole			
CaO			
CaS	0.0225		
$CaSO_4$	1.2775	1.3	1.3
Gas Phase, mole*			
S_2	0.27505 (22.4893)	0.2440 (20.8418)	0.1110 (10.1742)
S_4	0.002925 (0.2392)	0.02425 (2.0714)	0.051 (4.6746)
S_6	0.00005 (0.0041)	0.002475 (0.2114)	0.029 (2.6581)
S_8			
SO_2	0.9450 (77.2674)	0.90 (76.8754)	0.90 (82.4931)
CaS Conversion, %	100	100	100

* Values in parentheses indicate percent.

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TABLE 7. CASE IV (0.3 MOLE CaS, 1 MOLE CaO, 3 MOLES SO_2) (Continued)

Temperature	1300 K (1800°F)		
Reaction K Values			
$CaO + SO_2 \rightarrow CaSO_3$		0.52234	
$CaS + 2SO_2 \rightarrow CaSO_4 + S_2$		0.027907	
$CaS + 2SO_2 \rightarrow CaSO_4 + 1/2\ S_4$		0.002486	
$CaS + 2SO_2 \rightarrow CaSO_4 + 1/3\ S_6$		0.000931	
$CaS + 2SO_2 \rightarrow CaSO_4 + 1/4\ S_8$		0.000398	
$CaS + 3/2\ SO_2 \rightarrow CaSO_3 + 3/4\ S_2$		0.01666	
$CaS + 3/2\ SO_2 \rightarrow CaSO_4 + 3/8\ S_4$		0.002717	
$CaS + 3/2\ SO_2 \rightarrow CaSO_3 + 1/4\ S_6$		0.00130	
$CaS + 3/2\ SO_2 \rightarrow CaSO_3 + 3/16\ S_8$		0.000688	
$CaO + 3/2\ SO_2 \rightarrow CaSO_4 + 1/4\ S_2$		0.87496	
$CaS + 1/2\ SO_2 \rightarrow CaO + 3/4\ S_2$		0.03189	
Pressure, atm	1	10	100
Composition			
Solid Phase, mole			
CaO			
CaS	0.30	0.3	
$CaSO_4$	1.0	1.0	1.3
Gas Phase, mole*			
S_2	0.25 (14.2857)	0.25 (13.2857)	0.55 (37.9310)
S_4			
S_6			
S_8			
SO_2	1.5 (85.7143)	1.5 (85.7143)	0.9 (62.0690)
CaS Conversion, %	0.0	0.0	100.0

* Values in parentheses indicate percent.

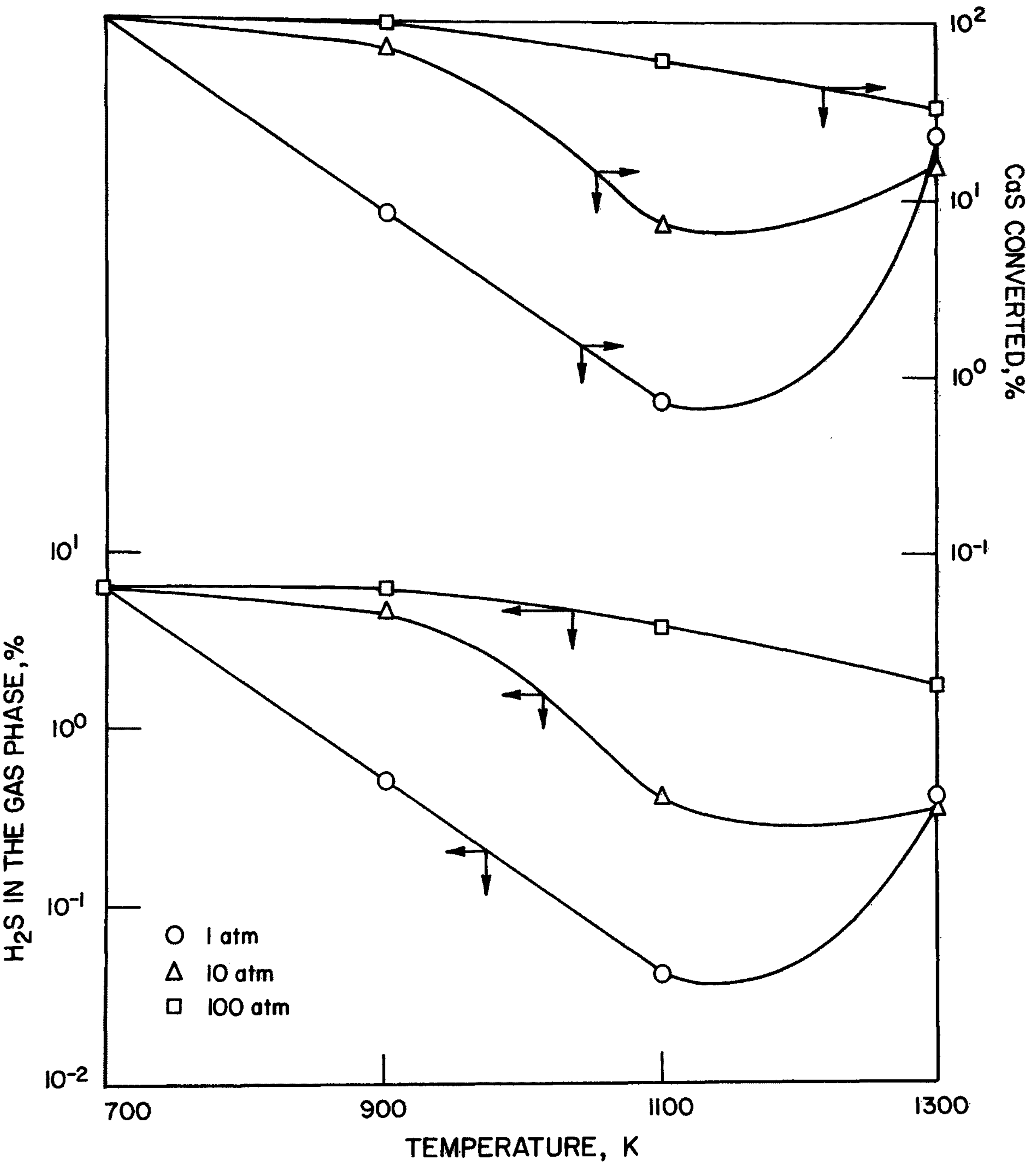
B-103-1603

TABLE 8. CASE V (0.3 MOLE CaS, 1 MOLE CaO, 1 MOLE O_2)

Temperature	700 K (800°F)	900 K (1160°F)	1100 K (1520°F)	1300 K (1880°F)
Reaction K Values				
$CaS + 2O_2 \rightarrow CaSO_4$	$e^{51.82}$	$e^{36.2}$	$e^{26.31}$	$e^{19.91}$
$CaS + 1/2O_2 \rightarrow CaO + 1/2S_2$	4.45×10^6	1.35×10^5	1.44×10^4	7.425×10^3
$CaS + 3/2O_2 \rightarrow CaSO_3$	$e^{38.60}$	$e^{25.73}$	$e^{18.72}$	$e^{14.32}$
Pressure, atm	1 10 100	1 10 100	1 10 100	1 10 100
Composition				
Solid Phase, mole				
CaS	—— 0.225 ——	—— 0.225 ——	—— 0.225 ——	—— 0.225 ——
CaO	—— 1.00 ——	—— 1.00 ——	—— 1.00 ——	—— 1.000 ——
$CaSO_4$	—— 0.075 ——	—— 0.075 ——	—— 0.075 ——	—— 0.075 ——
$CaSO_3$	--			
Gas Phase, mole				
O_2	—— 0 ——	—— 0 ——	—— 0 ——	—— 0 ——

Conclusion: The only reaction of importance is $CaS + 2O_2 \rightarrow CaSO_4$.

A-14-129



A-103-1599

Figure 8. Cas-CaO-CO_2-H_2O system.

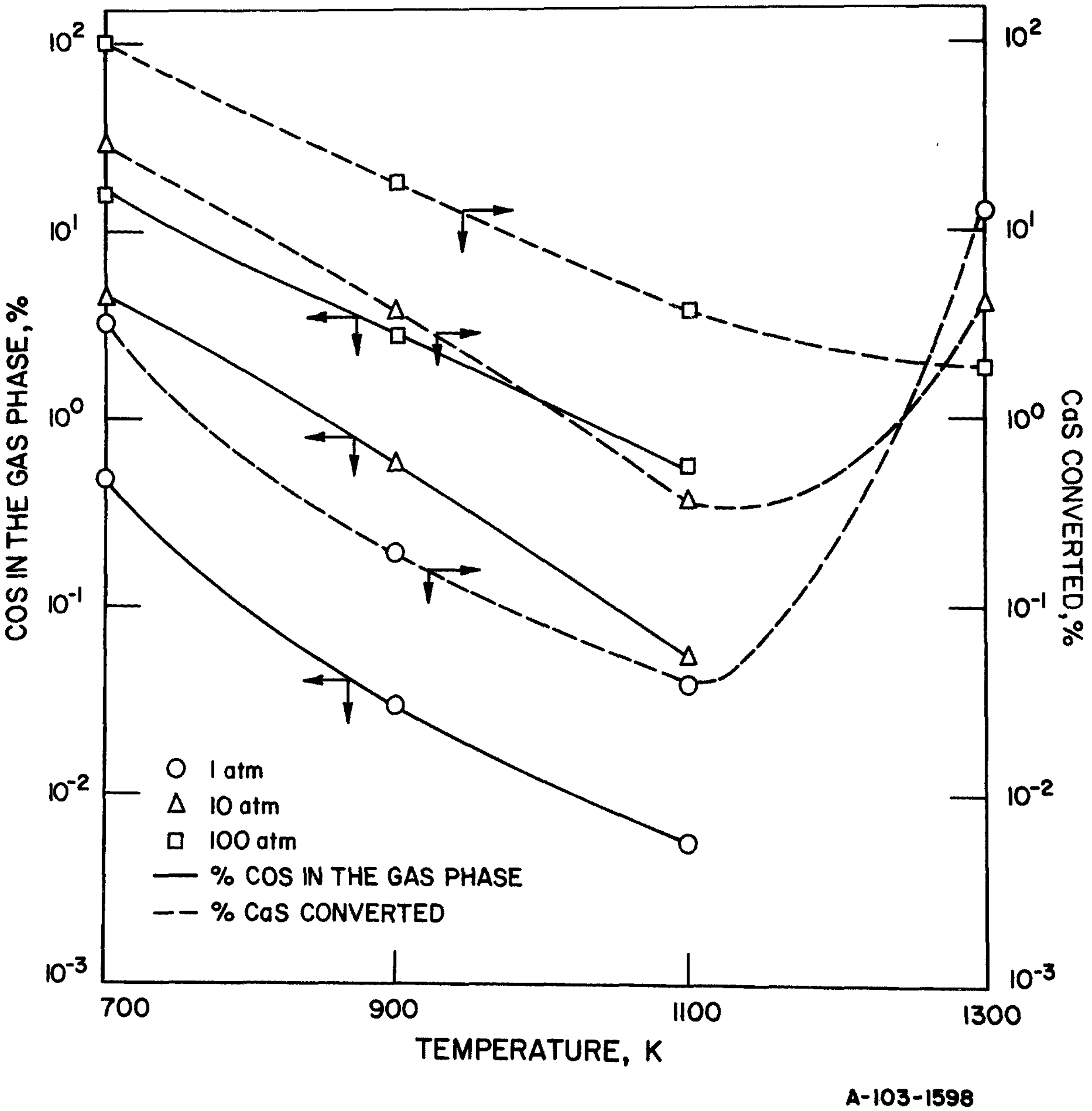


Figure 9. $CaO-CaS-CO_2$ system.

EQUIPMENT

PILOT UNIT

An existing pilot-development unit was renovated for use in the project. The unit is 10 inches in diameter and about 15 feet tall. A 6-inch pipe, 6 feet in length, was used as an inside overflow tube, so that the fluidized-bed section is 6 feet in height. The bottom was redesigned with a distributor plate that has nonweep nozzles. Figures 10 through 16 show the reactor configuration and design in addition to nozzle operating characteristics.

Material is screw-fed into the bottom of the reactor by a variable speed drive. Fluidizing gas (usually hydrogen) is introduced below the distribution plate, flows up through the nozzles, and fluidizes the material in the bed. When the material reaches the 6-foot level, it overflows the center pipe and falls into one of the receivers, as determined by the position of the diverter valve on the overflow line.

The bed is heated by external electric heaters. Six heating zones are controlled by temperature controllers. The gas flows out the top of the reactor, through a cyclone, a scrubber, and a knockout drum, and then out the stack. After the first runs, the cyclone was removed because tars were condensing in the unit. The dust loading was small and could be handled by the wet scrubber.

BATCH REACTOR

To gather background data while the pilot unit was being renovated, a batch reactor was set up. A flow diagram is shown in Figure 17. The reactor (shown schematically in Figure 17) is a 1-1/2 inch stainless-steel pipe with a sintered disk plate for fluidization. The reactor sits in a fluidized, heated sand bed. Preheated air fluidizes the sand. Nitrogen or hydrogen was used to fluidize the material charged to the reactor, with a rotameter for flow indication. A bubbler was used to condense tars and to trap solid particles before the gas was exhausted.

THERMOBALANCE

The thermobalance is a laboratory device that continuously measures the weight of a sample as it is being exposed to a controlled environment of temperature, pressure, and surrounding gas composition. It has a heated zone into which the sample can be lowered and then heated with a controlled time-temperature profile. If desired, rapid heat-up can be effected by preheating the unit to the desired temperature and then lowering the basket into the hot zone. Gas flow is large relative to the coal sample size so that large changes

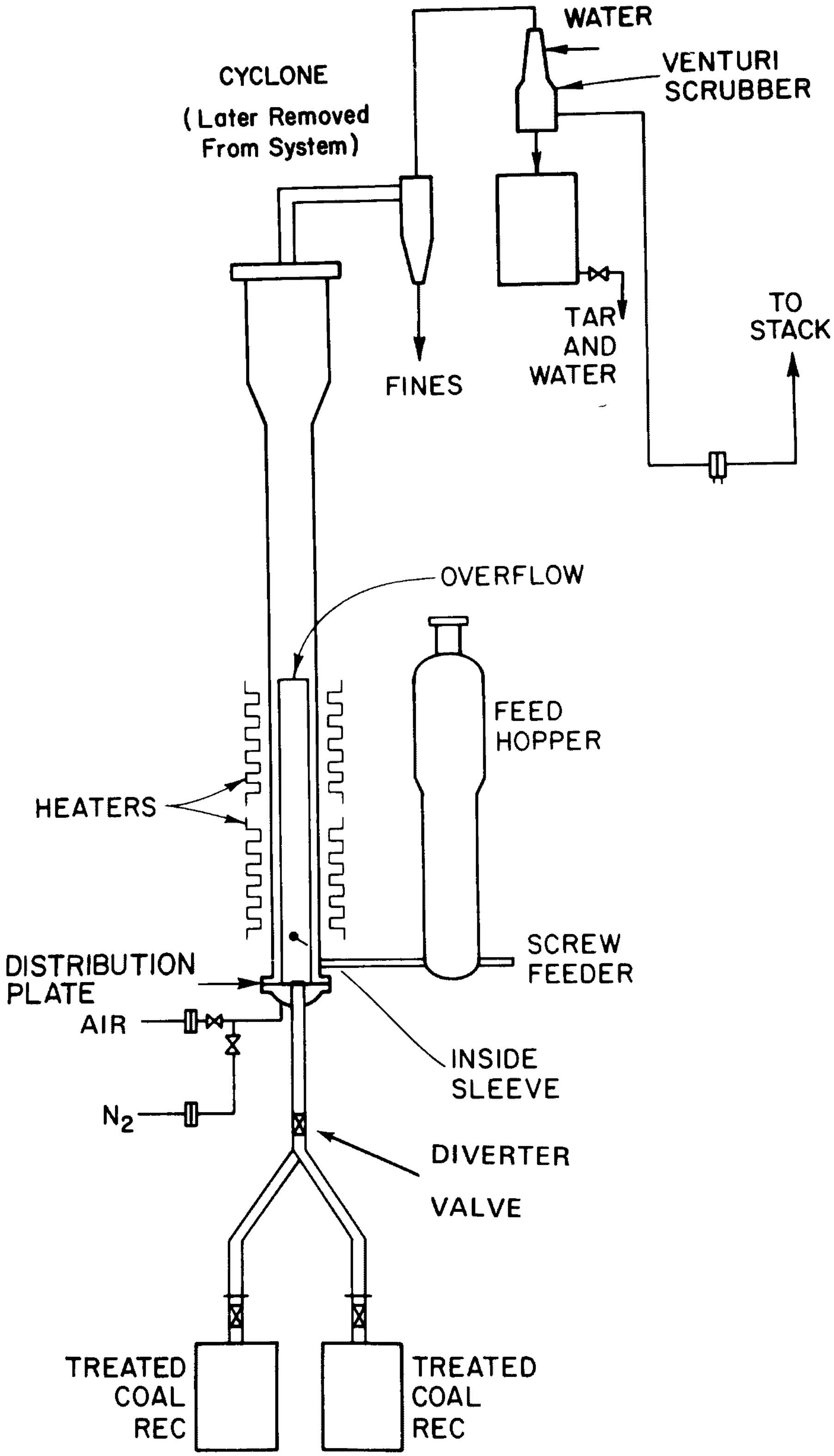


Figure 10. Reactor flow sheet.

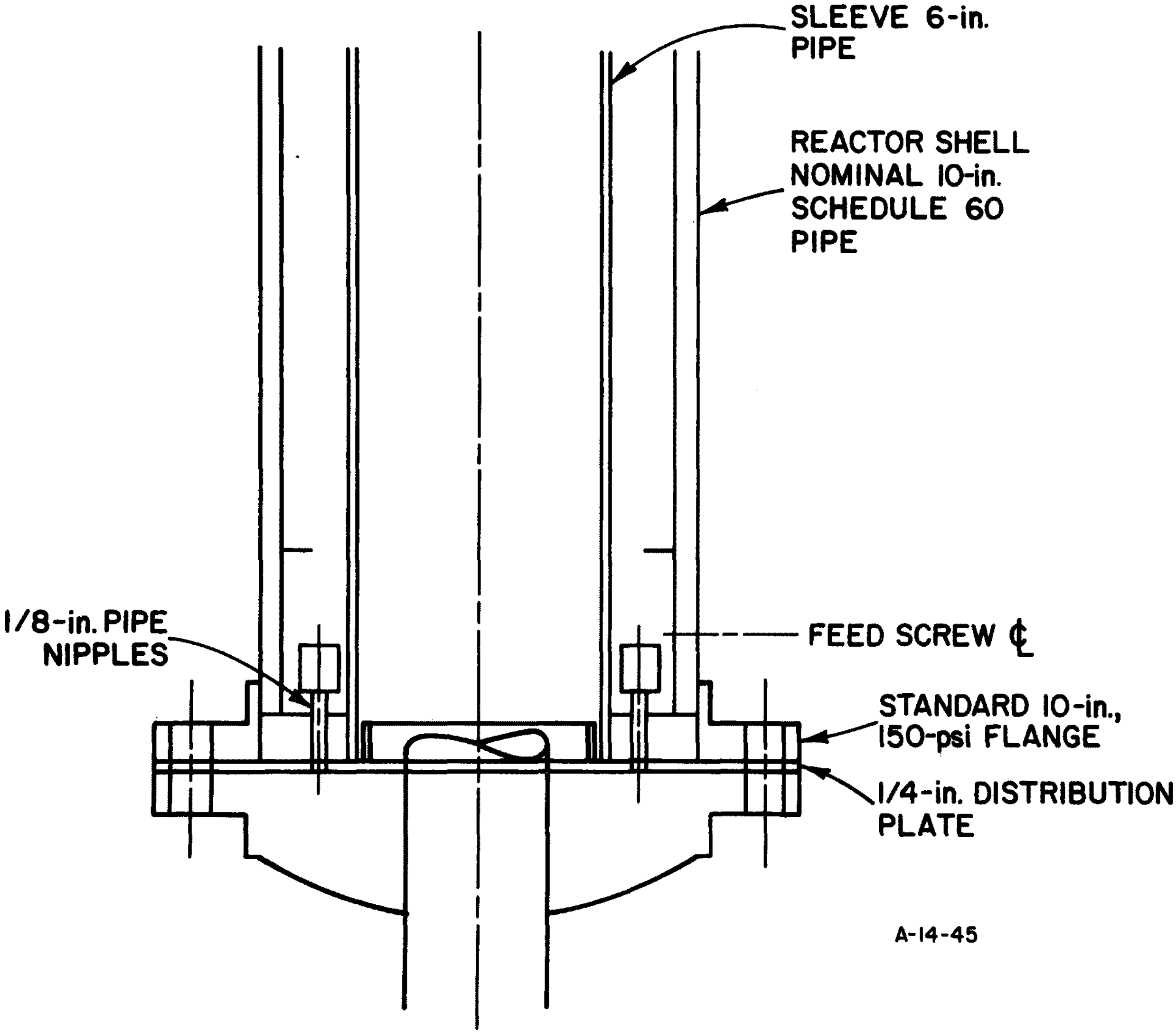


Figure 11. Distribution plate detail.

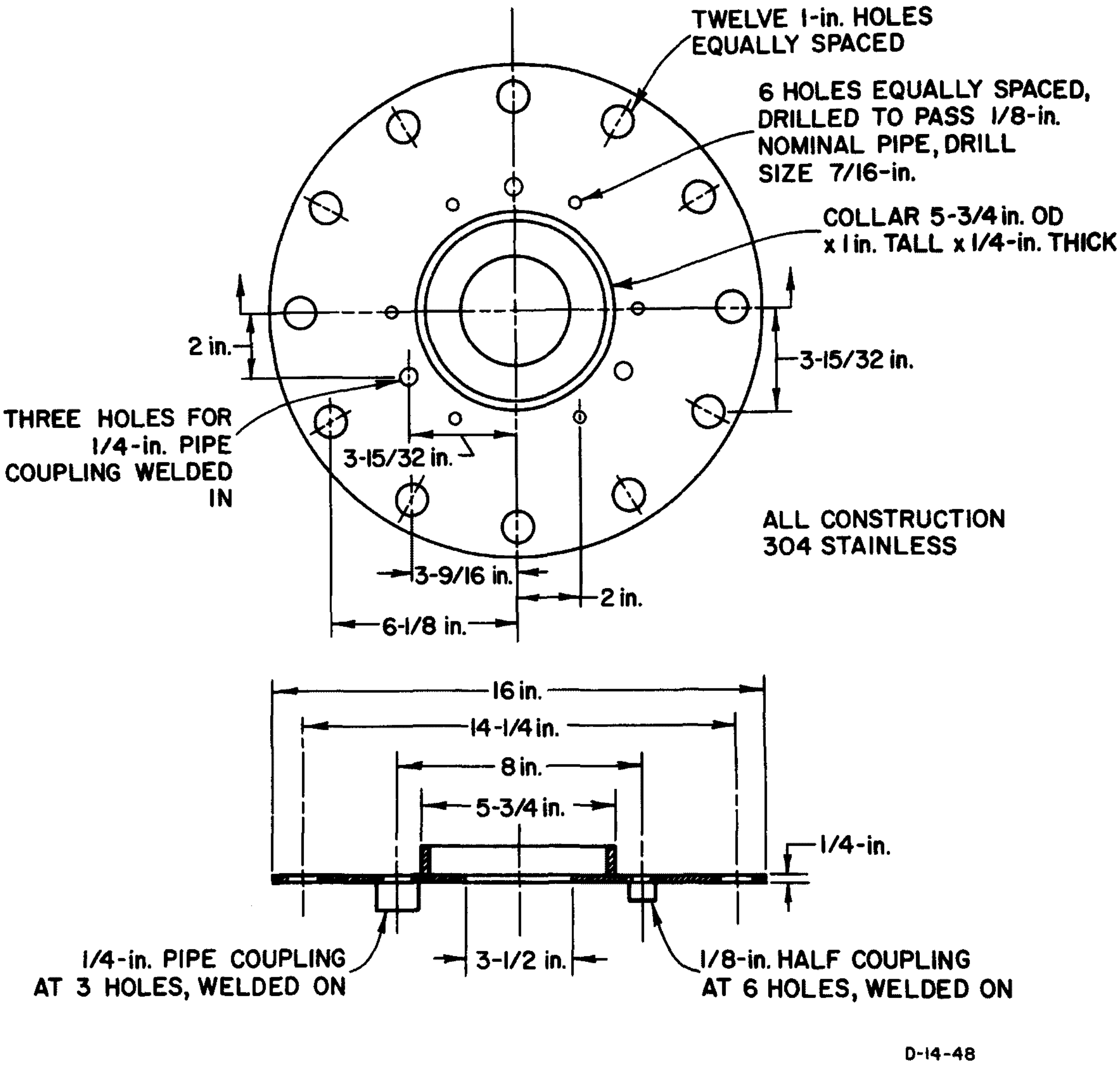


Figure 12. Distributor plate.

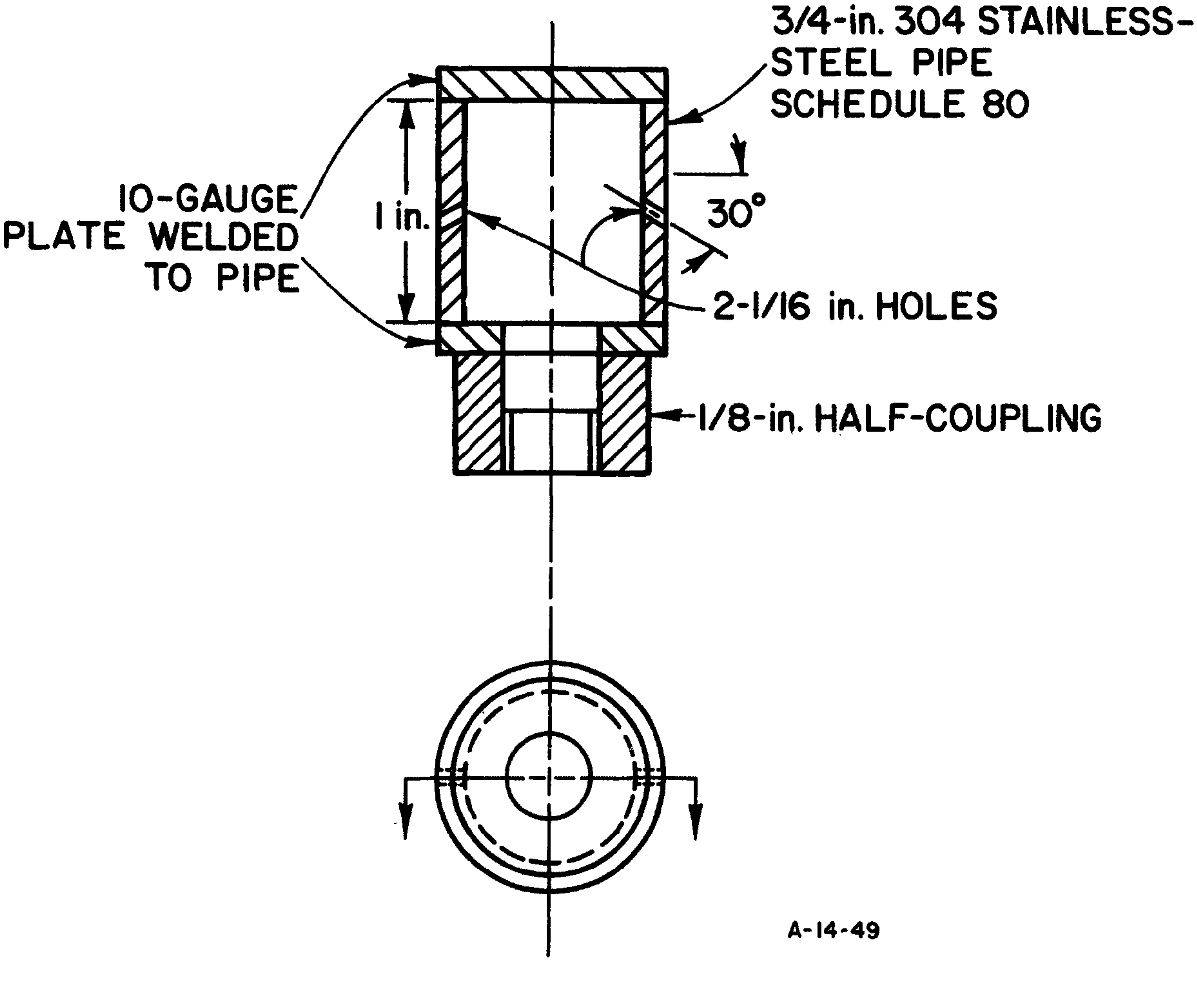


Figure 13. Distributor nozzles.

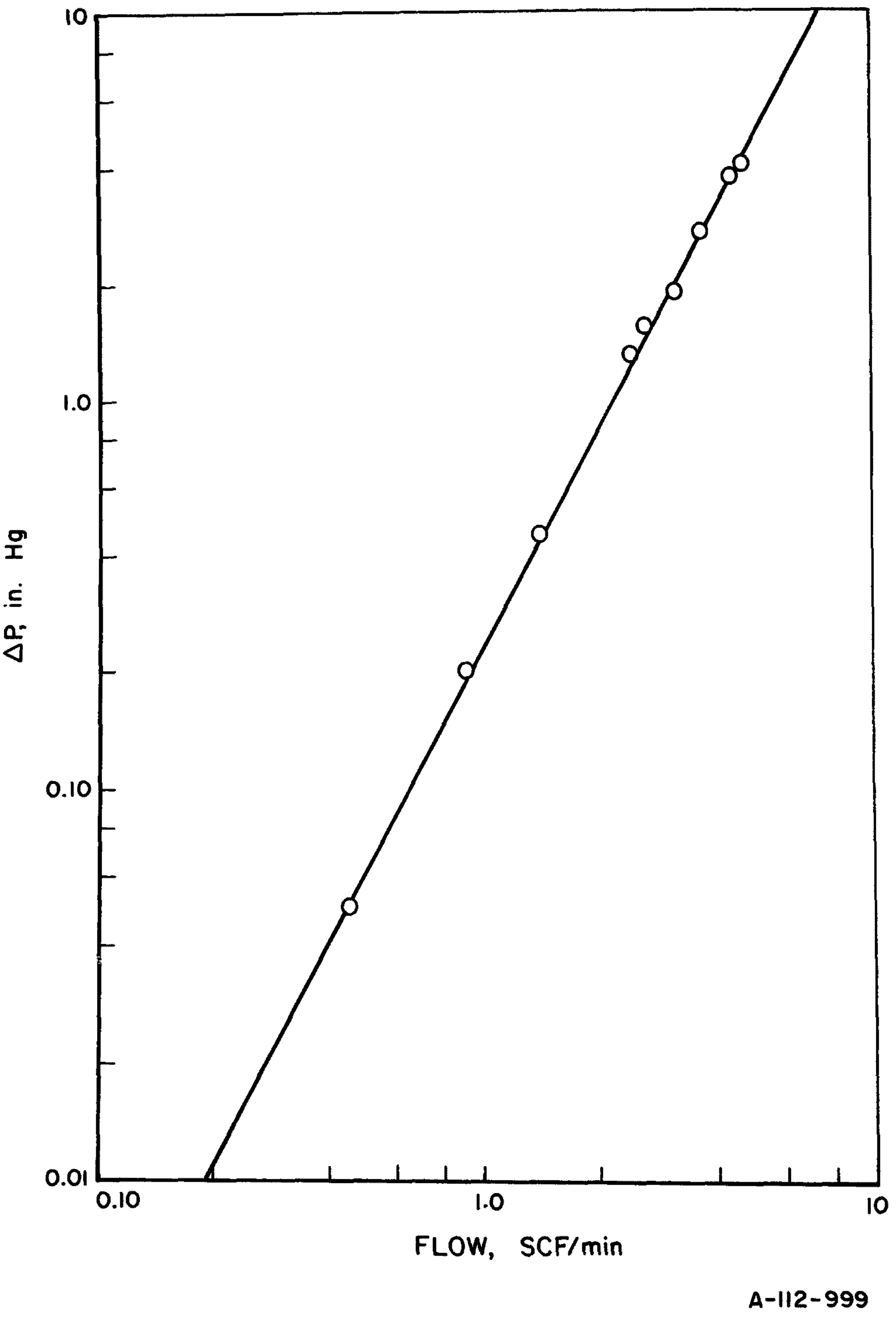


Figure 14. Flow of H_2 in distributor nozzle.

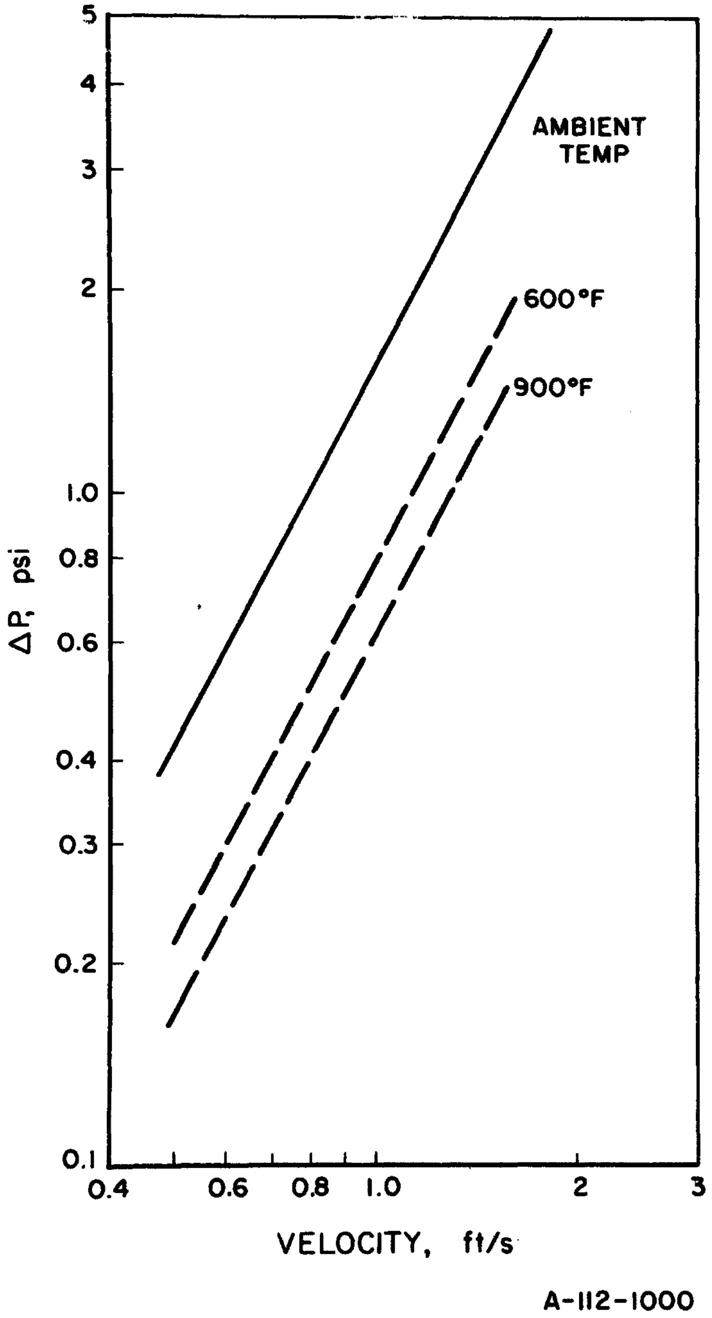
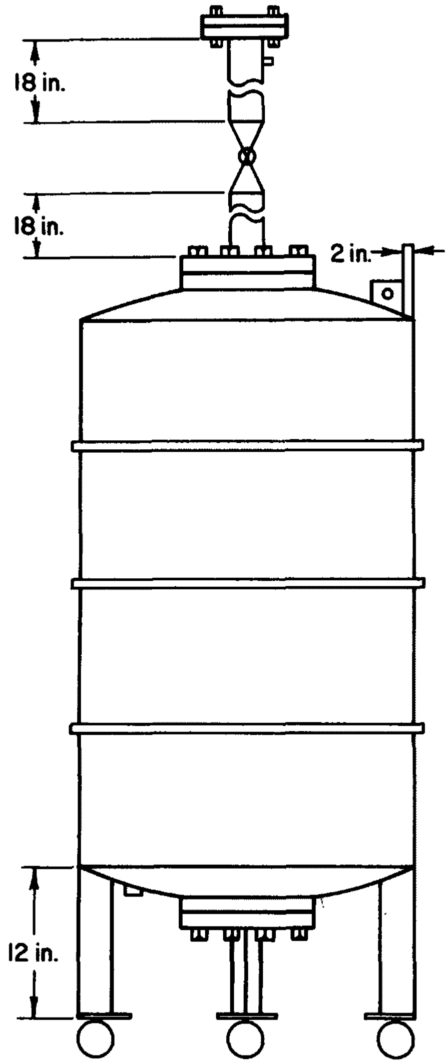


Figure 15. Distributor plate nozzle pressure drop versus reactor gas velocity.



FRONT VIEW

MATERIAL
304 SS [EXCEPT AS NOTED]

3-in. NIPPLES
TWO 3-in. SCH 40 NIP'S, 1 END N.P.T.;
ONE WITH 1/4-in. HALF-COUPLING

VALVE
HILLS-McCANNA TOP ENTRY 300 psi
SCREWED END, GRAPHITE SEAT,
3-in. BALL VALVE

LIFTING PLATE
2 in. x 2 in. x 3/8 in. ℞ WITH 1/2-in. Φ
HOLE O.C. IN-LINE (VERTICALLY)
WITH LEG [MILD STEEL]

HEADS
TWO 20-in. Φ 0.15-in.-THICK DISH HEADS
WITH FLANGES WELDED ON;
ONE WITH 1/2-in. HALF-COUPLING

RINGS
THREE 1/2-in. Φ BAR

SHELL
20-in. Φ SCH 5 PIPE, 30 in. LONG

FLANGES
ONE 3-in., 150-psi R.F. BLIND FLANGE
ONE 3-in., 150-psi SLIP-ON FLANGE
TWO 6-in., 150-psi SLIP-ON FLANGE
WITH BOLTS WELDED AS STUDS;
ONE 6-in., 150-psi R.F. BLIND FLANGE
ONE 6-in., 150-psi R.F. FLANGE WITH
HOLE FOR 3-in. PIPE

LEGS
THREE 2 in. x 2 in. x 1/4 in. ANGLE AND
3-3/4 in. x 4-5/8 in. x 1/4 in. THICK BASEPLATE
FOR WHEELS WITH FOUR 3/8-in. Φ HOLES
2-3/4 in. x 3-5/8 in. O.C. (MOUNT LEGS
120° APART) [MILD STEEL]

WHEELS
THREE 5-in. Φ SWIVEL CASTERS WITH
BRAKES

SHACKLE
3/8-in. SCREW PIN ANCHOR SHACKLE
[FORGED STEEL]

D-14-47

Figure 16. Treated coal receiver.

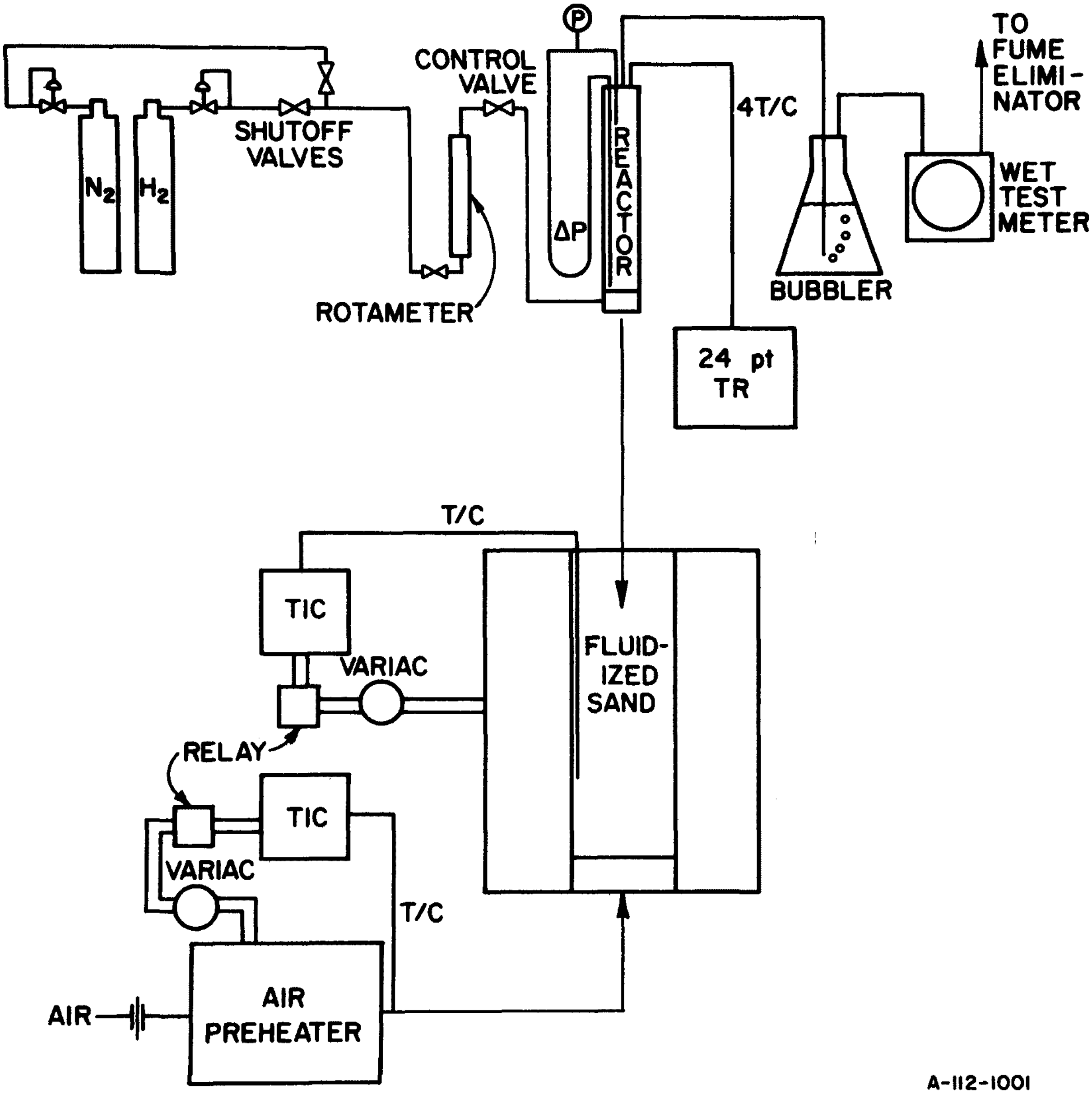


Figure 17. Batch coal desulfurization equipment.

in coal composition are associated with very little change in gas qualities. A flow sheet for the thermobalance test station is shown in Figure 18.

MODIFIED BATCH REACTOR

The batch reactor used in the first phase of the program was not as flexible in operation as desired. For this reason, a new reactor and heating unit was constructed.

A diagram of the new type of reactor is presented in Figure 19. With this type of reactor, material charging and discharging was simplified. The external heater was designed so that the elements heat the reactor directly. The elimination of the sand bed reduced the system mass; heat-up was faster and internal reactor temperatures were easier to control. A flow sheet for the new system is presented in Figure 20.

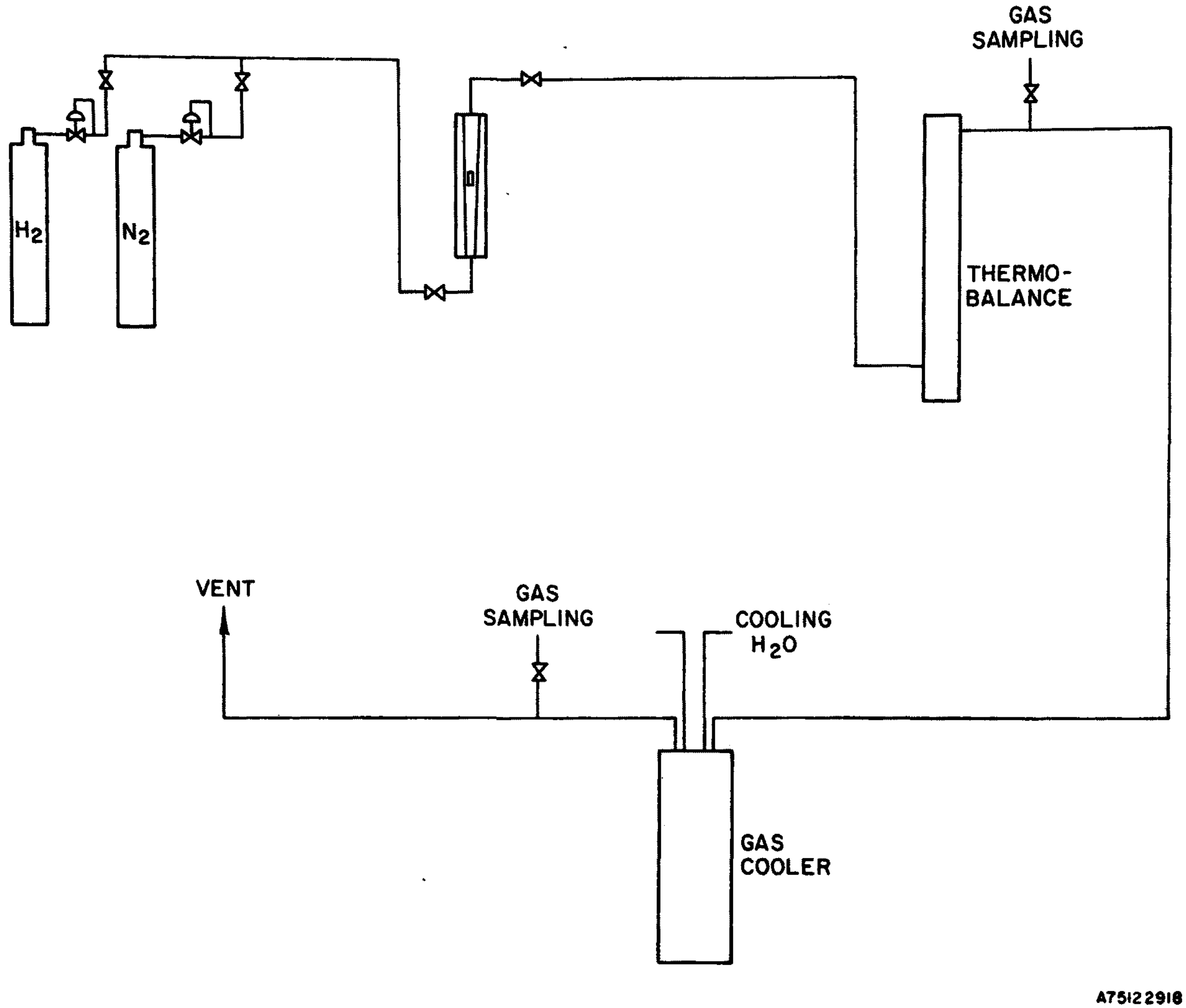


Figure 18. Flow diagram of thermobalance system.

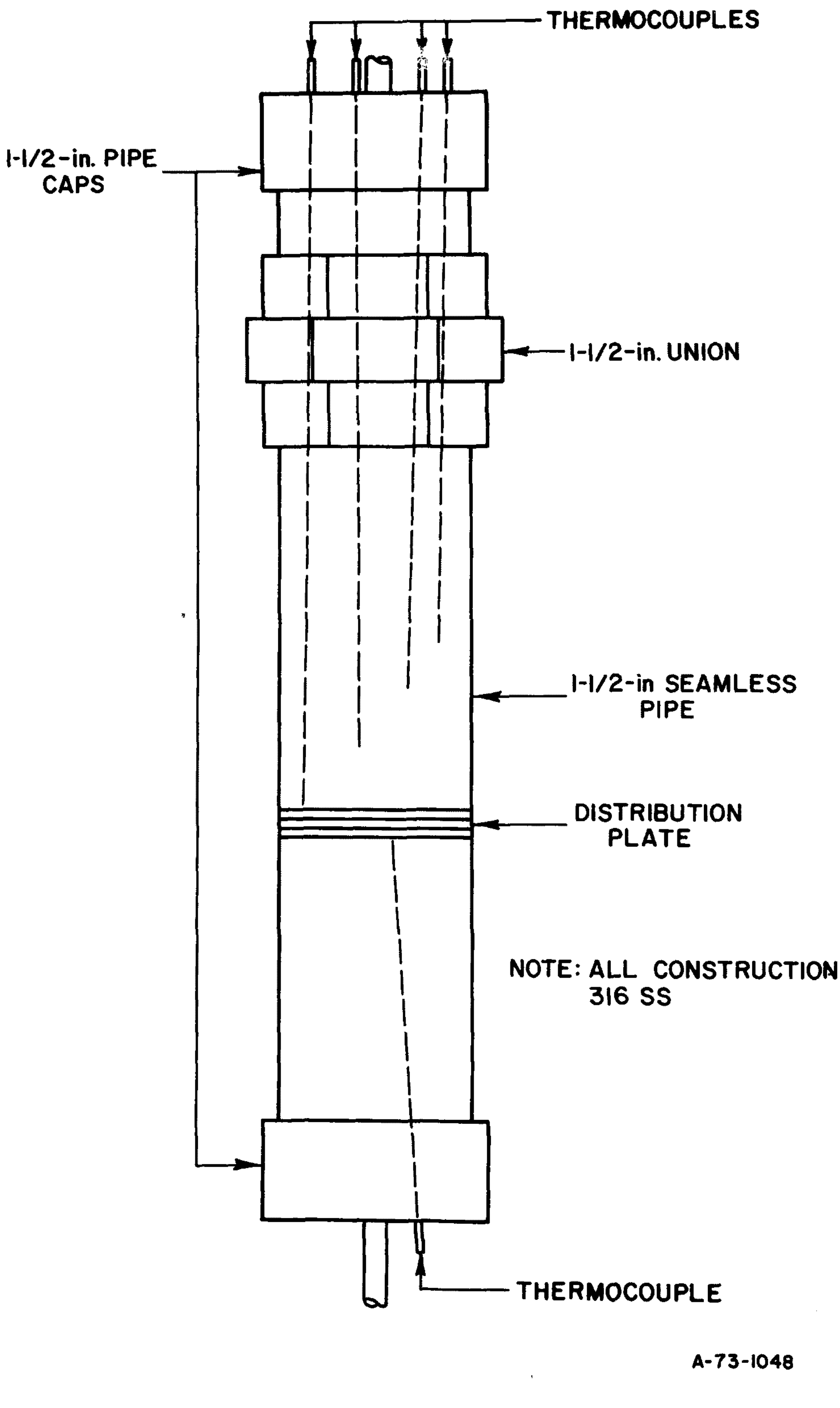


Figure 19. Modified batch reactor.

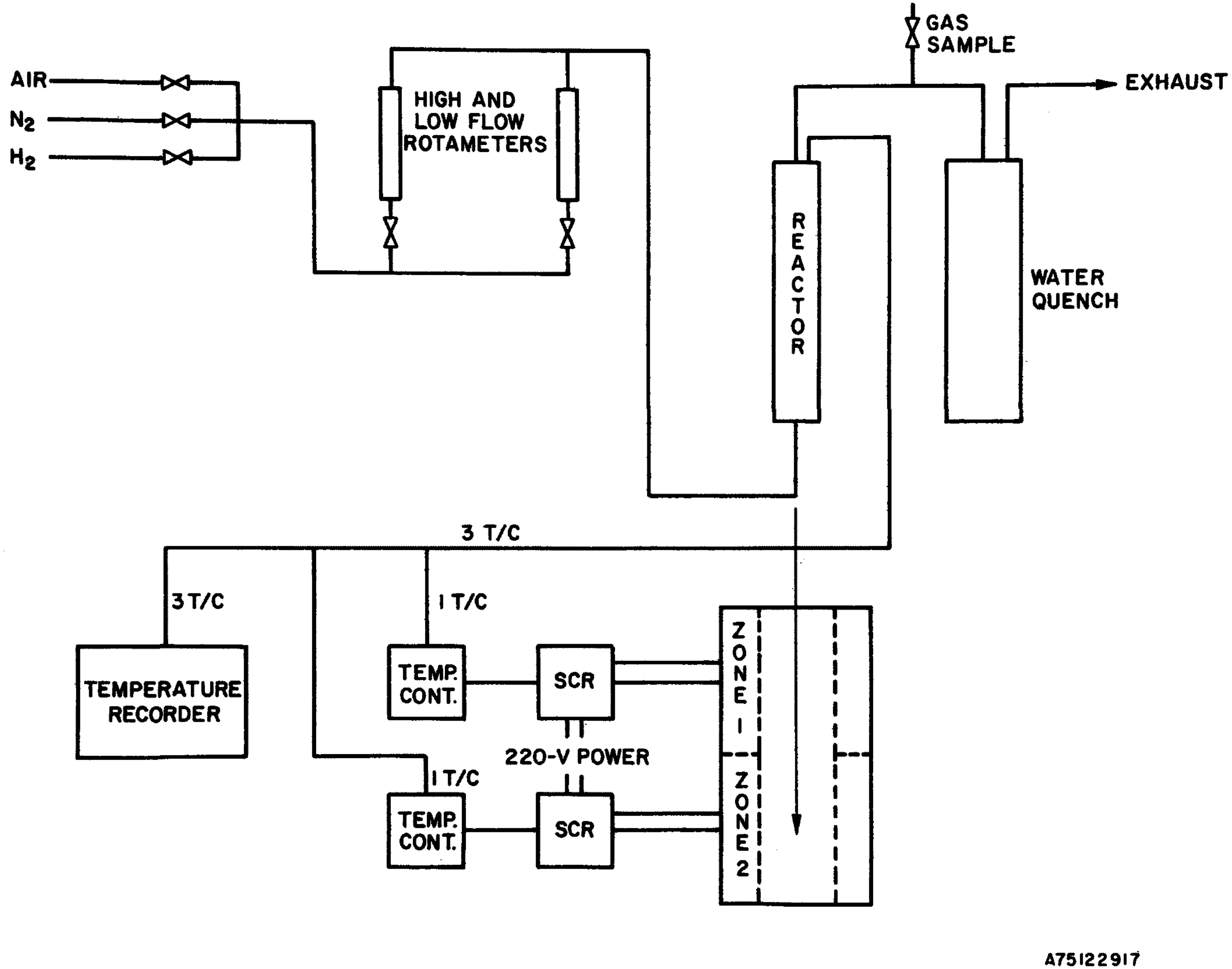


Figure 20. Modified batch reactor flow system.

LABORATORY PROCEDURES

Initially, samples were analyzed by standard ASTM methods. The coal-lime mixture was separated by a float-sink process in carbon tetrachloride, and each fraction was analyzed.

Total sulfur was determined by combusting the sample with a flux of magnesium oxide and sodium carbonate (Eschka reagent). The SO_2 generated was collected by the flux and, after dissolution, was precipitated as barium sulfate. The total sulfur content was then determined gravimetrically. A second sample was used to determine the sulfur by types. It was treated with HCl, and the H_2S evolved was precipitated as cadmium sulfide. This H_2S is assumed to correspond to the sulfide content of the sample. The liquid from the HCl treatment contained dissolved sulfate, which was precipitated with barium. The pyritic sulfur was not attacked by HCl in the first leach, but all the nonpyritic iron was removed. To determine the pyrite content, the sulfur was digested with concentrated nitric acid for 4 hours and the iron content determined titrametrically. In the standard technique, this iron is assumed to correspond to the pyrite content of the sample. The organic sulfur content was then determined by subtracting the sum of the other sulfur types from the previously determined total.

This analytical procedure is a lengthy process and is subject to sampling errors. Several other sources of error were also found:

a. The float-sink separation in carbon tetrachloride caused iron pyrite and iron sulfide (properly associated with the coal) to partially distribute in the lime fraction.

b. Treated residue samples cannot be ground without significant loss of calcium sulfide (caused by hydrolysis with atmospheric moisture).

c. Analyses of lime-pyrite mixtures resulted in apparently low pyritic sulfur determinations. Possibly the nitric acid digestion was insufficient for complete removal of this material.

d. Calcium sulfate formation from lime in the residue was possible during the combustion for total sulfur analysis. Any calcium sulfate formed would not be dissolved in the standard water dissolution of the flux.

These factors and others suggest that the standard ASTM procedures should be modified for this work.

Development of a new analytical procedure was undertaken, with emphasis on several improvements. Among these were quicker analysis, use of one sample for all work, and reproducibility. The following procedure resulted.

About 4 to 5 grams of the unground sample is treated in a flask with 6N HCl. The H_2S evolved flows through three cadmium carbonate traps and is precipitated as cadmium sulfide. This is further treated with HCl and iodine. Sulfide ($S^=$) is determined titrametrically.

The treated residue is filtered, giving a filtrate containing sulfate ($SO_4^=$), nonpyritic iron, and calcium (Ca^{++}). The residue is air-dried, ground in a diamonite mortar, and reextracted under reflux with 6N HCl. This second extraction removes additional small amounts of the $SO_4^=$ and nonpyritic iron. The two filtrates are combined and analyzed. The iron is precipitated from the solution as ferric hydroxide, then dissolved and analyzed colorimetrically. The filtrate, containing $SO_4^=$, is acidified, boiled, and barium sulfate precipitated by the addition of barium chloride. The precipitate is filtered, dried, and weighed. This gives a measure of the acid-soluble sulfate. The filtrate is also analyzed for Ca^{++} by atomic absorption.

After the second HCl extraction, the residue is air dried, intimately mixed with Eschka reagent, and fired at 800°C for several hours. The resulting mixture contains $SO_4^=$ from pyritic and organic sulfur; this sulfate is readily extracted in hot water. The iron originally present as pyrite appears as iron oxide (Fe_2O_3). The Eschka-water mixture is filtered to separate a solution containing $SO_4^=$ from the MgO-Fe_2O_3 residue. The filtrate is acidified and boiled; then barium chloride is added to precipitate the $SO_4^=$. Digestion followed by filtration and drying gives a measure of both pyritic plus organic sulfur. Pyritic sulfur is calculated from the iron in the Eschka residue. Organic sulfur is determined by the difference of [organic plus pyritic sulfur] minus pyritic sulfur, as calculated by the iron analysis.

Several chemicals were tested by this procedure. Reagent-grade zinc sulfide gave 96% to 98% recovery of theoretical $S^=$. Technical-grade calcium sulfide, specified as 80% to 85% CaS, gave 80% recovery of $S^=$, which is good agreement. A sample of pure iron pyrite was analyzed. Ninety-nine percent of the theoretical iron and 96.4% of the theoretical sulfur were obtained. Technical-grade iron sulfide gave 93.7% of the theoretical sulfide. NBS-certified coal (3.02±0.008% sulfur) gave 99.55% of theoretical sulfur by Eschka.

Figure 21 presents the revised analytical procedure, which was used to analyze samples from later tests.

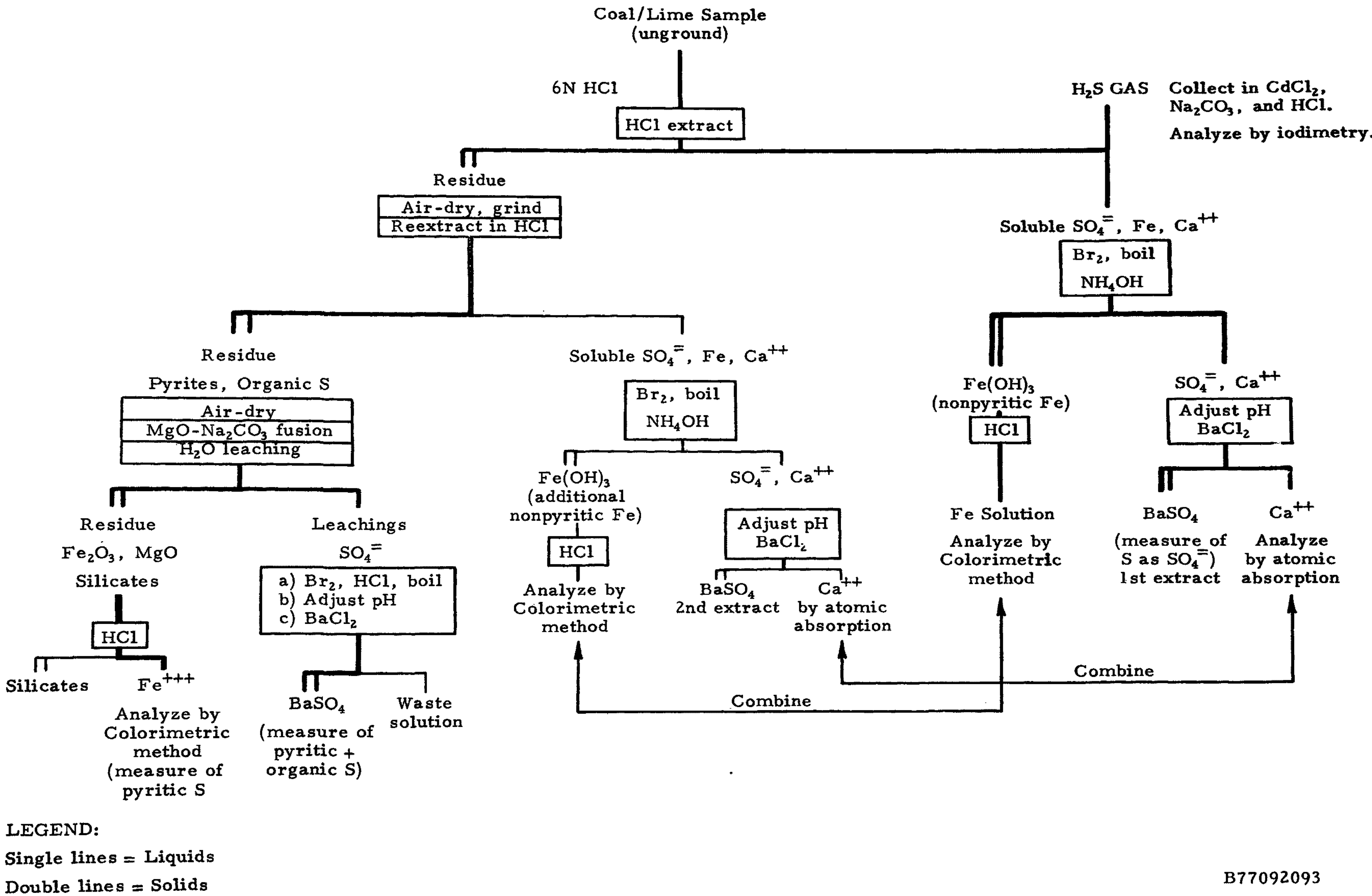


Figure 21. Laboratory procedure for the new analytical method.

TEST RUNS — START OF PHASE I

BATCH REACTOR

As previously noted, the batch reactor was used to gather preliminary data concerning the process while the pilot unit was being renovated for use in this program. A 100-gram charge was used in all the preliminary batch tests. The first tests used a mix of 4 parts coal to 1 part lime by weight. The coal used in these tests was the initial coal from the Illinois No. 6 seam. This ratio corresponds to about 400% of the stoichiometric lime requirement if the coal contains 4% sulfur. Laboratory analysis indicated that the lime was hydrating (from coal moisture) and carbonating before it could react with H_2S to give CaS. Therefore, the ratio was changed to 2 parts coal and 1 part lime for Run 14 and all subsequent tests. In one test, iron pyrite and calcium oxide were used as a mixture to prove the acceptor concept without interference from other coal-related effects.

In running a test, 100 grams of material was charged to the reactor, which was then lowered into the fluidized sand bed. All heaters were turned on, and the reactor was brought to the desired temperature with nitrogen fluidizing the sample. When the reactor temperature was reached, hydrogen was introduced for a specified time (1/2 hour, 1 hour). For base-line comparisons, similar runs were made using only nitrogen. The temperature ranged from 600° to 1000°F in 100°F increments.

After the specified time at temperature, the reactor was removed from the sand bed. If hydrogen had been used in the test, the system was purged with nitrogen. When the reactor was cool, it was opened, and the sample was removed and submitted to the laboratory for analysis.

PILOT-UNIT TESTS

Pilot-unit tests were started when the modification of the pilot unit was completed. Coal alone was used in the first six tests to determine its operating and fluidization characteristics. After these tests, a 2 to 1 mixture of coal and lime in the selected screen size was used for feed. The initial Illinois No. 6 coal was used in these tests.

Feed material was mixed and charged to the feed hopper before the run was started. The heaters were turned on, and the controllers were set for the run temperature. The gas flow was set to meet the required bed velocity for fluidization. The feed screw was turned on and the speed adjusted to provide the coal feed rate selected. The diverter valve, at the reactor discharge, was set so that discharged material went into the waste-material receiver. After the reactor bed was filled and the system was in steady-state operation, the diverter gate was switched, so that the discharged material went to the second receiver to ensure a good sample.

When enough sample was obtained, the diverter gate was switched back to the waste-material receiver. If the desired run was complete, the unit was purged with nitrogen and shut down. If other conditions were to be checked, the controls were changed and the receiver with the good sample exchanged for an empty. When the new conditions were met and the system was at steady-state, the diverter was again switched to obtain a sample at the new conditions. Several points can be checked with this technique, and only one heat-up and one cleanout are necessary. Feed rate and final temperatures were the primary parameters varied for the pilot tests. Samples from all tests were submitted to the analytical laboratory.

TEST RESULTS — BATCH UNIT

Batch tests were run with the feed types presented above except for Run 20, in which FeS_2 and CaO were used to test the getter concept. The test results and conditions are listed in Tables 9 through 12. The missing run numbers correspond to tests that were terminated early because of operational problems such as off-gas plugs, burned out heater elements, and controller malfunction.

Table 9 shows the data for the float (treated coal) portions of these tests. The results are presented in ascending temperatures for comparison purposes. Base runs were made with nitrogen to determine the effects of only heat on sulfur removal. In each set, the hydrogen shows better removal than nitrogen except at 700°F. No tests, however, show enough sulfur removal to yield an acceptable product, even at 1000°F and a ratio of 2 parts coal to 1 part lime. Problems with material separation prevented complete analysis of Runs 18 and 19.

Data for the sink portions of the tests are shown in Table 10. The high sulfide content of the separated sink fraction shows that pyrite reduction is being made. The sulfate content is caused by heavier, mineral elements of the coal reporting to the sink when separated. Part of the coal fraction (or coal tars adsorbed in the lime) also shows up in the sink portion, as evidenced by the carbon values.

Batch test Run 20 (Table 11) was made with FeS_2 instead of coal to determine the reduction of pyrite to sulfide-type sulfur. The results show that most of the FeS_2 was converted by FeS and CaS, as evidenced by the sulfide content and by the increase in nonpyritic iron in the treated sample. Some sulfur was lost during grinding; this was mostly caused by reaction of CaS with atmospheric water vapor, as can be determined by examining the results of the ground and unground samples.

Table 12 lists the analysis of gas samples taken during some batch test runs. Because only grab samples could be taken from a continuously-variable, batch situation, the analyses are not definitive, but give a representation of the distribution of the gas species. Evolution of H_2S is increased at higher temperatures. The longer-chain molecules containing sulfur are derived from the thermal decomposition of the coal, as are the carbon-bearing gases in the mass spectrometer analysis.

TABLE 9. FLOAT PORTION OF BATCH TESTS

Run No.				1	5	2	9	3	10	14
Temp, °F				600	600	700	700	800	800	800
Duration, min				30	30	30	30	30	30	30
Treatment Gas				H_2	N_2	H_2	N_2	H_2	N_2	H_2
Sample	Raw Coal	10 X 80 Coal	M.H. Lime	Reac Prod	Reac Prod	Reac Prod	Reac Prod	Reac Prod	Reac Prod	Reac Prod
Lab. Ident. No.		20907		20654	20657	20655	20679	20656	20680	21156
Sample Weight, g				39.54	46.7	49.19	56.00	43.36	56.55	60.50
Separated Fraction				Float	Float	Float	Float	Float	Float	Float
Weight recovered, g				30.13	36.06	32.01	46.7	33.00	46.2	33.85
Proximate Analysis, wt %										
Moisture	4.5-5.2	3.72	0.0	0.9	1.2	0.4	3.07	0.7	0.9	0.3
Ash	10.4-11.0	9.8	89.8	7.6	8.6	8.2	9.9	9.4	8.7	9.0
Volatile Matter	34.7-35.4	36.1		34.7	35.8	33.1		24.9		20.2
Fixed Carbon	49.1-49.7	51.38		56.8	54.4	58.3		65.0		70.5
Ultimate Analysis, wt %										
Ash (total dry)	10.88-11.60	10.20	89.81	7.66	8.72	8.20	10.21	9.43	8.83	9.03
Acid Insoluble			1.90				49.96		67.7	66.39
Calcium			66.41				9.75			5.30
Carbon	6.71-68.4	69.32	0.55	72.2	71.4	72.5	70.56	74.0	73.42	74.94
Hydrogen	4.66-4.70	4.72	1.25	4.76	4.72	4.59	4.84	4.14	3.99	3.60
Sulfur	3.05-3.23	2.62	0.08	1.87	2.49	2.26	2.09	1.90	2.32	1.99
Sulfide				0.0	tr	0.02		0.07	0.02	0.10
Sulfate		0.47		0.07	0.12	0.11	0.14	0.07	0.07	0.10
Pyritic		0.64		0.42	0.46	0.24	0.59	0.14	0.52	0.14
Organic		1.51		1.38	1.91	1.89	1.36	1.12	1.71	1.65
Oxygen (by difference)	11.76-12.14	11.89	7.64	12.36	11.50	11.18	10.86	9.27	9.69	8.78
Nitrogen	1.23-1.25	1.21	0.01	1.15	1.17	1.29	1.20	1.26	1.35	1.44
Carbon Dioxide			0.66				0.24		0.40	0.22
S as SO_2	6.10-6.46	5.24		3.74	4.98	4.52	4.18	3.80	4.64	3.98
Heating Value, (S free), Btu/lb	12276	12481		12920	12783	12875	12723	12860	12699	12718
$SO_2/10^6$ Btu	5.12	4.20		2.89	3.90	3.51	3.29	2.95	3.65	3.13
Type Mix (original)				Coal/ Lime	Coal/ Lime	Coal/ Lime	Coal/ Lime	Coal/ Lime	Coal/ Lime	Coal/ Lime
Ratio by Weight				4/1	4/1	4/1	4/1	4/1	4/1	2/1

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TABLE 9. FLOAT PORTION OF BATCH TESTS (Continued)

Run No.	12	16	18	19
Temp, °F	800	1000	900	900
Duration, min	60	30	30	30
Treatment Gas	N_2	H_2	H_2	H_2
Sample	Reac Prod	Reac Prod	Reac Prod	Reac Prod
Lab. Ident. No.	20736	21429	21743	21745
Sample Weight, g	57.3	54.7		
Separated Fraction	Float	Float	Float	Float
Weight recovered, g	47.6	30.6		
Proximate Analysis, wt %				
Moisture	0.7	0.8	1.4	1.2
Ash	8.4	11.4	9.1	13.8
Volatile Matter		15.4	21.9	13.7
Fixed Carbon		72.8	67.6	71.3
Ultimate Analysis, wt %				
Ash (total dry)	8.46	11.47	9.18	14.01
Acid Insoluble	65.3			
Calcium				
Carbon	73.50	75.22	74.95	74.24
Hydrogen	4.23	3.00	3.88	2.69
Sulfur	2.31	1.67		
Sulfide	0.01	0.11		
Sulfate	0.10	0.08	0.11	
Pyritic	0.57	0.06	0.22	
Organic	1.63	1.42		
Oxygen (by difference)	9.84	6.65		
Nitrogen	1.37	1.32	1.35	1.03
Carbon Dioxide	0.29	0.67		
S as SO_2	4.62	3.34		
Heating Value, (S free), Btu/lb	12834	12450		
$SO_2/10^6$ Btu	3.60	2.68		
Type Mix (original)	Coal/ Lime	Coal/ Lime	Coal/ Lime	Pretreated Coal/Lime
Ratio by Weight	4/1	2/1	2/1	2/1

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TABLE 10. SINK PORTION OF BATCH TESTS

Run No.		1	5	2	9	3	10	14
Temp, °F		600	600	700	700	800	800	800
Duration, min		30	30	30	30	30	30	30
Treatment Gas		H_2	N_2	H_2	N_2	H_2	N_2	H_2
Lab Ident. No.		20654	20657	20655	20679	20656	20680	21156
Sample Weight, g	M. H. Lime	39.54	46.7	49.19	56.00	43.36	56.55	60.50
Separated Fraction		Sink	Sink	Sink	Sink	Sink	Sink	Sink
Weight Recovered, g		4.16	8.50	8.07	8.64	8.44	10.35	26.65
Proximate Analysis, wt %								
Moisture	0.0	0.2		0.1	0.39	0.1	0.3	0.0
Ash	89.81				75.36		73.3	85.3
Ultimate Analysis, wt %								
Ash (total dry)	89.81				75.66		73.49	85.3
Acid Insoluble	1.90				4.44		9.00	3.91
Calcium	66.41				45.5			62.4
Carbon	0.55	2.52	3.4	8.49	3.58	12.4	10.65	5.80
Hydrogen	1.25		2.49	2.18	2.31	1.96	1.86	0.68
Sulfur	0.08	0.59	0.68	1.62	1.42	1.19	2.70	2.03
Sulfide		0.22	0.16	0.27	0.15	0.39	0.15	1.01
Sulfate		0.31	0.14	0.50	0.43	0.48	0.59	0.92
Pyritic		0.05	0.06	0.42	0.46	0.33	1.96	0.09
Organic		0.01	0.32	0.43	0.38	0.0	0.0	0.01
Oxygen (by difference)	7.64				14.89		8.47	2.30
Nitrogen	0.01		0.5		0.06	0.2	0.18	0.10
Carbon Dioxide	0.66				2.07		2.65	3.79
Type Mix (original)		Coal/ Lime	Coal/ Lime	Coal/ Lime	Coal/ Lime	Coal/ Lime	Coal/ Lime	Coal/ Lime
Ratio by Weight		4/1	4/1	4/1	4/1	4/1	4/1	2/1

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TABLE 10. SINK PORTION OF BATCH TESTS (Continued)

Run No.	12	16	18	19
Temp, °F	800	1000	900	900
Duration, min	60	30	30	30
Treatment Gas	N_2	H_2	H_2	H_2
Lab Ident. No.	20736	21430	21774	21746
Sample Weight, g	57.3	54.7		
Separated Fraction	Sink	Sink	Sink	Sink
Weight Recovered, g	9.7	24.1		
Proximate Analysis, wt %				
Moisture	0.22	0.5	0.0	0.0
Ash	71.4	82.9	86.0	93.0
Ultimate Analysis, wt %				
Ash (total dry)	71.54	83.32	86.07	93.2
Acid Insoluble	12.74			
Calcium				
Carbon	12.14	1.60	6.95	3.54
Hydrogen	1.79	1.14	1.36	0.43
Sulfur	2.90	0.99		
Sulfide	0.35	0.30		
Sulfate	0.76	0.55		
Pyritic	1.73	0.09		
Organic	0.06	0.05		
Oxygen (by difference)	8.41	10.65		
Nitrogen	0.23	0.06	0.09	0.01
Carbon Dioxide	2.99	2.24		
Type Mix (original)	Coal/ Lime	Coal/ Lime	Coal/ Lime	Pretreated Coal/Lime
Ratio by Weight	4/1	2/1	2/1	2/1

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TABLE 11. BATCH TEST RUN 20

Sample	Feed	Unground	Ground		
		Reactor Material			
Lab Ident. No.	21227	21227	21227	21227	21227
Separated Fraction	Total	Total	Total	Sink	Float
Proximate Analysis, wt%					
Moisture	0.0	0.0	0.0	0.3	0.2
Volatile Matter	0.0				
Ash	81.72	89.5	85.83	87.6	84.0
Ultimate Analysis, wt %					
Ash (Dry)	81.72	89.56	85.83	87.75	84.22
Carbon	0.0	0.26	0.05	0.05	0.18
Hydrogen	0.1	0.12	0.07	0.10	0.37
Sulfur	6.78	5.23	5.06	4.18	3.04
Sulfides	0.05	5.17	4.34	3.22	2.15
Pyrites	5.28	0.46	0.16	0.17	0.06
Oxygen	10.77	4.34	8.43	7.36	11.38
Nitrogen	0.01	0.05	0.02	0.01	0.01
Carbon Dioxide	0.62	0.44	0.54	0.55	0.80
Iron (Nonpyritic)	0.65	4.88	5.13	4.18	3.04

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TABLE 12. BATCH TEST GAS SAMPLE ANALYSIS

Run No.	14	18	19	20
Temperature, °F	800	900	900	900
Chromatograph, ppm, vol				
Hydrogen Sulfide	15.0	15.2	18.6	63.0
Carbonyl Sulfide	0.7	1.9	0.5	0.9
Ethyl Mercaptan	11.9	6.3	2.2	3.4
Dimethyl Disulfide	0.3	0.7	0.4	--
t-Amyl Mercaptan	0.2	10.5	1.0	--
Methylethyl Disulfide	1.1	--	--	--
Methyl Mercaptan	--	1.3	--	--
Thiophene	--	2.4	0.7	--
C_6 or Higher	--	28.5	--	--
Mass Spectrometer, mol %				
Nitrogen	25.3	16.3	16.7	24.0
Oxygen	6.8	--	--	--
Hydrogen	67.6	83.5	83.1	76.0
Argon	0.3	--	--	--
Carbon Dioxide	--	0.02	--	0.04
Methane	--	0.13	0.16	--
Ethane	--	0.03	--	--
Propane	--	0.01	--	--
n-Butane	--	0.02	--	--
Ethylene	--	0.01	--	--
Propylene	--	0.01	--	--

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TEST RESULTS — PILOT UNIT

The pilot-unit run conditions are listed in Table 13. The first six tests were made with coal (no lime) to check the fluidization, gas rates, devolatilization, and general operation at design conditions. It was found that the coal should be screened at —10+80 mesh. The maximum top size was selected to promote good fluidization, and the bottom size was selected to minimize the fines in the exhaust system. The gas velocity required was about 3.0 ft/s for satisfactory mixing and operation. Data from these runs and the time-temperature matrix are presented in Tables 14 through 25.

For Runs 7 through 14, the feed mixture was 2 parts coal (—10+80 mesh) to 1 part lime (—20+60 mesh). In Run 15 the same weight ratio was used, but the feed material size was all —80 mesh screen. Hydrogen was the fluidizing gas in all tests except No. 14; in this test, an attempt was made to add steam to the unit. This attempt was unsuccessful because the wet steam caused a large pressure drop across the distributor plates and the run was aborted. No further attempts to use steam were made because a change in the reactor configuration would be necessary.

In Runs 7 through 9C, material was fed to the unit at 50 lb/hr resulting in a reactor residence time of about 1 hour. The bed temperatures tested ranged from 750^{o} to 1000^{o}F in 50^{o}F increments. The feed rate was 100 lb/hr in Runs 10 and 11, and the temperatures were 1000^{o} and 900^{o}F. Runs 12A and 13 were made at 25 lb/hr and 1100^{o} and 900^{o}F. Run 12B was at 200 lb/hr and 900^{o}F. The final run with the fine material was made at 60 lb/hr and 900^{o}F. The time-temperature matrix for the pilot-unit runs is presented in Table 19. Lab analyses for Runs 7 through 9C are shown in Tables 20 through 25.

Run 7 (Tables 20 and 21) illustrates the reduction of the pyritic sulfur in the coal at 1000^{o}F. Sulfide-type sulfur has increased, evidence that the FeS_2 is being converted to FeS and CaS is being formed. In the float-sink separation, much of the sulfide-type sulfur is reporting to the sink portion. Some of the coal, or possibly tars absorbed by the lime, is in the sink fraction, causing the high carbon content. Also, some lime stayed with the float, as shown by the higher ash content of the float material as compared with the original coal.

Table 22 shows the analysis for Run 8A. This run is similar to Run 7 but the temperature was 100^{o}F lower. The results are much the same for both runs; although the pyritic sulfur has been attacked, the organic sulfur content has not changed appreciably, therefore, the overall sulfur content is still high.

Run 8B (Table 23) was made at still a lower temperature, 750^{o}F. The sulfur reduction was even less than in the previous runs. Pyritic sulfur was not reduced as much as in the other tests so more sulfur remains in the treated material.

Pilot runs 9A and 9B (Table 24) were made at 950^{o} and 850^{o}F, respectively. These data also show pyrite-sulfur reduction but the organic sulfur content of the coal is relatively unchanged. Again, this causes residual sulfur values that are higher than the desired values.

TABLE 13. PILOT-UNIT RUN CONDITIONS

Run No.	Feed Rate lb/hr	Temperature, °F	Gas	Material
1	33	Ambient	N_2	Raw coal
2	63.5	Ambient	N_2	10 X 80 mesh Coal
3	33.6	600	N_2	↓
4	66.7	800	N_2	↓
5	77.0	825	N_2	↓
6	50.0	850	H_2	↓
7	50.0	1000	H_2	{ 10 X 80 mesh Coal 20 X 60 mesh Lime
8A	50.0	900	H_2	↓
8B	50.0	750	H_2	↓
9A	50.0	950	H_2	↓
9B	50.0	850	H_2	↓
9C	50.0	800	H_2	↓
10	100.0	1000	H_2	↓
11	100.0	900	H_2	↓
12A	25.0	1100	H_2	↓
12B	200.0	900	H_2	↓
13	25.0	900	H_2	↓
14	50.0	900	H_2	↓
15	60.0	900	{ Steam + H_2	{ −80 mesh Coal −80 mesh Lime

TABLE 14. SIZE ANALYSES OF PILOT-UNIT TEST 2

Sample	Feed I	Feed II	Sample No. 5	4	3	2	1	Reactor
Description	Initial drum of feed	Final drum of feed	Initial treated coal in receiver (bottom) ~0 to 2/3 hr	~2/3 to 1-1/3 hr	~1-1/3 to 2 hr	~2 to 2-2/3 hr	Final treated coal in receiver (top) ~2 2/3 to 3-1/3 hr	Reactor residue at end of test
Lab Ident No.	20883	20884	20889	20888	20887	20886	20885	20891
Size Consist, wt % retained on stated size								
10	2.1	1.1	0.5	0.7	0.5	0.4	0.2	0.5
14	7.5	3.4	2.0	2.7	2.0	1.2	1.0	7.6
20	41.3	24.2	18.3	22.6	18.1	15.5	19.1	61.5
30	18.2	17.6	13.6	15.5	16.1	14.5	20.9	19.7
40	12.3	16.1	14.1	15.3	16.6	16.2	19.2	7.6
60	11.7	21.2	20.1	20.3	24.1	26.6	23.8	2.3
80	4.3	10.4	10.4	9.9	10.9	13.0	8.7	0.3
100	2.0	4.9	4.3	3.4	5.0	6.0	3.9	0.2
200	0.4	1.0	5.9	4.5	4.5	4.7	2.5	0.1
325	0.1	0.0	4.0	2.0	1.3	1.2	0.5	0.1
Pan	0.1	0.1	6.8	3.1	0.9	0.7	0.2	0.1

TABLE 15. SAMPLE ANALYSES FOR RUN 3 (N_2, 600°F, WITHOUT LIME)

Sample	Feed	Reactor	Receiver	Cyclone
Lab Ident No.	20907	20894	20893	20895
ANALYSIS:				
Proximate, wt %				
Moisture	3.72	0.7	0.7	5.2
Volatiles	36.1	32.8	31.2	31.7
Ash	9.8	13.1	11.0	20.0
Fixed Carbon	51.38	53.4	57.1	43.1
Ultimate, wt %				
Ash (dry)	10.20	13.20	11.03	21.14
Carbon	69.32	68.20	70.3	58.20
Hydrogen	4.76	4.36	4.26	3.67
Sulfur	2.62	2.55	2.64	3.39
Oxygen	11.89	10.59	10.58	12.66
Nitrogen	1.21	1.10	1.19	0.94
Carbon Dioxide	--	--	--	--
Bulk Density, lb/cu ft	48.9	51.3	39.3	26.8
Screen, % retained on				
10	0.0	1.3	0.9	0.0
14	0.6	3.1	1.7	0.3
20	16.4	26.5	20.6	0.3
30	14.6	18.1	18.4	0.3
40	17.0	16.7	19.8	0.0
60	26.4	20.7	23.8	0.3
80	15.5	8.5	8.7	0.3
100	7.1	3.3	3.0	0.3
200	2.1	1.6	2.4	8.3
325	0.1	0.1	0.5	17.6
Pan	0.2	0.1	0.2	72.3

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TABLE 16. SAMPLE ANALYSES FOR RUN 4 (N_2, 800°F, WITHOUT LIME)

Sample	Feed	Reactor	Receiver	Discharge Tube
Lab Ident No.	20907	20925	20926	20924
ANALYSIS:				
Proximate, wt %				
Moisture	3.72	0.4	0.00	0.6
Volatiles	36.1	20.1	23.1	19.4
Ash	9.8	17.8	14.8	8.7
Fixed Carbon	51.38	61.7	62.1	71.3
Ultimate, wt %				
Ash (dry)	10.20	17.89	14.81	8.77
Carbon	69.32	67.35	69.60	76.12
Hydrogen	4.76	3.43	3.79	3.58
Sulfur	2.62	2.47	2.39	1.77
Oxygen	11.89	7.60	8.14	8.27
Nitrogen	1.21	1.26	1.27	1.49
Carbon Dioxide	--	--	--	--
Bulk Density, lb/cu ft	48.9	36.21	34.4	27.0
Screen, % retained on				
10	0.0	2.2	1.5	10.3
14	0.6	8.2	1.8	9.6
20	16.4	40.8	14.5	23.4
30	14.6	21.1	17.0	14.1
40	17.0	13.6	20.7	13.7
60	26.4	10.0	26.6	15.8
80	15.5	2.5	10.7	6.4
100	7.1	0.8	4.1	2.8
200	2.1	0.5	2.7	2.6
325	0.1	0.2	0.3	0.7
Pan	0.2	0.1	0.1	0.6

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TABLE 17. PILOT-UNIT RUN 5 (N_2, 825°F)

	Coal Feed	Reactor Material	Coal Receiver Top	Coal Receiver Middle	Coal Receiver Bottom
ANALYSIS					
Proximate, wt %					
Moisture	3.72	0.5	0.4	0.8	0.7
Volatile	36.1	16.3	22.3	19.5	13.4
Ash	9.8	13.8	13.6	12.5	14.0
Fixed Carbon	51.38	69.4	63.7	67.2	71.9
Ultimate, wt %					
Ash (dry)	10.20	13.86	13.70	12.61	14.13
Carbon	69.32	72.82	70.49	72.61	75.10
Hydrogen	4.76	3.12	3.79	3.23	2.60
Sulfur	2.62	2.15	2.29	1.86	2.22
Oxygen	11.89	6.63	8.48	8.29	4.96
Nitrogen	1.21	1.42	1.25	1.40	0.99
Sulfur/Carbon Ratio	0.0378	0.0295	0.0325	0.0258	0.0296
Bulk Density, lb/cu ft	48.9	33.6	32.3	23.5	21.8
Screens, % retained on					
10	0.0	0.4	3.9	1.1	6.8
14	0.6	2.8	3.1	7.0	9.4
20	16.4	26.2	15.8	33.7	22.2
30	14.6	20.3	13.9	22.2	16.2
40	17.0	18.2	16.5	16.5	15.2
60	26.4	19.3	24.4	13.2	16.4
80	15.5	7.3	12.4	4.0	7.0
100	7.1	3.0	5.5	1.3	2.8
200	2.1	1.9	3.9	0.6	2.6
325	0.1	0.3	0.3	0.2	0.8
Pan	0.2	0.3	0.3	0.2	0.6

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TABLE 18. PILOT-UNIT RUN 6 (N_2 AND H_2, 850°F, 50 lb/hr COAL)

	Feed Coal	N_2 Treated	H_2 Treated	Reactor
ANALYSIS				
Proximate, wt %				
Moisture	3.72	0.5	0.3	0.7
Volatile	36.1	21.2	18.5	19.3
Ash	9.8	14.9	11.5	18.7
Fixed Carbon	51.38	63.4	69.7	61.3
Ultimate, wt %				
Ash (dry)	10.20	15.00	11.56	18.84
Carbon	69.32	69.20	73.24	66.24
Hydrogen	4.76	3.31	3.42	3.06
Sulfur	2.62	2.38	1.73	2.63
Oxygen	11.89	8.81	8.56	7.74
Nitrogen	1.21	1.30	1.49	1.31
Bulk Density, lb/cu ft	48.9	36.6	24.3	33.4
Screens, % retained on				
10	0.0	4.0	2.8	9.1
14	0.6	1.0	6.4	7.4
20	16.4	6.6	31.8	35.7
30	14.6	9.3	21.0	17.9
40	17.0	15.6	16.6	12.3
60	26.4	30.4	13.7	9.7
80	15.5	17.6	4.2	3.0
100	7.1	8.6	1.6	1.3
200	2.1	6.0	1.5	1.8
325	0.1	0.6	0.3	0.8
Pan	0.2	0.3	0.1	1.0

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TABLE 19. TIME-TEMPERATURE MATRIX FOR PILOT-UNIT RUNS

Feed Rate, lb/hr (Residence Time, min)	Temperature, °F						
	750	800	850	900	950	1000	1100
	Run Nos.						
25 (120)				13			12 A
50 (60)	8 B	9 C	6, 9 B	8 A	9 A	7	
100 (30)				11		10	
200 (15)				12 B			

TABLE 20. PILOT-UNIT RUN 7 (H_2, 1000°F, 50 lb/hr MIX)

	Feed Coal	Receiver Top	Receiver Middle	Receiver Bottom	Reactor
ANALYSIS					
Proximate, wt %					
Moisture	3.9	0.0	0.0	0.0	0.0
Volatile	37.4	10.1	11.4	11.7	10.1
Ash	9.6	65.9	51.3	46.7	64.4
Fixed Carbon	49.1	24.0	37.3	41.6	25.5
Ultimate, wt %					
Ash (dry)	9.98	65.93	51.31	46.77	64.41
Carbon	69.14	25.63	38.90	43.10	27.13
Hydrogen	4.46	1.16	1.63	1.75	1.30
Sulfur	3.33	2.17	2.12	2.70	2.44
Oxygen	11.91	4.66	5.33	4.88	4.25
Nitrogen	1.18	0.45	0.71	0.80	0.47
Bulk Density, lb/cu ft	49.3	47.3	30.9	29.4	39.7
Screens, % retained on					
10	0.1	0.2	1.7	2.0	1.1
14	0.6	0.7	9.1	13.6	7.6
20	14.5	5.1	22.0	28.1	21.4
30	14.0	7.6	14.9	14.0	12.7
40	16.0	18.2	18.5	15.5	22.1
60	26.6	31.1	20.2	16.2	23.5
80	16.2	15.4	6.5	4.6	6.0
100	7.9	6.8	2.7	1.8	1.8
200	3.6	10.2	3.0	2.8	2.0
325	0.2	3.4	0.9	0.9	1.0
Pan	0.3	1.3	0.5	0.5	0.8

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TABLE 21. PILOT-UNIT RUN 7, FURTHER DETAIL

	Coal Receiver Top Total	Coal Receiver Top Float	Coal Receiver Top Sink
Proximate Analysis, wt %			
Moisture	0.0	0.40	0.00
Volatile	10.1	14.80	
Ash	65.9	20.4	77.7
Fixed Carbon	24.0	61.4	
Ultimate Analysis, wt %			
Ash (dry)	65.93	20.46	77.76
Carbon	24.96	65.63	11.76
Hydrogen	1.16	2.77	0.91
Sulfur (total)	1.89	1.83	1.88
Sulfide	0.83	0.22	1.09
Sulfate	0.17	0.17	0.20
Pyritic	0.06	0.10	0.07
Organic	0.83	1.34	0.52
Oxygen	3.17	[illegible].12	4.04
Nitrogen	0.45	1.18	0.17
CO_2	2.44	1.01	3.48
Nonpyritic Iron	0.87	1.03	0.78

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TABLE 22. PILOT-UNIT RUN 8A (H_2, 900°F, 50 lb/hr MIX)

	Reactor Material	Coal Receiver Total	Coal Receiver Float	Coal Receiver Sink
Proximate Analysis, wt %				
Moisture	0.0	0.0		
Volatile	22.2	11.5		
Ash	28.4	66.6		
Fixed Carbon	49.4	21.9		
Ultimate Analysis, wt %				
Ash (dry)	28.41	66.63		
Carbon	54.60	22.86		
Hydrogen	3.23	1.32		
Sulfur (total)	2.18	1.80	1.92	1.70
Sulfide		0.84	0.03	0.85
Sulfate		0.26	0.09	0.16
Pyritic		0.12	0.21	0.11
Organic		0.58	1.59	0.58
Oxygen	10.57	3.97		
Nitrogen	1.01	0.43		
CO_2		2.72		
Bulk Density, lb/cu ft	41.3	52.1		
Screens, % Retained on				
10	0.1	0.1		
14	1.5	0.5		
20	31.3	3.7		
30	18.5	6.4		
40	17.2	21.1		
60	19.8	40.7		
80	6.3	15.1		
100	2.4	5.2		
200	2.2	5.2		
325	0.4	1.3		
Pan	0.3	0.7		

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TABLE 23. PILOT-UNIT RUN 8B (H_2, 750°F, 50 lb/hr MIX)

	Coal Receiver Total	Coal Receiver Float	Coal Receiver Sink
Proximate Analysis, wt %			
Moisture	0.0		
Volatile	19.7		
Ash	47.8		
Fixed Carbon	32.5		
Ultimate Analysis, wt %			
Ash (dry)	47.81		
Carbon	36.56		
Hydrogen	2.35		
Sulfur (total)	2.08	2.11	2.05
Sulfide	0.64	0.05	1.31
Sulfate	0.24	0.15	0.31
Pyritic	0.20	0.34	0.24
Organic	1.00	1.57	0.19
Oxygen	8.55		
Nitrogen	0.66		
CO_2	1.99		
Bulk Density, lb/cu ft	54.4		
Screens, % retained on			
10	0.0		
14	0.1		
20	2.6		
30	4.6		
40	13.9		
60	36.6		
80	19.5		
100	9.3		
200	9.6		
325	2.3		
Pan	1.5		

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TABLE 24. PILOT-UNIT RUNS 9A AND 9B (H_2, 950° AND 850°F, 50 lb/hr MIX)

	Run 9A			Run 9B		
	Total	Float	Sink	Total	Float	Sink
Proximate Analysis, wt %						
Moisture	0.0	0.9	0.00	0.0	1.1	0.00
Volatile	10.6	15.7		12.1	18.6	
Ash	68.5	16.8	81.00	60.7	14.7	84.5
Fixed Carbon	20.9	66.6		27.2	65.6	
Ultimate Analysis, wt %						
Ash (dry)	68.49	17.00	81.04	60.73	14.91	84.49
Carbon	23.93	67.44	6.45	28.95	68.16	4.39
Hydrogen	1.29	2.83	0.80	1.55	3.20	0.90
Sulfur (total)	1.91	1.95	1.80	1.58	1.92	1.31
Sulfide	1.00	0.14	1.22		0.16	0.79
Sulfate	0.28	0.20	0.27		0.15	0.33
Pyritic	0.08	0.15	0.10		0.19	0.11
Organic	0.55	1.46	0.21		1.42	0.08
Oxygen	1.03	8.56	6.29	4.69	9.38	5.65
Nitrogen	0.43	1.26	0.11	0.48	1.17	0.08
CO_2	2.92	0.96	3.51	2.02	1.26	3.18
Bulk Density, lb/cu ft	50.9			43.9		
Screens, % retained on						
10	0.5			0.3		
14	0.3			0.9		
20	1.4			3.8		
30	4.0			8.4		
40	18.9			25.5		
60	44.1			39.8		
80	17.6			13.0		
100	5.9			4.2		
200	5.4			3.1		
325	1.4			0.6		
Pan	0.5			0.4		

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TABLE 25. PILOT-UNIT RUN 9C (H_2, 800°F, 50 lb/hr MIX)

	Total	Float	Sink
Proximate Analysis, wt %			
Moisture	0.0	1.0	0.0
Volatile	17.3	21.6	--
Ash	44.4	10.6	83.6
Fixed Carbon	38.3	66.8	--
Ultimate Analysis, wt %			
Ash (dry)	44.44	10.74	83.61
Carbon	41.01	72.22	4.88
Hydrogen	2.29	3.69	0.58
Sulfur (total)	2.09	1.98	2.18
Oxygen	7.23	9.31	4.78
Nitrogen	0.68	1.39	0.09
CO_2	2.26	0.67	3.88
Bulk Density, lb/cu ft	45.3		
Screens, % retained on			
10	0.1		
14	0.2		
20	0.8		
30	3.6		
40	15.8		
60	39.0		
80	20.8		
100	8.8		
200	8.5		
325	1.6		
Pan	0.8		

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Run 9C (Table 25) at 800°F resulted in performance similar to the previous runs.

ANALYSIS OF TEST RESULTS

Figures 22 and 23 present the pyritic sulfur and organic sulfur contents of the samples at different temperatures. Both batch and pilot-unit tests caused the pyritic sulfur content to decrease as the temperature increased. However, in these tests the organic sulfur was not reduced enough to achieve the final content desired. Because the rate of organic sulfur removal was not faster than the devolatilization rate, the fraction of organic sulfur in the remaining treated coal was nearly constant.

CONCLUSIONS

Data from both the batch and pilot units indicated that, although some sulfur was being removed and the getter concept was viable, the degree of sulfur removal was insufficient. Sulfur reduction to values below 1% is necessary for the treated product to meet the Federal standards for SO_2 emission.

After a review of kinetic data (next section), it was decided to redirect the program to acquire more basic data on smaller-scale equipment.

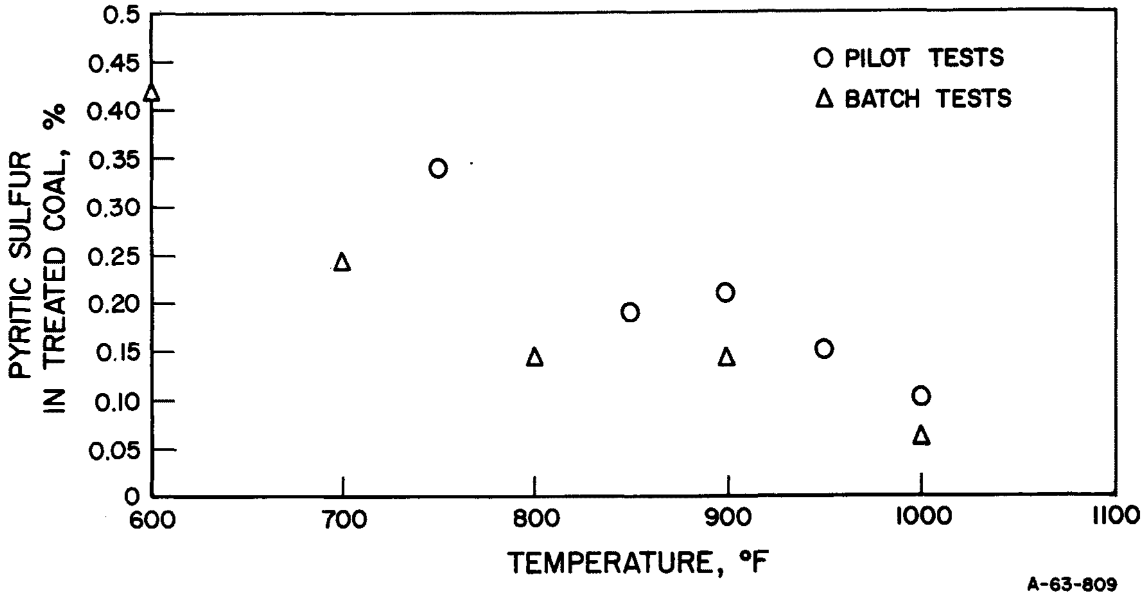

Figure 22. Percent pyritic sulfur in treated coal.

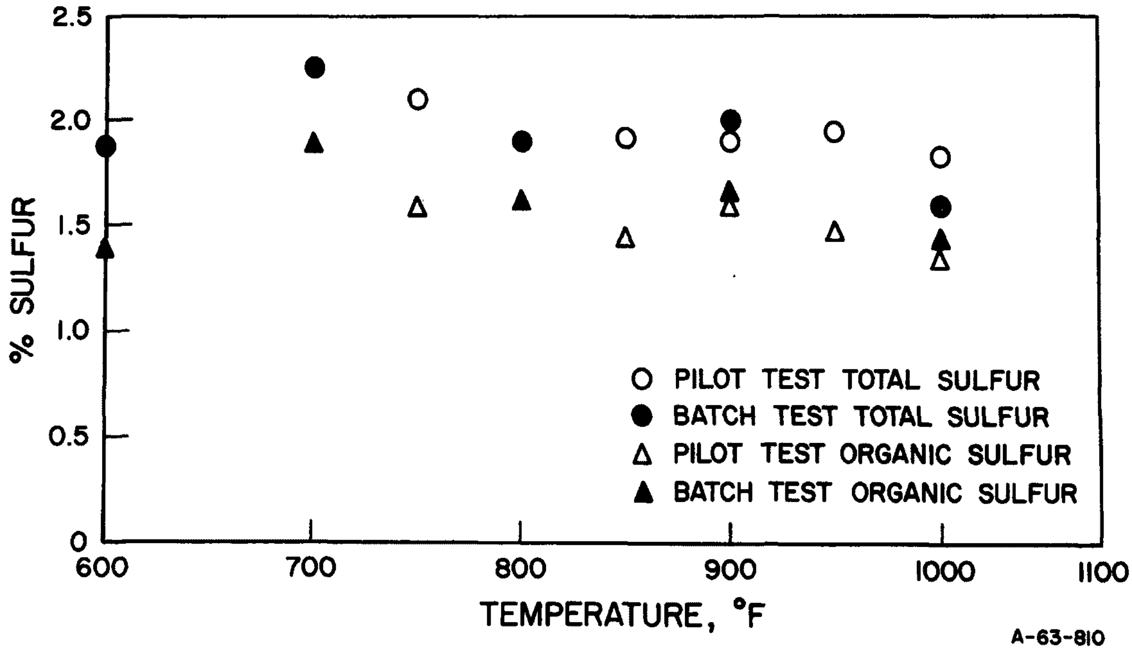

Figure 23. Percent total and organic sulfur in treated coal.

KINETIC STUDIES OF OUTSIDE DATA

The studies of Vestal and Johnston (1969) (6) indicate that much of the organic sulfur should be removed prior to pyrite decomposition. They confirm the work of Snow (1932) (5) that slow heat-up rates provide better sulfur release than fast heat-up. They also indicate that sulfur can be fixed into the carbon lattice in a reverse reaction. The configuration of the fluidized-bed reactor employed in this program caused rapid (about 100°-$500^{\circ}F/s$) heat-up from ambient to bed temperatures. These factors suggested that greater sulfur removals might be possible if the reactor configuration permitted slow heat-up and inhibited back-reaction. Therefore, a kinetic analysis of the data of Vestal and Johnston was made to determine potential sulfur removal made possible by this technique.

A short computer program was prepared to study the expected reactor operation based on the kinetic parameters reported by Vestal and Johnston (6). For the first studies, the assumption was made that these kinetics applied to the rapid heat-up in the pilot-unit, fluidized-bed reactor. A completely back-mixed reactor (a theoretically perfect fluidized bed) was assumed for the reactions; hydrogen and coal feed rates were similar to those used in the pilot-unit program. Temperature, residence time, and lime-to-coal ratio were the major parameters varied in this calculational program. Figures 24 through 28 illustrate the results.

Figure 24 shows the expected amount of pyritic sulfur remaining as a function of temperature and reaction time. Because the calculations assumed that there can be no back-reaction with hydrogen sulfide to remanufacture iron pyrite, pyrite removal should be independent of lime content. Significant pyrite removal should be achieved at 900° to $950^{\circ}F$ with sufficient reaction time. These results confirm the ability to decompose pyrite in the pilot unit.

Figure 25 presents the expected removal of nonfixed organic sulfur as a function of temperature and reaction time. This graph assumes no back-reaction of sulfur. It illustrates that the amount of available organic sulfur remaining in the coal will be quite low at $850^{\circ}F$ and a 30- to 60-minute reaction time. The kinetics do provide a mechanism for fixation of the available sulfur by a reaction of the coal char with H_2S. Figure 26 illustrates this effect. With large lime additions, the amount of sulfur fixation is negligible. This can be seen by comparing the data in Figure 25 (5-minute reaction time) with the largest lime addition of Figure 26. As lime addition is decreased, a significant portion of the previously available sulfur becomes fixed into the coal. Figure 27 illustrates sulfur fixation at various reaction times with stoichiometric excess-lime-addition rates, and Figure 28 illustrates the fixation with insufficient lime content.

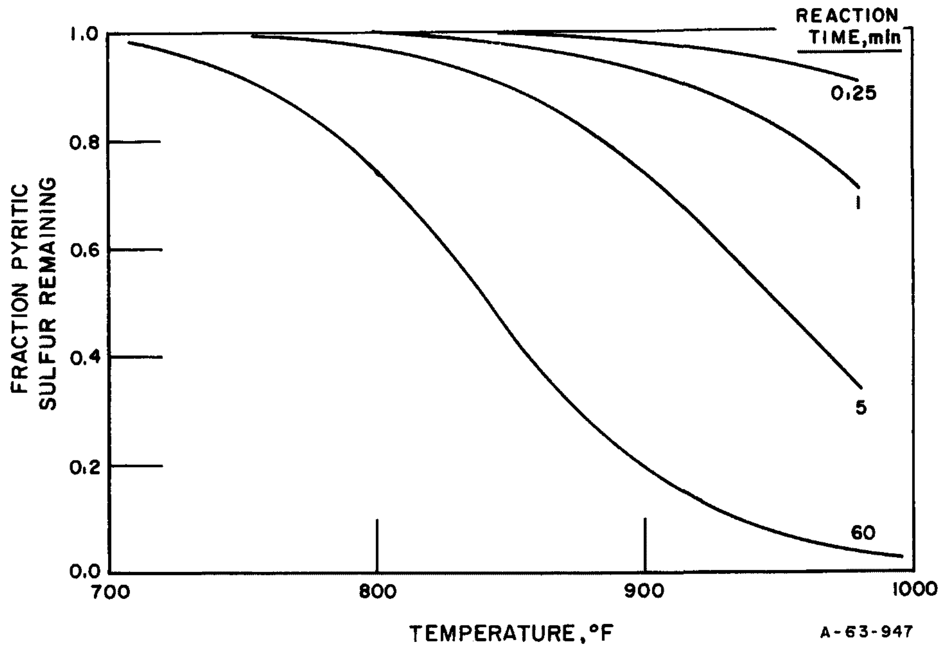

Figure 24. Removal of pyritic sulfur.

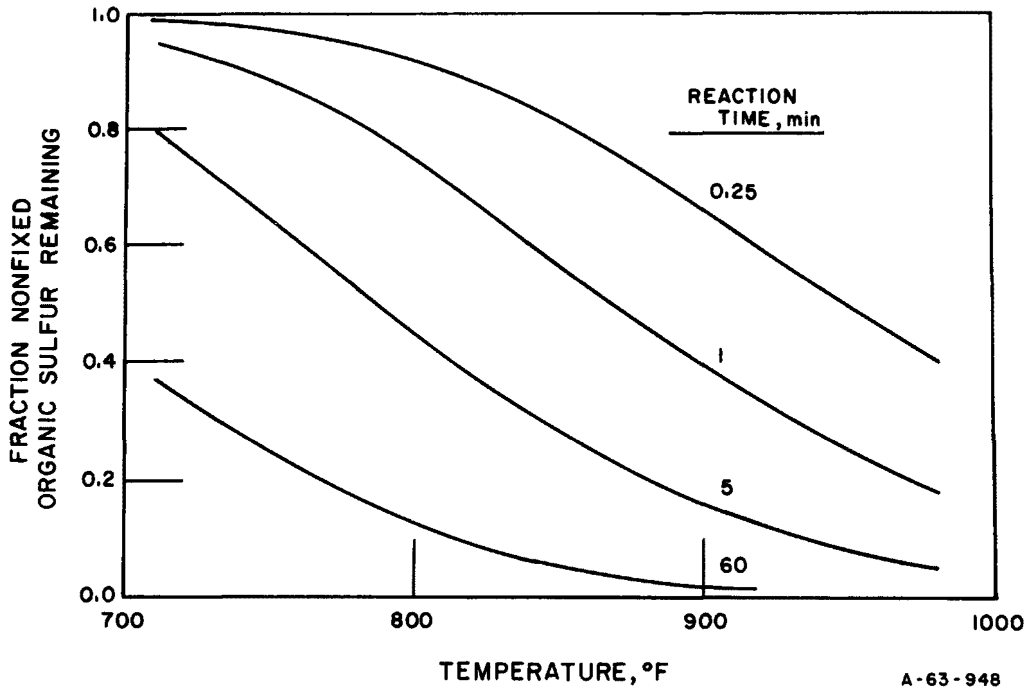

Figure 25. Removal of nonfixed organic sulfur.

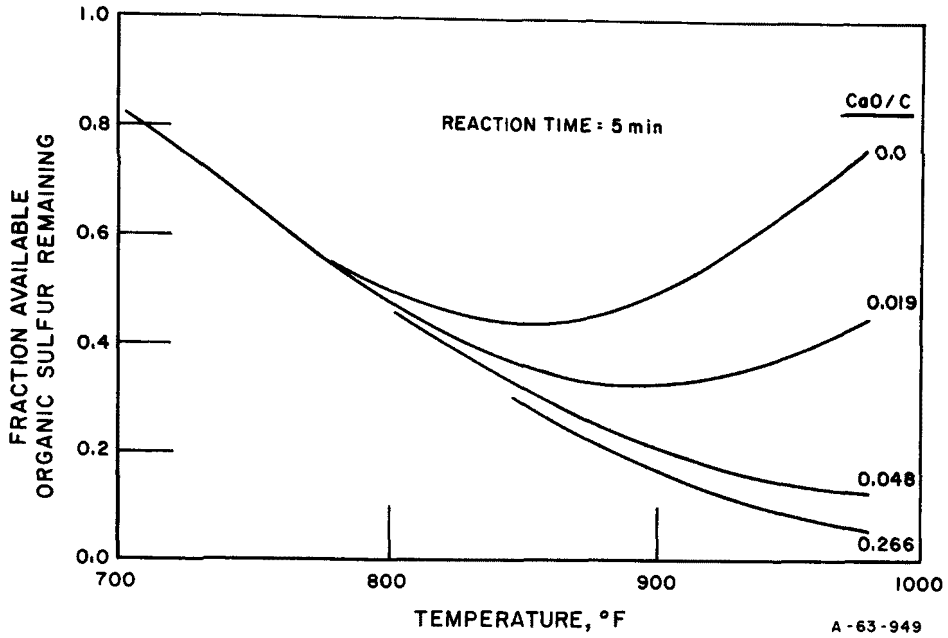

Figure 26. Fixation of available organic sulfur as a function of temperature and lime content.

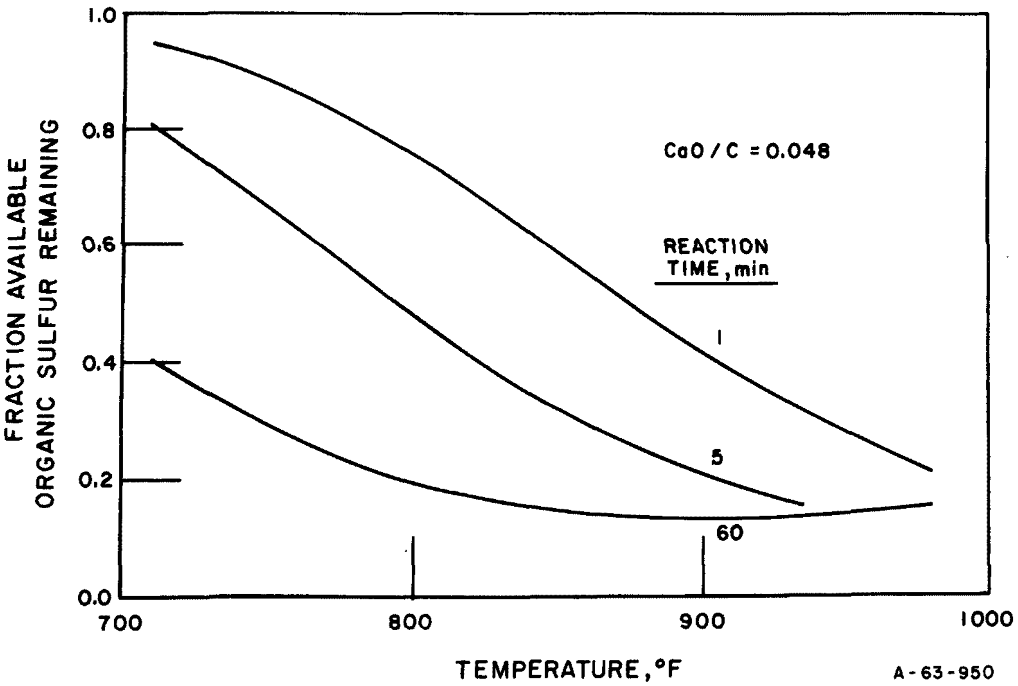

Figure 27. Fixation of organic sulfur with excess CaO present.

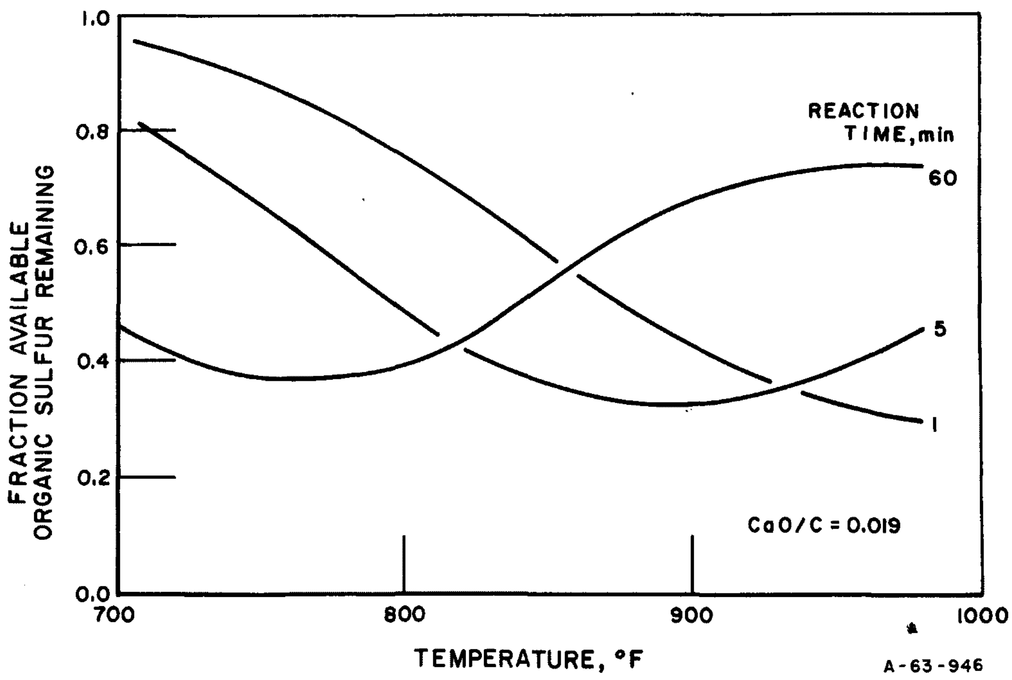

Figure 28. Fixation of organic sulfur with insufficient CaO present.

These graphs assume that the kinetic parameters reported by Vestal and Johnston (6) are applicable for the fast heat-up rate and isothermal bed characteristics of our pilot-unit reactor. The work in the initial program phase has confirmed their high fraction of pyritic sulfur removal, but the organic sulfur removal does not agree. Either the high heat-up rates fixed the organic sulfur and thus the kinetics did not apply, or the primary coal sample had a high percentage of previously fixed organic sulfur.

The calculational program was modified and evaluated for slow heat-up rates as opposed to the fast rates calculated above for fluidized-bed studies. Figures 29 and 30 present the mole fractions of the various sulfur constituents of the coal as the coal is heated in the presence of hydrogen at a rate of $9^{o}F/min$. In Figure 29, representing coal treatment without lime, one type of available organic sulfur is significantly removed at a temperature of $750^{o}F$; another, at $870^{o}F$. The hydrogen sulfide concentration of the gas at these temperatures is several thousand parts per million; therefore, some sulfur is being refixed into the coal.

The pyrites do not show significant decomposition at $900^{o}F$, confirming the observations made in this preliminary thermobalance work (discussed in the next section). Similarly, the iron sulfide formation is not yet high.

In Figure 30 the system was recalculated with large lime additions. Decomposition of the available organic sulfurs and pyrites must, of course, be similar to that in Figure 29 because no mechanism is given for back-reactions. Hydrogen sulfide concentration decreases because of the calcium sulfide formation. Consequently, the formation of fixed sulfur in the coal is reduced. The fixed sulfur appears to be decreasing at higher temperatures even before the iron sulfide is significantly decomposed.

The relative temperatures of fixed sulfur and iron sulfide decomposition shown in Figure 30 appear to contradict the original data in the Vestal and Johnston report (6). This may be due to the effect of lime on the decomposition of fixed sulfur or may be caused by the high sensitivity of the kinetic rate expressions to temperature. A slight error in the calculation of the decomposition rate or the initial presentation of the kinetic-rate data will have a significant effect on the resultant figures.

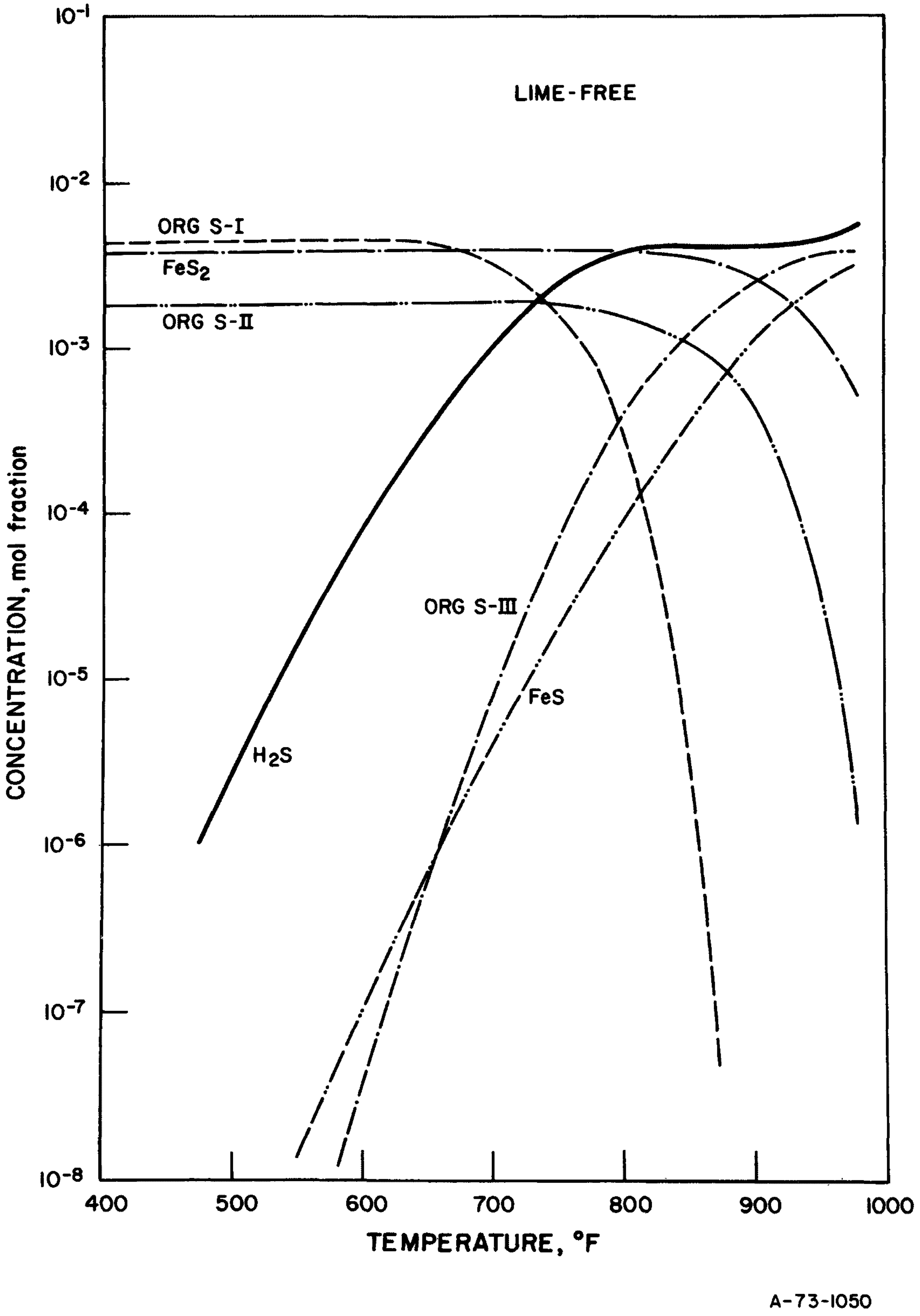

Figure 29. Coal sulfur fractions heated without lime in the presence of hydrogen.

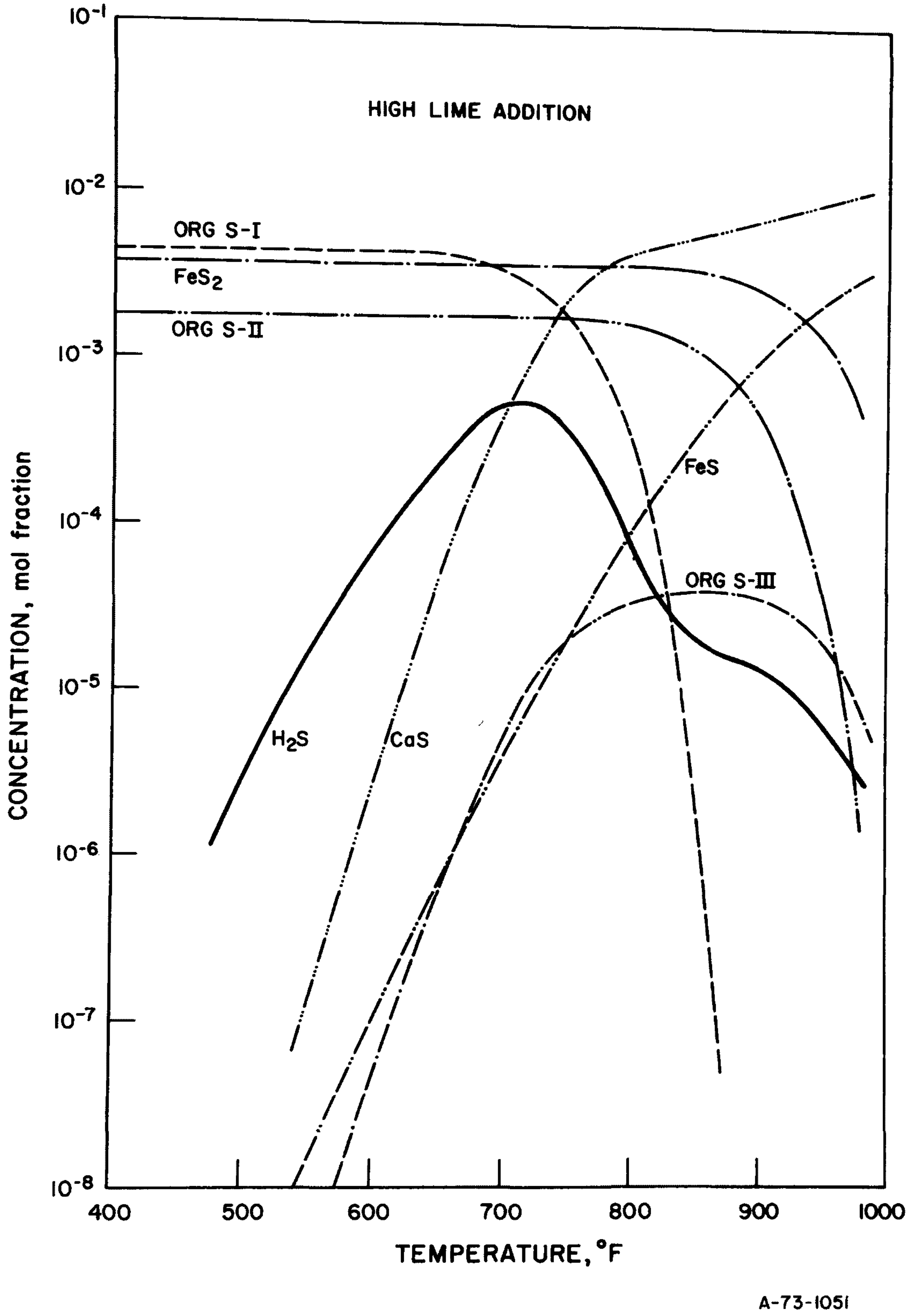

Figure 30. Coal sulfur fractions heated with high lime additions in the presence of hydrogen.

PROGRAM REDIRECTION — END OF PHASE I, START OF PHASE II

Considering the results from batch tests, pilot tests, and the kinetic studies, a change in the program was desirable. Two basic factors could have caused the discrepancy between the initial sulfur removal results and that reported by other investigators:

1. The primary coal sample, chosen for availability and substantial cost saving, was highly weathered. This weathering may have fixed some of the sulfur into the carbon lattice of the coal, making removal difficult.

2. The configuration of the pilot-unit reactor, with nearly instantaneous heat-up, may cause sulfur fixation.

Consequently, the program was redirected to evaluate these effects.

A thermobalance was used for initial testing. One was available for preliminary testwork with the initial coal sample. These tests were run with the thermobalance at a $10^{\circ}F$/min heat-up rate to $900^{\circ}F$ and 10 SCF/hr hydrogen flow. In each test, 1.8 grams of solid material was charged and the feed was screened to —10+20 mesh, a size governed by the mechanical requirements of the equipment.

The first test was operated with coal only, to obtain reference data on devolatilization and desulfurization of the coal in a hydrogen atmosphere. The second test used the standard coal-to-lime weight ratio of 2:1. However, the coal and lime contact was not good because there was no movement or mixing as in a fluidized-bed system. The third test was operated with a coal-to-lime ratio of 1:2 to increase the contact of the coal with the lime particles.

Laboratory analyses of the samples are presented in Tables 26 and 27. The total sulfur contents of the three feed samples were essentially identical, from 3.03% to 3.12%, when based on coal weight. This is a slightly higher percentage of sulfur than was shown in other tests, but the percentage may be consistent with the screen size fraction used (the larger particles appear to contain a greater fraction of sulfur).

In the first test the devolatilization was 25% and sulfur reduction was 45% of the original sulfur in the coal. Thirty-five percent of the organic sulfur was removed, and 53% of the pyritic sulfur decomposed.

The total sulfur loss to the gases decreased as lime was added, indicating sulfur recovery by the lime. In Test 3, for example, nearly all of the sulfur in the coal was recovered in the lime-coal residue. Also, because of volatile sorption into the lime pore structure, the devolatilization losses in Tests 2 and 3 were only about 21% of the original coal weight. In Test 2, the

TABLE 26. BASIC DATA — THERMOBALANCE RUNS

Test No.	CTB-1		CTB-2		CTB-3	
Coal/Lime Ratio	No lime		2:1		1:2	
Sample	Feed	Residue	Feed	Residue	Feed	Residue
Lab Ident. No.	21910	21911	21917	21918	21932	21933
Sulfur Composition, wt %						
Sulfide	0.00	0.05	0.00	0.21	0.00	0.16
Sulfate	0.36	0.10	0.27	0.22	0.15	0.19
Pyritic	1.06	0.66	0.90	0.50	0.41	0.36
Organic	1.69	1.47	0.85	0.70	0.48	0.31
Total	3.11	2.28	2.02	1.68	1.04	1.02
Weight, g						
Initial Sample		1.8440		1.9668		2.1070
Treated Sample		1.3839		1.6881		1.9585
Weight Loss, %		24.95		14.17		7.05

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TABLE 27. THERMOBALANCE RUNS — REDUCED DATA

Test No.	CTB-1			CTB-2			CTB-3		
Stream	Feed	Residue		Feed	Residue		Feed	Residue	
Weight Loss, fraction of coal	24.95			21.25			21.15		
	Sulfur Weight, based on 100-lb coal feed, lb		Sulfur Removal, %	Sulfur Weight, based on 100-lb coal feed, lb		Sulfur Removal, %	Sulfur Weight, based on 100-lb coal feed, lb		Sulfur Removal, %
Sulfide	0.0	0.038	--	0.0	0.27	--	0.0	0.45	--
Sulfate	0.36	0.075	79.2	0.405	0.28	30.0	0.45	0.529	(17.7)
Pyritic	1.06	0.49	53.3	1.35	0.64	53.3	1.23	1.00	26.2
Organic	1.69	1.10	34.7	1.27	0.97	24.0	1.44	0.86	40.0
Total	3.11	1.71	45.0	3.03	2.16	28.7	3.12	2.84	8.9

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percentage of pyrite reduction was similar to that of Test 1, but more organic sulfur remained in the residue. This might also be attributed to the sorption of volatile matter. Test 3, however, showed improved organic-sulfur removal and decreased pyritic removal.

Significant sulfur removal was achieved in these tests, as evidenced by the 45% reduction in Test 1 and the calcium sulfide manufactured in the other two tests. However, when devolatilization of the coal is considered, the net sulfur content of the treated coal calculates to about 2%. Removal of pyritic sulfur is not so great as in the pilot-unit tests because the sample was not maintained at the high temperature for an extended time.

SELECTION OF COAL FOR EXTENSIVE STUDY

The promising results from the three tests discussed above indicated that further thermobalance work was justified. Another unit was rebuilt for application in this work because the one used for the initial test was not available for extensive use.

The first runs in the rebuilt unit were made with the original, weathered Illinois No. 6 coal on hand. Four tests were made for unit shakedown and to establish operating procedures. Table 28 presents the data from the laboratory analyses for Runs TB-5 to TB-10. These were all made with a 2:1 coal-lime mixture, heated at 5°F/min to terminal temperatures of 700° to 1000°F. All tests were made with hydrogen except Run TB-5, which was made with nitrogen. A comparison of TB-5 with TB-8 shows the benefits of hydrogen usage at 900°F. The data indicate that as the temperature increased to 900°F the sulfur decreased.

Examination of the reduced data, calculated on a basis of 150 pounds of feed, (100 pounds of coal, 50 pounds of lime) shows formation of calcium sulfide. The calcium sulfide formation is proved because the amount of sulfur as sulfide is greater than the amount that would appear as ferrous sulfide from pyrite decomposition. Also, there is less sulfur in the residue than in the feed, indicating a loss (probably as H_2S) from the system, possibly because of relatively poor contact with lime and hydrogen sulfide. In the tests after TB-10, when lime was used, the ratio was changed to a 1:2 coal-lime mixture to improve the contact.

The next test series, TB-11 to TB-21, shown in Table 29, was performed on several new coal samples to select one sample for exhaustive testing. All the tests were run with the new 1:2 coal-lime mixture and were hydrogen-treated. They were heated at 5°F/min to 900°F, except TB-18 (800°F) and TB-20 (1450°F). Tests TB-19 and TB-20 were not held at the terminal temperatures, while the rest were held at the terminal temperature for 30 minutes.

Laboratory data and the values calculated in Table 29 were used for selection of the coal for further testing. Two lower rank coals, Montana subbituminous and North Dakota lignite, were excluded because their initial sulfur content was too low to respond to treatment. Similarly, the samples of Pittsburgh seam (Pennsylvania mine) and Illinois No. 6 were sufficiently low in original sulfur content that they would require less intense thermal exposure for sufficient sulfur release. Of the three coal samples remaining, the Western Kentucky No. 9 (an abundant Midwestern type) had the highest sulfur content and the highest after treatment, indicating that this coal would require the most extreme treatment conditions. These conditions, when determined, should be sufficient for the other coal materials available for initial

TABLE 28. THERMOBALANCE RUN DATA (ILLINOIS NO. 6 COAL)

Run No.			TB-5	TB-6	TB-7	TB-8	TB-9	TB-10
Coal Type	Illinois No. 6*							
Heating Rate, °F/min			5	5	5	5	5	5
Terminal Temperature, °F			900	700	800	900	1000	800
Holding Time, min			0	0	0	0	0	0
Lab Analysis, wt %	Coal	Feed mixture	Residue	Residue	Residue	Residue	Residue	Residue
H_2O								
Volatile Matter								
Sulfur, wt %, as								
Sulfide	0.00	0.00	0.06	0.05	0.30	0.50	0.72	0.34
Sulfate	0.32	0.21	0.08	0.12	0.10	0.10	0.07	0.10
Pyritic	0.89	0.60	0.73	0.41	0.27	0.16	0.20	0.20
Organic	1.79	1.20	1.09	1.09	0.98	0.82	0.81	0.97
Total	3.00	2.01	1.96	1.67	1.65	1.58	1.80	1.61
Weight, g								
Initial			4.6162	4.5115	4.2482	4.3311	4.1620	4.2689
Treated			4.0075	4.3042	3.7937	3.6153	3.4312	3.9038
Weight Loss, %								
Of Total Weight			13.18	4.59	10.70	16.53	17.56	8.55
Of Coal Weight			19.78	6.89	16.08	24.79	26.34	12.83
Reduced Data								
(100 lb Coal in Feed)								
Weight, lb	100.00	150.00	130.23	143.12	133.95	125.21	123.66	137.18
Sulfur Weight, lb, as								
Sulfide	0.00	0.00	0.08	0.07	0.40	0.63	0.89	0.47
Sulfate	0.32	0.32	0.10	0.17	0.13	0.13	0.09	0.14
Pyritic	0.89	0.89	0.95	0.59	0.36	0.20	0.25	0.27
Organic	1.79	1.79	1.42	1.56	1.31	1.03	1.00	1.33
Total	3.00	3.00	2.55	2.39	2.20	1.99	2.23	2.21
Sulfur Content, wt %, as								
Sulfide	0.00	0.00						
Sulfate	0.32	0.32						
Pyritic	0.89	0.89	1.18	0.63	0.43	0.27	0.34	0.31
Organic	1.79	1.79	1.77	1.68	1.56	1.37	1.36	1.53
Total	3.00	3.00	2.95	2.31	1.99	1.64	1.70	1.84

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*Weathered coal.

TABLE 29. THERMOBALANCE RUN DATA — VARIOUS COALS

Run No.	TB-11			TB-12			TB-13		
Coal Type	W. Kentucky No. 9			Indiana No. 5			Pittsburgh Seam (Pa.)		
Heating Rate, °F/min	5			5			5		
Terminal Temperature, °F	900			900			900		
Holding Time, min	30			30			30		
Lab Analysis, wt %	Coal	Mixture	Residue	Coal	Mixture	Residue	Coal	Mixture	Residue
H_2O	5.9			9.0			1.5		
Volatile Matter	33.4			34.5			27.6		
Sulfur, wt %, as									
Sulfide	0.00	0.00	0.54	0.00	0.00	0.21	0.00	0.00	0.11
Sulfate	0.07	0.02	0.04	0.07	0.02	0.16	0.04	0.01	0.04
Pyritic	2.30	0.77	0.11	2.02	0.67	0.16	1.08	0.36	0.14
Organic	0.97	0.32	0.38	1.24	0.41	0.29	0.26	0.09	0.06
Total	3.34	1.11	1.07	3.33	1.10	0.82	1.38	0.46	0.35
Weight, g									
Initial		5.0333			4.0500			4.3800	
Treated			4.4302			3.5607			3.9937
Weight Loss, %									
Of Total Weight			11.98			12.08			8.82
Of Coal Weight			35.95			36.24			26.46
Reduced Data (100 lb Coal Originally)									
Weight, lb	100.00	300.00	264.06	100.00	300.00	263.76	100.00	300.00	273.54
Sulfur Weight, lb, as									
Sulfide	0.00	0.00	1.43	0.00	0.00	0.55	0.00	0.00	0.30
Sulfate	0.07	0.07	0.11	0.07	0.07	0.42	0.04	0.04	0.11
Pyritic	2.30	2.30	0.29	2.02	2.02	0.42	1.08	1.08	0.38
Organic	0.97	0.97	1.00	1.24	1.24	0.76	0.26	0.26	0.16
Total	3.34	3.34	2.83	3.33	3.33	2.15	1.38	1.38	0.95
Sulfur Content, wt %, as									
Sulfide	0.00	0.00		0.00	0.00		0.00	0.00	
Sulfate	0.07	0.02		0.07	0.02		0.04	0.01	
Pyritic	2.30	0.77	0.45	2.02	0.67	0.65	1.08	0.36	0.52
Organic	0.97	0.32	1.56	1.24	0.41	1.19	0.26	0.09	0.22
Total	3.34	1.11	2.01	3.33	1.10	1.84	1.38	0.46	0.74
Wt % Original Sulfur Removed From Feed			61.4			64.6			60.9

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TABLE 29. THERMOBALANCE RUN DATA — VARIOUS COALS (Continued)

Run No.	TB-14			TB-15			TB-16		
Coal Type	Pittsburgh Seam (W. Va.)			Montana Subbituminous			Illinois No. 6		
Heating Rate, °F/min	5			5			5		
Terminal Temperature, °F	900			900			900		
Holding Time, min	30			30			30		
	Coal	Mixture	Residue	Coal	Mixture	Residue	Coal	Mixture	Residue
Lab Analysis, wt %									
H_2O	7.7			17.6			24.5		
Volatile Matter	33.8			35.7			32.0		
Sulfur, wt %, as									
Sulfide	0.00	0.00	0.10	0.00	0.00	0.02	0.00	0.00	0.01
Sulfate	0.05	0.02	0.06	0.00	0.00	0.04	0.04	0.01	0.08
Pyritic	1.49	0.50	0.11	0.29	0.10	0.10	0.21	0.07	0.16
Organic	1.37	0.46	0.33	0.37	0.12	0.06	0.28	0.09	0.00
Total	2.91	0.98	0.60	0.66	0.22	0.22	0.53	0.17	0.25
Weight, g									
Initial		4.5220			4.2117			4.7967	
Treated			3.9811			3.5817			4.0177
Weight Loss, %									
Of Total Weight			11.98			14.96			16.24
Of Coal Weight			35.96			44.88			48.72
Reduced Data									
(100 lb Coal Originally)									
Weight, lb	100.00	300.00	264.04	100.00	300.00	255.12	100.00	300.00	251.28
Sulfur Weight, lb, as									
Sulfide	0.00	0.00	0.26	0.00	0.00	0.05	0.00	0.00	0.02
Sulfate	0.05	0.05	0.16	0.00	0.00	0.10	0.04	0.04	0.20
Pyritic	1.49	1.49	0.29	0.29	0.29	0.26	0.21	0.21	0.40
Organic	1.37	1.37	0.87	0.37	0.37	0.15	0.28	0.28	0.00
Total	2.91	2.91	1.58	0.66	0.66	0.56	0.53	0.53	0.62
Sulfur Content, wt %, as									
Sulfide	0.00	0.00		0.00	0.00		0.00	0.00	
Sulfate	0.05	0.02		0.00	0.00		0.04	0.01	
Pyritic	1.49	0.50	0.45	0.29	0.10	0.47	0.21	0.07	0.78
Organic	1.37	0.46	1.35	0.37	0.12	0.27	0.28	0.09	0.00
Total	2.91	0.98	1.80	0.66	0.22	0.74	0.53	0.17	0.78
Wt % Original Sulfur Removed From Feed			60.1			37.9			24.5

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TABLE 29. THERMOBALANCE RUN DATA — VARIOUS COALS (Continued)

Run No.	TB-17			TB-18			TB-19		
Coal Type	W. Kentucky No. 9			Illinois No. 6			W. Kentucky No. 9		
Heating Rate, °F/min	5			5			5		
Terminal Temperature, °F	800			900			900		
Holding Time, min	30			30			30		
Lab Analysis, wt %	Coal	Mixture	Residue	Coal	Mixture	Residue	Coal	Mixture	Residue
H_2O	5.9			5.8			5.9		
Volatile Matter	33.4			24.8			33.4		
Sulfur, wt %, as									
Sulfide	0.00	0.00	0.57	0.00	0.00	0.05	0.00	0.00	0.47
Sulfate	0.07	0.02	0.06	0.00	0.00	0.02	0.07	0.02	0.04
Pyritic	2.30	0.77	0.57	1.14	0.38	0.23	2.30	0.77	0.36
Organic	0.97	0.32	0.30	0.04	0.01	0.00	0.97	0.32	0.26
Total	3.34	1.11	1.50	1.18	0.39	0.30	3.34	1.11	1.13
Weight, g									
Initial		4.0215			4.9714			3.9781	
Treated			3.7017			4.5853			3.6355
Weight Loss, %									
Of Total Weight			7.95			7.77			8.61
Of Coal Weight			23.85			23.30			26.30
Reduced Data (100 lb Coal Originally)									
Weight, lb	100.00	300.00	276.15	100.00	300.00	276.70	100.00	305.25	287.97
Sulfur Weight, lb, as			(Data not meaningful)						
Sulfide	0.00	0.00		0.00	0.00	0.13	0.00	0.00	1.31
Sulfate	0.07	0.07		0.00	0.00	0.05	0.07	0.07	0.11
Pyritic	2.30	2.30		1.14	1.14	0.62	2.30	2.30	0.72
Organic	0.97	0.97		0.04	0.04	0.00	0.97	0.97	1.00
Total	3.34	3.34		1.18	1.18	0.80	3.34	3.34	3.14
Sulfur Content, wt %, as									
Sulfide	0.00	0.00		0.00	0.00		0.00	0.00	
Sulfate	0.07	0.02		0.00	0.00		0.07	0.02	
Pyritic	2.30	0.77		1.14	0.38	0.81	2.30	0.77	0.98
Organic	0.97	0.32		0.04	0.01	0.00	0.97	0.32	1.36
Total	3.34	1.11		1.18	0.39	0.81	3.34	1.11	2.34
Wt % Original Sulfur Removed From Feed						47.5			48.5

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TABLE 29. THERMOBALANCE RUN DATA — VARIOUS COALS (Continued)

Run No.	TB-20			TB-21		
Coal Type	W. Kentucky No. 9			Illinois No. 6		
Heating Rate, °F/min	5			5		
Terminal Temperature, °F	1450			900		
Holding Time, min	30			30		
Lab Analysis, wt %	Coal	Mixture	Residue	Coal	Mixture	Residue
H_2O	5.9			6.6		
Volatile Matter	33.4			28.5		
Sulfur, wt %, as						
Sulfide	0.00	0.00	0.87	0.00	0.00	0.05
Sulfate	0.07	0.02	0.02	0.00	0.00	0.04
Pyritic	2.30	0.72	0.16	0.81	0.27	0.14
Organic	0.97	0.30	0.21	0.24	0.08	0.09
Total	3.34	1.04	1.26	1.05	0.35	0.32
Weight, g						
Initial		4.6539			4.8698	
Treated			3.9515			4.4626
Weight Loss, %						
Of Total Weight			15.09			8.36
Of Coal Weight			48.45			25.08
Reduced Data (100 lb Coal Originally)						
Weight, lb	100.00	321.03	272.59	100.00	300.00	274.92
Sulfur Weight, lb, as						
Sulfide	0.00	0.00	2.37	0.00	0.00	0.14
Sulfate	0.07	0.07	0.05	0.00	0.00	0.11
Pyritic	2.30	2.30	0.43	0.81	0.81	0.38
Organic	0.97	0.97	0.57	0.24	0.24	0.25
Total	3.34	3.34	3.42	1.05	1.05	0.88
Sulfur Content, wt %, as						
Sulfide	0.00	0.00		0.00	0.00	
Sulfate	0.07	0.02		0.00	0.00	
Pyritic	2.30	0.72	0.83	0.81	0.27	0.51
Organic	0.97	0.30	1.11	0.24	0.08	0.33
Total	3.34	1.04	1.94	1.05	0.35	0.84
Wt % Original Sulfur Removed From Feed			70.1			40.00

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evaluation. Therefore, the Western Kentucky No. 9 coal was selected for extensive study in this program.

THERMOBALANCE TESTS — WESTERN KENTUCKY NO. 9

Five runs, TB-22 to TB-26, were made with crushed and screened (—20+80 mesh) Western Kentucky No. 9 coal. This coal was mixed with lime for three tests; Runs TB-24 and TB-26 used coal only. The heat-up rate was 5°F/min to a terminal temperature of 800°F for Run TB-22 and 900°F for the others. All tests included holding the sample for 30 minutes at the terminal temperatures.

Data and calculations for these five runs are in Table 30. The sulfur removal ranged from 44% to 63% in these tests; however, the fraction of sulfur remaining in the treated coal was still too great to meet the requirements of direct combustion of the product. The lowest sulfur content was 1.73%, exceeding the limits. More severe treatment was necessary.

Two important facts were established in these tests. First, the sulfide content of the residues was much lower in the lime-free tests than in the tests with lime. This proves that calcium sulfide forms, but not so fast as the sulfur is released from the coal, as shown by an imbalance in total sulfur.

Second, the residue was caked in the sample basket and had to be broken up for removal and analysis. Poor solids-gas contact results from the caking and the reactions are inhibited; sulfur removal should be enhanced if the coal is noncaking.

A pretreatment step is required, for some coals, to prevent caking at the thermobalance conditions. The caking is caused by the tendency of the coal to become fluid at elevated temperatures. When partially fluid, the coal particles stick together. The coal can be pretreated by heating to a certain temperature, usually 750° to 800°F, in an atmosphere of air until a small quantity of oxygen has been consumed. Under these conditions, the "volatile matter" content of the coal is reduced and the coal no longer becomes fluid at the test temperature. Also, the coal particles form a skin, probably coke or char, that can be evaluated microscopically. This skin also inhibits caking. A batch reactor (modified) was used to pretreat coals for the test work.

Western Kentucky No. 9 coal is relatively easy to pretreat. The caking tendencies can be destroyed by heating the coal, fluidized with air at atmospheric pressure, to 750°F, reacting 1 SCF of oxygen per pound of coal. This coal can also be pretreated using inert nitrogen treatment at 750°F for 30 minutes. Associated with the pretreatment is a weight loss of 15% total (11% to 12% on a dry basis), including coal fines lost overhead. Volatile matter content is reduced from 33% to 35% in the coal to 27% to 28% in the pretreated coal. Its bulk density also decreases from about 50 lb/cu ft to approximately 35 lb/cu ft, because the particles tend to "puff." Other coals are pretreated in a similar manner but may require more air, longer exposure time, or higher temperatures.

TABLE 30. THERMOBALANCE RUN DATA (WESTERN KENTUCKY NO. 9)

Run No.		TB-22			TB-23	
Coal Type		W. Ky. No. 9			W. Ky. No. 9	
Heating Rate, °F/min		5			5	
Terminal Temperature, °F		800			900	
Holding Time, min		30			30	
Lab Analysis, wt %	Coal	Feed	Residue	Coal	Feed	Residue
H_2O	5.9			5.9		
Volatile Matter	33.4			33.4		
Sulfur, wt %, as						
Sulfide	0.00	0.00	0.30	0.00	0.00	0.59
Sulfate	0.07	0.02	0.07	0.07	0.02	0.05
Pyritic	2.30	0.77	0.34	2.30	0.77	0.32
Organic	0.97	0.32	0.34	0.97	0.32	0.30
Total	3.34	1.11	1.05	3.34	1.11	1.26
Weight, g						
Initial		4.5805			4.5869	
Treated			4.1764			4.1125
Weight Loss, %						
Of Total Weight			8.82			10.34
Of Coal Weight			26.48			31.02
Reduced Data (100 lb Coal Originally)						
Weight, lb		300.00	273.52		300.00	268.98
Sulfur Weight, lb, as						
Sulfide	0.00	0.00	0.82	0.00	0.00	1.59
Sulfate	0.07	0.07	0.19	0.07	0.07	0.13
Pyritic	2.30	2.30	0.93	2.30	2.30	0.86
Organic	0.97	0.97	0.93	0.97	0.97	0.81
Total	3.34	3.34	2.87	3.34	3.34	3.39
Sulfur Content, wt %, as						
Sulfide	0.00	0.00		0.00	0.00	
Sulfate	0.07	0.02		0.07	0.02	
Pyritic	2.30	0.77	1.26	2.30	0.77	1.25
Organic	0.97	0.32	1.26	0.97	0.32	1.17
Total	3.34	1.11	2.52	3.34	1.11	2.42
Wt % Original Sulfur Removed						
From Coal			44.3			50.0
From Feed			44.3			50.0

*No lime.

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TABLE 30. THERMOBALANCE RUN DATA (WESTERN KENTUCKY NO. 9) (Continued)

Run No.	TB-24*		TB-25		
Coal Type	W. Ky. No. 9		W. Ky. No. 9		
Heating Rate, °F/min	5		5		
Terminal Temperature, °F	900		900		
Holding Time, min	30		30		
Lab Analysis, wt %	Coal	Residue	Coal	Feed	Residue
H_2O	5.9		5.9		
Volatile Matter	33.4		33.4		
Sulfur, wt %, as					
Sulfide	0.00	0.72	0.00	0.00	0.36
Sulfate	0.07	0.05	0.07	0.02	0.04
Pyritic	2.30	0.64	2.30	0.77	0.18
Organic	0.97	1.09	0.97	0.32	0.37
Total	3.34	2.50	3.34	1.11	0.95
Weight, g					
Initial	4.2304			4.5726	
Treated		3.0028			4.0582
Weight Loss, %					
Of Total Weight		29.02			11.25
Of Coal Weight		29.02			33.74
Reduced Data (100 lb Coal Originally)					
Weight, lb	100.00	70.98		300.00	266.26
Sulfur Weight, lb, as					
Sulfide	0.00	0.51	0.00	0.00	0.96
Sulfate	0.07	0.04	0.07	0.07	0.11
Pyritic	2.30	0.45	2.30	2.30	0.48
Organic	0.97	0.77	0.97	0.97	0.99
Total	3.34	1.77	3.34	3.34	2.54
Sulfur Content, wt %, as					
Sulfide	0.00		0.00	0.00	
Sulfate	0.07		0.07	0.02	
Pyritic	2.30	0.64	2.30	0.77	0.72
Organic	0.97	1.09	0.97	0.32	1.49
Total	3.34	1.73	3.34	1.11	2.21
Wt % Original Sulfur Removed					
From Coal		63.5			56.0
From Feed		63.5			56.0

*No lime.

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TABLE 30. THERMOBALANCE RUN DATA (WESTERN KENTUCKY NO. 9) (Continued)

Run No.	TB-26*	
Coal Type	W. Ky. No. 9	
Heating Rate, °F/min	5	
Terminal Temperature, °F	900	
Holding Time, min	30	
Lab Analysis, wt %	Coal	Residue
H_2O	5.9	
Volatile Matter	33.4	
Sulfur, wt %, as		
Sulfide	0.00	0.73
Sulfate	0.07	0.00
Pyritic	2.30	0.75
Organic	0.97	1.03
Total	3.34	2.51
Weight, g		
Initial	3.8131	
Treated		2.7383
Weight Loss, %		
Of Total Weight		28.19
Of Coal Weight		28.19
Reduced Data (100 lb Coal Originally)		
Weight, lb	100.00	71.81
Sulfur Weight, lb, as		
Sulfide	0.00	0.52
Sulfate	0.07	0.00
Pyritic	2.30	0.54
Organic	0.97	0.74
Total	3.34	1.80
Sulfur Content, wt %, as		
Sulfide	0.00	
Sulfate	0.07	
Pyritic	2.30	0.75
Organic	0.97	1.03
Total	3.34	1.78
Wt % Original Sulfur Removed		
From Coal		61.7
From Feed		61.7

*No lime.

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A quantity of the Western Kentucky No. 9 coal was pretreated as described. The pretreated coal was then screened to −20+40 mesh for use in the thermobalance and batch reactor tests. All subsequent calculations for the tables are based on a coal-lime feed that is made by taking an initial 100 pounds of wet coal, pretreating it, and mixing the pretreated coal with lime (−60+80 mesh) in a 1:2 coal/lime ratio.

Results from a series of tests using pretreated coal are shown in Table 31. Sulfur removals of 65% to 90% were attained. The first two runs, TB-27 and TB-28, were heated at 5°F/min to 900°F terminal temperature and held for 30 minutes. Test TB-28 was run without lime. A reduction of pyritic sulfur was achieved with the formation of sulfide. Much more sulfide was made in the test with the lime than in the no-lime case. The organic sulfur reduction in these two tests, however, is about equal to the weight loss. The lower organic sulfur content in the residue from in the test with coal (no lime) may be due to sulfur-bearing oils and tars that are absorbed by the lime in the mixed-feed tests. These tests still yield a coal residue that is too high in sulfur.

Runs TB-30 and TB-31, also presented in Table 31, were heated to 1500°F at 5°F/min with no holding. As expected, weight losses were much higher at these temperatures. The residue from Test TB-30 has a lower sulfur content than most of the earlier runs; however, it is difficult to allocate the sulfur to the coal and lime when the residue is analyzed totally. Therefore, Test TB-31 was made at the same condition and the residue was separated by the float-sink method described earlier. The two fractions were then analyzed. The removal of sulfur and redistribution of the total original sulfur is nearly the same for Tests TB-30 and TB-31. The total amount of sulfur remaining after treatment (per 100 pounds of initial coal) is 1.84 pounds for Test TB-30 and 1.83 pounds for Test TB-31. The distribution of the sulfur by types is also similar. Assuming that the sulfide and sulfate remaining in the treated coal can be washed or mechanically separated, the coal residue contains only 0.66% total sulfur. This is an acceptable value depending upon the heating value of the coal residue.

For additional comparisons, three more tests, shown in Table 32, were run at a terminal temperature of 900°F and held for 30 minutes. The residue was separated by the float-sink method or screened at 50 mesh into +50 and −50 fractions. The sulfur data from the different separation techniques scattered widely; however, all sulfur contents were above the acceptable limits. The conclusion, at this point, is that 900°F is not severe enough treatment to effectively remove sulfur.

Table 33 lists the results and calculations from runs made at a heating rate of 5°F/min to a terminal temperature of 1500°F with no holding time. All tests show good sulfur removal with a range of 0.52% to 0.81% total sulfur in the coal residue (float or +50 mesh). Total weight loss (pretreatment and hydrogen treatment) is about 50%. Some of the loss is from the moisture content of the raw coal, and some losses will be recoverable as useful tars, oils, and gases from the process.

Two of the runs, TB-53 and TB-54, were made without lime. The residues were separated by the two methods as indicated in Table 33. This was done to

TABLE 31. THERMOBALANCE RUN DATA (PRETREATED WESTERN KENTUCKY NO. 9)

Run No.	Pretreatment		TB-27		TB-28*		TB-30		TB-31		
Coal Type	W. Ky. No. 9		Pretreated W. Ky. No. 9		Pretreated W. Ky. No. 9		Pretreated W. Ky. No. 9		Pretreated W. Ky. No. 9		
Heating Rate, °F/min			5		5		5		5		
Terminal Temp. °F	750		900		900		1500		1500		
Holding Time, min			30		30		0		0		
Lab Analysis, wt %	Coal	Pretreated Coal	Feed	Residue	Feed	Residue	Feed	Residue	Feed	Float	Sink
H_2O	5.9	0.8									
Volatile Matter	33.4	24.4									
Sulfur, wt %, as											
Sulfide	0.00	0.14	0.05	0.38	0.14	0.68	0.05	0.46	0.05	0.08	0.63
Sulfate	0.07	0.18	0.06	0.06	0.18	0.14	0.06	0.00	0.06	0.00	0.03
Pyritic	2.30	1.40	0.47	0.16	1.40	0.49	0.47	0.13	0.47	0.54	0.10
Organic	0.97	1.34	0.45	0.40	1.34	1.13	0.45	0.21	0.45	0.12	0.07
Total	3.34	3.06	1.03	1.00	3.06	2.44	1.03	0.80	1.03	0.74	0.83
Weight, g											
Initial	100.00		4.8760		3.1496		4.5381		4.5535		
Treated		85.54		4.5595		2.7452		4.0333		0.9946	3.0457
Weight Loss, %											
Of Total Weight		14.46		6.49		12.70		11.12		11.27	
Of Coal Weight		14.46		19.47		12.70		33.37		33.81	
Reduced Data											
(100 lb Original Coal)											
Weight, lb	100.00	85.54	256.62	239.96	85.54	74.67	256.62	228.08	256.62	56.05	171.65
Sulfur Weight, lb, as											
Sulfide	0.00	0.12	0.12	0.91	0.12	0.51	0.12	1.05	0.12	0.04	1.08
Sulfate	0.07	0.15	0.15	0.14	0.15	0.10	0.15	0.00	0.15	0.00	0.05
Pyritic	2.30	1.20	1.20	0.38	1.20	0.37	1.20	0.30	1.20	0.30	0.17
Organic	0.97	1.15	1.15	0.96	1.15	0.84	1.15	0.49	1.15	0.07	0.12
Total	3.34	2.62	2.62	2.39	2.62	1.82	2.62	1.84	2.62	0.41	1.42
Sulfur Content, wt %, as											
Sulfide	0.00		0.05				0.05		0.05		
Sulfate	0.07		0.06				0.06		0.06		
Pyritic	2.30	1.40	0.47	0.55	1.40	0.49	0.47	0.53	0.47	0.54	
Organic	0.97	1.34	0.45	1.39	1.34	1.13	0.45	0.86	0.45	0.12	
Total	3.34	2.74	1.03	1.94	2.74	1.62	1.03	1.39	1.03	0.66	
Wt %, Original Sulfur											
Removed From Feed				48.9		53.8		69.8		85.9	
Removed From Coal		29.6		59.9	29.6	63.8		76.3		88.9	

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*No lime.

TABLE 32. THERMOBALANCE RUN DATA (PRETREATED WESTERN KENTUCKY NO. 9 COAL, 900°F)

Run No.	Pretreatment		TB-34			TB-42			TB-33		
Coal	W. Ky. No. 9		Pretreated W.Ky. No. 9			Pretreated W.Ky. No. 9			Pretreated W.Ky. No. 9		
Heating Rate, °F/min				5			5			5	
Terminal Temperature, °F		750		900			900			900	
Holding Time, min				30			30			30	
Lab Analysis, wt %	Coal	Pretreated Coal	Feed	Float	Sink	Feed	+50	−50	Feed	+50	−50
H_2O	5.9	1.8									
Volatile Matter	33.4	32.3									
Sulfur, wt %, as											
Sulfide	0.00	0.13	0.04	0.07	0.33	0.04	1.22	0.27	0.04	0.86	0.22
Sulfate	0.07	0.19	0.06	0.00	0.07	0.06	0.01	0.04	0.06	0.05	0.04
Pyritic	2.30	2.87	0.96	0.50	0.29	0.96	0.64	0.00	0.96	1.00	0.11
Organic	0.97	1.29	0.43	1.04	0.17	0.43	1.36	0.21	0.43	0.92	0.09
Total	3.34	4.48	1.49	1.61	0.86	1.49	3.23	0.52	1.49	2.83	0.46
Weight, g											
Initial	100.00		4.2716			4.5483			4.1169		
Treated		85.54		0.9279	2.9854		1.1509	2.9930		1.0293	2.7387
Weight Loss, %											
Of Total Weight		14.46		7.94			7.94			7.82	
Of Coal Weight		14.46		23.81			23.83			23.47	
Reduced Data											
(100 lb Coal in Feed)											
Weight, lb	100.00	85.54	256.62	56.02	180.22	256.62	65.61	170.63	256.62	64.62	171.93
Sulfur Weight, lb, as											
Sulfide	0.00	0.11	0.11	0.04	0.59	0.11	0.80	0.46	0.11	0.56	0.38
Sulfate	0.07	0.16	0.16	0.00	0.13	0.16	0.01	0.07	0.16	0.03	0.07
Pyritic	2.30	2.45	2.45	0.28	0.52	2.45	0.42	0.00	2.45	0.65	0.19
Organic	0.97	1.10	1.10	0.58	0.31	1.10	0.89	0.36	1.10	0.59	0.15
Total	3.34	3.82	3.82	0.90	1.55	3.82	2.12	0.89	3.82	1.83	0.79
Sulfur Content, wt %, as											
Sulfide	0.00										
Sulfate	0.07										
Pyritic	2.30	2.87		0.50			0.64			1.00	
Organic	0.97	1.29		1.04			1.36			0.92	
Total	3.34	4.16		1.54			2.00			1.92	
Wt % Original Sulfur Removed From Feed				56.6			43.7			45.9	

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TABLE 33. THERMOBALANCE RUN DATA (PRETREATED WESTERN KENTUCKY NO. 9 COAL, 1500°F)

Run No.	Pretreatment		TB-35			TB-45			TB-52		
Coal Type	W. Kentucky No. 9		Pretreated W. Kentucky No. 9			Pretreated W. Kentucky No. 9			Pretreated W. Kentucky No. 9		
Heating Rate, °F/min			5			5			5		
Terminal Temperature, °F	750		1500			1500			1500		
Holding Time, min			0			0			0		
Lab Analysis, wt %	Coal	Pretreated Coal	Feed	+ 50	− 50	Feed	Float	Sink	Feed	Float	Sink
H_2O	5.9	1.8									
Volatile Matter	33.4	32.3									
Sulfur, wt %, as											
Sulfide	0.0	0.13	0.04	0.00	0.88	0.04	0.05	0.83	0.04	0.13	1.14
Sulfate	0.07	0.19	0.06	0.02	0.08	0.06	0.01	0.13	0.06	0.00	0.09
Pyritic	2.30	2.87	0.96	0.28	0.15	0.96	0.31	0.11	0.96	0.05	0.01
Organic	0.97	1.29	0.43	0.39	0.24	0.43	0.51	0.31	0.43	0.69	0.10
Total	3.34	4.48	1.49	0.69	1.35	1.49	0.88	1.38	1.49	0.87	1.34
Weight, g											
Initial	100.00		4.4377			4.4377			4.3962		
Treated		85.54		0.9085	2.9429		0.8339	3.2445		0.7817	2.9114
Weight Loss, %											
Of Total Weight		14.46		12.82			12.54			12.89	
Of Coal Weight		14.46		38.45			37.60			38.68	
Reduced Data											
(100 lb Coal Originally)											
Weight, lb	100.00	85.54	256.62	52.77	170.95	256.62	46.42	180.59	256.62	47.32	176.22
Sulfur Weight, lb, as											
Sulfide	0.00	0.11	0.11	0.00	1.50	0.11	0.02	1.50	0.11	0.06	2.01
Sulfate	0.07	0.16	0.16	0.01	0.14	0.16	0.01	0.23	0.16	0.00	0.16
Pyritic	2.30	2.45	2.45	0.15	0.26	2.45	0.14	0.20	2.45	0.02	0.02
Organic	0.97	1.10	1.10	0.21	0.41	1.10	0.24	0.56	1.10	0.33	0.18
Total	3.34	3.82	3.82	0.37	2.31	3.82	0.41	2.49	3.82	0.41	2.37
Sulfur Content, wt%, as											
Sulfide	0.00										
Sulfate	0.07										
Pyritic	2.30	2.87		0.28			0.31			0.05	
Organic	0.97	1.29		0.39			0.51			0.69	
Total	3.34	4.16		0.67			0.82			0.74	
Wt % Original Sulfur Removed From Feed				81.1			76.9			90.8	

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TABLE 33. THERMOBALANCE RUN DATA (PRETREATED WESTERN KENTUCKY NO. 9 COAL, 1500°F) (Continued)

Run No.	TB-53*			TB-54*			TB-57			TB-58		
Coal Type	Pretreated W. Kentucky No. 9			Pretreated W. Kentucky No. 9			Pretreated W. Kentucky No. 9			Pretreated W. Kentucky No. 9		
Heating Rate, °F/min	5			5			5			5		
Terminal Temperature, °F	1500			1500			1500			1500		
Holding Time, min	0			0			0			0		
Lab Analysis, wt %	Feed	+ 50	− 50	Feed	Float	Sink	Feed	Float	Sink	Feed	Float	Sink
H_2O												
Volatile Matter												
Sulfur, wt %, as												
Sulfide	0.13	0.44	2.00	0.13	0.15	2.13	0.04	0.06	0.24	0.04	0.14	0.67
Sulfate	0.19	0.00	0.00	0.19	0.00	0.02	0.06	0.02	0.40	0.06	0.00	0.14
Pyritic	2.87	0.34	0.18	2.87	0.45	0.10	0.96	0.00	0.06	0.96	0.45	0.01
Organic	1.29	0.19	1.22	1.29	0.07	0.36	0.43	0.81	0.43	0.43	0.36	0.38
Total	4.48	0.97	3.40	4.48	0.67	2.61	1.49	0.89	1.13	1.49	0.95	1.20
Weight, g												
Initial	4.7038			2.8771			4.6800			4.9088		
Treated		2.611	0.2407		1.4686	0.2936		0.1428	3.8901		0.8846	3.5508
Weight Loss, %												
Of Total Weight								13.83			13.64	
Of Coal Weight		38.29			38.75							
Reduced Data												
(100 lb Coal Originally)												
Weight, lb	85.54	48.41	4.38	85.54	43.66	8.73	256.62	7.92	215.78	256.62	44.20	177.42
Sulfur Weight, lb, as												
Sulfide	0.11	0.21	0.09	0.11	0.06	0.19	0.11	0.01	0.52	0.11	0.06	0.19
Sulfate	0.16	0.00	0.00	0.16	0.00	0.00	0.16	0.00	0.86	0.16	0.00	0.25
Pyritic	2.45	0.17	0.01	2.45	0.20	0.01	2.45	0.00	0.13	2.45	0.20	0.02
Organic	1.10	0.09	0.05	1.10	0.03	0.03	1.10	0.06	0.93	1.10	0.16	0.67
Total	3.82	0.47	0.15	3.82	0.29	0.23	3.82	0.07	2.44	3.82	0.42	1.13
Sulfur Content, wt%, as												
Sulfide												
Sulfate												
Pyritic		0.34			0.45			0.00			0.45	
Organic		0.19			0.07			0.81			0.36	
Total		0.53			0.52			0.81			0.81	
Wt % Original Sulfur Removed From Feed		93.2			94.0						78.8	

*No lime.

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determine the amount of treated material that would report to the lime portion (sink or −50 mesh) in the tests using mixed feed. In TB-53, 8.3% of the treated coal material remaining was −50 mesh, while 16.7% in TB-54 was in the sink portion. The treated material splits are assumed to occur in this way in the tests with lime. Also, the −50 and sink fractions have much higher sulfide and organic-type sulfur percentages than the +50 or float portions. This effect could be used in further sulfur reduction.

Run TB-57 was made with the pretreated material ground to −80 mesh and then mixed, treated, and separated. A disproportionately large portion of the treated material went to the sink portion of the separated material, making conclusions difficult.

The other runs (TB-35, TB-45, TB-52, and TB-58) were made with the usual coal-lime mix. They were screen- or float-separated as shown. Higher weight loss is experienced in the float-sink technique than in the screen separation, as illustrated by Runs TB-53 and TB-54. Assuming that the sulfide and sulfate can be removed by chemical or mechanical means, the coal-fraction sulfur content of these runs ranges from 0.52% to 0.82%. Heating values of 8,667 to 13,667 Btu/lb of treated material would give SO_2 emissions of 1.20 lb/10^6 Btu for these tests. Heating values from the early batch tests (Table 9) are 12,699 to 12,920 Btu/lb. If similar values are assumed for this material, only the higher sulfur content material would exceed the allowable limits.

The next set of runs, shown in Table 34, are those heated to 1500°F at 5°F/min and then held for 30 minutes at the final temperature. In Runs TB-61 and TB-63, nitrogen was used for initial preheat to 700°F and hydrogen to the end of the run. Runs TB-62 and TB-63, made with −80 mesh pretreated coal, have poor coal-fraction recovery. All tests show a lower total sulfur content, ranging from 0.36% to 0.75%, indicating that the holding time is beneficial. SO_2 emission again depends upon the heating value of the recovered coal portion, but is in the proper range.

Table 35 presents runs that were heated at 5°F/min to 1500°F, with no holding time, but had various feed or operational changes. Runs TB-59 and TB-60 were made with −80 mesh pretreated coal only. These tests exhibit a good final sulfur content (0.50% to 0.55%) indicating that the lime may not be imperative at elevated temperatures. The float-sink technique was used to determine how the finely ground material would separate. Losses to the sink fraction may cause a reevaluation of separation techniques when using lime.

Run TB-64 was made with the usual size coal and mixture, but was heated to 700°F with nitrogen and then with hydrogen the remainder of the time to the terminal temperature of 1500°F. The sulfur content of the product is in the higher end of the range and the separation was poor, indicating 1) this treatment is not beneficial, and 2) some sulfur reacts with the hydrogen at lower temperatures.

The pretreated coal feed for Run TB-65 was subjected to a 1:7 HNO_3 solution for 1 hour under reflux. These conditions are similar to the ASTM method for FeS_2 extraction. Afterward the coal was washed, filtered, dried, ground to −20+40 mesh, and mixed with lime in the usual ratio for the test. The

TABLE 34. THERMOBALANCE RUN DATA (PRETREATED WESTERN KENTUCKY NO. 9, 1500°F, 30 min)

Run No.	Pretreatment		TB-36			TB-37		
Coal Type	W. Kentucky No. 9		Pretreated W. Kentucky No. 9			Pretreated W. Kentucky No. 9		
Heating Rate, °F/min			5			5		
Terminal Temperature, °F	750		1500			1500		
Holding Time, min			30			30		
Lab Analysis, wt %	Coal	Pretreated Coal	Feed	Float	Sink	Feed	Float	Sink
H_2O	5.9	1.8						
Volatile Matter	33.4	32.3						
Sulfur, wt %, as								
Sulfide	0.00	0.13	0.04	0.00	0.95	0.04	0.04	0.99
Sulfate	0.07	0.19	0.06	0.06	0.05	0.06	0.01	0.06
Pyritic	2.30	2.87	0.96	0.49	0.04	0.96	0.23	0.08
Organic	0.97	1.29	0.43	0.26	0.32	0.43	0.32	0.23
Total	3.34	4.48	1.49	0.81	1.36	1.49	0.60	1.36
Weight, g								
Initial	100.00		4.6108			4.7242		
Treated		85.54		0.8837	3.2341		0.9266	3.1288
Weight Loss, %								
Of Total Weight		14.46		13.30			14.48	
Of Coal Weight		14.46		39.30			43.44	
Reduced Data (100 lb Coal Originally)								
Weight, lb	100.00	85.54	256.62	47.45	174.74	256.62	60.14	169.32
Sulfur Weight								
Sulfide	0.00	0.11	0.11	0.00	1.66	0.11	0.02	1.68
Sulfate	0.07	0.16	0.16	0.03	0.09	0.16	0.01	0.10
Pyritic	2.30	2.45	2.45	0.23	0.07	2.45	0.12	0.14
Organic	0.97	1.10	1.10	0.13	0.56	1.10	0.16	0.39
Total	3.34	3.82	3.82	0.39	2.38	3.82	0.31	2.31
Sulfur Content, wt %, as								
Sulfide	0.00							
Sulfate	0.07							
Pyritic	2.30	2.87		0.49			0.23	
Organic	0.97	1.29		0.26			0.32	
Total	3.34	4.16		0.75			0.55	
Wt % Original Sulfur Removed From Feed				78.9			84.5	

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TABLE 34. THERMOBALANCE RUN DATA (PRETREATED WESTERN KENTUCKY NO. 9, 1500°F, 30 min) (Continued)

Run No.	TB-61			TB-62*			TB-63*		
Coal Type	Pretreated W. Kentucky No. 9			Pretreated W. Kentucky No. 9			Pretreated W. Kentucky No. 9		
Heating Rate, °F/min	5			5			5		
Terminal Temperature, °F	1500			1500			1500		
Holding Time, min	30			30			30		
Lab Analysis, wt %	Feed	Float	Sink	Feed	Float	Sink	Feed	Float	Sink
H_2O									
Volatile Matter									
Sulfur, wt %, as									
Sulfide	0.04	0.32	0.80	0.04	0.10	0.78	0.04	0.23	0.64
Sulfate	0.06	0.01	0.11	0.06	0.00	0.12	0.06	0.05	0.14
Pyritic	0.96	{0.51}	{0.46}	0.96	0.36	0.13	0.96	0.00	0.11
Organic	0.43			0.43	0.00	0.40	0.43	0.71	0.40
Total	1.49	0.84	1.37	1.49	0.46	1.43	1.49	0.99	1.29
Weight, g									
Initial	4.6874			4.9800			4.8231		
Treated		0.9437	3.0926		0.1563	4.0783			
Weight Loss, %									
Of Total Weight		13.89			14.97			14.73	
Of Coal Weight		35.49			44.90			44.19	
Reduced Data									
(100 lb Coal Originally)									
Weight, lb	256.62	51.66	169.31	256.62	8.05	210.15	256.62	6.63	212.19
Sulfur Weight									
Sulfide	0.11	0.17	1.35	0.11	0.01	1.64	0.11	0.02	1.36
Sulfate	0.16	0.01	0.19	0.16	0.00	0.25	0.16	0.00	0.30
Pyritic	2.45	{0.26}	{0.78}	2.45	0.03	0.27	2.45	0.00	0.23
Organic	1.10			1.10	0.00	0.84	1.10	0.05	0.85
Total	3.82	0.44	2.32	3.82	0.04	3.00	3.82	0.07	2.74
Sulfur Content, wt %, as									
Sulfide									
Sulfate									
Pyritic		{0.51}			0.36			0.00	
Organic					0.00			0.71	
Total		0.51			0.36			0.71	
Wt % Original Sulfur Removed From Feed		93.2			99.2			98.7	

*–80 mesh pretreated coal.

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TABLE 35. THERMOBALANCE RUN DATA (PRETREATED WESTERN KENTUCKY NO. 9, 1500°F, 0 min)

Run No.	Pretreatment		TB-59*			TB-60*		
Coal Type	W. Kentucky No. 9		Pretreated W. Kentucky No. 9			Pretreated W. Kentucky No. 9		
Heating Rate, °F/min				5			5	
Terminal Temperature, °F	750			1500			1500	
Holding Time, min				0			0	
Lab Analysis, wt %	Coal	Pretreated Coal	Feed	Float	Sink	Feed	Float	Sink
H_2O	5.9	1.8						
Volatile Matter	33.4	32.3						
Sulfur, wt %, as								
Sulfide	0.00	0.13	0.13	0.19	0.54	0.13	0.14	0.83
Sulfate	0.07	0.19	0.19	0.00	0.00	0.19	0.00	0.29
Pyritic	2.30	2.87	2.87	0.30	0.26	2.87	0.27	0.00
Organic	0.97	1.29	1.29	0.24	0.28	1.29	0.25	0.49
Total	3.34	4.48	4.48	0.73	1.08	4.48	0.66	1.61
Weight, g								
Inttial	100.00		4.0071			3.9726		
Treated		85.54		1.4447	1.004		1.9371	0.4812
Weight Loss, %								
Of Total Weight		14.46						
Of Coal Weight		14.46		38.88			38.87	
Reduced Data								
(100 lb Coal Originally)								
Weight, lb	100.00	85.54	85.54	30.84	21.44	85.54	41.88	10.41
Sulfur Weight, lb, as								
Sulfide	0.00	0.11	0.11	0.06	0.12	0.11	0.06	0.09
Sulfate	0.07	0.16	0.16	0.00	0.00	0.16	0.00	0.03
Pyritic	2.30	2.45	2.45	0.09	0.05	2.45	0.11	0.00
Organic	0.97	1.10	1.10	0.07	0.06	1.10	0.10	0.05
Total	3.34	3.82	3.82	0.22	0.23	3.82	0.27	0.17
Sulfur Content, wt %, as								
Sulfide	0.00							
Sulfate	0.07							
Pyritic	2.30	2.87		0.30			0.27	
Organic	0.97	1.29		0.24			0.25	
Total	3.34	4.16		0.54			0.52	
Wt % Original Sulfur Removed From Feed				95.8			94.5	

*No lime.

TABLE 35. THERMOBALANCE RUN DATA (PRETREATED WESTERN KENTUCKY NO. 9, 1500°F, 0 min) (Continued)

Run No.	TB-64			TB-65			TB-66		
Coal Type	Pretreated W. Kentucky No. 9			Pretreated W. Kentucky No. 9			Pretreated W. Kentucky No. 9		
Heating Rate, °F/min	5			5			5		
Terminal Temperature, °F	1500			1500			1500		
Holding Time, min	0			0			0		
Lab Analysis, wt %	Feed	Float	Sink	Feed	Float	Sink	Feed	Float	Sink
H_2O									
Volatile Matter									
Sulfur, wt %, as									
Sulfide	0.04	0.16	0.53	0.01	0.08	0.21	0.00	0.34	0.60
Sulfate	0.06	0.00	0.16	0.02	0.00	0.11	0.01	0.03	0.09
Pyritic	0.96	0.37	0.01	0.34	0.35	0.05	0.37	0.73	0.13
Organic	0.43	0.38	0.40	0.52	0.21	0.20	0.65	0.23	0.43
Total	1.49	0.91	1.10	0.89	0.64	0.57	1.03	1.33	1.25
Weight, g									
Initial	4.8239			4.4535			4.4777		
Treated		0.7019	3.4910		0.5656	3.8879		0.0414	3.8316
Weight Loss, %									
Of Total Weight		13.08			13.36			13.50	
Of Coal Weight		39.24			40.08			40.50	
Reduced Data									
(100 lb Coal Originally)									
Weight, lb	256.62	37.34	185.71	256.62	28.24	194.10	300.00	2.78	256.72
Sulfur Weight, lb, as									
Sulfide	0.11	0.06	0.98	0.03	0.02	0.41	0.00	0.01	1.54
Sulfate	0.16	0.00	0.30	0.05	0.00	0.21	0.01	0.00	0.23
Pyritic	2.45	0.14	0.02	0.87	0.10	0.10	0.37	0.02	0.33
Organic	1.10	0.14	0.74	1.33	0.06	0.39	0.65	0.01	1.10
Total	3.82	0.34	2.04	2.28	0.18	1.11	1.03	0.04	3.20
Sulfur Content, wt %, as									
Sulfide									
Sulfate									
Pyritic		0.37			0.35			0.73	
Organic		0.38			0.21			0.23	
Total		0.75			0.56			0.96	
Wt % Original Sulfur Remove From Feed		92.7			95.8			97.1	

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treatment reduced the pyritic sulfur by over 50% and the total sulfur to 2.69%. After hydrogen treatment, the residue contained 0.56% pyritic plus organic sulfur, similar to other tests. Therefore, preremoval of pyrite by standard washing techniques is not beneficial.

For Run TB-66, the raw coal was treated with 1N $Fe_2(SO_4)_3$ (similar to the Meyers Process) for 11 hours and then crushed to —80 mesh and mixed with lime. The results are not conclusive because of the small amount of float material recovered. The float material did not have sulfur values as low as previous tests indicating (preliminarily) that utilization of the Meyers Process is not beneficial as a modification of this process. However, the $Fe_2(SO_4)_3$ treatment did prevent the agglomeration of the coal and may prove to be a substitute for air pretreatment.

Table 36 lists tests heated at 10°F/min to 1500°F, with one test being held for 30 minutes. Weight losses and separation values are consistent with other tests at this temperature. Residue sulfur contents are slightly higher with this heat-up rate, compared with tests at the slower heating rate (5°F/min). The increased coal residence time associated with the slower rate may have caused the improved sulfur removal. Table 37 presents data at a heat-up rate of 20°F/min: One test was held for 15 minutes, another was held for 30 minutes, and the rest had no holding time. Weight loss is as expected but the sulfur content is higher at 0.70% to 0.95%.

A series of tests, Table 38, was heated at 5°F/min to 1300°F; one test was held for 30 minutes. The results show slightly less weight loss, but the sulfur content is higher at 0.89% to 1.14%. Because this range is too high, it was concluded that 1300°F is not an adequate treatment temperature.

One test, TB-41 (Table 39), was heated at 20°F/min to 1600°F and held for 30 minutes. All of the parameters — weight loss, recovery, and final sulfur content — are no better than similar tests at 1500°F; therefore, it appears that no benefit is achieved from higher temperature.

The data on final sulfur content from all tests are presented in Figures 31 and 32. Figure 31 presents those tests heated at 5°F/min. Sulfur content definitely decreases as the temperature increases to 1500°F. No definite effect is discernible to prove the value of residence time at the final temperature.

The tests at higher heat-up rates, 10° and 20°F/min, presented in Figure 32, also exhibit a decrease in sulfur content but the decrease is not so great as in the tests at 5°F/min heat-up rate. Holding the test runs at the terminal temperature long enough to make the run times equal may depress this line to the level of the tests on Figure 31.

THERMOBALANCE TESTS — PITTSBURGH SEAM, WEST VIRGINIA

When the Western Kentucky No. 9 coal test series was concluded, a second coal was selected for a group of tests that would be definitive but not as exhaustive. Pittsburgh seam coal from a West Virginia mine was selected as an Eastern coal with a high-sulfur content.

TABLE 36. THERMOBALANCE RUN DATA (PRETREATED WESTERN KENTUCKY NO. 9, 10°F/min, 1500°F)

Run No.	Pretreatment		TB-44			TB-51			TB-46		
Coal Type	W. Ky. No. 9		Pretreated W. Ky. No. 9			Pretreated W. Ky. No. 9			Pretreated W. Ky. No. 9		
Heating Rate, °F/min				10			10			10	
Terminal Temperature, °F	750			1500			1500			1500	
Holding Time, min				0			0			30	
Lab Analysis, wt %	Coal	Pretreated Coal	Feed	Float	Sink	Feed	Float	Sink	Feed	Float	Sink
H_2O	5.9	1.8									
Volatile Matter	33.4	32.3									
Sulfur, wt %, as											
Sulfide	0.00	0.13	0.04	0.11	0.84	0.04	0.24	1.04	0.04	0.11	1.09
Sulfate	0.07	0.19	0.06	0.01	0.06	0.06	0.00	0.09	0.06	0.00	0.06
Pyritic	2.30	2.87	0.96	0.75	0.11	0.96	0.03	0.00	0.96	0.76	0.11
Organic	0.97	1.29	0.43	0.22	0.19	0.43	0.77	0.17	0.43	0.02	0.14
Total	3.34	4.48	1.49	1.09	1.20	1.49	1.04	1.30	1.49	0.89	1.40
Weight, g											
Initial	100.00		4.5669			4.4300			4.4200		
Treated		85.54		0.8950	3.1362		0.9141	3.0170		0.7773	3.0131
Weight Loss, %											
Of Total Weight		14.46		12.56			12.63			11.35	
Of Coal Weight		14.46		37.68			37.90			34.05	
Reduced Data (100 lb Coal Originally)											
Weight, lb	100.00	85.54	256.62	48.51	175.88	256.62	52.13	172.08	256.62	47.67	180.83
Sulfur Weight, lb, as											
Sulfide	0.00	0.11	0.11	0.05	1.48	0.11	0.12	1.79	0.11	0.05	1.97
Sulfate	0.07	0.16	0.16	0.00	0.11	0.16	0.00	0.15	0.16	0.00	0.11
Pyritic	2.30	2.45	2.45	0.36	0.19	2.45	0.02	0.00	2.45	0.36	0.20
Organic	0.97	1.10	1.10	0.11	0.33	1.10	0.40	0.29	1.10	0.01	0.25
Total	3.34	3.82	3.82	0.52	2.11	3.82	0.54	2.23	3.82	0.42	2.53
Sulfur Content, wt %, as											
Sulfide	0.00										
Sulfate	0.07										
Pyritic	2.30	2.87		0.75			0.03			0.76	
Organic	0.97	1.29		0.22			0.77			0.02	
Total	3.34	4.16		0.97			0.80			0.78	
Wt % Original Sulfur Removed From Feed				72.7			89.0			78.0	

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TABLE 37. THERMOBALANCE RUN DATA (PRETREATED WESTERN KENTUCKY NO. 9, $20^{o}F/min$, $1500^{o}F$)

Run No.	Pretreatment		TB-43			TB-47		
Coal Type	W. Kentucky No. 9		Pretreated W. Kentucky No. 9			Pretreated W. Kentucky No. 9		
Heating Rate, °F/min			20			20		
Terminal Temperature, °F	750		1500			1500		
Holding Time, min			0			0		
Lab Analysis, wt %	Coal	Pretreated Coal	Feed	Float	Sink	Feed	Float	Sink
H_2O	5.9	1.8						
Volatile Matter	33.4	32.3						
Sulfur, wt %, as								
Sulfide	0.00	0.13	0.04	0.27	0.81	0.04	0.28	0.80
Sulfate	0.07	0.19	0.06	0.00	0.08	0.06	0.04	0.14
Pyritic	2.30	2.87	0.96	0.84	0.20	0.96	0.36	0.09
Organic	0.97	1.29	0.43	0.04	0.24	0.43	0.54	0.25
Total	3.34	4.48	1.49	1.15	1.33	1.49	1.22	1.28
Weight, g								
Initial	100.00		4.5063			4.0954		
Treated		85.54		0.9437	3.0073		0.8857	2.7766
Weight Loss, %								
Of Total Weight		14.46		12.59			12.37	
Of Coal Weight		14.46		37.77			37.12	
Reduced Data (100 lb Coal Originally)								
Weight, lb	100.00	85.54	256.62	53.58	170.73	256.62	54.39	170.49
Sulfur Weight, lb, as								
Sulfide	0.00	0.11	0.11	0.14	1.38	0.11	0.15	1.36
Sulfate	0.07	0.16	0.16	0.00	0.14	0.16	0.02	0.24
Pyritic	2.30	2.45	2.45	0.45	0.34	2.45	0.20	0.15
Organic	0.97	1.10	1.10	0.02	0.41	1.10	0.29	0.43
Total	3.34	3.82	3.82	0.61	2.27	3.82	0.66	2.18
Sulfur Content, wt%, as								
Sulfide	0.00							
Sulfate	0.07							
Pyritic	2.30	2.87		0.84			0.36	
Organic	0.97	1.29		0.04			0.54	
Total	3.34	4.16		0.88			0.90	
Wt % Original Sulfur Removed From Feed				75.2			74.6	

TABLE 37. THERMOBALANCE RUN DATA (PRETREATED WESTERN KENTUCKY NO. 9, 20°F/min, 1500°F) (Continued)

Run No.	TB-50			TB-56		
Coal Type	Pretreated W. Kentucky No. 9			Pretreated W. Kentucky No. 9		
Heating Rate, °F/min	20			20		
Terminal Temperature, °F	1500			1500		
Holding Time, min	15			0		
Lab Analysis, wt %	Feed	Float	Sink	Feed	Float	Sink
H_2O						
Volatile Matter						
Sulfur, wt %, as						
Sulfide	0.04	0.36	0.96	0.04	0.25	0.30
Sulfate	0.06	0.06	0.14	0.06	0.00	0.08
Pyritic	0.96	0.40	0.02	0.96	0.04	0.00
Organic	0.43	0.47	0.22	0.43	0.72	0.32
Total	1.49	1.29	1.34	1.49	1.01	0.70
Weight, g						
Initial	4.1714			3.7436		
Treated		0.9013	2.7903		0.9515	2.3225
Weight Loss, %						
Of Total Weight		11.95			12.78	
Of Coal Weight		35.86			38.33	
Reduced Data						
(100 lb Coal Originally)						
Weight, lb	256.62	62.62	194.00	256.62	65.05	158.77
Sulfur Weight, lb, as						
Sulfide	0.11	0.23	1.86	0.11	0.16	0.47
Sulfate	0.16	0.04	0.27	0.16	0.00	0.13
Pyritic	2.45	0.25	0.04	2.45	0.03	0.00
Organic	1.10	0.29	0.43	1.10	0.47	0.51
Total	3.82	0.81	2.60	3.82	0.66	1.11
Sulfur Content, wt%, as						
Sulfide						
Sulfate						
Pyritic		0.40			0.04	
Organic		0.47			0.72	
Total		0.87			0.76	
Wt % Original Sulfur Removed From Feed		85.9			86.91	

TABLE 37. THERMOBALANCE RUN DATA (PRETREATED WESTERN KENTUCKY NO. 9, 20^{o}F/min, 1500^{o}F) (Continued)

Run No.	TB-55			TB-40		
Coal Type	Pretreated W. Kentucky No. 9			Pretreated W. Kentucky No. 9		
Heating Rate, °F/min	20			20		
Terminal Temperature, °F	1500			1500		
Holding Time, min	0			0		
Lab Analysis, wt %	Feed	Float	Sink	Feed	Float	Sink
H_2O						
Volatile Matter						
Sulfur, wt %, as						
Sulfide	0.04	0.22	0.69	0.04	0.34	1.18
Sulfate	0.06	0.00	0.07	0.06	0.00	0.05
Pyritic	0.96	0.56	0.00	0.96	0.33	0.03
Organic	0.43	0.39	0.33	0.43	0.37	0.28
Total	1.49	1.17	1.09	1.49	1.04	1.54
Weight, g						
Initial	4.5487			4.5438		
Treated		0.7746	2.4618		1.0533	3.0353
Weight Loss, %						
Of Total Weight		10.30			13.27	
Of Coal Weight		30.89			39.81	
Reduced Data						
(100 lb Coal Originally)						
Weight, lb	256.62	55.11	175.18	256.62	57.34	165.23
Sulfur Weight, lb, as						
Sulfide	0.11	0.12	1.18	0.11	0.19	1.95
Sulfate	0.16	0.00	0.12	0.16	0.00	0.08
Pyritic	2.45	0.31	0.00	2.45	0.19	0.05
Organic	1.10	0.21	0.56	1.10	0.22	0.46
Total	3.82	0.64	1.86	3.82	0.60	2.54
Sulfur Content, wt%, as						
Sulfide						
Sulfate						
Pyritic		0.56			0.33	
Organic		0.39			0.37	
Total		0.95			0.70	
Wt % Original Sulfur Removed From Feed		86.4			80.3	

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TABLE 38. THERMOBALANCE RUN DATA (PRETREATED WESTERN KENTUCKY NO. 9, 1300°F)

Run No.	Pretreatment		TB-39			TB-38		
Coal	W. Kentucky No. 9		Pretreated W. Ky. No. 9			Pretreated W. Ky. No. 9		
Heating Rate, °F/min				5			5	
Terminal Temperature, °F		750		1300			1300	
Holding Time, min				0			0	
Lab Analysis, wt %	Coal	Pretreated Coal	Feed	+50	−50	Feed	Float	Sink
H_2O	5.9	1.8						
Volatile Matter	33.4	32.3						
Sulfur, wt %, as								
Sulfide	0.00	0.13	0.04	0.30	0.69	0.04	0.00	0.62
Sulfate	0.07	0.19	0.06	0.00	0.10	0.06	0.00	0.08
Pyritic	2.30	2.87	0.96	0.53	0.00	0.96	0.88	0.02
Organic	0.97	1.29	0.43	0.47	0.47	0.43	0.24	0.42
Total	3.34	4.48	1.49	1.30	1.26	1.49	1.12	1.14
Weight, g								
Initial	100.00		4.4626			4.6853		
Treated		85.54		0.9832	2.9246		0.9805	3.2105
Weight Loss, %								
Of Total Weight		14.46		11.68			12.19	
Of Coal Weight		14.46		35.03			36.56	
Reduced Data								
(100 lb Coal in Feed)								
Weight, lb	100.00	85.54	256.62	57.02	169.63	256.62	52.72	172.62
Sulfur Weight, lb, as								
Sulfide	0.00	0.11	0.11	0.17	1.17	0.11	0.00	1.07
Sulfate	0.07	0.16	0.16	0.00	0.17	0.16	0.00	0.14
Pyritic	2.30	2.45	2.45	0.30	0.00	2.45	0.46	0.03
Organic	0.97	1.10	1.10	0.27	0.80	1.10	0.13	0.73
Total	3.34	3.82	3.82	0.74	2.14	3.82	0.59	1.97
Sulfur Content, wt %, as								
Sulfide	0.00							
Sulfate	0.07							
Pyritic	2.30	2.87		0.53			0.88	
Organic	0.97	1.29		0.47			0.24	
Total	3.34	4.16		1.00			1.12	
Wt % Original Sulfur Removed From Feed				71.8			68.5	

TABLE 38. THERMOBALANCE RUN DATA (PRETREATED WESTERN KENTUCKY NO. 9, 1300°F) (Continued)

Run No.	TB-48			TB-49		
Coal	Pretreated W.Ky. No. 9			Pretreated W.Ky. No. 9		
Heating Rate, °F/min		5			5	
Terminal Temperature, °F		1300			1300	
Holding Time, min		0			30	
Lab Analysis, wt %	Feed	Float	Sink	Feed	Float	Sink
H_2O						
Volatile Matter						
Sulfur, wt %, as						
Sulfide	0.04	0.20	0.91	0.04	0.24	0.61
Sulfate	0.06	0.00	0.05	0.06	0.00	0.12
Pyritic	0.96	0.56	0.13	0.96	0.56	0.06
Organic	0.43	0.33	0.12	0.43	0.58	0.31
Total	1.49	1.09	1.21	1.49	1.38	1.10
Weight, g						
Initial	4.3008			4.1520		
Treated		0.8317	2.9358		0.8177	2.8498
Weight Loss, %						
Of Total Weight		12.30			11.98	
Of Coal Weight		36.91			35.95	
Reduced Data						
(100 lb Coal in Feed)						
Weight, lb	256.62	49.69	175.36	256.62	50.37	
Sulfur Weight, lb, as						
Sulfide	0.11	0.10	1.60	0.11	0.12	1.07
Sulfate	0.16	0.00	0.09	0.16	0.00	0.21
Pyritic	2.45	0.28	0.23	2.45	0.28	0.11
Organic	1.10	0.16	0.21	1.10	0.29	0.54
Total	3.82	0.54	2.13	3.82	0.69	1.93
Sulfur Content, wt %, as						
Sulfide						
Sulfate						
Pyritic		0.56			0.56	
Organic		0.33			0.58	
Total		0.89			1.14	
Wt % Original Sulfur Removed From Feed		88.5			85.1	

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TABLE 39. THERMOBALANCE RUN DATA (PRETREATED WESTERN KENTUCKY NO. 9, 1600°F)

Run No.	Pretreatment		TB-41		
Coal Type	Western Kentucky No. 9		Pretreated Western Kentucky No. 9		
Heating Rate, °F/min				20	
Terminal Temperature, °F/min	750			1600	
Holding Time, min				30	
Lab Analysis, wt %	Coal	Pretreated Coal	Feed	Float	Sink
H_2O	5.9	1.8			
Volatile Matter	33.4	32.3			
Sulfur, wt %, as					
Sulfide	0.00	0.13	0.04	0.37	1.38
Sulfate	0.07	0.19	0.06	0.00	0.03
Pyritic	2.30	2.87	0.96	0.11	0.02
Organic	0.97	1.29	0.43	0.54	0.18
Total	3.34	4.48	1.49	1.02	1.61
Weight, g					
Initial	100.00		3.6476		
Treated		85.54		0.6887	2.4628
Weight Loss, %					
Of Total Weight		14.46		14.40	
Of Coal Weight		14.46		43.19	
Reduced Data					
(100 lb Coal Originally)	100.00	85.54	256.62	48.00	171.67
Weight, lb					
Sulfur Weight, lb, as					
Sulfide	0.00	0.11	0.11	0.18	2.37
Sulfate	0.07	0.16	0.16	0.00	0.05
Pyritic	2.30	2.45	2.45	0.05	0.03
Organic	0.97	1.10	1.10	0.26	0.31
Total	3.34	3.82	3.82	0.49	2.76
Sulfur Content, wt %, as					
Sulfide	0.00				
Sulfate	0.07				
Pyritic	2.30	2.87		0.11	
Organic	0.97	1.29		0.54	
Total	3.34	4.16		0.65	
Wt % Original Sulfur Removed From Feed				81.7	

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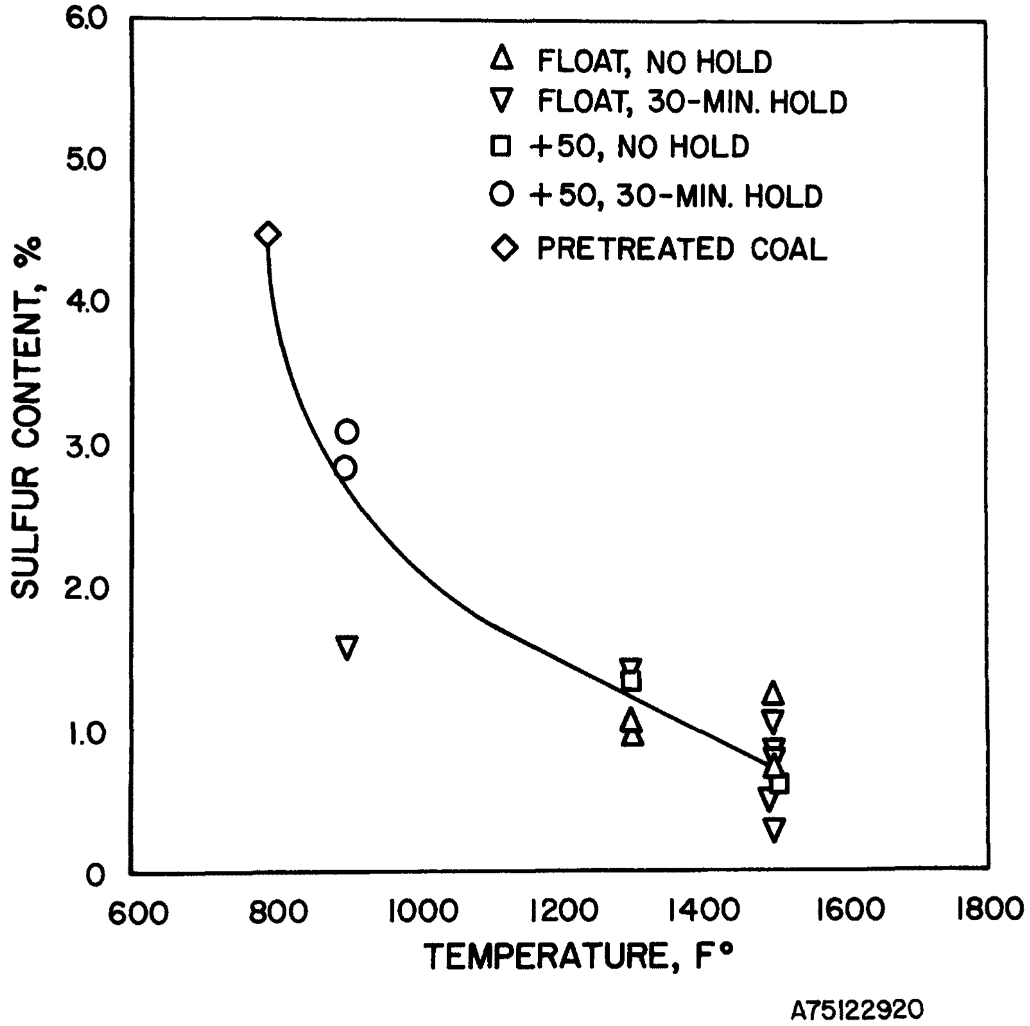

Figure 31. Thermobalance char-sulfur content at 5°F/min heating rate.

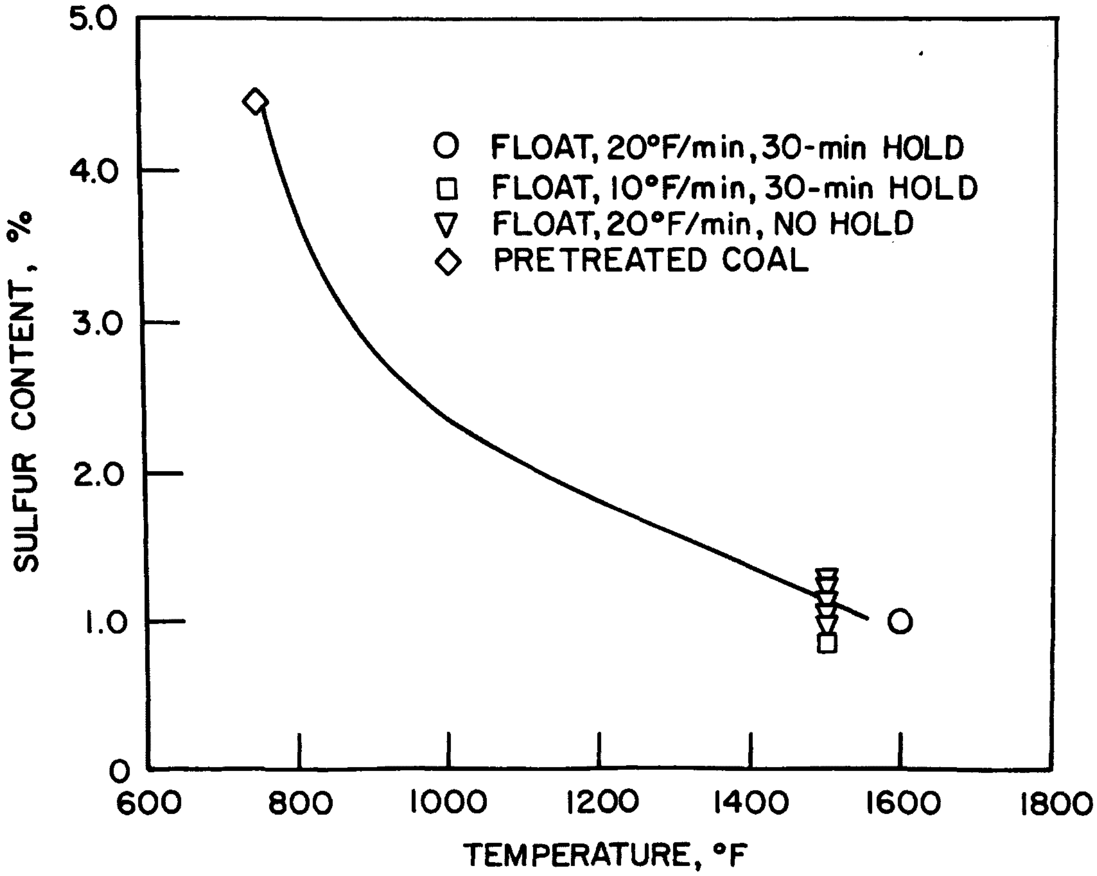

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Figure 32. Thermobalance char-sulfur content at 10° and 20°F/min heating rates.

A quantity of the coal was pretreated in the same way as the Western Kentucky No. 9. Results of the pretreatment and Run TB-67 are presented in Table 40. Weight losses are in the range expected (10% to 15%). The sulfur content of the treated coal was also low, comparable to the treated Midwestern coal. However, the feedstock was not pretreated adequately (compared with the Western Kentucky coal treated at the same condition) and the sample caked in the thermobalance test. Therefore, the sulfur content is not indicative of values that might be experienced if the coal were properly pretreated.

The pretreated material was subjected to a second air treatment, and thermobalance runs were made. The second pretreatment reduced the volatile content, but the coal still caked in all thermobalance tests. These data indicate that this sample of Pittsburgh seam coal is more agglomerating than the Western Kentucky coal.

Runs TB-68 to TB-70, in Table 41, were made with the double pretreated coal. All these tests were heated at $5^{o}F/min$ to $1500^{o}F$. Run TB-69 had a 30-minute holding time and nitrogen was used for the initial heat-up to $700^{o}F$ and then hydrogen to the run's end at $1500^{o}F$. The coal used for Run TB-70 was ground to —80 mesh before mixing. Sulfur reduction is good in Runs TB-68 and TB-69 despite the caking. The low recovery and high-sulfur content of the residue in Run TB-70 make obtaining the fine material unfeasible with these operating conditions.

A new sample of raw coal was screened and severely pretreated. The coal was heated to $750^{o}F$ with air and held at this temperature for 1 hour. Weight loss, including moisture, was over 18%. The volatile matter content was reduced to about 25% in the final material. This degree of pretreatment was sufficient because the treated coal did not cake in subsequent testing.

Thermobalance test Runs TB-71 and TB-75, Table 42, were made with this pretreated coal. Both were heated at $5^{o}F/min$ to $1500^{o}F$ with no holding. Run TB-71 was mixed with lime in the usual ratio; TB-75 used coal only. This coal, however, does not separate into float-sink portions as readily as the Western Kentucky No. 9; more of the coal goes into the sink portion. The sulfur content of the treated coal has been reduced near to the levels expected at these conditions based on past experience with Western Kentucky coal.

The pretreatment for the above tests was severe. To determine if less treatment would have sufficed, some coal was pretreated at less severe conditions — shorter time at $750^{o}F$.

The pretreated material was then used for Runs TB-72 to TB-74, presented in Table 43. Runs TB-73 and TB-74 were heated at $5^{o}F/min$ to $1500^{o}F$ with no holding. Run TB-73 was mixed with lime, while TB-74 was coal only. Both residues showed slight agglomeration, making the separation difficult. The sulfur was significantly reduced in both tests. Apparently, the lime is desirable because Run TB-74 shows a higher sulfur content; these results may, however, be masked by poorer separation.

In Run TB-72, a rapid heat-up procedure was used. The reactor was heated to $1500^{o}F$ and the basket was lowered into the heated zone. A large temperature

TABLE 40. THERMOBALANCE RUN DATA (PRETREATED PITTSBURGH SEAM, W. VA., 1500°F, 0 min)

Run No.	Pretreatment		TB-67		
Coal Type	Pittsburgh Seam, W. Va.		Pretreated Pittsburgh Seam, W. Va.		
Heating Rate, °F/min				5	
Terminal Temperature, °F	750			1500	
Holding Time, min				0	
Lab Analysis, wt %	Coal	Pretreated Coal	Feed	Float	Sink
H_2O	7.7	1.2	--	--	--
Volatile Matter	33.8	33.0	--	--	--
Sulfur, wt %, as					
Sulfide	0.00	0.09	0.03	0.29	0.42
Sulfate	0.05	0.10	0.03	0.06	0.12
Pyritic	1.49	1.24	0.41	0.02	0.00
Organic	1.37	1.42	0.47	0.45	0.16
Total	2.91	2.85	0.94	0.82	0.70
Weight, g					
Initial	100.00		4.7900		
Treated		85.64		1.2970	2.8236
Weight Loss, %					
Of Total Weight		14.36		13.97	
Of Coal Weight		14.36		41.92	
Reduced Data					
(100 lb Coal in Feed)					
Weight, lb	100.00	85.64	256.92	69.57	151.46
Sulfur Weight, lb, as					
Sulfide	0.00	0.08	0.08	0.20	0.64
Sulfate	0.05	0.08	0.08	0.04	0.18
Pyritic	1.49	1.05	1.05	0.01	0.00
Organic	1.37	1.20	1.20	0.31	0.24
Total	2.91	2.41	2.41	0.56	1.06
Sulfur Content, wt %, as					
Sulfide	0.00				
Sulfate	0.05				
Pyritic	1.49	1.24		0.02	
Organic	1.37	1.42		0.45	
Total	2.91	2.66		0.47	
Wt % Original Sulfur Removed From Feed				86.7	
Wt % Original Sulfur Removed From Original Coal		22.68		89.0	

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TABLE 41. THERMOBALANCE RUN DATA (DOUBLE PRETREATED PITTSBURGH SEAM, W. VA., 1500°F)

Run No.	Double Pretreatment		TB-68		
Coal Type	Pittsburgh Seam, W. Va.		Pretreated Pittsburgh Seam, W. Va.		
Heating Rate, °F/min				5	
Terminal Temperature, °F	750			1500	
Holding Time, min				0	
Lab Analysis, wt %	Coal	Pretreated Coal	Feed	Float	Sink
H_2O	7.7	1.1	--	--	--
Volatile Matter	33.8	32.0	--	--	--
Sulfur, wt %, as					
Sulfide	0.00	0.10	0.03	0.21	0.42
Sulfate	0.05	0.12	0.04	0.04	0.07
Pyritic	1.49	1.37	0.46	0.02	0.01
Organic	1.37	1.41	0.47	0.53	0.09
Total	2.91	3.00	1.00	0.80	0.59
Weight, g					
Initial			5.0814		
Treated				1.2166	3.1563
Weight Loss, %					
Of Total Weight				13.94	
Of Coal Weight				41.83	
Reduced Data					
(100 lb Coal in Feed)					
Weight, lb	100.00	83.92	251.76	60.28	156.38
Sulfur Wt, lb, as					
Sulfide	0.00	0.08	0.08	0.13	0.66
Sulfate	0.05	0.10	0.10	0.02	0.11
Pyritic	1.49	1.15	1.15	0.01	0.02
Organic	1.37	1.18	1.18	0.32	0.14
Total	2.91	2.51	2.51	0.48	0.92
Sulfur Content, wt %, as					
Sulfide	0.00	0.10			
Sulfate	0.05	0.12			
Pyritic	1.49	1.37		0.02	
Organic	1.37	1.41		0.53	
Total	2.91	3.00		0.55	
Wt % Original Sulfur Removed From Feed				86.9	
Wt % Original Sulfur Removed From Original Coal				88.7	

*–80 mesh.

TABLE 41. THERMOBALANCE RUN DATA (DOUBLE PRETREATED PITTSBURGH SEAM, W. VA., 1500°F) (Continued)

Run No.	TB-69		
Coal Type	Pretreated Pittsburgh Seam, W. Va.		
Heating Rate, °F/min	5		
Terminal Temperature, °F	1500		
Holding Time, min	30		
Lab Analysis, wt %	Feed	Float	Sink
H_2O	--	--	--
Volatile Matter	--	--	--
Sulfur, wt %, as			
Sulfide	0.03	0.30	0.60
Sulfate	0.04	0.00	0.03
Pyritic	0.46	0.02	0.00
Organic	0.47	0.52	0.16
Total	1.00	0.84	0.79
Weight, g			
Initial	4.9956		
Treated		0.9817	3.3146
Weight Loss, %			
Of Total Weight		14.00	
Of Coal Weight		42.00	
Reduced Data			
(100 lb Coal in Feed)			
Weight, lb	251.76	50.49	170.46
Sulfur Wt, lb, as			
Sulfide	0.08	0.15	1.02
Sulfate	0.10	0.00	0.05
Pyritic	1.15	0.01	0.00
Organic	1.18	0.26	0.27
Total	2.51	0.42	1.34
Sulfur Content, wt %, as			
Sulfide			
Sulfate			
Pyritic		0.02	
Organic		0.52	
Total		0.54	
Wt % Original Sulfur Removed From Feed		89.3	
Wt % Original Sulfur Removed From Original Coal		90.7	

*-80 mesh.

TABLE 41. THERMOBALANCE RUN DATA (DOUBLE PRETREATED PITTSBURGH SEAM, W. VA., 1500°F) (Continued)

Run No.	TB-70		
Coal Type	Pretreated Pittsburgh Seam, W. Va.*		
Heating Rate, °F/min		5	
Terminal Temperature, °F		1510	
Holding Time, min		0	
Lab Analysis, wt %	Feed	Float	Sink
H_2O	--	--	--
Volatile Matter	--	--	--
Sulfur, wt %, as			
Sulfide	0.03	0.00	0.36
Sulfate	0.04	0.28	0.08
Pyritic	0.46	0.03	0.01
Organic	0.47	1.40	0.30
Total	1.10	1.71	0.75
Weight, g			
Initial	4.7065		
Treated		0.1079	3.8968
Weight Loss, %			
Of Total Weight		14.91	
Of Coal Weight		44.73	
Reduced Data			
(100 lb Coal in Feed)			
Weight, lb	251.76	5.77	245.99
Sulfur Wt, lb, as			
Sulfide	0.08	0.00	0.88
Sulfate	0.10	0.02	0.20
Pyritic	1.15	0.00	0.02
Organic	1.18	0.08	0.74
Total	2.51	0.10	1.84
Sulfur Content, wt %, as			
Sulfide			
Sulfate			
Pyritic		0.03	
Organic		1.40	
Total		1.43	
Wt % Original Sulfur Removed From Feed		96.8	
Wt % Original Sulfur Removed From Original Coal		97.3	

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*–80 mesh.

TABLE 42. THERMOBALANCE RUN DATA (PRETREATED PITTSBURGH SEAM, W. VA., 1500°F, 0 min)

Run No.	Pretreatment		TB-71			TB-75*		
Coal Type	Pittsburgh seam, W. Va.		Pretreated Pittsburgh seam, W. Va.			Pretreated Pittsburgh Seam, W. Va.		
Heating Rate, °F/min				5			5	
Terminal Temperature, °F	750			1500			1500	
Holding Time, min				0			0	
Lab Analysis, wt %	Coal	Pretreated Coal	Feed	Float	Sink	Feed	Float	Sink
H_2O	7.7	1.0				--	--	--
Volatile Matter	33.8	24.8				--	--	--
Sulfur, wt %, as								
Sulfide	0.00	0.16	0.05	0.23	0.46	0.16	0.57	3.73
Sulfate	0.05	0.46	0.15	0.00	0.10	0.46	0.04	0.07
Pyritic	1.49	0.95	0.32	0.01	0.01	0.95	0.03	0.04
Organic	1.37	1.66	0.55	0.65	0.27	1.66	0.72	0.46
Total	2.91	3.23	1.07	0.89	0.84	3.23	1.36	4.30
Weight, g								
Initial	100.00		5.0400			2.7784		
Treated		81.81		0.6271	3.7766			
Weight Loss, %								
Of Total Weight		18.19		12.63			27.49	
Of Coal Weight		18.19		37.89				
Reduced Data								
(100 lb Coal in Feed)								
Weight, lb	100.00	81.81	245.43	30.54	183.89	81.81	42.83	16.48
Sulfur Weight, lb, as								
Sulfide	0.00	0.13	0.13	0.07	0.85	0.13	0.24	0.61
Sulfate	0.05	0.38	0.38	0.00	0.18	0.38	0.02	0.01
Pyritic	1.49	0.78	0.78	0.00	0.02	0.78	0.01	0.01
Organic	1.37	1.36	1.36	0.20	0.50	1.36	0.31	0.08
Total	2.91	2.65	2.65	0.27	1.55	2.65	0.58	0.71
Sulfur Content, wt %, as								
Sulfide		--		--				
Sulfate		--		--				
Pyritic		0.95		0.01			0.03	
Organic		1.66		0.65			0.72	
Total		2.61		0.66			0.75	
Wt % Original Sulfur Removed From Feed		26.46		92.45			87.92	
Wt % Original Sulfur Removed From Original Coal		26.46		93.13			89.00	

*No lime.

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TABLE 43. THERMOBALANCE RUN DATA (PRETREATED PITTSBURGH SEAM, W. VA.)

Run No.	Pretreatment		TB-72		
Coal Type	Pittsburgh Seam, W. Va.		Pretreated Pittsburgh Seam, W. Va.		
Heating Rate, °F/min				Rapid	
Terminal Temperature, °F	750			1500	
Holding Time, min				60	
Lab Analysis, wt %	Coal	Pretreated Coal	Feed	Float	Sink
H_2O	7.7	0.6			
Volatile Matter	33.8	31.6			
Sulfur, wt %, as					
Sulfide	0.00	0.04	0.01	0.62	0.65
Sulfate	0.05	0.10	0.03	0.00	0.00
Pyritic	1.49	1.27	0.42	--	0.01
Organic	1.37	1.56	0.52	0.35	0.18
Total	2.91	2.97	0.98	--	0.84
Weight, g					
Initial	100.00		4.5112		
Treated		88.80		3.8209	
Weight Loss, %					
Of Total Weight		11.20		15.30	
Of Coal Weight		11.20		45.90	
Reduced Data					
(100 lb Coal in Feed)					
Weight, lb	100.00	88.80	266.40	9.10	216.54
Sulfur Weight, lb, as					
Sulfide	0.00	0.04	0.04	0.06	1.41
Sulfate	0.05	0.09	0.09	0.00	0.00
Pyritic	1.49	1.13	1.13	--	0.02
Organic	1.37	1.39	1.39	0.03	0.39
Total	2.91	2.65	2.65	--	1.82
Sulfur Content, wt %, as					
Sulfide					
Sulfate					
Pyritic		1.27			
Organic		1.56			
Total		2.83			
Wt % Original Sulfur Removed From Feed		13.40			
Wt % Original Sulfur Removed From Original Coal		13.40			

* No lime.

TABLE 43. THERMOBALANCE RUN DATA (PRETREATED PITTSBURGH SEAM, W. VA.) (Continued)

Run No.	TB-73			TB-74*		
Coal Type	Pretreated Pittsburgh Seam, W. Va.			Pretreated Pittsburgh Seam, W. Va.		
Heating Rate, °F/min		5			5	
Terminal Temperature, °F		1500			1500	
Holding Time, min		0			0	
Lab Analysis, wt %	Feed	Float	Sink	Feed	Float	Sink
H_2O						
Volatile Matter						
Sulfur, wt %, as						
Sulfide	0.01	0.32	0.48	0.04	0.15	0.80
Sulfate	0.03	0.02	0.05	0.10	0.01	0.06
Pyritic	0.42	0.00	0.01	1.27	0.03	0.06
Organic	0.52	0.51	0.09	1.56	0.89	0.70
Total	0.98	0.85	0.63	2.97	1.08	1.62
Weight, g						
Initial	4.7455			3.5142		
Treated		4.0378				2.3601
Weight Loss, %						
Of Total Weight		14.91				32.84
Of Coal Weight		44.74				
Reduced Data						
(100 lb Coal in Feed)						
Weight, lb	266.40	80.48	146.20	88.80	32.81	26.83
Sulfur Weight, lb, as						
Sulfide	0.04	0.26	0.70	0.04	0.05	0.21
Sulfate	0.09	0.02	0.07	0.09	0.00	0.02
Pyritic	1.13	0.00	0.01	1.13	0.01	0.02
Organic	1.39	0.41	0.13	1.39	0.29	0.19
Total	2.65	0.69	0.91	2.65	0.35	0.44
Sulfur Content, wt %, as						
Sulfide						
Sulfate						
Pyritic		0.00			0.03	
Organic		0.51			0.89	
Total		0.51			0.92	
Wt % Original Sulfur Removed From Feed		84.53			88.68	
Wt % Original Sulfur Removed From Original Coal		85.91			89.68	

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* No lime.

gradient was imposed and a rapid heat-up was achieved. The sample was left for 1 hour and then removed. These conditions proved to be too rapid in heat-up and the sample was badly agglomerated. Complete analysis of the data was impossible.

Satisfactory sulfur content can be achieved by treatment of this coal; however, not enough data have been obtained to draw definitive conclusions as to sulfur removal. Pretreatment must be with longer residence and/or more air than with the Midwestern coals, resulting in higher weight loss in pretreatment.

The degree, or severity, of pretreatment differs for each coal. Some coals require only slight pretreatment and have relatively low weight loss. Others require more treatment and have higher weight loss.

The Western Kentucky No. 9 coal could be pretreated at 750^{o}F with 1 SCF O_2/lb of coal being consumed in 30 minutes. This is representative of the conditions necessary for pretreatment of coals from the Illinois Basin and results in about 10% weight loss. Coals such as the Pittsburgh seam require 750^{o}F temperature with 2 SCF O_2/lb of coal and from 30 minutes to 1 hour residence time. Weight loss for this treatment is usually 15% or more.

Each seam or mine may have its own characteristics such that pretreatment conditions are different for each.

BATCH REACTOR TESTS — WESTERN KENTUCKY NO. 9

The modified batch reactor described earlier was used to test the desulfurization concept in a fluidized-bed reactor. Information was taken from thermobalance runs to aid in establishing operating conditions for the unit. The fluidized-bed arrangement was expected to enhance gas-particle contact and increase sulfur removal. The feed coal, whether pretreated or not, was screened to —20+40 mesh and, when mixed, was 2 parts coal to 1 part lime of —60+80 mesh.

The first tests in the batch reactor were with nonpretreated Western Kentucky No. 9 coal. Table 44 lists the results of these tests. The heating rate was 5^{o}F/min to 900^{o}F, except Run BR-74-3 was heated to 1350^{o}F. All tests were held at their terminal temperatures for 30 minutes. A high hydrogen rate was used to simulate the gas flow conditions used in the pilot-unit. This flow was too high for the smaller unit, and excessive bed elutriation resulted. Some sulfur reduction in the residue took place, but this may be the result of concentrating the lime portion by flushing out the higher-sulfur-bearing coal fraction.

Later batch reactor runs were made with pretreated Western Kentucky No. 9 coal. To reduce entrainment losses, the hydrogen flow rate was reduced to yield a bed velocity of 0.35 ft/s at 900^{o}F and 0.5 ft/s at 1500^{o}F.

Runs BR-74-4 and BR-74-5, in Table 45, were made with the usual mixture of feedstock materials. Both tests were heated to 900^{o}F at 5^{o}F/min and held

TABLE 44. BATCH REACTOR RUN DATA (WESTERN KENTUCKY NO. 9)

Run No.	Coal	BR-74-1		BR-74-2		BR-74-3	
Coal Type	W. Ky. No. 9	W. Kentucky No. 9		W. Kentucky No. 9		W. Kentucky No. 9	
Heating Rate, °F/min		5		5		5	
Terminal Temperature, °F		900		900		1350	
Holding Time, min		30		30		30	
Lab Analysis, wt %	Coal	Feed	Residue	Feed	Residue	Feed	Residue
H_2O	5.9						
Volatile Matter	33.4						
Sulfur, wt %, as							
Sulfide	0.00	0.00	0.77	0.00	0.40	0.00	0.17
Sulfate	0.07	0.07	0.11	0.02	0.04	0.02	0.04
Pyritic	2.30	2.30	1.69	0.77	0.16	0.77	0.08
Organic	0.97	0.97	1.04	0.32	0.16	0.32	0.13
Total	3.34	3.34	3.61	1.11	0.76	1.11	0.42
Weight, g							
Initial	100.00	200.00		200.00		200.00	
Treated			158.00		167.00		110.00
Weight Loss, %							
Of Total Weight			21.00		16.50		45.00
Of Coal Weight			21.00		49.50		
Reduced Data (100 lb Coal in Feed)							
Weight, lb	100.00	100.00	79.00	300.00	250.50	300.00	165.00
Sulfur Weight, lb, as							
Sulfide	0.00	0.00	0.61	0.00	1.00	0.00	0.28
Sulfate	0.07	0.07	0.09	0.07	0.10	0.07	0.07
Pyritic	2.30	2.30	1.34	2.30	0.40	2.30	0.13
Organic	0.97	0.97	0.82	0.97	0.40	0.97	0.21
Total	3.34	3.34	2.86	3.34	1.90	3.34	0.69
Sulfur Content, wt %, as							
Sulfide	0.00	0.00		0.00		0.00	
Sulfate	0.07	0.07		0.07		0.07	
Pyritic	2.30	2.30	1.69	2.30	0.79	2.30	
Organic	0.97	0.97	1.04	0.97	0.79	0.97	
Total	3.34	3.34	2.73	3.34	1.58	3.34	
Wt % Original Sulfur Removed							
From Feed			35.3		76.0		
From Original Coal			35.3		76.0		

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TABLE 45. BATCH REACTOR RUN DATA (PRETREATED WESTERN KENTUCKY NO. 9, 900°F)

Run No.	Pretreatment		BR-74-4			BR-74-5	
Coal Type	W. Kentucky No. 9		Pretreated W. Kentucky No. 9			Pretreated W. Kentucky No. 9	
Heating Rate, °F/min				5		5	
Terminal Temperature, °F	750			900		900	
Holding Time, min				30		30	
Lab Analysis, wt %	Coal	Pretreated Coal	Feed	+ 50	− 50	Feed	Residue
H_2O	5.9	1.8					
Volatile Matter	33.4	32.3					
Sulfur, wt %, as							
Sulfide	0.00	0.13	0.04	0.80	0.49	0.13	0.86
Sulfate	0.07	0.19	0.06	0.07	0.03	0.19	0.06
Pyritic	2.30	2.87	0.96	0.36	0.19	2.87	0.49
Organic	0.97	1.29	0.43	1.06	0.03	1.29	1.17
Total	3.34	4.48	1.49	2.29	0.74	4.48	2.58
Weight, g							
Initial	100.00		150.00			100.00	
Treated		85.54		38.00	97.00		85.00
Weight Loss, %							
Of Total Weight		14.46		10.00			15.00
Of Coal Weight		14.46		30.00			15.00
Reduced Data (100 lb Coal in Feed)							
Weight, lb	100.00	85.54	256.62	65.01	165.95	85.54	72.71
Sulfur Weight, lb, as							
Sulfide	0.00	0.11	0.11	0.52	0.81	0.11	0.63
Sulfate	0.07	0.16	0.16	0.05	0.05	0.16	0.04
Pyritic	2.30	2.45	2.45	0.23	0.32	2.45	0.36
Organic	0.97	1.10	1.10	0.69	0.05	1.10	0.85
Total	3.34	3.82	3.82	1.49	1.23	3.82	1.88
Sulfur Content, wt %, as							
Sulfide	0.00		0.11			0.11	
Sulfate	0.07		0.16			0.16	
Pyritic	2.30	2.87	2.45	0.36		2.45	0.49
Organic	0.97	1.29	1.10	1.06		1.10	1.17
Total	3.34	4.16	3.82	1.42		3.82	1.66
Wt % Original Sulfur Removed From Feed				75.9			68.3

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for 30 minutes at the terminal temperature. Sulfur reduction was similar to the thermobalance tests at these conditions.

Table 46 presents runs heated at 5°F/min to 1500°F, with only Run BR-74-10 being held 30 minutes at the final temperature. The treated samples from Runs BR-74-9 and BR-74-10 were riffled into two parts, and then each part was screened or float-sink separated. The treated coal fractions show sulfur levels slightly higher than those from the thermobalance tests at this temperature. Weight losses from the batch reactor runs are higher, but the increased loss was probably caused by fluidization losses.

A lower terminal temperature, 1300°F, was used in Runs BR-74-8 and BR-74-11, shown in Table 47. Both tests were heated at 5°F/min, and Run BR-74-11 was held for 30 minutes at 1300°F. High material losses made the results from Run BR-74-8 inconclusive; however, Run BR-74-11 shows the percentage sulfur removal in the higher end of the range of values experienced in the 1500°F tests.

Table 48 lists data for Runs BR-74-12 and BR-74-13, heated to 1500°F at 10° and 20°F/min. No holding time was used in either test. The sulfur values are comparable to the batch reactor tests heated at 5°F/min with no holding, but are still higher than the thermobalance tests at the same condition. Further sulfur reduction may be possible by holding at the terminal temperature after using the higher heat-up rates.

Two runs, BR-74-18 and BR-74-19 (coal only), were exposed to a rapid heat-up to 1500°F, with Run BR-74-19 being held for 30 minutes (Table 49). The rapid heat-up is accomplished by turning full power to the heaters until the target temperature is reached. A rate of 65° to 70°F/min is possible by this procedure. Weight losses are lower than those usually found at 1500°F because of the shorter reaction time. Run BR-74-19 has the highest weight loss and lowest sulfur content as expected. Although the sulfur reduction has not been reduced to levels usually associated with these temperatures at lower heating rates, the data are promising. Run BR-74-19, held at 1500°F for 30 minutes, shows considerably lower sulfur content than Run BR-74-18. This indicates that rapid heat-up with much longer holding times may be as beneficial as lower heat-up rates.

The results of the batch reactor tests using pretreated Western Kentucky No. 9 coal are presented graphically in Figure 33. Total sulfur has been reduced significantly from the pretreated coal to the hydrogen-treated coal. Removal of sulfide and sulfate further depress the curve. The differences between 1300° and 1500°F are less than in the thermobalance tests and are probably due to better contact between gas and particles. Comparing Figure 33 with Figure 31, the overall sulfur level at 1500°F treatment is not as satisfactory in the batch reactor tests. Perhaps the much higher relative hydrogen flows in the thermobalance tend to release the "fixed" organic sulfur.

BATCH REACTOR TESTS — PITTSBURGH SEAM, WEST VIRGINIA

Four runs, BR-74-14 to BR-74-17, shown in Table 50, were made with Pittsburgh seam coal. Caking was evident in all of these tests, indicating

TABLE 46. BATCH REACTOR RUN DATA (PRETREATED WESTERN KENTUCKY NO. 9, 1500°F)

Run No.	Pretreatment		BR-74-6			BR-74-7		
Coal Type	W. Kentucky No. 9		Pretreated W. Kentucky No. 9			Pretreated W. Kentucky No. 9		
Heating Rate, °F/min				5			5	
Terminal Temperature, °F	750			1500			1500	
Holding Time, min				0			0	
Lab Analysis, wt %	Coal	Pretreated Coal	Feed	+ 50	− 50	Feed	Float	Sink
H_2O	5.9	1.8						
Volatile Matter	33.4	32.3						
Sulfur, wt %, as								
Sulfide	0.00	0.13	0.04	0.22	0.88	0.04	0.09	0.77
Sulfate	0.07	0.19	0.06	0.03	0.09	0.06	0.00	0.19
Pyritic	2.30	2.87	0.96	0.40	0.14	0.96	0.68	0.02
Organic	0.97	1.29	0.43	0.04	0.04	0.43	0.14	0.38
Total	3.34	4.48	1.49	0.69	1.15	1.49	0.91	1.36
Weight, g								
Initial	150.00		150.00			150.00		
Treated		85.54		27.50	96.00		22.04	96.86
Weight Loss %								
Of Total Weight		14.46		17.67			20.73	
Of Coal Weight		14.46		53.00			62.20	
Reduced Data								
(100 lb Coal Originally)								
Weight, lb	100.00	85.54	256.62	47.05	164.20	256.62	37.71	165.71
Sulfur Weight, lb, as								
Sulfide	0.00	0.11	0.11	0.10	1.44	0.11	0.03	0.75
Sulfate	0.07	0.16	0.16	0.01	0.15	0.16	0.00	0.18
Pyritic	2.30	2.45	2.45	0.19	0.23	2.45	0.26	0.02
Organic	0.97	1.10	1.10	0.02	0.07	1.10	0.05	0.37
Total	3.34	3.82	3.82	0.32	1.89	3.82	0.34	1.32
Sulfur Content, wt %, as								
Sulfide	0.00							
Sulfate	0.07							
Pyritic	2.30	2.87		0.40			0.68	
Organic	0.97	1.29		0.04			0.14	
Total	3.34	4.16		0.44			0.82	
Wt % Original Sulfur Removed From Feed				94.5			91.88	

TABLE 46. BATCH REACTOR RUN DATA (PRETREATED WESTERN KENTUCKY NO. 9, 1500°F) (Continued)

Run No.	BR-74-9					BR-74-10				
Coal Type	Pretreated W. Kentucky No. 9					Pretreated W. Kentucky No. 9				
Heating Rate, °F/min	5					5				
Terminal Temperature, °F	1500					1500				
Holding Time, min	0					30				
Lab Analysis, wt %	Feed	Float	Sink	+ 50	− 50	Feed	Float	Sink	+ 50	− 50
H_2O										
Volatile Matter										
Sulfur, wt %, as										
Sulfide	0.04	0.12	0.74	0.20	1.18	0.04	0.14	1.02	0.21	1.34
Sulfate	0.06	0.00	0.19	0.01	0.10	0.06	0.02	0.12	0.00	0.09
Pyritic	0.96	0.31	0.05	0.51	0.05	0.96	0.52	0.02	0.39	0.02
Organic	0.43	0.48	0.46	0.20	0.41	0.43	0.15	0.31	0.23	0.31
Total	1.49	0.91	1.44	0.92	1.74	1.49	0.83	1.47	0.83	1.76
Weight, g										
Initial	150.00					150.00				
Treated										
Weight Loss %										
Of Total Weight		← 31.33 →					← 14.73 →			
Of Coal Weight		← 93.99 →					← 44.20 →			
Reduced Data										
(100 lb Coal Originally)										
Weight, lb	256.62	47.44	128.78	38.56	137.66	256.62	51.39	167.38	59.25	159.52
Sulfur Weight, lb, as										
Sulfide	0.11	0.06	0.95	0.08	1.62	0.11	0.07	1.71	0.12	2.14
Sulfate	0.16	0.00	0.24	0.00	0.14	0.16	0.01	0.20	0.00	0.14
Pyritic	2.45	0.15	0.06	0.20	0.07	2.45	0.27	0.03	0.23	0.03
Organic	1.10	0.23	0.59	0.08	0.56	1.10	0.08	0.52	0.14	0.49
Total	3.82	0.44	1.84	0.36	2.39	3.82	0.43	2.46	0.49	2.80
Sulfur Content, wt %, as										
Sulfide										
Sulfate										
Pyritic		0.31		0.51			0.52		0.39	
Organic		0.48		0.20			0.15		0.23	
Total		0.79		0.71			0.67		0.62	
Wt % Original Sulfur Removed From Feed		90.0		92.7			90.80		90.31	

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TABLE 47. BATCH REACTOR RUN DATA (PRETREATED WESTERN KENTUCKY NO. 9, 1300°F)

Run No.	Pretreatment		BR-74-8				
Coal Type	W. Kentucky No. 9		Pretreated W. Kentucky No. 9				
Heating Rate, °F/min			5				
Terminal Temperature, °F	750		1300				
Holding Time, min			0				
Lab Analysis, wt %	Coal	Pretreated Coal	Feed	+ 50	− 50	Float	Sink
H_2O	5.9						
Volatile Matter	33.4						
Sulfur, wt %, as							
Sulfide	0.00	0.13	0.04	0.18	1.01	0.16	0.73
Sulfate	0.07	0.19	0.06	0.01	0.10	0.00	0.08
Pyritic	2.30	2.87	0.96	0.34	0.00	0.43	0.04
Organic	0.97	1.29	0.43	0.51	0.42	0.62	0.39
Total	3.34	4.48	1.49	1.04	1.53	1.21	1.24
Weight, g							
Initial	100.00		150.00				
Treated		85.54					
Weight Loss, %							
Of Total Weight		14.46	←		33.00		→
Of Coal Weight		14.46	←		99.00		→
Reduced Data							
(100 lb Coal Originally)							
Weight, lb	100.00	85.54	256.62	43.39	128.53	42.47	129.46
Sulfur Weight, lb, as							
Sulfide	0.00	0.11	0.11	0.08	1.30	0.07	0.95
Sulfate	0.07	0.16	0.16	0.00	0.13	0.00	0.10
Pyritic	2.30	2.45	2.45	0.15	0.00	0.18	0.05
Organic	0.97	1.10	1.10	0.22	0.54	0.26	0.50
Total	3.34	3.82	3.82	0.45	1.97	0.51	1.60
Sulfur Content, wt %, as							
Sulfide	0.00		0.11				
Sulfate	0.07		0.16				
Pyritic	2.30	2.87	2.45	0.34		0.43	
Organic	0.97	1.29	1.10	0.51		0.62	
Total	3.34	4.16	3.82	0.85		1.05	
Wt % Original Sulfur Removed From Feed				90.3		88.5	

TABLE 47. BATCH REACTOR RUN DATA (PRETREATED WESTERN KENTUCKY NO. 9, 1300°F) (Continued)

Run No.	BR-74-11				
Coal Type	Pretreated W. Kentucky No. 9				
Heating Rate, °F/min	5				
Terminal Temperature, °F	1300				
Holding Time, min	30				
Lab Analysis, wt %	Feed	+ 50	− 50	Float	Sink
H_2O					
Volatile Matter					
Sulfur, wt %, as					
Sulfide	0.04	0.23	0.94	0.12	0.64
Sulfate	0.06	0.02	0.13	0.02	0.23
Pyritic	0.96	0.44	0.04	0.62	0.04
Organic	0.43	0.33	0.52	0.25	0.50
Total	1.49	1.02	1.63	1.01	1.41
Weight, g					
Initial	150.00				
Treated					
Weight Loss, %					
Of Total Weight		← 14.26 →			
Of Coal Weight		← 42.78 →			
Reduced Data (100 lb Coal Originally)					
Weight, lb	256.62	52.00	168.02	48.80	171.22
Sulfur Weight, lb, as					
Sulfide	0.11	0.12	1.58	0.06	1.10
Sulfate	0.16	0.01	0.22	0.01	0.39
Pyritic	2.45	0.23	0.07	0.30	0.07
Organic	1.10	0.17	0.87	0.12	0.86
Total	3.82	0.53	2.74	0.49	2.42
Sulfur Content, wt %, as					
Sulfide	0.11				
Sulfate	0.16				
Pyritic	2.45	0.44		0.62	
Organic	1.10	0.33		0.25	
Total	3.82	0.77		0.87	
Wt % Original Sulfur Removed From Feed		89.5		89.0	

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TABLE 48. BATCH REACTOR RUN DATA (PRETREATED WESTERN KENTUCKY NO. 9, 10^{o} and 20^{o}F/min)

Run No.	Pretreatment		BR-74-12				
Coal Type	W. Kentucky No. 9		Pretreated W. Kentucky No. 9				
Heating Rate, °F/min			10				
Terminal Temperature, °F	750		1500				
Holding Time, min			0				
Lab Analysis, wt %	Coal	Pretreated Coal	Feed	+ 50	− 50	Float	Sink
H_2O	5.9	1.8					
Volatile Matter	33.4	32.3					
Sulfur, wt %, as							
Sulfide	0.00	0.15	0.04	0.23	1.06	0.11	0.54
Sulfate	0.07	0.19	0.06	0.01	0.04	0.03	0.21
Pyritic	2.30	2.87	0.96	0.43	0.01	0.40	0.05
Organic	0.97	1.29	0.43	0.32	0.34	0.31	0.49
Total	3.34	4.48	1.49	0.99	1.45	0.85	1.29
Weight, g							
Initial	100.00		150.00				
Treated		85.54					
Weight Loss, %							
Of Total Weight		14.46	18.47				
Of Coal Weight		14.46	55.42				
Reduced Data (100 lb Coal Originally)							
Weight, lb	100.00	85.54	256.62	59.78	149.44	45.61	163.61
Sulfur Weight, lb, as							
Sulfide	0.00	0.11	0.11	0.14	1.58	0.05	0.88
Sulfate	0.07	0.16	0.16	0.01	0.06	0.01	0.34
Pyritic	2.30	2.45	2.45	0.26	0.01	0.18	0.08
Organic	0.97	1.10	1.10	0.19	0.51	0.14	0.80
Total	3.34	3.82	3.82	0.60	2.16	0.38	2.10
Sulfur Content, wt %, as							
Sulfide	0.00						
Sulfate	0.07						
Pyritic	2.30	2.87		0.43		0.40	
Organic	0.97	1.29		0.32		0.31	
Total	3.34	4.16		0.75		0.71	
Wt % Original Sulfur Removed From Feed				88.2		91.6	

TABLE 48. BATCH REACTOR RUN DATA (PRETREATED WESTERN KENTUCKY NO. 9, 10^o and $20^oF/min$) (Continued)

Run No.	BR-74-13				
Coal Type	Pretreated W. Kentucky No. 9				
Heating Rate, °F/min	20				
Terminal Temperature, °F	1500				
Holding Time, min	0				
Lab Analysis, wt %	Feed	+ 50	− 50	Float	Sink
H_2O					
Volatile Matter					
Sulfur, wt %, as					
Sulfide	0.04	0.23	0.86	0.14	0.37
Sulfate	0.06	0.01	0.17	0.02	0.15
Pyritic	0.96	0.06	0.00	0.05	0.00
Organic	0.43	0.79	0.23	0.75	0.38
Total	1.49	1.09	1.26	0.96	0.90
Weight, g					
Initial	150.00				
Treated					
Weight Loss, %					
Of Total Weight	17.33				
Of Coal Weight	52.00				
Reduced Data (100 lb Coal Originally)					
Weight, lb	256.62	57.24	212.14	43.06	169.08
Sulfur Weight, lb, as					
Sulfide	0.11	0.13	1.82	0.06	0.63
Sulfate	0.16	0.01	0.36	0.01	0.25
Pyritic	2.45	0.03	0.00	0.02	0.00
Organic	1.10	0.45	0.49	0.32	0.64
Total	3.82	0.62	2.67	0.41	1.52
Sulfur Content, wt %, as					
Sulfide					
Sulfate					
Pyritic		0.06		0.05	
Organic		0.79		0.75	
Total		0.85		0.80	
Wt % Original Sulfur Removed From Feed		87.43		91.1	

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TABLE 49. BATCH REACTOR RUN DATA (PRETREATED WESTERN KENTUCKY NO. 9 RAPID HEATUP)

Run No.	Pretreatment		BR-74-18*		BR-74-19*	
Coal Type	W. Ky. No. 9		Pretreated W. Ky. No. 9		Pretreated W. Ky. No. 9	
Heating Rate, °F/min			Rapid		Rapid	
Terminal Temperature, °F			1500		1500	
Holding Time, min			0		30	
Lab Analysis, wt %	Coal	Pretreated Coal	Feed	Residue	Feed	Residue
H_2O	5.9	1.8				
Volatile Matter	33.4	32.3				
Sulfur, wt %, as						
Sulfide	0.00	0.13	0.13	0.98	0.13	1.41
Sulfate	0.07	0.19	0.19	0.06	0.19	0.03
Pyritic	2.30	2.87	2.87	0.19	2.87	0.06
Organic	0.97	1.29	1.29	1.47	1.29	1.06
Total	3.34	4.48	4.48	2.70	4.48	2.56
Weight, g						
Initial	100.00		150.00		150.00	
Treated		85.54		105.00		93.00
Weight Loss, %						
Of Total Weight		14.46		30.00		38.00
Of Coal Weight		14.46		30.00		38.00
Reduced Data						
(100 lb Coal in Feed)						
Weight, lb	100.00	85.54	85.54	59.88	85.54	53.03
Sulfur Weight, lb, as						
Sulfide	0.00	0.11	0.11	0.58	0.11	0.75
Sulfate	0.07	0.16	0.16	0.04	0.16	0.02
Pyritic	2.30	2.45	2.45	0.11	2.45	0.03
Organic	0.97	1.10	1.10	0.88	1.10	0.56
Total	3.34	3.82	3.82	1.61	3.82	1.36
Sulfur Content, wt %, as						
Sulfide						
Sulfate						
Pyritic		2.87		0.19		0.06
Organic		1.29		1.47		1.06
Total		4.16		1.66		1.12
Wt % Original Sulfur Removed From Feed				76.96		84.55

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* No lime.

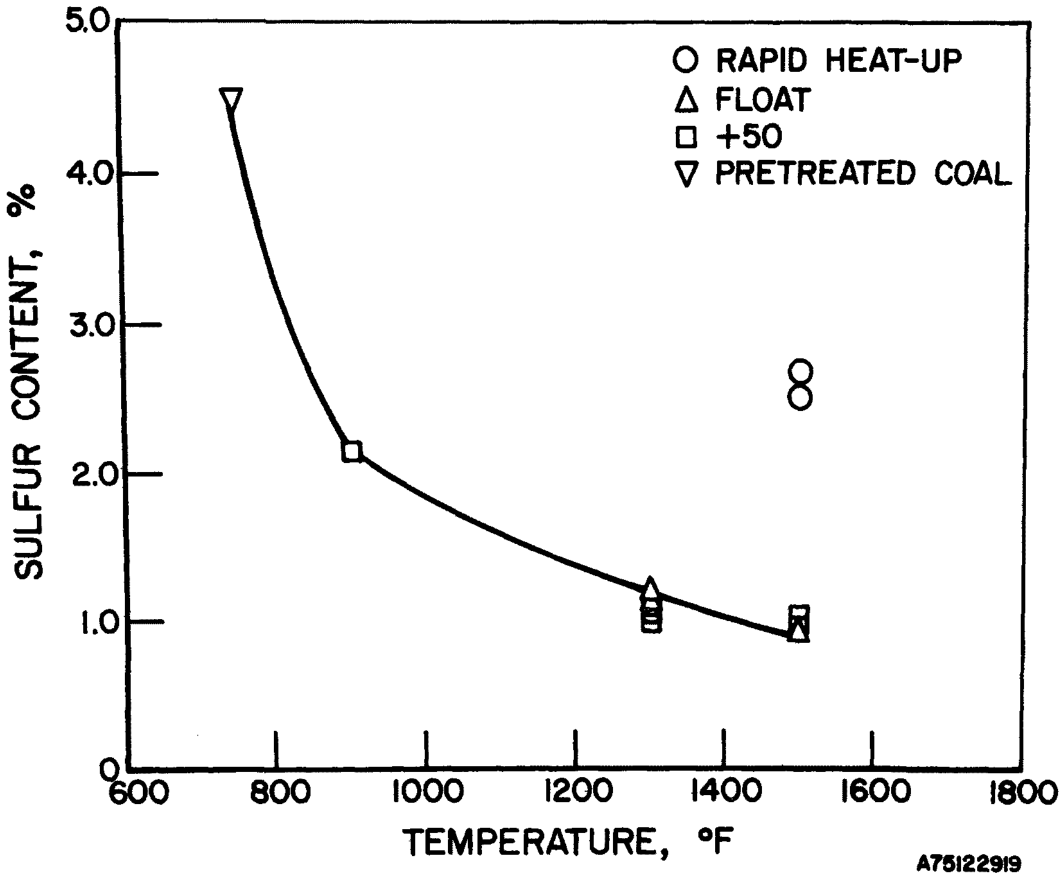

Figure 33. Batch reactor char-sulfur content.

TABLE 50. BATCH REACTOR RUN DATA (PRETREATED PITTSBURGH SEAM, W. VA.)

Run No.	Pretreatment		BR-74-14				
Coal Type	Pittsburgh seam, W. Va.		Pretreated Pittsburgh seam, W. Va.				
Heating Rate, °F/min					5		
Terminal Temperature, °F		750			1500		
Holding Time, min					0		
Lab Analysis, wt %	Coal	Pretreated Coal	Feed	+50	−50	Float	Sink
H_2O	7.7	1.2					
Volatile Matter	33.8	33.0					
Sulfur, wt %, as							
Sulfide	0.00	0.09	0.03	0.38	0.61	0.29	0.58
Sulfate	0.05	0.10	0.03	0.06	0.11	0.00	0.09
Pyritic	1.49	1.24	0.41	0.02	0.02	0.00	0.04
Organic	1.37	1.42	0.47	0.41	0.06	0.73	0.38
Total	2.91	2.85	0.94	0.87	0.80	1.02	1.09
Weight, g							
Initial	100.00		150.00				
Treated		85.64			126.60		
Weight Loss, %							
Of Total Weight		14.36			15.60		
Of Coal Weight		14.36			46.80		
Reduced Data							
(100 lb Coal in Feed)							
Weight, lb	100.00	85.64	256.92	97.93	118.91	52.63	164.21
Sulfur Wt, lb, as							
Sulfide	0.00	0.08	0.08	0.37	0.73	0.15	0.95
Sulfate	0.05	0.08	0.08	0.06	0.13	0.00	0.15
Pyritic	1.49	1.05	1.05	0.02	0.02	0.00	0.07
Organic	1.37	1.20	1.20	0.40	0.07	0.38	0.62
Total	2.91	2.41	2.41	0.85	0.95	0.53	1.79
Sulfur Content, wt %, as							
Sulfide	0.00	--		--		--	
Sulfate	0.05	--		--		--	
Pyritic	1.49	1.24		0.02		0.00	
Organic	1.37	1.42		0.41		0.73	
Total	2.91	2.66		0.43		0.73	
Wt % Original Sulfur Removed From Feed				82.57		84.23	
Wt % Original Sulfur Removed From Original Coal		22.68		85.57		86.94	

TABLE 50. BATCH REACTOR RUN DATA (PRETREATED PITTSBURGH SEAM, W. VA.) (Continued)

Run No.	BR-74-15					BR-74-16				
Coal Type	Pretreated Pittsburgh seam, W. Va.					Pretreated Pittsburgh seam, W. Va.				
Heating Rate, °F/min			5					5		
Terminal Temperature, °F			1500					1500		
Holding Time, min			30					0		
Lab Analysis, wt %	Feed	+50	−50	Float	Sink	Feed	+50	−50	Float	Sink
H_2O										
Volatile Matter										
Sulfur, wt %, as										
Sulfide	0.03	0.38	0.71	0.19	0.59	0.03	0.23	0.48	0.19	0.44
Sulfate	0.03	0.04	0.07	0.13	0.09	0.03	0.05	0.04	0.02	0.10
Pyritic	0.41	0.01	0.01	0.02	0.01	0.41	0.01	0.01	0.00	0.01
Organic	0.47	0.40	0.17	0.50	0.23	0.47	0.66	0.32	0.84	0.37
Total	0.94	0.83	0.96	0.84	0.92	0.94	0.95	0.85	1.05	0.92
Weight, g										
Initial	150.00									
Treated			126.00					120.30		
Weight Loss, %										
Of Total Weight			16.00					19.8		
Of Coal Weight			48.00					59.4		
Reduced Data										
(100 lb Coal in Feed)										
Weight, lb	256.92	90.50	125.31	42.38	173.43	256.92	97.79	108.26	56.78	149.27
Sulfur Wt, lb, as										
Sulfide	0.08	0.34	0.89	0.08	1.02	0.08	0.22	0.52	0.11	0.66
Sulfate	0.08	0.04	0.09	0.06	0.16	0.08	0.05	0.04	0.01	0.15
Pyritic	1.05	0.01	0.01	0.01	0.02	1.05	0.01	0.01	0.00	0.01
Organic	1.20	0.36	0.21	0.21	0.40	1.20	0.65	0.35	0.48	0.55
Total	2.41	0.75	1.20	0.36	1.60	2.41	0.93	0.92	0.60	1.37
Sulfur Content, wt %, as										
Sulfide		--		--			--		--	
Sulfate		--		--			--		--	
Pyritic		0.01		0.02			0.01		0.00	
Organic		0.40		0.50			0.66		0.84	
Total		0.41		0.52			0.67		0.84	
Wt % Original Sulfur Removed From Feed		84.65		90.87			72.60		80.08	
Wt % Original Sulfur Removed From Original Coal		87.28		92.44			77.32		83.51	

TABLE 50. BATCH REACTOR RUN DATA (PRETREATED PITTSBURGH SEAM, W. VA.) (Continued)

Run No.	BR-74-17*	
Coal Type	Pretreated Pittsburgh seam, W. Va.	
Heating Rate, °F/min	5	
Terminal Temperature, °F	1500	
Holding Time, min	0	
Lab Analysis, wt%	Feed	Treated Coal
H_2O		
Volatile Matter		
Sulfur, wt %, as		
Sulfide	0.09	0.72
Sulfate	0.10	0.05
Pyritic	1.24	0.09
Organic	1.42	1.05
Total	2.85	1.91
Weight, g		
Initial	150.00	
Treated		103.00
Weight Loss, %		
Of Total Weight		31.33
Of Coal Weight		31.33
Reduced Data (100 lb Coal in Feed)		
Weight, lb	85.64	58.81
Sulfur Wt, lb, as		
Sulfide	0.08	0.42
Sulfate	0.08	0.03
Pyritic	1.05	0.05
Organic	1.20	0.62
Total	2.41	1.12
Sulfur Content, wt %, as		
Sulfide		--
Sulfate		--
Pyritic		0.09
Organic		1.05
Total		1.14
Wt % Original Sulfur Removed From Feed		72.20
Wt % Original Sulfur Removed From Original Coal		76.98

*No lime in this test.

the coal had not been fully pretreated. Screen separation showed more +50 material recovered than initially charged. Lime has evidently been trapped by the caked coal particles and increased the weight of the +50 fraction. Because of this dilution with lime, the coal fraction appears to have a lower percentage of sulfur. The float portions of the first three tests show low sulfur but, again, this may be due to incomplete separation. Run BR-74-17 was made with coal only and, although the coal was badly caked, sulfur was still reduced to 1.14% in the final residue calculation. With the proper pretreatment, avoiding caking, it is expected that the sulfur can be reduced to levels comparable to Western Kentucky No. 9 coal.

GAS SAMPLE ANALYSIS

Batch Reactor

Analyses for batch reactor off-gas, on an air-free basis, are shown in Table 51. These data were taken from grab samples collected during the peak temperature period of the run. While not identical to the gas concentrations expected from a continuous operation, the species and distribution should be generally indicative of the off-gas to be obtained from a continuous unit. The H_2S is derived from reaction with coal sulfur, while the longer-chain molecules can be attributed to devolatilization.

Pilot Reactor Runs

Pilot reactor off-gas sample analyses are shown in Table 52. All of these runs were made at temperatures of 1200°F or lower. The gases containing sulfur are quite varied and many are devolatilization products only, caused by the lower operating temperature. No H_2S was detected in any of the samples and sulfur balances could not be made for these runs. Hydrogen sulfide is assumed to be lost to adsorption by the reactor and sample container or to condensation between sampling and analysis.

Modified Batch Reactor

Gas sample analyses for the modified batch reactor are shown in Tables 53 through 58. Tables 53 through 55 are for pretreated Western Kentucky No. 9 coal and Tables 56 through 58 are for pretreated Pittsburgh seam, West Virginia coal. For these data, grab samples were collected while the reactor was being heated; samples were taken when possible at temperatures of 800°, 1200°, and 1500°F.

Table 53 lists off-gas constituents at a reactor temperature of 800°F. The gas, as expected, is mostly hydrogen with some carbon species from the coal. No sulfur compounds were detected in the gas samples for the first four tests. The reason for this effect is unknown; perhaps the lime was effectively removing the sulfur-containing gases at the time the sample was taken. The runs in which sulfur was detected show several species, but no H_2S.

In Table 54, the analyses are shown for samples taken at 1200°F. These show generally higher values for the carbon species. However, the amounts of

TABLE 51. BATCH REACTOR GAS ANALYSIS — ILLINOIS NO. 6 COAL

Run No.	14	16	18	19	20
Mass Spectrometer Analysis, mol %					
Nitrogen	10.85	5.3	16.3	16.7	24.0
Carbon Monoxide		0.1			0.04
Carbon Dioxide			0.02		
Hydrogen	88.75	94.3	83.5	83.1	76.0
Methane		0.1	0.13	0.16	
Ethane			0.03		
Propane			0.01		
n-Butane			0.02		
Ethylene			0.01		
Propylene			0.01		
Toluene		0.14			
Argon	0.40	0.06			
Chromatograph Analysis, ppm					
Hydrogen Sulfide	15.0		15.2	18.6	63.0
Carbonyl Sulfide	0.7		1.9	0.5	0.9
Methyl Mercaptan			1.3		
Ethyl Mercaptan	11.9	2.2	6.3	2.2	3.4
Thiophene			2.4	0.7	
Dimethyl Disulfide	0.3		0.7	0.4	
t-Amyl Mercaptan			10.5	1.0	
Methylethyl Disulfide	1.1		28.5		
C_6 to C_8 Sulfides					

TABLE 52. PILOT REACTOR GAS ANALYSIS — ILLINOIS NO. 6 COAL

Run No.	VII	VIII A	VIII B	IX A	IX B	IX C	X	XI	XII A	XII B
Mass Spectrometer Analysis, mol %										
Nitrogen	1.65	1.95	1.72	3.13	2.53	1.03	1.3	1.5	1.81	2.09
Carbon Monoxide	1.77	1.61	1.60	2.19	2.07	1.84	2.5	1.8	2.17	2.56
Carbon Dioxide	0.16	0.03	0.03	0.17	0.03	0.01	0.09	0.03	0.34	0.03
Hydrogen	93.85	95.40	94.72	91.06	93.55	95.52	91.5	93.4	92.40	91.29
Methane	1.77	0.59	1.11	2.51	1.27	1.15	4.0	2.2	2.65	2.79
Ethane	0.19	0.05	0.17	0.27	0.14	0.09	0.21	0.29	0.18	0.41
$> C_2$	0.61	0.37	0.65	0.67	0.41	0.36	0.40	0.78	0.45	0.83
Chromatograph Analysis, ppm										
Carbonyl Sulfide				1.1	2.7	2.5	1.5	3.6		
Ethyl Mercaptan				0.4	2.6	2.6	0.9	4.7		
n-Propyl Mercaptan					1.1	1.2	0.4	1.6		
Thiophene				4.5	10.7	9.0	9.3	17.7		
Dimethyl Disulfide				1.6	2.1	4.6	0.3	8.7		
Methylethyl Disulfide				1.1	1.2	4.5	0.3	2.7		
Diethyl Disulfide				1.5	5.2	6.4	2.6			
$C_5H_{12}S$				13.8	38.9	34.8	28.1	43.9		
$C_6H_{14}S$				14.6	67.5	67.7	41.7	28.7		
$> C_6H_{14}S$				6.5	62.7	114.4	81.4	8.1		

TABLE 53. MODIFIED BATCH REACTOR GAS ANALYSIS (800°F) — PRETREATED WESTERN KENTUCKY NO. 9 COAL

Run No.	BR-74-7	BR-74-8	BR-74-9	BR-74-11	BR-74-12	BR-74-13
Mass Spectrometer Analysis, mol %						
Nitrogen	0.5		0.9	1.0	0.1	
Carbon Monoxide		0.1		0.1	0.1	
Carbon Dioxide				0.3		
Hydrogen	99.0	99.8	99.0	98.5	99.6	99.9
Methane	0.4	0.1	0.1	0.1	0.2	0.1
Ethane	0.1					
Chromatograph Analysis, ppm	*	*	*	*		
Carbonyl Sulfide					1.0	1.6
Carbon Disulfide					3.5	0.9
Dimethyl Sulfide						1.6
Thiophene					1.6	2.8
Dimethyl Disulfide					53.0	2.2
$C_5H_{12}S$					4.6	11.9
$C_6H_{14}S$					4.5	8.9

*No sulfur detected.

TABLE 54. MODIFIED BATCH REACTOR GAS ANALYSIS (1200°F) — PRETREATED WESTERN KENTUCKY NO. 9 COAL

Run No.	BR-74-7	BR-74-8	BR-74-11	BR-74-13
Mass Spectrometer Analysis, mol %				
Nitrogen	2.0	0.3	1.6	1.3
Carbon Monoxide	0.1	0.2	0.2	0.6
Carbon Dioxide	0.6		0.4	0.2
Hydrogen	96.8	98.7	97.4	97.2
Methane	0.5	0.8	0.4	0.7
Chromatograph Analysis, ppm		*		
Carbonyl Sulfide	1.0		2.0	1.6
Carbon Disulfide	1.0		0.2	0.4
Thiophene			0.4	

*No sulfur detected.

TABLE 55. MODIFIED BATCH REACTOR OFF-GAS ANALYSIS (1500°F) — PRETREATED WESTERN KENTUCKY NO. 9 COAL

Run No.	BR-74-7	BR-74-13
Mass Spectrometer Analysis, mol %		
Nitrogen	0.7	0.3
Carbon Monoxide	0.2	0.3
Carbon Dioxide	0.1	
Hydrogen	98.5	98.6
Methane	0.5	0.8
Chromatograph Analysis, ppm		
Carbonyl Sulfide	0.5	1.9
Carbon Disulfide	0.7	0.7

TABLE 56. MODIFIED BATCH REACTOR OFF-GAS (800°F) — PRETREATED PITTSBURGH SEAM (W. VA.) COAL

Run No.	BR-74-14	BR-74-15	BR-74-16
Mass Spectrometer Analysis, mol %			
Nitrogen	3.0	1.6	
Carbon Monoxide			0.4
Carbon Dioxide	0.3	0.5	99.5
Hydrogen	96.6	97.8	
Methane	0.1	0.1	0.1
Chromatograph Analysis, ppm			
Carbonyl Sulfide	1.0	1.3	660
Carbon Disulfide	1.8		95
Thiophene			12
$C_5H_{12}S$		1.0	100

TABLE 57. MODIFIED BATCH REACTOR OFF-GAS (1200°F) — PRETREATED PITTSBURGH SEAM (W. VA.) COAL

Run No.	BR-74-14	BR-74-15	BR-74-16
Mass Spectrometer Analysis, mol %			
Nitrogen	0.8	2.4	
Carbon Monoxide			0.3
Hydrogen	99.0	97.2	99.4
Methane	0.2	0.4	0.3
Chromatograph Analysis, ppm		*	*
Carbon Disulfide	0.6		

*No sulfur detected.

TABLE 58. MODIFIED BATCH REACTOR OFF-GAS (1500°F) — PRETREATED PITTSBURGH SEAM (W. VA.) COAL

Run No.	BR-74-14	BR-74-15	BR-74-15 (15 min into holding)
Mass Spectrometer Analysis, mol %			
Nitrogen	2.6	0.4	1.4
Carbon Monoxide		0.5	0.4
Carbon Dioxide	0.3		0.1
Hydrogen	96.9	98.7	97.9
Methane	0.2	0.4	0.2
Chromatograph Analysis, ppm			
Carbonyl Sulfide	0.7	0.5	2.3
Carbon Disulfide		1.5	0.9
Thiophene			3.8
$C_5H_{12}S$		0.8	1.8

sulfur gases are lower than in the same tests at 800°F. This effect may be due to reduced devolatilization at the higher temperature.

Analyses of gas samples at 1500°F are shown in Table 55. These are only slightly different than the 1200°F analyses and show very low sulfur content.

Table 56 shows analyses for off-gases at 800°F of the pretreated Pittsburgh seam, West Virginia coal. All analyses are typical except the sulfur types in BR-74-16. This test shows much higher values than any other tests and the results are unexplained.

Analyses of gases at 1200°F are shown in Table 57. Only a small amount of sulfur was detected in BR-74-14 and none was detected in the other two samples.

Table 58 shows analyses for gases at 1500°F. Once again, there are few sulfur-bearing gases and they are low in value.

The sampling and analysis of sulfur-bearing gases was inadequate for these tests. While balances can be made for the other coal constituents, it was not possible to make a sulfur balance for any of the runs. This is possibly caused by the reactivity of some of the species with their environment. The cooling of the sample between sampling and analysis may also be part of the problem. Future work must take these effects into account; a more complete analysis is required.

CONCLUSIONS

A pretreatment step is required for coals of the Midwestern and Eastern seams. This prevents agglomeration and caking in subsequent treatment for sulfur removal. The pretreatment also seems of benefit in removing sulfur.

Analysis of the hydrodesulfurization test results shows that with proper conditions of time, temperature, heating rate, etc., a substantial sulfur reduction is achieved. This is true for all the coals tested to date. Some coals require more severe conditions because of their original sulfur content or the seam location.

Use of lime as an acceptor may not be as beneficial as originally anticipated. While runs made with lime show less sulfur in the coal residue, there is also less residue recovered and some carbon loss to the lime fraction.

Gas analysis shows some heating value is available from the hydrocarbons present.

Further work is required before conclusively determining conditions for treatment of each coal, its final sulfur content, or the characteristics of the gaseous or any other stream from the process.

PROCESS CONCEPT

A process concept flow sheet, incorporating the results from the thermobalance and batch reactor runs for the Western Kentucky No. 9 coal, is presented in Figure 34. Streams not characterized have not yet been studied in the program. The data presented on Figure 34 are tentative; they are taken from an analysis of thermobalance and batch reactor tests that generate only small samples and are batch-type, not continuous as the process would be. The pilot unit, with a continuous feed and discharge system, will generate larger samples and better material and energy balances.

The process, as it is now conceived, yields a solid fuel meeting Federal EPA standards for direct combustion (1.2 lb SO_2/million Btu). The fuel contains 50% by weight of the input coal and 60% of the original carbon. Heat energy would be available from gas, tars, and oils generated both in the pretreater and hydrotreater. Carbon and hydrocarbon values in the lime would be used as a heat source for regeneration. Elemental sulfur would be a by-product.

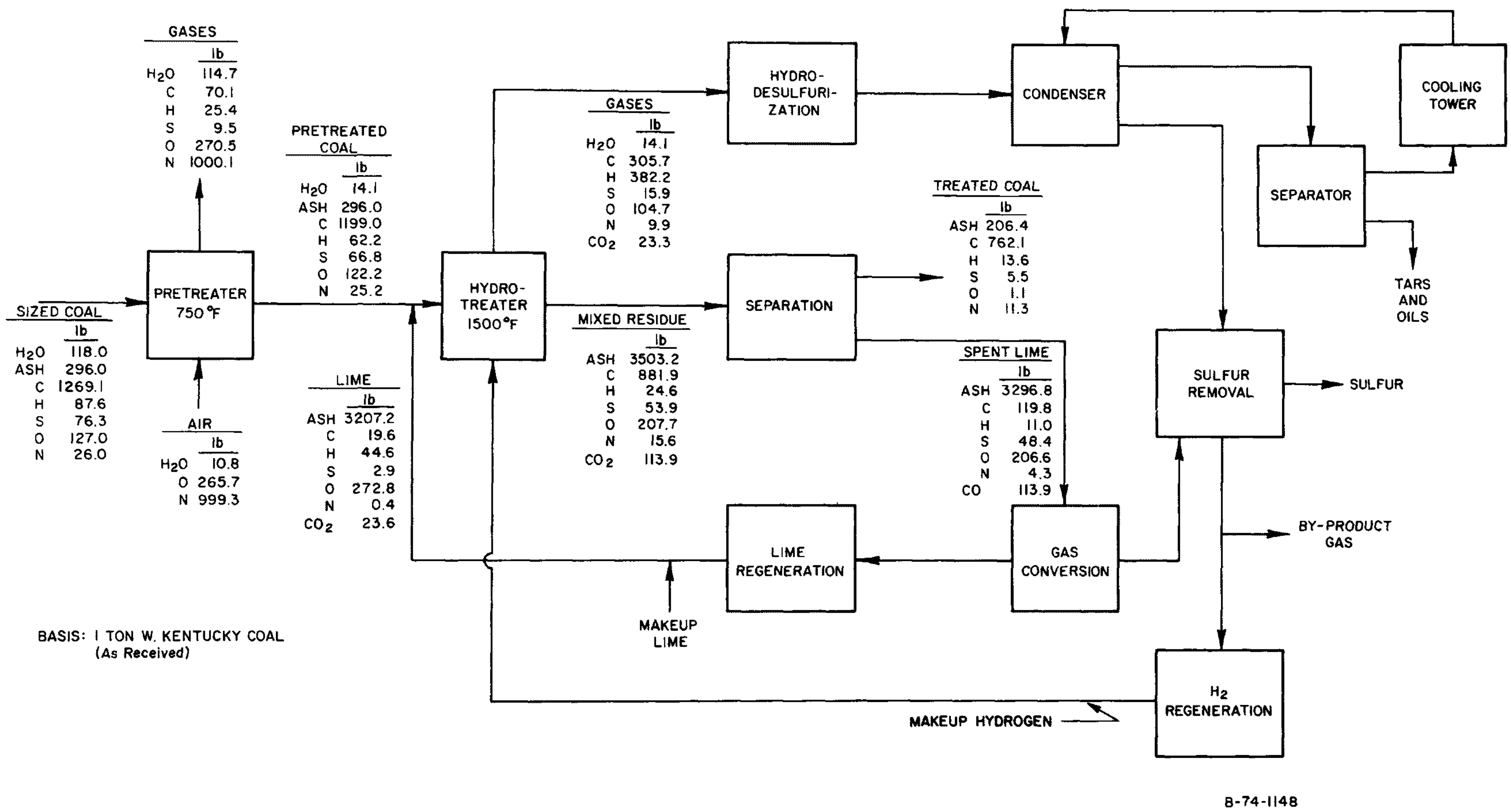

Figure 34. Flow sheet for proposed process.

FUTURE WORK

NECESSITY FOR LIME

One of the primary objectives to consider is the necessity of using lime. Some data indicate that the use of lime is not imperative; the process could be simplified if the lime were eliminated. Problems have been experienced with coal-lime separations, loss of carbon values to the lime, and capture of lime by the coal. These problems were not unexpected in the original plan for the process, but the effect is more pronounced than desirable.

Elimination of the lime would reduce the complexity of the process. The reactors could be made smaller, and gas usage would decrease because less material would be handled. Larger off-gas treatment facilities would be necessary to handle the increased sulfur in the off-gas. Studies must be made to determine which operating approach is economically and operationally superior.

OTHER COALS

Tests using other, typical sulfur-bearing coals should be made in the thermobalance and batch reactors. The results will be compared with results already obtained. The relative value of heating rates and holding times will be evaluated.

PILOT UNIT

Tests should be made on the 10-inch unit used previously. The larger scale operation and increased material generated are necessary for determining details to complete the process flow sheet. In particular, the determination and distribution of sulfur types in the off-gas during continuous operation is needed, so that treatment facilities can be designed.

If a heating rate must be imposed on the particle (other than the rapid heat-up in the fluidized-bed arrangement), the 10-inch unit will require modification. Further work is needed in the thermobalance and batch reactors to determine the optimum heat-up rate.

OVERALL CONCEPT DESIGN

When test work is completed, data would be used to generate an overall conceptual design for the process. This would include energy and material balances, economic studies, and all of the treatment steps to produce a low sulfur fuel from coal.

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16. ABSTRACT The report gives results of a program to develop, on bench and pilot scales, operating conditions for the key step in the IGT process to desulfurize coal by thermal and chemical treatment. This process, to date, uses the 'sulfur-getter' concept. (A sulfur-getter is a material that has a greater chemical affinity for sulfur than coal has.) Lime was the sulfur-getter for this program. In Phase I, a coal/lime mixture was experimentally treated at atmospheric pressure with a reducing gas in a heated, fluidized bed reactor, which could treat up to 200 lb/hr of mixture to 1200 F. The coal was Illinois No. 6, containing about 3% sulfur. Initial work resulted in the discovery that less sulfur was removed than expected. Two factors were believed responsible: the coal heat-up rate in the fluidized bed was nearly instantaneous, which appeared to cause organic sulfur fixation; and the coal showed signs of weathering (therefore, the total sulfur content was not readily available for hydrogen treatment). Phase II redirected the program to the operation of smaller scale units featuring: controlled heat-up rates, an increased number of tests over a broader range of conditions (with savings in time and manpower), and coal samples from several U.S. mines. A coal/lime mixture was treated with hydrogen, in batch reactors, to 1500 F. Tests indicated that lime treatment does not capture all sulfur released from the coal.

17. KEY WORDS AND DOCUMENT ANALYSIS

a. DESCRIPTORS	b. IDENTIFIERS/OPEN ENDED TERMS	c. COSATI Field/Group
Air Pollution	Air Pollution Control	13B
Coal	Stationary Sources	08G,21D
Conversion	IGT Process	14B
Desulfurization	Thermal Treatment	07A,07D
Calcium Oxides	Chemical Treatment	07B
Fluidizing		13H

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