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BENCH-SCALE DEVELOPMENT OF THE TRW PROCESS FOR CLEANING COAL (GRAVIMELT PROCESS)

Quarterly Technical Progress Report for the Period
November 1983—February 1984

March 1984

Work Performed Under Contract No. AC22-83PC63032

TRW Incorporated
Energy Technology Division
Redondo Beach, California

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QUARTERLY TECHNICAL PROGRESS REPORT
FOR THE PERIOD
NOVEMBER 1983 - FEBRUARY 1984

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WORK PERFORMED UNDER CONTRACT
DE-AC22-83PC63032

for
U.S. DEPARTMENT OF ENERGY
PITTSBURGH ENERGY TECHNOLOGY CENTER
P.O. BOX 10940
PITSSBURGH, PA 15236

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SUMMARY

This report presents progress for the second quarter of performance on Contract Number DE-AC22-83-PC63032. The effort includes Tasks 6 through 13 of a continuing program to demonstrate the TRW Gravimelt coal cleaning technology.

The technical effort this quarter has concentrated on defining an operable flow scheme, conducting the required supporting laboratory tests and establishing the performance of the bench scale centrifuge. Key to directing the development and scale-up activity, was the definition of the process flow scheme. Based on laboratory studies of the reaction and the washing/separation steps, it was concluded that a counter-flow reactor system was needed to make the separation of mineral-rich caustic from the processed coal. The absence of mineral matter should also improve the filtration of the processed coal. Each of the steps have been reviewed to determine where industry experience with similar operations may be able to reduce development effort or increase confidence.

Laboratory testing has established the general effect of impure caustic on the reaction rate and extent of ash and sulfur removal. It was found that within the expected range of moisture, sulfide and mineral matter build-up, the effects are small. Bench scale batches of processed Kentucky 11 coal verify lab scale results which produce coal meeting New Source Performance Standards (NSPS). For example, batches 1 to 3 gave sulfur levels ranging from 0.2 to 0.4 pounds of SO_x per million Btu (lb/mm Btu). Based on run-of-mine (ROM) sulfur, typically 8 to 12 lb SO_x/mm Btu, this is 1/6 to 1/2 the required NSPS levels. It also represents greater than 90% removal from the mine-cleaned level of 5 lbs SO_x/mm Btu. Counter-current flow simulation in laboratory batches is planned to verify the reaction effects. Planning for a bench scale size reactor system was initiated. It will generate counter-current flow, product coal for additional centrifuge and filter testing.

The bench-scale centrifuge was used to concentrate processed coal from caustic slurries in the range of 2 to 5% coal in 5 to 15% aqueous caustic. Centrifuge cakes generally were thick pastes with 35 to 40% solids. The first test of a slurry of about 20% coal in aqueous caustic also gave about a 35% solids product. Laboratory tests showed that concentration by filtration would have been very slow, probably as a result of gelatinous precipitates from the used caustic.

1.0 INTRODUCTION

This report presents progress for the second quarter of performance on Contract number DE-AC22-83PC63032 dated 17 August 1983 by the U.S. Department of Energy, Pittsburgh Energy Technology Center. The objective of this program is to develop and demonstrate the Gravimelt Process for the removal of sulfur and ash from coal. Under the program, selected processing steps and operations which comprise the process will be defined, experimentally tested and assessed to determine their efficacies and feasible use in the process. Processing operations or sections to be examined include: the leaching reactor, product filtering and washing, reactant regeneration and waste handling. Initially, the experimental evaluation of these processing operations will be conducted in laboratory and small bench-scale equipment and subsequently will be demonstrated in 20 pound per hour, non-integrated circuits. Engineering studies of other technologies applicable to the process scheme will also be performed and as appropriate, will be incorporated into a 20 pound per hour circuit. Experimental data, engineering analysis and interpretation of these results will be described and summarized in various reports and presentations. In this program, Tasks 6 through 13 are a continuation of Tasks 1 through 5 performed in the previous contract (Number DE-AC22-81PC42295) completed in June 1983.

2.0 ACCOMPLISHMENTS

The program will be conducted by performing a series of tasks which are identified in the Statement of Work (SOW). The SOW directs the Gravimelt Process development effort to follow up the previous five-task bench-scale study of the reactor and separation system with eight additional tasks. Tasks 6 through 9 relate to developing the process steps, Tasks 10 through 12 involve the 20 pound per hour demonstration and Task 13 is planning, reporting and management.

The SOW and the project plan provide detail about the content of each task. The following list shows the general task requirements:

Task 6 - Demonstrate key reactions in caustic and acid recycle.

Task 7 - Adapt the Mod II reactor to provide samples which determine efficacy of the process in reaching 90% ash and sulfur removal (parametric testing of three coals) and to provide data for the scaled-up reactor system for Tasks 10 through 12.

Task 8 - Test the solid/liquid separating devices needed in the washing stages.

Task 9 - Scale up the regeneration work defined in Task 6.

Task 10 - Engineer the 20 lb/hr units and prepare test plan.

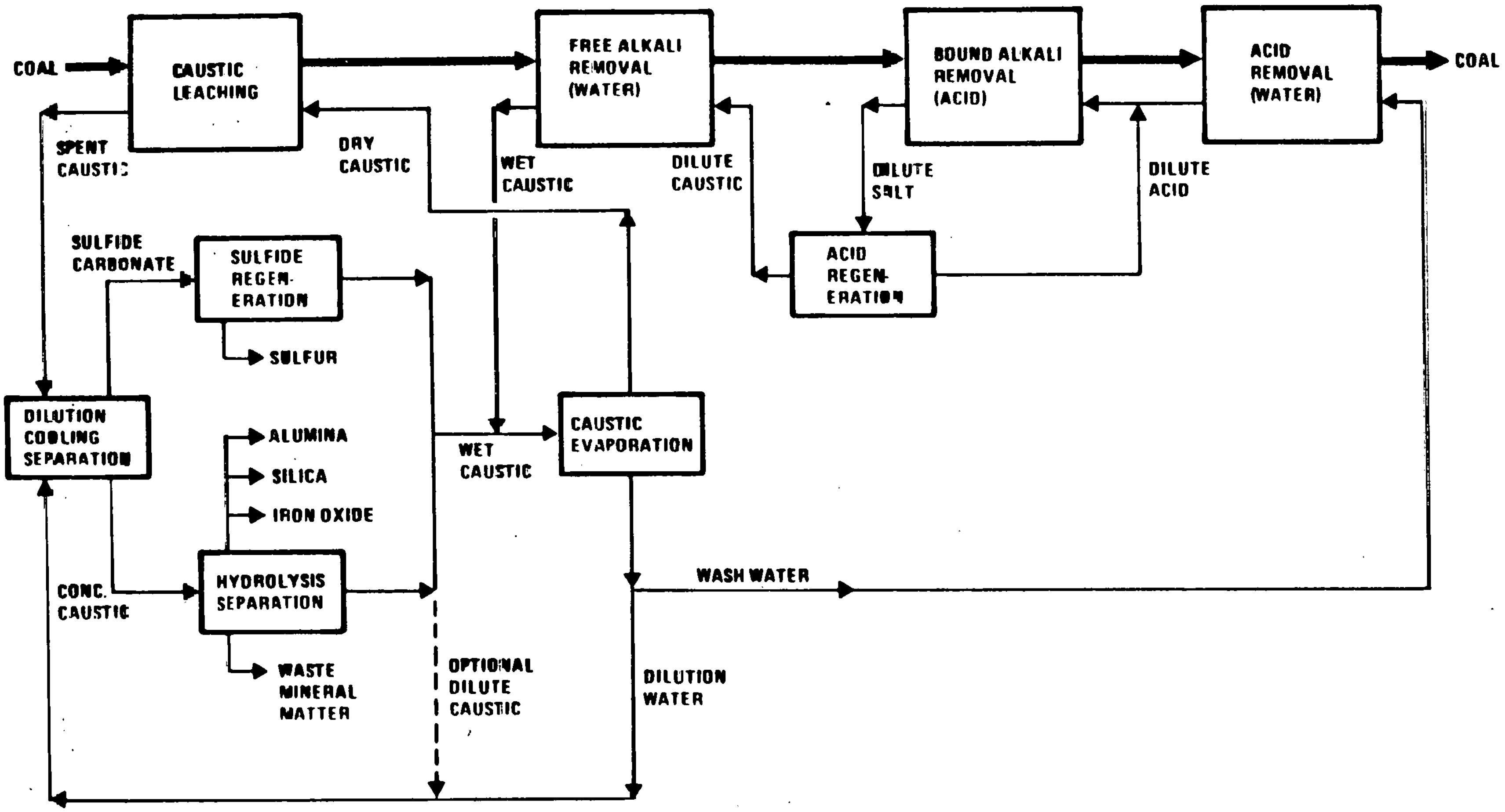
Task 11 - Construct and shakedown the 20 lb/hr units.

Task 12 - Operate the units.

During this reporting period most of the technical effort was performed under Task 6. As a result of these two quarters of effort the process diagram has been established and checked out. The reactor concept was modified based on the experimental findings.

In the sections that follow, the overall process concept will first be presented then the supporting Task 6 through Task 8 experimental data will be summarized.

FIGURE 1. GRAVIMELT PROCESS FLOW DIAGRAM



2.1 Process Description

The Gravimelt process consists of contacting coal with fluids in four sequential steps.

1. Coal is leached with molten caustic in a reactor system, to remove sulfur and mineral matter from the coal into the molten caustic.
2. Coal wetted with caustic, is removed from the reactor and washed with recycled water or dilute caustic to recover adhering caustic from the processed coal.
3. Coal is treated with acid the remove and recover alkali bound to the coal in the form of organic acid salts.
4. Coal is washed with distilled process recycle water to remove residual acid.

Effluent liquids from each of these four contacting steps must be reused either directly or after regeneration in order to complete the process flow sheet. Figure 1 presents the Gravimelt process with the four coal leaching steps shown across the top of the diagram interfacing with the liquid regeneration and recycle steps.

The following is a description of the Gravimelt Process shown in Figure 1.

In the first stage of the caustic leaching reactor system, coal is contacted with spent fused caustic in a wetting zone or vessel. The overflow coal is contacted with less spent caustic in several successive reaction zones or vessels. The overflow (float) coal from the next to last stage is contacted with fresh caustic in final reaction vessel to which fresh caustic is constantly added. Approximately 90% of the coal sulfur has dissolved in the fused caustic as sodium (mixed sodium and potassium) sulfide 95% of the coal mineral matter has dissolved in the fused caustic as alkali aluminate/silicate and about 1% of the coal carbon has been converted to sodium carbonate which is also soluble in the fused caustic. In addition, the coal rising to the top of the last reactor stage has about two weights of fused caustic absorbed both on the surface and within pores and cracks as well as some alkali bonded as sodium* carboxylate and sodium phenolates to the carbon

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* Throughout the description, sodium generally will include mixtures of sodium and potassium derived from the mixed NaOH/KOH caustic melt.

matrix. The amount of absorbed caustic at the same reaction conditions, is less for the more unreactive coals such as Upper Freeport seam and more for the more reactive coal such as Kentucky #11 seam and intermediate for coals such as Pittsburgh #8. Similar trends hold for the chemically bound alkali. The float from the final reaction stage is skimmed off into a pressure filter where the caustic content is reduced to the two weight level described above. The filtrate caustic contains little sulfide, mineral matter or carbonate as coal was treated in a counter current fashion with fresh caustic in the last stage. Therefore this caustic is returned to the final stage of the reactor system as fresh caustic. All of these steps occur within the caustic leaching box shown in the process diagram.

The filter cake, consisting of coal with about two weights of caustic, is washed in a counter current wash system by contact with increasingly dilute aqueous caustic. This contacting will remove most of the unbound, absorbed caustic and leave about two weight percent alkali metal which is ionically bounded to the coal. It is anticipated that these filtrations will proceed rapidly due to the very small amount of mineral matter remaining in the coal after counter current fused caustic extraction however, if problems occur as the pH of the wash section traverses the range of 13 to 9, other techniques may be utilized to avoid gel formation. The most concentrated aqueous caustic (first stage) is sent to the evaporator where it is concentrated along with freshly regenerated caustic and returned to the reactor system.

The coal is next washed with an aqueous acid solution to reduce the alkali content of the coal by hydrolyzing the ionically bound alkali. When the acid is sulfuric acid, the dilute salt is alkali sulfate which can be regenerated, for example, by electrolysis to recover the alkali as dilute caustic and the sulfate as dilute sulfuric acid for recycle. The alkali sulfate also may be handled in a water treatment plant by ionic exchange to convert the sodium content to sodium hydroxide and the sulfate content to amonium sulfate (with ammonia elution). The ammonium sulfate either becomes a fertilizer product of the process or may be heat treated to provide ammonia for recycle and sulfuric acid as a product of the process.

Coal from the acid wash step is washed with water from the caustic concentration evaporator to remove the residual acid. This water wet coal is the form of a filter (or centrifuge) cake is the process product which can be added to course coal (cleaned by conventional physical means) and shipped to market as is now essentially common practice in the coal preparation industry, where the coal fines are simply not cleaned or dried. Alternatively, the coal can be slurried with water to make coal water mixture after suitable additional grinding and addition of a stabilization package, or the coal can be bricketed for shipment as pure gravimelt coal.

Spent alkali drawn from the bottom section of the coal wetting portion of the reactor system contains the dissolved coal mineral matter, sulfide and carbonate. This fused caustic is diluted with water and cooled to precipitate sodium sulfide and carbonate. The precipitated sulfide and carbonate, which may contain coal fines and some mineral matter, is filtered away from the concentrated aqueous caustic. The filter cake is extracted with water to separate the water soluble alkali sulfide and carbonate from the residual coal fines which are added to the main coal stream for washing. These steps are conducted in the flow diagram box identified as "Dilution, Cooling, Separation".

One process stream from the previous step consists of dilute aqueous sulfide and carbonate. This stream is processed in the sulfide regeneration section to give elemental sulfur and dilute aqueous caustic. The regeneration steps include: carbon dioxide treatment of the aqueous sulfide to give hydrogen sulfide and alkali carbonate, converting the hydrogen sulfide to sulfur in a Claus plant, liming the alkali carbonate to dilute caustic and calcium carbonate, and decomposing the calcium carbonate to produce the carbon dioxide and lime used in the previous steps. The dilute aqueous caustic is evaporated and heated to produce dry caustic for recycle to the reaction system.

The second process stream from the "Dilution, Cooling, Separation" step is the concentrated aqueous caustic which is now low in sulfide and carbonate, but contains the dissolved mineral matter. The typical coal ash contains about 20% alumina from shale and clay, a similar amount of iron oxide from the reacted pyrite, 40% to 50% silica from shale, clay and quartz along with a few percent of alkali and alkaline earth oxides, titania and many other element at low levels. This stream resembles the stream that would be produced in the alumina industry if impure bauxite were totally dissolved in caustic. By adjusting conditions to those similar to the bauxite process, it may be possible to separate an alumina product from an iron oxide and silica by-product and other mineral waste material. The principal requirement of this process section is to provide suitable conditions for hydrolysis of the alkali aluminate/silicate/ferrite material to recover most of the alkali for recycle.

Most of the key steps have now been tested with simulated streams as a part of this project. Test results obtained during this reporting period are summarized in the next section.

2.2 Laboratory Testing

Through this reporting period, laboratory experiments have been competed through number GC59. A brief list giving the type and test conditions of each experiment is given in Table 1. Analytical results of the coal analyses are given in tabular form in the Appendix. In the discussions which follow selected runs from the Appendix will be grouped to show the comparisons.

Moisture Effects

Caustic as purchased is nominally anhydrous. In the case of sodium hydroxide, the moisture is less than 1% and probably a few tenths of percent. The "anhydrous" potassium hydroxide contains about 12% moisture regardless of the grade or source of supply. Thus, standard test runs contain 6% moisture in the 50/50 caustic blend. Loss of moisture from the melt occurs during an experiment and typically the final moisture level is about one-half the starting value. A more systematic look at the effect of moisture was undertaken. The resulting data are shown in Table 2. The effect of moisture on sulfur and ash removal appears to be small. Tests 21 and 15 for 1 hour and test 28 for 2 hours, show that standard wet caustic at 350°C, gives processed coal with slightly more than 1% sulfur and about 3/4% ash. Dry tests at 350°C for 1 and 2 hours (Tests 20, 7, 31, 53) give an average of 2/3% S an 3/4% ash.

The 4 hour tests (Test 29 wet and 30 dry) also show a small improvement in sulfur removal for the dry caustic, and as expected, both processed coals have correspondingly lower sulfur than coal from the 1 and 2 hour tests. Tests 32 and 33 with a higher level of KOH, had a higher moisture content in the wet test and drying still left about 3% moisture in the caustic. There appears to be no difference in the two results, but the increased KOH produces a somewhat more agressive caustic melt. As a result, the coal processed for 1 hour in wet 25/75 caustic has the same sulfur level as 4 hours in wet 50/50 caustic or 1 to 2 hours in dry 50/50 caustic.

Sulfur Effects

The effect of sulfide concentration in the caustic melt on coal cleaning was tested up to the 6% sulfur level. The 6% level was the calculated steady state reactor effluent concentration in the original co-current flow reactor

Table 1 - Bench Scale Gravimelt Laboratory Experiments

GC	Experiment (Descriptive notes at conclusion of list)
1	Sulfide Crystallization
2	Nickel Reactor - Sulfide Stability
3	Nickel Reactor - Sulfide Stability
4	Sulfide Crystallization
5	Acid Wash Ky No. 11, Mod II Batch 1, 50/50 (370/120)
6	Nickel Reactor - Sulfide Stability
7	Dry 50/50 Melt, Ky No. 11 (350/60)
8	Sulfide Crystallization
9	Sulfide Crystallization
10	Sulfide Crystallization
11	Sulfide Crystallization
12	Sulfide Crystallization
13	Sulfide Crystallization
14	Acid Wash Ky No. 11, Mod II Batch 1, 50/50 (370/120)
15	Standard 50/50 Melt, Ky No. 11 (350/60)
16	Ash Filtration (Precipitation by Cooling)
17	Used Caustic from Mod II after UF Runs, Ky No. 11 (350/60)
18	Sulfide Crystallization (Used Caustic)
19	Ash Filtration (Precipitation by Cooling)
20	Dry 50/50 Melt, Ky No. 11 (350/60) - GC 7 Repeat
21	Standard 50/50 Melt, Ky No. 11 (350/60) - GC 15 Repeat
22	Ash Filtration (Precipitation by Cooling)

(Cont'd)

GC	Experiment (Descriptive notes at conclusion of list)
23	Standard 50/50 Melt With 1% S as FeS_2, Ky No. 11 (350/60)
24	Standard 50/50 Melt With 2% S as FeS_2, Ky No. 11 (350/60)
25	Standard 50/50 Melt With 6% S as FeS_2, Ky No. 11 (350/60)
26	Standard 50/50 Melt With 6% S as Na_2S, Ky No. 11 (350/60)
27	Dry 50/50 Melt With 6% S as Na_2S, Ky No. 11 (350/60)
28	Standard 50/50 Melt, Ky No. 11 (350/120)
29	Standard 50/50 Melt, Ky No. 11 (350/240)
30	Dry 50/50 Melt, Ky No. 11 (350/240)
31	Dry 50/50 Melt, Ky No. 11 (350/120)
32	Standard 25/75 Melt, Ky No. 11 (350/60)
33	Dry 25/75 Melt, Ky No. 11 (350/60)
34	Standard 50/50 Melt With 10% Carbonate (350/60)
35	Standard 50/50 Melt With 10% Carbonate (370/60)
36	Acid Wash Ky No. 11, Mod II Batch 15, 50/50 (350/60)
37	Acid Wash Ky No. 11, Mod II Batch 15, 50/50 (350/60)
38	Standard 50/50 Melt, Ky No. 11 (370/60)
39	Standard 50/50 Melt, Ky No. 11 (370/120)
40	Acid Wash With Grinding, Pitt No. 8
41	Acid Wash With Grinding, Pitt No. 8
42	Acid Wash With Grinding, Pitt No. 8
43	Acid Wash With Grinding, Pitt No. 8
44	Standard 50/50 Melt With 9% Kaolinite, Ky No. 11 (370/60)
45	Standard 50/50 Melt With 9% Calcite, Ky No. 11 (370/60)
46	Acid Wash Ill No. 6
47	Acid Wash With Grinding, Ill No. 6

(Cont'd)

GC	Experiment (Descriptive notes at conclusion of list)
48	Acid Wash Pitt No. 8
49	Acid Wash With Grinding, Pitt No. 8
50	Standard 50/50 Melt with 13% Na_2SO_4, Ky No. 11 (350/60)
51	Acid Wash, Upper Freeport
52	Acid Wash With Grinding, Upper Freeport
53	Dry 50/50 Melt, Oven Dried Coal (170°C) Ky No. 11 (350/60)
54	Process Experiment, 80/20 Melt, Ky No. 11 (325/60)
55	Process Experiment, 80/20 Melt, Pitt No. 8 (350/60)
56	Standard 50/50 Melt With 1.5% Na_2SO_4, Ky No. 11 (350/60)
57	Standard 80/20 Melt, Double-Dip, Ky No. 11 (325/60+60)
58	Standard 80/20 Melt, Double-Dip, Pitt No. 8 (350/60+60)
59	Standard 80/20 Melt, Ky No. 11 (325/120)

Notes:

Caustic ratio, designated 50/50, 25/75 or 80/20, are the weight ratio of "as received" NaOH/KOH used for the reaction. The temperature, °C and reaction time in minutes are shown in parentheses, for example, (370/120) or (350/60). Some of the experiments did not involve the reaction of caustic and coal. These experiments involved: caustic sampling, sulfur forms analysis in molten caustic, acid washing of processed coal samples to extract mineral matter and caustic, ash precipitation and sodium sulfide crystallization. The latest tests involve multiple stage contact as part of the counter-current reactor simulation experimentation. Some of the coal experiments were repeated later and assigned new test numbers, for example, 20 repeats 7 and 21 repeats 15. In other cases the duplicates were performed consecutively and designated with an "A", for exmaple, 23 and 23A, 24 and 24A or 25 and 25A. These "A" experiments are not separately listed in this table.

TABLE 2. INFLUENCE OF MOISTURE ON PROCESSED COAL

Test No.	Moisture, %		Reaction Conditions Temp °C/Time, mm NaOH/KOH Ratio	Warner (ASTM) Analyses		
	Initial	Final		St,%	Ash,%	Btu/lb (MAF)
--	starting coal-Ky 11		--	3.25	11.16	14319
21	6.0	4.1		1.16	.85	13284
15	6.0	3.5	350°/60 50/50	1.15	.97	13595
	(duplicate sample)			1.04	.51	13853
20	.6	.1		.86	.86	12974
7	.1	0		.50	.47	12960
	(duplicate sample)			.50	.19	12942
28	6.0	3.0	350°/120 50/50	1.20	.75	13536
31	1.9	.9		.58	1.14	13497
29	6.0	1.9	350°/240 50/50	.70	1.09	13574
30	.6	-.4		.44	.18	13594
32	9.0	5.6	350°/60 25/75	.74	.86	13719
33	2.9	2.6		.77	.96	13594
53	~0	~0	350°/60 50/50 Vac. dry coal 170°	.72	.67	13735

design with the float coal contain one-half weight of caustic per weight of coal. Actual caustic to coal ratios were found to be about 2/1 resulting in a steady state sulfide level of about 1.5%. The current counter-current flow reactor system will have sulfide in the first stage near 2%, but an order of magnitude lower in the final stage. The results in Table 3 show that problems with sulfur removal would have been encountered at the 6% sulfide level, but little if any loss of efficiency occurs at 1% and 2%. The slightly lower sulfur from the 1% sulfide melt is most likely a result of drying the caustic during the pyrite reaction that preceded the coal treatment. Probably at 2% sulfide, the benefit of dry caustic was balanced by a slight reduction in removal efficiency.

Although the 6% sulfide tests are not the planned operating sulfide level, an effort was made to understand the results. Sulfur forms analysis showed that the increase in coal sulfur was not an increase in pyrite that would have indicated an incomplete reaction of the mineral added first to the melt. It was postulated that elemental sulfur may be formed by the pyrite/caustic reaction which would be picked up by the coal and appear as organic sulfur in the analysis scheme. Based on our oxydesulfurization experience, we extracted the product coal with toluene as an effective way to remove elemental sulfur. The results of the toluene treatment are as follows:

Sulfur Forms, % W/W

	S_p	S_s	S_o	S_T
25 Untreated	--	--	--	7.95
Toluene Extracted	.25	.50	3.35	4.10
25A Untreated	.12	.36	6.62	7.10
Toluene Extracted	.11	.76	3.35	4.22

Evidently not all of the sulfur is present as elemental sulfur, but some may be. No further effort is planned to interpret the sulfur increase at high sulfide concentrations.

TABLE 3. LABORATORY TESTS WITH CAUSTIC CONTAINING DISSOLVED SULFIDE

Test No.	Sulfur in Melt, %	Sulfur Forms, %				ASTM Ash,%	Btu/lb MAF
		S_p	S_s	S_o	S_T		
--	Starting coal	1.73	.02	1.46	3.25	11.16	14319
21	0	.12	.04	1.00	1.16	.85	13284
15	0	--	--	--	1.15	.97	13595
	(duplicate sample)	--	--	--	1.04	.51	13853
23	1% from FeS_2(1)	--	--	--	.81	.60	13499
23A	(duplicate test)	--	--	--	.84	.83	13745
24	2% from FeS_2	--	--	--	1.04	.94	13379
24A	(duplicate test)	--	--	--	1.32	1.47	13584
25	6% from FeS_2	--	--	--	7.95	1.79	13055
25A	(duplicate test)	.12	.36	6.62	7.10	1.28	12855
26	6% from Na_2S(2)	.14	.01	2.09	2.24	.96	13665
27	6% from Na_2S(3)	--	--	--	1.99	1.38	13749

(1) Mineral pyrite was first reacted with the caustic to the selected sulfur level. Probably some caustic drying also occurred during the pyrite reaction.

(2) Prepared by adding $Na_2S\cdot 9H_2O$. The resulting caustic was much wetter than usual. (Calculated 27.3% vs. 6% normal).

(3) Duplicate of Test 26 except the melt was dried overnight to an estimated 8% moisture.

Ash and Mineral Effect

Three tests were conducted to establish the level of emphasis that should be placed in studying ash and carbonate effects on coal cleaning efficiency. Test 34 used a synthetic blend of 10% carbonate added to the caustic. This was compared to Test 17 which had used caustic from the Mod II reactor, in which the caustic following the last (26th) batch, had been further contaminated by two batches of 40% ash, Upper Freeport, run-of-mine coal. Test 35 used the same synthetic melt as Test 34 but was conducted at 370° instead of 350°. Table 4 shows that both the used caustic (Test 17) and the synthetic blend (Test 34) gave similar results, but had less ash and sulfur removal than the tests with clean caustic. Increasing the reaction temperature to 370° restored the melt efficiency.

In the present counter-current flow reactor system, high ash content caustic will be in the first stage where mixing and wetting of the coal occurs. Ash levels in the first stage are estimated to be below 10% and probably below 5%. There will be a 3 or 4 fold decrease with each successive stage, and in the final stage, the caustic will contain a few tenths percent ash or less. Verification tests of the counter-current system will be performed.

TABLE 4. TESTS WITH ASH AND CARBONATE IN CAUSTIC

Test No.	Additives & Impurities	Temp °C	S, %	Ash, %	Btu/lb
--	starting coal - Ky 11	--	3.25	11.16	14319
21	None	350	1.16	.85	13284
15	None	350	1.15	.97	13595
	(duplicate sample)	350	1.04	.51	13853
17	Used - Mod 11	350	1.53	1.73	13839
34	10% $(Na/K)_2CO_3$	350	1.41	1.58	14168
35	10% $(Na/K)_2CO_3$	370	.94	.88	13882

2.3 Centrifuge Testing

One of the purposes of processing 26 batches of Kentucky 11 coal in the Mod II reactor was to obtain the large quantity of coal needed for centrifuge testing. Batches 15 through 26 were prepared at a single reaction condition (350°C/60 minutes). After samples of each batch were removed and stored, 437 pounds of the 478 pounds of caustic/coal product were dissolved in water to prepare dilute slurries for centrifuge tests.

Four slurry batches (CFG1-4) were prepared each using about one-fourth of the coal/caustic material dissolved in about 7 cubic feet of water to give a coal plus caustic concentration of about 20%. The processed coal is about one-fourth of the solid coal/caustic cake, and is therefore about 5% of the aqueous caustic slurry. Batch CFG1 was held for later blending of a master batch.

Batches CFG2 and 3 were fed at the rate of about 0.5 gpm to the centrifuge operating at 3000 rpm (about 750 g's). The centrifuge cake was a thick paste consistency with about 43% solids. Batch CFG 4 was split and each part diluted to about 10% caustic plus 3% coal. At the same centrifuge operating conditions, these each gave a centrifuge coke with 40% solids.

A fifth batch (CFG5) was prepared like batch CFG4 and diluted to about the same levels. These gave centrifuge cakes with 39% solids. Two additional batches were prepared at still greater dilution using coal from the Mod II reactor, Batches 1-11 processed at 370°C for 2 hours. Batch CFG6 was 6% caustic plus 2% coal and CFG7 was about 7% caustic plus 2% coal. These were separated at the same centrifuge operating conditions to yield cakes of 34% and 32% solids.

A summary of these seven batches of slurry and the main results of the centrifuge separation is given in Table 5.

From the centrifuge cakes obtained in separating Batches CFG2 through 7 plus 17.5 gallons of Batch CFG1, a master batch (CFG8) was prepared. It had a specific gravity of about 1.3 and had 20 to 25% coal in about 10 - 15% aqueous castic. This slurry did not flow well and plugged the feed lines. Water was added to reduce the specific gravity to 1.17 and centrifuge cakes of 30.5 to 36.3% solids were obtained during one hour of operation. Evaluation is not complete and mass balances will be difficult because a plug apparently developed just before the end of the one-hour test. The plug cleared itself, but caused a burst of centrate to mix with the centrifuge cake as the one-hour sample was being obtained.

The centrifuge speed was increased to 5000 rpm (about 2000 g's) for the next tests planned for slurry from this diluted (sp. gr. 1.17) Batch 8.

TABLE 5. CENTRIFUGE TESTS, DILUTE SLURRIES

Batch No.	Mod II Batches Numbers	Mod II Batches Wt, lb	Water Added ft^3	Water Added lb(calc)	Slurry sp.gr. g/cc	Centrifuge cake Wet, lb	Centrifuge cake % Solids
CFG1	26,25,24*	104.1	6.7	420	1.27(?)	--	--
CFG2	24*,23,22,21*	104.1	6.7	420	1.17	44.7	--
CFG3	21*,20,19*	104	6.7	420	1.16	56.5	42.7
CFG4	19*,18,17,16,15*	124.9	8.0	500	1.17	--	--
4A	20 gal	195(est)	2.0	125	1.10	28.3	40.3
4B	20 gal	195(est)	3.3	210	1.08	27.9	40.1
CFG5	15*,13,11	105.8	6.7	420	--	--	--
5A	25 gal	240(est)	3.5	220	1.09	28.6	38.9
5B	Remainder	285(est)	4.6	290	1.10	36.5	38.0
CFG6	10	36.7	7.1	440	1.06	24.1	33.7
CFG7	9	42.7	6.7	420	1.07	26.4	32.0

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* These coal batches were partly used in each of two centrifuge batches. Other coal batches were totally used except for a nominal 1 pound sample.

APPENDIX

COAL ANALYSIS DATA

This Appendix lists the coal analysis data obtained from Warner Labs in Cresson, Pennsylvania for coal samples produced in the program to date.

Table A-1 gives analyses for 9 of the 26 batches of coal prepared in the Mod II reactor and reported in the first quarter. Toward the middle of this table are analyses for specially, washed coal samples and at the bottom of the table, starting coal analyses obtained during this program are given.

Table A-2 gives results for laboratory tests through Test GC59.

Each Table gives the following information:

- o <u>Analysis Date</u> - The date shown in the Warner analysis report mailed to TRW.
- o <u>Mod II Batch No or GC Test No</u> - These are the batch number for the Mod II test or the sequential test number for the laboratory tests. When the numbers are followed by numbers/letters in parenthesis, the analysis was on a coal sample that had treatment other than the usual water, dilute sulfuric acid, and water washes. These are detailed later under Special Treatment of Coals.
- o <u>C, H, N, O</u> - These are the elemental analyses corrected for moisture and reported on a dry, moisture - free basis. Oxygen is obtained by difference, i.e., the found values for C, H, N, total sulfur and ash are deducted from 100% to give the oxygen value. Oxygen therefore contains the net of all errors.
- o S_p, S_s, S_o, S_T - These are obtained by standard techniques routinely used for unprocessed coal samples. Briefly stated the sulfate sulfur, S_s, is the hydrochloric acid extractable sulfur. The pyrite sulfur, S_p, is the additional sulfur extractable with nitric acid. The organic sulfur, S_o, is obtained by subtracting S_p and S_s from the total sulfur S_T (or simply S) and therefore contains the net of all analysis errors.
- o <u>Ash</u> - Obtained by standard temperature/time heating programs to oxidize the coal and obtain the residue. The temperature normally is 750° to 800°C in air.

- FC, VM - Are the fixed carbon and volatile matter obtained in standard pyrolysis tests and corrected to a dry basis with separate moisture analysis. The fixed carbon is obtained by subtracting ash and VM from 100% and contains the net of their measurement errors.
- Btu/lb(MF) and (MAF) - This is the heat of combustion of the sample corrected for moisture (MF) or for both moisture and ash (MAF). Some reports give moisture and mineral matter for (MMF) values. This is a better value for comparison, but mineral matter is difficult to determine and does not directly relate to ash values.
- Na, K, Fe - These are determined by analysis of the residue from low temperature ashing of coal samples by standard ASTM methods.
- 500° Na, K and 750° Na, K - These were special determinations which were ashed at 500° or 750°C in platinium crucibles for analysis. The weight of ther 500° and 750° ash is also reported.

Special Treatment of Coal

Table A-1 lists 10 analyses of coal from Batch 1 (Mod II reactor) which had special processing. These are briefly described.

(W2) - The processed sample was washed twice with water only. Without the usual acid wash free and bound alkali remained with the coal to give the high ash value.

(HCL) - Dilute hydrochloric acid was substituted for sulfuric acid. It gave essentially identical sulfur and ash analyses.

(SO_2) - Dilute aqueous SO_2 (sulfurous acid) was substituted for sulfuric acid. A higher value of both ash and sulfur was observed.

(14LA) and (14ALA) - The coal was first acid washed at a pH of about 6 in duplicate tests. The ash and sulfur were both higher than normal.

(14) and (14A) - These are the GC laboratory numbers for this pair of tests. After the low acid (LA) washes the coals were sulfuric acid washed in the normal way (pH about 0 to 1). The ash and sulfur values appear to be about the reverse of those previously obtained but are low in any case.

(170) - Starting coal was vacuum dried at 170°C prior to being used in Test GC53.

(250), (300) - Starting coal was dried at 250°C and 300°C to obtain composition and weight loss data. These will be reacted in dry caustic in the near future.

(dup) - Addition analysis on the same coal sample were performed.

(W), (W3), (LA) - As part of the studies to examine the coal washing steps, processed coal was analyzed after a single water wash (W), after three water washes (W3) and after low acidity washing (LA) at pH about 6.

Starting Coals

The Upper Freeport coal was obtained for the previous program in two forms. Run-of-mine coal had about 40% ash and cleaned coal had about 10% ash. Following the 26 batches of Kentucky 11 coal in the Mod II reactor, the caustic was purposely made high in ash by processing two batches of ROM Upper Freeport coal. This "extra dirty" caustic was used in Test GC 17 and for some of the ash/caustic separation studies. In addition the ROM Upper Freeport coal was float-sink separated to recovery a high-ash material for other ash studies. Table A-1 shows the analysis of the 75% ash UF, Sink fraction.

Both the Pittsburgh 8 and the Kentucky 11 samples are from the coal repository and have been tested on previous programs.

TABLE A-1. BENCH SCALE AND STARTING COAL ANALYSES

Analysis Date	Mod II Batch No	Warner Lab Analyses - % W/W Moisture Free Basis											Btu/lb		500°,% W/W		750°,% W/W		Ash	
		C	H	N	O	S_p	S_s	S_o	S_T	Ash	FC	VM	MF	MAF	Na	K	Na	K	500°	750°
9-24-83	1					.03	.03	.09	.14	.64	30.57	68.79	11838	11914			.056	.091		
10-6-83	1	75.43	3.32	1.66	18.84				.10	.65					.089	1.60				
12-9-83	1					.02	.21	.26	.49	.30	30.42	69.28	12287	12324						
10-26-83	2	79.34	3.39	1.61	15.25	.04	.04	.16	.25	.17	27.37	72.46	12645	12666	1.49	1.29			.12	.16
12-9-83	2					.02	.02	.35	.38	.46	29.92	69.62	12087	12143						
1-10-84	2								.36	.21	28.88	70.91	12151	12177						
12-9-83	3					.01	.01	.22	.25	.09	26.95	72.96	12666	12677						
11-1-83	7	80.52	3.65	1.76	13.30				.58	.18	24.86	74.96	13318	13342						
10-20-83	10	80.20	3.28	1.67	14.19	.08	.05	.25	.38	.28	24.12	75.60	13034	13070						
11-10-83	14								.58	.44			13515	13575						
12-9-83	14					.02	.38	.38	.80	.18	29.13	70.69	13228	13253						
1-10-84	14								.51	.50	29.12	70.38	13256	13322						
10-20-83	15	79.02	4.54	1.77	13.03	.15	.03	.72	.90	.75	31.22	68.03	13488	13590						
11-1-83	20	79.75	4.71	1.75	12.22				.98	.60	31.29	68.11	13762	13846						
11-1-83	26	79.73	5.02	1.73	11.80				1.21	.52	33.65	65.63	13943	14016						
Special Processing																				
9-29-83	1(W2)					.09	.02	.01	.12	25.08	29.18	45.74	8873	11842			2.74	5.23		
10-6-83	1(W2)	57.10	2.56	1.22	14.00				.05	25.07					11.54	7.26				
9-28-83	1(HCL)					.05	.01	.11	.17	.65	34.29	65.06	11215	11288			.025	.045		
10-6-83	1(HCL)	72.15	2.99	1.56	22.58				.08	.64					.095	.162				
10-26-83	1(SO_2)	71.22	3.20	1.64	18.38	.04	.03	.51	.58	4.99			10979	11556	.46	1.22	.57	1.48	4.99	3.62
10-26-83	(dup)	70.97	3.21	1.57	18.29	.04	.03	.44	.52	5.44			10922	11550	.64	1.40	.68	1.55	5.82	4.75
10-26-83	1(14LA)								.63	3.33			10768	11140						
10-26-83	1(14)								.49	.08			11356	11365						
10-26-83	1(14ALA)								.51	4.23			10866	11345						
10-26-83	1(14A)								.41	.27			11376	11407						
Starting Coal Analysis																				
11-15-83	UF,Sink								3.69	75.04			2564	10271						
2-16-84	P8	69.66	5.22	1.27	8.91				4.32	10.61			12870	14397						
9-28-83	K11					1.73	.02	1.46	3.21	11.16	38.57	50.27	12721	14319			.040	.191		
10-6-83	K11	69.88	5.04	1.42	9.25										.27	.30				
2-22-84	K11	70.92	4.97	1.46	9.50				3.09	10.06			12849	14286						
2-22-84	K11(170)	69.15	4.70	1.44	9.45				3.40	11.87			10042	11395						
2-24-84	(dup)												12424	14098						
2-22-84	K11(250)	70.45	4.81	1.53	8.72				3.28	11.19			12714	14316						
2-22-84	K11(300)	70.33	4.78	1.51	8.92				3.25	11.21			12756	14368						

TABLE A-2. LABORATORY SCALE COAL ANALYSES

Analysis Date	GC Test No.	Warner Lab Analyses - % W/W Moisure Free Basis											Btu/lb		% W/W (MF)		
		C	H	N	O	S_p	S_s	S_o	S_T	Ash	FC	VM	MF	MAF	Na	K	Fe
10-20-83	7	77.42	4.12	1.66	15.82	.10	.03	.37	.50	.47	32.12	67.41	12899	12960			
11-1-83	(dup)	77.29	4.04	1.68	16.30				.50	.19	31.96	67.85	12916	12942			
10-26-83	15	79.46	4.90	1.71	11.81	.06	.03	1.06	1.15	.97			13463	13595			
11-1-83	(dup)	79.54	4.75	1.73	12.43				1.04	.51	33.30	66.19	13783	13853			
11-1-83	17	77.90	4.91	1.72	12.21				1.73	1.53	34.68	63.79	13627	13839			
11-7-83	20	77.79	3.98	1.61	14.90				.86	.86	30.79	68.35	12863	12974			
11-8-83	21	76.90	4.64	1.48	14.96	.12	.04	1.00	1.16	.85	36.12	63.03	13171	13284			
11-10-83	23								.81	.60			13418	13499			
11-10-83	23A								.84	.83			13632	13745			
11-10-83	24								1.04	.94			13254	13379			
11-10-83	24A								1.32	1.47			13384	13584			
11-10-83	25								7.95	1.79			12821	13055			
11-10-83	25A								7.10	1.28			12690	12855			
11-21-83	(dup)					.12	.36	6.62									
11-15-83	26								2.24	.96			13534	13665			
11-21-83	(dup)					.14	.01	2.09									
11-15-83	27								1.99	1.38			13558	13749			
11-15-83	28								1.20	.25			13434	13536			
11-15-83	29								.70	1.09			13426	13574			
11-15-83	30								.44	.18			13569	13594			
11-22-83	31								.58	1.14			13344	13479			
11-22-83	32	79.40	4.57	1.67	12.77				.74	.86			13602	13719			
12-21-83	33	79.11	4.26	1.60	13.29				.77	.96			13464	13594			
12-20-83	34								1.41	1.58			13943	14168			
12-20-83	35								.94	.88			13760	13882			
1-31-84	53								.72	.67			13644	13735			
2-22-84	(dup)	79.88	4.57	1.78	12.10				.79	.88							
2-8-84	54(W)	44.11	4.32	.71	8.43				1.25	41.17							
2-8-84	54(W3)	70.16	5.22	1.17	9.22				4.26	9.98			11444	12712			
2-15-84	54(LA)	77.38	5.12	1.46	11.41				1.54	3.09			13647	14082			
2-13-84	54								1.35	.64			14043	14134			
2-8-84	55(W)	38.54	4.42	.78	4.32				.84	51.10							
2-15-84	55(W3)	75.12	4.97	1.42	5.99				1.75	10.74			13239	14832			
2-15-84	55(LA)	78.92	5.12	1.95	9.05				1.79	3.18			13972	14431			
2-15-84	55	79.58	5.23	1.66	10.18				1.78	1.50			14146	14373			
2-15-84	57(W)								1.14	5.04			13589	14309	.95	.57	1.01
2-15-84	57								1.26	.74			13911	14016	.05	.04	.25
2-15-84	58(W)								.83	4.64			13586	14247	.93	.50	1.00
2-15-84	58								.77	.44			13912	13974	.04	.03	.12
2-15-84	59(W)								1.22	6.63			13202	14140	1.14	.65	1.76
2-15-84	59								1.25	.93			13576	13704	.07	.07	.50

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