DOE/PC/91257--T26

MOLTEN-CAUSTIC-LEACHING (GRAVIMELT)
SYSTEM INTEGRATION PROJECT

QUARTERLY REPORT FOR JULY THROUGH SEPTEMBER, 1989

CONTRACT NUMBER DE-AC22-⁸⁶PC91257

OCTOBER 10, 1989

PREPARED BY APPLIED TECHNOLOGY DIVISION
SPACE AND TECHNOLOGY GROUP
ONE SPACE PARK
REDONDO BEACH, CA 90278

PREPARED FOR
U.S. DEPARTMENT OF ENERGY
PITTSBURGH ENERGY TECHNOLOGY CENTER
P.O. BOX 10940 - MS/922-206
PITTSBURGH, PA 15236

DISCLAIMER

This report was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor any agency thereof, nor any of their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof.

DISTRIBUTION OF THIS DOCUMENT IS UNLIMITED

MASTER

DISCLAIMER

Portions of this document may be illegible in electronic image products. Images are produced from the best available original document.

1. EXECUTIVE SUMMARY

Operation of the Gravimelt Integrated Test Circuit for desulfurization and demineralization of coal has been completed. A 48-test process matrix was performed over 750 hours of operational time resulting in production of 3,000 pounds of treated coal suitable for further test and evaluation.

Analysis of the several thousand data is underway. Assessment of coal material balance data shows an average 98% closure with 2% conversion of coal to humics and phenolics, 3% conversion to hydrogen and methane and 3 1/2% loss as carbonate.

Assessment of sulfur forms data shows a mean residual puritic sulfur of 0.022% for Pittsburgh No. 8 seam coal and 0.01% for Kentucky No. 9. Organic sulfur removal was dependent on conditions with lowest at 0.08% after processing in the plant. The mean sulfate sulfur level was 0.28% with a standard deviation of only 0.06%.

2. INTRODUCTION AND PROCESS DESCRIPTION

TRW, under sponsorship of the Department of Energy's Pittsburgh Energy Technology Center (Contract No. DE-AC22-86-PC91257) is evaluating the Gravimelt Process in commercial equipment installed in an Integrated Test Circuit. The circuit is located at the TRW San Juan Capistrano test site in California.

The process utilizes a melt of sodium hydroxide or mixtures of sodium and potassium hydroxides at temperatures of 325° to 415°C to remove virtually all of the sulfur and mineral matter from coal. The results of an initial ten weeks of shakedown and operation of the integrated test circuit show that Eastern coals can be treated to meet New Source Performance Standards for sulfur oxides control while providing a product with heat content of 14,000 Btu per pound or greater and an ash content as low as a few hundreds of a percent.

The process is seen as a potential replacement for the costly flue gas desulfurization systems contemplated for smaller utilities and industrial boilers. The product coal might also displace oil in some turbine and diesel engines and may have application as an inexpensive preactivated or activated carbon for extraction of pollutants from waste water and can potentially be used to clean-up and concentrate radioactive or toxic waste. Process and plant descriptions are presented in the next two sections.

2.1 Process Description

A schematic of the Gravimelt process is shown in Figure 1. Feed coal is first combined with a mixture of dry sodium hydroxide or mixed sodium and potassium hydroxides in a rotary kiln reactor where the mixture is heated to reaction temperatures of 325° to 415°C causing the caustic to 1) become sorbed in the coal matrix, 2) react and then 3) dissolve the coal sulfur and mineral matter.

The reaction mixture exits the rotary kiln in the form of pellets which are next washed with water in a countercurrent separation system of filters and centrifuges. As an example, the use of four weights of wash water per weight of coal results in a coal cake containing up to two parts of wash water per part of coal exiting the last stage of the countercurrent system, and also a 50 percent aqueous reacted caustic solution exiting the first stage of filtration which contains nearly all of the coal-derived silicon, aluminum, carbonate and sulfur content. The coal-derived iron (usually 2-3 percent of the weight of the coal) and a small amount of sodium and/or potassium (0.1-2 percent of the weight of the coal) remains with the coal exiting the countercurrent filtration system.

The coal cake is next washed to remove the residual iron and caustic with, for example, three weights of process water, again in a countercurrent mode. Sulfuric acid is added to the first stage to dissolve the residual alkali and iron hydroxide. A typical coal cake entering the acid wash filtration train contains two (or as little as one-half) weights of sorbed water while the product coal exiting the train contains one tenth to one weight of sorbed water. Where two weights of wash water enter the acid wash section on the coal cake and the product coal carries one weight of water, the acid extract leaving the first stage of the acid wash section consists of four weights of water containing 250 to 5,000 ppm of mixed sodium and potassium and 5,000 to 10,000 ppm of iron.

All of the iron sulfate and a portion of the alkali sulfates in this stream can be removed by a sequence of heating and lime treatment to form insoluble minerals. The water can be recycled.

The aqueous caustic is limed at 40° to 125°C to remove the coal derived minerals and carbonate, and the purified liquid is sent to a caustic evaporator where two weights of wash water are recovered for recycle to the first wash train while producing anhydrous caustic for reuse in extraction of coal.

TRW Gravimelt Process

Figure 1. Gravimelt Process Flow Schematic

2.2 Integrated Test Circuit Description

The test circuit consists of six unit operations (see Figure 1) which together provide a continuous system for leaching coal and regenerating the caustic reactant and wash water. These units are a) a kiln for reacting molten caustic with coal, b) a seven stage water washing section for recovering caustic from the coal, c) a three stage acid washing section for removing the last traces of metals and alkali and providing an ultra pure coal product, d) a water treatment section to provide either dischargeable or recyclable water, e) a regeneration section to provide purified aqueous caustic and f) an evaporator section to provide molten caustic for recycle to the kiln reactor.

The integrated test circuit facility contains more than 160 pieces of equipment including filters, centrifuges, tanks, reactors, feeders and the kiln and rising film evaporator. It occupies 3,700 square feet and is fitted with more than 6,000 feet of piping, 425 valves, 80 instruments and controls as well as a control room with computer control and data acquisition and reduction system.

3. PROJECT DESCRIPTION

The objective of this project is to design, construct and operate an integrated test circuit (as shown in Figure 1) for evaluation of the Gravimelt Process and production of desulfurized and demineralized coal samples.

The project consists of eight tasks for planning, design, equipment procurement, construction and shakedown, test planning, operation, data assessment and management.

4. PROJECT ACCOMPLISHMENTS

Assessment of data for coal hydrocarbon material balance, sulfur forms remaining in processed coal and formation of humics and phenolics is presented in the sections to follow. More than 4000 analyses were obtained on process streams such as product coal, intermediate coal, slurries, filter cakes and filtrates during 750 hours of matrix testing. The cost of the analyses and assessment of the analyses, as shown below, constituted 45% of the total budget for plant operation, sample analysis and data assessment. In order to restrict these costs to the 45% level and not reduce budget for operation, it was necessary to limit analyses of process streams. Thus, stream data points are often used to cover a wide range of operating hours and computations are sometimes used, based on data, for material balance calculations.

4.1 Coal Material Balance

The coal material balances for all nine MCL runs, subsequent to shakedown, are shown in Table 1. These material balances are based on the coal feed to the rotary kiln, and the washed coal product and kiln discharge coal product collected, all obtained from the operation log book and corrected to MAF coal, using feed coal and product coal analysis data. In addition, data from the MCL operations show that approximately 2% of the feed coal was converted to volatiles (mainly methane and hydrogen) in the kiln gas, and another 2% to humics and phenolics. These are used as the basis for estimating the amount of volatiles and humics and phenolics in each run.

Analysis of the kiln discharge product and the spent caustic both show that on the average, approximately 15% of the caustic feed was converted to carbonates. The amount of coal carbon in carbonates is computed using the 15% caustic feed conversion rate, the caustic/coal feed ratio, and the percentage of carbon in carbonates. The sulfur removed from coal is computed from the difference of sulfur content of the feed coal and the sulfur contents of the washed coal product and kiln discharge coal product.

The amount of coal fines collected is estimated using the 120 lb per hour caustic solution rate, the total hours of operation of the caustic wash section in each run, and the concentration of coal fines in the caustic solution sent to the bag filters (where coal fines were collected). Except for Runs 2, 3 and 4, the amount of coal fines is based on a 0.435% coal fines concentration in the caustic wash solution. The 0.435% coal fines concentration in caustic solution was obtained from the average of Run 1 data. For Runs 2 and 3, coal fines concentrations of 0.122% and 0.057% from the analysis of the caustic wash solution are used. For Run 4, the amount of coal fines is the sum of the coal fines collected on the bag filters (46.60 lb on dry basis) and the residual coal fines that passed through these bag filters (85.43 lb). The amount of residual coal fines was exceptionally high for Run 4, because an average of 0.85% coal fines concentration was found in the filtered caustic wash solution, probably due to the use of filter media of incorrect mesh size during the operation of the vacuum filter. The amount of coal fines in caustic solution fluctuated during the operation of each run, and would be significantly reduced if the two vacuum filters were in operation and with the proper filter media.

Table 1. Coal Material Balance

	<u>Run 1</u>	<u>Run 2</u>	<u>Run 3</u>	<u>Run 4</u>	<u>Run 5</u>
Coal product (1b MAF)	270.4	306.9	84.3	313.9	454.3
Kiln discharge coal (1b MAF)	111.4	119.4	488.8	179.0	8.3
Volatiles in kiln gas (1b)	14.2	13.3	17.1	13.9	16.4
Humics and phenolics (1b)	14.2	13.3	17.1	17.3	16.4
Carbon in carbonates (1b)	21.8	25.5	33.4	31.3	35.6
Coal fines in bag filters (1b)	53.8	8.8	3.2	132.0	54.9
Sulfur removed from coal (1b)	22.3	20.2	30.9	23.8	25.9
Coal left in wash section (1b MAF)	25.0	25.0	25.0	25.0	25.0
Coal left in kiln (1b MAF)	47.3	29.5	15.9	6.0	33.5
Total coal product and coal derivatives (1b)	580.4	561.9	715.7	742.2	670.3
Coal feed to kiln (1b MAF)	611.0	577.8	734.0	743.1	711.2
Mass balance closure (%)	95.0	97.2	97.5	99.9	94.2

Table 1. Coal Material Balance (Continued)

	<u>Run 6</u>	<u>Run 7</u>	<u>Run 8</u>	<u>Run 9</u>
Coal product (lb MAF)	556.4	323.6	401.0	251.3
Kiln discharge coal (lb MAF)	386.4	68.2	168.1	30.0
Volatiles in kiln gas (lb)	26.9	12.2	16.7	9.7
Humics and phenolics (lb)	26.9	12.2	16.7	9.7
Carbon in carbonates (lb)	33.8	29.5	28.6	36.2
Coal fines in bag filters (lb)	34.3	50.6	52.2	42.4
Sulfur removed from coal (lb)	35.9	18.2	29.1	18.5
Coal left in wash section (lb MAF)	25.0	25.0	25.0	25.0
Coal left in kiln (lb MAF)	8.1	8.6	5.7	4.9
Total coal product and coal derivatives (lb)	1133.7	548.1	743.1	427.7
Coal feed to kiln (lb MAF)	1155.9	533.7	758.7	417.2
Mass balance closure (%)	98.1	102.7	97.9	102.5

The amount of coal left in the wash section at the end of each run is estimated to be 25 lbs. This is derived by first estimating that the amount of process solutions left in the wash tanks at the end of run would be 514 lb (8 tanks x 14 gallons per tank x 50% full x 8.34 lb/gallon x 1.1 specific gravity), and then using an average 3.8% coal concentration in the solution (obtained from Run 1 data). The amount of coal left in the wash tanks is, therefore, 19.5 lb. The 25 lb estimate includes allowance for some additional coal left in centrifuges and process piping. The amount of coal left in the rotary kiln at the end of each run is estimated from review of the operation log book data. For five of the nine runs, the equivalent of one hour of feed material was left inside the rotary kiln at the end of each run. For Runs 1, 2, 3 and 5, however, it appears that large quantities of feed material were still left inside the kiln, because the kiln was shut off shortly after the transfer of additional coal/caustic to the feed hopper.

As shown in Table 1, excellent mass balance closure is obtained for each of the nine runs, ranging from 94.2% for Run 5 to 102.7% for Run 7. For the nine runs combined, the total coal product and coal derivatives amounted to 6,123 lb, and the total coal feed to the rotary kiln was 6,243 lb. The resulting combined mass balance closure is 98.1%

4.2 Sulfur Form Analysis

Samples of kiln discharge coal and washed coal product from selected MCL runs were analyzed to determine the forms of residual sulfur present in MCL coal. A secondary objective for this analysis was to resolve whether sulfate sulfur was formed in kiln processing, or as a result of subsequent wash by dilute sulfuric acid. Therefore, some of the samples were only analyzed to determine sulfate sulfur and total sulfur. If sulfates were formed in kiln processing, it may be possible to delineate the operating conditions that suppress sulfate formation. If sulfates were formed by dilute sulfuric acid wash, then it may be necessary to consider alternate washing schemes in order to further reduce residual sulfur levels in MCL coal.

The sulfur form analysis results are presented in Table 2. As shown in this table, the amount of sulfate sulfur in MCL coal appears to remain invariant of coal type or processing conditions. The mean sulfate sulfur level for the MCL coal samples is 0.28%, with a standard deviation of only 0.06%.

Ten sets of sulfate sulfur data are compared in Figure 2, with each set representing kiln discharge (KD) coal versus washed coal product (CP) data from the same run. The comparisons show higher KD than CP sulfate sulfur levels in 6 data sets, same KD and CP sulfate sulfur level in 1 data set, and lower KD than CP sulfate levels in 3 data sets. In addition, the Pittsburgh No. 8 and the Kentucky NO. 9 coal feed only contains 0.04% and 0.02-0.06% sulfate sulfur, respectively. These indicate that sulfate sulfur in MCL coal is formed in kiln processing, and

Table 2. Sulfur Form Analysis Results

<u>Run</u>	<u>Coal Type</u>	<u>Sample Type</u>	<u>% Sulfate Sulfur Mean</u>	<u>Std Dev.</u>	<u>Data Pts</u>	<u>% Pyritic Sulfur</u>	<u>% Organic Sulfur</u>	<u>% Total Sulfur</u>
4C1	PITT 8	CP	0.24	0.08	2	0.04	0.47	0.74
6B1	PITT 8	CP	0.29	-	1	0.01	1.05	1.35
6D1	PITT 8	CP	0.28	0.01	2	0.02	1.09	1.38
7A	KENT 9	CP	0.35	0.08	3	0.01	0.22	0.59
7A	KENT 9	KD	0.29	0.09	3	-	-	0.73
7B	KENT 9	CP	0.27	-	1	-	-	0.56
7B	KENT 9	KD	0.35	-	1	-	-	0.63
7C	PITT 8	CP	0.26	-	1	-	-	0.54
7C	PITT 8	KD	0.26	-	1	-	-	-
7D	PITT 8	CP	0.21	-	1	-	-	0.38
7D	PITT 8	KD	0.36	-	1	-	-	0.66
7E	PITT 8	KD	0.29	0.04	3	-	-	1.50
8A	PITT 8	CP	0.28	-	1	0.02	0.55	0.85
8A	PITT 8	KD	0.34	0.03	4	-	-	0.80
8B	PITT 8	CP	0.21	-	1	0.07	1.00	1.37
8C	PITT 8	CP	0.13	-	1	0.03	0.61	0.77
8D	PITT 8	CP	0.25	0.07	2	0.03	0.56	0.80
8E	PITT 8	CP	0.23	-	1	0.02	0.52	0.76
8F	PITT 8	CP	0.36	0.10	3	0.01	0.63	0.92
8F	PITT 8	KD	0.35	-	1	-	-	1.01
9A	PITT 8	CP	0.27	-	1	0.01	0.60	0.88
9A	PITT 8	KD	0.33	0.03	3	-	-	0.97
9A1	PITT 8	CP	0.30	0.03	2	0.01	0.41	0.72
9A1	PITT 8	KD	0.41	-	1	-	-	0.79
9B	PITT 8	CP	0.26	0.03	3	0.003	0.35	0.62
9B	PITT 8	KD	0.28	0.08	1	-	-	1.25
9C	PITT 8	CP	0.30	0.02	6	0.002	0.19	0.49
9C	PITT 8	KD	0.19	-	1	-	-	0.23

 For pyritic and organic sulfur, an "-" indicates no data.

Figure 2. Comparison of Sulfate Sulfur in Kiln Discharge Coal and Washed Coal Product

not due to washing by dilute sulfuric acid. It also appears that in at least some of the runs, downstream washing removes part of the sulfate sulfur initially formed. Thus, these sulfate level comparisons provide evidence of the effectiveness of the countercurrent washing scheme in the integrated MCL plant.

The sulfate in MCL coal is probably present as iron sulfate, formed from the thiosulfate derived from the reaction of sodium or potassium hydroxide with coal pyritic sulfur:

The above reaction indicates that 1/8 of the pyritic sulfur could be converted to thiosulfate and subsequently to iron sulfate, which apparently cannot be readily removed from coal by washing with water or dilute sulfuric acid. For Pittsburgh No. 8 coal, the 1.69% pyritic sulfur and 0.04% sulfate sulfur in the coal feed could result in 0.25% sulfate sulfur in MCL coal. Similarly, the 1.84% pyritic sulfur and 0.02-0.06% sulfate sulfur in Kentucky No. 9 coal feed could result in 0.27% sulfate sulfur in MCL coal. These sulfate sulfur levels are approximately the same as the average 0.28% sulfate levels determined from the MCL coal samples.

This retention of sulfate sulfur can therefore be reduced by utilizing low pyrite (highly cleaned) coals in the Gravimelt Process. For example, coal deep cleaned to 0.5% pyritic sulfur, but containing any amount of organic sulfur should be reducible to 0.1% organic sulfur (see below), 0.02% pyritic sulfur (also, see below) and 0.07% sulfate sulfur (see above) for a total sulfur of 0.19%.

The data presented in Table 2 also show that in almost every case, the pyritic sulfur in MCL coal has been reduced to extremely low levels. The mean residual pyritic sulfur level is 0.022% for Pittsburgh coal, and 0.01% for Kentucky coal. These represent 98.7% and 99.5% removal of the pyritic sulfur present in the Pittsburgh and Kentucky coals fed to the rotary kiln.

The amount of residual organic sulfur in MCL coal is strongly dependent on processing conditions. The lowest organic sulfur level found is 0.08% from a Run .9C coal product sample. The effects of processing conditions on sulfur removal will be discussed in detail in a separate section of the final report.

4.3 Formation Of Humic Acid And Phenolics

Soluble organic compounds present in the spent caustic solutions are classified as humic materials if they precipitate upon acidification, and as phenolic materials if they remain soluble upon acidification. Data on the conversion of coal feed to humics are presented in Table 3. Data on the conversion to phenolics are not reported because of analytical and sampling problems.

Table 3. Formation of Humic Acid

Run	Coal Type	KOH/ NaOH	Leach Temp., °C*	% Coal Converted to Humics			
				Mean	Std Dev.	Data Pts	Range
1B	PITT 8	1	259	0.533	-	1	0.533
1C	PITT 8	1	279	0.794	1.041	3	0.105-1.992
1D	PITT 8	1	279	1.231	0.676	4	0.278-1.872
2B	PITT 8	1	259	0.249	0.148	2	0.144-0.354
2C	PITT 8	1	296	0.067	0.060	3	0.027-0.136
2D	KENT 9	1	296	0.236	-	1	0.236
2E	KENT 9	1	307	0.039	-	1	0.039
3B1	PITT 8	1	307	0.507	0.392	6	0.066-1.02
3C1	PITT 8	1	307	0.217	-	1	0.217
4C1	PITT 8	0	290	3.97	-	1	3.97
4C2	PITT 8	0	302	5.38	0.445	2	5.06-5.69
4C3	PITT 8	0	323	1.74	-	1	1.74
5B1	PITT 8	0	302	3.17	-	1	3.17
5B3	PITT 8	0	237	10.4	-	1	10.4
5C5	KENT 9	0	298	1.67	-	1	1.67
5C4	KENT 9	0	223	5.95	-	1	5.95
5D3	KENT 9	0	252	2.49	-	1	2.49
8A	PITT 8	1	395	1.94	-	1	1.94
8B	PITT 8	1	395	1.20	-	1	1.20
8C	PITT 8	0	403	0.744	0.276	2	0.548-0.939
8D	PITT 8	0	417	1.14	-	1	1.14
8E	PITT 8	0	389	1.27	-	1	1.27
8F	PITT 8	0	384	1.24	-	1	1.24
9A1	PITT 8	1	407	1.17	-	1	1.17
9B	PITT 8	1	415	0.209	-	1	0.209
9C	PITT 8	0	419	0.318	0.319	2	0.093-0.524

* Leaching temperature is based on temperatures measured by the thermocouple prob placed in either Zone 1 (Runs 4 and 5) or Zone 2 (Runs 8 and 9) of the rotary kiln. For Runs 1 to 3, the leaching temperature is estimated by assuming a 131° temperature difference between the Zone 1 kiln wall and the caustic/coal mixture.

Data on the conversion of coal feed to humics are also plotted in Figure 3 as a function of the caustic/coal temperature in Zone 1 (Runs 1 to 5) or Zone 2 (Runs 8 and 9) of the rotary kiln. The nitrogen flow was concurrent with the coal/caustic flow in Runs 1 to 5, and countercurrent to the coal/caustic flow in Runs 8 and 9. The net result was that in Runs 1 to 5, the temperature difference between the kiln wall and the coal/caustic mixture in Zone 1 was typically 131°C. By comparison, the temperature difference between the kiln wall and the coal/caustic mixture in Zone 2 was only in the 19-32°C range in Runs 8 and 9. For Runs 1 to 5, the leaching temperature would increase in the subsequent zones of the rotary kiln and would be higher than the temperature indicated by the Zone 1 probe sensor. For Runs 8 and 9, the leaching temperature in all four zones of the rotary kiln would be approximately the same as indicated by the Zone 2 probe sensor.

Based on the data from Runs 4C1, 4C2, 5B1, 5B3, 5C4 and 5D3, formation of humics appears to be maximum when only sodium hydroxide was used and when Zone 1 leaching temperatures were near or below 300°C. When mixed caustic was used for leaching, the maximum conversion of coal feed to humics was less than 2%. However, at leaching temperatures higher than 384°C, the conversion to humics was about the same whether sodium hydroxide or mixed caustic was used, and an average of 0.96% of the coal feed was converted to humics. At these temperatures, humics formation appears to decrease with leaching temperature. At leaching temperatures in excess of 415°C (Runs 9B and 9C), the data also show that low conversions of only 0.2-0.3% of the coal feed to humics are achievable.

At Zone 1 leaching temperatures near or below 300°C, humics formation was also low when mixed caustic was used (Runs 1 to 3). Even though the average leaching temperature was higher than that for Zone 1, these data suggest that it is possible to achieve low humics formation under mild leaching conditions.

5. PLANNED ACTIVITIES

During the next quarter coal will be packaged for shipment and process wastes will be disposed. Data assessment will be continued and topical reports will be prepared for test planning, shakedown and operation.

Figure 3. Effect of Leaching Temperature on Conversion to Humics