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32548-6003-UT-00

MASTER

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PROJECT FOR
LABORATORY STUDY FOR REMOVAL OF ORGANIC
SULFUR FROM COAL

U.S. DOE CONTRACT
NO. DE-AC22-80PC30141

QUARTERLY TECHNICAL PROGRESS REPORT
JANUARY 15, 1981

TRW
DEFENSE AND SPACE SYSTEMS GROUP

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1.0 MAJOR ACCOMPLISHMENTS

The following is a list of the major accomplishments for the fourth quarter of 1980.

1. It was found that molten sodium hydroxide (in place of mixed sodium and potassium hydroxides) followed by dilute sulfuric acid wash gave Gravimelt coal with the usual amount of sulfur and mineral matter removal but there was no MAF heat content loss over the small amount required for replacement of sulfur atoms by oxygen atoms in the coal structure - e.g., these samples had both measured heat content and MAF heat content in excess of 14000 Btu/lb. Therefore, the selectivity of the Gravimelt Process appears to be very high.
2. It was found that demineralized and desulfurized Gravimelt coal has significantly less alkali metals content than the input coal.
3. Kentucky No. 11 coal was reduced in sulfur content to a level of 0.10 lbs of sulfur (0.20 lbs of sulfur dioxide)/10⁶ Btu with an ash content of 0.21% in a cumulative reaction time of 60 minutes. This represents a 96% reduction in sulfur and a 97% reduction in ash. This product is significantly lower in sulfur content and ash than are typical synthetic or conventional liquid boiler fuels.
4. The Gravimelt Process was tested on Illinois No. 6 coal giving essentially identical results to those previously obtained for the Kentucky No. 11 coal under the same conditions (89% reduction in sulfur and 97% reduction in ash).
5. A technology for the regeneration of spent caustic has been identified within the tanning industry which corresponds to most of our Gravimelt Process requirements.

2.0 LABORATORY EXPERIMENTATION

2.1 GRAVIMELT EXPERIMENTATION

A series of experiments were conducted using the Gravimelt Process with NaOH, KOH and a mixture of KOH/NaOH melts. The equipment utilized are the stirred reactors described in previous quarterly reports. Coal and caustic were heated to temperatures where the caustic melts becomes a liquid which extracts sulfur from the coal. When stirring is stopped, the coal rises to the top of the mixture due to its buoyancy relative to the caustic. Thus, upon cooling, the coal is easily separated from the main body of the caustic. Two coals were evaluated in this series, Kentucky No. 11 coal recently furnished by Tennessee Valley Authority under the auspices of our DOE Project Officer Scott Taylor, and Illinois No. 6 coal obtained from the Oxydesulfurization program.

This experimentation consisted of a series of runs to evaluate the effect of time-temperature and various processing parameters upon sulfur or ash removal from the coal. Specifically, runs were conducted between 250°C and 370°C using reaction times ranging from 5 to 60 minutes. Included in this was one run utilizing a triple extraction (20 minutes each) with KOH/NaOH melt resulting in a reduction of total sulfur to 0.1 lbs S/10⁶ Btu which is a 96% reduction. Six runs were made consisting of three sets of duplicate experiments to investigate the effect of acid washing after Gravimelt extraction with either NaOH, KOH or a mixture of KOH/NaOH melts.

2.1.1 Kentucky No. 11 Coal Studies

TIME TEMPERATURE EFFECTS

Experimental runs were made to evaluate the effect of varying the reaction temperature and reaction time upon the sulfur removal from Kentucky No. 11 coal. The majority of the runs were made using mixed KOH/NaOH melt. Limited extractions were made with NaOH or KOH. Each of the experiments were conducted by heating and stabilizing the reactor and melt at the

desired temperature after which the coal was added. The reaction was run for the prescribed time and immediately cooled by immersing the reactor in an ice bath.

Table 1 presents a summary of the experimental data obtained in the above described experimentation, plus additional experimental data presented in the last quarterly which comprises an initial data based for statistical evaluation.

Multiple regression analyses using lbs sulfur/ 10^6 Btu as the dependent parameter related to time and temperature was conducted using 20 data points*(NaOH/KOH melt) for the regression, including the control sample. Table 2 presents the computer printout showing the coefficients of the regression equation as well as a comparison of observed vs predicted lbs/ 10^6 Btu as a function of time and temperature. The resulting equation is:

$$\text{lbs S}/10^6 \text{ Btu} = 3.01 - .0063(^{\circ}\text{C}) - .0048(\text{minutes})$$

which closely approximates the experimental data of Table 2.

MULTIPLE GRAVIMELT EXTRACTION

A triple extraction of the coal with fresh mixtures of KOH/NaOH melt was performed in 20 minute increments at 370°C for a total retention time of 60 minutes (Table 3). It is seen that total sulfur level was reduced to $0.11\text{ lbs}/10^6$ Btu (96% reduction) accompanied by a 7% reduction in MAF heat content. This represents a further reduction from 89% achieved with double extraction using NaOH, as presented in the last quarterly. The product coal contained only 0.21% ash (a 97% reduction).

Two Gravimelt extractions using NaOH and KOH/NaOH melts were performed to obtain samples of processed coal for the DOE Project Officer. A summary of the analyses data obtained from the processed samples is given in Table 4. Post extraction processing consisted of water washing only. The samples and analyses were delivered in December 1980.

*Some data as contained in Table 1 were obtained after the regression analysis was performed. These are noted in Table 1.

TABLE 1. POUNDS SULFUR/10⁶ BTU AS A FUNCTION OF TEMPERATURE AND TIME

MELT	Time (Min)	Temp, °C			
		250	315	340	370
KOH/NaOH	5				0.84
	10				0.47
					0.65
	20	1.73	1.03	0.75	0.40
					0.40
					0.50
					0.67
					0.37*
					0.57*
					0.56
					$\bar{x}=0.50$
					$\sigma=0.11$
	30		0.92	0.84	
	40				0.23 (Double extraction 20 min each)
	60	1.32*	0.84	0.63	0.25
			0.70	0.55	0.10* (Triple extraction 20 min each)
				0.60	
				$\bar{x}=0.59$	
				$\sigma=0.04$	

NaOH *	20				0.69
					0.63
					0.62
					0.68
					0.58
					$\bar{x}=0.64$

KOH *	20				0.44
					0.24
					0.26
					$\bar{x}=0.31$
					$\sigma=0.11$

* Data not included in regression analysis.

TABLE 2. MULTIPLE REGRESSION OF GRAVIMELT TREATED
KENTUCKY NO. 11 COAL*

	REG COEFF	STANDARD ERROR	BETA COEFF
R(0)	3.0118763E+00		
R(1)	-6.3133116E-03	4.8470413E-04	-9.0070339E-01
R(2)	-4.7631937E-03	1.8182277E-03	-1.8115539E-01

STANDARD ERROR OF ESTIMATE = 1.6252973E-01

COEFFICIENT OF DETERMINATION = 9.2352471E-01

	OBSERVED	PREDICTED	RESIDUAL
Y(1)	2.7000000E+00	2.8856101E+00	-1.8561010E-01
Y(2)	2.5000000E-01	3.8384609E-01	-1.3384609E-01
Y(3)	4.0000000E-01	5.7437384E-01	-1.7437384E-01
Y(4)	4.0000000E-01	5.7437384E-01	-1.7437384E-01
Y(5)	5.0000000E-01	5.7437384E-01	-7.4373837E-02
Y(6)	2.3000000E-01	4.7910996E-01	-2.4910996E-01
Y(7)	6.7000000E-01	5.7437384E-01	9.5626163E-02
Y(8)	4.7000000E-01	6.2200577E-01	-1.5200577E-01
Y(9)	8.4000000E-01	6.4582174E-01	1.9417826E-01
Y(10)	6.5000000E-01	6.2200577E-01	2.7994225E-02
Y(11)	8.4000000E-01	7.0351463E-01	1.3648537E-01
Y(12)	6.0000000E-01	5.6061881E-01	3.9381186E-02
Y(13)	5.5000000E-01	5.6061881E-01	-1.0618814E-02
Y(14)	7.5000000E-01	7.5114656E-01	-1.1465632E-03
Y(15)	6.3000000E-01	5.6061881E-01	6.9381186E-02
Y(16)	9.2000000E-01	8.8028735E-01	3.9712648E-02
Y(17)	8.4000000E-01	7.3739154E-01	1.0260846E-01
Y(18)	7.0000000E-01	7.3739154E-01	-3.7391540E-02
Y(19)	1.0300000E+00	9.2791929E-01	1.0208071E-01
Y(20)	1.7300000E+00	1.3445979E+00	3.8540214E-01

*Reference Table 1

TABLE 3. MULTIPLE GRAVIMELT* EXTRACTION OF KENTUCKY NO. 11

RUN	LBS/10 ⁶ BTU	ASH	BTU/LB		CUMULATIVE TIME, MIN.
			DRY	MAF	
CONTROL	2.7	7.9	13182	14314	0
1	0.67	7.04	12775	13742	20
2	0.23	8.69	12274	13443	40
3	0.10	6.84	12425	13338	60
		0.21**			

* 1:1 NaOH/KOH, 700°F, 20 minutes each

** % Ash after H₂SO₄ wash

TABLE 4. REMVOAL OF SULFUR FROM KENTUCKY MINE NO. 11 COAL BY THE GRAVIMELT PROCESS*

RUN	MELT TREATMENT	CONTENT				HEAT CONTENT		% w/w			
		LBS S/10 ⁶ BTU (DRY)				BTU/LB		ASH	VOLATILE MATTER	FIXED CARBON	NITROGEN
		S _t	S _p	S _s	S _o	DRY	MAF				
Control	None	2.7	1.2	0.0	1.44	13182	14314	7.9	36.8	56.0	1.54
68	KOH/NaOH	0.37	0.11	0.01	0.25	12342	13359	7.6	31.2	61.2	1.61
70	NaOH	0.62	0.09	0.01	0.52	13617	14499	6.1	35.4	58.5	1.67

* 20 minutes @ 370°C

2.1.2 Illinois No. Coal

Illinois No. 6 coal was treated as the first in a planned series of investigations to evaluate five coals by the Gravimelt Process. Two sets of duplicate runs consisting of treatment with NaOH and KOH/NaOH melts were completed at 370°C for 20 minutes each. These data are shown in Table 5. It is seen that the KOH/NaOH melt data (Experiment 69 and 69a) are nearly identical. The two NaOH melt runs, Nos 71 and 71a are not identical. We believe that run 71a was anomolous in either retention time or analysis. Note complete absence of heat content loss for runs 71 and 71a.

2.1.3 Processing Studies - Kentucky No. 11

Areas relating to processing effects upon sulfur and ash removal other than time-temperature were investigated.

Six runs were made consisting of three sets of duplicate experiments to investigate the effect of acid washing after Gravimelt extraction with either NaOH, KOH or a mixture of KOH/NaOH melts. Each extraction was made for 20 minutes at 370°C. In each case, the coal was removed from the reactor and subjected to both water washes and dilute sulfuric acid washes. The samples were oven dried and submitted for analysis. The data are presented in Table 6. It is seen that the ash content of the coal is significantly reduced which verifies data reported in the second quarterly. Additionally, except for Experiment 74a* the Na and K are effectively equal to or less than the starting coal after acid treatment.

Note that the MAF heat content of the initially NaOH extracted coals was decreased only slightly, while the KOH/NaOH runs showed a typical 7% decrease and pure KOH a 9% decrease. The slight heat content decreases is almost exactly that expected for removal of sulfur atoms from coal and replacement with oxygen. It appears that NaOH treatment is most effective at removing both mineral matter and sulfur without loss of heat content.

*The higher ash content is presumably due to faulty washing.

TABLE 5. REMOVAL OF SULFUR FROM ILLINOIS NO. 6 COAL BY THE GRAVIMELT PROCESS*

RUN	MELT TREATMENT	CONTENT LBS S/10 ⁶ BTU (DRY)				HEAT CONTENT BTU/LB		ASH % w/w
		S _t	S _p	S _s	S _o	DRY	MAF	
Control	None	2.81	1.23	0.01	1.57	12250	14257	12.0
69	KOH/NaOH	0.30	0.10	0.01	0.19	12857	13651	5.8 (0.52)**
69a	KOH/NaOH	0.27	0.09	0.01	0.17	12913	13610	5.1 (0.52)**
71	NaOH	0.36	0.07	0.01	0.28	13433	14288	6.0
(71a	NaOH	0.73	0.14	0.01	0.58	13376	14391	7.1)

* 20 minutes @ 370°C

** 10% H₂SO₄ wash

TABLE 6. ACID WASHING OF GRAVIMELT* EXTRACTED KENTUCKY NO. 11 COAL

EXPERIMENT	MELT	#/10 ⁶ BTU	ASH	BTU/LB		RESIDUAL ON COAL	
			% w/w	DRY	MAF	Na	K
Control	-	2.7	7.9	13182	14314	.05	0.14
72	NaOH/KOH**	0.57	0.51	13517	13517	.05	0.1
72a	NaOH/KOH	0.56	0.16	13361	13383	.01	.01
73	NaOH	0.68	0.32	14068	14113	.02	0.004
73a	NaOH	0.58	0.23	14023	14055	.02	.001
74	KOH	0.24	0.53	12897	12965	.01	.02
(74a	KOH	0.26	1.14	12723	12869	.19	.11)
						$\bar{x} = .02^{***}$	$\bar{x} = .01^{***}$
						$\sigma = .02$	$\sigma = .01$

* Temperature: 370°C
Time : 20 minutes

** 50/50 KOH/NaOH melt

*** Does not include Experiment 74a

2.3 CAUSTIC REGENERATION

Initial experimentation has been conducted to support caustic regeneration of the wash waters from the Gravimelt Process. In summary, the wash water from the first coal wash is expected to contain the bulk of removed caustic. In addition, dissolved sulfides (Na,K) and some ash will be contained therein. Subsequent water washes prior to neutralization will contain lesser amounts of caustic and ash while, the acid wash and subsequent water washes will contain the majority of ash material.

Studies to date have been directed to regeneration of caustic solutions containing sulfides. Removal of the sulfide will be most expeditiously accomplished by liming and removal as a sulfate prepared by solution oxidation of the sulfide. Mellor* states that

"In solution, sodium sulfide is oxidized by oxygen largely to thiosulphate, small quantities of sulfite and sulfate are also being formed⁹⁶⁻⁹⁸. The rate of reaction of sodium sulfide with oxygen is almost doubled by heavy metal catalysts such as Mn, Co, Fe or Cu⁹⁹. Ferric hydroxide will also oxidize sodium sulfide solutions to sulfite¹⁰⁰."

Oxidation of sulfides in industry to recover waste waters, from the tanning industry is state-of-the-art. In the tanning industry solutions of sodium sulfide made alkaline with either sodium hydroxide or lime are oxidized with air to produce sulfate which precipitates as gypsum and regenerate the caustic.

We contacted Clow Corporation (Waste Treatment Division), Florence, KY. Clow Corporation provides equipment packages for the oxidation of sulfides to sulfates which are basically air or oxygen blown sparging systems with added manganese for catalytic oxidation of sulfide in solution. This is basically our approach except it is expected that inherent iron extracted from the coal will provide the catalyst. Laboratory studies are now in progress.

*Comprehensive Treatise of Inorganic Chemistry, Vol 11, Supplement 11, Li, Na (Page 983).

2.2 EVALUATION OF ESCHKA AND BOMB SULFUR ANALYSES FOR DETERMINATION OF SULFUR IN COMPOUNDS EXPECTED TO BE EXTRACTED DURING GRAVIMELT PROCESSING

I. EXPERIMENTAL CONDITIONS:

- GM-60 ● NaOH/KOH heated to 700°F for 20 minutes then cooled.
Calculated S in melt: None
- GM-61 ● NaOH/KOH + Na₂S·9H₂O heated to 700°F for 20 minutes then cooled.
Calculated S in melt: 1.1% w/w
- GM-62 ● NaOH/KOH + K₂SO₄ heated to 700°F for 20 minutes then cooled.
Calculated S in melt: 1.0% w/w

In each case the cooled melt was retrieved from the reactor and sampled. Analyses were conducted by Warner Labs.

S IN MELT, % w/w

Exp	Calc.	Bomb Method	Eschka Method
GM60	0	0.1	0.01
GM61	1.1	1.2	1.1
GM62	1.0	1.2	0.9

II. CONCLUSIONS

1. Sulfur in sulfur compounds, extracted into molten caustic during Gravimelt coal desulfurization, can be accurately measured by either the Bomb or Eschka methods.
2. This confirms the accuracy of Gravimelt sulfur material balance measurements reported in Table 5 of the October 15 Quarterly Report.

3.0 GRAVIMELT CONCEPTUAL DESIGN FOR SULFUR REMOVAL

The following pages present the preliminary conceptual design for a Gravimelt Process producing coal for a 1000 MWe power plant. This case does not include the second step of the Gravimelt Process for mineral matter removal by acid extraction. This preliminary design will serve as a base case for future designs after the assumptions made in this design have been tested in the laboratory. This design will also point out areas where the overall process economics are sensitive to estimated capital costs and operating parameters. The following pages include a design basis, heat and material balance, brief process description, capital cost estimate and estimated annual operating costs.

3.1 DESIGN BASIS

3.1.1 Feed Coal

The Gravimelt process is designed to provide coal feed to a 1000 MWe power plant assuming a power plant efficiency of 36% based on the higher heating value of the coal feed. Using the 36% efficiency or 9483 Btu/KWe the required coal output from the Gravimelt process is 9483 MM Btu/hr. It is assumed that the coal feed to the Gravimelt process is nominal 1/8 inch X 0, mine cleaned Kentucky No. 11 coal. For the purposes of this study it is assumed that the coal feed has been dried to three percent moisture and the coal product from the Gravimelt process will also be dried to three percent moisture. Table 7 shows the analysis of the feed coal used in this study.

3.1.2 Molten Caustic Reactor

The chemical desulfurization of the coal by reaction with an 80% molten caustic mixture with a 1:1 mole ratio of KOH and NaOH occur in a nickel reaction vessel at atmospheric pressure and 715°F. Based on laboratory results it is assumed that 90% of the coal sulfur is converted to K_2S and Na_2S . The reactor is sized to provide 30 minutes residence time for the coal slurry which has four parts caustic to one part coal. It is known that a portion of the coal will be volatilized upon heating to the

TABLE 7. FEED COAL ANALYSIS

WARNER LABORATORIES, INC.

EST. 1923

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CRESSON, PA. 16630

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DATE: 8-29-80
WARNER NO. 660753

000 000-0000
TRW SYSTEMS, BLDG. 01
ROOM 2151 ONE SPACE PARK
REDONDO BEACH, CALIF.

SAMPLE ID: TVA #2

OPERATING CO.:
SAMPLED BY:
MINE:
LOCATION:

DATE SAMPLED:

DATE RECEIVED: 8/25/80

WEATHER:
GROSS WEIGHT:

OTHER ID: P. O. 642670CG BA

CERTIFICATE OF ANALYSIS

	AS RECEIVED	DRY BASIS
MOISTURE	7.27%	XXX
ASH	7.19%	7.75%
SULFUR	3.20%	3.45%
BTU/LB	12314	13279
NAF BTU/LB		14395
PYRITIC SULFUR	1.66%	1.80%
SULFATE SULFUR	.01%	.01%
ORGANIC SULFUR	1.52%	1.64%

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reaction temperature. For the purpose of this study it is assumed that the volatilized gases will contain seven percent of the heat value in the feed coal and this material will have an average heating value of 18,000 Btu/lb. The above assumptions are subject to confirmation by the ongoing laboratory work on this program.

3.1.3 Coal Recovery

It is assumed that the coal slurry from the reactor can be screened to contain 50% coal prior to the addition of water for cooling and washing. It is also assumed that the washing of the coal to recover the caustic and sulfides can be done using two rotary drum filters in series with a counter-current washing arrangement to minimize the wash water requirements. The assumed wash water requirement is one pound water per pound of dry coal. From the filters the coal is further dewatered to 18% moisture prior to thermal drying to a level of three percent moisture. The heating value of the recovered coal is 13,106 Btu/lb after the removal of sulfur and volatiles. As part of the laboratory program, the assumptions made here will be checked to better determine the operating parameters for dewatering and washing of the reacted coal.

3.1.4 Caustic Regeneration

The aqueous caustic solution from the filter is reacted with lime and oxygen to convert the potassium and sodium sulfide to calcium sulfate. It is assumed that 75% of the lime feed to the regenerator will be utilized in the conversion to sulfate. Oxygen is provided by feeding compressed air with an excess of 100% of that required to oxidize the sulfide to sulfate. The reaction is carried out in a stirred nickel reactor with a 30 minute residence at an estimated equilibrium temperature of 297°F. The insoluble sulfate salts and unreacted lime are removed from the solution by thickening and filtration and the caustic solution is reconcentrated by evaporation for recycle to the caustic reactor.

3.1.5 Product Coal

The coal product from the process has a heating value of 13,106 Btu/lb which is slightly less than the feed coal due to the removal of volatile

material and the replacement of sulfur by oxygen in the coal by the de-sulfurization reaction. The sulfur content of the product coal is 0.37% on a dry weight basis plus the small amount of residual sulfide salts remaining on the coal after washing.

3.2 PROCESS DESCRIPTION

For the purpose of discussion, the Gravimelt process design has been divided into three functional sections: Caustic reaction, coal recovery, and caustic regeneration. A process flow diagram for the preliminary design is presented in Figure 1. The process material balance is given in Table 8.

3.2.1 Caustic Reaction Section

The caustic reaction section consists of equipment necessary to feed dried coal to the caustic reactor, react the coal with the molten caustic, heat the recycle caustic to the reactor and recover the volatile fuels evolved from the coal during the reaction. A dried coal gravity is fed from coal silos to the reactors by conveyors at the rate of about 400 TPH. The feed coal is a 1/8 inch X 0 mine cleaned Kentucky No. 11 coal. For the feeding of coal, the caustic reaction, and the coal screening, the plant has been divided into five trains. Each train is provided with coal feed silos which have the capacity to store 24 hours of feed coal. The coal is fed from the silos to the reactors using conveyors where the coal is contacted with the molten caustic solution at 715°F and atmospheric pressure in an agitated nickel reactor. Each of the five reactors sized to provide 30 minute residence time for the coal are 15 feet diameter by 23.5 feet high. The caustic feed rate to the reactor is 1448 TPH which allows a 4:1 ratio of caustic to coal. The feed caustic enters the reactor at 769°F providing enough heat to raise the temperature of the feed coal to 715°F and volatilize the water present in the coal and hydrocarbons equal to seven percent of the heat content of the feed coal. Water is removed from the vent gas using a 295 ft² condenser on each reactor. The vent gases are then compressed to 100 psig in a single 3500 HP compressor where more water is removed and the gaseous and liquid fuels are recovered for process

Figure 1. Process Flow Diagram

TABLE 8. MATERIAL BALANCE

STREAM	1 COAL FEED	2 VOLATILE VENT	3 REACTOR EFFLUENT	4 FEED CAUSTIC	5 RECYCLE CAUSTIC	6 COAL SLURRY	7 SLURRY DRUM REFLUX	8 FILTER FEED SLURRY	9 WASH FILTRATE
COAL, TPH									
MAF	344.40		330.38			330.38		330.38	
S	13.38		1.34			1.34		1.34	
ASH	30.06		30.06			30.06		30.06	
VOLATILE		20.03							
H ₂ O	12.00	18.76							
TOTAL	399.83	38.79	361.78			361.78		361.78	
CAUSTIC, TPH									
KOH			609.75	630.83	457.32	152.44		202.69	50.25
NaOH			434.76	449.79	326.07	108.69		144.52	35.83
K ₂ S			82.83	62.12	62.12	20.71		27.53	6.83
Na ₂ S			58.64	43.98	43.98	14.66		19.49	4.83
H ₂ O			261.13	261.13	195.85	65.28	85.15	329.32	264.04
TOTAL			1,447.11	1,447.85	1,085.33	361.78	85.15	723.55	361.78
TOTAL TPH	399.83	38.79	1,808.89	1,447.85	1,085.33	723.56	85.15	1,085.33	361.78
(CONTINUED)									

TABLE 8. (CONTINUED)

STREAM	10 WASH WATER	11 FILTER CAKE	12 CENTRATE	13 CENTRIFUGE CAKE	14 DRIED COAL	15 REGENERATOR FEED	16 LIME FEED	17 REGENERATOR EFFLUENT
COAL, TPH								
MAF		330.38		330.38	330.38			
S		1.34		1.34	1.34			
ASH		30.06		30.06	30.06			
VOLATILE								
H ₂ O								
TOTAL		361.78		361.78	361.78			
CAUSTIC, TPH								
KOH		.42	.237	.185	.185	152.02		173.04
NaOH		.30	.169	.132	.132	108.39		123.37
K ₂ S		.06	.032	.025	.025	20.65		
Na ₂ S		.04	.023	.018	.018	14.62		
H ₂ O	361.78	180.07	101.01	79.05	11.19	246.99		172.74
CaO							28.01	
Ca(OH) ₂								9.25
CaSO ₄								50.99
TOTAL	361.78	180.89	101.47	79.42	11.55	542.67	28.01	529.39
TOTAL	361.78	542.67	101.47	441.20	373.33	542.67	28.01	529.39
(CONTINUED)								

TABLE 8. (CONTINUED)

STREAM	21 THICKNER OVERFLOW	22 THICKNER UNDERFLOW	23 WASH WATER	24 FILTRATE	25 SOLIDS TO DISPOSAL	26 EVAPORATOR FEED	27 MAKE UP KOH/NaOH	28 EVAPORATOR BOTTOMS	29 EVAPORATOR WATER
CAUSTIC, TPH									
KOH	150.82	22.22		22.13	.09	172.95	.56	173.51	
NaOH	107.53	15.84		15.77	.07	123.30	.42	123.72	
K ₂ S									
Na ₂ S									
H ₂ O	150.56	22.18	60.24	52.46	29.96	203.02	.25	65.28	137.99
Ca(OH) ₂		9.25			9.25				
CaSO ₄		50.99			50.99				
TOTAL	408.91	120.48	60.24	90.36	90.36	499.27	1.23	362.52	137.99

STREAM	18 REGENERATION AIR	19 REGENERATOR VENT	20 CONDENSATE
O ₂	47.95	23.97	
N ₂	157.29	157.92	
H ₂ O	1.55	66.80	52.09
TOTAL	207.42	248.69	52.09

use. It is not known at this time the quantity of fuel which will be recovered as liquid. An analysis of the volatile material will be included as part of the ongoing laboratory program.

The desulfurization of the coal forming sulfide salts is accomplished by the following reactions:

The reacted coal slurry from the reactors overflows to five nickel screens where the liquid material is removed to leave a coal containing 50% caustic solution. The caustic solution is recycled to the reactor after reheating in the recycle caustic heater where both the recycle caustic and the re-generated caustic from the evaporator are heated to 769°F. The caustic heater with a fired duty of 317 MM Btu/hr uses fuel recovered from the volatile vent stream at the reactor. For this analysis it has been assumed that all equipment contacting the caustic solution will be of nickel construction. The possibility of using less noble and less expensive material will be studied as part of the laboratory program.

3.2.2 Coal Recovery Section

The coal slurry from the screens containing 50 wt. % coal is fed to a slurry tank where it is combined with the wash filtrate from the filter/washing operation. The slurry tank is an 19,500 gallon agitated nickel vessel which is sized to provide 10 minutes residence time for the coal slurry. The slurry is cooled by the 180°F wash water from the filters and a reflux condenser which condenses and cools the vapor boiled off from the slurry to 175°F before recycle back to the tank which is operating at about 320°F. The assumed 320°F boiling temperature for the solution is subject to confirmation in the laboratory. The overhead condenser duty is 180 MM Btu/hr requiring approximately 6440 ft² of surface area. The cooled slurry containing about 33 wt. % coal is fed to two trains of two rotary drum vacuum filters in series for dewatering and washing. The four filters require a total of 1200 BHP for the filter drives and vacuum systems. The filters are arranged to wash the coal countercurrently using one ton of

water per ton of dry coal with the fresh wash water used as feed for the 2nd stage filter. The wash filtrate from the second stage filter is used to reslurry the coal cake from the first stage filter and the filtrate from the second stage filter is used as the wash water for the first stage filter. The wash filtrate from the first stage filter is used to make up the coal slurry in the slurry tank. The filtrate from the first stage filter, approximately a 50% caustic solution containing most of the sulfide salts, is fed to the regenerator for the reaction with lime and oxygen. It is assumed that in all stages of filtration the coal will be dewatered to contain 0.5 lb solution per pound of coal. The washed coal cake from the filter containing 33% moisture is further dewatered to 18% moisture content using two 350 hp solid bowl centrifuges. The coal cake from the centrifuges contains 362 TPH coal with about 79 TPH moisture. The moisture on the coal cake at this point has been washed to contain about 370 lb/hr KOH, 260 lb/hr NaOH, and about 86 lb/hr sulfide salts. The coal cake from the centrifuges is then dried in a fine coal drier requiring about 309 MM Btu/hr of fuel assuming a 65% thermal efficiency. The drier will use coal and recovered volatiles as fuel to dry the product coal to three percent moisture. The overall sulfur content of the coal product including the residual sulfide salts is 0.36 wt. %.

3.2.3 Caustic Regeneration Section

In the caustic regeneration section the filtrate from the coal recovery section is reacted with slaked lime and air to precipitate the sulfate salts and regenerate NaOH and KOH via the following overall reactions:

The regeneration is carried out in two 25,000 gallon nickel reactors which provide 30 minute residence time for the slurry of lime and caustic. Oxygen for the reaction is supplied from two 3900 HP air compressors. The exothermic reactions provide enough heat to vaporize about 52 TPH water from the slurry which maintains an operating temperature of 297°F. The slurry effluent from the reactors, containing unreacted $\text{Ca}(\text{OH})_2$ and CaSO_4 ,

is fed to a 200 ft diameter thickener where the underflow is concentrated to a slurry which is 50 wt. % solids. The thickener overflow goes to the evaporator for concentration to 80 wt. % caustic. The thickener underflow is pumped to a two stage countercurrent vacuum filter system for dewatering and washing. The filter arrangement is similar to that used for the coal washing and requires about 250 HP for the filter drums and vacuum system. The system requires one ton of wash water per ton of solids and the solid cake from the system contains 33 wt. % moisture. The filtrate and wash filtrate from the system is collected and pumped to the evaporator with the thickener overflow. The solids from the system containing CaSO_4 and Ca(OH)_2 are sent to a disposal site.

The diluted caustic solution from the filter and thickner are fed to a double effect nickel evaporator for concentration to 80 wt. % before recycle back to the caustic reactor. Each effect of the evaporator system will require about 5400 ft² of heat transfer surface and the overall steam requirement is estimated at 205,000 lb/hr. A package steam generator is provided to produce the steam at 600 psig and 600°F.

3.2.4 Heat Balance

The heat input to the plant as coal feed is equal to 10,300 MM Btu/hr based on 13,280 Btu/lb coal (moisture free). The heat output as product coal is equal to 9483 MM Btu/hr based 13,106 Btu/lb (moisture free). The fuel recovered from the volatilized coal is equal to 721 MM Btu/hr which is used in process and charged to the process as an operating cost. An additional 143 MM Btu/hr is required for the plant heating requirements which are summarized in Table 9.

Table 10 summarizes the overall efficiency of the plant including the purchased additional fuel and the required electric power. From Table 4 we see that the estimated thermal efficiency is about 90%.

3.3 EQUIPMENT LIST/CAPITAL COSTS

The capital equipment required for the Gravimelt process are listed along with estimated 1980 costs in Table 11. The following references are used as a basis for equipment sizing and costing information.

TABLE 9. FUEL REQUIREMENTS

Heat Available	MM Btu/hr
Volatiles	<u>721</u>
Total	721
Heat Required	
Caustic Heater	317
Coal Dryer	308
Steam Generator	<u>239</u>
	1,131
Additional Fuel Required	143

TABLE 10. THERMAL EFFICIENCY

Heat In	MM Btu/hr
Feed Coal	10,300
Purchased Fuel	143
Electric Power @ 3412 Btu/kw	<u>52</u>
Total	10,495
Heat Out	
Product Coal	<u>9,483</u>
Total	9,483
Efficiency = 90%	

- Perry, "Chemical Engineers Handbook", 5th edition
- Guthrie, K.M., Process Plant Estimating, Evaluation, and Control; 1974
- Internal TRW Costing Data

All costs were escalated to mid 1980 using the Marshall and Swift cost index provided in Chemical Engineering publications. The costs listed in Table 12 are installed equipment costs which include the F.O.B. equipment cost, foundations, supports, piping, instrumentation, other miscellaneous equipment, and construction labor. The total installed cost for the Gravimelt process is \$51 MM. Using this number for installed cost the total invested capital is presented in Table 6. The total capital investment is equal to \$74.1 MM which is equivalent to \$74.10/KWe for the 1000 MWe power plant.

3.4 OPERATING COSTS

Table 13 presents the operating costs for the Gravimelt process based on 330 operating days per year. The costs are presented as annual costs and dollars per ton of product coal produced. An operating cost of coal at \$1.30 Btu is taken for the coal feed to the Gravimelt process which is in excess of the coal required for the 1000 MWe power plant. This excess coal is volatilized in the caustic reactor and recovered as fuel gas and liquid fuels which is used in the Gravimelt process for heating purposes.

The additional fuel required is listed as a utility cost for the 143 MM Btu/hr required for process use. The total non-capitalized operating cost for the Gravimelt process is \$34 million per year which is equal to \$11.49/ton of coal product. Using a capital charge equal to 16% of the total plant investment for depreciation and cost of capital the total amortized annual operating cost is \$45.8 million or \$15.50/ton of coal product. For comparison, a second column is shown in Table 12 where the capital charges are equal to 20% of the total plant investment. In this case the total operations cost is equal to \$48.8 million per year or \$16.50 per ton of coal product.

TABLE 11. CAPITAL COST ESTIMATES

	\$1,000 (1980)
<u>Reaction Section</u>	
Reactor w/mixers	6,315
Coal Silos	2,493
Conveyors	326
Feeders	111
Solid Separators	3,542
Pumps	278
Vent Compressor	898
Vent Condenser	351
Recycle Heater	5,233
Total Reactor Section	19,547
<u>Coal Recovery Section</u>	
Slurry Tank w/mixer	799
Overhead Condenser	466
Condensate Drum	70
2 Stage Filter System	4,000
Centrifuge	6,214
Coal Dryer	6,489
Interstage Slurry Tank w/mixer	335
Slurry Pumps	261
	18,634
<u>Caustic Regeneration Section</u>	
Lime Silos	600
Lime Conveyors	570
Lime Feeder	350
Regenerator	1,969
Thickner	1,098
Filter System	1,034

(CONTINUED)

TABLE 11. (CONTINUED)

Air Compressor	2,107
OVMC Condenser	122
Evaporator	3,325
Steam Generator	1,273
Pumps	425
	<hr/> 12,873
Total Installed Cost	\$51,054

TABLE 12. CAPITAL COST SUMMARY

	<u>\$ 10⁶</u>
Installed Equipment	51.05
Engineering & Design @ 10% of Capital Equipment	5.11
Contractors Overhead and Profit @ 22% of Capital Equipment	11.23
Contingency @ 10% of Installed Equipment & Engineering & Design & Overhead & Profit	6.74
	<hr/>
Total Invested Capital	74.13

TABLE 13. OPERATING COSTS

BASIS 330 Operating days/year		Annual Cost \$/Ton	
		\$ Million	Coal Product
Raw Materials			
Coal @ \$1.30/MM Btu		7.42	2.51
KOH @ \$378/ton		1.67	.56
NaOH @ \$160/ton		0.53	.18
Lime @ \$32/ton		7.10	2.40
Solids Disposal		4.29	1.45
Utilities			
Power @ 2.5¢/KW		3.02	1.02
Fuel @ \$1.30/MM Btu		1.48	.50
Boiler Feedwater @ 65¢/1000 lb		0.06	.02
Process Water @ 40¢/1000 gal		0.43	.15
Cooling Water @ 4.5¢/1000 gal		1.21	.41
Labor 15 positions @ \$8/hr		1.05	.36
Supervision @ 15% of operating labor		0.16	.05
General Overheads @ 60% of Labor & Supervision		0.73	.25
Maintenance		2.22	.75
@ 3% of Total Plant Investment			
Taxes and Insurance		2.22	.75
@ 3% of Total Plant Investment			
Operating Supplies		0.39	.13
@ 20% of Operating Labor			
Total Non-Capitalized Operating Cost		33.98	11.49
Capital Charges @ 20% Total Plant Investment		14.83	5.01
@ 16% Total Plant Investment		11.86	4.01
Total Amortized Operating Cost		48.81	16.50
		45.84	15.50

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