DOE/PC/91257-T27

MOLTEN-CAUSTIC-LEACHING (GRAVIMELT)
SYSTEM INTEGRATION PROJECT

QUARTERLY REPORT FOR OCTOBER THROUGH DECEMBER, 1989

CONTRACT NUMBER DE-AC22-⁸⁶PC91257
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JANUARY 10, 1990

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1. EXECUTIVE SUMMARY

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

Analysis of the large quantity of data collected continued during the current quarter. Assessment of trace elements in the feed and product coal for two runs (one with Pittsburgh No. 8 coal and one with Kentucky No. 9 coal) indicates that greater than 96% of the silicon, iron and aluminum was removed for both coals. A trace element analysis for 21 elements is presented in this quarterly.

Selected samples of the product coal were placed in a GN_2 -purged oven for six hours at 140°F to remove about 15% of the moisture from the samples. These samples were repackaged in 55-gallon drums and shipped to DoE.

Data from shakedown was analyzed in detail with particular attention paid to coal product quality (sulfur and ash), carbonate and humic acid formation, particle size distribution, liquid sample analysis, and wash train performance.

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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 the 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 pre-activated 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

TRW Gravimelt Process

Figure 1. Gravimelt Process Flow Schematic

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 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.

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, the kiln, and the 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 a 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

Analysis of the large quantity of data collected continued during the current quarter. (More than 4000 analyses had been obtained in previous quarters on process streams such as product coal, intermediate coal, slurries, filter cakes and filtrates during 750 hours of matrix testing.) Assessment of trace elements in the feed and product coal for two runs (one with Kentucky No. 9 coal and one with Pittsburgh No. 8 coal) indicates that greater than 96% of the silicon, iron and aluminum was removed for both coals. The presence of twenty-one trace elements was assessed.

Selected samples of the product coal were placed in a GN_2 -purged oven for six hours at 140°F to remove about 15% of the moisture from the samples. These samples were repackaged in 55-gallon drums and shipped to DoE.

Data from shakedown was analyzed in detail with particular attention paid to coal product quality (sulfur and ash), carbonate and humic acid formation, particle size distribution, liquid sample analysis, and wash train performance.

4.1 TRACE ELEMENT ANALYSIS OF COAL

Assessment of trace elements in the feed and product coal for two runs (Run 7A with Kentucky No. 9 coal and Run 9C with Pittsburgh No. 8 coal) was performed. These two coals were subjected to a series of analysis as follows:

- Quantitative analysis for Na, K, Cl and F
- Semiquantitative analysis for any remaining cations.

The above analysis required different sample preparation techniques which were as follows:

- Quantitative Na and K analysis - used ASTM D2795 which is a muffle ash at 750°C followed by a H_2SO_4 -HF digestion.
- Quantitative Cl and F analysis - used a Parr oxygen bomb combustion over standard anion eluent. Solutions were analyzed directly by ion chromatography.
- Semiquantitative Emission Spectrographic Analysis (ES) - the coal ash sample, which was ultimately analyzed, was obtained from the parent coal using a low temperature ($<130^\circ\text{C}$) oxygen plasma procedure. The ash, after plasma ashing, was removed and submitted to Pacific Spectrochemical for ES analysis. (Note: low temperature ashing is used to retain elements normally lost using high temperature muffle ashing techniques).

The quantitative results obtained for Na, K, Cl and F are presented in Table 1. The ES results reduced to a mg/g basis are summarized in Table 2 for 21 elements.

4.2 DRYING OF PRODUCT COAL

Selected sample bags of MCL product coal were placed in a GN_2 -purged coal drying oven (about eleven bags per load) for six hours, with the oven set at its minimum temperature of 140°F . This removed about 15% of the moisture from the samples. The samples were repackaged in new plastic bags and relabeled with the new weight. The dried samples were placed in nine 55-gallon steel drums for shipment to DoE. Table 3 is a list of all coal samples that were dried and shipped to DoE. The total weight shipped is summarized in Table 4.

Eight of the selected sample bags listed in Table 3 for Pittsburgh No. 8 Run 4C1 3-7-89 12:45 through 19:15 were not dried because they could not be located in the storage drums. Samples from Kentucky No. 9 Run 7A 5-1-89 20:15 through 22:15 and Pittsburgh No. 8 Run 9A 5-30-89 17:15 through 19:15 (about 10 pounds dry basis of each coal) were dried and placed in an "MCL repository" for future use and analysis.

4.3 SHAKEDOWN RUN TEST RESULTS

4.3.1 Coal Product Quality

The shakedown test was run with a 1:1 caustic/coal feed, using 50:50 KOH/NaOH and 14 mesh Pittsburgh No. 8 coal. During the shakedown test on 12/15/1988, the rotary kiln was operated with wall temperatures of $346\text{--}350^\circ\text{C}$ in Zone 1, $336\text{--}346^\circ\text{C}$ in Zone 2, and $331\text{--}338^\circ\text{C}$ in Zones 3 and 4. The coal product samples analyzed for product quality were all processed by the rotary kiln during this time period, even though some of the kiln processed coal was later fed to the wash train on 12/16/1988. The residence time of the caustic/coal mixture in the heated zones of the rotary kiln was approximately 2 hours.

Coal product samples were obtained during the shakedown test for analysis. The analysis results presented in Table 5 show an average residual sulfur content of 2.52% (dry basis) in the coal product, which corresponds to 46.19% sulfur dioxide (per unit heat content) removal based on coal feed to the rotary kiln, or 68.22% sulfur dioxide removal based on run-of-mine coal. The average residual ash content of the coal product was 2.76%, which corresponds to 76.10% ash removal. The substantial, but relatively modest sulfur and ash removals for MCL processing were due to the mild operating temperatures in the rotary kiln, which were necessary during the shakedown test. As shown in Figure 2, there is good correlation between the sulfur content and ash content of the coal product:

$$\% \text{ sulfur} = 2.1941 + 0.1165 \% \text{ ash}$$

Table 1. Quantitative Cation and Anion Analysis

Coal Analysis, % wt/wt Dry Coal Basis

<u>Element</u>	<u>Feed Ky 9</u>	<u>Feed Pitt 8</u>	<u>Prod Ky 9</u>	<u>Prod Pitt 8</u>
Na	0.034	0.060	0.012	0.022
K	0.15	0.20	0.025	0.013
Cl	0.16	0.11	0.0090	0.0105
F	0.0027	0.0050	0.0017	0.0044

Table 2. Removal of Minor and Trace Elements from Coal
Semiquantitative Emm Spectr Analysis, mg/g dmf

	FEED KYN 9	FEED PITT 8	PROD KYN 9	PROD PITT 8	%REM KYN 9	%REM PITT 8
Si	40	55	1.6	1.1	96	98
Fe	8.8	16	0.24	0.12	97	99
Al	9.7	13	0.26	0.09	97	99
Mg	0.5	0.63	0.024	0.009	95	99
Mn	0.045	0.1	0.0037	0.003	92	97
Ca	0.57	3.4	0.013	0.046	98	99
K	2	2	0.24	0.0035	88	100
Ti	0.63	0.43	0.26	0.19	59	56
Cr	0.045	0.03	0.014	0.017	69	43
Ba	0.2	0.2	0.003	0.0035	99	98
B	0.026	0.05	0.0018	0.001	93	98
Pb	0.02	0.02	0.0054	0.024	73	-20
Mo	0.004	0.004	0.0044	0.003	-10	25
Sn	0.004	0.004	5E-05	5E-05	99	99
V	0.008	0.027	0.0018	0.002	78	93
Cu	0.007	0.023	0.003	0.006	57	74
Na	0.44	0.37	0.1	0.15	77	59
Zr	0.023	0.055	0.015	0.018	35	67
Co	0.002	0.002	0.0015	0.001	25	50
Sr	0.025	0.069	0.0008	0.001	97	99
Cl	0.16	0.11	0.01	0.01	94	90

Clorine analysis by cation anion method

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Table 3.
MCL PRODUCT COAL DRYING

PAGE 1

RUN NO.	RUN DATE	SAMPLE TIME	PRE DRY WT. gm	POST DRY WT. gm	% MOIST. REMOVED	NET SHIP WT. gm	CALC DRY WT	TYPE COAL	SHIPPING DRUM NO
2C	02/08/89	00:20	4837	4053	16.2	3978	2395	PITTS 8	107
2C	02/08/89	01:20	4854	4148	14.5	4073	2385	PITTS 8	107
2C	02/08/89	02:20	3882	3198	17.6	3123	1924	PITTS 8	107
2C	02/08/89	03:20	4256	3569	16.1	3494	2101	PITTS 8	107
2C	02/08/89	04:20	3770	3224	14.5	3149	1842	PITTS 8	107
2C	02/08/89	05:20	3692	2980	19.3	2905	1838	PITTS 8	107
2C	02/08/89	06:20	3506	2887	17.7	2812	1734	PITTS 8	107
2C	02/08/89	07:20	3407	2834	16.8	2759	1678	PITTS 8	107
2C	02/08/89	08:15	3904	3171	18.8	3096	1944	PITTS 8	107
2C	02/08/89	09:20	3995	3414	14.5	3339	1955	PITTS 8	107
2C	02/08/89	10:20	3997	3321	16.9	3246	1977	PITTS 8	107
2C	02/08/89	11:20	1810	1335	26.2	1260	885	PITTS 8	107
2C	02/08/89	12:20	1694	1261	25.6	1186	825	PITTS 8	107
2C	02/08/89	13:20	1345	934	30.6	859	640	PITTS 8	107
2C	02/08/89	14:20	1815	1428	21.3	1353	884	PITTS 8	107
2C	02/08/89	15:20	2995	2575	14.0	2500	1451	PITTS 8	107
2C	02/08/89	16:20	3618	3149	13.0	3074	1751	PITTS 8	107
2C	02/08/89	17:20	3753	3275	12.7	3200	1816	PITTS 8	107
2C	02/08/89	18:20	4114	3601	12.5	3526	1991	PITTS 8	107
2C	02/08/89	19:20	3958	3427	13.4	3352	1925	PITTS 8	107
2C	02/08/89	20:20	3909	3390	13.3	3315	1899	PITTS 8	107
2C	02/08/89	21:20	3591	2892	19.5	2817	1788	PITTS 8	107
2C	02/08/89	22:20	3624	3081	15.0	3006	1773	PITTS 8	107
2C	02/08/89	23:20	3818	3238	15.2	3163	1872	PITTS 8	107
2C	02/09/89	00:20	3589	3084	14.1	3009	1747	PITTS 8	88
2C	02/09/89	01:20	4175	3544	15.1	3469	2051	PITTS 8	88
2D	02/09/89	02:20	4257	3602	15.4	3527	2095	KY9	109
2D	02/09/89	03:20	4270	3563	16.6	3488	2112	KY9	109
2D	02/09/89	04:20	4250	3604	15.2	3529	2089	KY9	109
2D	02/09/89	05:20	4367	3916	10.3	3841	2087	KY9	109
2D	02/09/89	10:20	3651	1500	58.9	1425	1467	KY9	96
2D	02/09/89	11:20	3943	1650	58.2	1575	1609	KY9	96
2D	02/09/89	12:20	3787	1590	58.0	1515	1546	KY9	96
2D	02/09/89	13:20	3717	1552	58.2	1477	1510	KY9	96
2D	02/09/89	14:20	3946	1620	58.9	1545	1591	KY9	96
2D	02/09/89	15:20	4014	1688	57.9	1613	1644	KY9	96
2D	02/09/89	16:20	3888	3286	15.5	3211	1910	KY9	96
2D	02/09/89	17:20	4076	3184	21.9	3109	2048	KY9	96

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Table 3
MCL PRODUCT COAL DRYING

PAGE 2

RUN NO.	RUN DATE	SAMPLE TIME	PRE DRY WT. gm	POST DRY WT. gm	% MOIST. REMOVED	NET SHIP WT. gm	CALC DRY WT	TYPE COAL	SHIPPING DRUM NO
2D	02/09/89	18:20	4728	3742	20.9	3667	2378	KY9	96
2D	02/09/89	19:20	5530	4633	16.2	4558	2745	KY9	96
2D	02/09/89	20:20	3788	3191	15.8	3116	1862	KY9	96
2D	02/09/89	21:20	5122	4066	20.6	3991	2579	KY9	96
2D	02/09/89	22:20	5815	4757	18.2	4682	2912	KY9	96
2E	02/09/89	23:20	5839	5132	12.1	5057	2837	KY9	96
2E	02/10/89	00:20	5883	5258	10.6	5183	2831	KY9	96
2E	02/10/89	01:20	5266	4408	16.3	4333	2613	KY9	96
2E	02/10/89	02:20	4977	4289	13.8	4214	2437	KY9	96
2E	02/10/89	03:20	5008	4445	11.2	4370	2414	KY9	96
2E	02/10/89	04:20	4754	3862	18.8	3787	2377	KY9	96
2E	02/10/89	05:20	4889	4257	12.9	4182	2381	KY9	96
2E	02/10/89	06:20	4790	4196	12.4	4121	2324	KY9	96
2E	02/10/89	07:20	4915	4195	14.6	4120	2416	KY9	109
2E	02/10/89	08:20	5426	4563	15.9	4488	2689	KY9	109
2E	02/10/89	09:20	5681	5039	11.3	4964	2745	KY9	109
2E	02/10/89	10:20	5433	4842	10.9	4767	2616	KY9	96
2E	02/10/89	11:20	5422	4656	14.1	4581	2663	KY9	96
2E	02/10/89	12:20	5372	4742	11.7	4667	2601	KY9	98
2E	02/10/89	13:20	5347	4947	7.5	4872	2508	KY9	98
2E	02/10/89	14:20	5212	4611	11.5	4536	2519	KY9	98
2E	02/10/89	14:50	2865	2534	11.6	2459	1366	KY9	98
3B1	02/23/89	05:15	1922	1557	19.0	1482	934	PITTS 8	107
3B1	02/23/89	06:15	2145	1836	14.4	1761	1029	PITTS 8	107
3B1	02/23/89	07:15	2377	2001	15.8	1926	1152	PITTS 8	107
3B1	02/23/89	08:15					0	PITTS 8	88
3B1	02/23/89	09:15					0	PITTS 8	88
3B1	02/23/89	10:15					0	PITTS 8	88
3B1	02/23/89	11:15					0	PITTS 8	88
3B1	02/23/89	12:15					0	PITTS 8	88
3B1	02/23/89	13:15		10895		10820	4761	PITTS 8	88
3B1	02/23/89	14:15		10288		10213	4494	PITTS 8	88
3B1	02/23/89	15:15		6434		6359	2798	PITTS 8	88
3B1	02/23/89	16:15					0	PITTS 8	88
3B1	02/23/89	17:15					0	PITTS 8	88
3B1	02/23/89	18:15					0	PITTS 8	88
3B1	02/23/89	19:15					0	PITTS 8	88
3B1	02/23/89	20:15					0	PITTS 8	88

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Table 3
MCL PRODUCT COAL DRYING

PAGE 3

RUN NO.	RUN DATE	SAMPLE TIME	PRE DRY WT. gm	POST DRY WT. gm	% MOIST. REMOVED	NET SHIP WT. gm	CALC DRY WT	TYPE COAL	SHIPPING DRUM NO
3B1	02/23/89	21:15					0	PITTS 8	88
3B1	02/23/89	22:15					0	PITTS 8	88
3B1	02/23/89	23:15					0	PITTS 8	88
3B1	02/24/89	00:15					0	PITTS 8	88
3B1	02/24/89	01:15					0	PITTS 8	88
3B1	02/24/89	02:15					0	PITTS 8	88
3B1	02/24/89	03:15					0	PITTS 8	88
3B1	02/24/89	04:15					0	PITTS 8	88
3B1	02/24/89	05:15					0	PITTS 8	88
3B1	02/24/89	06:15					0	PITTS 8	88
3B1	02/24/89	07:15					0	PITTS 8	88
3B1	02/24/89	08:15					0	PITTS 8	88
3C1	02/24/89	09:15					0	PITTS 8	88
3C1	02/24/89	10:15					0	PITTS 8	88
3C1	02/24/89	11:15					0	PITTS 8	88
3C1	02/24/89	12:15					0	PITTS 8	88
3C1	02/24/89	13:15	3570	3246	9.1	3171	1683	PITTS 8	107
4C1	03/07/89	20:15	4043	3639	10.0	3564	1924	PITTS 8	120
4C1	03/07/89	21:15	4780	4359	8.8	4284	2262	PITTS 8	120
4C1	03/07/89	22:15	4370	3902	10.7	3827	2094	PITTS 8	120
4C1	03/07/89	23:15	4823	4356	9.7	4281	2298	PITTS 8	120
4C1	03/08/89	00:15	4720	4335	8.2	4260	2222	PITTS 8	120
4C1	03/08/89	01:15	4964	4527	8.8	4452	2351	PITTS 8	120
4C1	03/08/89	02:15	5223	4860	7.0	4785	2438	PITTS 8	120
4C1	03/08/89	03:15	5246	4785	8.8	4710	2486	PITTS 8	120
4C1	03/08/89	04:15	4257	3723	12.5	3648	2063	PITTS 8	120
4C1	03/08/89	05:15	5112	4528	11.4	4453	2468	PITTS 8	120
4C1	03/08/89	06:15	4624	4191	9.4	4116	2196	PITTS 8	120
7A	05/01/89	23:15	5555	4524	18.6	4449	2783	KY9	98
7A	05/02/89	00:15	4555	4124	9.5	4049	2165	KY9	98
7A	05/02/89	01:15	4476	4022	10.1	3947	2137	KY9	98
7A	05/02/89	02:15	4809	4353	9.5	4278	2288	KY9	98
7A	05/02/89	03:15	4743	4302	9.3	4227	2253	KY9	98
7A	05/02/89	04:15	4356	3945	9.4	3870	2068	KY9	98
7A	05/02/89	05:15	3898	3480	10.7	3405	1863	KY9	98
7A	05/02/89	06:15	3153	2740	13.1	2665	1522	KY9	98
7A	05/02/89	07:15	2641	2110	20.1	2035	1305	KY9	98
7A	05/02/89	08:15	2784	2302	17.3	2227	1365	KY9	98

RUN NO.	RUN DATE	SAMPLE TIME	PRE DRY WT. gm	POST DRY WT. gm	% MOIST. REMOVED	NET SHIP WT. gm	CALC DRY WT	TYPE COAL	SHIPPING DRUM NO
7A	05/02/89	09:15	3301	2977	9.8	2902	1562	KY9	98
7A	05/02/89	10:15	3386	2857	15.6	2782	1659	KY9	108
7A	05/02/89	11:15	3534	3095	12.4	3020	1704	KY9	108
7A	05/02/89	12:15	4209	3757	10.7	3682	2015	KY9	108
7A	05/02/89	13:15	5045	4222	16.3	4147	2501	KY9	108
7A	05/02/89	14:15	5560	5126	7.8	5051	2617	KY9	108
7A	05/02/89	15:15	5213	4697	9.9	4622	2491	KY9	108
7A	05/02/89	16:15	5457	4890	10.4	4815	2619	KY9	108
7A	05/02/89	17:15	6443	5917	8.2	5842	3047	KY9	108
7A	05/02/89	18:15	5674	5180	8.7	5105	2691	KY9	108
7A	05/02/89	19:15	4937	4348	11.9	4273	2390	KY9	108
7A	05/02/89	20:15	4855	4269	12.1	4194	2352	KY9	108
7A	05/02/89	21:15	4744	4321	8.9	4246	2247	KY9	108
7A	05/02/89	22:15	4939	4272	13.5	4197	2413	KY9	98
7A	05/02/89	23:15	4426	3906	11.7	3831	2136	KY9	98
7A	05/03/89	00:15	5111	4312	15.6	4237	2527	KY9	108
7A	05/03/89	01:15	4318	3920	9.2	3845	2046	KY9	108
7A	05/03/89	02:15	4287	3984	7.1	3909	1996	KY9	108
7A	05/03/89	03:15	4386	3839	12.5	3764	2126	KY9	108
7A	05/03/89	04:15	4260	3795	10.9	3720	2043	KY9	108
7A	05/03/89	05:15	4722	4347	7.9	4272	2219	KY9	108
7A	05/03/89	06:15	5046	4425	12.3	4350	2449	KY9	108
7A	05/03/89	07:15	4235	3770	11.0	3695	2032	KY9	108
7A	05/03/89	08:15	4332	3963	8.5	3888	2042	KY9	108
7A	05/03/89	09:15	3539	2953	16.6	2878	1743	KY9	109
7A	05/03/89	10:15	3389	2980	12.1	2905	1629	KY9	109
7A	05/03/89	11:15	4434	3893	12.2	3818	2146	KY9	109
7A	05/03/89	12:15	5079	4420	13.0	4345	2476	KY9	109
7A	05/03/89	13:15	4761	4171	12.4	4096	2310	KY9	109
7A	05/03/89	14:15	4955	4501	9.2	4426	2353	KY9	109
7A	05/03/89	15:15	5130	4529	11.7	4454	2482	KY9	109
7A	05/03/89	16:15	5651	4993	11.6	4918	2737	KY9	109
7A	05/03/89	17:15	5665	5083	10.3	5008	2718	KY9	109
7A	05/03/89	18:15	5531	4592	17.0	4517	2754	KY9	109
7A	05/03/89	19:15	4980	4403	11.6	4328	2406	KY9	109
7A	05/03/89	20:05	4978	4481	10.0	4406	2379	KY9	109
7A	05/03/89	21:15	4260	3595	15.6	3520	2098	KY9	108
7A	05/03/89	22:15	4050	3516	13.2	3441	1968	KY9	108

RUN NO.	RUN DATE	SAMPLE TIME	PRE DRY WT. gm	POST DRY WT. gm	% MOIST. REMOVED	NET SHIP WT. gm	CALC DRY WT	TYPE COAL	SHIPPING DRUM NO
7A	05/03/89	23:15	5309	4576	13.8	4501	2602	KY9	108
7A	05/04/89	00:15	4896	4370	10.7	4295	2351	KY9	109
7A	05/04/89	01:15	4637	4390	5.3	4315	2128	KY9	109
7A	05/04/89	02:15	4562	4208	7.8	4133	2139	KY9	109
7A	05/04/89	03:15	4429	3777	14.7	3702	2174	KY9	109
7A	05/04/89	04:15	4017	3563	11.3	3488	1929	KY9	109
7A	05/04/89	05:15	3908	3502	10.4	3427	1864	KY9	109
7A	05/04/89	06:15	3783	3171	16.2	3096	1863	KY9	109
7A	05/04/89	07:15	4118	3694	10.3	3619	1965	KY9	109
7A	05/04/89	08:15	4310	3969	7.9	3894	2021	KY9	109
7B	05/04/89	10:15	4625	4005	13.4	3930	2256	KY9	98
7B	05/04/89	11:15	4500	3910	13.1	3835	2190	KY9	98
7B	05/04/89	12:15	4010	3493	12.9	3418	1945	KY9	98
7B	05/04/89	13:15	3908	3112	20.4	3037	1955	KY9	98
7B	05/04/89	14:15	3583	3004	16.2	2929	1762	KY9	98
7B	05/04/89	15:15	3616	3001	17.0	2926	1785	KY9	98
7B	05/04/89	16:15	3515	2816	19.9	2741	1751	KY9	98
7B	05/04/89	17:15	3593	3012	16.2	2937	1767	KY9	98
7B	05/04/89	18:15	3333	2803	15.9	2728	1634	KY9	98
7C	05/04/89	20:15	3689	3041	17.6	2966	1826	PITTS 8	120
7C	05/04/89	21:15	3509	2984	15.0	2909	1715	PITTS 8	120
7C	05/04/89	22:15	3314	2867	13.5	2792	1605	PITTS 8	120
7C	05/04/89	23:15	3603	3075	14.7	3000	1760	PITTS 8	120
7C	05/05/89	00:15	3753	3199	14.8	3124	1836	PITTS 8	120
7C	05/05/89	01:15	3541	3174	10.4	3099	1685	PITTS 8	120
7C	05/05/89	02:15	2701	2372	12.2	2297	1290	PITTS 8	120
7C	05/05/89	03:15	2235	1831	18.1	1756	1090	PITTS 8	120
7C	05/05/89	04:15	1377	926	32.8	851	653	PITTS 8	120
7C	05/05/89	05:15	1517	1199	21.0	1124	730	PITTS 8	120
7C	05/05/89	06:15	1486	1129	24.0	1054	717	PITTS 8	120
7C	05/05/89	07:15	2029	1640	19.2	1565	989	PITTS 8	120
7D	05/05/89	08:15	2656	2220	16.4	2145	1296	PITTS 8	120
7D	05/05/89	09:15	2580	2048	20.6	1973	1275	PITTS 8	107
7D	05/05/89	10:15	2185	1784	18.4	1709	1066	PITTS 8	120
7D	05/05/89	11:15	1574	1223	22.3	1148	761	PITTS 8	120
7D	05/05/89	12:15	1088	791	27.3	716	510	PITTS 8	120
7D	05/05/89	13:15	1465	1167	20.3	1092	703	PITTS 8	120
7D	05/05/89	14:15	1562	1206	22.8	1131	755	PITTS 8	120

RUN NO.	RUN DATE	SAMPLE TIME	PRE DRY WT. gm	POST DRY WT. gm	% MOIST. REMOVED	NET SHIP WT. gm	CALC DRY WT	TYPE COAL	SHIPPING DRUM NO
8D1	05/17/89	23:15	4869	4230	13.1	4155	2373	PITTS 8	112
8D1	05/18/89	00:15	5445	5020	7.8	4945	2562	PITTS 8	112
8D1	05/18/89	01:15	5197	4729	9.0	4654	2467	PITTS 8	112
8D1	05/18/89	02:15	5155	4686	9.1	4611	2448	PITTS 8	112
8D1	05/18/89	03:15	5390	4989	7.4	4914	2528	PITTS 8	112
8D1	05/18/89	04:15	5374	4768	11.3	4693	2594	PITTS 8	112
8D1	05/18/89	05:15	3855	3474	9.9	3399	1831	PITTS 8	112
8D1	05/18/89	06:16	3955	3618	8.5	3543	1861	PITTS 8	112
8D1	05/18/89	07:15	3615	3155	12.7	3080	1747	PITTS 8	112
8D1	05/18/89	08:15	2696	2347	12.9	2272	1294	PITTS 8	112
8D1	05/18/89	09:15	2689	2325	13.5	2250	1295	PITTS 8	112
8D1	05/18/89	10:15	2711	2243	17.3	2168	1328	PITTS 8	112
8D1	05/18/89	11:15	2955	2558	13.4	2483	1426	PITTS 8	112
8D1	05/18/89	12:15	3766	3373	10.4	3298	1795	PITTS 8	112
8F	05/19/89	05:15	4097	3491	14.8	3416	2008	PITTS 8	120
8F	05/19/89	06:15	3344	2944	12.0	2869	1606	PITTS 8	120
8F	05/19/89	07:15	4130	3584	13.2	3509	2008	PITTS 8	120
8F	05/19/89	08:15	4014	3314	17.4	3239	1990	PITTS 8	120
8F	05/19/89	09:15	4918	4447	9.6	4372	2342	PITTS 8	120
8F	05/19/89	10:15	3115	2657	14.7	2582	1516	PITTS 8	120
8F	05/19/89	11:15	3911	3295	15.8	3220	1924	PITTS 8	120
8F	05/19/89	12:15	3548	3014	15.1	2939	1736	PITTS 8	120
8F	05/19/89	13:15	4628	4168	9.9	4093	2208	PITTS 8	120
8F	05/19/89	14:15	3469	3035	12.5	2960	1673	PITTS 8	88
8F	05/19/89	15:15	4172	3438	17.6	3363	2071	PITTS 8	88
8F	05/19/89	16:15	3365	2887	14.2	2812	1637	PITTS 8	88
8F	05/19/89	17:35	3780	3376	10.7	3301	1805	PITTS 8	88
9A	05/30/89	14:15	6740	5812	13.8	5737	3314	PITTS 8	119
9A	05/30/89	15:15	2444	1930	21.0	1855	1206	PITTS 8	119
9A	05/30/89	16:15	2039	1456	28.6	1381	1003	PITTS 8	119
9A	05/30/89	20:15	3395	2918	14.1	2843	1650	PITTS 8	119
9A	05/30/89	21:15	3483	3058	12.2	2983	1677	PITTS 8	119
9A	05/30/89	22:15	3212	2559	20.3	2484	1598	PITTS 8	119
9A	05/30/89	23:15	4086	3551	13.1	3476	1985	PITTS 8	119
9A	05/31/89	00:15	4027	3567	11.4	3492	1935	PITTS 8	119
9A	05/31/89	01:15	3901	3354	14.0	3279	1903	PITTS 8	112
9A	05/31/89	02:15	3934	3443	12.5	3368	1902	PITTS 8	112
9A1	05/31/89	03:15	3558	2871	19.3	2796	1770	PITTS 8	112

RUN NO.	RUN DATE	SAMPLE TIME	PRE DRY WT. gm	POST DRY WT. gm	% MOIST. REMOVED	NET SHIP WT. gm	CALC DRY WT	TYPE COAL	SHIPPING DRUM NO
9A1	05/31/89	04:15	3865	3330	13.8	3255	1883	PITTS 8	112
9A1	05/31/89	05:15	3514	3044	13.4	2969	1703	PITTS 8	112
9A1	05/31/89	06:15	4651	4037	13.2	3962	2266	PITTS 8	112
9A1	05/31/89	07:15	4554	4027	11.6	3952	2196	PITTS 8	112
9A1	05/31/89	08:15	5094	4666	8.4	4591	2406	PITTS 8	112
9A1	05/31/89	09:15	3661	2863	21.8	2788	1834	PITTS 8	88
9A1	05/31/89	10:15	3121	2417	22.6	2342	1559	PITTS 8	88
9A1	05/31/89	11:15	2932	2237	23.7	2162	1464	PITTS 8	88
9A1	05/31/89	12:15	2556	1819	28.8	1744	1270	PITTS 8	88
9B	05/31/89	14:15	2877	2501	13.1	2426	1384	PITTS 8	116
9B	05/31/89	15:15	3446	2970	13.8	2895	1674	PITTS 8	116
9B	05/31/89	16:15	3393	2871	15.4	2796	1660	PITTS 8	116
9B	05/31/89	17:15	3187	2826	11.3	2751	1522	PITTS 8	116
9B	05/31/89	18:15	2409	2047	15.0	1972	1164	PITTS 8	116
9B	05/31/89	19:15	2472	2112	14.6	2037	1193	PITTS 8	116
9B	05/31/89	20:15	2576	2057	20.1	1982	1271	PITTS 8	107
9B	05/31/89	21:15	3158	2720	13.9	2645	1531	PITTS 8	116
9B	05/31/89	22:15	3265	2865	12.3	2790	1569	PITTS 8	116
9C	06/01/89	00:15	3906	3403	12.9	3328	1893	PITTS 8	116
9C	06/01/89	01:15	4407	3911	11.3	3836	2120	PITTS 8	116
9C	06/01/89	02:15	4188	3520	16.0	3445	2065	PITTS 8	116
9C	06/01/89	03:15	4317	3803	11.9	3728	2084	PITTS 8	116
9C	06/01/89	04:15	3912	3408	12.9	3333	1896	PITTS 8	116
9C	06/01/89	05:15	3843	3296	14.2	3221	1876	PITTS 8	116
9C	06/01/89	06:15	3057	2635	13.8	2560	1480	PITTS 8	116
9C	06/01/89	07:15	3454	3054	11.6	2979	1656	PITTS 8	116
9C	06/01/89	08:15	3142	2633	16.2	2558	1540	PITTS 8	116
9C	06/01/89	09:15	3656	3196	12.6	3121	1766	PITTS 8	116
9C	06/01/89	10:15	3743	3400	9.2	3325	1768	PITTS 8	116
9C	06/01/89	11:15	3850	3337	13.3	3262	1870	PITTS 8	116
9C	06/01/89	12:15	3361	2956	12.0	2881	1615	PITTS 8	116
9C	06/01/89	13:15	3407	2979	12.6	2904	1643	PITTS 8	116
9C	06/01/89	14:15	3430	2908	15.2	2833	1678	PITTS 8	116
9C	06/01/89	15:15	3752	3223	14.1	3148	1829	PITTS 8	116
9C	06/01/89	16:15	3776	3059	19.0	2984	1880	PITTS 8	116
9C	06/01/89	17:15	3525	3043	13.7	2968	1712	PITTS 8	116
9C	06/01/89	18:15	3626	3134	13.6	3059	1761	PITTS 8	116
9C	06/01/89	19:15	3128	2626	16.0	2551	1532	PITTS 8	116

09-Nov-89

Table 3
MCL PRODUCT COAL DRYING

PAGE 8

RUN NO.	RUN DATE	SAMPLE TIME	PRE DRY WT. gm	POST DRY WT. gm	% MOIST. REMOVED	NET SHIP WT. gm	CALC DRY WT	TYPE COAL	SHIPPING DRUM NO
9C	06/01/89	20:15	2806	2303	17.9	2228	1380	PITTS 8	116
9C	06/01/89	21:15	3415	2930	14.2	2855	1662	PITTS 8	116
9C	06/01/89	22:15	3883	3166	18.5	3091	1931	PITTS 8	116
9C	06/01/89	23:15	3756	3316	11.7	3241	1806	PITTS 8	116
9C	06/02/89	00:15	4083	3702	9.3	3627	1934	PITTS 8	116
9C	06/02/89	01:15	4056	3447	15.0	3372	1990	PITTS 8	119
9C	06/02/89	02:15	3887	3418	12.1	3343	1874	PITTS 8	119
9C	06/02/89	03:15	3379	2682	20.6	2607	1685	PITTS 8	119
9C	06/02/89	04:15	3637	3200	12.0	3125	1750	PITTS 8	119
9C	06/02/89	05:15	3728	3275	12.2	3200	1797	PITTS 8	119
9C	06/02/89	06:15	3540	3009	15.0	2934	1731	PITTS 8	119
9C	06/02/89	07:15	3861	3292	14.7	3217	1890	PITTS 8	119
9C	06/02/89	08:15	3156	2769	12.3	2694	1516	PITTS 8	119
9C	06/02/89	09:15	3334	2759	17.2	2684	1644	PITTS 8	119
9C	06/02/89	10:15	3764	3298	12.4	3223	1817	PITTS 8	119
9C	06/02/89	11:15	4177	3709	11.2	3634	2006	PITTS 8	119
9C	06/02/89	12:15	4083	3741	8.4	3666	1920	PITTS 8	119
9C	06/02/89	13:15	3787	3357	11.4	3282	1817	PITTS 8	119
9C	06/02/89	14:15	3813	3211	15.8	3136	1875	PITTS 8	119
9C	06/02/89	15:15	3213	2845	11.5	2770	1536	PITTS 8	119
9C	06/02/89	16:15	3463	3074	11.2	2999	1656	PITTS 8	119
9C	06/02/89	17:15	3155	2666	15.5	2591	1542	PITTS 8	119
9C	06/02/89	18:15	2587	2191	15.3	2116	1255	PITTS 8	119

Table 4. MCL Product Coal Summary

SHIP DRUM NO.	TYPE COAL	NET SHIP WT LBS
096	KY9	176.5
098	KY9	200.8
108	KY9	218.1
109	KY9	247.0
107	PITTS 8	173.9
112	PITTS 8	173.4
116	PITTS 8	214.7
119	PITTS 8	173.8
120	PITTS 8	244.9

TOTAL SHIP WT KY9	842.4
TOTAL SHIP WT PITTS 8	980.7

TOTAL DRY WT KY 9	486.0
TOTAL DRY WT PITTS	631.0

Table 5. Quality of Coal Product from Shakedown Test

SHAKEDOWN TEST - INTEGRATED TEST CIRCUIT PITTSBURGH NO. 8 COAL

14m x 0 with 1:1 Caustic (KOH/NaOH), approx reaction time of 2 hrs

DATE	TIME	LOCTN	% MOISTURE	% VOLATILES	% ASH	% S	Btu/lb*	% Change** VOLATILES	SO2/ MMBtu	SO2 Rem fr ROM,%	SO2 Rem fr feed,%	Ash Rem,%
Run of Mine Coal									11.10			
Feed Coal			2.82	38.6	11.57	4.27	13016		6.55			
12-15	2330	Plntexit	36.04	40.11	1.96	2.43	14376	-6.27	3.38	69.57	48.48	83.06
12-15	2400	Plntexit	34.55	40.47	1.79	2.40	14401	-5.60	3.33	70.00	49.20	84.53
12-16	0030	Plntexit	35.16	40.91	1.74	2.42	14408	-4.62	3.36	69.77	48.80	84.96
12-16	0115	Plntexit	33.85	40.84	1.74	2.41	14408	-4.78	3.34	69.89	49.01	84.96
12-16	0200	Plntexit	33.59	40.19	1.82	2.44	14397	-6.22	3.39	69.49	48.34	84.27
12-16	0330	Plntexit	34.14	39.31	1.86	2.42	14391	-8.24	3.36	69.73	48.74	83.92
12-16	0400	Plntexit	25.86	41.20	2.24	2.37	14335	-3.45	3.30	70.24	49.60	80.64
12-16	0500	Plntexit	19.74	41.72	2.71	2.39	14266	-1.76	3.35	69.84	48.93	76.58
12-16	0600	Plntexit	19.74	41.59	2.67	2.52	14272	-2.11	3.53	68.22	46.18	76.92
12-16	0630	Plntexit	19.39	41.97	2.92	2.52	14235	-0.96	3.54	68.13	46.04	74.76
12-16	0700	Plntexit	17.82	40.15	3.06	2.57	14215	-5.12	3.61	67.46	44.89	73.55
12-16	0730	Plntexit	21.26	40.38	2.72	2.51	14265	-4.91	3.52	68.33	46.36	76.49
12-16	0800	Plntexit	19.15	42.40	2.69	2.56	14269	-0.18	3.58	67.71	45.31	76.75
12-16	0830	Plntexit	14.92	41.96	3.27	2.59	14184	-0.62	3.65	67.13	44.34	71.74
12-16	0850	Plntexit	20.91	41.13	2.93	2.56	14234	-2.93	3.59	67.63	45.18	74.68
12-16	0930	Plntexit	19.25	39.37	3.11	2.56	14207	-6.91	3.60	67.57	45.07	73.12
12-16	1030	Plntexit	11.43	40.14	4.19	2.72	14049	-4.02	3.87	65.15	40.98	63.79
12-16	1130	Plntexit	17.58	41.53	3.13	2.55	14205	-1.78	3.59	67.69	45.28	72.95
12-16	1230	Plntexit	22.15	40.24	3.25	2.57	14187	-4.72	3.62	67.39	44.78	71.91
12-16	1430	Plntexit	18.99	41.10	3.72	2.62	14118	-2.20	3.71	66.60	43.43	67.85
12-16	1600	Plntexit	10.69	40.65	4.54	2.71	13998	-2.44	3.87	65.15	40.99	60.76
Averages			23.15	40.83	2.76	2.52	14258	-3.80	3.53	68.22	46.19	76.10

* Heat content based on 14664 Btu/lb (MAF) determined from 2 samples, and recalculated to MF basis for individual samples.

** % change in volatiles is on MAF coal basis.

Figure 2. Correlation Between Product Coal Sulfur and Ash Content

with a correlation coefficient of 0.923. This good correlation indicates that the operating conditions that favor sulfur removal also facilitate ash removal.

In addition to analysis of total sulfur, two coal product samples were also analyzed for sulfur forms. The sulfur forms for these two samples are compared with those for the feed coal as follows, all on dry basis:

<u>Sample</u>	<u>% Pyritic S</u>	<u>% Sulfate S</u>	<u>% Organic S</u>
Feed	1.69	0.04	2.54
No. 1	0.20	0.02	2.15
No. 2	0.85	0.02	1.43

The sulfur forms analysis results show that under the mild operating temperatures, insoluble sulfate is not formed in the MCL process, and that some removal of organic sulfur takes place before the complete removal of pyritic sulfur. The two coal product samples were taken from two time periods (1 hour and 15 minutes apart) with the same operating conditions. The difference in the pyritic and organic sulfur contents for these two samples was probably caused by the difference in local operating parameters. For example, Sample No.1 might be processed with a higher local caustic/coal ratio and shorter residence time as compared to Sample No. 2.

The heating values of the coal product samples in Table 5 were computed based on the 14664 Btu/lb (MAF basis) determined from the analysis of two samples, and the ash content of the individual coal product samples. On a MAF basis, the heating value of the feed coal is 14719 Btu/lb. Thus, there is only 0.37% loss in heating value from MCL processing.

The average volatile content of the coal product was 40.83% on dry basis, or 41.99% on MAF basis. The volatile content of the feed coal is 38.6% on dry basis, or 43.65% on MAF basis. The average loss in volatiles is therefore only 1.66%, or 3.8% relative to the feed coal.

The moisture content of the coal product was very low, ranging from 10.69% to 36.04%. The average moisture content was 23.15%. This low moisture content was the result of the mild operating conditions in the shakedown test. As shown in Figure 3, there is good correlation between the moisture content and ash content of the coal product:

$$\% \text{ moisture} = 48.975 - 9.34 \% \text{ ash}$$

with a correlation coefficient of -0.920. This good correlation suggests that the mild operating conditions which lead to more modest ash removal would also lead to lower moisture content for the coal product, probably because the resulting product would be associated with fairly low porosity and surface area. The moisture content can also be correlated with

Figure 3. Relationship Between Product Coal Moisture Content and Ash Content

particle size of the coal product. As shown in Figure 4, the moisture content of the coal product increases with increasing percentage of coal product passing through 200 mesh, because the greater surface area of the finer coal particles would lead to higher moisture retention.

The changes in the carbon, hydrogen, nitrogen and oxygen content of coal after MCL processing are presented in Table 6 on moisture-, ash- and sulfur-free (MASF) basis. For comparison, the analysis results from the two operational runs conducted in 1986 for Pittsburgh No. 8 are also included in this table. These results show that under the mild operating conditions of the shakedown test, there were only small changes in the elemental makeup of the MCL coal from the feed coal, and the hydrogen loss was only about 0.6%. For Runs 1 and 6 conducted in 1986, the changes in the hydrogen and oxygen content of the product coal were significantly greater.

4.3.2 Carbonate Formation

Carbonate is formed by the reaction of molten caustic with coal carbon in the presence of oxygen. During the shakedown run, selected kiln discharge (KD) samples and spent caustic solution (C-201 centrate) samples were collected and analyzed for carbonate and caustic compositions. These composition data were used to compute the fraction of caustic converted to carbonate, as well as the fraction of coal or coal carbon converted to carbonate. The computations were based on the following equations:

$\text{KOH} + \text{NaOH feed} = \text{KOH} + \text{NaOH in product} + \text{KOH} + \text{NaOH used for sulfur and ash removal}$

$\text{Carbonate formed} = \text{K}_2\text{CO}_3 + \text{Na}_2\text{CO}_3 \text{ in product} - \text{K}_2\text{CO}_3 + \text{Na}_2\text{CO}_3 \text{ in caustic feed}$

For 50:50 KOH/NaOH feed, 1 lb of KOH+NaOH converted to carbonate would result in 1.2783 lb of potassium and sodium carbonate. Therefore,

$$\% \text{ of caustic converted to carbonate} = \frac{100 \times \text{carbonate formed}}{1.2783 \times \text{KOH} + \text{NaOH feed}}$$

In reducing the data, the following compositions of the solid caustic mixture were used: 92.42% sodium and potassium hydroxide, 3.37% sodium and potassium carbonate, and 4.21% water. These are the average compositions of the mixed caustic fed to the rotary kiln, as determined from the analysis of nine samples.

It was also assumed that the carbon in the carbonate formed was derived from the carbon in the coal feed. For 50:50 KOH/NaOH feed, 1 lb of KOH+NaOH reacts with 0.25718 lb of coal carbon to form carbonate. Since the caustic feed contains only 92.42% sodium and potassium hydroxide and only part of this hydroxide is converted to carbonate, the percentage of coal feed converted to carbonate was calculated as follows:

Figure 4. Relationship Between Product Coal Moisture Content and Particle Size

Table 6. Carbon, Hydrogen, Nitrogen and Oxygen Content Change

Sample	Carbon (MASF)		Hydrogen (MASF)		Nitrogen (MASF)		Oxygen (MASF)	
	%, w/w	% Change	%, w/w	% Change	%, w/w	% Change	%, w/w	% Change
Feed	85.46	-	6.17	-	1.57	-	6.80	-
No.1	85.63	0.17	5.56	0.61	1.46	0.11	7.35	0.55
No.2	85.32	0.14	5.51	0.66	1.45	0.12	7.72	0.92
Run 1*	81.68	3.78	4.74	1.43	1.51	0.06	11.27	4.47
Run 6*	81.43	4.03	3.05	3.12	2.73	1.16	12.45	5.65

 * Runs 1 and 6 were tests conducted in 1986. The reaction temperatures for Runs 1 and 6 were 320°C and 400°C, respectively.

$$\% \text{ coal converted to carbonate} = \frac{0.25718 \times 92.42 \times \text{carbonate formed}}{1.2783 \times \text{KOH+NaOH feed}}$$

In Table 7, data on carbonate formation from 4 KD samples and 4 C-201 centrate samples are presented. For the KD samples, the average conversion of caustic to carbonate was 5.01%, which corresponds to an average conversion of 1.19% of the feed coal to carbonate. For the C-201 centrate samples, data from one non-representative sample were not used in computing average values. On this basis, the average conversion of caustic to carbonate was 5.05%, which also corresponds to an average conversion of 1.20% of the feed coal to carbonate. Therefore, the KD and the spent caustic samples both indicate identical, low conversions of caustic and coal carbon to carbonate.

The low conversions of caustic and coal carbon to carbonate was due to the relatively low operating temperatures in the rotary kiln. In addition, operating with a low caustic/coal ratio of 1.0 might also lead to low conversion to carbonates.

4.3.3 Humic Acid

Humic acid analysis was performed on two of the liquid samples collected during the shakedown test. The concentration of humic acid in the C-301 (the first centrifuge in the acid wash section) centrate sample was 0.26 mg/g, which corresponds to 0.35% of the feed coal converted to humic acid. For the caustic regenerator effluent sample, the humic acid concentration was determined to be 3.1 mg/g, which corresponds to 4.1% of the feed coal converted to humic acid. These data show that most of the humic acid would be found in the spent caustic and not in the acid wash. The total 4.5% conversion of feed coal to humic acid is indicative of the mild kiln operating temperatures during the shakedown run. Humics formation is known to decrease with increasing temperature. It is thought that the humics, which are polycarboxy organics, dissolved in the caustic even under mild conditions used in shakedown. Under more severe operating conditions, the humics would decarboxylate to insoluble coal-like particles and exit the plant as coal product.

4.3.4 Particle Size Distribution

Particle size distribution data for the feed coal and processed coal are presented in Table 8. Representative data from Table 7 are plotted in Figure 5 to provide better illustration of the effects of MCL processing on coal particle size. The data plotted are derived from the experimental data, assuming that the coal particles follow a logarithmic-probability distribution of the form:

$$\text{Cumulative \% by Weight Undersize} = 50 [1 + \text{erf}(\log (X/X')/s)]$$

Table 7. Carbonate Formation

<u>Sample</u>	<u>Date/Time</u>	<u>% Hydroxide</u>	<u>% Carbonate</u>	<u>% Caustic to Carbonate</u>	<u>% Coal to Carbonate</u>
KD	1212/1640	44.09	7.74	7.93	1.885
KD	1213/1530	40.57	1.98	0.52	0.124
KD	1215/0130	50.58	4.27	2.74	0.651
KD	1215/0215	36.87	7.10	8.83	2.099
			Mean	5.01	1.190
			Std Dev.	4.02	0.955
C-201	1215/0400	7.60	0.85	4.38	1.041
C-201	1215/0700	2.39	0.25	3.95	0.939
C-201	1216/0700	0.30	0.13	19.63	4.666
C-201	1216/1229	11.18	1.73	6.81	1.619
			Mean*	5.05	1.200
			Std Dev.	1.54	0.367

* The C-201, 1216/0700 sample contained unusually low hydroxide concentration, and was not representative of the shakedown operation. Small variations in this concentration could lead to large changes in computed carbonate conversion values. Therefore, data from this sample were not used in computing the mean carbonate conversion.

Table 8. Coal Particle Size Distribution

Sample	Date/Time	Cumulative % Retained on Screen*					Pan 0
		40 mesh 0.425mm	60 mesh 0.250mm	80 mesh 0.180mm	100 mesh 0.150mm	200 mesh 0.075mm	
Feed	1212	47.0	64.0	71.4	75.2	85.3	100
KD	1214/0130	37.9	56.0	63.8	68.1	80.3	100
KD	1214/0830	39.7	56.7	63.8	68.1	79.7	100
T-101	1214/0805	8.5	33.0	47.1	55.7	77.1	100
C-201	1214/0550	19.5	41.4	53.3	60.0	75.9	100
C-201	1214/0805	13.9	35.3	50.3	58.8	80.4	100
C-201	1214/0815	28.9	53.6	65.9	72.5	87.6	100
CP	1216/0115	1.5	2.3	3.3	5.0	12.2	100
CP	1216/0200	1.0	2.1	3.3	6.2	16.0	100
CP	1216/0400	1.3	2.1	3.3	4.8	20.5	100
CP	1216/0700	1.8	9.4	19.9	28.3	56.7	100
CP	1216/1130	1.3	6.1	12.9	18.7	44.3	100
CP	1216/1600	3.7	19.6	40.4	54.7	85.3	100

* The screen sizes are given in both mesh size (40 mesh to pan) and in the size of the corresponding screen opening (0.425 mm to zero).

Figure 5. Particle Size Distribution for Feed Coal and Coal Product

where X = particle size, X' = parameter with dimension of size, s = standard deviation parameter, and erf = normal probability function or error function. The parameters X' and s were determined from linear regression of the experimental data. In all cases, it was found that the experimental data can be well represented by the logarithmic-probability function. This indicates that the logarithm of the coal particle size is normally distributed.

The data presented in Table 8 and Figure 5 show that there is little or no size reduction for the coal particles after processing in the rotary kiln, based on examination of the kiln discharge (KD) coal particle size data. However, there is significant size reduction for the coal particles from the downstream operations, including: the dissolver loop pump around and initial centrifuge, as indicated by the T-101 (dissolver tank) data and C-201 (first centrifuge in caustic wash section) data; and subsequent washing, centrifuge and pump around, as indicated by the coal product (CP) data.

The C-201 data show that in the dissolver loop pump around and after the first centrifuge, only the larger coal particles have been reduced in size, and there is no significant size reduction for coal particles less than 0.075 mm (200 mesh). About 47% of the feed coal particles were greater than 0.425 mm (40 mesh). By comparison, only 13.9 to 28.9% of the C-201 coal particles were greater than this size.

The washing, centrifuge and pump around operations downstream of C-201 appear to further reduce the size of coal particles in all size ranges, as illustrated in Figure 5. In the C-201 coal product, only about 20% of the coal particles were smaller than 0.075 mm (200 mesh). In the final coal product, an average of 61% of the coal particles were smaller than this size, and an average of only 1.8% of the coal particles were greater than 0.425 mm (40 mesh).

With the additional operation of the two vacuum filters to remove most of the spent caustic from MCL coal before centrifuge separation, it may be possible to lessen coal particle size reduction by reducing the number of centrifuge stages, or by reducing centrifuge speed and minimizing shear generated in pump around loops and stirring of the coal slurry.

4.3.5 Process Liquid Analysis

Three liquid samples were collected on 12/16/1988, 12:40 and analyzed to determine the partition of aluminum, silicon, iron, sodium and potassium in the wash sections. These liquid samples included an effluent sample from the caustic regenerator (T-401), a centrate sample from the first centrifuge in the acid wash section (C-301), and an effluent sample from the lime contactor (T-602). The analysis results for these samples are presented in the following table, along with computed concentration

levels in the spent caustic, assuming that all the mineral matter removed (an average of 76.1%) are in solution:

<u>Sample</u>	<u>Al(mg/L)</u>	<u>Si(mg/L)</u>	<u>Fe(mg/L)</u>	<u>Na(mg/L)</u>	<u>K(mg/L)</u>	<u>pH</u>
T-401 Effluent	2090	3190	1100	No Data	No Data	12.9
C-301 Centrate	14	<20	160	21.1	4.2	1.7
T-602 Effluent	<3	<3	<0.2	17.8	3.3	No Data
Spent Caustic (Computed)	707	1261	1233	20647	25033	---

These analysis results show that almost all the aluminum and silicon in the coal feed were found in the caustic regenerator effluent. For this shakedown run, only about 13% of the iron in the coal feed was partitioned to the acid wash section. This result is atypical of the findings from later operational runs, where most of the iron was found in the acid wash section.

The sodium and potassium concentrations in the C-301 centrate totaled 25.3 mg/L, as compared to 45680 mg/L estimated for the spent caustic. This indicates that most of the caustic was effectively removed from the coal product in the caustic wash section. This also implies that the estimated caustic loss through the acid wash section would be only $25.3/45680$, or 0.055% of the input caustic. The final coal product contained an average of 23.15% moisture. Using this moisture content and the 25.3 mg/L alkali concentration in the C-301 centrate, it is estimated that the final coal product would only contain $25.3 \times 0.2315 = 5.9$ ppm alkali from the MCL process.

The T-601 effluent data show that lime treatment of the waste water from acid wash would effect almost total removal of the iron, but little or no additional removal of sodium and potassium salts. The treated water also contained very low levels of aluminum and silicon, and may be suitable for recycle as wash water.

The flow rates for the T-401 effluent, C-301 centrate, and the spent caustic stream were all the same, and constituents of the spent caustic were essentially split between the T-401 effluent and C-301 centrate. Therefore, the total concentrations of a constituent in the T-401 effluent and the C-301 centrate should be equal to its estimated concentration in the spent caustic. Comparison of the process liquid and estimated spent caustic concentrations show that there is excellent agreement between the measured and computed iron concentrations. The total measured iron concentration is 1260 mg/L versus the computed iron concentration of 1233 mg/L in the spent caustic. The total measured concentration levels of aluminum and silicon, however, are each about 2.5 to 3.0 times higher than the corresponding computed concentration values. This could be the result

of inadequate mixing in the caustic regenerator during the shakedown test, so that the measured aluminum and silicon concentrations in the T-401 effluent sample were not representative.

4.3.6 Wash Train Performance

The wash train during the shakedown test includes 5 centrifuge stages in the caustic wash section and 3 centrifuge stages in the acid wash section. The performance of the centrifuges can be evaluated from measurements of coal particles in the centrates and cake moisture in the coal product. The effectiveness of the wash train can be determined from measurements of alkalinity and pH as the washing progresses downstream.

The average pH, coal particle concentration, and the concentrations of sodium and potassium hydroxide and sodium and potassium carbonate in the centrate (C) and centrifuge feed slurry (S) at various centrifuge stages are presented in Table 9. As expected, the pH in both the centrate and the slurry decreased from C-201 to C-205, as washing progressed in the caustic wash section. In the acid wash section, the pH in both the centrate and the slurry increased from C-301 (where sulfuric acid solution is separated) to C-303 (where the fresh water is separated), again as expected. The pH in the centrate from C-303 was almost neutral. Similarly, Table 9 also shows the general decrease in both hydroxide and carbonate concentrations from C-201 to C-205. The hydroxide concentration decreased from 5.60% in the C-201 centrate to 6.7 ppm in the C-205 centrate. In Figure 6, the hydroxide and carbonate concentration is plotted against the pH for the caustic wash water. The plot shows that there is good correlation between alkalinity concentration and pH. Both the measured alkalinity concentration (sum of the hydroxide and carbonate concentrations) and the pH suggest the effectiveness of the wash stations in removing caustic from coal in the caustic wash section, and in removing acid from coal in the acid wash section.

Except in the C-201 centrate, the concentrations of coal particles in the centrifuge centrates were very low. Separation in the first centrifuge was not as good because of the smaller density difference between the concentrated caustic solution and the coal product. With the additional operation of the two vacuum filters, the caustic concentration in the first centrifuge will be significantly lower and separation in this centrifuge is expected to improve accordingly. The average concentration of coal particles in the C-202 to C-205 centrate was 0.038%, as compared to the average coal particle concentration of 1.42% in the C-202 to C-205 slurry. For the acid wash section, the average concentration of coal particles in the centrates was 0.035%, as compared to the average coal particle concentration of 1.80% in the slurry. Thus, these centrifuges performed well and showed good separation. In addition, the average cake moisture of only 23.15% in the final coal product is also an indication of the good performance of the centrifuges in removing liquid from the solid product.

Table 9. Centrifuge Centrate and Slurry Characteristics

<u>Sample</u>	<u>pH</u>	<u>% Coal</u>	<u>% NaOH+KOH</u>	<u>% Na₂CO₃+K₂CO₃</u>
C-201/C	14.0	0.38	5.60	0.73
C-202/C	11.5	0.01	0.073	0.032
C-203/C	11.0	0.081	0.13	0.21
C-204/C	10.8	0.022	0.031	0.093
C-205/C	10.0	0.038	0.00067	0.042
C-201/S	13.8	1.93	3.09	0.54
C-202/S	12.3	2.62	0.31	0.057
C-203/S	11.0	1.45	0.062	0.33
C-204/S	10.6	0.33	0.029	0.097
C-205/S	9.7	1.26	0.032	0.029
C-301/C	1.7	0.04	--	--
C-302/C	4.9	0.05	--	--
C-303/C	6.7	0.015	--	--
C-301/C	2.1	1.78	--	--
C-302/C	3.4	2.09	--	--
C-303/C	6.4	1.52	--	--

 * C indicates centrate and S indicates slurry

Figure 6. Relationship Between Alkalinity Concentration and pH in Caustic Wash Water

Excellent liquid removal was attained even for C-201, where the moisture to coal ratio in the two cake samples collected was only 0.51 and 0.96. The moisture content of this coal cake was significantly lower than the expected 2:1 moisture to coal ratio for the coal cake exiting the caustic wash section, and even lower than the expected 1:1 moisture to coal ratio for the final washed coal product.

5. PLANNED ACTIVITIES

During the next quarter, the process wastes will be disposed of. Data assessment will continue, topical reports will be prepared for test planning, shakedown and operation, and the draft final report will be completed.