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Hydrothermal Pretreatment of Coal before Molten Caustic Leaching

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ABSTRACT

A hydrothermal pretreatment of coal samples before caustic leaching results in efficient sulfur removal using reduced amounts of caustic and to recovery of a higher fraction of the energy content of the feed coal than caustic leaching without the pretreatment. Pretreating an Illinois No. 6 coal with boiling water followed by a float-sink separation using 50% aqueous NaOH as the heavy medium, and then leaching the floated coal with only the caustic adhering to the float portion (less than 1 part caustic to 1 part water to 1 part coal) at 390°C for 15 minutes led to the same residual levels of sulfur in the cleaned coal (0.5%) as was obtained performing the float-sink procedure and leaching procedures on a non-prewashed coal using 2.4 parts caustic to 1 part coal. When prewashed Illinois No. 6 coal was leached with lesser amounts of caustic, the energy recoveries in the cleaned coal were about 5-10% higher than when non-prewashed coal was leached with the larger amounts of caustic.

1. BACKGROUND

During the molten caustic leaching (MCL) of coal, caustic reacts with inorganic species and organosulfur compounds present in coal to form water-soluble alkali metal salts [1-4]. Subsequent washings of the resulting coal-caustic cakes with water and dilute acid leads to recovery of a very low-sulfur, low-ash coal product and to recovery of a spent caustic solution from which caustic for use in treating additional coal can be recovered [5-6]. MCL conditions such as the use of 2 parts caustic to 1 part coal, leaching temperatures of about 390°C, and reaction intervals of 2-3 hours have been shown to be effective for removing over 90% of the ash and sulfur from coal. Despite the technical success of MCL, use of large amounts of expensive reagents such as NaOH and severe conditions lead to high costs [7].

Previous work at the Ames Laboratory has led to more economical MCL conditions. For example, it has been shown that for many coals, sulfur can be removed using NaOH alone as a leachant rather than more expensive NaOH-KOH mixtures [8]; and that leaching in two stages, 250°C for 1 hour followed by 390°C for a few seconds, leads to as efficient of sulfur removals as leaching for several

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hours at a high temperature [9]. And, a combination float-sink-leaching process (FLP) developed at the Ames Laboratory requires the use of far lower amounts of NaOH, and significantly less severe leaching conditions than used in MCL [10]. In the FLP, 50% aqueous NaOH solutions are used as the heavy medium for float-sink separation of coal, the float fraction and only the aqueous caustic adhering to it are then heated to 390°C, and as soon as that temperature is reached, the reaction is terminated, the coal-caustic cake is washed with water, and the recovered aqueous caustic is reused without treatment for leaching additional coal samples.

The more difficult step in the mechanism of removal of sulfur by any caustic leaching procedure appears to be gaining access to sulfur groups. During the 2-stage leaching procedure, improved access results from partially disrupting the coal structure. In the companion studies to the current work [11], the literature was evaluated in an attempt to identify potentially more economical procedures for disrupting coal structures. Exploratory studies were performed in an effort to determine if identified conditions or reagents actually had the potential for more economical desulfurization of coal samples. The most economical of the identified procedures proved to be hydrothermal pretreatment, which involves prewashing coal with boiling water. In the current work this procedure was studied.

2. EXPERIMENTAL

2.1 Feed Coals

The properties of feed coals studied are given in Table 1. The 1186 coal was obtained from the Monterrey Mine in southern Illinois in November of 1986. This coal was prewashed at the mine. The IBC 101 coal was obtained from the Illinois State Geological Survey.

Table 1
Analyses of Illinois No. 6 Feed Coal Samples (moisture-free basis)

Coal	Sulfur, %				SO ₂	Ash	Heat	Moisture
	Total	Organic	Pyrite	Sulfate	lb/MMBtu	%	Btu/lb	%
1186	3.76	2.66	0.55	0.55	6.27	10.7	11,996	9.3
IBC 101	4.51	3.35	1.14	0.02	7.15	10.2	12,615	15.3

2.2 Float-Sink Procedure

Two similar procedures were used for performing float-sink separations. In the first of these, 12.5 g samples of Illinois No. 6 coal were placed in centrifuge tubes, 40 ml (60 g) of 50% NaOH solution was added, and the mixture was shaken until the coal was wet with the caustic solution. Sets of four tubes were then centrifuged at 2000 rpm for 10 minutes. The float portions were removed from the tube and

Figure 1.
Reactor used for leaching coal.

placed in an Inconel reaction crucible (Figure 1). The liquid middle layers (middlings), which contained some dispersed coal, were also added to the same crucible. And, the sink portions were washed from the bottom of the centrifuge tubes onto a filter paper in a Buchner funnel, washed with water, dried, weighed, and retained for analysis. In some tests, the mixture of coal and 50% caustic in the centrifuge tube was sonicated for 5 minutes before centrifugation. In other instances, a wetting agent (Mazowet DF, PPG Mazer Chemical) was added to the coal in each tube just before the caustic was introduced. In some instances small aliquots of the floated coal and middlings fractions were titrated potentiometrically to determine the caustic content, and other aliquots were analyzed for sulfate by ion chromatography. In the second float-sink separation procedure, 100 g of coal was mixed with 500 g of 50% NaOH, and the resulting slurry was divided among four large centrifuge tubes. The mixture was then separated and processed as described above.

2.3 Single-Stage Leaching Procedure

Mixtures of coal and aqueous caustic middlings were placed in an Inconel crucible, a thermocouple was immersed into the coal-caustic mixture,

a purge line was installed above the levels of coal-caustic, the crucible was sealed, and a nitrogen purge was commenced at a flow rate of 30 ml/min at atmospheric pressure. The nitrogen purge was maintained throughout the run. After 5 minutes of purging, the sealed crucible was placed in a preheated vertical tube furnace. The temperature of the coal-caustic was monitored until a temperature of 390°C was reached, and that temperature was maintained for an interval ranging from zero minutes to 1 hour. The still-sealed crucible was then removed from the furnace and immersed in a vat of chilled water. The temperature of the coal-caustic was monitored until it cooled to below 50°C.

2.4 Two-Stage Leaching Procedure

The same procedure was used as for single-stage leaching except that the coal-caustic mixture was heated to 250°C, that temperature was maintained for 1 hour, the temperature was then increased to 390°C, and the crucible was removed from the reactor as soon as the coal-caustic mixture reached 390°C.

2.5 Processing of Leached Coal

After the coal-caustic mixtures had cooled to below 50°C, the nitrogen purge was discontinued, the crucible was opened, and the bulk of the coal-caustic cake was removed and placed in a 1000-ml beaker. The residual coal-caustic mixture adhering to the sides and bottom of the crucible was removed by repeated washings with boiling water. These washings were combined with the coal-caustic cake in the beaker. The volume of water was adjusted to about 500 ml, the resulting slurry of coal-caustic was stirred and heated to near boiling for 5 minutes, and it was then vacuum-filtered through Whatman No. 41 filter paper in a Buchner funnel. The coal was washed on the filter with an additional 500 ml of boiling water. The recovered coal was then removed from the filter, slurried with 500 ml of 10% hydrochloric acid, and the mixture heated and stirred for 5 minutes. The acid-washed coal was then vacuum-filtered using Whatman No. 41 filter paper and washed on the filter with an additional 500 ml of boiling water.

2.6 Cleaned Coal Products

The cleaned coal was placed on a watch glass and dried at 100°C overnight. The recovered coal was then weighed and ground to <60 mesh. An aliquot was analyzed for total sulfur using a Fisher Total Sulfur Analyzer, a second aliquot was analyzed for heating value by the ASTM procedure using a Parr Adiabatic Bomb Calorimeter, and a third aliquot was analyzed for ash content by the ASTM procedure.

2.7 Sink Fractions

Sink fractions were washed from the centrifuge tubes onto a filter paper, vacuum-filtered, washed on the filter with boiling water, dried at 100°C, and analyzed for ash content, heating value, and total sulfur. The filtrates from some sink fractions were analyzed for sulfate by ion chromatography.

2.8 Hydrothermal Pretreatment of Coal Samples

Coal samples were placed in a beaker with water and the mixture brought to a boil for 1 h.

3.0 RESULTS AND DISCUSSION

3.1 Prewashing of Coal with Boiling Water

Experiments were performed to compare the removal of sulfur and the recovery of coal and energy obtained from IBC 101 and 1186 coal samples with and without prewashing with boiling water. As shown by the data in Table 2, with the 1186 coal sulfur reductions were comparable on the prewashed coal leached with half as much caustic, and coal and energy recoveries were consistently better. With the IBC 101 coal, however, sulfur reductions were only slightly better on the non-prewashed 1186 coal using 2 parts caustic to 1 part coal than on the prewashed coal using 1 part caustic to one part coal. With the IBC 101 coal, coal and energy recoveries were again enhanced by prewashing the coal with boiling water, but prewashing was not able to completely overcome the effects of reduced caustic on sulfur reductions.

Table 2

Residual sulfur, coal recovery, and heating value recovery in Illinois No. 6 coal samples with and without prewashing with boiling water before MCL.

MCL Conditions	Prewashed Coal			Non-Prewashed Coal		
	S, %	Recovery, %		S, %	Recovery, %	
		Coal	BTU		Coal	BTU
	1:1 NaOH:Coal			2:1 NaOH:Coal		
1186 Feed Coal	3.8	100	100	3.8	100	100
390°C/60 min	0.8	62	71	0.6	56	65
390°C/30 min	0.6	66	73	---	---	---
390°C/15 min	0.7	66	77	0.6	56	69
390°C/ 0 min	2.0	68	77	1.1	44	47
IBC 101 Feed Coal	4.5	100	100	4.5	100	100
390°C/60 min	1.0	69	79	0.7	63	71
390°C/30 min	0.9	70	80	0.7	63	73
390°C/15 min	0.8	66	77	0.7	64	75
390°C/ 0 min	1.1	73	84	1.1	64	75
2-stage	1.1	60	71	0.8	63	74

Additional studies were performed in which coal samples were prewashed with boiling water and then subjected to a float-sink pretreatment using 50% aqueous caustic as the heavy medium. In these studies, shown in Table 3, prewashing the 1186 coal again led to as good of sulfur reductions using 1 part caustic to 1 part coal as were attained without prewashing using 1.8-2.4 parts caustic to 1 part coal. Energy and coal recoveries were markedly higher when the prewashed coal was leached with one part caustic than when the non-prewashed coal was leached with larger amounts of caustic. With the IBC 101 coal, the same trends are obvious. Prewashed coal leads to just as acceptable of sulfur reductions when leached with 1 part caustic as are obtained leaching non-prewashed coal with greater amounts of caustic, and coal and energy recoveries are better.

Table 3

Residual sulfur in Illinois No. 6 coal after float and sink of prewashed and non-prewashed samples followed by MCL.

MCL Conditions	Prewashed Coal			Non-Prewashed Coal					
	Recovery, %			Recovery, %			Recovery, %		
	S, %	Coal	BTU	S, %	Coal	BTU	S, %	Coal	BTU
	1:1 NaOH:Coal			2.4:1 NaOH:Coal			1.8:1 NaOH:Coal		
1186 Feed Coal	3.8	100	100	3.8	100	100	3.8	100	100
390°C/60 min	0.2	61	75	0.2	50	55	0.5	55	64
390°C/30 min	---	---	---	0.4	46	53	0.4	56	63
390°C/15 min	0.2	60	70	0.4	51	57	0.5	55	63
390°C/ 0 min	0.4	66	75	0.5	49	56	---	---	---
IBC 101 Feed Coal	4.5	100	100	4.5	100	100	4.5	100	100
390°C/60 min	0.5	65	74	0.6	51	58	---	---	---
390°C/30 min	0.4	67	77	---	50	55	---	54	63
390°C/15 min	0.4	69	79	0.2	---	---	0.8	---	---
390°C/ 0 min	0.4	---	---	---	---	---	---	---	---
2-stage	0.2	60	71	---	---	---	0.6	60	69

4.0 CONCLUSIONS

◆ Hydrothermal pretreatment of coal, which involves only prewashing coal samples with boiling water, before the float-sink procedure allows sulfur to be removed efficiently using lower caustic to coal ratios.

◆ Hydrothermal pretreatment of coal samples before the float-sink procedure leads to a higher recovery of energy and coal than performing the same procedure on coal samples without the pretreatment.

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