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Separation by Countercurrent Washing of Coal-Caustic Mixtures during Chemical Coal Cleaning

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Abstract

Leaching coal with molten sodium hydroxide at 370–390°C converts most of the sulfur and mineral components of the coal into soluble species. The unreacted caustic and soluble components are then separated from the cleaned coal by a series of washing and filtration steps. A laboratory-scale simulation of a 6-stage countercurrent washing and filtration procedure was performed on Illinois No. 6 and Kentucky No. 11 coal samples that had been leached with molten sodium hydroxide. The mass of filter cakes and filtrates during each wash cycle and the concentrations of all major components of the caustic solutions were determined in each process stream. The countercurrent washing procedure resulted in a relatively clean coal and a final filtrate with a caustic concentration close to the desired 50%. However, after several coals had been processed, filtration rates decreased markedly and the mass of filtrate recovered also decreased. This was due to a build-up of a precipitate, consisting predominantly of Na_2CO_3, on filter cakes in the middle stages of the countercurrent process step. Process modifications to avoid this build-up are proposed.

INTRODUCTION

Advanced physical coal-cleaning procedures are available to reduce the ash and pyritic sulfur content of coal, but chemical cleaning is required to reduce the organic sulfur levels in coal by a significant amount. Several chemical coal-cleaning processes are being developed (*1–4*). The gravimelt or molten caustic leaching (MCL) process being developed by TRW with the help of the Ames Laboratory and the Pittsburgh Energy Technology Center is at the most advanced state of development. MCL has proven capable of routinely removing more than 90% of both the sulfur and ash from physically cleaned feed coal samples (*5–9*).

TRW is currently conducting continuous pilot-plant-scale tests (at 20 lb/h) of the MCL process. The Ames Laboratory is focusing on laboratory-scale tests of individual process steps, generation of process design data, and the development of analytical methods applicable to MCL process streams.

A schematic for the MCL process is shown in Fig. 1. During the leaching reaction, sulfur and mineral components of coal react with molten caustic to form carbonates, sulfides, sulfites, sulfates, silicates, ferrates, and aluminates (*10, 11*) which are subsequently washed from the coal in the water and acid washing steps. Typical molten caustic leaching conditions are: sodium hydroxide alone or equal-weight mixtures of sodium and potassium hydroxide as the caustic; 2 to 2.5 parts caustic to 1 part coal; a leaching temperature of 370–400°C; and a leaching time of 1 to 3 h.

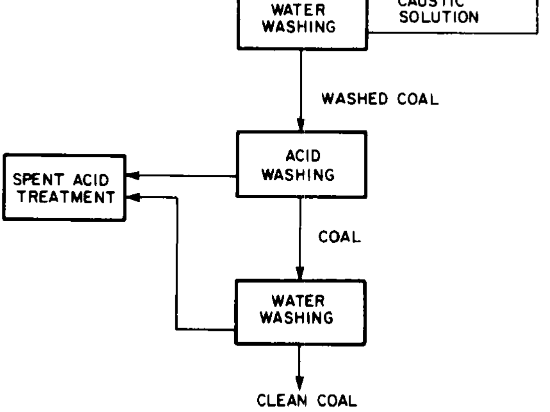

FIG. 1. Schematic flow diagram of the molten caustic leaching process.

During the water-washing step of the MCL process, soluble impurities such as carbonates, silicates, and aluminates are removed from the coal. In addition, excess caustic is recovered for subsequent reprocessing and reuse. In developmental studies, water washing with large volumes of hot water resulted in the removal of essentially all caustic and other soluble species from coal samples. Subsequent acid washing removed ionically bound alkali metals and acid-soluble iron salts from the coal, and a final water washing removed residual acid from the coal samples.

For the economical cleaning of coal, water washing must involve only small volumes of water to minimize the cost of evaporation from recovered caustic. However, that small volume of water must also remove essentially all soluble salts and alkaline materials from the coal in order to minimize acid consumption in the subsequent acid-washing step. TRW has proposed a countercurrent water-washing procedure designed to produce a 50% caustic solution while removing essentially all soluble salts from the coal-caustic cakes emerging from the leaching reactor (*12*).

In this countercurrent scheme (depicted in Fig. 2), coal moves from left to right while water moves from right to left. Net inputs are coal cakes containing 2 parts caustic to 1 part coal on the left and water on the right. Net outputs are cleaned coals on the right and 50% caustic solutions on the left. According to design, coal-caustic cakes from the reaction step are first washed with a 30% caustic solution yielding a 50% filtrate and a coal wet with 50% caustic solution. The filtrate from this first stage is reprocessed. The coal cake is then washed with a 15% caustic solution yielding a 30% filtrate and a coal cake wet with 30% caustic. The 30% caustic solution is used for the initial washing of the next coal-caustic

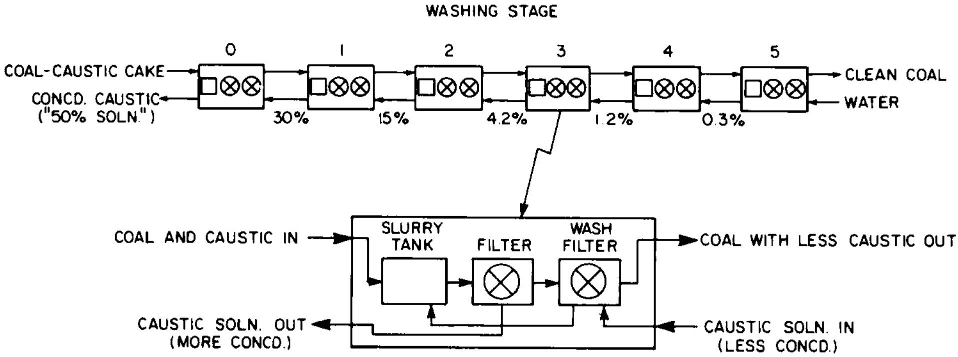

FIG. 2. TRW-designed countercurrent washing procedure.

cake. The coal cake is washed with progressively more dilute caustic solutions and finally with water. At each stage the filtrate is used to wash the following coal sample. The washing steps must produce a highly concentrated and relatively pure caustic solution in order to minimize energy required for the subsequent evaporation, to decrease the regeneration requirements, and to maintain the effectiveness of the recycled dry caustic.

In work reported herein, the Ames Laboratory has conducted laboratory-scale tests of the TRW-designed countercurrent washing procedure on two coals leached under two slightly different but typical MCL conditions. Each processing step, each solution concentration, and all volumes were scaled down precisely from those designed by TRW in order to yield a simulation producing results from which predictions of full-scale performance can be made.

EXPERIMENTAL

Preliminary Studies

Preliminary experiments were conducted to characterize and quantify the amounts of unreacted caustic and water-soluble components formed as the result of reactions between coal and caustic. The 50-g samples of Illinois No. 6 coal and Kentucky No. 11 coal were reacted with 100 g NaOH at 380°C for 2 h. The resulting coal-caustic cakes were washed with 2 L boiling water, and the alkaline solutions were analyzed for water-soluble components. Table 1 shows the properties of the feed coals used in these preliminary studies and the subsequent countercurrent washing studies.

TABLE 1
Properties of Feed Coal

Property	Illinois No. 6	Kentucky No. 11
Moisture	7.0%	3.3%
Ash	13.3%	9.1%
Total sulfur:	4.1%	3.1%
Pyritic sulfur	1.03%	0.96%
Sulfatic sulfur	0.12%	0.46%
Organic sulfur	2.95%	1.68%
Heating value, Btu/lb	11,799	13,213

Countercurrent Washing Studies

Eleven 50-g samples of Kentucky No. 11 coal and 11 50-g samples of Illinois No. 6 coal were each reacted with 100-g portions of sodium hydroxide. The Kentucky coal samples were reacted at 370°C for 2 h and the Illinois coal samples at 370°C for 1 h. The resulting coal cakes were stored under a nitrogen atmosphere for periods ranging from 16 to 48 h until countercurrent washing commenced.

The countercurrent washing procedure followed the TRW-designed protocol depicted in Fig. 2. The Kentucky No. 11 coal–caustic samples were all processed with solutions heated to 80°C. The first Kentucky No. 11 coal sample was slurried with 30% virgin sodium hydroxide solution in a 1000-mL beaker and the slurry filtered through a Whatman No. 41 filter paper in a Buchner funnel. The process was repeated, following the steps indicated in Fig. 2, with progressively more dilute caustic solutions and finally with water. The remaining 10 samples of Kentucky No. 11 coal-caustic cakes were slurried with filtrates from previously washed samples. This procedure produced 11 water-washed coal samples, 11 concentrated caustic solutions, and 11 intermediate wash solutions which were in process when the eleventh coal was washed. The 11 Illinois No. 6 coal-caustic samples were washed in an identical manner except that room temperature solutions were used.

Analyses of Countercurrent Washing Streams

During the countercurrent washings of coal–caustic samples, the weights of each filter cake and filtrate were measured. Hydroxide, carbonate, and total alkalinity were determined in aliquots of each concentrated caustic stream and of each intermediate process stream resulting from the countercurrent washing by potentiometric titration. Total sulfur was determined in aliquots of these same samples by ion chromatography following oxidation of all sulfur forms to sulfate with peroxide (*13*). Sodium was determined in aliquots of these same streams and in additional samples resulting from the subsequent acid washing of the water-washed coal samples by ion chromatography. Iron and silicon were determined in aliquots of the concentrated caustic streams, the streams in process, and the acid wash streams by spectrophotometry utilizing the 1,10-phenanthroline (*14*) and molybdenum blue (*15*) procedures, respectively. Aluminum was determined in aliquots of all streams by atomic absorption spectrometry. Sulfur was determined in cleaned coal samples using a Fisher total sulfur analyzer, and ash was determined using the standard ASTM procedure.

RESULTS AND DISCUSSION

Extensive Water Washing

Preliminary studies showed that essentially identical results were obtained when the Kentucky No. 11 and the Illinois No. 6 coal samples were leached under similar conditions and then washed extensively with large volumes of water. As shown in Table 2, the recoveries of clean coal, the conversions of caustic to carbonate, and the levels of iron, silicon, and aluminum in the recovered caustic solutions were essentially identical with both coals.

Observations during Countercurrent Washing

Serious problems were encountered during countercurrent washing of both the Illinois No. 6 and Kentucky No. 11 coal samples. It was found that the filtration times increased from about 4 to 5 min with the initial coal samples up to 20 to 50 min for the final ones. The recoveries of concentrated caustic solutions decreased as progressively more coal

TABLE 2

Characterization of Water-Soluble Compounds in Coal–Caustic Cakes (by weight, in grams)

Parameter	Illinois No. 6 coal	Kentucky No. 11 coal
Feed coal	50	50
Recovered dry coal	29	29
Feed NaOH	100	100
Recovered unreacted NaOH	54	44
NaOH converted to Na_2CO_3	33	35
NaOH reacted with sulfur and ash	13	21
Wash solution:		
Iron	0.24	0.22
Sulfur	1.7	1.4
Silicon	1.4	1.2
Aluminum	2.2	2.8

samples were washed by countercurrent. The filter cakes from both coals became hard and impermeable as more coal samples were washed. And with both coals, as progressively more coal samples were washed, the consumption of acid in the subsequent acid-washing step increased.

Filter Cake Weight Buildups

The relative weights of the filter cakes produced during countercurrent washing increased as more coal samples were washed. As shown in Fig. 3, during washing of the first Kentucky No. 11 coal sample, filter cake weights ranged from three to four times the weight of coal contained in the cake at each stage of countercurrent washing. This was expected because coals were wet with about two volumes of caustic solutions having densities ranging from about 1.5 for 50% caustic to 1.0 for water. However, as more coal samples were washed, the relative weights of the filter cakes increased, reached a maximum of about 12 times the weight of coal in the cakes, and the maximum shifted toward later filters. Very similar results were obtained with the washing of the Illinois No. 6 coal. The relative weights of the filter cakes for the eleventh sample of this coal are also depicted in Fig. 3.

Carbonate Precipitation

The increased filter cake weight indicated a build up of an insoluble, fluid-retaining material. This material was identified as sodium carbonate. During countercurrent washing of coal samples, the coal cakes move from left to right. Initially the coal cakes are in contact with concentrated caustic solutions. Carbonate is only sparingly soluble in concentrated caustic (*16*) and thus remains precipitated on the coal and moves with the coal toward the right. However, in the final stages of countercurrent washing, coal cakes are in contact with more dilute caustic and finally water. Carbonate is extremely soluble in water and thus dissolves and moves with the water back toward the earlier stages of countercurrent washing. The net effect is that during countercurrent washing carbonate does not exit with the concentrated caustic solutions because it is insoluble, and it does not exit with the coal because it is extremely soluble in the water used for washing the coal. Thus, it remains in the countercurrent process and its levels build up as progressively more coal samples are washed.

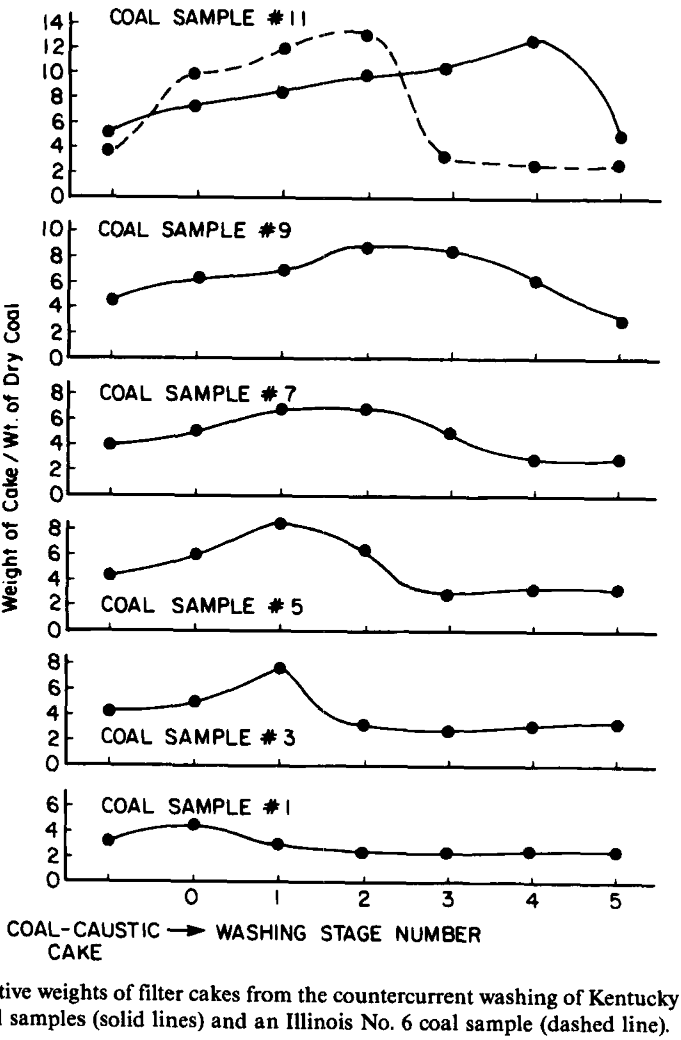

FIG. 3. Relative weights of filter cakes from the countercurrent washing of Kentucky No. 11 coal samples (solid lines) and an Illinois No. 6 coal sample (dashed line).

The massive build up of carbonate during countercurrent washing contributes to the increased filtration times observed. In addition, the build up of carbonate results in the retention of more fluids in the filter cake and causes the decreased recovery of caustic solutions. Hydrated carbonates form cementlike precipitates, which accounts for the increased hardness and decreased permeability of filter cakes as countercurrent washing progresses. Finally, carbonate levels increase to the extent that their nonequilibrium solubility in water is exceeded, and for the final coal samples the carbonates exit with the coal and lead to increased acid consumption in the next process step.

Recovery of Concentrated Caustic

Despite the carbonate-caused problems with countercurrent washing of coal samples, the concentration of recovered caustic approached the designed levels of 50%, as shown in Fig. 4 for the Kentucky No. 11 coal samples. Virtually identical results were obtained with the Illinois No. 6 coal.

However, the amounts of caustic solution recovered did not approach the design levels. As shown in Fig. 5, the amount of caustic solution recovered from the washing of the first Kentucky No. 11 coal sample was about 90% of predicted, the recovery then dropped precipitously with the second coal sample and dropped steadily thereafter. Overall, only about half as much caustic solution was recovered as was predicted by the TRW design. Similar low recoveries of caustic solutions were encountered with the Illinois No. 6 coal. With this coal, the eleventh sample processed yielded only 10% of the predicted amount of caustic solution.

Impurities in Caustic Soltuions

Concentrated caustic solutions recovered during the countercurrent washing of both the Illinois No. 6 and the Kentucky No. 11 coals were remarkably free of impurities. Iron, silicon, aluminum, and sulfur levels in concentrated caustic streams were all in the range from 0.1 to 0.3%. At these concentration levels the only reprocessing of recovered caustic required before reuse would be evaporation to dryness. Carbonate levels in the spent caustic solutions were likewise low, ranging from about 1 to 2%. Again, these levels were sufficiently low for the reuse of evaporated caustic without any reprocessing.

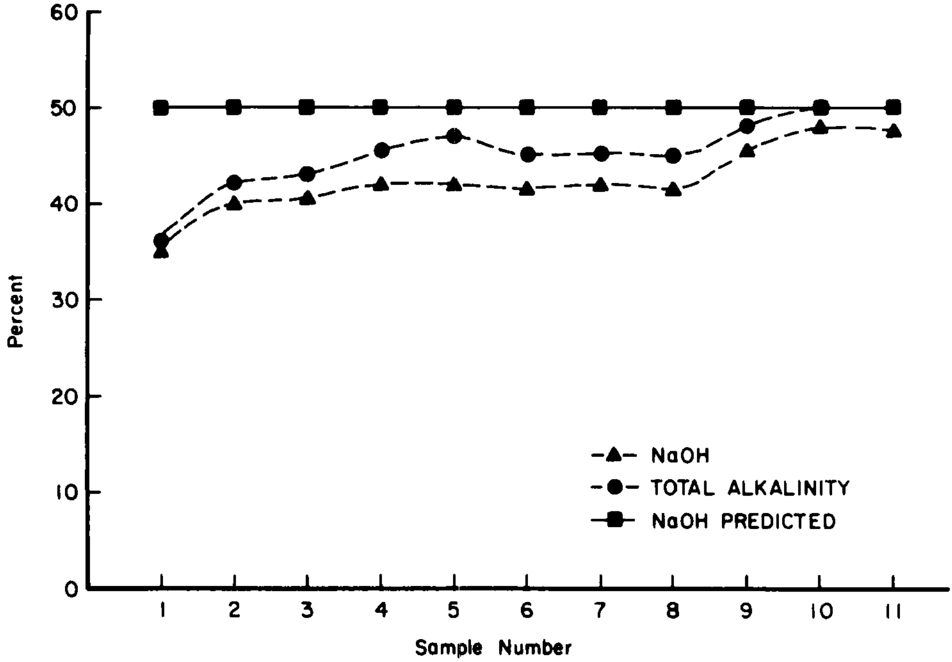

FIG. 4. Percent of NaOH in concentrated caustic solutions recovered from the countercurrent washing of Kentucky No. 11 coal samples.

Streams in Process at the End of the Run

Caustic solutions in process at the time the eleventh coal samples were washed were found to contain significantly higher levels of total alkalinity than was predicted by the TRW design (Fig. 6). This was, of course, expected because the amounts of caustic recovered were low. As shown in Fig. 7, a significant amount of the alkalinity contained in these in process streams was in the form of carbonate for the Kentucky No. 11 coal. Essentially identical results were obtained with the Illinois No. 6 coal samples.

Water-Washed Coal Samples

Cleaned coal samples produced by molten caustic leaching followed by countercurrent washing consumed relatively large amounts of acid in

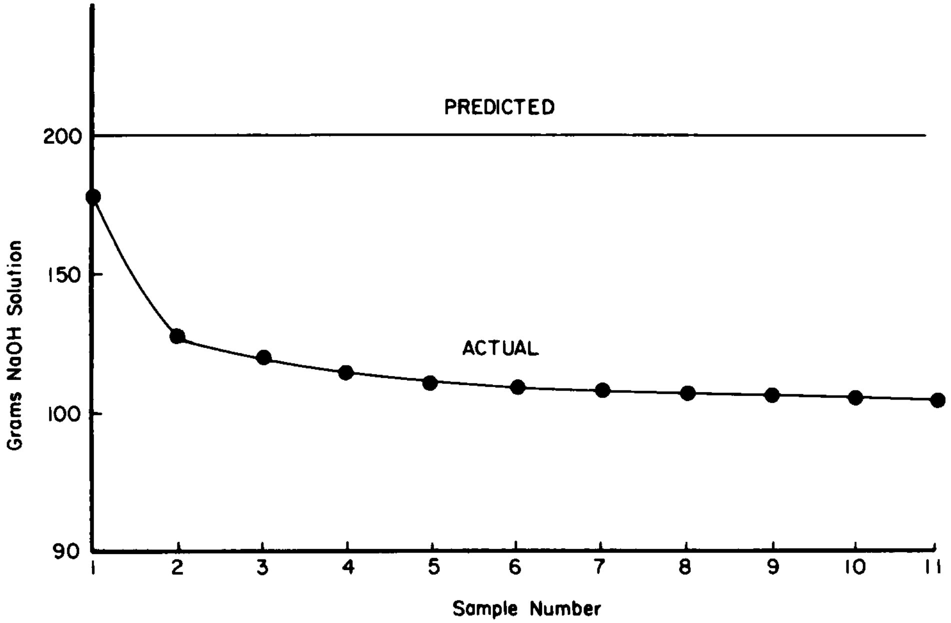

FIG. 5. Amounts of concentrated caustic solution recovered from the countercurrent washing of Kentucky No. 11 coal samples.

the subsequent acid-washing step. This step is designed for the removal of low levels of alkali metals ionically bound to the coal surface and low amounts of iron salts that are insoluble in basic and neutral water-wash solutions. Hence, very little acid should be consumed. From the curves in Fig. 8, it can be seen that the amount of acid consumed by the first coal sample washed was indeed quite low, but the amount nearly doubled by the third coal sample and increased by a factor of 10 by the time the eleventh coal sample was washed.

As shown in Fig. 9, the cleaned coal produced using the countercurrent washing procedure exhibited sulfur removals approaching the 90% levels that are typical of molten caustic leaching followed by extensive water washing. Ash removals were, however, lower than the 95% levels obtained on the same coals which were leached and subsequently washed extensively with water.

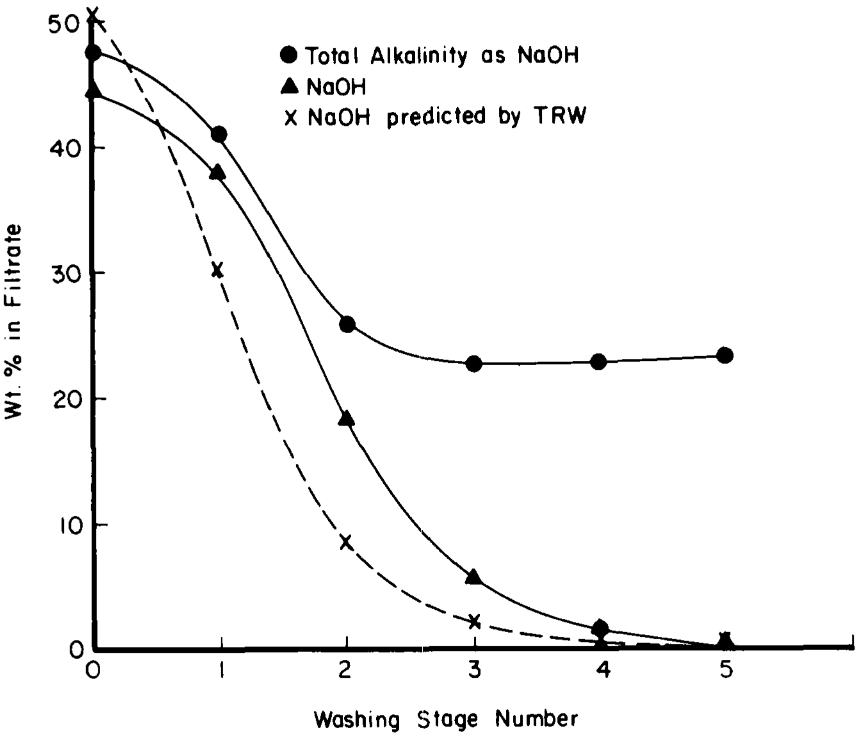

FIG. 6. Alkaline species in intermediate streams in process after the last Kentucky No. 11 coal sample has been washed.

Proposed Modifications to Countercurrent Washing

Overall the countercurrent washing procedure is effective in producing a concentrated caustic solution and a relatively clean coal. The precipitation of carbonate, however, is a serious problem which must be dealt with in order for countercurrent washing to become feasible. Five alternatives have been identified as means for reducing or eliminating the carbonate problems.

1. The suppression of carbonate formation during the molten caustic leaching step would reduce the amount of carbonate entering the countercurrent step and thereby lessen the precipitation problem. Work at the Ames Laboratory (*17*, *18*) has shown that pretreatment

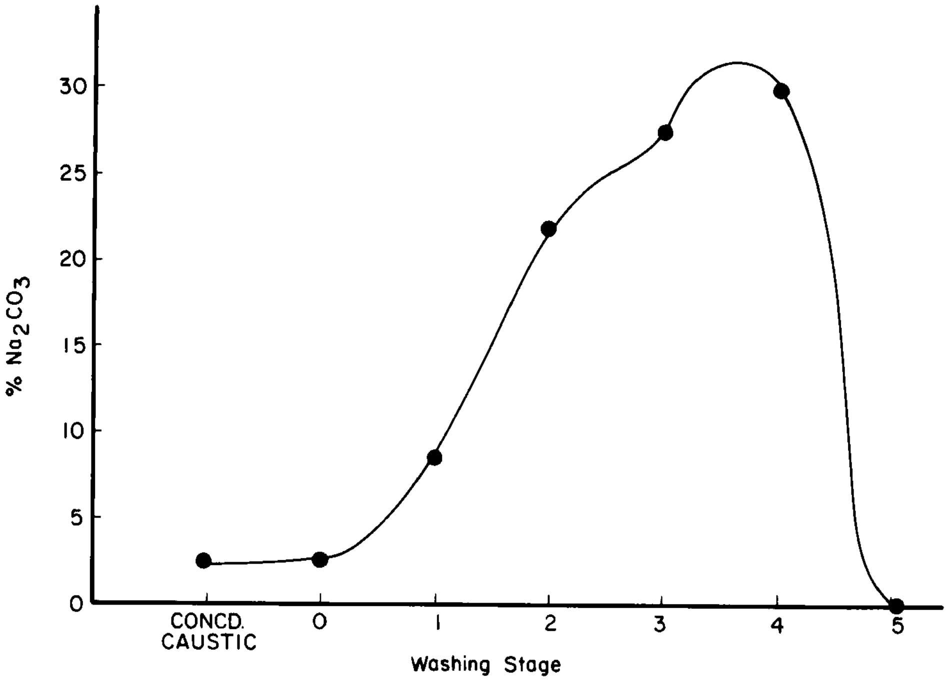

FIG. 7. Sodium carbonate concentrations in intermediate streams in process after the last Kentucky No. 11 coal sample has been washed.

of coal by low-temperature devolatilization and rigorous exclusion of contact with air during leaching can reduce carbonate formation by 70%.

2. Side streams from the countercurrent washing procedure can be removed and treated to remove carbonate and then reintroduced into the process. Work at the Ames Laboratory has shown that lime treatment of sodium hydroxide containing side streams from countercurrent washing procedures will indeed reduce levels of carbonate in those streams by significant amounts.
3. As an alternative to lime treatment, the carbonate-containing dilute caustic streams and essentially carbonate-free concentrated caustic streams could be removed from the process and blended to produce solutions from which much of the carbonate would precipitate and could be removed by filtration.
4. Concentrated caustic solutions could be removed from the counter-

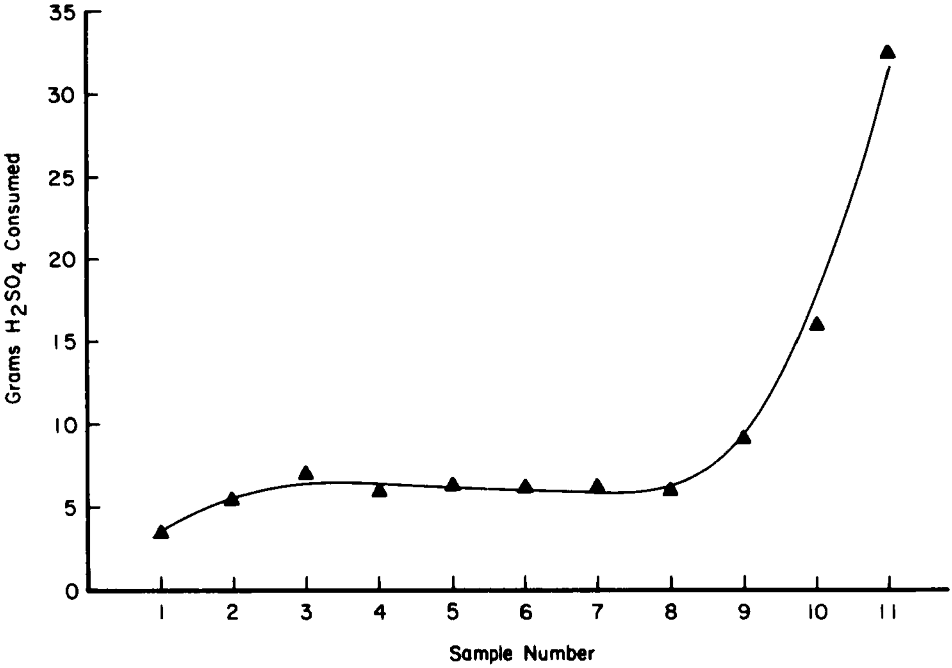

FIG. 8. Acid consumption during the acid washing of Kentucky No. 11 coal samples that have been water washed by the countercurrent procedure.

current washing procedure at lower caustic concentrations in which carbonate would be more soluble. The increased cost of water evaporation from these solutions would have to be weighed against the costs of other alternatives.

5. Potassium or other cations forming carbonates which are more soluble in caustic solution could be added to caustic solutions, as in NaOH-KOH mixtures.

CONCLUSIONS

Countercurrent washing procedure produced a relatively clean coal and an early 50% concentrated caustic solution. The coal sulfur removal ranged from 80 to 90% and ash removal averaged about 80%. Comparable results were obtained for Illinois No. 6 and Kentucky No. 11 coal samples.

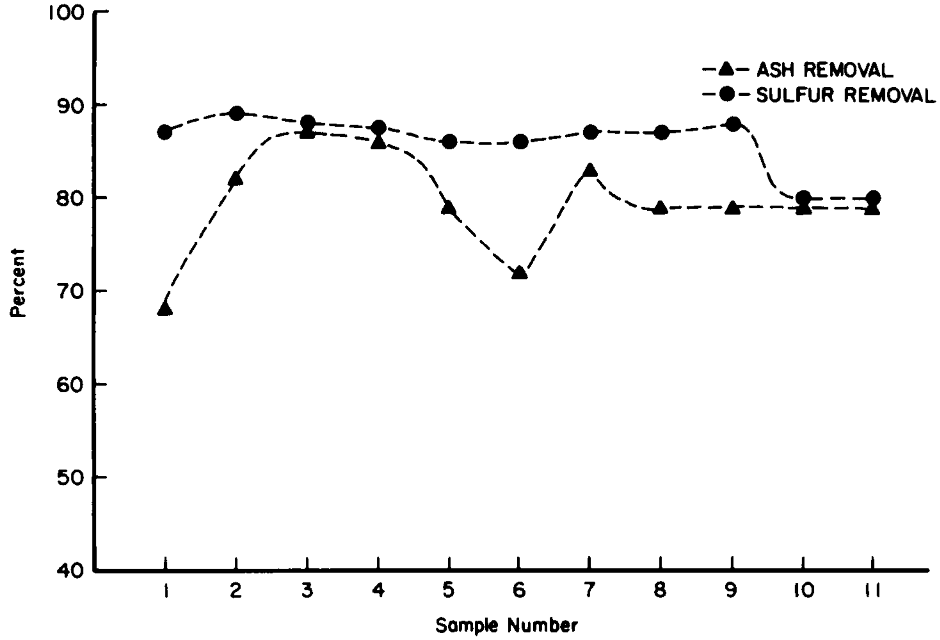

FIG. 9. Percent ash and sulfur removal from Kentucky No. 11 coal samples washed by the countercurrent procedure.

The concentrated caustic solution produced from the countercurrent washing was relatively low in impurities and contained less than 1% of Al, Si, Fe, and S, with Na_2CO_3 concentrations at about 1 to 2%.

With the processing of 11 coal samples, a serious problem of Na_2CO_3 precipitation was encountered. This resulted in reduced filtration rates, low recovery of spent caustic solution, and plugging of filters. In a continuous process, additional precipitation of other salts could lead to the same problems.

If carbonate formation cannot be eliminated, the countercurrent washing procedure needs to be modified to separate and remove the precipitate containing these carbonates. The suppression of carbonate formation during MCL is the most promising area for further research.

Acknowledgments

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