29
9-18-90 JS ②

IS-4970
UC 102

FOSSIL ENERGY

AMES LABORATORY

REGENERATION OF ALKALI IN CAUSTIC DESULFURIZATION SYSTEMS

FOSSIL ENERGY QUARTERLY REPORT

April 1, 1988 - June 30, 1988

R. Markuszewski, G. A. Norton, and C. D. Chriswell

Ames Laboratory
Iowa State University
Ames, Iowa 50011-3020

Date Transmitted: September 1988

DO NOT MICROFILM
COVER

Prepared for:
Pittsburgh Energy Technology Center
Pittsburgh, Pennsylvania

Operated for the U. S. Department of Energy
under contract No. W-7405-ENG-82

Printed in the United States of America

Available from
National Technical Information Service
U.S. Department of Commerce
5265 Port Royal Road
Springfield, VA 22161

IS--4970

DE90 017298

REGENERATION OF ALKALI IN CAUSTIC DESULFURIZATION SYSTEMS

Fossil Energy Quarterly Report

April 1, 1988 - June 30, 1988

R. Markuszewski, G. A. Norton, and C. D. Chriswell

Ames Laboratory*
Iowa State University
Ames, Iowa 50011

Date Transmitted: September 1988

Prepared for : Pittsburgh Energy Technology Center
Pittsburgh, Pennsylvania

Project Monitor: M. Nowak

*Operated for the U. S. Department of Energy
by Iowa State University
under Contract No. W-7405-Eng-82.

LB

REGENERATION OF ALKALI IN CAUSTIC DESULFURIZATION SYSTEMS
Fossil Energy Quarterly Report, IS-4970
April 1, 1988 - June 30, 1988

R. Markuszewski, G. A. Norton, and C. D. Chriswell
Ames Laboratory, Iowa State University

ABSTRACT

Experiments on precipitating double salts using model spent acid solutions indicated that 90% or more of the solids present in the solution could be precipitated at 80°C as natrojarosite ($NaFe_3(SO_4)_2(OH)_6$) and gypsum ($CaSO_4 \cdot 2H_2O$). The precipitate yield and the removal of iron and sulfate increased dramatically as the pH was increased from 1.1 to about 1.5. Natrojarosite and gypsum formed at pH values of 1.4 to 1.7, while mostly gypsum was detected at the other pH values studied. Maximum sodium removals of only about 70% were obtained, even though initial iron concentrations in the solutions were 25% in excess of those theoretically required for complete precipitation of sodium as natrojarosite. Although iron and sulfate could be effectively removed at pH 1.5-2.3, optimum sodium removal occurred within the narrow pH range of 1.5-1.6. Maximum precipitate yields were obtained within about 6 hours, with at least 80% of the iron and sulfate and about 60-75% of the sodium being removed.

A spent acid stream obtained from the laboratory simulation of counter-current washing of caustic-treated coal, performed at Ames, was also tested for precipitate formation at 80°C for 6 hours at a pH of 1.5. Results from this test are pending complete evaluation, but initial visual observations indicated that the spent acid behaved similarly to the model solutions. Additional tests on precipitating another double salt, sideronatrite ($Na_2Fe(SO_4)_2OH \cdot 3H_2O$), from model solutions indicated that the precipitation

of sideronatrite is probably not a viable option for treating spent acid streams from the MCL Process. However, from a technical standpoint, the precipitation of natrojarosite looks very promising.

Results of other experiments on model solutions containing NaOH, KOH, and carbonate and having compositions similar to those of actual spent caustic streams indicated that liming did not effectively precipitate carbonate. These results, which were in agreement with previously reported results obtained with actual spent caustic solutions, need further explanation.

REGENERATION OF ALKALI IN CAUSTIC DESULFURIZATION SYSTEMS

R. Markuszewski, G. A. Norton, and C. D. Chriswell

OBJECTIVE

The overall objective of this project is to develop and test feasible reaction pathways for regenerating the spent caustic and acid streams used to remove sulfur and ash from coal in the molten caustic leaching (MCL) process being developed by TRW in California. Economic considerations of the MCL process necessitate regeneration and recycling of the reagents from each of the cleaning steps in order to minimize the consumption of expensive chemicals. Also, the rejuvenation procedures may enhance the cleaning efficiencies of the reagents and minimize the amount of residue remaining on the cleaned coal. As an integral part of these tasks, modern instrumental methods are used, or developed if needed, in order to acquire chemical information pertaining to the regeneration of reagents and to the chemistry and mechanisms of coal cleaning. This information will provide insight into possible economical and technological improvements in the coal cleaning and reagent regeneration processes.

PROGRESS

Treatment of Spent Acid Streams by Double Salt Precipitation

In double salt precipitation experiments with model compounds performed previously (1), 1.25 g of Na_2SO_4 and 14.0 g of $Fe_2(SO_4)_3$ were added to 250 ml of water. The Na_2SO_4 concentration was the maximum level predicted by TRW (2). The $Fe_2(SO_4)_3$ concentration was chosen so that the level of ferric iron was 25% in excess of that theoretically (based on stoichiometry) required for the complete removal of sodium by precipitation as natrojarosite ($NaFe_3(SO_4)_2(OH)_6$). Consequently, the actual $Fe_2(SO_4)_3$ concentrations were 5 to 10 times higher than those predicted by TRW (2). The desired pH values were maintained during the tests by adding $CaCO_3$ to neutralize H_2SO_4 released during the precipitation reactions. Several tests were performed using reaction times of 1, 3, 6, and 9 hours, temperatures of 80°C and 95°C, and pH values of 1.1, 1.3, 1.4, 1.5, 1.6, 1.7, 1.9, and 2.3. The precipitates from these tests were filtered, air-dried, and analyzed subsequently by x-ray diffraction (XRD), while the filtrates were retained for analyses for iron, sodium, sulfate, and calcium by other techniques.

Precipitate yields and the removals of iron and sulfate as a function of pH were reported previously (1). Those results indicated that 90% or more of the solids ($CaCO_3$, Na_2SO_4, and $Fe_2(SO_4)_3$) present in the solution could be precipitated as natrojarosite and gypsum ($CaSO_4 \cdot 2H_2O$) within 6 hours at 80°C. The precipitate yield increased dramatically as the pH was increased from 1.1 to about 1.5 and was due primarily to the increase in pH rather than to the increased amounts of $CaCO_3$ used at the higher pH values. The trends for iron and sulfate removal as a function of pH were similar to the trend observed for the precipitate yield, with dramatic increases in removal being observed as the pH was increased from about 1.1 to 1.5. Analyses of the precipitates by XRD indicated that natrojarosite and gypsum were formed at pH values of 1.4 to 1.7, while mostly gypsum was detected at the other pH values studied. No other mineral phases were detected in any of those precipitates. Thus, mostly gypsum precipitated at pH 1.1, but sulfate ions in the solution were not depleted substantially because of the low yield of precipitate. At pH 1.4, the precipitate yield was higher, and both natrojarosite and gypsum formed in significant quantities. At pH values of 1.5 and 1.7, yields were near a maximum, and substantial amounts of iron and sulfate were removed as natrojarosite and gypsum. At pH values of 1.9 and 2.3, the removal of iron and sulfate remained high, even though XRD analyses indicated that little or no natrojarosite was formed. The removal of sulfate remained high at those pH values because it was being precipitated as gypsum. Because iron removals were high and since the corresponding precipitates were orange, it is believed that amorphous iron-containing compounds were precipitated at those pH values, even though no iron-bearing phases were detected by XRD.

In the current work reported for this quarter, results are presented for the sodium analyses on the filtrates obtained from these tests described above. In addition, results are now reported for precipitate yields and the removals of sodium, iron, and sulfate as a function of reaction time and at the two reaction temperatures studied.

The removal of sodium as a function of pH at 80°C with reaction times of 6 hours is shown in Figure 1. For comparative purposes, the previously reported (1) trends for iron and sulfate removal are also included. To simplify the graph, and in order to more clearly depict typical trends that can be anticipated, average values at each pH were used for each of the constituents. As can be seen, maximum sodium removals of only 65-70% were obtained, even though the initial iron concentration in the solution was 25% in excess of that theoretically required for complete precipitation of sodium as natrojarosite. These results correlate well with the XRD results, which indicated that relatively little natrojarosite precipitated above pH 1.7 or below pH 1.4.

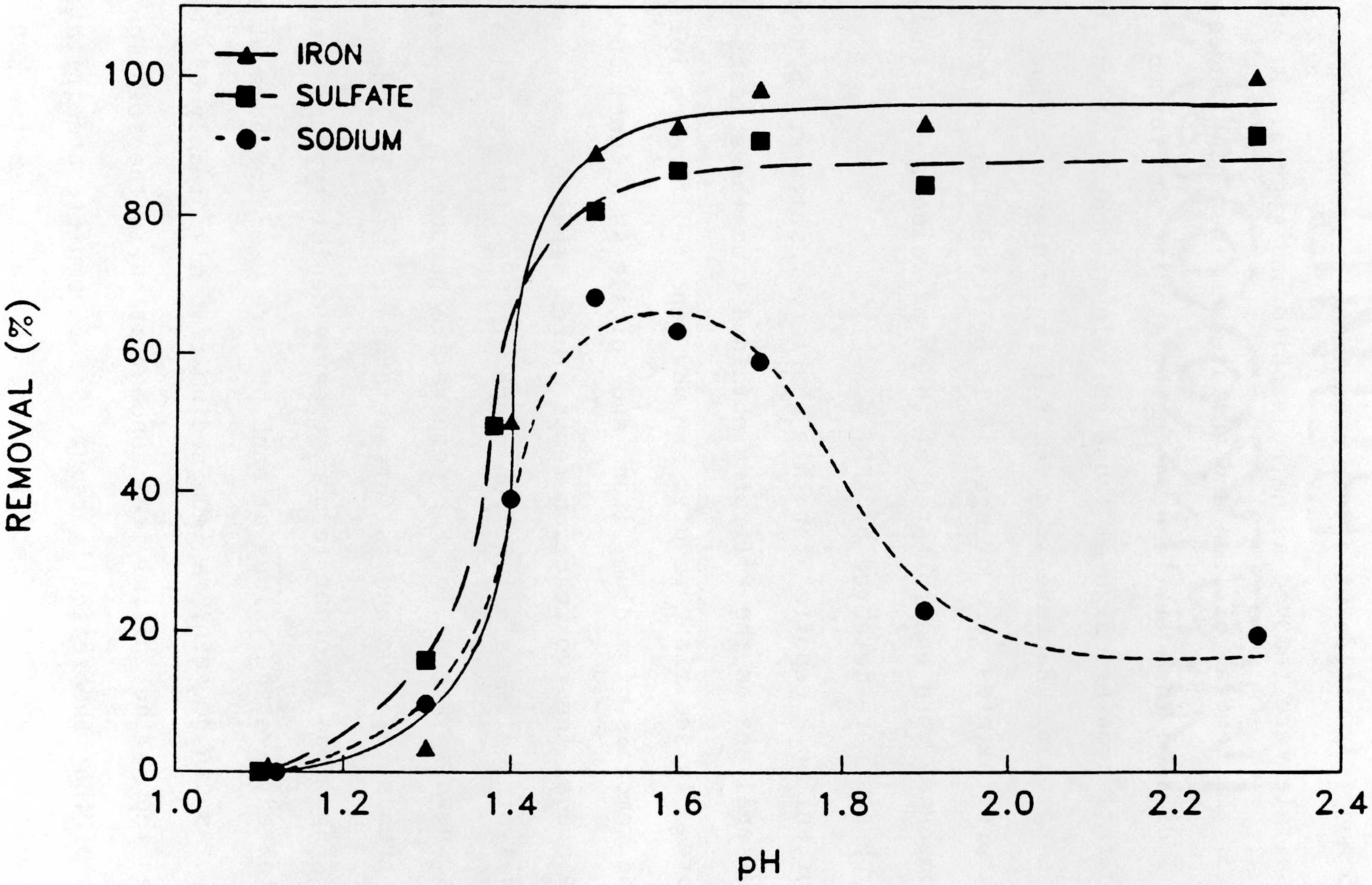

Figure 1. Iron, sulfate, and sodium removal as a function of pH. Solutions were heated at 75-80°C for 6 hours.

Precipitate weights and the amount of $CaCO_3$ added to the solution (for pH adjustment) as a function of time are shown in Figure 2. In each case, maximum precipitate yields were obtained within about 6 hours, and the increase in yield with increased reaction time was primarily a function of time rather than the increased amounts of $CaCO_3$ added at the longer reaction times. At reaction temperatures of about 80°C, precipitation was more rapid at a pH of 1.7 than at a pH of 1.5, as shown by the fact that maximum yields were obtained within 3 hours at a pH of 1.7. However, results for sodium removal at this pH showed a relatively large amount of data scatter, suggesting that a pH of 1.7 may be a borderline value for effectively precipitating natrojarosite. Based on duplicate runs which were performed at some of the pH values, iron and sulfate removals were generally reproducible to within ±5% (relative). The sodium removals were generally reproducible to within ±10% (relative) or less, except at pH 1.7 in which case the results for sodium removal varied by as much as 30% (relative) from the mean. This is probably because, under the conditions studied, the pH value of 1.7 is critical, and even slight deviations from this pH have large effects on natrojarosite formation.

The removal of total iron, sulfate, and sodium from the model solutions as a function of time is depicted in Figure 3. From these results, it is evident that at least 80% of the iron and sulfate and 60-75% of the sodium were precipitated after about 6 hours. A pH of 1.5 appeared to be more effective at removing sodium than a pH of 1.7. It is possible that a minimum iron, sodium, or sulfate concentration in the solution is necessary to effectively precipitate natrojarosite. Thus, iron levels may have decreased to a point where natrojarosite could not be effectively precipitated.

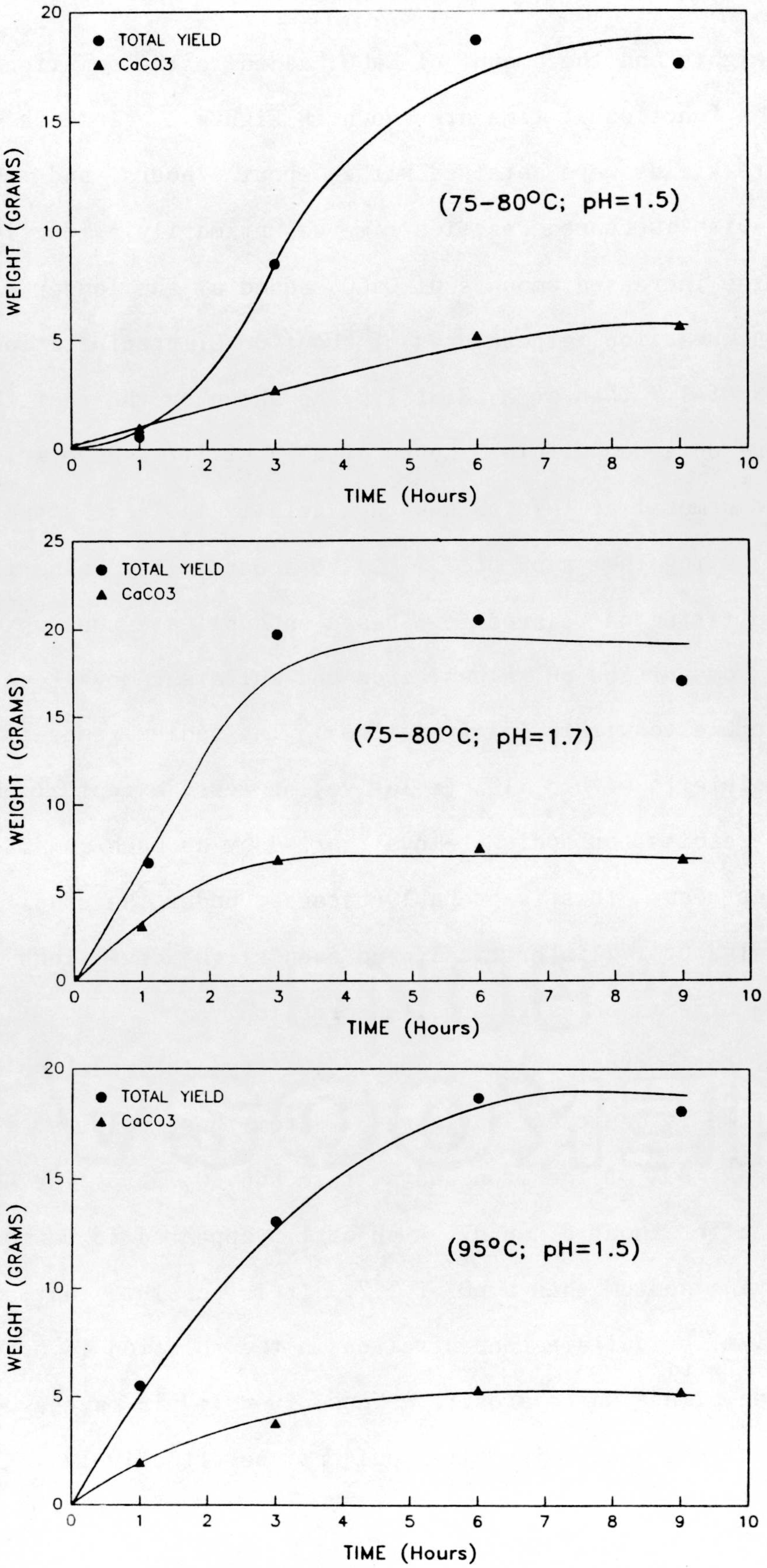

Figure 2. Precipitate yield (grams) and $CaCO_3$ (grams) added as a function of time at various temperatures and pH values.

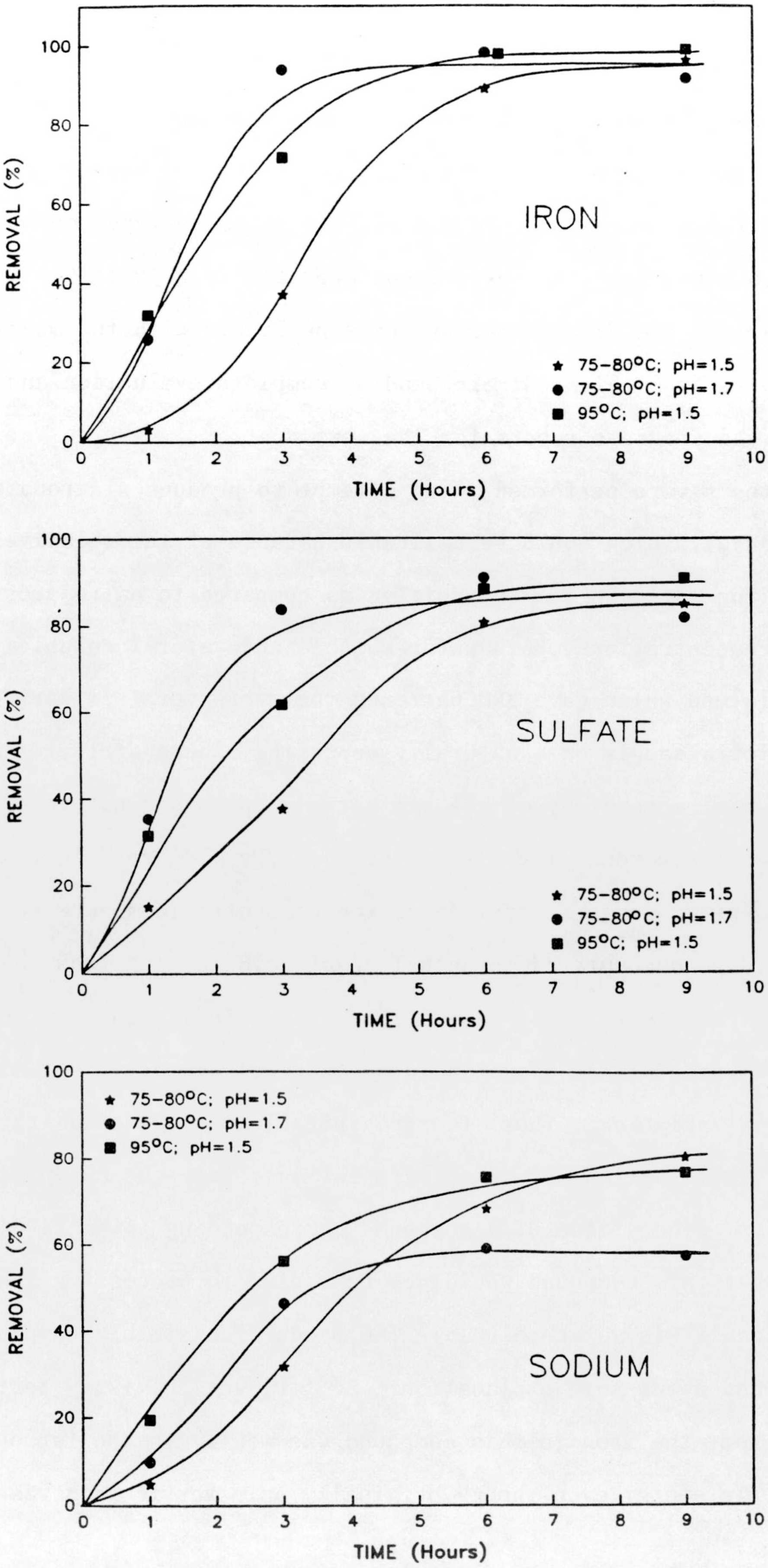

Figure 3. Iron, sulfate, and sodium removal as a function of reaction time at various temperatures and pH values.

As a follow-up to the experiments with model solutions, a test was run in which actual spent acid from a laboratory simulation of the countercurrent washing procedure proposed by TRW was heated at 80°C for 6 hours at a pH of 1.5 in an attempt to precipitate jarosite-type compounds. Based on visual observations, the experiment appeared to go well and appeared to behave in the same manner as the experiments with the model solutions. Results from this test are pending complete evaluation and will be discussed in the progress report for the next quarter.

Additional tests were performed in an attempt to produce sideronatrite ($Na_2Fe(SO_4)_2OH \cdot 3H_2O$), which would be desirable because of the relatively high sodium-to-iron ratio in its composition as compared to natrojarosite. Using high ion concentrations, both water-soluble and water-insoluble compounds were formed which gave XRD patterns that were very similar to those obtained for a sample of a naturally occurring sideronatrite. However, the crystal morphology of the synthetic samples did not resemble that of the mineral sideronatrite. In these tests, yields were low, reaction times were at least several days, ion concentrations were much higher than would be encountered in actual spent acid samples from the MCL process, and the results were not easily reproduced, indicating that the properties of the precipitate appeared to be extremely sensitive to a number of process variables. Thus, the precipitation of sideronatrite is probably not a viable option for treating spent acid from the MCL process.

In some tests, good yields of a compound corresponding to $Na_6Fe(SO_4)_4$ were obtained, but this compound would not be useful in processing spent acid streams since it is water-soluble. The production of this compound was surprising and needs some explanation. So far, wet chemistry tests have confirmed that the iron in this compound was mostly in the ferrous rather than ferric state, even though originally only ferric iron was added to the solutions.

Removal of Carbonate from Countercurrent Washing Streams

In work reported previously (3), elevated levels of carbonate were found in intermediate streams arising from laboratory countercurrent washing of coal that had been leached with caustic. In previous tests, when only NaOH was used as the leaching caustic, the carbonate in the intermediate-wash caustic streams could be precipitated by liming. However, in those tests, when a NaOH/KOH mixture was used to leach the coal, liming did not effectively remove carbonate.

In current work, model solutions containing NaOH, KOH, and carbonate, and having compositions similar to that of actual spent caustic streams, were treated with $Ca(OH)_2$ to determine whether liming can effectively precipitate carbonate. As for the previous experiments with the actual spent caustic solutions, results indicated that liming did not effectively precipitate carbonate from the solutions containing NaOH and KOH. Further solubility studies are needed to explain these results. But, on first glance, these observations point to possible complications in the caustic regeneration if a mixed caustic is used for the MCL process.

Formation of Humics During the MCL Stage

Illinois No. 6 coal was reacted with NaOH using a 2:1 caustic-to-coal weight ratio at temperatures of 150 to 450°C in increments of 50°C. After leaching the coal under a nitrogen atmosphere for one hour, the reacted coal/caustic mixture was washed with water. The resulting spent caustic solution was acidified with HCl and the humic material which precipitated was filtered and air-dried. As expected, the recovered levels of humic materials initially increased with increasing leaching temperature. The levels of recovered humic materials reached a maximum value at a leaching temperature of about 300°C. As was also anticipated, based upon our previous work, the levels of recovered humic materials decreased with increasing leaching temperature above 300°C. These findings are consistent with a previously proposed mechanism in which humic materials are formed at elevated temperatures and are then subsequently degraded at higher temperatures (4). The total amount of crude humic materials recovered at 300°C was equivalent to a significant fraction of the original weight of the leached coal, which was not anticipated. Studies are currently being performed to determine the composition of these crude humic materials and to confirm the very high recoveries.

FUTURE WORK

Precipitates from the studies on forming double salts in model spent acid solutions will be analyzed for sodium, iron, sulfate, and calcium. Results of these analyses will provide useful supplemental information which will help to more fully evaluate double salt precipitation as a means of treating spent acid streams from the MCL process. In addition, the evaluation will be completed of the results from chemical and mineralogical analyses obtained for the double salt precipitation experiment using spent acid from the countercurrent washing (performed at Ames Laboratory) of caustic-treated coal. This will allow results to be compared between real and model spent acid solutions.

Studies on dissolved organic compounds in caustic streams will continue in order to more fully evaluate conditions for their formation and the potential effect on caustic regeneration.

LITERATURE CITED

1. R. Markuszewski, G. A. Norton, and C. D. Chriswell, "Regeneration of Alkali in Caustic Desulfurization Systems," Fossil Energy Quarterly Report, January 1, 1988 - March 31, 1988, IS-4961, Ames Laboratory, Iowa State University, Ames, Iowa.

2. TRW Energy Division, "Bench Scale Development of the TRW Process for Cleaning Coal (Gravimelt Process). Topical Report for Task 8: Solid-Liquid Separation," TRW Document No. 42419-6015-UT-00, January 1986.

3. N. D. Shah, C. D. Chriswell, and R. Markuszewski, "Separation by Countercurrent Washing of Coal-Caustic Mixtures During Chemical Coal Cleaning," Separation Science and Technology, 1988, in press.

4. E. J. Jensen, N. Melnyk, J. C. Wood, and N. Berkowitz, Adv. Chem. Ser. 55, 621 (1966).

DISTRIBUTION LIST

Ames Laboratory Document Library Iowa State University Ames, Iowa 50011 - 3020	(6)
Chicago Operations Patent Counsel 9800 South Cass Avenue Argonne, Illinois 60439	(1)
Technical Information Center U. S. Department of Energy P. O. Box 62 Oak Ridge, Tennessee 37830	(30)
PETC (R. Hucko) (K. Rhee) (M. Nowak) (A. Deurbrouck)	(4)
US DOE - Washington (W. Jones) (R. Pennington) (S. Spadone) (J. Batchelor) (J. Siegel)	(5)
Fossil Energy Office Ames Laboratory 321 Spedding Hall Iowa State University Ames, Iowa 50011	(20)
R. Markuszewski	(10)
Fossil Energy Principal Investigators (D. Birlingmair) (L. Burkhart) (W. Buttermore) (C. Chriswell) (G. Norton) (J. McClelland) (W. Straszheim) (J. Verkade) (T. Wheelock)	(9)