IS--5021

DE91 004098

SONIC ENHANCEMENT OF PHYSICAL AND CHEMICAL CLEANING OF COAL

Fossil Energy Quarterly Report

July 1, 1989 - September 30, 1989

W. H. Buttermore, B. J. Slomka, and M. R. Dawson

Ames Laboratory*
Iowa State University
Ames, Iowa 50011

Date Transmitted: October, 1989

Prepared for: Pittsburgh Energy Technology Center
Pittsburgh, Pennsylvania

Project Monitor: Jacqueline Balzarini

*Ames Laboratory is operated for the U. S. Department of Energy by Iowa State University under Contract No. W-7405-ENG-82.

MASTER

gmp

DISTRIBUTION OF THIS DOCUMENT IS UNLIMITED

SONIC ENHANCEMENT OF PHYSICAL AND CHEMICAL CLEANING OF COAL

Fossil Energy Quarterly Report, IS-5021

July 1, 1989 - September 30, 1989

W. H. Buttermore, B. J. Slomka, and M. R. Dawson

Ames Laboratory, Iowa State University

ABSTRACT

During this reporting period, laboratory tests were performed to investigate the effects of coal particle size on the sonically enhanced desliming of Illinois No. 6 coal. Desliming removes fine clay particles which can interfere with surface-controlled cleaning processes, and thus it is an important step prior to beneficiation procedures such as flotation or oil agglomeration. A 10-kHz Swen Sonic near-field apparatus, configured for continuous-rinse desliming of coal in the presence of sonic waves, was used in the tests. Ash content of the sonically dislodged undersize material ranged from 55.0% to 86.9% by weight. Comparison of data for sonically deslimed coal and the initial wet-sieved sample showed ash content reduced from 22.2 to 16.5% by weight as a result of exposure to pulsed sonic energy at a 50-second total sonication time. Calculated recoveries of heating value ranged from 97.6% to as high as 99.8%, depending on the particle size of coal treated. Desliming of isolated coal-mineral composite particles resulted in preferential liberation of mineral-rich undersize material. The sonically dislodged undersize particles contained from 2.2 to 2.8 times more ash-forming minerals (by weight) than the starting coal-mineral composite particles. The ash content of the undersize material varied between 24.2 and 31.2% by weight, showing no systematic decrease as the sonication time increased.

Laboratory-scale flotation tests using a Hallimond tube were performed to study the effects of coal oxidation and sonic pretreatment of oxidized coals on the surface-controlled cleaning of coal. The experiments revealed a significant decrease in floatability of closely sized, narrow specific gravity fractions of the Illinois No. 6 coal as a result of oxidation in dry air at 150° C for 150 hours. Sonication of the oxidized coal in aqueous slurry for 30 seconds using the 10-kHz probe significantly improved floatability. Washing oxidized coal with water effected only marginal improvements in floatability. FTIR analysis indicated that sonication reduced the quantity of oxidized material on the coal surface measured in the carbonyl region of the IR spectra.

Other experiments were conducted this quarter to determine the effect of sonication on coal and pyrite surfaces. These experiments involved the use of linear potential sweep voltammetry on pyrite and coal electrodes, and zeta potential experiments which included the development of a new

method for the zeta potential determination of easily oxidizable materials such as sulfides and some coals. Results from voltammetry experiments, using a mineral pyrite electrode, indicate that sonication is effective in removing the elemental sulfur from the surface of oxidized pyrite, thereby exposing additional metal oxide. Both these factors indicate that sonication should be effective in depressing the flotation of oxidized pyrite. Actual flotation experiments will be conducted to confirm this finding.

OBJECTIVE

The purpose of this project is to improve the efficiency and reduce the cost of coal preparation processes. The primary objective of this project is to enhance the physical and chemical separation of sulfur and ash-forming mineral matter from coal through the novel application of sonic energy.

APPLIED COAL CLEANING TESTS

Effect of Coal Particle Size on the Sonically Enhanced Desliming of Illinois No. 6 Coal

Sample Preparation. A bulk sample of coal was prepared by wet-grinding a 3/8 x 0 inch run-of-mine Illinois No. 6 coal to 8-mesh top size. The minus 8-mesh material was further wet-sieved to obtain particle size fractions ranging from 8 to 100 mesh (U.S.) for desliming studies. Wet-sieving ensured removal of loosely clinging undersize material from the particle surfaces. The particle size distribution and the ash content values for the wet-sieved product are given in Table 1.

Table 1. Characterization by size fraction of minus 8-mesh Illinois No. 6 coal wet-sieved sample.

<u>U.S. Sieve</u>	<u>Wt.%</u>	<u>Ash (wt.%)</u>
8 x 16	35.0	20.4
16 x 30	17.6	19.1
30 x 50	12.1	22.2
50 x 100	8.1	24.1
-100	27.3	-

Desliming Apparatus and Procedure. For testing the effects of coal particle size on desliming in the presence of sonic waves, the 10-kHz Swen Sonic near-field apparatus was configured to allow for continuous rinse operation. According to an earlier established procedure¹, the coal sample is retained in the space between radiators by a 200-mesh (74 μ m) stainless steel screen filter installed at the fluid exit of the apparatus. The undersize material dislodged by sonication is continuously removed from the apparatus as an aqueous suspension. The presence of undersize material, as well as its approximate concentration in the effluent, was continuously monitored by an in-line photometric turbidity detector. This feature provides a rapid means to monitor the completeness of rinsing following sonication. Samples of undersize material removed by single, short sonic pulses were collected and analyzed for ash content. Sonic energy was delivered to the sample as 10 pulses of 5-second duration. The sonic pulse intensity was 10.4 watt/inch². In each 5-minute cycle, the coal sample was flushed for 4 minutes and 55 seconds following 5-second sonic pulse.

In a typical test, 120 g of coal was used. A flow of deionized water was provided to rinse the sample at a constant rate of 1.0 L/min. Effluent was collected at predetermined time intervals. Undersize material was filtered on glass porous discs to facilitate subsequent quantitative analysis. Deslimed coal recovered from the apparatus was filtered on 2.5- μ m filter paper. Both products were dried under nitrogen at 110°C for 4 hours. Ash and moisture contents were determined for samples of sufficient quantity.

Results. Figure 1 shows the ash content of minus 200-mesh materials as a function of sonication time. For each particle size fraction studied, the observed ash content of liberated material is high at the beginning of the process and decreases as the sonic pulses are repeated. The finest particle size fraction studied, i.e., 50 x 100-mesh, shows the most selective removal of ash-forming minerals throughout the entire 50-second period of sonication time. In this size range, the ash content of the dislodged material decreased from 86.9% by weight for the first pulse to 73.2% for the last sonic pulse delivered. The coarser particles studied, i.e., 30 x 50, 16 x 30, and 8 x 16-mesh, show a similar qualitative trend except for a sudden decrease in ash content of the undersize material at sonication

Figure 1. Sonically Enhanced Desliming of the Illinois No. 6 Coal.

times longer than 35 seconds in the case of the 8 x 16-mesh fraction. Most likely this decrease marks the onset of dispersing a significant quantity of coal along with the removal of ash-forming minerals. Perhaps sonication under these conditions is more effective in breaking coal of this size range, or perhaps coal in this size range contains fragments or macerals more easily broken by sonic energy. Table 2 summarizes the overall effect of coal particle size on the sonically enhanced desliming of Illinois No. 6 coal, both in terms of heating value recovery and relative reduction of the ash content of coal.

The data clearly show that the heating value recovery decreases as the particle size decreases. However, for all the particle sizes studied, the overall heating value recovery remains at very high levels, i.e., above 97% as a result of sonic desliming. As indicated in Table 2, the highest relative reduction of ash-forming minerals (over one-quarter of the initial quantity removed) was obtained for the 30 x 50-mesh fraction at a very high recovery of heating value of 99.5%.

Table 2. Coal Particle Size Effect on the Desliming of the Illinois No. 6 Coal in the Presence of 10-kHz Sonic Waves.

<u>U.S. Sieve</u>	<u>Percent Ash of Deslimed Coal</u> (wt.%)	<u>MAF Coal Recovery</u> (%)	<u>Ash Content Reduction</u> (%)
8 x 16	17.9	99.8	12.3
16 x 30	17.3	99.6	9.4
30 x 50	16.5	99.5	25.7
50 x 100	20.5	97.6	14.9

Desliming of Middlings. A sample of Illinois No. 6 middlings was prepared to study the behavior of coal-mineral composites during desliming in the presence of sonic waves. To obtain a 'pure' fraction of coal-mineral composites, wet-sieved 16 x 100-mesh particles were separated in aqueous

CsCl solutions at specific gravities of 1.30 and 1.80. This procedure ensured that the middlings material did not contain all-mineral particles. Analysis indicated 11.1% ash content for the separated 1.30 x 1.80 middlings material. The desliming test procedure, including the sonic pulse sequence and collection of the undersize material liberated, was identical to that described above. Figure 1 includes a plot of the ash content of the middlings undersize material as a function of sonication time. Ash content values from 24.2 to 31.2% by weight were obtained, and showed no clear trend of decreasing with sonication time. Comparison with ash content of the middlings before desliming, i.e., 11.1% by weight, indicates a considerable degree of selectivity for sonic desliming. It can be concluded that as a result of exposure to intense near-field sonic energy, the ash-forming mineral constituents in coal-mineral composites are from 2 to 3 times more readily dispersed than their coal counterparts. The MAF coal recovery was 96.8%.

Flotation Response Tests. Laboratory-scale flotations using a Hallimond tube were performed to study the sonic treatment of oxidized coals prior to surface-controlled cleaning. A modified version of a Hallimond tube with a porous frit installed at the bottom was used according to the procedure described earlier². Coal samples of 1.000 g were placed inside the flotation tube, covered with 150 ml of deionized water and conditioned by magnetic stirring for 3 minutes. Flotation was effected by flowing purified nitrogen through the pulp at 20 ml/minute. No flotation reagents were used in these tests.

Light fractions (specific gravity less than 1.45) of wet-sieved 70 x 100-mesh Illinois No. 6 coal were used in this series of tests to focus the effect of sonication on predominantly coal rather than coal and mineral surfaces. The +1.45 specific gravity fraction comprises 64.8% wt. of this coal and represents 77.7% of energy available in all gravity fractions. Procedures for preparation of samples, oxidation, and sonic pretreatment were described in detail earlier².

The results of flotation tests are shown in Figures 2-5 for four specific gravity fractions. Each figure includes flotation rate curves for

Figure 2. Recovery vs. Time for Fresh, Oxidized, Oxidized then Sonicated, and Reference Samples of 1.30 Float Specific Gravity Fraction of Illinois No. 6 Coal.

Figure 3. Recovery vs. Time for Fresh, Oxidized, Oxidized then Sonicated, and Reference Samples of 1.30 x 1.35 Specific Gravity Fraction of Illinois No. 6 Coal.

Figure 4. Recovery vs. Time for Fresh, Oxidized, Oxidized then Sonicated, and Reference Samples of 1.35 x 1.40 Specific Gravity Fraction of Illinois No. 6 Coal.

Figure 5. Recovery vs. Time for Fresh, Oxidized, Oxidized then Sonicated, and Reference Samples of 1.40 x 1.45 Specific Gravity Fraction of Illinois No. 6 Coal.

150 hours at 150° C, oxidized material exposed to sonication, and a reference test in which oxidized material was exposed to the same laboratory procedure as the sonicated samples, except for energizing the source of sonic waves.

Results for the 1.30-float fraction, illustrated in Figure 2, indicate that sonication is effective in restoring the floatability of oxidized coal to a level near that of fresh coal. FTIR analysis performed by Dr. J. F. McClelland indicated that sonication reduced the quantity of oxidized material on the coal surface measured in the carbonyl region of the IR spectra. For the specific gravity fractions 1.30 x 1.35 and 1.35 x 1.40, sonication of oxidized coal particles resulted in improvements of floatability to levels exceeding those of the fresh samples. This is an indication of possible residual surface oxidation of the fresh samples. Compared to the floatabilities of the corresponding oxidized samples, these improvements are dramatic. As can be seen from Figures 3 and 4, the initial flotation rates differ by as much as 3 times. Results for the heaviest fraction studied, i.e., 1.40 x 1.45, illustrated in Figure 5, showed significant, however less pronounced, improvement in floatability over the oxidized and the reference sample. Reduced recoveries observed for this sonicated, heavier fraction may reflect the result of sonication on combined coal and mineral particles, where sonication enhances the floatability of the organic fraction but depresses the flotation of encapsulated minerals. Another possibility is the segregation by gravity of macerals less easily treated with sonic energy. Additional experiments are underway to determine the effectiveness of sonic treatment for removing surface oxidation from Pittsburgh Seam and Upper Freeport coals.

Assessment of Possible Fundamental Mechanisms Responsible for Sonic Enhancement of Physical Coal Cleaning Processes

Experiments were conducted this quarter to determine the effect of sonication on coal and pyrite surfaces. These experiments involved the use of linear potential sweep voltammetry on pyrite and coal electrodes, and zeta potential experiments which included the development of a new method for the zeta potential determination of easily oxidizable materials such as sulfides and some coals.

Effect of sonication of pyrite oxidation surfaces. In collaboration with T. Chmielewski and D. Birlingmair, voltammetric measurements were made using pyrite electrodes to electrochemically determine the effect of sonication on pyrite surfaces. In these experiments, voltammetry is used to determine the type and relative amount of oxidation products on a pyrite surface.

Oxidation reactions are driven on the surface of a pyrite electrode by applying a positive potential. When the potential is reversed and scanned linearly, a reaction is indicated by current flow, as the newly created oxidation products are reduced. Different oxidation products are reduced at different potentials, the reaction rate is reflected by the current at a given potential. It has been demonstrated^{3,4} that a thin iron-oxide layer forms spontaneously when freshly created surface of pyrite is exposed to air. Further oxidation of pyrite leads to the formation of elemental sulfur on the pyrite surface. Because sulfur is hydrophobic, difficulties result in the selective flotation of coal from associated pyrite. It has also been shown⁴ that when elemental sulfur is removed from the surface of pyrite as soluble oxy-sulfur ions, a hydrated hydrophilic metal-oxide layer remains which would be expected to inhibit the flotation of pyrite.

The sample preparation and analytical method is described in a report by Birlingmair et al.⁵ Sonic energy was applied at a frequency of 7 kHz, using a transducer supplied by the Raytheon Company. Sonication was under water, with the sample on the transducer face, and pulsed for three intervals of 5 seconds each, for a total sonic exposure of 15 seconds.

The results of experiments performed at a pH of 4.6 are shown in Figure 6. In this figure, the solid line represents a cathodic sweep of the freshly polished pyrite electrode. For the dashed line, the electrode was oxidized by applying a potential of +0.5 volts vs. SCE for 7 minutes before the cathodic sweep. The dotted line was generated by oxidizing the pyrite electrode as before, then sonicating the electrode before the cathodic sweep.

For the oxidized sample curve (dashed), two prominent peaks are seen, one at -0.15 volts and a broader peak between -0.5 and -0.6 volts. Based on

Figure 6. Voltammograms for a mineral pyrite electrode at pH=4.6.

thermodynamic calculations^{4,6}, the peak at -0.15 volts is attributed to reactions of iron oxidation products. The dashed curve in this region shows an indication of a "doublet" peak. The cause of this is uncertain. The broader peak at -0.55 is attributed to the reduction of elemental sulfur which was formed during the 7-minute oxidation period. From the dotted curve, sonication can be seen to have two effects on pyrite surface oxidation products: 1) a substantial reduction of elemental sulfur on the pyrite surface and 2) a slight increase in the amount of reactable iron-oxy and iron-hydroxy products.

The results of this experiment indicate that sonication is effective in reducing the elemental sulfur on the surface of oxidized pyrite and in increasing the amount of exposed metal oxide. Both these factors suggest that sonication should be effective in depressing the flotation of oxidized pyrite. Flotation studies will be conducted to confirm this finding. Tests are also planned to examine the effect of sonication of oxidized coal surfaces using voltammetry, if appropriate modifications can be made to fabricate test electrodes made of coal.

A new method for determining of the effect of sonic energy on the zeta potential of easily oxidizable materials. During this quarter a new method was developed for determining the zeta potential of easily oxidizable materials such as pyrite and some coals. Problems had been encountered during earlier attempts to determine the zeta potential of pyrite and some coals. Earlier analyses using a flow-through Zeta Reader apparatus lacked reproducibility. Measurements were then made using a micro-cell and a Lazer Zee Meter manufactured by Pen-Kem Inc. Although the data collected on similar machines has been reported in the literature for some coals^{7,8}, it was found that the zeta potential analyses of easily oxidizable materials, particularly pyrites, lacked reproducibility. The source of the problem was determined to be pH change and zeta potential change due to the continuing oxidation of samples even after several hours of equilibration time. A method has now been developed which utilizes a closed-system with argon purge. It includes: deoxygenated pH solution containers, closed-system equilibration cells, pH-measurement cell, sonication cell, and a micro-electrophoresis cell with an argon reservoir. This new method promises to be a valuable tool in the predictive studies of pyrite behavior. Results of

the effect of sonication on the zeta potential of pyrite and coal will be correlated with micro-flotation studies and reported when complete, along with a description of the zeta potential measurement method.

FUTURE WORK

Additional experiments are planned to determine the effect of sonic exposure on the desliming, zeta potential, and surface oxidation of Pittsburgh seam coal. Work will also continue on the construction and preliminary testing of a 20-ft column flotation apparatus to be used in evaluating the effect of sonic treatment on minus-200-mesh coals.

REFERENCES

1. Buttermore, W. H., B. J. Slomka and M. R. Dawson, "Sonic Enhancement of Physical and Chemical Coal Cleaning", Fossil Energy Quarterly Report IS-4998, January 1, 1989 - March 31, 1989.
2. Buttermore, W. H., B. J. Slomka and M. R. Dawson, "Sonic Enhancement of Physical and Chemical Coal Cleaning", Fossil Energy Quarterly Report IS-5006, April 1, 1989 - June 30, 1989.
3. Birlingmair, D., T. Chmielewski and J. Pollard, "Chemical Pretreatment of Coal in a Stirred Ball Mill", Fossil Energy Quarterly Report, July 1, 1989 - September 30, 1989.
4. Hamilton, I. C. and R. Woods, 1981, An investigation of surface oxidation of pyrite by linear potential sweep voltammetry, J. Electroanal. Chem., 188:327-343.
5. Hewett, R. L., 1968, Proc. Aust. Instn. Min. Met., 226:73.
6. Arbiter, N., 1978, The physical chemistry of mineral-reagent interactions in sulfide flotation, proceedings of symposium held at College Park, Md., U.S.B.M. ICC 8818, pp. 144-9.
7. Kelebek, S., T. Salman and G. W. Smith, 1982, An Electrokinetic Study of Three Coals, Canadian Metallurgical Quarterly, 21:205-209.
8. Wen, W. W. and S. C. Sun, 1977, An Electrokinetic Study on the Amine Flotation of Oxidized Coal, Society of Mining Engineers, AIME, 262:174-180.

END

DATE FILMED

12 / 11 / 90