

LOWERING THE SULFUR AND ASH CONTENTS OF HIGH-SULFUR COALS
BY PEROXIDE-ACID TREATMENT

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INTRODUCTION

Considerable effort has been devoted in recent years to upgrading high-sulfur coals by both physical and chemical methods. Some methods are mild, selectively removing mineral components without significantly altering the organic matter. The more drastic methods break down the coal structure, separating it into an inorganic sludge and an organic product essentially not coal. As a recently publicized example, high-gradient magnetic separation has been proposed as a technique for removing pyrite and other weakly paramagnetic minerals from slurried coal.¹ The Bureau of Mines' froth flotation process² removes pyrite and other minerals by taking advantage of differences in density and wettability of these undesirable substances and organic material. A method known as Meyer's Process³ involves up to six leaches of pulverized coal with ferric salt solution at about 100° C, converting pyrite to sulfate and elemental sulfur. A more vigorous chemical method⁴ requires leaching finely pulverized coal with aqueous alkali at about 225° C in a closed system under an inert atmosphere, followed by treatment with strong acid and leaching with water. The still more vigorous PAMCO process⁵ involves dissolution of coal in solvent at elevated temperature, hydrogen treatment, physical separation of undissolved matter, and vacuum distillation of the dissolved products.

Our laboratory is investigating methods for upgrading shale oil and high-sulfur coal by mild oxidation. Currently, experiments are being conducted with two types of oxidation systems--one using oxygen, which shows promise as a method for upgrading shale-oil distillates,⁶ and the other using mixtures of H₂O₂ and acid, which may be useful for upgrading both shale oil and coal. This report describes results of treating several high-sulfur coals with solutions of H₂O₂ in H₂SO₄ or with H₂SO₄ alone. Acid concentrations ranged from 0.1 N to 0.5 N, H₂O₂ concentrations ranged from 7 to 17 percent, and treating periods ranged from 1 to 72 hours. Most of the tests were conducted at ambient temperature, but in one test series, the solutions were warmed to speed up the reaction.

EXPERIMENTAL PROCEDURES

Coals and Sample Preparation

Five different high-sulfur, high-volatile bituminous coals, representing a wide range of sulfur contents, sulfur types, and ash contents, were obtained from the Pittsburgh Energy Research Center. These were (A) Pittsburgh Seam, St. Clairsville, Ohio; (B) Pittsburgh Seam, Pittsburgh, Pennsylvania; (C) Illinois No. 5 Bed; (D) Hastie, Iowa Bed; and (E) Ft. Scott, Oklahoma Bed. Each coal as received was first screened through a 32-mesh screen to separate fine and coarse material. The plus 32-mesh material was crushed in a ceramic mill jar with Burundum cylinders; that which passed through the 32-mesh screen was combined with the initially separated fine material, and the plus 32-mesh material was returned to the mill jar for further crushing. This process was repeated until the entire sample was reduced to minus 32 mesh.

Reagents and Analytical Procedures

Reagents

H_2O_2 (30 percent), H_2SO_4 , and HCl were ACS reagent grade. $\text{Ce}(\text{SO}_4)_2$ was certified 0.1000 N solution standardized against primary standard iron wire. Treating solutions were prepared by dilution based on label values.

Coal Analyses

Proximate and ultimate composition and heating values were determined by standard methods⁷ at the Bureau of Mines Coal Analysis Laboratory, Pittsburgh Energy Research Center.

Determination of Extracted Iron

An aliquot of filtered spent treating solution was transferred to a 125-ml Erlenmeyer flask, 2-ml 6 N H_2SO_4 was added, the mixture was heated to boiling, and 0.5 N KMnO_4 solution was added dropwise until the pink color persisted for at least 2 minutes. After addition of 10-ml of 6 N HCl , the solution was again brought to a boil, reduced by the Zimmerman-Reinhardt method, and titrated with 0.1 N cerate solution using Ferroin indicator. A blank titer was determined on the reagents, subtracted from the sample titers, and the net titers calculated as Fe.

Treating Procedures

Varying the Treating Time

Ten-gram samples of coal A were shaken at ambient temperature in 500-ml Pyrex Erlenmeyer flasks with 100-ml portions of solution, which were 17 weight-percent H_2O_2 and 0.3 N H_2SO_4 . Treating times were 2, 4, 19, 24, 48, and 72 hours. One sample was treated with 0.5 N H_2SO_4 alone for 72 hours. After treating, each mixture was filtered with the aid of vacuum through a fine-porosity fitted glass funnel, and the coal was washed several times with water until a small portion of wash showed little or no sulfate content. Each treated coal and a portion of the untreated coal were dried for 2 hours in a vacuum dessicator at 80° C and analyzed for proximate and ultimate composition and heating value. The combined filtrates and washes from each coal sample were analyzed for iron content.

Varying Hydrogen Peroxide Concentration

Thirty-gram samples of coal A were treated for 2 hours in the manner previously described with 100-ml portions of solution, each 0.1 N in H_2SO_4 but with different concentrations of H_2O_2 in each. Hydrogen peroxide concentrations were 7, 9, 11, 13, 15, and 17 percent. After filtering and washing, the coals were dried and analyzed, and the extracted iron was determined in each filtrate.

Treating Coals Containing Different Proportions of Inorganic and Organic Sulfur

Coals B, C, D, and E, ranging in pyrite sulfur content from less than 1 percent to more than 4 percent and ranging in organic sulfur content from 1 percent to 3 percent, were treated for 1 hour with 15 percent H_2O_2 solutions that were 0.3 N H_2SO_4 and with 0.3 N H_2SO_4 alone. The volume of treating solution was 250-ml and the sample weight was 50 grams in each test. The treating and workup procedures were the same as previously described.

Repetitive Treating

Coals B and C were treated with 250-ml portions of 0.3 N H_2SO_4 -10 percent hydrogen peroxide as follows: Three 50-gram samples of each coal were first treated as previously described for 1 hour at ambient temperature. After filtering the three mixtures, one sample was worked up for analysis, and the other two were retreated with fresh solution for 3 hours at 55° C. After filtering the remaining two, one was worked up for analysis; the last sample was treated a third time with fresh solution for 7 hours at 85° C., filtered, and worked up for analysis.

RESULTS AND DISCUSSION

Analyses of samples of coal A before and after treating for 2 to 72 hours are shown in table 1. Acid-peroxide treatment caused a 49-percent decrease in sulfur content and a 32-percent

TABLE 1. - Results¹ of treating high-sulfur coal A with H_2O_2 - H_2SO_4 or with H_2SO_4 alone

Treating time, hr	Treating solution ²		C	H	N	S	O	Ash	Heating value, Btu/lb	Extracted Fe, wt-pct of coal
	H_2O_2 , wt-pct	H_2SO_4 , N								
	Untreated coal		68.9	4.8	1.1	4.5	7.9	12.8	12,460	0
2	17	0.3	74.8	5.0	1.3	2.3	7.8	8.7	---	1.92
4	17	.3	75.2	5.0	1.3	2.0	7.9	8.6	---	2.27
19	17	.3	75.4	5.0	1.3	1.9	8.4	8.0	13,310	2.32
24	17	.3	75.1	4.9	1.3	2.0	8.3	8.4	---	2.33
48	17	.3	75.0	5.0	1.3	2.0	8.5	8.2	---	2.39
72	17	.3	74.8	5.0	1.3	2.0	9.0	7.9	13,380	2.45
72	0	.5	72.3	4.8	1.2	3.9	7.5	10.8	12,890	.31

¹ Ultimate analyses and heating values on a dry basis.

² 100-ml solution per 10 grams of minus 32-mesh coal, ambient temperature.

decrease in ash content in 2 hours; thereafter, sulfur and ash contents decreased slowly to minimums of 44 and 62 percent, respectively, of original values. Values of iron extracted followed a similar trend, which indicated that most improvements in composition were substantially accomplished in 2 to 4 hours. Heating values of the treated samples were about 7 percent higher than that of the untreated coal. The sample treated for 72 hours with 0.5 N H_2SO_4 alone showed a modest increase of 3.5 percent in heating value and decreases of only 13 percent in sulfur and 16 percent in ash. It is apparent that this treatment for 72 hours had less effect on the coal than 2 hours of treatment with acid-peroxide, which demonstrates the importance of H_2O_2 in the solution.

Another series of tests on the same coal indicates the importance of sulfuric acid in the treating solution. In these tests conducted for 2 hours at ambient temperature, the initial concentrations of hydrogen peroxide were varied from 7 to 17 percent; initial sulfuric acid concentration was 0.1 N in each solution. The results, shown in table 2, show that at peroxide concentrations greater than 7 percent, very little further change in coal composition was achieved. At 17 percent peroxide concentration, comparison of these results with the results of 2 hours treating shown in table 1 indicate that the solution with the higher acid concentration was more effective in removing iron and sulfur and in lowering ash content. The analyses of sulfur forms show that only mineral sulfur was affected by acid-peroxide under these conditions. Neither organic sulfur nor nitrogen contents were appreciably affected by these treatments, and the increased heating values indicate there was little or no attack on organic components.

TABLE 2. - Composition¹ of high-sulfur coal A before and after treating with H₂O₂-H₂SO₄ solution

Treating H ₂ O ₂ , wt-pct	Solution ² H ₂ SO ₄ N	Ultimate analysis, wt-pct						Sulfur forms, wt-pct			Heating value, Btu/lb	Extracted Fe, wt-pct of coal
		C	H	N	S	O	Ash	SO ₄	Pyr.	Org.		
Untreated coal		68.9	4.8	1.1	4.5	7.9	12.8	0.41	2.30	1.79	12,460	0
7	0.1	73.0	5.0	1.2	3.3	8.0	9.5	.06	1.44	1.80	13,150	1.15
9	.1	73.0	5.0	1.2	3.1	8.4	9.4	.06	1.22	1.82	13,160	1.37
11	.1	72.9	5.0	1.2	3.1	8.5	9.3	.01	1.31	1.78	13,130	1.31
13	.1	73.3	5.0	1.2	2.9	8.6	9.0	.05	1.12	1.73	13,180	1.39
15	.1	73.3	5.1	1.2	2.8	8.3	9.3	.08	.94	1.78	13,170	1.41
17	.1	73.3	5.0	1.2	2.9	8.4	9.2	.09	1.04	1.77	13,200	1.50

¹ Ultimate analyses and heating values on a dry basis.

² 200-ml solution per 30 grams of minus 32-mesh coal, 2 hours at ambient temperature.

To test the effectiveness of acid-peroxide treatment on coals having widely different proportions of sulfur types, 50-gram samples of four coals were treated for 1 hour at ambient temperature with 250-ml volumes of either 15 percent H₂O₂-0.3 N H₂SO₄ or 0.3 N H₂SO₄ alone. Results are shown in table 3. In all cases acid-peroxide treatment was more effective than treatment with acid alone in terms of reducing sulfur and ash contents and increasing heating values. As previously observed, only the sulfate and pyrite sulfur were removed. Treatment of coal C with 0.3 N H₂SO₄ removed iron equivalent to 2 weight-percent of the sample, the source of which was not pyrite. Calculated as iron oxide, this amount of iron would account for the difference in ash content in this acid-washed sample and the untreated coal. In general, dilute sulfuric acid treating removed varying amounts of mineral matter, including sulfates and nonpyrite iron, but had no apparent effect on pyrite. In every case, acid-peroxide solution removed more mineral than acid alone and removed most of the pyrite but had no apparent effect on organic matter under these mild conditions.

To test the effects of multiple treatments, 50-gram samples of coals B and C were treated with one, two, or three 250-ml portions of a solution which was 10 weight-percent H₂O₂ in 0.3 N H₂SO₄. Reactions in second and third treatments were quite slow at ambient temperature, and the flasks were warmed to expedite peroxide decomposition. Analyses of the treated samples and of the untreated coals are shown in table 4 and show that these coals suffered some loss in quality when treated for a second and third time, characterized by a trend toward lower carbon contents and heating values accompanied by rising oxygen and ash contents. Even though the pyrite contents of the coals had decreased after the third treatment to less than 10 percent of the original contents, the amounts removed by repeated treatment were relatively small. Both coals show a modest decrease in organic sulfur content after treating a second and third time. The change in coal C is more significant, amounting to a decline of 11 percent of the organic sulfur present in the coal after the first treatment. The results indicate that continued exposure to acid-peroxide after pyrite or other reactive minerals are removed leads to oxidative attack on the organic matter.

Although the main object of these experiments was to gauge the potential of a strongly oxidizing system for demineralizing coal, rather than to examine the chemistry in detail, some observations of mainly chemical interest emerged. Treatment of the coals used in this work with 10 to 15 percent H₂O₂ solution for 1 to 2 hours at ambient temperature had very little effect on coal composition. The foregoing experiments demonstrate that in the concentrations employed, only the mixture of H₂O₂ and H₂SO₄, but neither reagent alone, is capable of attacking pyrite or

TABLE 3. - Analyses¹ of coals before and after treating with H_2O_2 - H_2SO_4 or with H_2SO_4 alone

Coal	Treating solution ²		Ultimate analysis, wt-pct						Sulfur forms, wt-pct			Heating value, Btu/lb	Extracted Fe, wt-pct of coal
	H_2O_2 , wt-pct	H_2SO_4 , N	C	H	N	S	O	Ash	SO_4	Pyr.	Org.		
B	Untreated coal		71.8	5.1	1.4	1.8	8.2	11.7	0.06	0.74	1.00	12,990	0
	0	0.3	72.3	5.0	1.4	1.8	8.0	11.5	.04	.79	.97	12,960	0.04
	15	.3	73.5	5.0	1.4	1.1	8.2	10.8	.02	.08	1.00	13,060	.63
C	Untreated coal		69.8	4.7	1.3	3.6	11.0	9.6	.08	1.06	2.46	12,590	0
	0	.3	71.5	4.9	1.3	3.6	10.1	8.6	.01	1.11	2.48	12,800	.08
	15	.3	72.0	5.0	1.3	2.7	11.5	7.5	.06	.09	2.55	12,860	1.02
D	Untreated coal		58.7	4.6	1.0	8.7	9.9	17.1	2.00	3.93	2.77	10,700	0
	0	.3	65.7	4.9	1.1	7.9	6.5	13.9	.51	4.45	2.94	11,900	2.06
	15	.3	68.9	5.1	1.2	4.4	10.8	9.6	.29	1.15	2.96	12,360	4.38
E	Untreated coal		73.7	5.3	1.6	4.1	6.7	8.6	.48	2.05	1.57	13,300	0
	0	.3	75.9	5.5	1.6	3.8	6.4	6.8	.07	1.94	1.79	13,770	.46
	15	.3	77.0	5.6	1.7	2.5	8.0	5.2	.04	.58	1.88	14,040	1.56

¹ Ultimate analyses and heating values on a dry basis.² 250-ml solution per 50 grams minus 32-mesh coal, ambient temperature for 1 hour.TABLE 4. - Effects of repeated treatment with 10-percent H_2O_2 -0.3 N H_2SO_4 on the composition¹ of two high-sulfur coals

Coal	Total treatments ²	Ultimate analysis, wt-pct						Sulfur forms, wt-pct			Heating value, Btu/lb	Extracted Fe, wt-pct of coal
		C	H	N	S	O	Ash	SO_4	Pyr.	Org.		
B	Untreated	71.8	5.1	1.4	1.8	8.3	11.6	0.06	0.74	1.00	12,990	0
	1	73.3	5.1	1.4	1.2	8.2	10.8	.01	.11	1.08	13,090	0.60
	2	72.5	5.0	1.4	1.0	9.3	10.8	.0	.04	.96	12,980	.72
	3	71.5	5.0	1.4	1.0	9.9	11.2	.0	.03	.97	12,630	.74
A	Untreated	69.8	4.7	1.3	3.6	11.0	9.6	.08	1.06	2.46	12,600	0
	1	72.9	5.1	1.3	2.8	10.3	7.6	.06	.16	2.58	12,900	.84
	2	72.7	5.0	1.4	2.6	11.3	7.0	.08	.08	2.44	12,840	1.22
	3	70.1	4.6	1.3	2.5	14.3	7.2	.11	.10	2.29	12,240	1.14

¹ Ultimate analyses and heating values on a dry basis.² Each treatment 250-ml solution per 50 grams minus 32-mesh coal. First treatment, 1 hour at ambient temperature; second treatment, additional 3 hours at 55° C; third treatment, additional 7 hours at 85° C.

demineralizing coal to the extent observed. It is therefore reasonable to postulate that peroxysulfuric acid, H_2SO_5 , is formed in equilibrium quantity in the mixture and plays an important role in the reaction. However, the expected initial H_2SO_5 concentration would be extremely low in the solution employed in this work because of the low H_2SO_4 concentration and the low value of the equilibrium constant measured by Monger and Redlich.⁸ Further, in view of the rapid decomposition of H_2O_2 in contact with high-sulfur coal and the apparent low rate of H_2SO_5 formation,⁸ it is difficult to reconcile the amount of peroxyacid expected in the treating solutions with the amounts of pyrite and other minerals removed unless it is assumed that substances in coal catalyze peroxyacid formation. This catalytic effect has been observed for a number of metal ions and for sulfates,⁸ and so could be expected in mixtures of H_2O_2 , H_2SO_4 , and coal. The principle reactions are therefore visualized as catalytic formation of H_2SO_5 and oxidation of pyrite with competing peroxide decomposition by metal ions. After removal of most of the active metals and sulfates from coal, oxidative attack on the organic matter becomes significant as indicated by analyses of coal subjected to repeated acid-peroxide treatment (table 4).

Evolution of small amounts of hydrogen sulfide was detected when coals were treated with acid-peroxide, although none was detected when using H_2SO_4 or H_2O_2 alone. Its presence in the strongly oxidizing media was surprising. Acid concentrations were apparently too low to produce H_2S from pyrite, in view of the selective extraction of sulfate from coal with ~ 3 N HCl, which is not expected to attack pyrite.⁷ Nalwalk and coworkers⁹ report that decomposition of coal with 30 percent H_2O_2 slowly oxidized pyrite to sulfate, but no evolution of H_2S was mentioned either in this work or that of Ward.¹⁰ The formation of H_2S cannot be conveniently explained as a result of H_2SO_5 formation because it is apparently a weaker acid than sulfuric acid.⁸ However, the formation of H_2S in minute quantities, whatever the reaction path, is not expected to be important in the overall reaction.

Further experimentation is in progress to determine the most effective concentrations of peroxide and sulfuric acid for coal demineralization. On the premise that peroxysulfuric acid is the most effective reagent and in order to increase its initial concentration, the concentration of sulfuric acid must be considerably higher than used in the initial experiments described in this work.

CONCLUSIONS

Treatment of high-sulfur coals with H_2SO_4 - H_2O_2 solution lowers the sulfur and ash contents of the coals by removing pyrite, iron, and other minerals, leading to fuels of higher heating value. No significant attack on organic constituents occurs at ambient temperature before minerals susceptible to oxidation have been removed. Acid-peroxide treatment apparently has potential as a method for demineralizing high-sulfur coals.

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