

DISSOLUTION OF SULFUR COMPOUNDS IN COAL AND COAL-DERIVED PYRITE
WITH PERCHLORIC ACID

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ABSTRACT

Knowledge of the ease by which various sulfur forms contained in coal can be removed during treatment under oxidizing conditions can be used as a guideline for controlling process conditions during desulfurization. To investigate these properties, perchloric acid was chosen as the oxidizing agent because its potential can be varied by changing its concentration. The stepwise oxidation of an Illinois #6 coal and a coal-derived pyrite was effected by carrying out the reactions in a modified Bethge apparatus to control the boiling point and thus the concentration and oxidizing power of perchloric acid. Sulfur was determined as sulfate in the reaction mixture. Volatile sulfur gases were trapped in an aqueous hydrogen peroxide scrubber and determined as sulfate. Sulfatic sulfur and the other forms of sulfur in coal were clearly delineated. Some delineation was made between pyritic sulfur and organic sulfur. However, the anticipated delineation between various organic sulfur forms was not observed. Total sulfur was recovered from the reaction of coal with boiling concentrated perchloric acid at 203°C. The oxidation of large samples of pyrite (>0.1 g) produced a yellow precipitate identified as ferric hydroxide sulfate.

INTRODUCTION

Of the various methods proposed for the desulfurization of coal, several have involved the use of oxidizing conditions. By knowing the ease with which the various sulfur species in coal can be removed, the oxidation conditions used during a process could be optimized for maximum sulfur removal and recovered heat content. The ease of removal of sulfur species in coal can be measured by using perchloric acid as an oxidizing agent. This paper discusses the reaction of perchloric acid with sulfur in coal and in a coal-derived pyrite and the relationship of the sulfur products produced in these reactions.

It was hoped that by varying the boiling point of perchloric acid, and thus its concentration, some delineation among the various forms of sulfur in coal could be made. Perchloric acid was chosen as an oxidizing agent because the apparent reduction potential of perchloric acid can be varied by changing its concentration as a function of boiling temperature. In this manner, stepwise oxidation of the sulfur species could be performed by varying the reduction potential of the oxidizing agent. Smith (1) has demonstrated that the apparent reduction potential of perchloric acid rises slowly as the boiling point and concentration increase. McGowan and Diehl (2,3) have used this property of perchloric acid to oxidize the kerogen of Green River oil shale.

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Total sulfur in coal has been determined previously using perchloric acid in combination with other acids. Smith and Deem (4) used a combination of nitric acid and perchloric acid to oxidize the coal and then determined sulfate in the resulting solution. They reported that the sulfur results were low, possibly due to inefficient precipitation of barium sulfate from perchloric acid solution. In light of the present study and studies by Kahane (5) and Bethge (6), the low results were probably due to loss of a volatile sulfur compound. Spielholtz and Diehl (7) oxidized coal with a mixture of perchloric acid and periodic acid. In that study, sulfur gases were trapped in 3% H₂O, which was then added to the perchloric acid solution, boiled to fumes of perchloric acid, and the total sulfur was determined as sulfate. The total sulfur values were consistent with those determined by ASTM procedures. However, there was a foaming problem with some coals. Those coals that foamed generally caused an explosion with boiling concentrated (70-72%) perchloric acid, but explosions were avoided if a starting concentration of ~68% perchloric acid was used. Being aware to this danger, special precautions were taken during the course of the present work. Markuszewski et al. (8,9) have determined total sulfur in coal using a mixture of nitric, phosphoric, and perchloric acids for the dissolution and determining sulfate in the resulting solution by nephelometry. As shown in the present work, addition of phosphoric acid inhibits the formation of volatile sulfur gases.

The present investigation consisted of four series of experiments. The first was the oxidation of an as-received Illinois #6 coal, the second was the oxidation of a finely ground sample of the same Illinois #6 coal, the third was the oxidation of 1.0-g samples of coal-derived pyrite, and the fourth was the oxidation of 0.06-g samples of the coal-derived pyrite. To follow the course of the oxidation, the amount of solid remaining after the reaction, the amount of sulfate sulfur in the aqueous phase, and the amount of sulfur collected from the vapor phase during the reaction were monitored.

EXPERIMENTAL

The Illinois #6 (IL 6) coal used in this study came from the Captain Mine, Percy, Illinois, and is described further in the Ames Laboratory Coal Library report (10). Perchloric acid oxidations of the coal were performed on as-received and on ground samples. Grinding was performed to make the sample more homogeneous. The coal-derived pyrite (CP 1) was separated from an Iowa coal during cleaning (Chuang et al., 1980). The sample was ground to -16 mesh, with at least 75% being -100 mesh. Acids used were commercial reagent grade. All perchloric acid oxidations were done with a modified Bethge apparatus, described by McGowan and Diehl (2), in a hood and behind an explosion shield.

Several different samples were oxidized with perchloric acid of varying concentration and boiling point. In the tables, the sample designations IL 6 and CP 1 are followed by the boiling point of the perchloric acid used to oxidize a particular sample. A lower case letter following the boiling point indicates that more than one

reaction was run at that boiling point employing different experimental conditions.

For the oxidation experiments, perchloric acid was added to the Bethge apparatus, and the boiling point adjusted to the desired temperature. By varying the initial amount of perchloric acid added, a final volume of approximately 50 mL was obtained. After cooling, 5 or 10 mL of phosphoric acid was added for some of the pyrite oxidations. A weighed sample of the coal or pyrite was placed in the Bethge apparatus, and a gas absorption bottle containing 100 mL of 15% H_2O_2 was added to the top of the Bethge apparatus (this absorption bottle was not used on the as-received coal samples). Using nitrogen as a purge gas, the reaction vessel was heated and the stable reaction temperature was noted. The reaction was allowed to proceed for 1.5 hours, and then the heat was removed. For the ground coal samples foaming was a problem. To overcome this foaming problem, the heat was removed when foaming began and reapplied when foaming ceased. Eventually, foaming ceased completely, and the reaction mixture was allowed to reach the boiling point. The system was purged for 30 minutes with nitrogen. The solution in the absorption bottle, designated with an end letter "G", was boiled to insure oxidation of the sulfur to sulfate and to reduce the volume to 25 mL. The samples were then diluted to 50 mL and the sulfate was determined by ion chromatography. After cooling, the reaction mixture was filtered. The solid phase, designated with an end letter "S", was dried at 60° in a vacuum oven and weighed. The percentage undissolved material was calculated. The aqueous phase, designated with an end letter "P", was diluted to 250 mL and analyzed for sulfate by nephelometry.

The solid samples were analyzed for sulfur by the Analytical Services of Ames Laboratory. IL 6 was analyzed by the ASTM procedure. CP 1 was analyzed for total sulfur using a Fisher Total Sulfur Analyzer. It was assumed that all of the sulfur existed as pyritic sulfur in the pyrite sample. The results of these analyses appear in Table 1.

In the aqueous phase of each reaction, sulfate was determined by precipitation with barium and the turbidity of the resultant barium sulfate suspension was measured spectrophotometrically. Since some of the aqueous phases contained a solid material, the solutions were allowed to sit at least overnight, and the sample used for the analysis was pipetted from the supernatant liquid. Since most of the solutions were also colored, the absorbance of the sample without added barium was measured and subtracted from the absorbance of the test solutions.

RESULTS AND DISCUSSION

The sulfate results from the aqueous phases of the as-received coal and the ground coal samples appear in Table 2 and Table 3, respectively. At temperatures of 150° and below, the sulfate content in the aqueous phase is constant and in the range of sulfatic sulfur reported by the ASTM procedure. This is native sulfate in the coal which may have undergone some oxidation since the ASTM assay. Above 150°, the sulfate

content begins to increase rapidly up to 165°, reaching a point which is somewhat below the assay for sulfatic plus pyritic sulfur. The increase then slows with increased temperature to a value somewhat less than the total sulfur assay.

Note that the results for the ground sample appear to have more "noise" than the as-received sample at temperatures of about 170° and especially at 203°. This was probably due to the foaming of samples about 170° and the lowering of the temperature until foaming ceased. Hence, these reactions spent more time at lower temperatures, where the production of sulfur gases was favored. The as-received samples did not have a foaming problem. There were some high results for two of the reactions with as-received coals. These results were most likely due to a sampling problem with the as-received coal, i.e., a large particle of pyrite was observed in some of the 1-g samples which would give an unrepresentative high sulfur value for that sample. Thus, the as-received coal posed a sampling problem which was alleviated by grinding the sample. However, the ground coal had a problem with foaming.

For the ground coal reactions and for one as-received coal reaction, the gases produced during the reaction were bubbled through a solution containing 15% H_2O_2 . Based on the sulfate determined using ion chromatography, the production of sulfur gases was low at low temperatures, increased as the temperature increased, and then decreased as the temperature increased above 170°C. This indicated that sulfur gases were produced at low temperatures when the oxidizing ability of perchloric acid was low. As the oxidizing ability of perchloric acid increased, the production of sulfate was favored. The low results at 170° and 203°C appeared to be due to an unidentified systematic error introduced on the same day of analysis. The high result at 203° was apparently due to the large amount of time this particular sample spent at lower temperatures to overcome the foaming problem described earlier for the ground coals. There are several sulfur compounds that could be produced in these reactions. Bethge (6) proposed that hydrogen sulfide, sulfur dioxide, and carbonyl sulfide were likely gases produced. Since some sulfur gases are produced at 130°C where perchloric acid has very little oxidizing ability, some native sulfide may have been converted to hydrogen sulfide. The data for the total sulfur recovered (the sum of the sulfate in the aqueous solution and the trapped sulfur gases) indicated that approximately 95% of the total sulfur was recovered at 180° and 100% was recovered at 190° and above.

In order to ascertain the effect of perchloric acid on FeS_2 , several samples of a coal-derived pyrite were dissolved. In the first series, 1-g samples of pyrite were used so that a large amount of sulfate would be produced making the determination of sulfate in a large excess of perchloric acid easier. The results appear in Table 4. At temperatures below 164°, the reactions proceeded as expected. However, above 164° a yellow precipitate formed. The amount of precipitate produced increased as the boiling point of perchloric acid increased, with the maximum amount produced at 203°. When 2 reactions were run on 0.1-g samples at 203°, the yellow precipitate formed again, but the

relative amount was significantly smaller. The precipitate was filtered, vacuum dried at 60°, and analyzed by a scanning electron microprobe (SEM) to reveal the presence of iron and sulfur as the major components of the solid. Since SEM can detect all elements above neon, oxygen was not eliminated as a component, but chlorine was eliminated. X-ray diffraction analysis proved the solid to be ferric hydroxide sulfate, $\text{Fe}(\text{OH})(\text{SO}_4)$. Analysis of the solid produced at 194° gave a result of 17.6% total sulfur (theoretical is 18.99% sulfur). Recognizing the presence of silica and residual coal impurities, this result was remarkably close. There are many ferric hydroxy sulfates known which vary mostly by hydration but also by the ratio of iron, hydroxide and sulfate; all of these compounds are yellow and precipitate from acid solution (12). Sulfate was also determined in the aqueous phases using nephelometry; however, no correlations could be made.

Since no yellow precipitate was formed during the coal oxidations, it was decided to oxidize CP 1 samples that would correspond in size to the amount of pyrite known to be in the coal sample, i.e., 0.06-g. Several reactions were run, some with the addition of phosphoric acid in an attempt to drive the dissolution of pyrite by forming an iron-phosphate complex. Phosphoric acid has been used with perchloric acid to speed the dissolution of iron ores (13).

The results of these reactions appear in Table 5. Microscopic observation of the solid material from each reaction showed that no yellow precipitate formed during these reactions. The percentage of undissolved material was determined for each reaction except those at 203°C; the undissolved material for 203° reactions was quite small and existed as small white crystals, probably quartz. In general, the addition of phosphoric acid does not increase the dissolution of pyrite at low temperatures (150-160°C). In fact, phosphoric acid appears to inhibit dissolution at these temperatures. Even though over 90 percent of the sample was dissolved by perchloric acid at 155-160°, the remaining solid still contained a small amount of pyrite. However, no pyrite was observed at 170° or at 203°. Sulfate was determined in the aqueous phase using nephelometry and in the peroxide trap using ion chromatography. With no phosphoric acid present, total sulfur recovered approached 100% for boiling points of 160° and above (total sulfur in the sample was assayed at 42.77%). The presence of phosphoric acid at 160° produced a much lower sulfur recovery, but the presence of phosphoric acid at 203° produced a sulfur recovery identical to that for perchloric acid alone at 203°, both approaching 100%. The presence of phosphoric acid at 203° did inhibit the formation of sulfur gases. Only 0.1% sulfur was recovered in the peroxide trap, while 39.9% sulfur was recovered as sulfate in the aqueous phase.

CONCLUSIONS

Sulfatic sulfur in coal can be removed by perchloric acid that has no oxidizing ability other than the hydrogen ion. Any hot acid should remove sulfate. Sulfatic sulfur in coal can be determined by using perchloric acid with a boiling point below 150°, and measuring the sulfate in the reaction mixture. Boiling perchloric acid at 160°, approximately 1.5 volts (14), is required to remove 100% of the pyrite.

However, at this temperature, some oxidation of the organic material will also occur. About 80% of the pyrite can be removed at 150°, approximately 1.3 volts, without significant oxidation of the organic material. A boiling point of 180°, approximately 1.7-1.8 volts, is necessary to remove the organic sulfur. However, at this temperature the organic material has been oxidized to the point dissolution. Total sulfur in coal can be determined with boiling concentrated perchloric acid. Two forms of sulfur are produced as reaction products: sulfur which is retained in solution as sulfate and a sulfur-containing gas which can be removed in a peroxide trap. Both forms of sulfur need to be measured for the determination of total sulfur. Since phosphoric acid inhibits the formation of sulfur gases at 203°, it may be possible to determine total sulfur without measuring the sulfur trapped by the peroxide solution.

The oxidation of pyrite can produce a precipitate of ferric hydroxide sulfate if the concentration of iron and sulfate are high enough. A 0.06-g sample of pyrite does not form a precipitate; a 0.1-g sample will form a small amount, and a 1.0-g sample will form a large amount of precipitate. The oxidation of a 1.0-g sample of coal which contains approximately 0.06-g of pyrite does not form any observable precipitate. It is possible that a small amount of sulfate may be tied up with iron in the reaction mixtures of the coal and 0.06-g pyrite samples. This may account for the fact that the results for sulfur recovery never quite approach the theoretical (even though they are within 5% of the theoretical).

Clear delineation has been made between sulfatic sulfur and the other forms of sulfur. Some delineation has been made between pyritic sulfur and organic sulfur. The anticipated delineation among the various forms of organic sulfur was not achieved.

LITERATURE CITED

1. Smith, G. F., "The Dualistic and Versatile Reaction Properties of Perchloric Acid," Analyst, 80, 16, 1955.
2. McGowan, C. W. and Diehl, H., "The Oxidation of Green River Oil Shale with Perchloric Acid. Part I - The Reaction of Green River Oil Shale with Perchloric Acid of Varying Concentration and Boiling Point," in print Fuel Proc. Tech.
3. McGowan, C. W. and Diehl, H., "The Oxidation of Green River Oil Shale with Perchloric Acid. Part II - The Analysis of Oxidation Products," in print Fuel Proc. Tech.
4. Smith, G. F. and Deem, A. G., "Determination of Sulfur in Coal by Perchloric Acid Method," Ind. Eng. Chem., Anal. Ed., 4, 227, 1932.
5. Kahane, E., "Determination of Sulfur in Rubber," Caoutchouc et Gutta-Percha, 24, 13549, 1927.
6. Bethge, P. O., "Apparatus for the Wet Ashing of Organic Matter," Anal. Chim. Acta., 10, 317, 1954.

7. Spielholtz, G. I. and Diehl, M., "Wet Ashing of Coal with Perchloric Acid Mixed with Periodic Acid for the Determination of Sulphur and Certain Other Constituents," Talanta, 13, 1002, 1966.
8. Markuszewski, R., Wheeler, B. C., Johnson, R. S., and Hach, C. C., "Rapid Dissolution of Coal for Analysis for Sulfur, Iron, and Other Elements," Am. Chem. Soc. Div. Fuel Chem. Preprints 28(4), 292ff (1983).
9. Kilpatrick, P. and Markuszewski, R., "Rapid Determination of Sulfur and Iron in Coal," presented at the Iowa Academy of Science Meeting, Iowa City, IA, April 27-28, 1984.
10. Biggs, D. L., et al., "Status Report of the Collection and Preparation of Coal Samples for the Ames Laboratory Coal Library," presented at the Coal Sample Bank Workshop, Atlanta, GA, March 27-28, 1981.
11. Chuang, K. C., Chen, M.-C., Greer, R. T., Markuszewski, R., and Wheelock, T. D., "Pyrite Desulfurization by Wet Oxidation in Alkaline Solutions," Chem. Eng. Commun. 12(1-3), 137-159 (1981).
12. Posnjak, E. and Merwin, H. E., "The System, $Fe_2O_3-SO_3-H_2O$," J. Am. Chem. Soc., 44, 1965, 1922.
13. Diehl, H., Quantitative Analysis, Oakland Street Science Press, Ames, Iowa, 2nd edition, 1974, 232.
14. Smith, G. F., "The Wet Chemical Oxidation of Organic Compositions Employing Perchloric Acid With-or-Without Added $HNO_3-H_5IO_6-H_2SO_4$," The G. Frederick Smith Chemical Co., Inc., Columbus, Ohio, 1965.

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Table 1. Sulfur Assays for Coal and Pyrite Samples (in %)

Sample	Sulfatic Sulfur	Pyritic Sulfur	Organic Sulfur	Total
IL 6	0.26	2.41	2.17	4.85
CP 1	----	42.77 ^a	----	42.77

^a Assumed that all sulfur was pyritic.

Table 2. Oxidation of As-Received Illinois #6 Coal with Perchloric Acid

Sample	Sample Weight (g)	Boiling Point (°C)	Reaction Temperature (°C)	Reaction Time (hr)	Undissolved Material (%)	Sulfur Aqueous As SO ₄ ²⁻ (%)
IL6-130	0.9751	134	126	1.5	91.34	0.39
IL6-140	1.0213	144	135	1.5	93.77	0.46
IL6-151	0.9991	155	146	1.5	99.43	1.26
IL6-160	0.9960	164	157-61	1.5	88.91	2.44
IL6-169	0.9513	173	166	1.5	52.93	6.68
IL6-170	1.0269	174	166-7	1.5	59.09	3.21
IL6-179	1.0048	183	174-1	1.5	17.96	3.56
IL6-180	0.9718	184	175-1	1.5	12.44	4.71
IL6-190	1.0408	194	183	1.5	8.50	3.98
IL6-200a	0.1431	203	202	0.5	7.41	4.30
IL6-200b	0.0408	203	202	1.0	7.89	4.54

Table 3. Results of the Oxidation of the Ground Coal with Perchloric Acid

Sample	Sample Weight (g)	Boiling Point (°C)	Reaction Temp. (°C)	Reaction Time (hr)	Undissolved Material (%)	Sulfur Aqueous As SO ₄ ²⁻ (%)	Sulfur As Gas (%)	Total Sulfur (%)
IL6-130b	0.9897	130	124-5	1.5	93.63	0.39	0.17	0.56
IL6-140b	1.0023	140	131	1.5	91.38	0.41	0.66	1.07
IL6-150b	1.0146	150	140-38	1.5	90.62	0.49	1.44	1.93
IL6-160b	0.9996	160	152	1.5	81.18	1.87	1.78	3.65
IL6-170b	0.9904	170	162-3	1.5	31.50	2.65	0.03 ^a	2.68
IL6-171b	0.9936	171	162-3	1.5	34.95	2.78	0.31 ^b	3.09
IL6-180c	1.0181	180	174	1.5	14.24	3.06	1.37	4.43
IL6-190b	0.9945	190	178-7	1.5	9.03	4.07	1.03	5.10
IL6-203a	0.9974	203	196-9	1.3	6.94	3.01	1.59	4.60
IL6-203b ^c	1.0190	203	201	1.5	7.19	3.43	0.10 ^a	3.53

^a These two samples were run on the same day. All samples run on the ion chromatograph that day appeared to be low.

^b This sample went dry during processing and H₂SO₄ was lost.

^c This sample used the coarse, as-received coal.

Table 4. Results of the Oxidation of 1-g Pyrite Samples with Perchloric Acid

Sample	Sample Weight (g)	Boiling Point (°C)	Reaction Temp. (°C)	Reaction Time (hr)	Undissolved Material (%)	Sulfur Aqueous As SO_4^{2-} (%)
CP1-140	1.0042	144	139	1.5	47.92	4.13
CP1-150	1.0063	154	149	1.5	11.54	13.6
CP1-160	1.0027	164	156-8	1.5	11.60	13.2
CP1-170	1.0185	174	164-6	1.5	19.75 ^a	12.3
CP1-180	0.9922	184	175-8	1.5	57.11 ^a	6.4
CP1-190	1.0089	194	186-8	1.5	101.5 ^a	---
CP1-200a	0.9794	203	202	1.5	83.29 ^a	---
CP1-200b	1.0177	203	202	0.33	78.01 ^a	---
CP1-200c	0.1010	203	203	0.67	3.47 ^a	---

^a A yellow precipitate was produced during the reaction.

Table 5. Results of the Oxidation of 0.06-g Samples of Pyrite

Sample	Sample Weight (g)	H ₃ PO ₄ Added to HClO ₄	Boiling Point (°C)	Reaction Temp. (°C)	Reaction Time (hr)	Undissolved Material (%)	Sulfur Aqueous (%)	Sulfur As Gas (%)	Total Sulfur (%)
CP1-150b	0.0577	0	154	152-3	1.5	3.12	21.7	----	----
CP1-150c	0.0658	5 ^a	150	145	1.5	22.49 ^c	6.4	28.6	35.3
CP1-156a	0.0613	5 ^b	156	144-52 ^d	1.5	15.2	9.3	----	----
CP1-160b	0.0604	0	164	157-64 ^d	1.5	2.98	27.3	----	----
CP1-160c	0.0609	10 ^b	160	152	1.5	20.0	12.0	20.7	32.9
CP1-160d	0.0614	0	160	149	1.5	7.3	17.3	22.8	40.1
CP1-170b	0.0574	0	170	161-66	1.5	1.4	19.5	22.5	42.0
CP1-203b	0.0622	0	203	203	1.0	---	35.9	3.9	39.8
CP1-203c	0.0566	5 ^a	203	200	1.5	---	39.9	0.1	40.0

^a Added after boiling point adjustment.

^b Added before boiling point adjustment.

^c Oven temperature reached 170° during drying process causing oxidation.

^d Condensate escape during reaction.