

PRE-OXIDATION AND PERCHLOROETHYLENE (PCE) DESULFURIZATION OF ILLINOIS COALS
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INTRODUCTION

A pre-combustion coal desulfurization process using perchloroethylene (PCE) at 120°C to remove up to 70% of the organic sulfur has been claimed by the Midwest Ore Processing Co. (MWOPC). The importance of oxidation and drying conditions as well as temperature control is stressed by the developers (Lee et al., 1991; Leehe and Sehgal, 1988). According to MWOPC, this process gives higher organic sulfur removal from Ohio and Indiana coals than from Illinois coals.

Over the past few years, the ISGS and Eastern Illinois University (EIU) have jointly developed analytical methods to measure forms of sulfur in PCE extracts of high-sulfur Illinois coals (Buchanan et al., 1990). Some elemental sulfur and limited amounts of organic sulfur have been removed from oxidized Illinois coals during these studies; however, these sulfur removals were much lower than those reported by MWOPC. Several hypotheses may explain these differences, but to date, limited data addressing these hypotheses have been reported. MWOPC postulated that the organic sulfur removed was mainly aliphatic, and that the organic sulfur in Illinois coals may contain less aliphatic sulfur than other coals tested. We have hypothesized that errors in interpreting data from American Society for Testing and Materials analysis methods (ASTM) may account for the higher organic sulfur removal reported by the MWOPC. For example, elemental sulfur extracted by the PCE can be derived from the pre-oxidation of pyrite, but this elemental sulfur will be erroneously reported as organic sulfur by the ASTM analysis. Furthermore, the high chlorine content in the PCE-treated material could decrease its suitability for combustion.

One goal of this study was to independently confirm the organic sulfur removal from high-sulfur Illinois coals with the PCE desulfurization process reported by the MWOPC. Another goal was to verify the forms-of-sulfur determination using the ASTM method for evaluation of the MWOPC process. The overall commercial value of this process also depends on removal of the chlorine from the PCE-treated coal residue. Chlorine up-take during PCE desulfurization, and techniques for removal of chlorine from the process residue, also were investigated.

EXPERIMENTAL

Samples - An oxidized Ohio 5/6 coal was provided by Mr. C. Kulik of Electric Power Research Institute. Coals identified as IBC-101, -102, -104, -106 were obtained from the Illinois Basin Coal Sample Program (Kruse, et al., 1991). Mineral pyrite was provided by Mr. R.H. Shiley, an ISGS staff member.

Procedures

Ambient oxidation (laboratory weathering) - During ambient oxidation, samples (IBC-104 coal and mineral pyrite) were stored in a container under room air at laboratory conditions for periods of both 2 weeks and greater than 5 years for coal and for more than 3 years for a pyrite sample.

PCE extraction of oxidized samples of coals IBC-104 and Ohio 5/6 - Azeotropic drying was conducted prior to each PCE extraction. This was accomplished by adding the sample to well-stirred PCE at 70 to 100°C in an open flask, heating the mixture until all of the water was removed and the temperature in the flask rose to 121°C. The temperature was maintained at 121°C for 30 minutes to complete the extraction. The residue coals from PCE extraction were isolated by hot filtration. The feeds and products from these operations were subjected to both ASTM and X-ray absorption near edge structure (XANES) analyses. The PCE extracts were analyzed for elemental sulfur by high performance liquid chromatography (HPLC).

Short-term air oxidation/PCE extraction - Oxidation in air in the presence of PCE was conducted by bubbling filtered air through a coal/PCE slurry with and without water at a specified temperature for a selected length of time. After oxidation, the temperature was increased to 121°C and maintained for 30 minutes. The extracts produced from PCE extraction were then isolated from the residues by hot filtration. After purification, the PCE extracts were analyzed by HPLC for elemental sulfur contents.

ASTM forms-of-sulfur analysis - In the ASTM D-2492 procedure (1991), the sample (-60 mesh) is first digested with a dilute HCl solution. The acidic solution is filtered and sulfatic sulfur is precipitated and quantified as BaSO₄. After washing with distilled water, the HCl-free residue is digested with dilute HNO₃. The solution is filtered and the volume adjusted for atomic absorption (AA) determination of iron, which is then calculated as pyritic sulfur. At this point, all the iron from pyrite (FeS₂) should have been removed and analyzed. To obtain total sulfur, a separate split of coal sample is combusted in a Leco model SC32 total sulfur analyzer equipped with an on-line IR detector which is used to monitor SO₂ production. Organic sulfur is obtained by taking the difference between total sulfur content and the sum of pyritic and sulfatic sulfur contents. Any elemental sulfur present appears as organic sulfur since it is not reported as pyritic or sulfatic sulfur.

Elemental sulfur determination - Elemental sulfur in the PCE extract was first purified by passing the solution through a Florisil column. Sulfur was then determined with a Perkin-Elmer Model LC65 HPLC with an ultraviolet - visible light (UV-VIS) detector.

X-ray absorption near-edge structure (XANES) analysis - This method has been developed (Huffman et al., 1991) for the quantitative determination of all major forms of sulfur in coal, both organic and inorganic. The method is based on a least-squares analysis of the X-ray absorption near-edge structure (XANES). This analysis produces a series of peaks that represent 1s → np photoelectron transitions. Because the major sulfur forms occurring in coal (pyrite, elemental sulfur, organic sulfide, thiophene, sulfoxide, sulfone, and sulfate) have characteristic s → p transition energies, the relative peak areas contributed to the XANES spectrum by each sulfur species can be determined. Aliphatic sulfur is represented by organic sulfide, aromatic compounds by thiophene, and oxidized organic sulfur species by sulfoxide and sulfone. These peak areas are converted to weight percentages of sulfur using calibration constants derived from XANES data from standard compound mixtures. Since XANES derives the signal from the bulk of the sample, detailed information concerning the aliphatic, aromatic, and oxidized forms of organic sulfur removed during PCE desulfurization can be obtained.

Dechlorination and chlorine analysis - Procedures for chlorine removal from the PCE-extracted coals were examined. An ISGS proprietary method was used to remove chlorine from the processed residues. The chlorine contents of the treated products were determined by a Leco CL350 chlorine analyzer.

RESULTS AND DISCUSSION

PCE desulfurization and sulfur analyses by ASTM and HPLC methods - PCE desulfurization was conducted on short-term (2 weeks) and long-term (> 5 years) air-oxidized IBC-104 coal samples and an oxidized Ohio 5/6 coal sample. The results of the ASTM analyses of the desulfurization products and the HPLC analyses of the PCE extracts are shown in Table 1. Coal oxidation before PCE extraction produces more elemental sulfur to be extracted. The ASTM data also show a reduction in both total sulfur and organic sulfur after PCE extraction of the highly oxidized coal samples.

The sample from two weeks oxidation indicates no total sulfur reduction with an undetectable amount of elemental sulfur by HPLC analysis of the PCE extract. The increase in organic sulfur content of this sample as shown by ASTM analysis appears to be an error of the ASTM analysis. Considering the ASTM forms-of-sulfur determination (ASTM D-2492, 1991), the error in organic sulfur determination is associated with the errors from sulfate, pyrite, and total sulfur determinations. The changes in the two-week oxidized sample after PCE extraction may be too small to offset these errors. However, the sample from a long-term (> 5 years) ambient oxidation shows a noticeable reduction in both total sulfur (20%) and organic sulfur (10%), and a noticeable amount of elemental sulfur (0.07%) obtained by PCE extraction. Similar reductions in sulfur content of the residues and increases in extracted elemental sulfur were obtained for the highly oxidized Ohio 5/6 sample. The reduction in total sulfur was 20% and in organic sulfur was 21%, and 0.10% elemental sulfur was obtained by PCE extraction.

PCE desulfurization and sulfur analyses by XANES and ASTM methods - Least-squares sulfur K-edge XANES analysis was utilized to resolve organic sulfur into aliphatic, aromatic, and oxidized forms. To take the most precise data on sulfur forms, the data from XANES analysis were combined with wt% pyritic sulfur in coal from the ASTM analysis. The results are listed in Table 2. The data show that two-week oxidation has little effect on elemental sulfur extraction, which is consistent with the HPLC analysis result. However, these data do not identify any form of organic sulfur reduction.

The five-year oxidized sample (Table 2) differs significantly from the two-week oxidized sample in that 35% of the pyritic sulfur has been oxidized to sulfate and to a small amount of elemental sulfur. In addition, the principal forms of organic sulfur appear to be 10% lower in the five-year oxidized sample than in the two-week oxidized sample, suggesting that organic sulfur has been oxidized to some extent. Oxidized organic sulfur (0.13%) observed by the XANES analysis supports the indication that organic sulfur has been partially oxidized during this long-term air oxidation. The XANES data also indicate that PCE treatment removes all the elemental sulfur and about half of the oxidized organic sulfur. The apparent difference in sulfate content before and after PCE extraction is attributed to water washing after the PCE treatment, which removes soluble sulfates.

The Ohio 5/6 sample behaves similarly to the IBC-104 coal in that the PCE treatment removes all the elemental sulfur and 71% of the oxidized organic sulfur. The treatment has little or no effect on other forms of sulfur. As was the case with the coal previously discussed, the large decline in sulfate content is attributed to aqueous washing after PCE extraction.

Overall, the results indicate that oxidation is important to subsequent PCE desulfurization.

The effects of process conditions (time, temperature, and oxidation) on the amounts of elemental sulfur obtained by PCE extraction - In addition to ambient oxidation, various short-term, air-oxidation effects (achieved by varying the amount of water, temperature, and time) were examined. As indicated in Table 3 for a partially oxidized coal O-IBC-101, bubbling air through a suspension of coal in hot PCE with water present produces more elemental sulfur (0.10%) in the extract than the run conducted under the same condition without water present (0.06%). Without water present, as seen in the two runs of O-IBC-101 coals, bubbling air at 90°C for two hours does not produce additional elemental sulfur. A similar trend is observed for a fresh sample of IBC-104 (F-IBC-104). The run that was conducted with water present (at 90°C bubbling air for two hours) shows a 2-fold increase in elemental sulfur production (0.02%), whereas, the run that was conducted without water present (at 24°C bubbling air for two hours) shows no change in elemental sulfur production. Among all the IBC-104 coal samples, the sample which underwent long-term ambient oxidation has the most elemental sulfur (0.07%).

The results of this investigation indicate that the presence of water during oxidation enhances elemental sulfur production. This implies that the oxidation process can be speeded up by maintaining moist conditions during oxidation.

Dechlorination - A steam-stripping technique has been reported to give a PCE residue from Illinois Herrin (No. 6) coal with a chlorine content of 0.9% (Atwood and Leehe, 1991). This level of chlorine in the treated coal would be considered unacceptable by coal users.

Various methods for chlorine removal from the PCE process residues were examined. The amount of chlorine remaining in the PCE-extracted coals was determined. Without any washing, a PCE-extracted coal had a chlorine content as high as 4.68%, as indicated in Table 4. An ISGS proprietary method was developed to remove excess PCE. This method can totally remove PCE and give PCE-extracted coal with a chlorine content as low as 0.03%.

ASTM forms of sulfur in fresh and oxidized coal samples - Four coals from the Illinois Basin Coal Sample Program (IBCSP) were oxidized under ambient conditions. The forms of sulfur in coals with and without oxidation were then analyzed by the ASTM method. The analyses were performed at the same time with the same instrumental calibration, and by the same operator. The results (Table 5) indicated that the oxidized samples show a noticeable decrease in pyritic sulfur, a noticeable increase in sulfatic sulfur, and a slight increase in "organic sulfur". Total sulfur content in the coals remains unchanged, but the decrease in the amount of pyritic sulfur appears to be equal to the sum of the increases in the amount of sulfatic and organic sulfur. This variation is consistent for all four coal samples analyzed.

In a separate study, a sample of oxidized pyrite (OPY) was extracted with PCE. The OPY was prepared by subjecting a pure sample of pyrite to ambient oxidation for more than three years. The oxidized sample was mixed with inert celite for the purpose of diluting the sample for analysis. The diluted sample was then used for PCE extraction. The ASTM analysis of the oxidized sample shows 0.28% "organic sulfur," 0.32% of sulfatic sulfur, and 3.53% of pyritic sulfur (Table 6). After PCE extraction, this ASTM "organic sulfur" disappears, and the PCE extract shows elemental sulfur (0.03%) from HPLC analysis. These data suggest that during oxidation, pyrite in the coal is oxidized. Part of the pyritic sulfur is converted to a sulfatic form and part to the elemental form. Perchloroethylene is known to be an efficient solvent for elemental sulfur extraction. Thus, the elemental sulfur removed by PCE extraction apparently originated with oxidation of pyrite. This elemental sulfur will be credited as

"organic sulfur" by the ASTM analysis. This explains why an increase in "organic sulfur" content was observed by ASTM analysis of the oxidized coal samples, and why over-estimation of "organic sulfur" removal by PCE desulfurization of highly oxidized coal samples could occur. Overall, the results of these oxidation studies confirm the hypothesis that oxidation produces elemental sulfur that complicates the interpretation of data on organic sulfur removal by PCE desulfurization obtained from ASTM forms-of-sulfur analyses.

CONCLUSIONS

Oxidation of coals was found to affect subsequent PCE desulfurization. Not only pyritic sulfur but also some of the organic sulfur in coal is oxidized. Elemental sulfur produced from pyrite oxidation and some oxidized forms of organic sulfur are amenable to removal by PCE desulfurization.

The uncertainty in an organic sulfur content calculated by the ASTM method includes the separate errors of the sulfate, pyrite, and total sulfur determinations. A high value for ASTM organic sulfur results from oxidation of coal. Air oxidation of pyrite in coal produces PCE-extractable elemental sulfur. This elemental sulfur is interpreted as "organic sulfur" using the ASTM method for forms-of-sulfur determination.

The data indicate that the ASTM-2492 analytical method for forms-of-sulfur determination is inadequate for interpreting "organic sulfur" removal by PCE desulfurization.

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Table 1. Elemental sulfur from PCE extraction and ASTM forms of sulfur in short-term and long-term air oxidized coals before and after PCE extraction.

Sample	Wt %, moisture-free, whole-coal basis				
	Sulfatic	Pyritic	Organic	Total	S°
IBC-104, un-oxidized	0.03	2.44	1.66	4.13	
IBC-104, 2 wks oxid, before PCE extract	0.12	2.17	1.68	3.97	
IBC-104, 2 wks oxid, after PCE extract and dechlorination	0.05	2.18	1.75 ^{+4%}	3.98 ^{+0.3%}	0.00
IBC-104, >5 yrs oxid, before PCE extract	0.87	1.40	1.84	4.11	
IBC-104, >5 yrs oxid, after PCE extract and dechlorination	0.25	1.40	1.66 ^{-10%}	3.31 ^{-20%}	0.07
Oxidized Ohio 5/6, before PCE extract	0.63	0.79	2.08	3.50	
Oxidized Ohio 5/6, after PCE extract and dechlorination	0.28	0.87	1.64 ^{-21%}	2.79 ^{-20%}	0.10

^{-20%}, % of reduction in total sulfur or organic sulfur; S°, elemental sulfur in PCE extracts by HPLC analysis, in wt% on moisture-free, whole-coal basis.

Table 2. Analysis of sulfur forms by XANES in three oxidized coals before and after PCE desulfurization.

Sample	Wt %, moisture-free, whole-coal basis					
	Pyritic	S°	Sulfide	Thiophenic	Oxid	Sulfatic
IBC-104, 2 wks oxid, before PCE extraction	2.17	0.00	0.61	1.07	0.00	0.12
IBC-104, 2 wks oxid, after PCE extract and dechlorination	2.18	0.00	0.61	1.12	0.00	0.07
IBC-104, >5 yrs oxid, before PCE extract	1.40	0.17	0.54	0.86	0.13	1.01
IBC-104, >5 yrs oxid, after PCE extract and dechlorination	1.40	0.00	0.56	0.88	0.07	0.40
Oxidized Ohio 5/6, before PCE extract	0.79	0.26	0.50	1.00	0.14	0.81
Oxidized Ohio 5/6, after PCE extract and dechlorination	0.87	0.00	0.54	1.04	0.04	0.30

* All data were obtained from least-squares sulfur K-edge XANES analysis with the exception of pyritic sulfur which was obtained from the ASTM analysis; oxid., sulfoxide and sulfone.

Table 3. The effects of oxidation conditions on the amount of elemental sulfur removed by PCE extraction

Starting coal	PCE/H ₂ O (mL/mL)	Oxidation Method	Time	Temp.(°C)	S* %
F-IBC-104	100/0	none	-	-	0.01
F-IBC-104		long-term ambient-air oxidation	> 5 yrs	Room	0.07
F-IBC-104	100/0	bubbling air, 20 mL/sec	2 hrs	24	0.01
F-IBC-104	100/20	bubbling air, 20 mL/sec	2 hrs	90	0.02
O-IBC-101	100/0	none	-	-	0.06
O-IBC-101	100/0	bubbling air, 20 mL/sec	2 hrs	90	0.06
O-IBC-101	100/20	bubbling air, 20 mL/sec	2 hrs	90	0.10

F-IBC-104, un-oxidized IBC-104 coal; O-IBC-101, slightly ambient-oxidized IBC-101 coal; S*, elemental sulfur by HPLC analysis of PCE extracts, in wt%, moisture-free, whole-coal basis.

Table 4. Results of chlorine removal from PCE-extracted residues of an un-oxidized (F-IBC-104-PCE) and an oxidized (O-IBC-104-PCE) coal.

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Sample	Method of washing	Total Chlorine (%)
F-IBC-104		0.03
F-IBC-104-PCE	NONE	4.68
F-IBC-104-PCE	Water	2.96
F-IBC-104-PCE	Proprietary A	0.17
F-IBC-104-PCE	Proprietary B	0.03
O-IBC-104-PCE	Proprietary B	0.03
O-IBC-104-PCE	Proprietary B	0.03

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Total chlorine contents are in weight percent, moisture-free, whole-coal basis.

Table 5. ASTM forms of sulfur in oxidized and un-oxidized IBCSP coal samples.

Coal Sample		ASTM forms of sulfur (weight %, moisture free, whole-coal basis)			
		Sulfatic	Pyritic	Organic	Total
IBC-101	A	0.05	1.20	3.10	4.35
	B	0.54	0.54	3.30	4.38
IBC-102	A	0.06	2.20	1.00	3.26
	B	1.12	0.81	1.34	3.27
IBC-104	A	0.03	2.40	1.70	4.13
	B	0.84	1.33	2.00	4.17
IBC-106	A	0.02	1.80	1.90	3.72
	B	0.57	1.00	2.25	3.82

A, un-oxidized, preserved under nitrogen; B, oxidized.

Table 6. Sulfur in an oxidized pyrite before and after PCE extraction.

Sample	ASTM forms of sulfur weight %, moisture-free, Celite-diluted sample				S %
	Sulfatic	Pyritic	Organic	Total	
Oxidized pyrite ^a , before PCE extraction	0.32	3.53	0.28	4.13	na
Oxidized pyrite, after PCE extraction	0.35	3.68	0.01	4.04	0.03

^a Long-term (> 3 years) ambient air oxidized pyrite, 10% in Celite (an inert additive for the purpose of diluting the sample for analysis); S^o, elemental sulfur in PCE extracts by HPLC analysis, in wt% on moisture-free, celite diluted sample.