PROJECT TITLE:
SULFUR REMOVAL FROM HIGH-SULFUR ILLINOIS COAL BY LOW-TEMPERATURE PERCHLOROETHYLENE (PCE) EXTRACTION

ICCI Project Number: 91-1/2.2A-3P
Principal Investigator: M.-I. M. Chou, Illinois State Geological Survey (ISGS)
Funded Co-investigator: D.H. Buchanan, Eastern Illinois University (EIU)
Other Co-investigators: J.W. Stucki, University of Illinois, G.P. Huffman and F.E. Huggins, University of Kentucky
Project Monitor: D.D. Banerjee, CRSC

ABSTRACT

The Midwest Ore Processing Co. (MWOPC) has reported a precombustion coal desulfurization process using perchloroethylene (PCE) at 120°C to remove up to 70% of the organic sulfur. However, this process has not been proven to be as successful with Illinois coals as it has been for Ohio and Indiana coals. Also, the high levels of organic sulfur removals observed by the MWOPC may be due to certain errors involved in interpreting data from the American Society For Testing and Materials (ASTM) forms of sulfur analysis. The purposes of this research are to independently confirm and possibly to improve the organic sulfur removal from Illinois coals with the PCE desulfurization process and to verify the forms-of-sulfur determination using the ASTM method for the PCE process evaluation. Problem that limits commercial application of the PCE process is the high chlorine content in the PCE-treated coals. Hence, to develop a dechlorination procedure to remove excess PCE from the PCE-treated coal is an additional goal of this investigation.

MWOPC's results have been repeated on fresh IBC-104 coal. Oxidation of coals was found to affect subsequent PCE desulfurization. Elemental sulfur is more amenable to removal by PCE. Ohio 5/6 coal appears to produce elemental sulfur more readily than Illinois coal during oxidation. Data from X-Ray Diffraction spectroscopy indicate that sulfate in the oxidized Illinois IBC-104 coal is mainly in gypsum form, whereas, sulfate in oxidized Ohio 5/6 sample is mainly in szomolnokite form. These data suggest that the oxidation reaction for Ohio 5/6 coal might occur under catalytic conditions which readily convert pyrite to produce FeSO₄ and elemental sulfur. The higher elemental sulfur content in that coal results in higher ASTM organic sulfur removal by PCE extraction. From mass balance calculation, 96% of the total sulfur and greater than 95% of total iron were accounted for during our PCE tests with both long-term ambient-oxidized IBC-104 coal and ambient-oxidized Ohio 5/6 coal.

The amount of elemental sulfur generated during short-term oxidation of coal or pyrite is controlled by reaction temperature, moisture conditions, and a proprietary oxidant we introduced. The elemental sulfur produced during ambient air oxidation appears to originate mainly from pyrite oxidation. This elemental sulfur complicates the material balance concerning organic sulfur removal when depending on ASTM analysis alone. A washing procedure to remove PCE from the PCE-treated coals was developed which produced coals with chlorine contents as low as 0.03%.

This project is funded by the U. S. Department of Energy (PETC) and by the Illinois Department of Energy and Natural Resources as part of their cost-shared programs.
EXECUTIVE SUMMARY

The development of economical and practical processes to remove both organic and pyritic sulfur under mild reaction conditions would be highly beneficial to the Illinois coal industry. The Midwest Ore Processing Co. (MWOPC) has reported a precombustion desulfurization process operating at 120°C using perchloroethylene (PCE) to remove up to 70% of the organic sulfur as elemental sulfur. The MWOPC stresses the importance of oxidation and drying conditions as well as temperature control. The process is effective in extracting organic sulfur and separating pyrite fines from coal by float-sink; the process can be operated at low temperatures with minimal loss of solvent (Leehe et al., 1988 and 1989; Lee et al., 1990) and was reported to effectively remove organic sulfur from high-sulfur coals obtained from Ohio and Indiana. However, it has not yet proven to be as successful with Illinois coals (Lee et al., 1990; Buchanan et al., 1990). The MWOPC process evaluation was based on the ASTM data interpretation.

Over the past few years, the Illinois State Geological Survey (ISGS) and Eastern Illinois University (EIU) have jointly developed analytical methods to measure forms of sulfur in the PCE extracts from PCE extraction of high-sulfur Illinois coals. Some elemental sulfur and limited amounts of organic sulfur have been removed from oxidized Illinois coals during these studies; however, these sulfur removals (<32%) were much lower than those reported by the MWOPC (>43%). Several hypotheses may explain these differences, but to date, no experimental support has been reported. MWOPC assumed that organic sulfur removal was due mainly to the removal of aliphatic sulfur, and that the aliphatic sulfur component of organic sulfur in the Illinois coals may be less than that of the other coals tested. We have postulated that certain errors in interpreting ASTM data may result in higher organic sulfur removal reported by the MWOPC.

One hypothesis underlying the ASTM analysis is that elemental sulfur extracted by the PCE may be that derived from pyrite oxidation during coal preoxidation, not organic sulfur removed by the PCE. The ASTM forms of sulfur analysis does not distinguish between organic sulfur and elemental sulfur. Another hypothesis is that preoxidation of coal may convert pyrite into PCE-extractable sulfur, and a pyrite-derived form of iron not extractable by HCl but extractable by HNO₃. If so, this iron would be counted as pyritic sulfur during the ASTM analysis. Since the ASTM "pyritic sulfur" appears to remain constant and the ASTM organic sulfur is obtained by the difference between total sulfur and the sum of pyritic sulfur and sulfatic sulfur, this calculation would lead to an error in interpreting the ASTM results, making it appear that the removal of sulfur by PCE extraction is organic in nature.

The goals of this research are: (1) to independently confirm and possibly to improve the organic sulfur removal from Illinois coals with the PCE desulfurization process developed by the MWOPC, (2) to verify the forms-of-sulfur determination using ASTM method for the PCE desulfurization process evaluation, and (3) to develop a procedure to remove excess PCE from PCE-treated coals. This is a joint effort by the ISGS, EIU, the University of Illinois at Urbana/Champaign (UI-UC), and the University of Kentucky (UK). Tasks 1 to 5 were completed in the first year, and tasks 6 to 8 will be carried out in the second year.
PCE desulfurization, in the beginning of this investigation, was evaluated by measuring the level of total sulfur reduction in the PCE-treated coals and by measuring the amounts of elemental sulfur obtained in the PCE extracts. The removal of this sulfur from coal is enhanced by a preoxidation treatment. The extractable elemental sulfur obtained from a long-term ambient oxidized IBC-104 coal is 25 to 75 times greater than that from the unoxidized or short-term oxidized coal samples.

Larger scale (50g) PCE desulfurizations on a short-term and a long-term ambient oxidized IBC-104 coal, and on an ambient oxidized Ohio 5/6 coal were conducted to obtain enough sample for ASTM analysis, ASTM-independent sulfur analyses and a mass balance analysis. The data from ASTM-independent sulfur analyses were examined and compared to that of the ASTM analysis. XANES analyses indicate that long-term ambient oxidation may have oxidized some organic sulfur in coal, and that PCE desulfurization removes all the elemental sulfur from coals. The results also suggest that no principal (aliphatic and aromatic) forms of organic sulfur in coal was removed by PCE. This is supported by the data from a wet chemical analysis which uses a lithium aluminum hydride (LAH) reduction to delineate the interference of elemental sulfur during organic sulfur determination by a combustion technique.

Data from X-Ray Diffraction spectroscopy indicate that sulfate in long-term ambient oxidized IBC-104 coal is mainly in gypsum form, whereas, sulfate in oxidized Ohio 5/6 coal is mainly in szomolnokite form. These data suggest that the ambient oxidation reaction for Ohio 5/6 coal might occur under catalytic conditions which readily convert pyrite to produce FeSO₄ and elemental sulfur. This interpretation also supports the observation obtained during the short-term oxidation study that Ohio 5/6 coal appears to more readily produce elemental sulfur than Illinois coal. Oxidation of coals was found to facilitate subsequent PCE desulfurizations, and the higher elemental sulfur content in that coal results in higher ASTM organic sulfur removal by PCE extraction.

The results from the mass balance calculation indicate that 96% of the total sulfur and greater than 95% of total iron were accounted for during our PCE desulfurization tests with both long-term ambient-oxidized IBC-104 coal and ambient-oxidized Ohio 5/6 coal.

PCE desulfurization under various short-term oxidation conditions was examined. The results of this oxidation study show that the increase in elemental sulfur is related to reaction temperature, moisture conditions, and the presence of a proprietary oxidant we introduced. These are three key operating variables reported or alluded to by Lee et al. at University of Akron and Leehe et al. at MWOPC. Coal oxidation produces more elemental sulfur in coals to be removed by PCE extraction. The elemental sulfur produced during ambient air oxidation appears to originate mainly from pyrite oxidation. This elemental sulfur complicates the material balance concerning organic sulfur removal when depending on ASTM analysis alone. The source of the increased elemental sulfur and the nature of the pyritic and organic sulfur in the sample treated by the technique using our proprietary oxidant are currently under investigation. Finally, a washing procedure to remove PCE from the PCE-treated coals was developed which produced coals with chlorine contents as low as 0.03%.

Pages 4 through 28 contain proprietary information.