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TECHNICAL REPORT
September 1 through November 30, 1994

Project Title: **ADVANCED CHARACTERIZATION OF FORMS OF CHLORINE, ORGANIC SULFUR, AND TRACE ELEMENTS IN AVAILABLE COALS FROM OPERATING ILLINOIS MINES**

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ABSTRACT

A set of 34 as-shipped coal samples from operating Illinois mines is available for this study to determine the forms of chlorine and sulfur and leachability of chlorine during wet grinding and froth flotation. The forms of chlorine may be inorganic, ionic, and organic. The forms of organic sulfur will include organic sulfide and thiophenic sulfur. Chlorine can be leached from coal during wet grinding. The potential for removal of chlorine from the samples during fine (-200 mesh) and ultrafine (-400 mesh) wet-grinding and during froth flotation designed primarily for removal of pyrite and ash will be determined. In addition, the organic/inorganic affinities of trace elements in as-shipped Illinois coals will be assessed so that the current physical coal cleaning results may be better interpreted.

This is a cooperative effort among the Illinois State Geological Survey, University of Kentucky, and Western Kentucky University. In this quarter, coal samples were prepared and delivered to the co-investigators. X-ray absorption near-edge structure (XANES), a non-destructive method, is being applied to analyze forms of chlorine and forms of organic sulfur, and for analyses of trace elements at UK. Experiments on temperature-programmed thermogravimetry with Fourier transform infrared (TGA-FTIR) is being employed at WKU to further investigate chlorine speciation.

EXECUTIVE SUMMARY

A major problem with the use of Illinois Basin coals is the presence of sulfur and chlorine containing compounds. Effective removal of sulfur (S) and chlorine (Cl) in coal prior to combustion or conversion is a primary goal of the Illinois coal industry. In addition to Cl and S, the presence of trace elements in coal is another concern for future use of coal.

Both U.S. and British researchers have studied chlorine removal by water leaching. Among those examined, the most important factors that affect chlorine removal are forms of chlorine, particle size, and leaching temperature. The overall goal of this study is to characterize the forms of chlorine in all Illinois coals currently being produced and assess the degree of chlorine removal by processes such as fine grinding (both with and without heating) and froth flotation operations. Current and past studies have evaluated the trace element contents in all of these coals both before and after fine coal cleaning. This project will focus on a direct method to study organic/inorganic associations of some trace elements in coal including uranium (U) and vanadium (V).

The goals of this study are (1) to determine forms of chlorine (inorganic, ionic, and organic) and forms of organic sulfur (organic sulfide and thiophenic sulfur) in as-shipped coals from Illinois mines using XANES, (2) to obtain basic data on chlorine removal during fine (-200 mesh) and ultrafine (-400 mesh) wet-grinding of coals and during froth flotation designed primarily for removal of pyrite and ash, and (3) to evaluate the technique of XANES for direct assessment of the organic/inorganic affinities of trace elements in as-shipped Illinois coal so that current froth-flotation cleaning efforts may be better interpreted.

Specific objectives are:

A Prepare as-shipped coals from all operating Illinois mines for analyses (ISGS).

B Establish representative data on major forms of chlorine (inorganic, ionic, and organic) in as-shipped Illinois coal using XANES, a non-destructive analytical method (UK and ISGS).

C Estimate the degree of leachability of chlorine from the as-shipped coals during fine and ultrafine wet-grinding and during froth flotation processes (ISGS).

D Evaluate strategies for managing the chlorine-rich waste water generated as a result of physical fine coal cleaning (ISGS).

E Perform coal porosity measurements and TGA-FTIR analysis on selected coals and establish a relationship, if any, among coal porosity, forms of chlorine, and chlorine leachability for the coal samples (ISGS and WKU).

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F Establish representative data on forms of organic sulfur (organic sulfide and thiophenic sulfur) in as-shipped coals of Illinois mines using XANES (UK and ISGS).

G Evaluate the technique of XANES for direct assessment of forms/associations of some trace elements in as-shipped Illinois coal in order to better interpret the current physical coal cleaning results (UK and ISGS).

This is a cooperative effort among the ISGS, UK, and WKU. The project consists of eight tasks. In this quarter, the as-shipped coal samples were prepared and submitted to co-investigators. Additional ASTM analysis on these samples is being performed at the ISGS. Chlorine leachability tests, and evaluation strategies for disposition of chlorine-enriched water generated as a result of coal cleaning will be initiated in the next quarter. The analyses of forms of chlorine, forms of organic sulfur including elemental sulfur, sulfone, and sulfoxides if they are present, and trace elements by XANES are in progress. Experiments with temperature-programmed TGA-FTIR is being performed at WKU. The TGA-FTIR profiles will be examined with focus on establishing relationship, if any, between the chemical/physical properties of coals and the statutes of chlorine in coals.

GOALS AND OBJECTIVES

The goals of this study are (1) to determine forms of chlorine (inorganic, ionic, and organic) and forms of organic sulfur (organic sulfide and thiophenic sulfur) in as-shipped coals from Illinois mines, (2) to obtain basic data on chlorine removal during fine (-200 mesh) and ultrafine (-400 mesh) wet-grinding of coals and during froth flotation designed primarily for removal of pyrite and ash, and (3) to evaluate the technique of XANES for direct assessment of the organic/inorganic affinities of trace elements in as-shipped Illinois coal so that current froth-flotation cleaning efforts may be better interpreted.

Specific objectives are:

A Prepare as-shipped coals from all operating Illinois mines for analyses (ISGS).

B Perform characterization tests and establish representative data on major forms of chlorine (inorganic, ionic, and organic) in as-shipped Illinois coal using XANES, a non-destructive analytical method (UK and ISGS).

C Estimate the leachability of chlorine from selected as-shipped coals during fine and ultrafine wet-grinding and during froth flotation processes (ISGS).

D Evaluate strategies for managing the chlorine-rich waste water generated as a result of physical fine coal cleaning (ISGS).

E Perform coal porosity measurements and TGA-FTIR analysis on selected coals and establish a relationship, if any, among coal porosity, forms of chlorine, and chlorine leachability for the coal samples (ISGS and WKU).

F Perform XANES data analysis and establish representative data on forms of organic sulfur (organic sulfide and thiophenic sulfur) in coals of the Illinois Basin (UK and ISGS).

G Evaluate the technique of XANES for direct assessment of forms/associations of some trace elements in as-shipped Illinois coal for better interpretation of the current physical coal cleaning results (UK and ISGS).

INTRODUCTION AND BACKGROUND

The chlorine content of Illinois coals generally increases with the burial depth of the coal seam. As the shallow deposits are depleted, future coal production will likely come from deeper, higher chlorine deposits. Utilities will be interested in the effects of using these higher chlorine coals. Extensive data have been generated on British coals to correlate corrosion of boilers at power plants with chlorine content and other parameters of coal. However, data with respect to boiler corrosion problems associated with burning Illinois coals is very limited. The question of whether or not chlorine in Illinois coals really causes corrosion has not yet been satisfactorily answered. However, because of the general concern about chlorine in coal, the presence of chlorine in Illinois coals could have a negative impact on their marketability.

In addition to chlorine, the presence of sulfur in Illinois coals has long been a major concern for the end users of these coals. High-sulfur Illinois coals contain significant amounts of both organic and pyritic sulfur. On the average, about half of the sulfur in high-sulfur Illinois coals exists as pyritic sulfur. Literature indicates that fine grinding and physical cleaning of some coals may achieve removal of up to 95% of pyrite from coal. Literature also indicates the possibility of achieving 70% or more chlorine removal during leaching of finely ground coals. Thus, the problems of pyrite and chlorine in coals may be resolved by a combination of physical coal cleaning and thermal treatment processes. Organic sulfur, which often makes up the other half of sulfur in Illinois coal, cannot be removed by physical coal cleaning. Removing the organic sulfur requires that the molecular structure of the coal be significantly altered. It is anticipated that organic sulfide (weakly bonded sulfur) is more easily removed from coals than thiophenic sulfur (strongly bonded sulfur). If a mild thermal or chemical method can be found to achieve 50% reduction in organic forms of sulfur in coal, a fuel of less than 1.5% sulfur may be derived from a high-sulfur Illinois coal containing 4% total sulfur. This integrated process should remove the majority of pyrite and chlorine during physical coal cleaning and part of the organic sulfur, presumably organic sulfides, from coals during mild thermal or chemical cleaning. For such an integrated process or other advanced coal utilization processes to be successfully developed, a detailed understanding of the fundamental associations of organic sulfur and chlorine in coal is needed.

The current American Society for Testing and Materials (ASTM) standard method can determine the total chlorine content, but not the forms of chlorine in coal. In many previous attempts at determining the forms of chlorine in coals, indirect methods were used, and some mixed results were reported. For example, Hamling and Kaegi in 1984 stated that chlorine in coal samples from one of the high-chlorine Illinois mines was predominantly in the form of organic chloride(s), and the organically associated chlorine does not apparently contribute to boiler corrosion and fouling problems. Others suggested that chlorine in coals occurs in two major forms;

chloride anions from NaCl dissolved in the pore water of coal, and chloride anions adsorbed on the inner surfaces of the micropores in macerals (organic fraction of the coal). It is clearly desirable to confirm previous interpretations about chlorine in coal and generate representative data with a more direct method of determination.

As with chlorine analysis, the current standard methods for sulfur analysis in coal are based on the ASTM procedures. They are basically adequate for analyzing total, pyritic and sulfatic sulfur in raw coal. However, they do not provide a direct measurement of total organic sulfur, nor are they able to indicate the chemical forms of organic sulfur in coal. Solvent extraction, oxidation, and thermal degradation techniques have been attempted to characterize organic sulfur in compounds in coal. These techniques often suffer from uncertainty of characterizing the original nature of the organic functional group. Furthermore, extracted and thermally evolved molecules may represent only a small portion of the macromolecules of coal. While a detailed characterization of organic sulfur compounds in coal is not presently possible, the direct non-destructive x-ray absorption near-edge spectroscopy (XANES) method provides the greatest promise for group type classification of forms of organic sulfur in coal. This method can be used to analyze both the forms of chlorine and forms of organic sulfur in the same tests.

In addition to chlorine and sulfur, the presence of trace elements in coal is another possible concern for future use of coal. Utilities using Illinois coals currently are exempt from having to consider trace element emissions. This, however, may eventually change after the U.S. EPA completes its risk analyses and establishes emission standards.

EXPERIMENTAL PROCEDURES

Preparation of as-shipped coal samples - A set of 21 as-shipped coal samples was prepared for forms of chlorine and forms of organic sulfur analyses by XANES. All the samples were ground to pass 100% through a 60 mesh screen, however, they contain greater than 90% in 100 mesh according to the particle size analysis by the MicroTrac II analyzer.

Preparation of size-fractionated coal samples - Size fractionated coal samples, -200 mesh and -400 mesh, were prepared from four Illinois coals and four British coals. A Selective-Uniform Particle Size Grinder was used. Coal sample (-60 mesh) and glass beads were placed into a glass jar that was secured in the grinder. The grinding time of about five minutes was required to prepare a -200 mesh sample and about eight minutes for the -400 mesh sample.

In addition, a set of samples at -200, and -400 mesh obtained from a previous study (Demir et al. 1994, 1994a) through wet-grinding as the feed for froth-flotation cleaning are available for this study. Total chlorine content of these samples are being analyzed by the ASTM procedure. The procedure uses high temperature combustion and chloride ion determination by a selective chloride ion-electrode. The data will serve as background information for conducting further coal chlorine leachability tests in Task 3.

RESULTS AND DISCUSSIONS

Samples preparation (Task 1) was the main focus in this quarter. Among the available 34 as-shipped coal samples, eighteen samples have chlorine content greater than 0.12% with the values ranged between 0.15% to 0.49%. In addition to these eighteen samples, three additional samples from low-chlorine coal production with chlorine content of 0.12%, 0.08%, and 0.02% respectively were also chosen. These twenty-one coal samples from four Illinois geological localities represent Illinois coal production of low, medium, and high chlorine contents. These samples will be analyzed for forms of chlorine and forms of organic sulfur by XANES.

The results of our previous study indicate the difference in HCl evolution profiles between Illinois and British coals. This difference could be attributed to the possible differences in chemical or physical properties of the coals. For the purpose of examining the relationship, if any, between the chemical/physical properties of the coals and the existing statues of chlorine in the coals, size fractionated coal samples were prepared for TGA-FTIR analysis.

The as-shipped coal samples and size fractionated coal samples were submitted to co-investigators. Additional ASTM analysis on these samples is being performed at the ISGS. Chlorine leachability tests and the task to evaluate strategies for disposition of chlorine-enriched water generated as a result of coal cleaning will be initiated in the next quarter.

DISCLAIMER STATEMENT

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