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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

The goals of the study are (1) to use X-ray absorption near-edge spectroscopy (XANES) 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 via froth flotation at fine (-200 mesh) and ultrafine (-400 mesh) particle sizes, and (3) to evaluate XANES for direct assessment of the organic/inorganic affinities of trace elements.

This is a cooperative effort among the Illinois State Geological Survey, the University of Kentucky, and Western Kentucky University. In this quarter, chlorine leachability during fine wet grinding of 21 coal samples was examined. The results show a general improvement in chlorine removal by grinding coals to -200 mesh, but do not show further improvement by additional grinding to -400 mesh. The chlorine and sulfur spectra of five coals, each from a distinct geographic location in Illinois, were examined. The chlorine XANES spectra for the five coals are similar and chloride anion was determined to be the predominant form of chlorine. The sulfur XANES data for the same coals show that a majority (61% to 82%) of organic sulfur in the coals is contributed from thiophenic sulfur. The distribution of organic sulfur shows that the high sulfur coals tend to have more organic sulfide than low sulfur coals. A more detailed interpretation may be possible after a complete analysis of all the samples selected. Evaluating the possibility of XANES for direct assessment of the organic/inorganic affinities of trace elements in an Illinois coal was completed.

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EXECUTIVE SUMMARY

A major problem with the use of Illinois Basin coals is the presence of sulfur and chlorine containing compounds. Fully characterizing the forms and the occurrence of these compounds may lead to economic methods for their removal. 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 X-ray absorption near-edge spectroscopy (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).

- 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 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 Illinois State Geological Survey (ISGS), University of Kentucky (UK), and Western Kentucky University (WKU).

In this quarter, the chlorine and sulfur XANES spectra of five coals, each from a distinct geographic region in Illinois, were examined. The chlorine XANES spectra for five coals examined are very similar and show chloride anions are the predominant form of chlorine. The sulfur XANES data for the same coals indicate that a majority (61% to 82%) of organic sulfur in the coals occurs as thiophenic sulfur. The distribution of organic sulfur occurring as organic sulfide and thiophenic sulfur was examined. The results show that the high sulfur coals, in general, contain more organic sulfide with the amounts equal to about 29% to 39% of the total organic sulfur, whereas the low sulfur coals contain less organic sulfide with the amounts equal to about 18% to 20% of the total organic sulfur. Whether this difference in organic sulfur distribution reflects the difference in rank of the coal samples, or some other factor remains to be determined. A more detailed interpretation may be possible after analysis of all the samples is completed.

Preliminary study on the trace metals in coal by XANES analysis was completed. For some of the elements, such as As and Zn, examined, the present XANES database provides a definitive interpretation of the predominant mode of occurrence of the element in question in the specific sample of Illinois #6 coal (C-32778) investigated. For the other elements (Ti, V, Cr, Mn), the database on XANES spectra is still too limited to allow a definitive interpretation; however, the data obtained on these elements are sufficient to rule out many of the mineralogical possibilities that have been previously suggested by other investigators.

Total chlorine of the coal samples before and after fine (-200 mesh) and ultra fine (-400 mesh) wet grinding was determined. The results show a general improvement in chlorine removal by grinding coals to -200 mesh. In comparison to the results of -200 mesh samples, Grinding coals to -400 mesh from -200 mesh did not significantly improve chlorine removal. The effect of froth flotation/release analysis on the Cl contents of the 21 coals ground to -200 and -400 mesh sizes is under investigation.

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 X-ray absorption near-edge spectroscopy (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

Task 1: Prepare coal sample (ISGS).

Among the available 34 as-shipped coal samples, eighteen samples have chlorine content greater than 0.12% with values between 0.15% to 0.49%. In addition to these eighteen samples, three samples from low-chlorine coal production with chlorine content of 0.12%, 0.08%, and 0.02% respectively were chosen for this project. These twenty-one coal samples from four Illinois geological localities represent Illinois coal production of low, medium, and high chlorine contents. A split of the coal samples were ground to pass 100% through a 60 mesh screen and used to analyze forms of chlorine and forms of organic sulfur by ASTM procedures and XANES. A second split of the selected 21 coal samples was passed through a jaw crusher and then a roll crusher to reduce the particle size of the coal to < 3/8" and -4 mesh, respectively, for the leachability tests.

Partially combusted coal samples were prepared from two coals, an Illinois coal C-32795 and a British coal C-33500. The coal sample was placed in a constant temperature zone of a Lindberg tube furnace. Under a flow of air, the furnace temperature was increased from room temperature to 200°C and remained at 200°C for 30 minutes at which point the first sample was collected. After the first sample was taken out, the temperature was increased to 250°C and held at 250°C for 30 minutes in order for the second sample to be collected. This stepwise heating was continued and a sample was collected at each 50°C interval until the final temperature of 1000°C was reached. These partially combusted samples were submitted to the University of Kentucky for XANES analysis.

Task 2: Perform characterization tests and establish representative data on chlorine forms using ASTM procedures (ISGS) to obtain total chlorine and XANES (UK) to determine forms of chlorine.

Total chlorine analysis of the as shipped coals and products of wet grinding was completed by ASTM procedures which uses high temperature combustion and chloride ion determination by a selective chloride ion electrode.

Chlorine X-ray absorption fine structures (XAFS) spectra were obtained from all samples at beam-line X19A of the National Synchrotron Light Source (NSLS), Brookhaven National Laboratory. The spectra were obtained from the samples as-received by suspending them in the monochromatic X-ray beam in ultrathin (6 μm) polypropylene baggies. The chlorine XAFS spectra were collected in fluorescence geometry using a (Farcel) Lytle-type fluorescent detector with nitrogen as the ionization gas and helium in the sample chamber. The beam-line was operated in

the focussed spot mode, although the spot was de-focussed somewhat in order to obtain a better sampling of the coal and char samples. Each spectra consisted of about 500 points collected at energies between about 50 eV below the chlorine edge (2825 eV) to about 300 eV above the edge. Dilute samples of sodium chloride in boric acid were used as the primary, standards for the chlorine edges. The principal peak position of the derivative XANES spectrum of NaCl were defined as the zero points of energy for the purpose of calibrating the chlorine XANES spectra. All spectra were collected and stored in a MicroVAX computer at NSLS and were transferred electronically to a similar computer at the University of Kentucky for analysis.

In this quarter, the chlorine spectra for five coals, one from each geological location, were examined. As is normally done, the raw XAFS data were first calibrated with respect to the primary standard (NaCl), then normalized to the edge step, corrected for background slope above and below the edge, and finally divided into separate XANES and extended X-ray absorption fine structures (EXAFS) regions. Analysis of the EXAFS regions of these spectra is generally not very informative, so that the analysis reported here deals only with the XANES region, that is, the structure within about 20 eV of the chlorine K absorption edge.

Task 3: Estimate the degree of leachability of the chlorine with fine or ultrafine wet grinding as in advanced physical coal cleaning processes (ISGS).

All of the 21 samples prepared for leachability test were wet-ground to -200 mesh size, and 3 of the 21 samples were also wet-ground to -400 mesh size. To reduce the particle size of the samples to -200 mesh, about 700 grams of each 4 mesh coal was mixed with 700 ml of tap water and ground in a rod mill for 30 minutes. The coal slurry was filtered, and air-dried. To achieve -400 mesh particle size, about 700 grams of each of the selected -4 mesh coals was mixed with 700 grams of water and ground in a rod mill for 60 minutes. The coal slurry was filtered and air-dried. A split of the filter cakes were tested for particle size distribution. Total chlorine content of these samples were analyzed by the ASTM procedure. The data will serve as background information for conducting further coal chlorine leachability tests on one selected coal sample.

Task 4: Design and evaluate strategies for managing the waste water generated from the leaching tests (ISGS).

The purpose of this task is to perform an economic evaluation of disposing Cl enriched process water used in wet-grinding of the coals in physical coal cleaning. The task is in progress and four basic options will be evaluated.

Task 5: Perform TGA-FTIR analysis and establish representative patterns of chlorine evolution from Illinois coal under pyrolysis and combustion conditions (WKU and ISGS).

This task is in progress, and the results will be reported in the next quarter.

Task 6: 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).

Sulfur XAFS spectra were obtained from all samples at beam-line X19A of the National Synchrotron Light Source (NSLS), Brookhaven National Laboratory. The spectra were obtained using the same procedure used in Task 2, but dilute samples of elemental sulfur were used as the primary standards for the sulfur edges. The principal peak position of the elemental sulfur XANES spectrum (2472 eV) was defined as the zero point of energy for the purpose of calibrating the sulfur XANES spectra.

Sulfur XANES spectra are used as input to a least-squares fitting program that interactively fits a set of lorentzian-gaussian shaped peaks and an arctangent step function the spectral region between -8 eV to +16 eV. A standardized procedure is followed that first fits a highly constrained description of the peaks and step to the data and then the constraints are progressively removed as the overall fit comes closer and closer to the data. The initial input parameters and the fitting procedure have been developed empirically over the last four years or so. The final output of the least-squares program is a list of positions and areas of the peaks defined in the least-squares fitting. The identity and approximate percentage of sulfur in each form can be derived from the peak positions and areas respectively obtained in the least-squares fitting. As has been shown in various studies (Huffman, 1991; Huggins, 1993) the position of the peak reflects the valence state of the form of sulfur and increases in the order: pyrrhotite (-2.0 eV), pyrite (-0.6 eV), elemental sulfur (0.0 eV), aliphatic sulfide (0.7 eV), thiophenic derivatives (1.4 eV), sulfoxides (3.5 eV), sulfone (8.0 eV), sulfonate (9.0 eV), and sulfate (10.2 eV). As discussed in detail elsewhere (Huggins, 1993), the pyritic sulfur is by far the poorest determined form by this method, and it is recommended that an alternatively determined value be used in place of the XANES determined pyritic sulfur. Once this is done, the non-pyritic sulfur in the coal can be subdivided among the non-pyritic forms according to the XANES results with an have an accuracy of about $\pm 10\%$.

In this quarter, the sulfur spectra of five coals, one from each geological location, were examined.

Task 7: Perform preliminary tests on trace metal and their organic/inorganic affinity in coals using XANES.

The technique used to determine the mode of occurrence was XAFS spectroscopy, a synchrotron-based technique that is direct, nondestructive, and informative for very dilute levels (5-10 ppm). The XAFS spectra obtained from the different elements in the coal sample are divided into two separate regions: the XANES region and the EXAFS region. The XANES region is used directly as a fingerprint, whereas the EXAFS region is mathematically manipulated further to obtain a radial structure function (RSF) which will provide information on the coordination environment of the element. For trace elements, the EXAFS structure is usually only useful if the element is somewhat concentrated (>50 ppm) or if the element is surrounded by heavy elements. Hence, as a consequence of this and other complications, the interpretation of the elemental mode of occurrence is based solely on the XANES region in many instances.

Six different trace elements have been examined: Cr, Mn, Zn, and As were investigated at beam-line IV-3 at the Stanford Synchrotron Radiation Laboratory (SSRL), whereas Ti and V were investigated at beamline X-19A at the National Synchrotron Light Source (NSLS) at Brookhaven National Laboratory. Essentially identical experimental practice was carried out at the two synchrotron facilities. Samples of the coal were exposed to monochromatic X-rays and the fluorescent radiation emitted in response to the X-ray absorption process was detected in a 13 Ge-element solid-state detector. Normally, a scan was made from about 100 eV below the K absorption edge of the element of interest to as much as 1,000 eV above the K-edge. The individual signals recorded in each channel of the 13 Ge-element detector were combined into a single spectral scan. In addition, multiple scans were made for most elements and these scans were also combined to provide a single spectrum for each element. Hence, for most elements, the spectra represent between 3 and 5 hours of spectral accumulation time.

RESULTS AND DISCUSSIONS

Chlorine analysis by XANES

The chlorine XANES spectra for five coals, one from each geographic location, were examined in this quarter. The chlorine XANES spectra (Figure 1, left) of the samples appear to be very similar which show a predominant form of chlorine as chloride anions. These anions may be in solution and have significant interaction with maceral surfaces presumably via ionic functional groups, such as quaternary amines or oxygen functional groups anchored via cations.

The same samples were also heated to 125°C for 24 hours and the chlorine XANES spectra (Figure 1, right) re-measured. Some subtle differences are apparent between the two sets of spectra: (i) the shape of the main peak becomes less pointed and flatter at its apex upon heating and (ii) the rise from the minimum at about 10 eV to 20 eV is much more pronounced in the original coal spectra than in the heated samples. This may mean that the chloride anions have lost some of the water molecules in their coordination sphere (Huggins and Huffman, 1995).

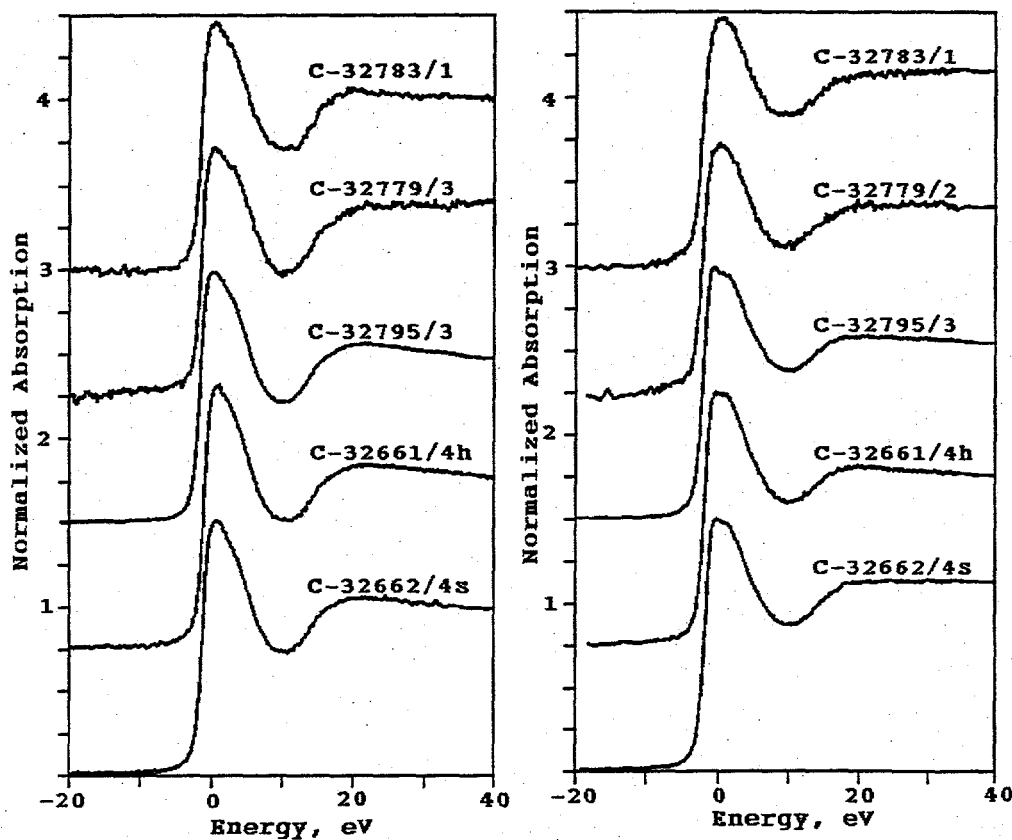


Figure 1: XANES spectra of five Illinois coals from different geographic locations (left) and their heat-treated samples (right).

The XANES spectra for the partially combusted coal samples show significant changes in the form of chlorine (and concentration) with increasing char preparation temperature (Figure 2). In addition, there are differences between the variation of chlorine in the British coal compared to that in the Illinois coal. A small peak at about 12.5 eV is apparent in the spectra of the chars formed at 200 to 350°C from the British coal that is diagnostic of the formation of NaCl. This feature is absent from the spectra of chars from the Illinois coal. Above 350°C, spectra of chars from both coals show a prominent peak at about -1 eV that dominates the spectra in the range 400 - 600°C. Above 600°C, the spectra degrade in quality, as virtually all of

the chlorine has been evolved from the samples. The peak position and shape of the spectrum for the spectra around 400°C are similar to those noted (Huggins and Huffman, 1995) for chlorine in organic (aromatic) compounds. However, other less similar chlorine forms (hypochlorite, e.g. NaOCl) could be possible. The possible presence of organic chlorine in these chars raises some interesting speculation as to where it comes from. Alternative possibilities are: (i) it was present in the coal originally, but at such a low level (<10% of the total chlorine) that it did not register in the Cl XANES spectrum of the coal until the more volatile forms of chlorine had been evolved during low-temperature char preparation; or (ii) it was formed by reaction between the char and HCl evolved during char preparation. This phenomena, the appearance of "organic" chloride, was not seen in a previous investigation (Huggins and Huffman, 1995) which was done by in situ heating under helium followed by XANES Cl analysis. In that study, however, the heating temperature was low, reaching only 350°C.

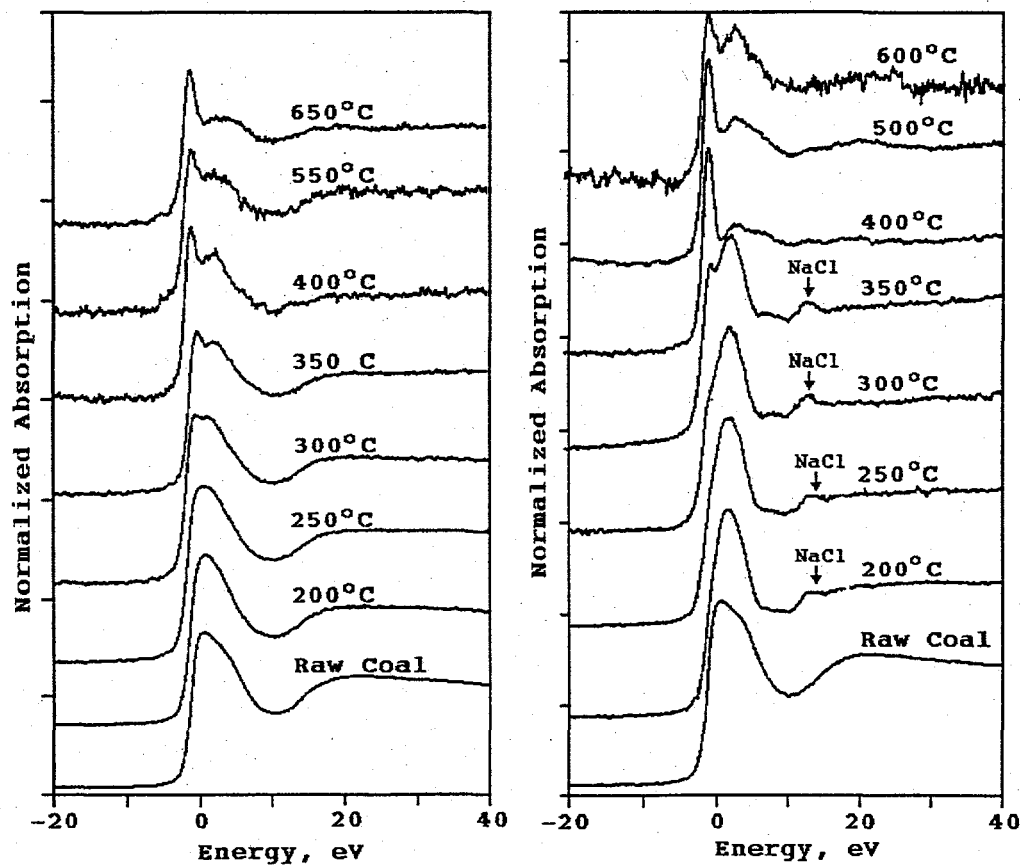


Figure 2: XANES spectra of samples obtained from stepwise heating of an Illinois Coal (left) and a British coal (right).

A procedure for quantification of different forms of chlorine, similar to that applied to sulfur, has not been established because most coals appear to have only one major form of chlorine, ionic chloride. However, visual inspection of the chlorine XANES spectra of certain char samples indicates the presence of at least three co-existing forms of chlorine at temperatures around 300°C. Also, suites of char samples prepared at different temperatures in air exhibited subtle forms of chlorine that appeared to be varied with both temperature and country of origin. A detailed examination of these interesting phenomena is recommended.

Chlorine leachability during fine and ultrafine wet grinding

Analysis of particle size distribution on coal ground for 30 minutes showed in the range of 90% -200 to -270 mesh. A few of the samples showed in the range of 90% -325 mesh and 80% -500 mesh. In that case grinding was repeated with reduced time, less than 30 minutes, to achieve a particle size distribution of about 90% -200 mesh. Data on particle size distribution of coal ground for 60 minutes indicated a particle size of 85 to 90% -400 mesh.

Table 1 tabulates Cl contents in the 21 samples before and after they were ground wet in the rod mill. Grinding to -200 mesh reduced the Cl contents of those coals of regions 1 and 3 by 17 to 67%. With exceptions of one coal from regions 2 and 4H, and three coals from region 4S, reduction of the particle size to -200 mesh made very little difference in the Cl contents of the samples from regions 2, 4H, and 4S. One sample (C-32793) from region 4S lost 30% of its Cl when it was ground to -200 mesh. Grinding three of the coals to -400 mesh resulted in 31% to 58% reductions in their Cl contents. However, when it is compared to the -200 mesh samples, grinding to -400 mesh did not give any significant improvement in chlorine leaching efficiency.

In general, improvement in chlorine leaching was observed by grinding coals to -200 mesh. This is the case for all the coals from regions 1 and 3, one coal from regions 2 and 4H, and three coals from region 4S. In comparison to the -200 mesh samples, grinding coals to -400 mesh did not give any significant improvement in chlorine removal.

The effect of froth flotation/release analysis on the Cl contents of the same 21 coals ground to -200 and -400 mesh sizes will be included in the next quarterly report.

Table 1: Cl content of coals before and after wet grinding

Coal	Region	Cl (weight % dry coal)		
		Feed	-200 mesh product	-400 mesh product
C-32777	1	0.12	0.04	0.05
C-32782	1	0.15	0.07	
C-32783	1	0.16	0.07	
C-32779	2	0.08	0.05	
C-32815	2	0.02	0.03	
C-32784	3	0.39	0.28	
C-32795	3	0.45	0.35	
C-32796	3	0.38	0.24	
C-32801	3	0.35	0.29	0.24
C-32802	3	0.29	0.24	
C-32803	3	0.32	0.24	
C-32661	4H	0.26	0.27	
C-32665	4H	0.13	0.14	
C-35776	4H	0.15	0.12	
C-32662	4S	0.35	0.37	
C-32663	4S	0.21	0.20	
C-32772	4S	0.24	0.26	
C-32775	4S	0.17	0.22	
C-32780	4S	0.21	0.19	
C-32781	4S	0.19	0.20	
C-32793	4S	0.20	0.13	0.13

Sulfur analysis by XANES

Sulfur XANES spectra from five coal samples representative of a particular region in the Illinois coal-fields were examined in this quarter. Results of the least-squares fitting are summarized in Table 2 for all five samples. Most samples also indicated the presence of sulfate (12 - 15% of the nonpyritic sulfur), derived presumably from pyrite oxidation.

Table 2. Percentages of Sulfur in Selected Coal Samples Derived from XANES Analysis

Coal	% Coal Total Sulfur	% of Total Sulfur			% Organic Sulfur	
		Pyritic Sulfur*	Sulfate	Thiophene	Organic Sulfide	Organic Sulfide
C-32783	4.41	21	10	42	27	39
C-32779**	4.20	16	1	51	28	35
C-32795	0.73	10	12	64	14	18
C-32801	1.98	38	9	37	16	30
C-32661	2.89	35	8	40	16	29
C-32662	1.51	35	11	43	11	20

*By ASTM analysis.

**Also contains 3 sulfoxide

The data (Table 2) indicate that 61% to 82% of the organic sulfur in the Illinois coals is contributed from thiophenic sulfur and the remaining 18% to 39% of the organic sulfur in coals is contributed from sulfide sulfur. Variation on the distribution of coal organic sulfur between organic sulfide sulfur and thiophenic sulfur for the five samples were examined. In general, about 29% to 39% of the organic sulfur in high sulfur coals is attributed to sulfide sulfur, whereas about 18% to 20% of the organic sulfur in low sulfur coals is attributed to sulfide sulfur. Whether this difference in organic sulfur distribution reflects the difference in rank of the coal samples, or some other factor remains to be revealed. Various semi-quantitative variation in sulfur forms have been observed, but a more detailed interpretation can not be given until a complete analysis of all the samples is accomplished.

Trace metal analysis by XAFS/XANES

This task focuses on a survey to determine what elements are capable of being successfully studied by the XANES technique and can possibly be interpreted for the "form" of the element (organic/inorganic affinity) in the coal. Using the average trace element concentrations data obtained previously (Demir et al., 1993) as a guide, a representative Illinois No. 6 coal sample (C-32778) was chosen for this study. The data obtained for several elements are described as follows:

Titanium - There is a relatively weak pre-edge peak at about 3 eV and a broad main peak between 20 and 30 eV that consists of two components. However, because no sharp minor features are discernable in the spectrum and because the small pre-edge peak does not exhibit any apparent splitting, virtually all common minerals (rutile, anatase, sphene, Tiillitc, etc.) can be eliminated as being a major contribution to this

spectrum. The spectrum is very similar to that from Ti in other Illinois #6 coals (e.g. Argonne Premium coal sample) that have been examined previously (Huggins et al., 1993).

Vanadium - This is the first attempt to measure V in coal by XAFS/XANES, and there are no database to draw upon to interpret the spectrum obtained; however, fortunately, a V-rich (500 to 2000 ppm) Kentucky #9 coal was studied extensively by Maylotte et al. (1981). There is no similarity between the spectrum of Illinois coal and that of the standard compounds reported by Maylotte. However, there are similarities between the V K-edge coal spectra, especially the float fraction, of Kentucky #9 coal and that of the Illinois #6 coal. The sharp pre-edge feature at about 4 eV in the spectrum is indicative of either a highly distorted V^{3+} environment or an unusual V^{4+} compound.

Chromium - A very weak pre-edge peak at about 2 eV above the K-edge calibration zero-point indicates that all (>95%) of the chromium is present as Cr^{3+} ; there is no evidence for the more toxic Cr^{6+} oxidation state. The detection limit is about 5% for this ratio of the oxidation states. The Cr spectrum for the Illinois #6 coal is similar to those for chromium in most bituminous coals (Huggins et al., 1993; Huffman et al., 1994). Such a spectrum of the Illinois coal is tentatively identified as a result derived from a chromium oxyhydroxide ($CrOOH$) phase.

Manganese - UK database does contain the Mn spectrum in Illinois #6 Argonne Premium coal sample (APCS). The current spectrum is quite different from that of the APCS coal and, except for the weak feature at about 17 eV, appears to have a profile that is more similar to that of Mn in a lignite (Beulah lignite, ND). Additional efforts are required for examination of this element in coal before a definitive conclusion can be made.

Zinc - This is a strong spectrum and is clearly derived largely from zinc sulfide (ZnS). The spectrum is consistent with that seen for other Illinois #6 coals. We have also examined a few coals from outside the Illinois Basin containing much less zinc. Surprisingly, perhaps, their Zn XANES spectra do not resemble that of zinc sulfide, but suggest an oxygen environment around the zinc. The radio structure function (RSF) that provides coordinate environment of the element was examined. The RSF derived from the EXAFS region for Zn in the Illinois #6 coal (C-32778) is also very similar to that from a ZnS standard.

Arsenic - A recently prepared sample of the Illinois #6 coal as well as its extensively oxidized sample were examined. In both spectra, two distinct peaks can be seen, indicating two different forms of arsenic present in these samples. The peak to the negative side of 0 eV arises from arsenic in pyrite, while the higher energy peak arises from an arsenate (AsO_4^{3-}) phase, formed by oxidation of the pyritic arsenic (Huggins et al., 1993; Huffman et al., 1994). These assignments are confirmed by

examining the RSF derived from the EXAFS region. Although the noise level is high for the arsenic XAFS spectrum of this sample, the RSFs for the two spectra do correctly locate the major peak for the dominant forms at about 2.05 Å for arsenic in pyrite and at about 1.30 Å for the arsenate anion.

In summary, for some of the elements examined, such as As and Zn, the present XAFS data provide a definitive interpretation of the predominant mode of occurrence of the element in question in the specific sample of Illinois #6 coal (C-32778) investigated. For the other elements (Ti, V, Cr, Mn), the database on XAFS spectra of trace elements in coal is still too limited to allow a definitive interpretation; however, the data obtained on these elements are sufficient to rule out many of the mineralogical possibilities that have been suggested previously (Swaine, 1990).

SUMMARY

The chlorine XANES spectra for five coals examined in this quarter are very similar which show a predominant form of chlorine as chloride anions. The sulfur XANES data for the same coals indicate that a majority of (61% to 82%) organic sulfur in the Illinois coals is contributed from thiophenic sulfur. In general, high sulfur coals contain more organic sulfide, about 29% to 39% of their total organic sulfur, than the low sulfur coals, about 18% to 20% of their organic sulfur. Whether this difference in organic sulfur distribution reflects the difference in rank of the coal samples, or some other factor remains to be revealed. Various semi-quantitative variation in sulfur forms have been observed, but a more detailed interpretation can not be given until a complete analysis of all the samples is accomplished.

In trace metals XAFS/XANES analysis, for some of the elements, such as As and Zn, examined, the present XAFS database provides a definitive interpretation of the predominant mode of occurrence of the element in question in the specific sample of Illinois #6 coal (C-32778) investigated. For the other elements (Ti, V, Cr, Mn), the database on XAFS spectra of trace elements in coal is still too limited to allow a definitive interpretation; however, the data obtained on these elements are sufficient to rule out many of the mineralogical possibilities that have been suggested previously (Swaine, 1990).

The results of leaching study show a general improvement in chlorine removal by grinding coals to -200 mesh. This is the case for all the coals from regions 1 and 3, one coal from regions 2 and 4H, and three coals from region 4S. In comparison to the results of -200 mesh samples, grinding coal to -400 mesh did not give any significant improvement in chlorine leaching efficiency. The effect of froth flotation/release analysis on the Cl contents of the same 21 coals ground to -200 and -400 mesh sizes is under investigation.

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DISCLAIMER STATEMENT

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PROJECT MANAGEMENT REPORT
December 1, 1994 through February 28, 1995

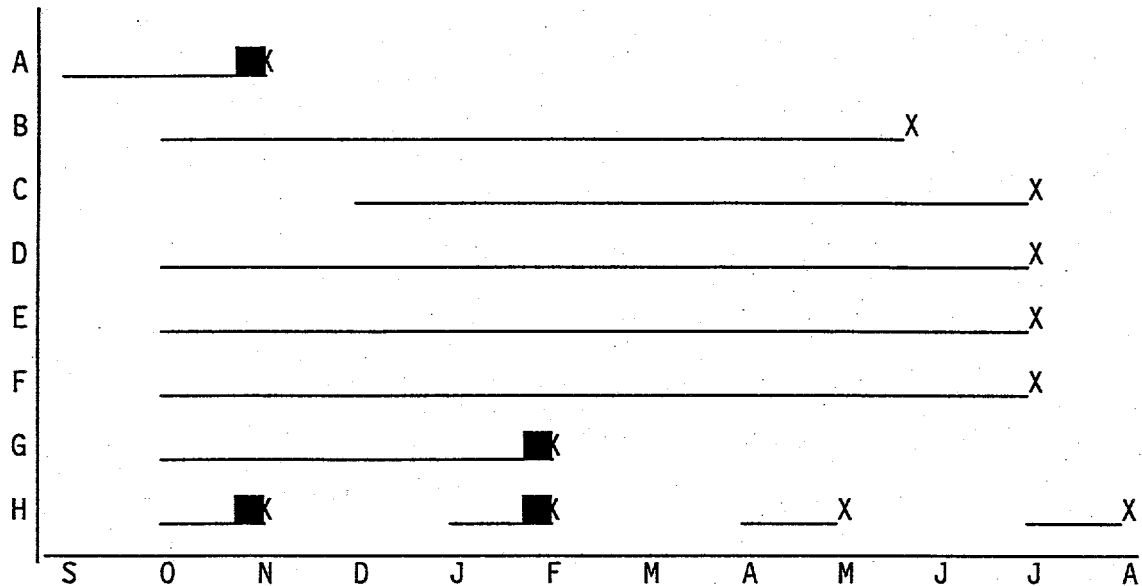
Project Title: **ADVANCED CHARACTERIZATION OF FORMS OF CHLORINE,
ORGANIC SULFUR, AND TRACE ELEMENTS IN AVAILABLE
COALS FROM OPERATING ILLINOIS MINES**

DOE Cooperative Agreement Number: DE-FC22-92PC92521 (Year 3)
ICCI Project Number: 94-1/1.2C-2P
Principal Investigator: M.-I.M. Chou, Illinois State Geological
Survey (ISGS),
Other Investigators: I. Demir, R.R. Ruch, J.M. Lytle, S.
Bhagwat, and C.L. Chou (ISGS); F.E.
Huggins and G.P. Huffman, University of
Kentucky (UK); W.P. Pan, Western
Kentucky University (WKU).
Project Manager: Ken K. Ho, ICCI

COMMENTS

Analyses services from various laboratories have not yet been paid. These works are in progress but payments are made on a cost reimbursement basis after the works are completed.

SCHEDULE OF PROJECT MILESTONES



Milestones:

- A. Coal sample preparation (Task 1)
- B. XANES for forms of Cl analysis and ASTM analyses (Task 2)
- C. Chlorine leaching studies (Task 3)
- D. Chlorine-enriched waste water analysis (Task 4)
- E. TGA-FTIR analysis of evolution profiles of Cl-containing compounds in coal (Task 5)
- F. XANES for forms of organic sulfur analysis (Task 6)
- G. XANES for trace elements analysis (Task 7)
- H. Technical project management reports prepared and submitted (Task 8)

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EXPENDITURES - EXHIBIT B

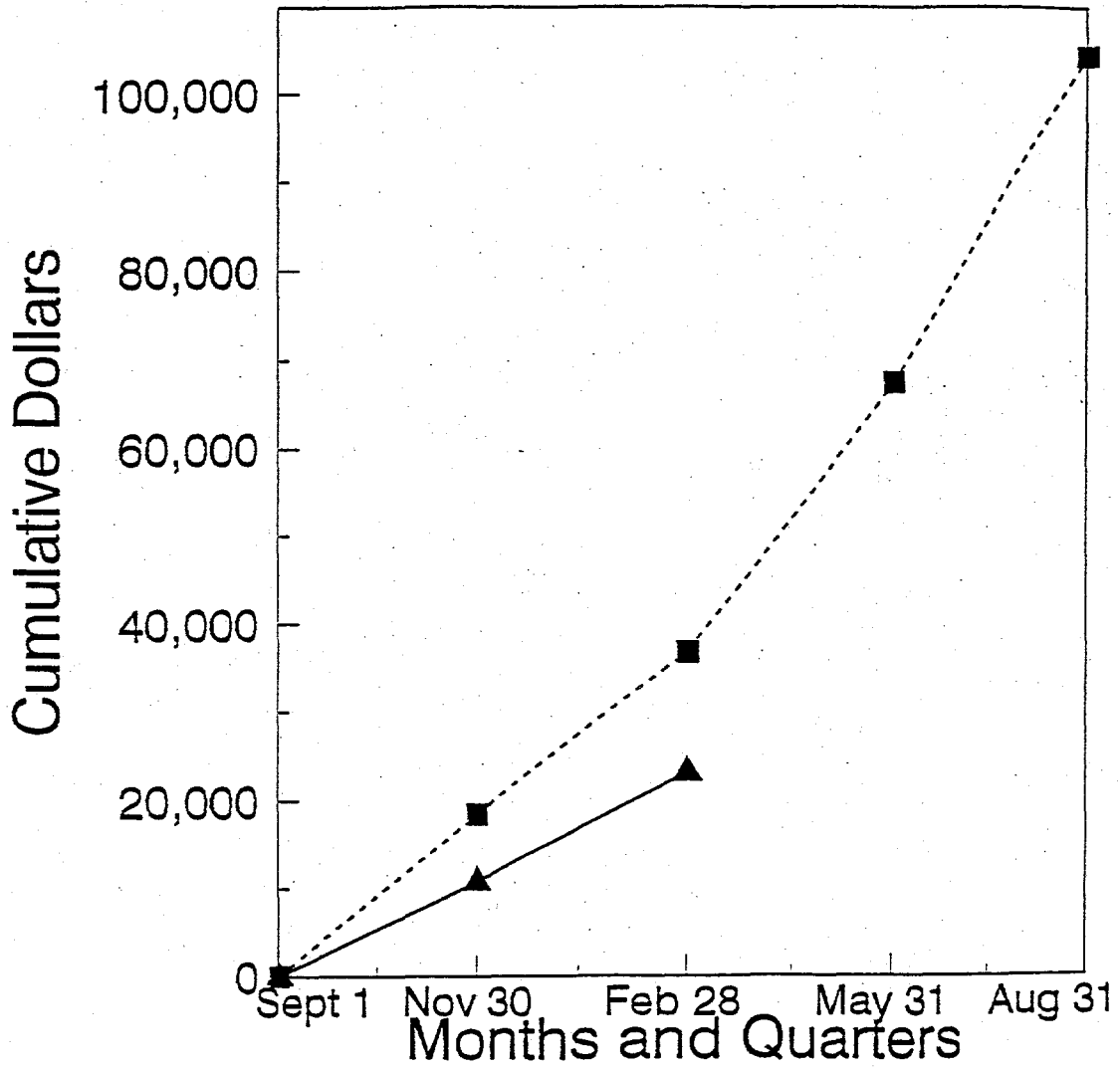
Cumulative Projected and Estimated Expenditures by Quarter

Quarter*	Types of Cost	Direct Labor	Fringe Benefits	Materials and Supplies	Travel	Major Equipment	Other Direct Costs	Indirect Costs	Total
Sep. 1, 1994 to Nov. 30, 1995	Projected	8,920	1,984	500	0	0	5,383	1,679	18,466
	Estimated	7,136	1,587	200	0	0	893	982	10,798
Sep. 1, 1994 to Feb. 28, 1995	Projected	17,840	3,968	800	0	0	10,766	3,337	36,711
	Estimated	11,658	2,593	847	857	0	5,063	2,102	23,120
Sep. 1, 1994 to May 31, 1995	Projected	26,759	5,952	2,000	600	0	26,049	6,136	67,496
	Estimated								
Sep. 1, 1994 to Aug. 31, 1995	Projected	35,683	7,938	2,500	1,200	0	47,548	9,487	104,356
	Estimated								

*Cumulative by Quarter

COST BY QUARTER - EXHIBIT C

ADVANCE CHARACTERIZATION OF FORMS OF CHLORINE,
ORGANIC SULFUR, AND TRACE ELEMENTS IN AVAILABLE
COALS FROM OPERATING ILLINOIS MINES



Projected Expenditures Actual Expenditures

Total ICCI Award \$ 104,356