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TECHNICAL REPORT
March 1 through May 31, 1995

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.

In the last quarter, chlorine leachability during fine wet grinding of 21 coal samples was examined. In this quarter, the effect of froth flotation/release analysis (FF/RA) on the Cl contents of coals ground to -200 and -400 mesh sizes is completed. The results indicate that a combination of wet grinding and FF/RA reduced Cl contents in most samples from regions 1,2, and 3 by 29-81% and in one sample from region 4S by 60%. The chlorine and sulfur spectra of 21 coals, from five distinct geographic locations in Illinois, were examined. The chlorine XANES spectra for the coals are similar and chloride anion was determined to be the predominant form of chlorine. The sulfur XANES data for these coals show that a majority (61% to 82%) of organic sulfur in the thiophenic form. The ratios of thiophenic sulfur to total organic sulfur show a correlation with sample location. For samples from regions 1 and 2, the ratios are relatively lower (61% to 64%), whereas, for samples from regions 3, 4H, and 4S, the ratios are relatively higher (64% to 82%). A more detailed interpretation in these correlations will be discussed in the next report.

DISCLAIMER

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).

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).

In last quarter, total chlorine of the coal samples before and after fine (-200 mesh) and ultra fine (-400 mesh) wet grinding was examined. In this quarter, the effect of froth flotation/release analysis (FF/RA) on the Cl contents of coals ground to -200 and -400 mesh sizes is completed. The results of the FF/RA indicate that FF procedure further reduced Cl in most of the ground samples from regions 1, 2, and 3 by 4-60%. A reduction of 38% in Cl content was observed for one sample (C32793) from region 4S; no reduction was observed for other samples from region 4S and region 4H. A combination of wet grinding and FF/RA reduced Cl contents in most samples from regions 1,2, and 3 by 29-81% and in one sample from region 4S by 60%.

The chlorine and sulfur XANES spectra of twenty-one coals, from four distinct geographic regions in Illinois, were examined. The chlorine XANES spectra of the coals examined are very similar and show chloride anions are the predominant form of chlorine. The XANES sulfur spectra show that major forms of sulfur present in most samples consist of pyritic sulfur, organic (aliphatic) sulfide, thiophenic sulfur, and sulfate sulfur. Other forms, oxidized organic sulfur forms and elemental sulfur, if present, are relatively minor. The distribution of organic sulfur occurring as organic sulfide and thiophenic sulfur was further examined. The sulfur XANES data indicate that a majority of organic sulfur in the coals occurs as thiophenic sulfur (61% to 82%). The ratios of thiophenic sulfur to total organic sulfur show a correlation with sample location (region). For samples from regions 1 and 2, the ratios are relatively lower (61% to 64%), whereas, for samples from the other three regions, the ratios are relatively higher (64% to 82%). 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 will be discussed in the next quarter.

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).

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 (Chou, 1991). 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 (ASTM, 1991) 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.

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 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 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.

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.

The 21 samples ground to -200 mesh and 3 samples ground to -400 mesh were then cleaned using a froth floatation / release analysis procedure (FF/RA) (Fig. 1). The clean concentrates (floats) from each FF/RA test were combined to obtain a composite products that had the 80% combustibles of the total combustibles (in the feed).

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 in physical coal cleaning. The fundamental will be based on a 500 MW power plant over one year, and data includes chlorine removal, fresh water required for chlorine removal, and waste water generated. Three basic options are being examined for the disposal of the waste water.

Task 5: 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).

The progress on this task was slightly interrupted. This is due, partially, to some difficulties in equipment modification and to temporally shot down of the facility at the Applied Research Laboratory of the ISGS for building remodeling.

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 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 has been obtained for all of the 21 test coals.

Sulfur XANES spectra from the coal samples were used as input to a least-squares fitting program (EDGFIT) that iteratively fits a set of lorentzian-gaussian shaped peaks and an arctangent step function to 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 leastsquares fitting. As has been shown in various studies (Huffman et al., 1991; Huggins et al.,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), thiophene derivatives (1.4 eV), sulfoxides (3.5 eV), sulfone (8.0 ev), sulfonate (9.0 eV), and sulfate (10.2 eV). Results of the least-squares fitting are summarized in Table 2 for all 21 samples and the final fitting of each sample is also attached. As discussed in detail elsewhere (Huggins et al.,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 XAFS-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 accuracy of about +10%.

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.

RESULTS AND DISCUSSIONS

XANES CHLORINE ANALYSIS

Analysis of the chlorine XANES spectra has been completed on the 21 coal samples. The chlorine XANES spectra for all the coals are similar and chloride anion was determined to be the predominant form of chlorine. The identity of the positive counter ions with which the chlorine anions are associated in the coals could not be unambiguously determined from XANES spectra.

CHLORINE REMOVAL BY FROTH FLOTATION/RELEASE ANALYSIS

The effects of wet grinding on the chlorine contents of the test coals was reported in the second quarterly report. The effect of froth floatation/release analysis procedure (FF/RA) on chlorine content is reported in Table 1. The FF/RA procedure further reduced Cl in most of the ground samples from regions 1, 2, and 3 by 4-60%. A reduction of 38% in Cl content was observed for one sample (C32793) from region 4S; no reduction was observed for other samples from region 4S and region 4H. A combination of wet grinding and FF/RA reduced Cl contents in most samples from regions 1,2, and 3 by 29-81% and in one sample from region 4S by 60%.

PRELIMINARY WASTE WATER EVALUATION

Wet grinding of coal to 80% -200 mesh could reduce its chlorine content from 25 to 40% (Chou, 1992). The chlorine content of coal was reduced from 0.42% to 0.25% in the filter cake. For effective chlorine reduction, the chlorine content of the wash water must not exceed 1 mg/Ml (Chou, 1992). Based on these finds, strategies to manage the water quantities from the process were examined. Preliminary calculations indicate that a ton of coal subjected to wet grinding, in which its chlorine content is reduced from 0.42% to a range from 0.25% or 0.33% will generate 1.8 lbs. to 3.4 lbs. of chlorine that must be carried away in the water.

If chlorine concentration in water is not to exceed 1 mg/Ml, the process would generate 0.9 tons to 1.7 tons of waste water per ton of wet-ground coal.

Table 1: Cl content of wet-ground coals before and after FF/RA procedure

Coal	Region	Cl (weight % dry coal) Feed	-200 mesh product	-400 mesh product	FF/RA products -200 mesh	FF/RA products -400 mesh
C-32777	1	0.12	0.04	0.05	0.03	0.03
C-32782	1	0.15	0.07		0.03	
C-32783	1	0.16	0.07		0.03	
C-32779	2	0.08	0.05		0.02	
C-32815	2	0.02	0.03		0.04	
C-32784	3	0.39	0.28		0.24	
C-32795	3	0.45	0.35		0.27	
C-32796	3	0.38	0.24		0.18	
C-32801	3	0.35	0.29	0.24	0.25	0.23
C-32802	3	0.29	0.24		0.24	
C-32803	3	0.32	0.24		0.25	
C-32661	4H	0.26	0.27		0.28	
C-32665	4H	0.13	0.14		0.14	
C-35776	4H	0.15	0.12		0.13	
C-32662	4S	0.35	0.37		0.37	
C-32663	4S	0.21	0.20		0.21	
C-32772	4S	0.24	0.26		0.29	
C-32775	4S	0.17	0.22		0.22	
C-32780	4S	0.21	0.19		0.18	
C-32781	4S	0.19	0.20		0.20	
C-32793	4S	0.20	0.13	0.13	0.08	0.08

About 1 million tons of clean coal is required to operate a 500 MW power plant for one year. Processing this quantity of coal would generate waste water quantities of 0.9 million tons to 1.7 million tons each year. The essential precondition to such an operation is the availability of these quantities of fresh water on site at an affordable cost. This study will attempt an estimate of the cost of fresh water on site.

The study will focus on three basic strategies to manage the chlorine-rich waste water:

1. Store water in a seepage free pond with a possible lime treatment for increasing the pH value,

2. Inject the waste water into geologically safe formations, and

3. Treat the waste water by reverse osmosis to produce highly purified and possibly potable water.

Cost estimates for each of the tree strategies will be submitted in the final report along with the discussion of the pros and cons of the strategy.

Preliminary estimates indicate that the pond size requirements will be substantial. If pond depth is assumed to be 3 m. (10 ft.), the pond dimensions would range from 550 m square to 750 m square just to accommodate the water quantities generated each year. Actual pond dimensions are likely to be modified due to evaporation as well as expected precipitation of up to 75 cms. Injecting large quantities of water into geologic formations would require availability of such a formation, and the cost will depend on the drilling depth.

Water purification by reverse osmosis is expensive. Therefore, this option would require special conditions of water scarcity and will be treated as an outside possibility as a strategy to manage the waste water problem.

SULFUR XANES ANALYSIS

The sulfur XANES spectra of the 21 coal samples were recorded and analyzed in this quarter. The data are listed in Table 2. The sulfur XANES spectra of three samples (C32782, C32665, and C32776) were unintentionally recorded twice and least-squares fitting of these duplicate spectra were done before it was realized that they were duplicate spectra. Hence, such spectra provide a useful test of the reproducibility of the least-squares fitting analysis procedure. These data are also listed in Table 2. It is reassuring to find that there is good agreement between these results, even for the pyritic sulfur.

There are notable variation in the ratio of thiophenic sulfur to total organic sulfur among the samples (61% to 82%). The variation appears to be related to sample locations. As shown in Table 2, the ratios for samples from region 1 and 2 are relatively lower (61% to 64%), whereas, the ratios for samples from the other three regions are relatively higher (64% to 82%). This correlation will be examined further including total sulfur content and coal rank of the samples. The results will be reported in the next quarter.

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

	% Coal	% of Total Sulfur				% Organic Sulfur
Coal	Total Sulfur*	Pyritic Sulfur	Sulfate	Thiophenic Sulfur	Organic Sulfide	Thiophenic Sulfur
C-32777	3.14	22	2	47	27	64
C-32782	3.90	18	7	47	27	64
C-32782	3.90	20	7	46	28	62
C-32783	4.41	21	9	42	27	61
C-32779	4.20	16	1	51	28	65
C-32815	3.73	27	4	42	25	63
C-32784	1.79	34	18	30	13	70
C-32795	0.73	10	12	64	14	82
C-32796	1.05	45	4	38	13	75
C-32801	1.98	38	9	37	16	70
C-32802	3.12	25	5	46	24	66
C-32803	2.54	28	6	45	21	68
C-32661	2.89	35	8	40	16	71
C-32665	2.73	34	8	40	18	69
C-32665	2.73	35	7	41	16	72
C-32776	3.13	29	6	42	22	66
C-32776	3.13	33	6	39	22	64
C-32662	1.51	35	11	43	11	80
C-32663	2.18	30	21	30	13	70
C-32772	2.38	40	7	39	14	74
C-32775	2.98	38	6	40	16	71
C-32780	3.32	26	7	47	20	70
C-32781	3.02	38	6	43	13	77
C-32793	1.64	41	10	35	14	71

*By ASTM analysis.
**Also contains 3 sulfoxide

SUMMARY

The results of the froth floatation/release analysis (FF/RA) tests indicate that FF procedure further reduced Cl in most of the ground samples from regions 1, 2, and 3 by 4-60%. A reduction of 38% in Cl content was observed for one sample (C32793) from region 4S; no reduction was observed for other samples from region 4S and region 4H. A combination of wet grinding and FF/RA reduced Cl contents in most samples from regions 1,2, and 3 by 29-81% and in one sample from region 4S by 60%.

The forms of chlorine and sulfur in twenty-one Illinois basin coal samples have been determined from their sulfur K-edge XANES spectra using the least-squares fitting method. The chlorine XANES spectra for all the coals are similar and chloride anion was determined to be the predominant form of chlorine. The identity of the positive counter ions with which the chlorine anions are associated in the coals could not be unambiguously determined from XANES spectra.

The XANES sulfur spectra show that major forms of sulfur present in most samples consist of pyritic sulfur, organic (aliphatic) sulfide, thiophenic sulfur, and sulfate sulfur. Other forms, oxidized organic sulfur forms and elemental sulfur, if present, are relatively minor. The ratios of thiophenic sulfur to total organic sulfur were examined. The ratios show a correlation with sample location (region). For samples from regions 1 and 2, the ratios are relatively lower (61% to 64%), whereas, for samples from the other three regions, the ratios are relatively higher (64% to 82%).

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PROJECT MANAGEMENT REPORT
March 1 through May 31, 1995

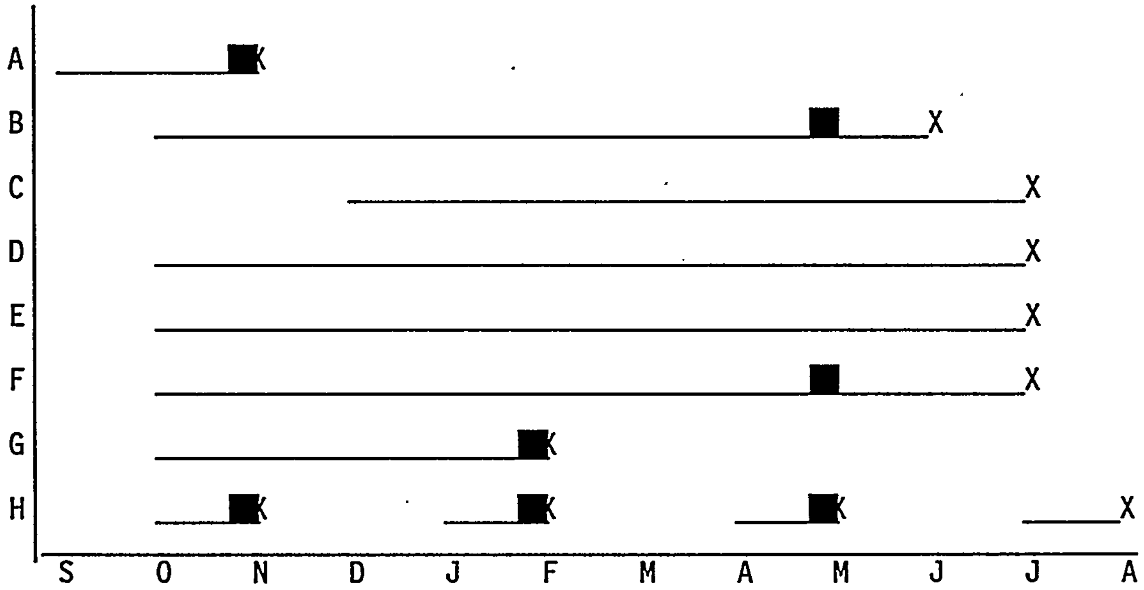
Project Title: **ADVANCED CHARACTERIZATION OF FORMS OF CHLORINE, ORGANIC SULFUR, AND TRACE ELEMENTS IN AVAILABLE COALS FROM OPERATING ILLINOIS MINES**

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).
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. Perform porosity and TGA-FTIR analyses (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)

EXPENDITURES - EXHIBIT B

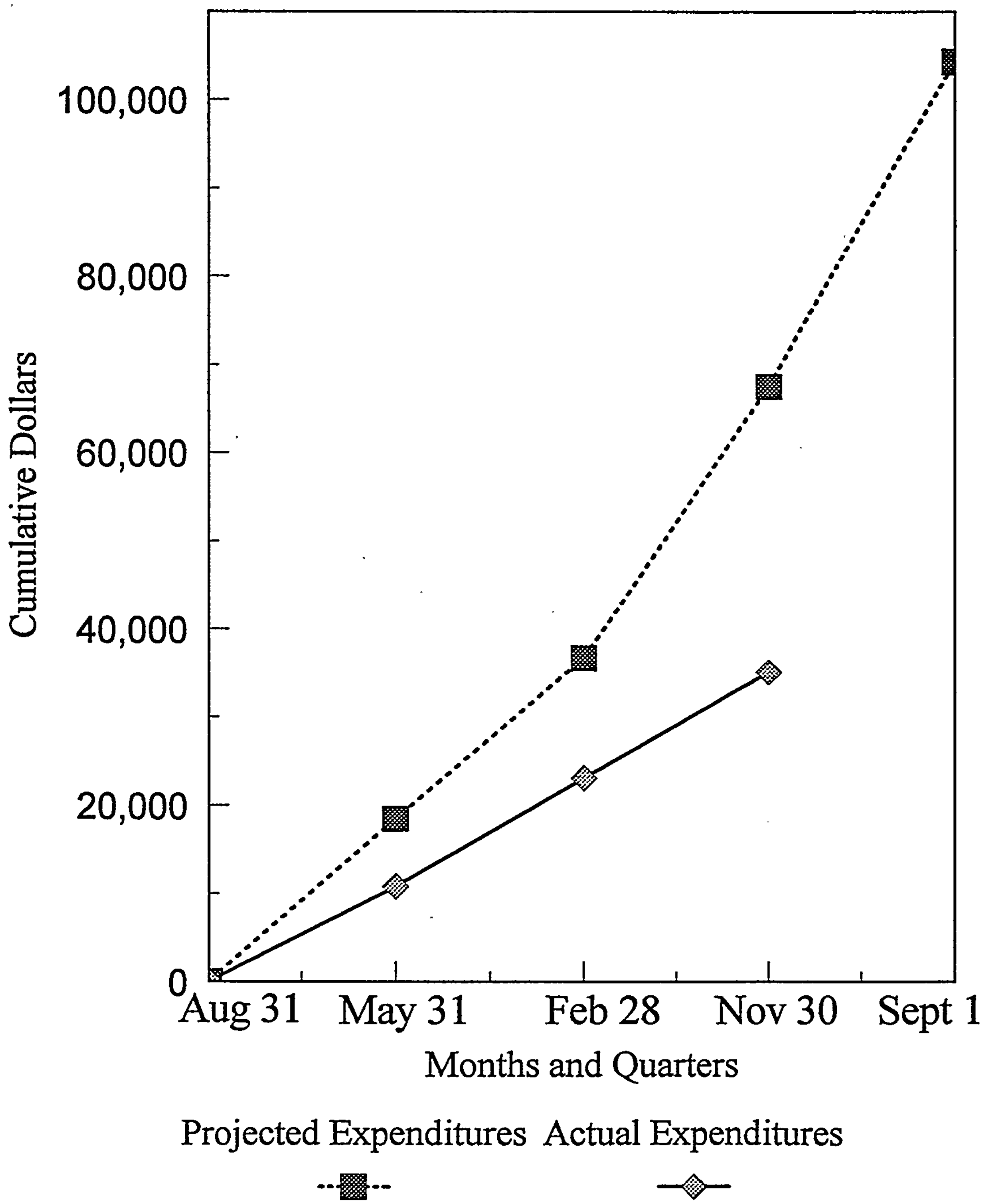
Cumulative Projected and Estimated Expenditures by Quarter

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	17,763	3,956	1,119	1,364	0	7,687	3,189	35,078
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



Total ICCI Award $ 104,356