

XANES SPECTROSCOPIC CHARACTERIZATION OF SELECTED ELEMENTS IN DEEP-CLEANED FRACTIONS OF KENTUCKY #9 COAL

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INTRODUCTION

Cleaning of pulverized (-200 mesh) coal is a potentially cost-effective strategy for removing mineral matter and associated minor and trace elements from coal prior to combustion, thereby minimizing the release of pollutants to the atmosphere during combustion. Of special concern are those trace elements designated as potential hazardous air pollutants (HAPs) in the 1990 Amendments to the Clean Air Act¹. Various physical and chemical cleaning methods have been examined with regard to their efficiency for removal of trace elements from coal. Although the mode of occurrence is recognized to be a key factor in determining the behavior of a given element with respect to a specific cleaning method, no study, as far as we are aware, has attempted to include such information.

In this study, a finely ground sample of Kentucky #9 coal from the Illinois coal basin region in western Kentucky has been subjected to a combination of physical cleaning and chemical leaching methods. Each generated fraction has then been characterized using proton-induced X-ray emission (PIXE) spectroscopy to determine the bulk chemical composition and X-ray absorption fine structure (XAFS) spectroscopy to determine information relevant to the elemental mode of occurrence for selected elements. As we will show, inclusion of the mode of occurrence information explains much of the variable efficiency exhibited with respect to the cleaning process by different elements. Conversely, the superior efficiency of column flotation for removal of mineral matter from clean coal provides samples in which the elements exist almost entirely in organic association. Such samples have proven to be invaluable for generating the XAFS spectral signatures for elements in organic association.

EXPERIMENTAL

(a) Coal Cleaning Studies: A 50 kilogram sample of Kentucky #9 coal was made available for this study by the Big Rivers Utility company. The coal, originally consisting of 1" lumps, was dried and crushed to 28 mesh. A representative kilogram sample of the 28 mesh coal was then ground to 80% passing 60 mesh, from which two head samples of 150 grams each were prepared and submitted for analysis. Samples were then prepared for gravity separation testing and release analysis, the results of which are described elsewhere².

A representative sample was then ground to 90% passing 325 mesh to constitute the fine coal sample. Aliquots of this sample were subjected to separation by flotation in a Denver cell and also in a 2"-diameter "Ken-Flote" column³ into float and tailings fractions. The float fraction from the Denver cell was then used as feed for hydrothermal leaching tests that were conducted in a 1 liter autoclave at 110°C and 300 psi. Four samples were prepared: samples were exposed for 15 and 60 minutes to either a 10% acid (H₃PO₄) or basic (NaOH) medium. The overall sample scheme and sample labelling notation are shown in Figure 1. Sufficient samples of each fraction were obtained for proximate analysis, chemical analysis by PIXE spectroscopy, and element speciation analysis by XAFS spectroscopy.

(b) PIXE Spectroscopic Analysis: Each generated sample in the scheme shown in Figure 1 was analyzed by thick-target PIXE spectroscopy using the dual-energy irradiation procedure⁴. NIST coal and fly-ash SRMs were used to monitor the accuracy and precision of the trace element measurements. Results for the SRMs and detection limits for the PIXE measurements are given elsewhere⁴; further details of PIXE analysis can be found in the preceding paper in this volume.

(c) XAFS Spectroscopic Analysis: XAFS spectroscopy of selected elements in the samples generated according to the scheme shown in Figure 1 was carried out either at the National Synchrotron Light Source (NSLS) in Brookhaven National Laboratory, NY, or at the Stanford Synchrotron Radiation Laboratory (SSRL) at Stanford University, CA. Similar experimental procedures were used at both of these facilities; these procedures have been described in detail in previous publications^{5,6}. The XAFS spectra from elements in coal were collected in fluorescence geometry using a thirteen-element germanium detector developed principally for

trace element investigation⁷. Spectra were obtained typically from 100 eV below the K-edge of the element under investigation to as much as 500 eV above the edge. As is usually done, the XAFS spectra were subdivided into separate X-ray absorption near-edge structure (XANES) and extended X-ray absorption fine structure (EXAFS) regions. In many instances, particularly when the concentration of the element was less than about 50 parts-per-million (ppm), the EXAFS signal was too weak to be reliably interpreted and interpretation of the mode of occurrence of an element was based exclusively on the XANES region.

The XANES spectra shown in this paper have been prepared from the raw XAFS spectroscopic data in the usual manner: the spectra are first normalized to the edge step and any slope in the data is removed by fitting spline functions to the pre-edge and post-edge regions and subtracting the pre-edge background extended beneath the overall spectrum. Each spectrum shows a zero-point of energy that is defined by the position of the same absorption edge in a standard material, the spectrum of which is collected at the same time as the spectrum from the coal. For the elements discussed in this paper, these zero points are defined in standard materials as follows: potassium (3608.4 eV, KCl), calcium (4038.1, calcite CaCO₃), titanium (4966 eV, Ti metal foil), vanadium (5465 eV, V metal foil), chromium (5989 eV, Cr in stainless steel), manganese (6539 eV, Mn metal foil), arsenic (11867 eV, As₂O₃). ⁵⁷Fe Mössbauer spectroscopy, rather than Fe XAFS spectroscopy, was used to examine the different forms of iron in some of the fractions shown in Figure 1 because this method is more definitive for elucidating details regarding the iron minerals present in coal.

Table 1: PIXE Analytical Data for Head, Float and Tailings Samples from Denver Cell and "Ken-Flote" Column Flotation Tests

	Sample				
	Head	DC-1	DC-2	CF3-1	CF3-2
Wt fraction, wt%	100.00	72.33	27.67	83.17	16.83
Ash content, wt%	18.29	5.69	50.88	3.56	84.20
Sulfur, wt%	2.96	2.25	5.49	2.94	6.29
Elements in ppm					
Na	5010	2523	--	4233	5852
Mg	5392	2381	10006	3456	20743
Al	19463	8479	57138	11705	103127
Si	45258	15197	129760	17462	222744
S	29095	22446	54905	19432	62873
Cl	3632	1113	--	1529	244
K	4181	1418	10019	1135	15962
Ca	2597	1592	34524	1107	41068
Ti	1249	931	2430	711	2797
V	159	59	187	36	133
Cr	40	31	84	19	98
Mn	37	43	491	21	401
Fe	18173	13465	78278	8612	55967
Ni	21	25	67	19	55
Cu	8	17	47	12	44
Zn	47	20	154	13	108
Ga	7	5	11	3	10
As	10	14	100	10	50
Br	22	26	27	12	12
Sr	41	21	75	15	23

RESULTS AND DISCUSSION

A. Cleaning Efficiency:

Coal characterization data and PIXE analysis data on elemental concentrations are summarized for the different float and tailings fractions in Table 1. The two flotation methods are both efficient at separating the inorganic matter from organic matter, but the column flotation test is definitely the better of the two methods. This is also illustrated in Figure 2, which provides a direct comparison of the two methods. In general, the float/tailings difference indicators in this figure are longer for the column flotation method than for the Denver cell method for most of the elements. It is also instructive to examine the tailings/float concentration ratio for individual elements (or equivalently comparing the length of the indicators in Figure 2) to that for the

overall ash. The elements that exceed or equal the overall ash ratio are Ca and Mn; those that are slightly less than the overall ash ratio are Al, Si, K, and Zn in both tests, and Fe along with As in the case of the Denver cell test. Not surprisingly, sulfur shows a small value for the ratio because over 40% of the element is organically bound. However, there is a group of elements consisting of Ti, V, Cr, Ni, Ga, that also have relatively short indicators, suggesting that significant fractions of these elements might also be in organic association.

Attempts to mass balance individual elements in these flotation experiments vary from good to poor and certainly the differences for a number of elements are much larger than can be attributed to experimental errors in the PIXE analysis. The most significant problem would appear to be segregation of the heavy minerals (pyrite, calcite) in the feed sample as the largest variations between the flotation experiments are exhibited by calcium, manganese and iron. In particular, the calculated feed composition for the column flotation experiment has significantly lesser amounts of these elements and somewhat more Al and Si (derived from excess clays?) than that for the Denver cell flotation test.

B. The Lithophile Elements:

XANES spectra of Ti, V, Cr, and Mn showed quite different spectra for the float and tailings fractions (e.g for Mn, Figure 3). Whereas the XANES spectra of the tailings fractions could be attributed to principally (>80%) illite for Ti, V and Cr, and to a mixed mineralogical occurrence for Mn (25% Mn/illite and 75% Mn/calcite), the spectra of the float fractions did not match the spectra of any mineral standard examined and distinct organically associated forms were inferred to exist for these four elements. For Ti and Cr, the closest matches appeared to be a poorly crystalline oxide or oxyhydroxide, a possibility raised in earlier studies⁸ of V in Kentucky #9 coal. For Mn, the spectrum of the float fraction was altered significantly by application of both the base and acid leaching tests and the Mn content was also reduced in both tests. This suggested the presence of two organically associated forms of Mn: one that was soluble in acid; the other soluble in base.

Examination of the XANES spectra of calcium, a major element, also showed distinctly different spectra for the tailings and float fractions. The spectra of the tailings fractions were clearly dominated by Ca as calcite, whereas the spectra of the float fractions were similar to that observed for carboxyl-bound Ca in low-rank coals⁹. Interestingly, K XANES spectra of all fractions, whether float or tailings, were identical to that of K in illite. The fact that illitic Ti, V, and Cr spectra were only seen for the tailings fraction and not for the float fraction suggests that there are two generations of illite in the coal: one generation is coarse and/or easily separated from the coal (e.g. partings) and contains all of the minor elements; the other generation is fine, can not be separated easily from the organic matter, and is essentially devoid of significant Ti, V, and Cr. These two illite forms might represent coarse detrital and fine-grained authigenic generations of illite in the coal, respectively.

C. The Chalcophile Elements:

In contrast to the lithophile elements, the two chalcophile elements examined, Fe and As, were found in the same forms in both the tailings and float fractions. Both Fe and As are found in association with pyrite and its oxidation products in all fractions. Arsenic occurs as a substitutional replacement for sulfur in the pyrite structure and as arsenate. The arsenate form is more prevalent in the float fractions (Figure 4), consistent with the fact that smaller particle sizes of pyrite are both more likely to be found in the float fractions and to be more oxidized than large particle sized pyrite. The Mössbauer data for iron tells a very similar story. Iron in oxidized form (principally jarosite) is relatively more common compared to iron as pyrite in the float fractions than in the tailings fractions. There is an approximate linear correlation between the fraction of oxidized arsenic and the fraction of Fe as jarosite for all the samples examined. This relationship would imply perhaps that the arsenate is incorporated in the jarosite structure, presumably by substitution of the arsenate group for the sulfate group in the jarosite structure.

CONCLUSIONS

The results of this study demonstrate convincingly that Ca, Ti, V, Cr and Mn in Kentucky #9 coal occur in both a mineralogical and an organic association. For Ti, V, and Cr the mineralogical association consists principally of substitution in the cation layers in the clay mineral illite, whereas Mn substitutes mainly for Ca in calcite, which is the major mineral occurrence for calcium. The organic association has not been so clearly identified, but is consistent with the elements present in oxygen coordination, either at individual isolated ion-exchange sites on maceral surfaces, or in microparticles of poorly crystalline oxide or oxyhydroxide minerals. For Ti, V, and Cr, this organic association represents approximately 50% of the occurrence of these elements in this particular sample of Kentucky #9 coal. In contrast to the five lithophile elements, the chalcophile elements, Fe and As, appear to occur almost

exclusively in pyrite or its oxidation products in all fractions of this coal. Such occurrences readily explain the relatively poor separation of some of these elements (Ti, V, Cr) in flotation tests.

Finally, this investigation demonstrates that information on elemental modes of occurrence from XAFS spectroscopy is a very useful supplement for the interpretation and understanding of results from coal cleaning studies. Conversely, the mineral-rich and mineral-poor fractions generated in the course of such studies provide the means for a much better understanding of elemental occurrences based on XAFS spectroscopy. This serendipitous relationship will be exploited for investigation of other coals and cleaning processes.

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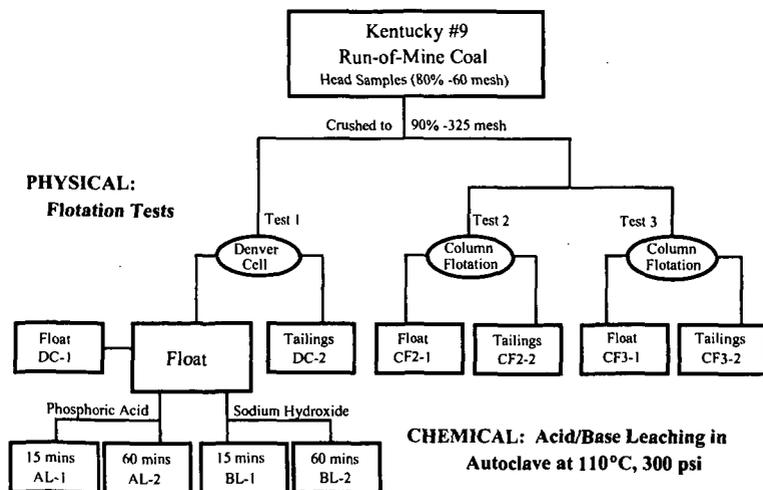


Figure 1: Scheme for physical and cleaning tests performed on the as-mined sample of Kentucky #9 coal to generate float, tailings, and leached fractions.

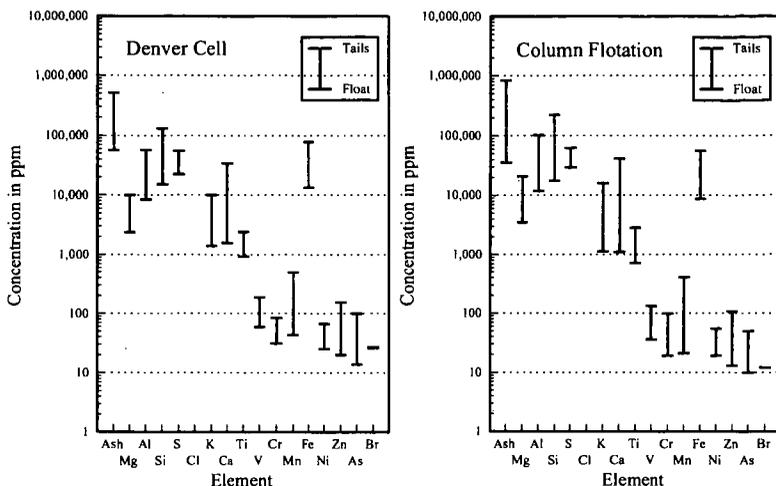


Figure 2: Comparison of the relative efficiency of the segregation of elements in Kentucky #9 coal between float and tailings fractions generated in the Denver cell test and in the "Ken-Flote" column flotation test.

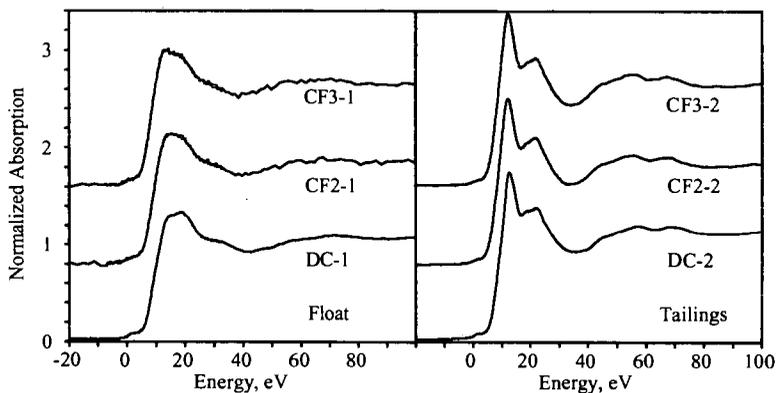


Figure 3: Mn XANES spectra of float and tailings fractions of Kentucky #9 coal.

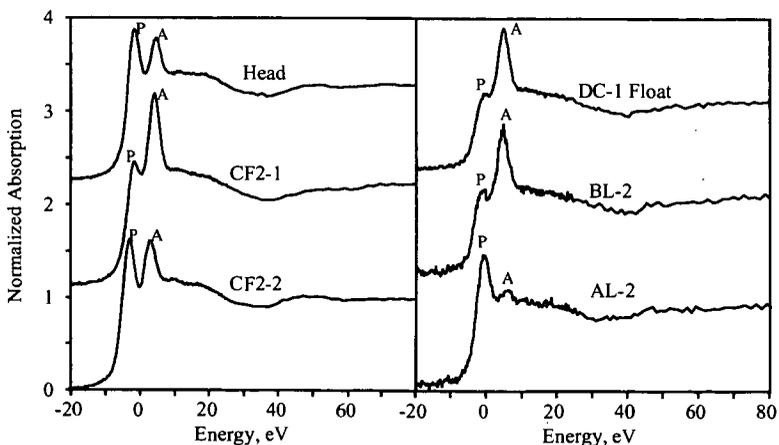


Figure 4: As XANES spectra of various fractions of Kentucky #9 coal.