

INVESTIGATION OF THE BEHAVIOR OF POTENTIALLY HAZARDOUS TRACE ELEMENTS IN KENTUCKY COALS AND COMBUSTION BYPRODUCTS

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INTRODUCTION

The minor- and trace-element content of coal is of great interest because of the potentially hazardous impact on human health and the environment resulting from their release during coal combustion. Of the one billion tons of coal mined annually in the United States, 85-90% is consumed by coal-fired power plants.¹ Potentially toxic elements present at concentrations as low as a few $\mu\text{g/g}$ can be released in large quantities from combustion of this magnitude. Of special concern are those trace elements that occur naturally in coal which have been designated as potential hazardous air pollutants (HAPs) in the 1990 Amendments to the Clean Air Act.²

The principle objective of this work was to investigate a combination of physical and chemical coal cleaning techniques to remove 90 percent of HAP trace elements at 90 percent combustibles recovery from Kentucky #9 coal. Samples of this coal were first subjected to physical separation by flotation in a Denver cell. The float fraction from the Denver cell was then used as feed material for hydrothermal leaching tests in which the efficacy of dilute alkali (NaOH) and acid (HNO₃) solutions at various temperatures and pressures was investigated. The combined column flotation and mild chemical cleaning strategy removed 60-80% of trace elements with greater than 85% recovery of combustibles from very finely ground (-325 mesh) coal. The elemental composition of the samples generated at each stage was determined using particle induced X-ray emission (PIXE) analysis. PIXE is a rapid, instrumental technique that, in principle, is capable of analyzing all elements from sodium through uranium with sensitivities as low as 1 $\mu\text{g/g}$.

EXPERIMENTAL PROCEDURE

Sample Preparation

A sample of run of mine coal from the Kentucky #9 seam was collected at the mine site, and split into subsamples as needed. Each subsample was then ground to -325 mesh and a 5% (w/v) slurry was prepared. The slurry was subjected to Denver flotation, and the float fraction was employed as the feed sample for hydrothermal leaching using either a NaOH or HNO₃ solution in a 1 liter autoclave reactor. The duration, temperature, and pressure of the chemical leaching process were varied to ascertain their influence, if any, on the removal of trace elements. Each clean coal sample was dried at 50°C overnight, and pressed into a 1 mm x 19 mm pellet for elemental analysis.

PIXE Analysis

A schematic of the PIXE analysis system at Element Analysis Corporation is shown in Figure 1. A dual energy irradiation is performed on each sample with the X-ray detector in two positions for data collection. During the high-energy (2.1 MeV) irradiation, the detector is in a close-in position with a thick absorber and during the low-energy (1.6 MeV) irradiation, the detector is in a backed-out position with no absorber. Variable charge collection at these two energies/positions allows for spectrum balance and flexibility in the analysis on either the high- or low-energy ends of the X-ray spectrum.

Protons enter the target chamber by passing through a 0.30 mil Kapton window and the X-rays exit through a 0.1 mil Mylar window that is at 45 degrees relative to the beam. The beam, which is at an angle of 23° relative to the sample surface, is swept over the target to irradiate a 16 mm diameter area. The sample chamber is flushed with helium at atmospheric pressure to reduce sample heating and charging and each sample is irradiated for 15 minutes. A typical PIXE spectrum of a coal sample is shown in Figure 2. Data analysis is performed using a modified version of the GUPIX³ PC-based software package. In order that the accuracy and precision of the measurements may be assessed, the results for the PIXE analysis of 7 samples of the NIST 1635a Subbituminous Coal standard reference material are presented in Table 1.

RESULTS & DISCUSSION

In general, HNO₃ was more effective than NaOH in reducing elemental concentrations for all elements except V and Ga. The increase in the concentration of Cu and Cr in certain tests was attributed to corrosion of fittings in the autoclave reactor.

Table 1. Results for NIST SRM 1635a Subbituminous Coal

Element	PIXE Result ^a	Certified Value ^b
Sodium	0.21 ± 0.02 %	(0.24 ± 0.02 %)
Magnesium	760 ± 71 ppm	(1040 ± 130 ppm)
Aluminum	0.30 ± 0.02 %	(0.29 ± 0.03 %)
Silicon	0.60 ± 0.03 %	(0.59 ± 0.05 %)
Sulfur	0.39 ± 0.02 %	0.33 ± 0.03 %
Potassium	113 ± 11 ppm	(96 ± 16 ppm)
Calcium	0.69 ± 0.02 %	(0.54 ± 0.03 %)
Titanium	213 ± 8 ppm	(202 ± 6 ppm)
Chromium	1.2 ± 0.9 ppm	2.5 ± 0.3 ppm
Manganese	19.8 ± 1.2 ppm	21.4 ± 1.5 ppm
Iron	0.23 ± 0.01 %	0.239 ± 0.005 %
Nickel	Below LOD	1.74 ± 0.10 ppm
Copper	3.1 ± 0.2 ppm	3.6 ± 0.3 ppm
Zinc	4.6 ± 0.9 ppm	4.7 ± 0.5 ppm
Selenium	Below LOD	0.9 ± 0.3 ppm
Bromine	1.3 ± 0.3 ppm	(1.4 ± 0.4 ppm)
Strontium	129 ± 9 ppm	(121 ± 19 ppm)

^aAverage and standard deviation of the analysis of 7 samples

^bValues in parentheses are the recommended or consensus values

The degree to which elements are removed by coal cleaning processes depends to a great extent on their mode of occurrence or chemical association in the coal. Although the exact composition can vary greatly from one coal to the next, generalizations have been made concerning common modes of occurrence for trace elements in coal.¹ For example, the fact that Mg, Ca, Mn, and Sr have a carbonate association would explain their efficient removal since the solubilities of carbonates increase in acidic solutions. Moreover, elements known to have an association with pyrite, Fe, S, As, Zn, Ni, and Ga, all show a significant decrease in concentration. Similarly, a considerable reduction in elements known to be strongly associated with silicates, Si, Al, Mg, and K, was observed. Elements thought to have a significant organic association were removed less efficiently by HNO₃. In these samples, those elements were V, Cr, Ti, and Cu. X-ray absorption fine structure spectroscopy of Kentucky #9 coal has indicated a partial organic association for V, Cr, and Ti. Although the association of Cu has not been determined in these samples, Cu is known to have partial organic associations in other coals.

An increase in the duration and pressure of the hydrothermal leaching process showed negligible improvement in the reduction of elemental concentrations for some elements and only slight improvements for others. Thus, it appears these variables have minimal impact on the effectiveness of this coal cleaning process.

SUMMARY

The variable with the greatest impact on hydrothermal leaching appears to be the leaching agent itself. A significant reduction in the concentration of many elements was observed with the use of 2% HNO₃. On the other hand, increasing the reaction time from 15 minutes to 1 hour and/or the vessel pressure from 100 psi to 300 psi had only a slight impact on the removal of hazardous elements in coal.

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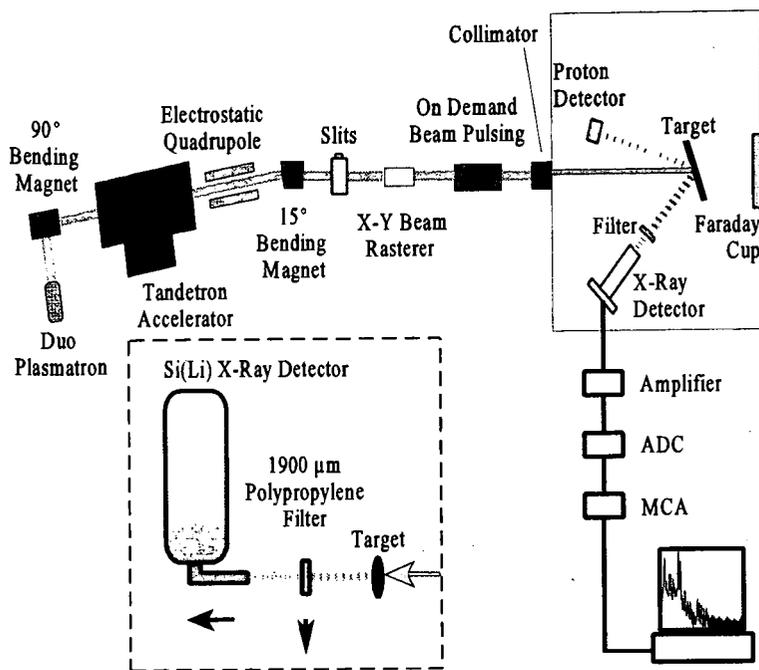


Figure 1. Schematic diagram of PIXE system.

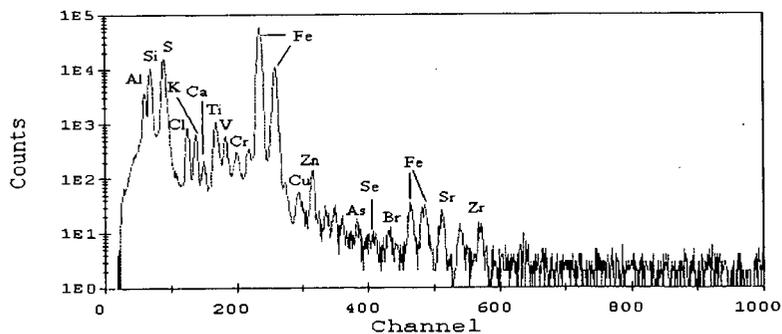


Figure 2. Typical PIXE spectrum of coal.