

APPLICATION OF SELECTIVE LEACHING TECHNIQUE FOR MAJOR, MINOR, AND TRACE ELEMENT ANALYSIS IN COAL

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INTRODUCTION

The abundance and association of major, minor, and trace inorganic constituents in coal must be determined to predict their fate during combustion and gasification. In addition, the inorganic composition of coal influences the properties of the ash produced that, in turn, affects the usability of ash. The adverse effects of the inorganic components (ash-forming species) on coal utilization system performance include the formation of fine particulate that is difficult to collect, ash fouling and slagging, and conversion and erosion. Recently, selected metals that are present in coal were identified as air toxics. The 1990 Amendments to the Clean Air Act identified 189 hazardous air pollutants, including many trace metals. Therefore, the fate of trace metals considered to be air toxics is increasing in importance. Knowledge of the abundance and association of inorganic constituents is necessary in predicting the inorganic species behavior in coal in a given process. Chemical fractionation, in combination with other analytical techniques such as computer-controlled scanning electron microscopy (CCSEM), is used in models to predict the formation and ash deposition properties.

The inorganic components in the higher-rank coals (anthracite and bituminous) are primarily present in mineral phases. Whereas, the inorganic components in low-rank coals can be associated as discrete mineral phases, coordinated metal ions, and cations bound to carboxyl groups or in clays (1). The major mineral phases found in coal include aluminosilicates, carbonates, sulfides, and sulfates. Much of the Si, Al, and K is found in the aluminosilicate minerals such as clay minerals, with Si also found in quartz. Clays may also adsorb some trace elements such as Cs, Li, and Rb. Sulfide minerals such as pyrite can contain the trace elements arsenic, cadmium, cobalt, chromium, copper, mercury, manganese, molybdenum, nickel, lead, and selenium (2, 3). Carbonate minerals such as calcite, siderite, dolomite, and ankerite contain magnesium, calcium, and iron, but may also have trace amounts of manganese, strontium, and barium present.

The organic coal portion of coal consists of carboxylic acid, phenolic hydroxyl, mercapto, and imino groups which are able to bond with several trace elements. Cations of sodium, calcium, magnesium, potassium, barium, iron, manganese, strontium, and zinc bond to the carboxyl group to produce carboxylate salts (3). The trace elements are generally associated with both the organic and the mineral matter. In the mineral portion of coal, the trace elements can be found as discrete minor minerals, as replacement ions in minerals, or adsorbed on clays (2).

This paper discusses the application of a selective leaching technique known as chemical fractionation to coal. The method described is a modification of a leaching method by Miller and Given (4). Chemical fractionation is used to determine the distribution of elements among the organic and mineral phases in coal based on the differences in solubilities of coal constituents in three separate, stirred solutions: deionized water, 1 M ammonium acetate (NH₄OAc), and 1 M hydrochloric acid (HCl) as shown in Figure 1. A representative 140-gram sample of coal is ground to -200 mesh (<74 micrometers) and then vacuum dried to a constant weight. A 35-gram portion of coal is ashed at 750°C and the ash content is determined. A sample is analyzed for the major, minor, and trace elements. The remainder of the coal is then subjected to successive extraction treatments. The first extraction treatment uses 4 mL of deionized water per gram of coal and is stirred in a covered beaker at room temperature for 24 hours. The sample is vacuum-filtered and

rinsed with deionized water. About 35 grams of the coal residue is removed and dried for ash content determination, and an analysis on the ash for the major, minor, and trace elements is performed by energy-dispersive x-ray fluorescence (EDXRF) utilizing direct excitation and three secondary excitation conditions (aluminum, titanium, and germanium). The filtrate is then acidified and transferred to a 125-mL volumetric flask, made up to volume, and stored for further analysis by inductively coupled plasma emission spectroscopy (ICP) and atomic absorption (AA).

Four mL of 1 M NH_4OAc per gram of coal is then added to the beaker containing the remaining 70 grams of coal residue. The sample is stirred and heated at 70°C for 24 hours. The sample is then vacuum-filtered and rinsed with deionized water. The filtrate is acidified and saved. The 1 M NH_4OAc extraction procedure is repeated two additional times. The filtrates from the three successive NH_4OAc extractions are combined, transferred to a 500-mL volumetric flask, made up to volume, and stored for analysis by AA. About 35 grams of residue coal is removed and dried. The residue coal is used for determination of the ash content, and major, minor, and trace constituents are determined on the ash by EDXRF.

To the remaining coal residue, 4 mL of 1 M HCl per gram of coal is added, stirred, and heated at 70°C for 24 hours. The sample is vacuum-filtered and rinsed with deionized water. The filtrate is acidified and saved. The 1 M HCl extraction procedure is repeated once more. The filtrate from both HCl extractions is combined, transferred to a 300-mL volumetric flask, made up to volume, and stored for analysis by AA. The coal residue is then dried. A portion of the dried coal residue is used for ash content determination, and the remainder is ashed and analyzed by EDXRF for the major, minor, and trace elements.

RESULTS AND DISCUSSION

The chemical fractionation procedure uses deionized water to extract the water-soluble minerals, such as halite (NaCl) and thenardite (Na_2SO_4). The cations associated on ionic exchange sites of carboxylic acids in the organic portion of coal are removed by ammonium acetate. Hydrochloric acid extracts elements that are associated with acid-soluble minerals, such as calcite (CaCO_3), dolomite ($\text{CaMg}(\text{CO}_3)_2$), and siderite (FeCO_3), and organic coordination complexes. The elemental constituents remaining in the residue presumably are associated with the insoluble minerals, such as clays (aluminosilicates), quartz (SiO_2), and pyrite (FeS_2).

Table 1 summarizes the chemical fractionation results obtained from five coals ranging in rank from lignite to bituminous. The ash produced by ashing (at 750°C) the chemical fractionation residues was analyzed using a Fisons 770 EDXRF system, and the mass balance was completed by normalizing to zero silicon loss. The results indicate that sodium is the only element that is consistently and appreciably extracted in the water treatment. The sodium is probably present in the coals as sodium chloride (halite), and sodium sulfate (thenardite), and, in the Beulah coal, may be present in the water inherent in the lignite.

Calcium, magnesium, and sodium in all five coals, along with some potassium in two of the coals, are removed primarily in the ammonium acetate extraction. These elements are usually found in salts of organic acids in coals. They may also be found in minerals such as gypsum which is soluble in both water and ammonium acetate, or they may be associated with ion-exchange sites in clays.

The hydrochloric acid leaching extracted a majority of the iron and aluminum that was removed during the chemical fractionation process. Much of the remainder of the calcium and magnesium that was left after the ammonium acetate leaching was removed by the hydrochloric acid extraction. These elements were probably associated with the carbonate minerals calcite and dolomite which are acid-soluble. A small amount of titanium in two of the coals was also leached out of the coal during the hydrochloric acid extraction. The hydrochloric acid extraction removes elements that exist in organic coordination complexes such as Al^{3+} and Fe^{3+} and in acid-soluble minerals such as carbonates.

The bituminous coals differed from the lignite and subbituminous coals in that less sodium and magnesium were extracted, indicating an association of sodium with the insoluble mineral fraction of the coal. A larger portion of the aluminum remains in the bituminous coals than in the lignite or subbituminous coals, suggesting that the aluminum is not associated with a coordinate site, or that there is a better developed crystalline structure of the clays such as illite and montmorillonite.

The iron in all of the coals is located in the acid-soluble or the insoluble fractions. Computer-controlled scanning electron microscopy (CCSEM) analysis of the coals indicates the percent of pyrite to be as follows: Beulah - 30%, Black Thunder - 11%, Rochelle - 2%, Illinois No. 6 - 36%, and Pittsburgh No. 8 - 13%. This indicates a direct relationship between the pyrite content and the iron content after leaching. The iron leached by HCl can be attributed to the dissolution of siderite (FeCO_3). This is the most evident in the Rochelle subbituminous coal.

The weathering of Pittsburgh No. 8 has caused some minerals such as pyrite to oxidize. Therefore, the oxidized iron was removed in the hydrochloric leaching, but aluminum was not because aluminum is not readily oxidized. The aluminum was removed in the lignite and bituminous coals, due to aluminum being organically associated.

Arsenic and mercury, according to Norton and others (5) and Ciocco and others (6), are strongly associated with pyrite and other sulfide minerals. Finkelman (7) and Galbreath and others (8) also have indicated that mercury is present in coal as a sulfide. Chromium is reported to be associated with clay minerals (9). Table 2 indicates that arsenic is primarily removed by hydrochloric acid, while only a small portion of chromium is removed. However, the majority of mercury and chromium are not leached out and are associated with the insoluble fraction of coal, indicating an association with pyrite or silicates.

SUMMARY

Few water-soluble minerals were found in the coals studied. The water-soluble minerals are likely limited to halite (NaCl); gypsum ($\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$), found in the Pittsburgh No. 8 and Illinois No. 6 coals; and sylvite (KCl), found in the Beulah and Illinois No. 6 coals. A small amount of iron was removed from the bituminous coals, most likely from hematite (Fe_2O_3).

High levels of calcium, magnesium, and sodium were removed by ammonium acetate (NH_4OAc). These elements are associated with ion exchange sites of the carboxylic acids in the organic portion of the coal. The lower-grade coals studied contained more organically associated elements.

Iron, calcium, and magnesium are the most commonly removed elements in the acid leaching. The loss of these elements can be attributed to the dissolution of calcite (CaCO_3), dolomite ($\text{CaMg}(\text{CO}_3)_2$), and siderite (FeCO_3). The Illinois No. 6 coal had very few elements removed by HCl, indicating few carbonate minerals in the coal and the probable association of mercury and chromium with pyrite and silicates. The calcium present was either in the form of gypsum ($\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$), an accessory element in clays, or organically associated.

In order to predict the behavior of the inorganic portions of the coal during combustion, it is necessary to know how the elements are distributed between the organic and inorganic portions of the coal. The chemical fractionation process helps to define this distribution. The organically associated elements will be freed during the earliest stages of combustion and will react with the inorganic phases as combustion continues. This will have an effect on fouling and slagging within the boiler, reducing plant efficiency. By thorough characterization and careful selection of coals, coal-burning plants can increase efficiency and, in some cases, reduce pollution containing trace elements.

REFERENCES

1. Benson, S.; Holm, P. "Comparison of Inorganic Constituents in Three Low-Rank Coals," *Ind. Eng. Chem. Prod. Res. Dev.* **1985**, *24*, 145-149.
2. Martines-Tarazona, M.; Spears, D.; Tascon, J. "Organic Affinity of Trace Elements in Austrian Bituminous Coals," *Fuels* **1992**, *71*, 909-917.
3. Swaine, D.J. "The Organic Association of Elements in Coals," *Organic Geochemistry* **1992**, *18* (3), 259-261.
4. Miller, R.N.; Given, P.H. *Ash Deposits and Corrosion Due to Impurities in Combustion Gases*, Bryers, R.H., Ed.; Hemisphere Publishing Corp.: Washington, DC, 1977; p 39.
5. Norton, G.A.; Markuszewski, R.; Buttermore, W.H. "The Removal and Control of Trace Elements in Coal and Coal Wastes," *In Proceedings of the International Conference on Elemental Analysis of Coal and Its By-Products*; 1991, p 270-288.
6. Ciocco, M.V.; Morsi, B.I.; Araujo, G.; Chiang, S.H. "Trace Elements Removal Using a Selective Coal Agglomeration Process," *In Proceedings of the Ninth Annual International Pittsburgh Coal Conference*; 1992, p 299-305.
7. Finkelman, R.B.; Stanton, R.W. "Identification and Significance of Accessory Minerals from a Bituminous Coal," *Fuel* **1977**, *57*, 763-768.
8. Galbreath, K.C.; Brekke, D.W. "Feasibility of Combined Wavelength-Dispersive/Energy-Dispersive Computer-Controlled Scanning Electron Microscopy for Determining Trace Metal Distribution," *In Draft Proceedings of the Trace Elements Workshop: Trace Element Transformations in Coal-Fired Power Systems*; Scottsdale, Arizona, 1993.
9. Wiese, R.G., Jr.; Muir, I.; Fyfe, W.S. "Trace Element Siting in Iron Sulfides from Coal Determined by Secondary Ion Mass Spectrometry," *Energy Source* **1990**, *12*, 251-264.

TABLE 1
Chemical Fractionation Results

Coal - Beulah - Lignite					
Elements	Initial, ppm	% Removed by H ₂ O	% Removed by NH ₄ OAc	% Removed by HCl	% Remaining
Aluminum	8,100	0	0	33	67
Iron	3,400	0	0	20	80
Titanium	270	0	0	9	91
Calcium	18,000	0	74	24	2
Magnesium	4,600	0	87	6	7
Sodium	5,800	13	87	0	0
Potassium	230	7	43	3	47
Coal - Black Thunder - Subbituminous					
Elements	Initial, ppm	% Removed by H ₂ O	% Removed by NH ₄ OAc	% Removed by HCl	% Remaining
Aluminum	8,400	0	26	42	32
Iron	1,800	0	0	75	25
Titanium	400	0	0	0	100
Calcium	9,900	0	72	28	0
Magnesium	3,000	0	64	35	1
Sodium	290	27	62	8	3
Potassium	140	0	48	0	52
Coal - Rochelle - Subbituminous					
Elements	Initial, ppm	% Removed by H ₂ O	% Removed by NH ₄ OAc	% Removed by HCl	% Remaining
Aluminum	8,300	0	0	18	82
Iron	4,600	0	0	96	4
Titanium	2,000	0	0	0	100
Calcium	8,800	0	64	35	1
Magnesium	2,900	0	57	37	6
Sodium	450	11	76	5	8
Potassium	230	0	0	0	100
Coal - Illinois No. 6 - Bituminous					
Elements	Initial, ppm	% Removed by H ₂ O	% Removed by NH ₄ OAc	% Removed by HCl	% Remaining
Aluminum	15,900	0	0	0	100
Iron	21,100	9	0	0	91
Titanium	610	0	0	2	98
Calcium	5,900	19	74	0	7
Magnesium	750	3	6	0	91
Sodium	1,400	47	17	3	33
Potassium	1,800	2	2	2	94
Coal - Pittsburgh No. 8 - Bituminous					
Elements	Initial, ppm	% Removed by H ₂ O	% Removed by NH ₄ OAc	% Removed by HCl	% Remaining
Aluminum	12,300	0	0	0	100
Iron	5,200	4	0	39	57
Titanium	580	0	0	0	100
Calcium	330	15	63	10	12
Magnesium	3,300	0	13	15	72
Sodium	420	11	23	0	66
Potassium	1,200	0	0	0	100

TABLE 2
Illinois No. 6 Filtrate Analysis by AA

Elements	% Removed by H ₂ O	% Removed by NH ₄ OAc	% Removed by HCl	% Remaining
Arsenic	<7	7	68	18
Chromium	1	1	26	72
Mercury	<24	5	<3	68

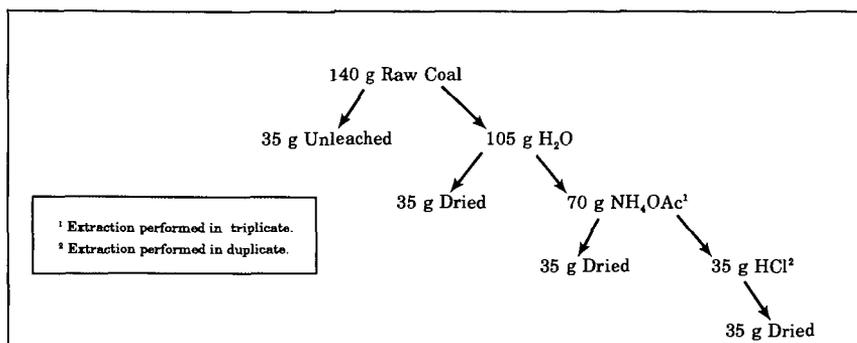


Figure 1. Chemical fractionation procedure.