



Quantification of the modes of occurrence of 42 elements in coal

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ABSTRACT

A series of 20 coal samples were subjected to sequential leaching with ammonium acetate, hydrochloric acid, hydrofluoric acid, and nitric acid to quantify the modes of occurrence of about 42 elements. The results indicate that within a coal rank the leaching behavior of many elements are broadly similar. However, the behavior of many elements varies between bituminous and subbituminous coals. While the leaching behavior of most elements is consistent with previous mode of occurrence interpretations there were a number of unanticipated results. About 75% of the arsenic in bituminous coals appears to be associated with sulfides, probably pyrite, however only 40% of the arsenic in the low rank coals appears to be associated with pyrite. In the bituminous coals we interpret that about 60% of the beryllium is associated with silicates, but in the low rank coals only 30% is silicate associated. In the bituminous coals 25% of the magnesium is associated with carbonates, but in the low rank coals 75% of the magnesium is in the carbonates. Fifty-five percent of the molybdenum was associated with the sulfides in the bituminous coals and in the low rank coals 65% was in the silicates. In the bituminous coals the rare earth elements (REE) are predominantly in the phosphate minerals (70% for the light REE and 50% for the heavy REE) but in the low rank coals the REE (50–60%) are associated with the clays. Sodium is predominantly (80%) associated with silicates in the bituminous coals and with the organics (65%) in the low rank coals. Titanium appears to occur more in the clays (65% bituminous, 70% low rank) than in oxides (35% bituminous, 15% low rank). Tungsten is in the sulfides (50%) in the bituminous coals but in the clays (60%) in the low rank coals. Uranium is associated with the silicates (40%) and insoluble phases such as zircon (30%) in the bituminous coals, but is associated with the organics (55%) in the low rank coals. Many of these rank differences reflect a higher detrital input and greater sulfide mineralization of the bituminous coals.

1. Introduction

The mode of occurrence of an element (also referred to as the element form or species) in coal is an important parameter as it is the mode of occurrence that will dictate the behavior of the element during coal combustion, beneficiation, conversion, weathering, leaching or any other chemical reaction that the coal undergoes (Finkelman, 1993a; Finkelman, 1993b). The behavior of the element will, in turn, determine how it will impact the environment, human health, technologic performance, and byproduct recovery. The mode of occurrence of the elements in coal can also provide insights into the source of the element and some of the changes that occurred during coalification (Orem & Finkelman, 2003).

The importance of the modes of occurrence of trace elements in coal is attested to by the number of published articles addressing this issue. Recent examples include: (Cheng et al., 2014; Dai et al., 2014a; Dai et al., 2014b; Dai et al., 2015a; Dang et al., 2016; Fang et al., 2014;

Gürdal, 2011; Huggins et al., 2009; Karayigit et al., 2017; Li et al., 2010; Liu et al., 2015; Riley et al., 2012; Sia & Abdullah, 2012; Tian et al., 2013; Vesper et al., 2008; Zhou et al., 2014).

Information on the modes of occurrence of elements in coal goes back more than a century to the first identification of minerals in coal (for example, (Des Cloizeaux, 1880)). Early attempts to determine the mode of occurrence of elements in coal took the form of estimating the organic/inorganic affinity of the elements based largely on the behavior of the element during density separation experiments (for example, (Zubovic et al., 1960; Zubovic et al., 1961)). The pioneering work of Gluskoter et al. (Gluskoter et al., 1977) represented one of the first attempts to systematize this knowledge. Most of the work from this time was qualitative or, at best, semi-quantitative in nature. For modes of occurrence information to have more practical value and for the information to be used in a predictive manner, quantitative data are necessary.

This paper summarizes previous studies which attempted to

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Table 1
Sample information.

Sample	Bed	State/Country	Rank	Ash yield (%)
PG	Pittsburgh	Pennsylvania	Bituminous	23.8
PF401	Pittsburgh	Pennsylvania	Bituminous	15.5
PF701	Pittsburgh	West Virginia	Bituminous	14.6
PF801	Lower Kittanning	Pennsylvania	Bituminous	35.5
PF901	Upper Freeport	Pennsylvania	Bituminous	27.5
KY	Broaz	Kentucky	Bituminous	14.0
AP	Warrior Basin	Alabama	Bituminous	57.4
EL	?	Eastern Interior	Bituminous	37.5
CLB	Lower Bakerstown	Maryland	Bituminous	6.5
CAN	?	Canada	Bituminous	10.1
Brazil	?	Brazil	Bituminous	39.8
LON (GW)	Gascoigne-Wood #2	Great Britain	Bituminous	15.8
AUS	Wyee	Australia	Bituminous	23.7
AUS2	?	Australia	Bituminous	21.3
PR	Rosebud	Montana	Subbituminous	11.3
CORD	Wyodak	Wyoming	Subbituminous	7.9
CQR	Antelope	Wyoming	Subbituminous	5.95
CQC	Antelope	Wyoming	Subbituminous	5.9
Wyodak	Wyodak	Wyoming	Subbituminous	6.9
ND	Fort Union	No. Dakota	Lignite	10.0

quantify the modes of occurrence of 42 elements in coal. The interpretations presented here are based primarily on a selective leaching protocol developed by Finkelman and Simon (Finkelman & Simon, 1984) and refined by Palmer et al. (Palmer et al., 2000). The leaching protocol is briefly described below, and applied to 20 coal samples also described below (Table 1). However, the interpretations of the elements modes of occurrence have been aided by more than a combined 50 years of experience that the authors gained from the analysis of thousands of coal samples encompassing a very broad range of rank, quality, geographic location, stratigraphic distribution, and chemical composition. Most of the coal samples obtained by the U.S. Geological Survey (USGS) were analyzed in the USGS laboratories in Denver, CO by Inductively Coupled Mass Spectroscopy (ICP-MS) and Optical Emission Spectroscopy Mass Spectroscopy (OES-MS) and many samples were analyzed by optical petrography, scanning electron microscopy with energy dispersive X-ray analyzers, electron microprobe analysis, ion probe analysis, X-ray diffraction, selective leaching, density separation, etc. Initial characterization (Finkelman, 1978; Finkelman, 1981a; Finkelman, 1981b) simply tried to identify the modes of occurrence of the trace elements in coal. Subsequent efforts (Finkelman, 1994) presented this information in a semi-quantitative mode. Finally, the selective leaching protocol was incorporated in an effort to quantify the elements modes of occurrence.

Selective leaching is an indirect approach to determining the mode

Table 2
Modes of occurrence of elements in high Rank (Bituminous) coals.

Elements	Modes of occurrence
Aluminum	90% silicate , 10% organic association
Antimony	55% sulfide, 25% silicate, 10% monosulfide, 10% organic association and/or other phase
Arsenic	70% pyrite , 15% clays, 15% monosulfides, organic association and/or other phase
Barium U.S.	40% silicate, 15% carbonate, 45% barite, phosphate, organic association
Barium non-U.S.	60% silicate, 15% carbonate, 25% barite, phosphate, organic association
Beryllium	60% silicate, 40% organic, oxyhydroxide, or clay
Bromine	70% organic, 10% silicate, 20% ^a
Calcium	70% carbonate , 20% organic, 5% silicate, 5% phosphate, etc.
Cadmium	65% monosulfides (mainly sphalerite), 25% pyrite, 10% silicate
Cesium	100% silicate
Chromium	75% silicate, 10% sulfide, 10% organic association, 5% oxide
Cobalt	35% monosulfides, 20% silicate, 20% sulfide, 20% organic association
Copper	45% pyrite, 30% chalcopryrite, 20% clays, 5% organic association
Hafnium	70% zircon, 25% clay, 5% other phase
Iron	50% sulfides (pyrite), 25% carbonates, 20% silicates, 5% other Phase Note: the Australian coals have more carbonate iron and less sulfide iron.
Lead	55% monosulfides (galena), 35% pyrite, 5% silicate, 5% other phase
Lithium	90% silicate , 10% insoluble phases, organic association
Magnesium	30% silicate, 25% calcite, 25% ankerite/dolomite, 20% organic association
Manganese (N. A.)	50% calcite, 25% clays, 15% siderite, 10% organic association
Manganese (non-N.A.)	85% calcite, 10% silicate, 5% organic association
Mercury	90% sulfide (primarily pyrite) , 10% all other forms
Molybdenum	55% sulfide, 30% silicate, 15% carbonate, sulfate, organic association
Nickel	30% clays, 25% pyrite 30% linnaeite group and other monosulfides, 15% organic association, sulfates, carbonates,
Phosphorus	95% phosphates , 5% organic association
Potassium	95% silicate
Light Rare Earths	70% phosphates, 20% clays, 10% carbonates, organic association
Heavy Rare Earths	50% phosphates, 20% clays, 30% organic association, carbonates
Rubidium	90% silicate, 10% other phase
Scandium	90% silicates , 5% organic, 5% ^a
Selenium	70% sulfides and selenides, 30% organic association, shielded sulfides and selenides
Sodium	80% silicate (primarily clays) , 20% organic association
Strontium	50% phosphates, carbonates, 25% silicate, 25% organic association
Tantalum	75% oxides, 25% silicates
Titanium	65% clays, 35% Ti-oxides
Tungsten	50% sulfide, 35% silicate, 15% organic association, etc.
Uranium	40% silicate, 30% insoluble minerals such as zircon, 15% phosphates, 5% carbonates, 5% organic association
Vanadium	65% silicates, probably clays, 35% organic association, etc.
Zinc	45% sphalerite, 30% pyrite, 25% silicates
Zirconium	70% zircon, 25% clay, 5% other phase

Bold = High degree of confidence, non-bold = moderate degree of confidence, *italics* = low degree of confidence. The numbers indicate our estimate of the proportion of that element occurring in that phase.

^a Indicates uncertainty in determining the mode of occurrence.

of occurrence of an element. Direct determination of the mode of occurrence of an element is generally restricted to analyzing individual mineral grains or micrometer-sized areas (microbeam techniques) or, as in XAFS (X-ray Absorption Fine-Structure analysis), the technique is limited in the number of elements that can be determined. Although indirect, the selective leaching procedure offers the opportunity to quantify the modes of occurrence. The elements in coal may be present in many different forms; for example, they may occur in silicates, sulfides, carbonates, oxides, phosphates, sulfates, phosphates, selenides, halides, etc. or they may be bound to the surfaces of minerals or the organic matter. Some elements occur dissolved in fluids in the coal. Elements may occur in amorphous phases and in different organic associations. Each of these forms could respond differently to individual solvents or the order of solvent application. However, for the selective leaching procedure to have practical advantages, a limited number of solvents have to be selected. We chose four solvents: ammonium acetate, hydrochloric acid, hydrofluoric acid, and nitric acid. We recognize that each of these solvents could dissolve more than one phase. For example, ammonium acetate could release elements from mineral or organic ion exchange sites, water soluble phases, and some carbonates. Hydrochloric acid will attack carbonates, monosulfides, and sulfates. The elements remaining in the residue following the leaching procedure could be in acid insoluble phases, in minerals that were shielded from the solvents by the encasing organic matter (see (Willett et al., 2003)), or they may be associated with the organic matter. By ‘organically associated’ we are referring to those elements that are chemically bound to the carbon matrix and those elements that are so intimately enmeshed in the organics that, for all intents and purposes they behave as if they were chemically bound to the carbon matrix (Finkelman, 1981a; Finkelman, 1981b). This would include nano-minerals (Silva & da Boit, 2011).

Despite these complications and limitations we believe that the selective leaching protocol can provide reliable quantitative information on the modes of occurrence of elements in coal. The interpretations presented in the following discussions and in Tables 2 and 3 are our best estimates based on a limited number (20) of samples. It may be somewhat unrealistic to expect that a single number can reflect the percentage of an element in a particular mode of occurrence in coal. Experience has shown that for most elements there is substantial variability in its modes of occurrence even within a single coal bed and there are obvious differences in modes of occurrence with rank. Nevertheless, we offer these approximations to document what we consider to be the results of the current state-of-the-art and to stimulate discussion on the quantification of the modes of occurrence. For most elements, the modes of occurrence are presented as an association with major mineral groups (e.g. sulfides, silicates, carbonates, etc.) and with the organic component. Where we have additional evidence we will suggest the specific mineral species that is likely to host the element.

2. Methodology

The concentrations of the elements in each of the 20 samples were determined on separate splits by at least one of the following techniques: instrumental neutron activation analysis (INAA), cold vapor atomic absorption (CVAA) on whole coal and inductively-coupled plasma-atomic emission spectroscopy (ICP-AES) and –mass spectroscopy (ICP-MS) on 525 °C coal ash. The analytical procedures are described by Bullock et al. (2002). The results from the coal ash analysis were converted to a whole coal basis. Chemical data for duplicate 5 g coal samples, ground to pass 60 mesh, were sequentially leached at room temperature with 35 ml each of 1 N ammonium acetate ($\text{CH}_3\text{COONH}_4$), 3 N hydrochloric acid (HCl), and concentrated hydrofluoric acid (HF; 48%) in 50 ml polypropylene tubes. Each tube was shaken for 18 h using a motorized wrist shaker. Because gas can form during some of the leaching procedures due to decomposition of

Table 3

Modes of occurrence of elements in Low Rank Coals.

Elements	Modes of occurrence
Aluminum	65% silicate , 35% organic association
Antimony	50% silicate, 20% sulfide, 10% monosulfide, 20% organic association, other
Arsenic	40% pyrite , 30% organic, 15% silicate, 15% monosulfides, carbonates
Barium	75% carbonate, 10% silicate, 15% <i>organic association, sulfate, phosphate</i>
Beryllium	30% silicate , 60% <i>organic, oxyhydroxide, or clay</i>
Bromine	80% organic, 10% silicate, 10% ^a
Calcium	60% carbonate, 35% organic association, 5% silicate
Cadmium	80% monosulfides (sphalerite), 10% pyrite, 10% silicate
Cesium	80% silicate , 20% organic association
Chromium	75% silicate, 10% sulfide, 10% organic, 5% oxide
Cobalt	30% organic, 25% monosulfides, 25% clays, 15% pyrite
Copper	30% pyrite, 30% chalcopryrite, 20% clays, 20% organic association
Hafnium	70% zircon, 25% clay, 5% other phase
Iron	60% carbonate & other, 20% sulfide, 15% silicate, 5% organic association
Lead	50% monosulfides (galena), 10% pyrite, 25% silicates, 15% other phase
Lithium	70% silicate , 30% organic association, insoluble phases
Magnesium	60% organic association, 30% calcite, 10% silicate
Manganese	75% calcite, 10% silicate, 5% siderite, 10% organic association
Mercury	75% sulfide (primarily pyrite) , 25% organic association and other phase
Molybdenum	65% silicate, 15% sulfide, 20% organic association, etc.
Nickel	30% organic association, 30% monosulfides, sulfates, carbonates, 20% clays, 20% sulfides
Phosphorus	85% phosphates , 15% organic association
Potassium	75% silicates , 50% organic association,
Light Rare Earths	60% clays, 20% phosphates, 20% carbonates, organic association
Heavy Rare Earths	50% clays, 25% phosphates, 25% organic association, carbonates
Rubidium	85% silicate , 15% other phase
Scandium	95% silicate, 5% organic association
Selenium	75% organic, 20% sulfides and selenides, 5% silicate
Sodium	65% organic association, 35% clay, salts, pore water
Strontium	50% organic association, 50% phosphates, carbonates
Tantalum	60% oxides, 40% silicates
Titanium	70% clays, 15% Ti-oxides, 15% organic association
Tungsten	60% silicate, 20% sulfide, 20% organic association, other phase
Uranium	55% organic association, 35% silicates, 5% phosphates, 5% insoluble phases such as zircon
Vanadium	50% silicate, 50% organic association, other phase
Zinc	55% sphalerite, 15% pyrite, 15% silicates, 15% organic association
Zirconium	70% zircon, 25% clay, 5% other (organic association?)

Bold = High degree of confidence, non-bold = moderate degree of confidence, *italics = low degree of confidence*. The numbers indicate our estimate of the proportion of that element occurring in that phase.

^a Indicates uncertainty in determining the mode of occurrence.

carbonates, sulfides, and other minerals, each tube was enclosed in a polyethylene bag closed with a plastic coated wire strap. The sample was then enclosed in a second polyethylene bag also closed with a plastic coated strap. The bags allow the gas to escape the bag, but prevents release of liquid. In the final step of the process the residual material (primarily mineral free coal particles and pyrite) was placed in an Erlenmeyer flask and shaken with 2 N nitric acid (HNO_3) for 18 h. This change in the last step was necessary because the conical bottoms of the polypropylene tubes trapped much of the very small and heavy pyrite grains and the much lighter and generally larger grains of coal shielded them from the nitric acid. The flat bottom of the Erlenmeyer

flask greatly increased the surface area interaction of the pyrite and the nitric acid causing all but some micron sized pyrite grains to be dissolved. The density difference between pyrite and demineralized coal is significant and the volume of unreactive demineralized coal is large, thus causing the coal to stick to the conical bottom test tubes and limiting access of the nitric acid to the pyrite. The use of the flask method solved these problems. This was confirmed by SEM study of polished sections made from the residues. The flask method is a standard ASTM method for pyritic sulfur. Modifying this method for use in other steps would have required intensive method development which we felt would not likely improve results.

The sequence of solvents was adopted so that exchangeable cations would be removed first by the ammonium acetate; cations associated with the carbonates and monosulfides would then be removed by the HCl; and cations associated with the silicates would be removed by HF. Finally, elements associated with the disulfides would be removed by using HNO₃. In this procedure unleached cations may be ‘shielded’ mineral grains that are completely encapsulated by the coal matrix, or they may be associated with insoluble mineral phases, or associated with the organic matrix (Fig. 1).

Representative splits of approximately 0.5 g of residual solid were removed after each step for instrumental neutron activation analysis and for Hg analysis by cold vapor atomic absorption. The leachates were reduced in volume to about 2–3 ml and then diluted with 2 N HCl to 60 ml and saved for analysis by ICP-AES and ICP-MS. Chemical data for the leachates and residues were used to derive percentages of each element leached by each of the four solvents as follows: The concentration of each element in solution (C_s) in $\mu\text{g}/\text{ml}$ was converted to the concentration dissolved (C_d) using the weight dissolved (W_d) where $W_d = W_b - W_e$. W_b is the weight in grams of the coal at the beginning of each leaching step and W_e is the weight of the coal residue after leaching, rinsing, and drying. The residues were analyzed in the same manner as the original coals. C_d was then calculated as follows $C_d = C_s \cdot V / W_d$ where V is the volume (60 ml). The percent leached for each element in each sample was then calculated as $C_d / C_o \times 100$, where C_o is the concentration of each element in the original unleached sample. The calculated percentages were then used to quantify the modes of occurrence of the elements. By comparing data from the residual fractions with data from the solutions, we estimate an absolute error of 1–10% with an average error of about 5%.

According to Tewalt et al. (Tewalt et al., 2010) during the period when some of these analyses were conducted, USGS required that the maximum adjustment of instrument values, guided by calibration standards, was not allowed to exceed 10%. However, in some cases, the Inorganic Geochemistry Laboratory released data that were adjusted by > 10% and (or) were not constrained by an adequate number of control standards. Original instrument values no longer exist for about 80% of the analyses during this period; therefore, the acceptability of drift corrections for most of the samples analyzed cannot be determined. For these reasons, the data from the USGS Inorganic Geochemistry Laboratory should be used with care.

For each of the elements we present a figure that graphically portrays the proportion of the element leached by each of the four solvents.

3. Samples

The samples were randomly chosen and divided to represent bituminous and lower rank coals. For some elements we noted a difference in leaching behavior between the U.S. or North American bituminous coals and the non-U.S. or non-North American coals.

4. Modes of occurrence

4.1. Aluminum (Al)

The average concentration of aluminum in U.S. coals is 1.5 wt%

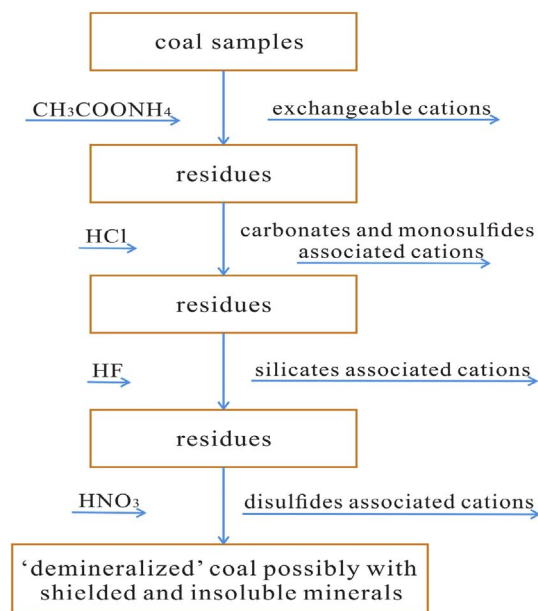


Fig. 1. Diagram of solvent extraction procedure.

(Orem & Finkelman, 2003).¹ The coal geochemistry literature mentions a wide range of Al-bearing minerals. The most common are clays, primarily kaolinite, illite, and mixed-layer clays. Other Al-bearing minerals that have been described from coal include zeolites, phosphates such as the crandallite group, sulfates, oxides, feldspars, gibbsite, boehmite, diaspore, etc. (Finkelman, 1981a; Finkelman, 1981b). Finkelman and Simon (1984) ‘demineralized’ a sample of Illinois #6 coal using HCl, HF and HNO₃. They then low-temperature ashed the demineralized coal and looked at the residue with a transmission electron microscope. They found amorphous sheets high in aluminum and concluded that this aluminum had been part of the organic structure. Li et al. (Li et al., 2007) using electron microprobe element mapping, concluded that ‘clean’ (i.e. mineral-free) vitrinite in low-rank Australian coals contains as much as 0.5% aluminum.

Aside from Dai et al. (Dai et al., 2006a; Dai et al., 2012a) there has been little discussion of the modes of occurrence of aluminum in coal. This is somewhat surprising because aluminum can have environmental impacts, byproduct potential, and technological impacts. The lack of focus on this element may be due to the assumption that most of the aluminum in coal is associated with clays. The leaching data from this study supports this assumption.

The behavior of aluminum in the selective leaching procedure is consistent. For all but one bituminous coal sample, at least 75% of the aluminum was leached by HF (Fig. 2). On average, HF removed nearly 85% (range 45–95%) of the aluminum from 12 bituminous coal samples. About 15% percent of the aluminum was unleached by the solvents and we interpret that this aluminum is either organically bound, associated with insoluble phases or is associated with clays that were shielded from the solvents by the organic matter. Most of the aluminum leached by the HF is undoubtedly associated with the ubiquitous clays observed in most coals by optical petrography, scanning electron microscopy, X-ray diffraction, etc.

Aluminum was leached by HCl in only one bituminous coal sample (5% of sample KY). However, HCl removed from 10 to 35% (average: nearly 25%) of the aluminum in all six low-rank coals. This aluminum probably occurred in organic association or as soluble inorganic phases such as amorphous oxyhydroxides. In the low-rank coals, 50 to 85% (average: 65%) of the aluminum was leached by HF. This is

¹ Citing the U.S. average value for an element in coal is intended only to provide the reader with a frame of reference.

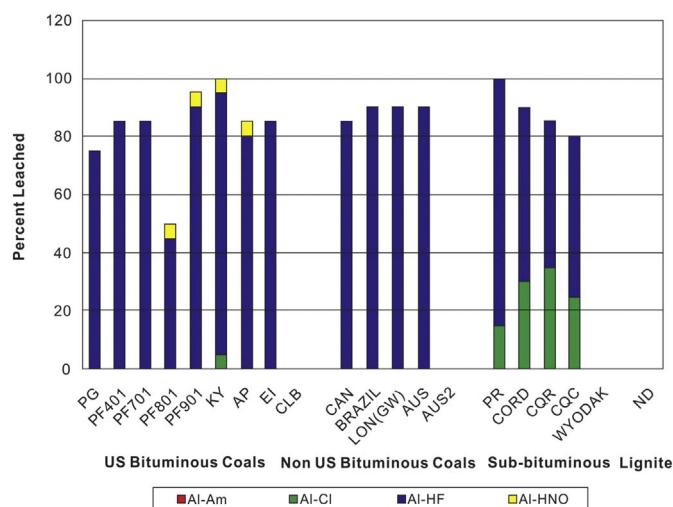


Fig. 2. Sequential leaching results for aluminum.

significantly lower than the 85% aluminum removed by HF from the bituminous coals. The sum of HF + HCl leached aluminum (90%) from the low-rank coals is slightly higher than the total aluminum leached by HF from the bituminous coals (85%). It is possible that the organically bound (HCl leachable) aluminum was lost during uprinking or that the organically bound aluminum was used in the formation of neogenic clays such as kaolinite during uprinking.

It should be noted that the bituminous coals contain considerably more aluminum (2.75 wt%, average of 11 samples) than do the low rank coals (0.5 wt%, average of four samples). The higher aluminum content is a reflection of the abundance of aluminosilicates in the higher ash yield (24.5% vs. 8%) of the bituminous coals.

4.2. Antimony (Sb)

The average concentration of antimony in U.S. coals is 1.2 ppm (Orem & Finkelman, 2003). (Finkelman, 1981a; Finkelman, 1981b) did not detect any antimony-bearing minerals in the coals that he studied. In reviewing the literature he noted that in sink-float experiments, antimony reported to the sink fractions and concluded that antimony in coal is largely associated with the sulfide minerals. Finkelman (Finkelman, 1994) concluded that antimony may be present in solid solution in pyrite and as minute accessory sulfide minerals, such as stibnite, dispersed throughout the organic matrix, and some may be organically bound. However, he acknowledged a low level of confidence, because of the paucity of direct mode of occurrence data. Subsequent studies further confirmed Finkelman's (Finkelman, 1994) conclusions, for example, highly-elevated Sb in a Xinren coal (Guizhou, China; 3860 ppm, on a whole coal basis) and a Wulantuga coal (Inner Mongolia, China; 240 ppm, on a whole coal basis) occurs in getchellite and pyrite respectively (Dai et al., 2006b; Dai et al., 2012b).

In the selective leaching experiments (Fig. 3) ammonium acetate extracted 5–10% of the antimony from two bituminous coal samples and 35% from the AUS sample. HCl extracted 15% (range 0–40%) of the antimony from the bituminous coals. HF extracted slightly > 15% (range 10–35%) of the antimony from the bituminous coals and nitric acid extracted 20% (range 10–45%). The total amount of antimony leached from the 14 coal samples averaged 55% (range 40–70%).

Ammonium acetate extracted 5% and 15% of the antimony from two of the six low rank coals and HCl extracted 5% from two of the samples. HF extracted 35% (range 30–40%) and nitric acid extracted 10% (range 0–20%) of the antimony from the six low rank coals. The total antimony extracted from the low rank coals was 50% (range 40–60%).

Based on these results it appears that the modes of occurrence of

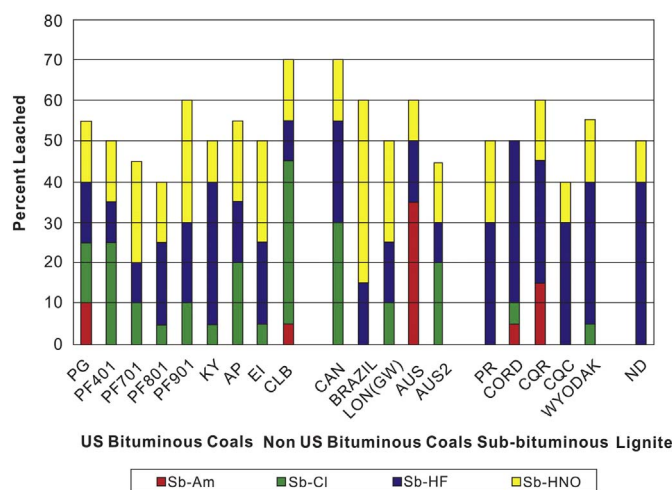


Fig. 3. Sequential leaching results for antimony.

antimony are more complex than previously studies indicated. We interpret our data to indicate that the antimony extracted by the HCl from the bituminous coals was associated with monosulfides or oxidized disulfides (primarily pyrite). The antimony extracted by the nitric acid was, almost certainly, associated with sulfides. There does appear to be a small, but consistent, amount of antimony associated with silicates. The total amount of antimony extracted never exceeded 70%. Although some of the unleached antimony may be associated with shielded sulfides or insoluble phases we cannot rule out the possibility of organically associated antimony. The fact that the bituminous coals have, on average, higher antimony (1.0 ppm) than do the low rank coals (0.3 ppm) is consistent with some of the antimony in the bituminous coals being associated with epigenetic sulfide mineralization.

4.3. Arsenic (As)

The average concentration of arsenic in U.S. coal is 24 ppm (Orem & Finkelman, 2003). Arsenic has attracted considerable attention because of the widespread and severe health problems caused by exposure to high levels of arsenic in drinking water in Bangladesh, West Bengal, India, China, Argentina, Mexico, and elsewhere (Smedley & Kinniburgh, 2005). Arsenic mobilized from coal combustion has also caused severe health problems in China (Belkin et al., 1997) and in the former Czechoslovakia (Bencko & Symon, 1977).

Although much of the older literature cites arsenopyrite as the primary mode of occurrence of arsenic in coal (Crossley, 1946; Finkelman, 1981a; Finkelman, 1981b; Francis, 1961; Stach et al., 1975) and Minkin et al. (Minkin et al., 1984) found no evidence for this association and concluded that most of the arsenic in coal is associated with pyrite. Swaine (Swaine, 1990) acknowledged that most arsenic in coal is associated with pyrite, but concluded that some coals contain arsenic in other forms such as organic, clay, and phosphate associations. Kolker et al. (Kolker et al., 2000), using an integrated analytical approach including X-ray absorption fine structure analysis, selective leaching, and electron microprobe analysis found that pyrite was the principal host of arsenic in most of the samples they analyzed, but in a low rank coal the arsenic appeared to be organically associated. They also concluded that the small amounts of arsenates found in the coal were derived from the oxidation of arsenic-bearing pyrite. There are many reports of arsenic in coal associated with pyrite (e.g. (Dai et al., 2012b)) and a number of reports of rare and unusual arsenic modes of occurrence such as that of getchellite (AsSbS₃) (Dai et al., 2006b).

In a unique sample of coal from China containing 35,000 ppm arsenic, Finkelman et al. (Finkelman et al., 1999) found that a substantial portion of the arsenic was organically associated. Belkin et al. (Belkin

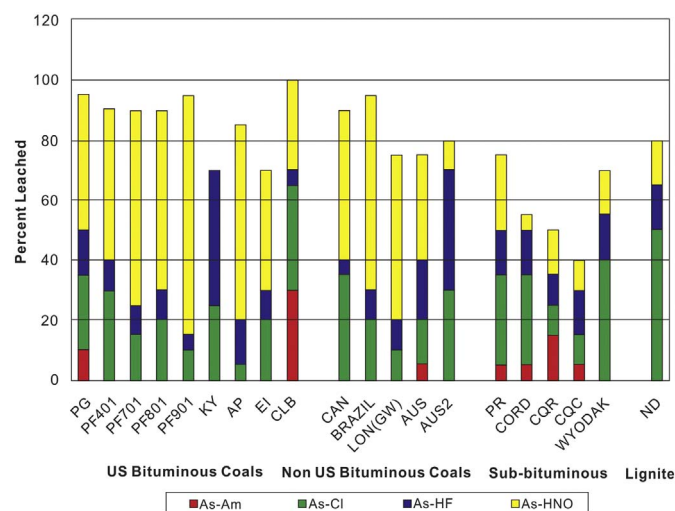


Fig. 4. Sequential leaching results for arsenic.

et al., 1997) analyzed about 25 coal samples that they had collected from several locations within Guizhou Province. In several samples the arsenic (as arsenate) was primarily associated with the organic fraction. Belkin et al. (Belkin et al., 1997) also found a wide variety of As-bearing mineral phases in the coal samples. Pyrite was the most common sulfide, occurring as framboids, euhedral crystals, and in irregular shapes. The range of arsenic concentrations in pyrite, determined by electron microprobe analyses, ranged from the detection limit (~100 ppm) in unaltered framboids to about 4.5 wt% in grains adjacent to arsenopyrite crystals. They also found arsenic in clays, phosphates, and sulfates. Kolker et al. (Kolker et al., 2006) summarized the modes of occurrence of arsenic in coal and concluded that arsenic is generally the most abundant trace element in pyrite and marcasite, with highly variable concentrations. In bituminous coals, pyrite generally accounts for the largest fraction of arsenic, with smaller proportions in the organic matter and in other minerals. Lower rank coals generally have a larger proportion of organically-bound arsenic.

In the current study, ammonium acetate leached 10 to 30% of the arsenic from only two bituminous coal samples (Fig. 4). HCl leached 20% (range 5–35%), HF extracted 15% (5–45%) of the arsenic and nitric acid removed 45% (0–80%) from the 14 bituminous coal samples. The total amount of arsenic removed was 85% (70–100%).

It is likely that the ammonium acetate leached arsenic was present as oxidized (arsenate) arsenic. It is possible that the HCl leachable arsenic was primarily from oxidized arsenic-bearing pyrite (Huggins et al., 2002), although some could have been associated with monosulfides and perhaps some carbonates. The nitric acid leachable arsenic was associated with the sulfides (most probably pyrite). The arsenic leached by HF was likely associated with the silicate minerals (probably clays). We infer that some of the unleached arsenic was organically associated, but some may be due to 'shielded' sulfides.

In the six low rank coals ammonium acetate extracted about 5% (0–15%) of the arsenic, HCl removed 30% (10–50%), HF leached 15% (10–15%), and nitric acid extracted 15% (5–25%). The total amount of arsenic leached from the low rank coals was 60% (40–80%).

Clearly, there is a difference in the modes of occurrence of arsenic between the bituminous coals and in the low rank coals. The percentage of nitric acid leachable arsenic (sulfide association) is considerably lower in the low rank coals (15% vs. 45%) and the percentage of unleached arsenic is higher (40% vs. 15%). We assume that the ammonium acetate leachable arsenic was organically bound and that a portion (15%) of the HCl leachable arsenic was from oxidized arsenic-bearing pyrite, a portion (10%) was from monosulfides and carbonates, and 5% was organically bound. We further assume that 5% of the unleached arsenic was associated with shielded monosulfides, etc. and

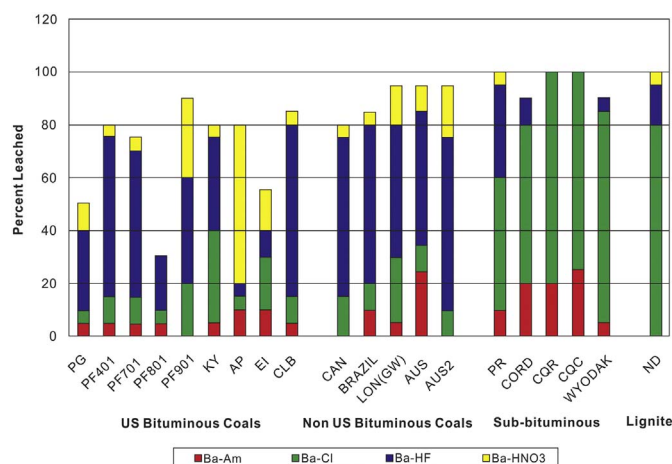


Fig. 5. Sequential leaching results for barium.

15% with shielded fine-grained pyrite, the remainder (20%) being organically associated.

It should be noted that the average arsenic content of the six low rank coals (1.8 ppm samples) is considerably lower than the average for the 14 bituminous coals (15.8 ppm). This implies that arsenic may be added to the coal during the coalification process, most likely as epigenetic sulfides.

4.4. Barium (Ba)

The average concentration of barium in U.S. coal is 170 ppm (Orem & Finkelman, 2003). Barium occurs in coal in multiple forms. Swaine (Swaine, 1990) cites the occurrence of barite (BaSO_4), barytocelestine, witherite (BaCO_3), gorceixite in coal and in organic association in low rank coals through carboxyl groups. (Finkelman, 1981a; Finkelman, 1981b)) reports the occurrence of barite, barytocalcite, alsonite (both $\text{BaCa}(\text{CO}_3)_2$), Ba-feldspars, gorceixite and other Ba-bearing cradellite group minerals which have subsequently been reported by in many publications (e.g. (Brownfield et al., 1986; Bytnar & Makowska, 2017; Ward et al., 1996)). (Finkelman, 1981a; Finkelman, 1981b)) also acknowledged that some organically associated barium certainly a possibility in low rank coals.

Data from the selective leaching studies (Fig. 5) show that about 5% (0–25%) of the barium in bituminous coals is ammonium acetate soluble. HCl extracted 15% (5–35%) of the barium from these coals. HF extraction showed a marked difference between the U.S. bituminous coals (35%, range 5–65%) and the non-U.S. bituminous coals (60%; range 50–65%). Nitric acid leached 15% (0–60%) from the 14 bituminous coals. The total Ba extracted was 70% (30–90%) from the U.S. bituminous coals and 90% (80–95%) from the non-U.S. bituminous coals.

Higher amounts (average 15%; range 5–25%) of the barium are extracted by ammonium acetate from the six low rank coals. Barium exhibits a distinct rank difference with HCl leaching. About 75% (20–89%) of the barium is leached by HCl from the lower rank coals. HF extracted 10% (0–50%) of the barium from these coals and nitric extracted only 5% from each of two of the low rank coals. The total amount of barium extracted was 95% (80–100%).

We interpret the ammonium acetate soluble barium to have been organically bound but some may have been associated with carbonates that are slightly soluble in the ammonium acetate or in ion exchange sites in clays. The HCl leachable barium is likely to be largely derived from carbonate minerals. This suggestion is supported by the leaching data for calcium (see calcium discussion below). About 50% of the Ca in the low rank coals is leached by HCl in contrast to about 35% leached from the bituminous coals. The HF leachable barium is likely from clays

and, to a lesser degree, feldspars. It is interesting to note the difference between the amount extracted by HF from the U.S. bituminous coals (35%) and from the non-U.S. bituminous coals (60%). The modest amount of Ba extracted by HNO_3 may be from barite and crandallite minerals. Although both Palache et al. (Palache et al., 1951) and Sinkankus (Sinkankus, 1972) agree that barite is insoluble in acid and crandallite is only very slightly attacked by acids. It is possible that small particle size of these minerals would enhance their solubility, but the authors' experience is that crandallite group minerals are among the larger minerals found in coal, although (Dai et al., 2015b)) found that crandallite/goyazite group minerals varied from $< 1 \mu\text{m}$ to tens of μm s in the Muli coal on the Tibetan Plateau. The unleached barium is, therefore, more likely to be associated with insoluble phases such as barite (Willett et al., 2003), soluble Ba-bearing phases shielded from the solvents by the organic matrix, and organically bound barium.

4.5. Beryllium (Be)

The average concentration of beryllium in U.S. coal is 2.2 mg/kg (Orem & Finkelman, 2003). Coal combustion may be the primary source of beryllium in the environment, accounting for $> 90\%$ of the U.S. beryllium emissions (Adriano, 2001). Beryllium can be harmful when inhaled, although health problems caused by beryllium are primarily from industrial exposure (Grandjean, 1998).

Because of the relatively low concentration and low atomic weight (atomic number 4), beryllium is undetectable by electron microbeam instruments, and thus direct determination of its mode of occurrence is difficult. (Finkelman, 1981a; Finkelman, 1981b)) stated that few elements so consistently report to the organic (lighter) fractions in sink-float experiments. He concluded that there was abundant evidence in the literature indicating a strong organic affinity for beryllium. Swaine (Swaine, 1990) stated that beryllium is organically associated in most coals. Both (Finkelman, 1981a; Finkelman, 1981b)) and Swaine (Swaine, 1990) cite exceptions to this generalization. Recently, Dai et al. (Dai et al., 2015c) detected a significant proportion of hydrous beryllium sulfate ($\text{BeSO}_4 \cdot 4\text{H}_2\text{O}$) to be present in several coal samples from Yunnan Province, China.

Querol et al. (Querol et al., 1998; Querol et al., 2001), however, found conflicting data on the mode of occurrence of beryllium in several coals. In these studies of coal samples from Australia, Great Britain, and the U.S., results from density separations and from selective leaching were combined. For most elements there was good to excellent agreement between the modes of occurrence interpretations based on the density separation and on selective leaching results; however, there was a significant discrepancy for beryllium and molybdenum. The leaching protocol indicated a dominant Al-silicate association for beryllium in all three samples, but results from the density separation technique were more consistent with an organic association (Querol et al., 1998; Querol et al., 2001). They concluded that 48% of the beryllium in the sample from Great Britain was associated with aluminosilicates and 52% was organically associated. In the sample for the U.S., 30% of the beryllium was associated with aluminosilicates and 70% with the organics and in the sample from Australia 28% of the beryllium was associated with aluminosilicates and 72% with the organics. Nevertheless, they stated that research is necessary to resolve the discrepancy in the apparent mode of occurrence of beryllium as determined by density separation techniques and as determined by selective leaching procedures. Palmer et al. (Palmer et al., 1998) offers an explanation for these apparent discrepancies. They suggest that submicroscopic particles of Be-silicate dispersed within the organic matrix of the coal could explain why Be is concentrated in the lightest density fractions and leached by HF.

Results from the selective leaching procedures indicate a distinct rank difference in the mode of occurrence of beryllium (Fig. 6). In the 11 bituminous coals 10% (range 2–20%) of the Be was leached by HCl and about 60% (30–80%) was leached by HF. The total Be leached was

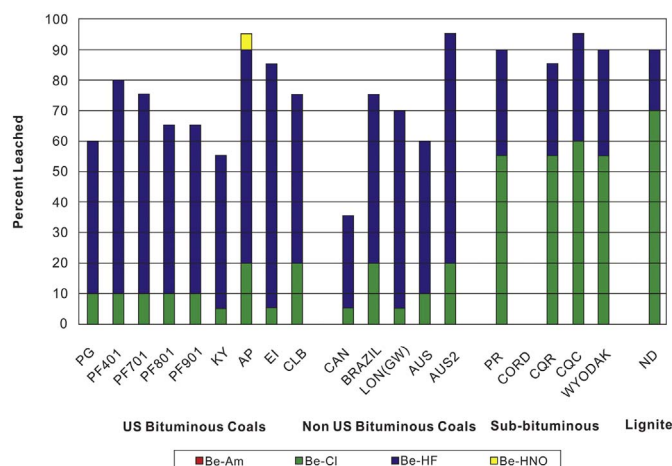


Fig. 6. Sequential leaching results for beryllium.

70% (35–95%). Subbituminous sample PR behaved very much like the bituminous coals, but in the other five low rank coals 60% (55–70%) of the beryllium was leached by HCl and only 30% (20–35%) was leached by HF. The total amount of beryllium leached from the five low rank coals was 90% (85–95%).

The HF leachable beryllium indicates an association with silicate minerals. The 30% HCl leachable beryllium in the bituminous coals and the 70% removed by HCl from the low rank coals may be loosely bound beryllium associated with the organics, clays, or as oxyhydroxides.

The behavior of Be follows that of aluminum (Goldschmidt, 1954) (see Fig. 2 and the aluminum discussion above). Like aluminum, some of the beryllium may occur in organic association, as loosely held cations in clays, or in HCl soluble inorganic phases such as amorphous oxyhydroxides in the low rank coals. As coalification progresses this beryllium may be mobilized and incorporated into neogenic clays such as kaolinite.

4.6. Bromine (Br)

The average content of bromine in U.S. coal is 17 ppm (Orem & Finkelman, 2003). (Finkelman, 1981a; Finkelman, 1981b)) reviewed the literature on bromine in coal and estimated that almost all of the Br is organically associated.

Selective leaching data for bromine are varied (Fig. 7). Ammonium acetate removed about 15% of the bromine from ten U.S. bituminous coals, however, the range was broad (0–55%). There are data for only three low rank coals, so no averages will be given. In these three coals

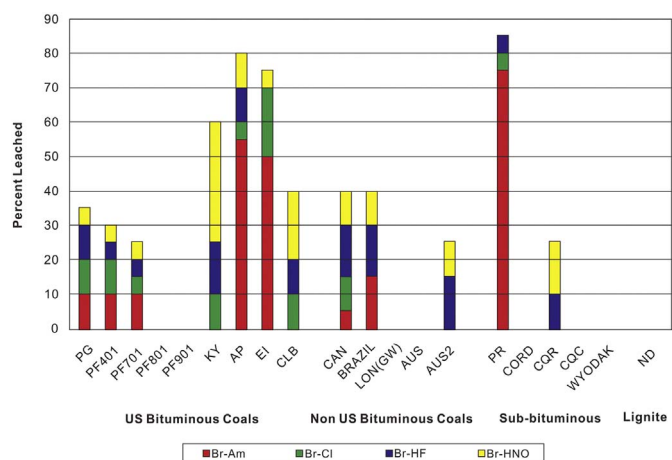


Fig. 7. Sequential leaching results for bromine.

ammonium acetate extracted 75% of the bromine from one sample. HCl, HF, and HNO₃ each removed about 10% of the Br with the total bromine leached ranging from 25 to 85%. Assuming that the unleached bromine and the bromine leached by the ammonium acetate was organically bound these data indicate that at least 70% of the bromine in the bituminous coals and as much as 80% in the low rank coals was associated with the organic components. It is not clear in which phases the HCl and HNO₃ soluble bromine was associated with.

4.7. Calcium (Ca)

The average concentration of calcium in U. S. coal is 0.46 wt% (Finkelman, 1993a; Finkelman, 1993b). The literature contains little discussion on the modes of occurrence of calcium in coal. The lack of discussion is not due to the uniformity of calcium's mode of occurrence, as was the case for aluminum, but rather for the sheer abundance of different forms of calcium that occur in coal. (Finkelman, 1981a; Finkelman, 1981b)) lists > 30 minerals found in coal containing calcium. These include a variety of silicates, phosphates, carbonates, sulfates, and oxalates (CaC₂O₄). Moreover, in low-rank coals much of the calcium can occur in organic association as humates (Bouska, 1981). Li et al. (Li et al., 2007) using electron microprobe element mapping concluded that 'clean' (i.e. mineral-free) vitrinite in low-rank Australian coals contains as much as 1.5% calcium. Because of the variety of mineral types potentially containing calcium and the different responses to the solvents it is difficult to interpret the leaching data for calcium with a high degree of confidence. Dai et al. (Dai et al., 2015d) deduced that a proportion of the calcium in occurred either in the organic matter (a ca-oxalate was detected by XRD) or as dissolved ions in the pore water.

In this study 20 to 80 (average of 50%) percent of the calcium was leached by ammonium acetate from 13 bituminous coals (Fig. 8). Palmer et al. (Palmer et al., 2002) has shown that the ammonium acetate can leach calcium from carbonates in coal, but ion exchangeable calcium in organics or in clays cannot be ruled out. We have assumed that most (2/3^{rds}) of the ammonium acetate leached calcium was derived from carbonate dissolution and the remainder was organically bound. It seems reasonable that the calcium is leached from ubiquitous calcite than from rarer calcium-bearing minerals such as smectites. Ten to 60% (average: 35%) of the calcium was leached by hydrochloric acid. This calcium is, most likely associated with carbonates. However, it is possible that some of this calcium was leached from phosphates or sulfates. Hydrofluoric acid leached small amounts (5 to 15%) of calcium from three samples and nitric acid leached calcium (5 to 20%) from four samples. We believe that the nitric acid leachable calcium represents shielded carbonates, sulfates, and phosphates that were not

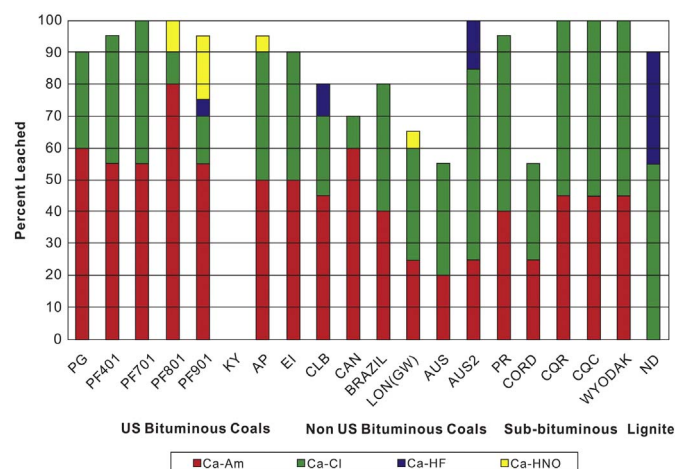


Fig. 8. Sequential leaching results for calcium.

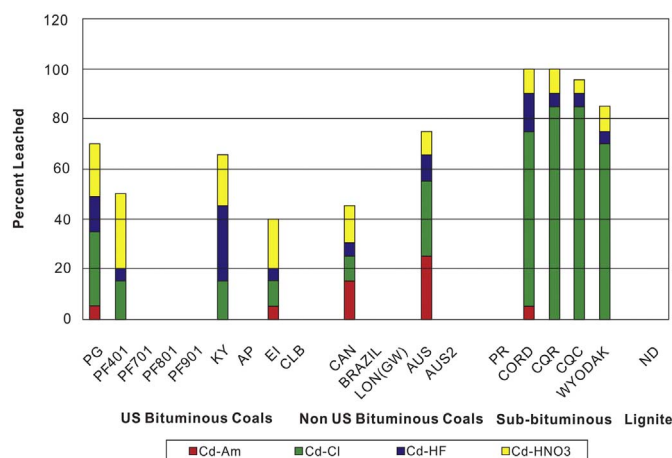


Fig. 9. Sequential leaching results for cadmium.

leached earlier in the process. The total calcium leached from the bituminous coals was 85% (range 55–100%). We interpret the unleached calcium to be from shielded minerals or to be organically bound.

In the lower rank coals 0 to 45% (average: 35%) of the calcium was leached by ammonium acetate. We interpret that most of this calcium (25%) was organically bound and that 10% of the calcium was derived from dissolved carbonates. Thirty to 55% (average: 50%) of the calcium was leached by HCl. HF leached calcium (35%) from only one sample (ND) and nitric acid did not leach calcium from any of the samples. The total amount of calcium leached was 90% (55–100%). The unleached calcium is most likely organically bound.

4.8. Cadmium (Cd)

The average concentration of cadmium in U.S. coals is 0.47 ppm (Orem & Finkelman, 2003). (Finkelman, 1981a; Finkelman, 1981b)) concluded that the bulk of cadmium in coal is associated with sphalerite. Swaine (Swaine, 1990) also reported that cadmium is predominantly associated with sphalerite, but notes that cadmium may also be associated with other minerals.

Selective leaching data was obtained for cadmium on only 10 coal samples (Fig. 9). Ammonium acetate extracted about 10% (0–25%) of the cadmium from six bituminous coals. HCl extracted 20% (10–30%) of the cadmium, HF extracted 10% (5–30%) and HNO₃ extracted about 20% (10–30%). Curiously, the total recovery for the low-rank coals was higher than those for the bituminous coals (95% vs. 60%). In the low-rank coals most of the cadmium (78%) was leached by HCl, with about 10% being leached by HF and nitric acid.

We believe that the ammonium acetate soluble cadmium was released from oxidized sulfides (probably pyrite) as was the nitric acid soluble cadmium. Based on the common occurrence of fine-grained sphalerite (Finkelman, 1985) in coal, we estimate that perhaps 25% of the 40% of the unleached cadmium is in shielded sulfides, such as sphalerite. The remainder of the unleached cadmium (15%) may be in pyrite.

We infer from the leaching data for the four low-rank coals that 80% of the cadmium is associated with monosulfides (primarily sphalerite), 10% with pyrite, and 10% with the silicates.

Because, the average concentration of cadmium in the bituminous coals (0.8 ppm) is ten times the concentration in the low rank coals (0.07), we conclude that the increased cadmium in the bituminous coals is primarily associated with epigenetic pyrite.

4.9. Cesium (Cs)

The average amount of cesium in U.S. coal is 1.1 ppm (Orem & Finkelman, 2003). According to (Finkelman, 1981a;

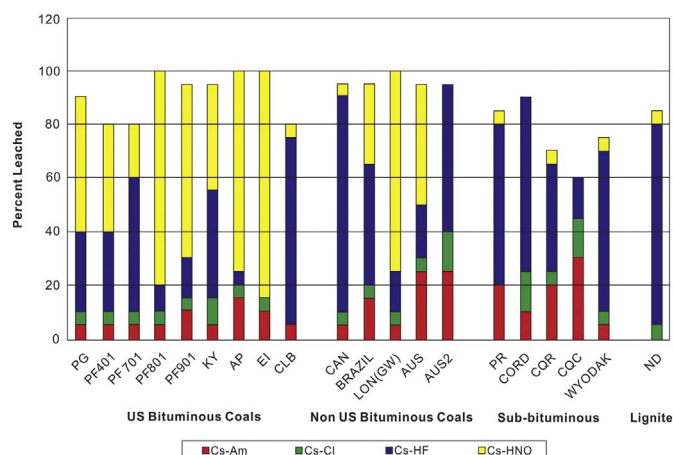


Fig. 10. Sequential leaching results for cesium.

Finkelman, 1981b)) the literature data on cesium in coal, although sparse, is mostly consistent with an inorganic association, likely in clays, feldspars, or micas (see also (Dai et al., 2015c)). This would be consistent with the fact that cesium is geochemically related to potassium and rubidium.

In the selective leaching experiments, nearly 95% (range 80 to 100%) of the cesium was leached by the solvents from the bituminous coals (Fig. 10). It is likely that the remaining 5% is in insoluble or mineral grains shielded from the solvents thus suggesting no organic association. Ammonium acetate leached about 10% (5–15%) of the cesium from the bituminous coals, and HCl leached about 5% (5–15%). The ammonium acetate leachable cesium may have been in exchangeable sites in clays. For most of the bituminous coals discussed in this paper nitric acid (45% leached; range 0–85%) was more effective than HF (35% leached; range 0–80%). As it is geochemically unusual for cesium to be associated with sulfide minerals we conclude that: 1) the HF solubilized, but didn't dissolve all of the silicates and the nitric acid completed the leaching of the solubilized silicates; or 2) the cesium precipitated as a fluoride phase that was subsequently dissolved by the nitric acid. Despite the diverse leaching behavior of the cesium in the bituminous coals, we conclude that virtually this entire element is associated with the silicate minerals.

In the low-rank coals about 15% (range 5–30%) of the cesium was leached by the ammonium acetate. HCl leached 10% (0–15%) of the cesium, HF leached 52.5% (15–75%) and nitric acid leached about 5% (0–5%). The total cesium leached from the low rank coals was 80% (60–90%). These data indicate that there is some organically-bound cesium in these coals as it is unlikely that there are more insoluble cesium-bearing phases in the low rank coals than in the bituminous coals. The high proportion of ammonium acetate leachable cesium plus the HCl leachable cesium may be due to organically-bound cesium or to cesium in exchangeable sites on clays. We estimate that about 80% of the cesium in the low-rank coals is associated with silicate minerals and as much as 20% may be organically bound.

4.10. Chromium (Cr)

The average concentration of chromium in U.S. coals is 15 ppm (Orem & Finkelman, 2003). (Finkelman, 1981a; Finkelman, 1981b)) concluded that chromium is likely to be associated with the clays, but that some chromium is probably associated with spinel group minerals such as chromite. Swaine (Swaine, 1990) reported that it is reasonable to expect some organic association of chromium especially in low-rank coals. Finkelman (Finkelman, 1994) concluded that there is insufficient data to specify the modes of occurrence of chromium in coal. Using XAFS technology Huggins et al. (Huggins et al., 2000) found that chromium in coal occurs in clays, as Cr-oxy-hydroxides in the organic

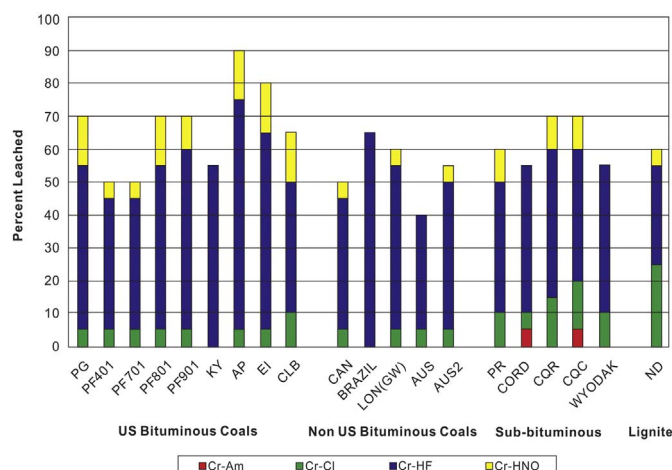


Fig. 11. Sequential leaching results for chromium.

matter, and a small amount in spinels. All of the chromium in coal is trivalent, but combustion can convert some of the chromium in the coal to the carcinogenic hexavalent form in the fly ash (Earthjustice, 2011; Sheps et al., 1997).

There was no ammonium acetate leachable chromium in the bituminous coals and HCl leached only 5% (0–10%) of the Cr (Fig. 11). HF leached 45% (range 35–70%) and nitric acid removed about 10% (0–15%). The total amount of chromium leached by the solvents was slightly > 60% (40–90%). It is likely that the ammonium acetate leachable chromium was in exchangeable sites in clays. The nitric acid leachable chromium may very well have been associated with sulfide minerals. The HF leachable chromium is certainly associated with clay minerals. The main question is what is the mode of occurrence of the nearly 40% of the chromium that was not leached by the solvents? We are inclined to attribute most of this chromium to silicates shielded from the solvents and to insoluble phases such as spinels, though this would account for only a small portion of the total chromium in the coal. Certainly some of the unleached chromium may be present in the organic matter as oxyhydroxides.

HCl removed about 10% (5–25%) of the chromium, HF leached 40% (30–45%), and nitric acid removed about 5% of the chromium. The total chromium leached from the low-rank coals was about the same as for the bituminous coals, 60% (55–70%). As the leaching behavior of chromium in the low-rank coals is quite similar to its behavior in the bituminous coals, we are inclined to apply the same mode of occurrence interpretations. The one difference is that there may be more ion-exchangeable chromium in the low-rank coal clays.

4.11. Cobalt (Co)

The average concentration of cobalt in U.S. coals is 6.1 ppm (Orem & Finkelman, 2003). (Finkelman, 1981a; Finkelman, 1981b)) reported that most of the cobalt in coal is associated with the sulfides such as pyrite and linnaeite group minerals and that some cobalt is associated with clays. Swaine (Swaine, 1990) agrees, but also suggested that some cobalt may be associated with the organic matter. Finkelman (Finkelman, 1994) concludes that there is still a high degree of uncertainty as to the modes of occurrence of cobalt in coal. An unusual mode of occurrence of cobalt (cattierite; CoS) has been reported by Dai et al. (Dai et al., 2015e).

Unfortunately, the leaching behavior of cobalt does not resolve this uncertainty (Fig. 12). Ammonium acetate removed about 5% (0–15%) of the cobalt from all but two bituminous coal samples (CLB and CAN) 60 and 50% of the cobalt was leached, respectively. HCl removed 25% (10–40%) of the cobalt from the bituminous coal samples. HF leached 15% (0–25%) and nitric acid removed 15% (5–25%). The total cobalt

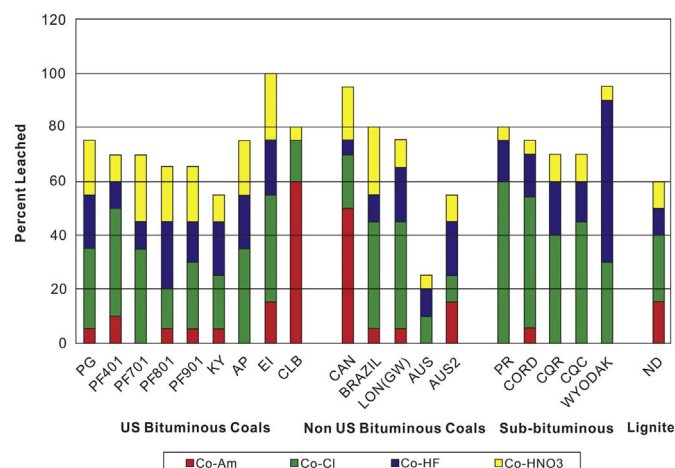


Fig. 12. Sequential leaching results for cobalt.

leached was 70% (25–100%).

The HCl soluble cobalt may be from oxidized sulfides, acid-soluble monosulfides, ion-exchangeable Co in clays, and perhaps some carbonate-associated cobalt. The cobalt leached by HF is likely to have been associated with the clays. The nitric acid leached cobalt is likely sulfide-associated cobalt and is less significant than previously assumed by (Finkelman, 1981a; Finkelman, 1981b)) and Swaine (Swaine, 1990). Even allowing for some Co-bearing minerals being shielded by the organics, there appears to be a significant proportion (at least 20%) of the cobalt with an organic association. It is significant to note that 45% and 35% of the nickel (see nickel discussion below) was extracted from the CLB and CAN samples, respectively, by ammonium acetate. Perhaps this leachable cobalt and nickel is from oxidized linnaeite group minerals. We assume that the ammonium acetate leachable cobalt (5%), most (20%) of the HCl leachable cobalt and some (10%) of the unleached cobalt was associated with monosulfides. The HF leachable cobalt and some (5%) of the unleached cobalt was likely associated with clays. The nitric acid leachable cobalt and some of the unleached cobalt was likely associated with pyrite.

Ammonium acetate removed 5% and 15% of the cobalt from two of the six low rank coals. HCl removed 40% (range 25–60%) of the cobalt from the low rank coals. HF removed 20% (10–40%) of the cobalt, and nitric acid leached only 7.5% (5–10%) of the cobalt. The total cobalt removed from the low-rank coals was 75% (60–95%).

The HCl soluble cobalt could be from oxidized sulfides, acid-soluble monosulfides, ion-exchangeable cobalt in clays, and perhaps some carbonate-associated cobalt. The higher proportion of HCl leachable cobalt in the low-rank coals may reflect a greater amount of ion-exchangeable cobalt. The cobalt leached by HF is likely to have been associated with the clays. The nitric acid leached cobalt, which is likely sulfide-associated cobalt, is less significant than previously assumed. Even allowing for some Co-bearing minerals being shielded by the organics, there appears to be a significant proportion (at least 20%) of the cobalt with an organic association.

4.12. Copper (Cu)

The average Copper content in U.S. coal is 16 ppm (Orem & Finkelman, 2003). (Finkelman, 1981a; Finkelman, 1981b)) concluded, "...significant amounts of copper occur as chalcopryrite in most coals, but organically bound copper may be important in low rank coals." Swaine (Swaine, 1990) concurs saying, "So the mode of occurrence of copper in most coals is probably as a sulfide, usually, chalcopryrite, and associated with organic matter, especially in low-rank coals."

In the selective leaching experiments (Fig. 13) almost 20% (range

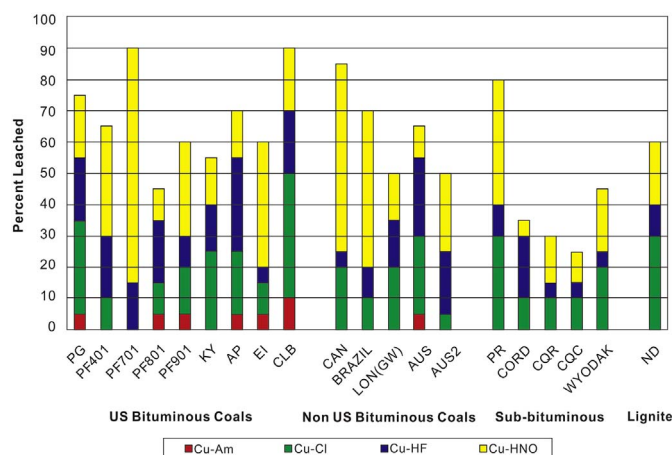


Fig. 13. Sequential leaching results for copper.

5–40%) of the copper in the bituminous coals was leached by HCl, slightly less than what was leached by HF (15%, range 5–30%) and 30% (10–75%) was leached by HNO₃. About 65% (50–95%) of the total copper was leached by the solvents. We interpret these data to indicate that about 20% of the copper is associated with HCl soluble monosulfides (probably chalcopryrite), 30% with HNO₃ soluble disulfides (likely pyrite), 15% may be associated with silicates (probably clays), and most of the 35% unleached Cu is trapped in shielded fine-grained sulfides.

The leaching behavior of the low rank coals was similar for HCl with about 20% (range 10–30%) removed and for HF with 15% (5–30%) leached. In contrast only 20% (5–40%) of the copper was extracted by nitric acid and the total copper leached was 50% (25–80%) indicating a higher proportion of organically associated copper.

4.13. Hafnium (Hf)

The average hafnium content in U.S. coals is 0.7 ppm (Orem & Finkelman, 2003). The chemical properties of hafnium are quite similar to those of zirconium (see zirconium section below) and these elements are invariably found in the same minerals (Goldschmidt, 1954). Zircon is one of the most ubiquitous accessory minerals in coal and is insoluble in acid. Using SEM-EDX, (Finkelman, 1981a; Finkelman, 1981b)) detected small amounts of Hf in zircons in several coals and concluded that the bulk of the hafnium in coals is associated with this mineral. Swaine (Swaine, 1990) also reported the occurrence of hafnium in zircons.

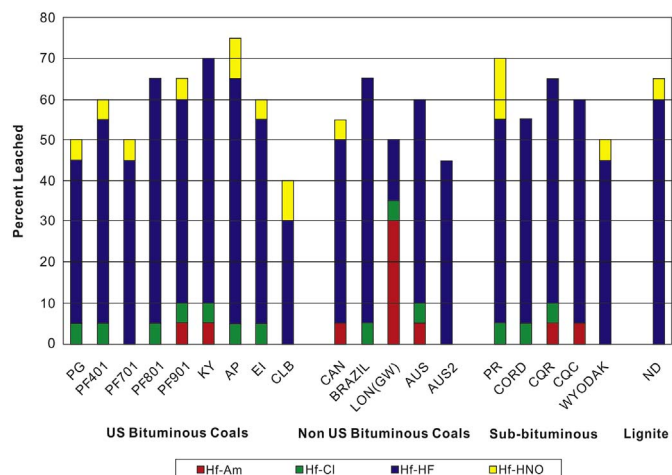


Fig. 14. Sequential leaching results for hafnium.

The selective leaching data (Fig. 14) indicate that hafnium leaching by hydrofluoric acid is nearly identical for the bituminous and low-rank coals. 30% of the hafnium was leached by ammonium acetate from only one sample (LON GW). About 5% (0–5%) of the hafnium was leached by HCl, about 50% (15–60% for the bituminous coals and 40–55% for the low rank coals) was leached by hydrofluoric acid, and about 5% (0–10% and 5–15%) was leached by nitric acid. The total amount of hafnium leached was 60% (40–75% for the bituminous coals and 45–70% for the low rank coals).

Some of the hydrofluoric acid-leachable hafnium was likely associated with clays, but some may have been associated with poorly crystalline (metamict?) zircons that were attacked by the hydrofluoric acid. We have assumed that the HCl soluble hafnium and half of the hydrofluoric acid soluble hafnium was associated with clays. We infer from the observation that the leaching behavior of hafnium was nearly identical in the bituminous coals and in the low rank coals that there is little to no organically bound hafnium. We suggest that the 40% unleached hafnium was associated primarily with acid-insoluble zircons.

4.14. Iron (Fe)

Iron is present at the 1.3 wt% level in U.S. coal (Orem & Finkelman, 2003). It has long been known that iron occurs in numerous, different forms in coal. Finkelman (1981b) reported that the following iron-bearing minerals were found in coal: sulfides (pyrite, marcasite, melnikowite, chalcopyrite, pyrrhotite, arsenopyrite, bornite); micas (biotite, glauconite); clays (montmorillonite, vermiculite, mixed layer, chlorites); carbonates (ankerite, siderite); silicates (garnet, pyroxene, amphiboles, olivine, tourmaline, staurolite, chrysotile, epidote); oxides (magnetite, hematite, goethite, lepidocrocite, limonite, ilmenite, chromite); numerous sulfates (melanterite, rozenite, coquimbite, roemerite, siderite, jarosite, natrojarosite); phosphates (messelite). Bouska (Bouska, 1981) reports that humbaltite, a hydrous iron oxalate occurs in low-rank coal. Dai et al. (Dai et al., 2015d) found ferroselite and eskebornite in Chinese coals, and using electron microprobe analysis Li et al. (Li et al., 2007) found organically-bound iron in coal macerals.

Selective leaching results (Fig. 15) indicate multiple modes of occurrence for iron in all 20 samples. For the bituminous coals there was no ammonium acetate leachable iron. The HCl leachable Fe ranged from 5 to 80% with an average of about 30%. Excluding the two Australian coals with 75 and 80% HCl extractable iron, the average is 25%. The HCl leachable iron is likely associated with the carbonate minerals, but could also be from monosulfides, phosphates, and sulfates. From 5 to 40% of the Fe (average: 20%) was leached by HF. This iron was associated with the silicates. Nitric acid extracted 0 (an Australian coal) to 80% (average about 45%; 50% excluding the two Australian coals).

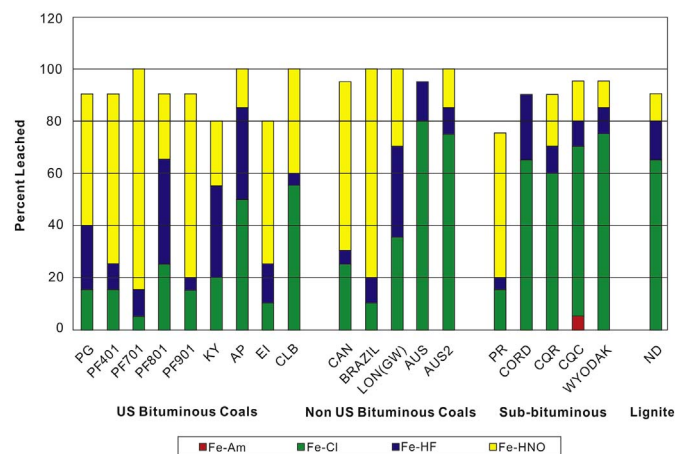


Fig. 15. Sequential leaching results for iron.

The nitric acid leachable iron is almost certainly associated with the sulfide minerals, likely pyrite. The total amount of iron extracted by the selective leaching protocol ranged from 80 to 100% (average: almost 95%). The unleached iron is likely to be a combination of organically associated iron, iron in insoluble minerals such as oxides, and iron in soluble phases that were shielded by the organic matter.

In the low rank coals essentially none of the iron was extracted with ammonium acetate and 15 to 75% (average: 60%) of the Fe was extracted by HCl. From 5 to 25% (average: 12.5%) of the iron was extracted by HF, and from 0 to 55% (average: 20%) was leached by nitric acid. The low rank coals have significantly higher proportion (60% for the low rank coals versus 20% for the bituminous coals) of iron associated with carbonates or other HCl soluble phases and a corresponding lower proportion of sulfide associated iron (20% for the low rank coals versus 50% for the bituminous coals), although there are significant variation with nitric acid leachable iron in both ranks of coal. The total amount of iron extracted by the selective leaching protocol ranged from 85 to 95% (average: 90%). The unleached iron may be a combination of organically associated iron, iron in insoluble minerals such as oxides, and iron in soluble phases such as pyrite that were shielded by the organic matter.

Except for the Wyodak sample, the low rank coals had much lower total iron (0.32 wt%) than did most bituminous coals (average: 1.5 wt %). It is therefore likely that the higher proportion of nitric acid leachable iron in the bituminous coals is due to the addition of epigenetic iron-bearing sulfide minerals during the coalification process.

4.15. Lead (Pb)

The average concentration of lead in U.S. coals is 11 ppm (Orem & Finkelman, 2003). (Finkelman, 1981a; Finkelman, 1981b)) concluded that lead in coal is inorganically bound and noted that substantial amounts of lead in the Appalachian Basin coals occurs as PbSe (claustalite). However, in most other coals (Finkelman, 1981a; Finkelman, 1981b)) reported that the dominant mode of occurrence for lead was as galena (PbS) with some lead occurring in sulfates, carbonates, phosphates, and silicates, especially in sulfide-poor coals. Swaine (Swaine, 1990) suggested that lead may occur in pyrite, and that an organic association in low-rank coals would be possible. Finkelman (Finkelman, 1994) had a high level of confidence in concluding that lead in coal occurred predominantly as sulfides or in association with sulfide minerals.

The selective leaching results (Fig. 16) indicated that essentially no lead was removed by ammonium acetate. HCl removed 40% (range 10–80%) of the lead from the bituminous coals. HF removed 5% (0–15%) of the lead and nitric acid removed about 20% (0–50%) of the lead from the bituminous coal samples. The total lead extracted from

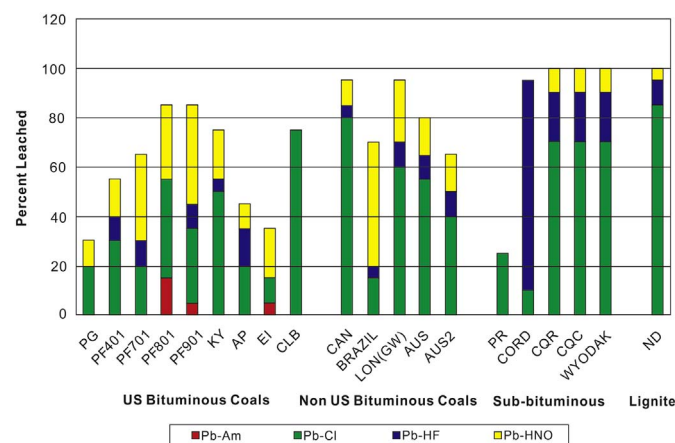


Fig. 16. Sequential leaching results for lead.

the bituminous coals was 70% (30–95%).

These data indicate that there is only a minor amount (5–10%) of silicate-associated lead in the bituminous coals. The data are consistent with most of the lead in coal being associated with HCl soluble monosulfides such as galena and clusthalite, although some lead associated with carbonates and phosphates cannot be excluded. Some of the lead (as much as 20%) is probably associated with pyrite. There may be a small amount of organically associated lead. The low total (70%) for leachable lead in the bituminous coals may be due to a significant portion of the lead occurring as micron-sized grains of galena and clauthalite (Dai et al., 2006a; Finkelman, 1985; Hower & Robertson, 2003); these grains may have been enmeshed in the organic matrix and thus shielded from the solvents.

For the six low rank coals HCl removed 55% (10–85%) of the lead, HF extracted 25% (10–85%), and nitric acid removed 5% (0–5%) of the lead. The total about of lead extracted by the solvents was 85% (25–100%).

In the low rank coals there appears to be a greater proportion of the lead associated with the silicates, although this interpretation is dominated by a single sample (CORD). Compared to the bituminous coals, less lead is associated with pyrite. The low rank coals have considerably less lead (< 4 ppm) than do the bituminous coals (18 ppm). It is likely that during the coalification process lead was added to coal through epigenetic mineralization of sulfides. This suggestion is supported by the fact that the lead content of the bituminous coals is 18.6 ppm and that of the low rank coals is 6.2 ppm.

4.16. Lithium (Li)

The average amount of Li in U.S. coal is 16 ppm (Orem & Finkelman, 2003). Because Li is generally not detectable by microbeam analysis, (Finkelman, 1981a; Finkelman, 1981b)) stated that the lack of data precludes any definitive statements on the modes of occurrence of lithium in coal. He did conclude that it is likely that much of the lithium is associated with the clays and some may be found with the detrital micas and tourmalines.

Selective leaching results (Fig. 17) indicates that HF leached 80% (65–95%) of the lithium from the 14 high-rank coals, but only 60% (15–90%) from the low-rank coals. > 85% (70–95%) of the lithium was removed by the solvents from the high-rank coals. The range for the low rank coals was much greater: 15–100% with an average of 62.5%. Ammonium acetate, HCl, and nitric acid removed relatively small amounts of lithium. We suggest that in most coals about 90% of the lithium is associated with the clays and micas and the remainder is either associated with the organics or acid-insoluble phases such as tourmaline. In some low-rank coals the proportion of organically-bound lithium may be as high as 50%.

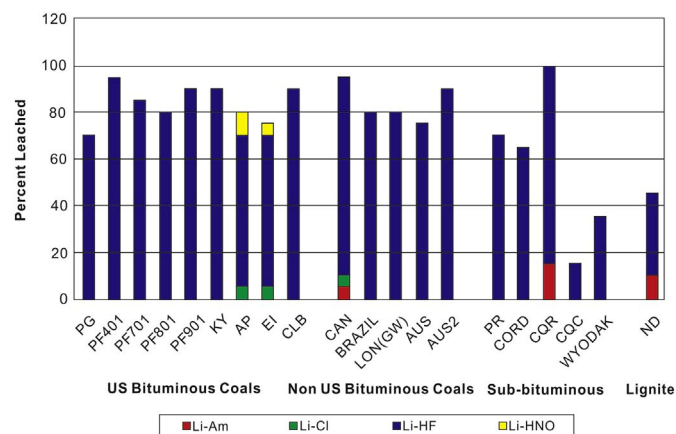


Fig. 17. Sequential leaching results for lithium.

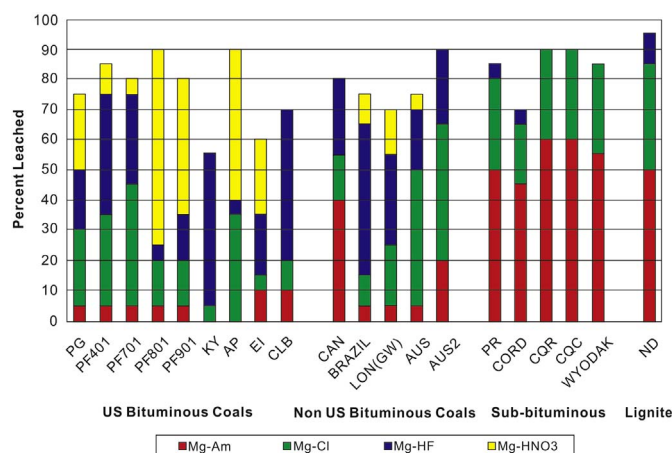


Fig. 18. Sequential leaching results for magnesium.

The concentration of lithium in the 14 bituminous coals (44 ppm) is considerably higher than that of the low rank coals (6 ppm). This is consistent with lithium being associated with detrital silicates in the higher ash yield bituminous coals.

4.17. Magnesium (Mg)

Magnesium is present at the 0.11 wt% level in U.S. coal (Orem & Finkelman, 2003). Bouska (Bouska, 1981) indicates that magnesium is primarily associated with the inorganic fraction of coal. Zubovic (1966) reported that this element in coal was due primarily to accumulation of detrital mineral and rock fragments. Finkelman (1981b) reported that the following magnesium bearing minerals were found in coal: micas (biotite, glauconite, talc); clays (montmorillonite, vermiculite, mixed layer, chlorites); carbonates (ankerite, siderite, dolomite and rare magnesite); silicates (garnet, pyroxene, amphiboles, olivine, tourmaline, staurolite, chrysolite); oxides (spinel); and rare sulfates and halides (bischofite).

Selective leaching results (Fig. 18) suggest multiple modes of occurrence for magnesium in all the samples. For the bituminous coals the percentage of ammonium acetate leachable magnesium ranged from 0 to 40% with an average of about 10%. The ammonium acetate leachable magnesium may be associated with the organic constituents or with the carbonates. The HCl leachable magnesium ranged from 5 to 45% with an average of about 20%. This magnesium is likely associated with the carbonate minerals such as calcite. From 5 to 50% of the magnesium (average: 25%) was leached by HF. This magnesium was associated with the silicates, probably with mixed-layer clays. From 0 to 65% of the magnesium (average: about 20%) was leached by nitric acid. It is likely that this magnesium was associated with ankerite and/or dolomite. Both minerals are present in coal and are only sparingly soluble in HCl (Palache et al., 1952). A total of about 75% (55–90%) percent of the total magnesium was leached by the selective leaching protocol. The remaining 25% of the magnesium is likely associated with the organics, although it is possible that some of the magnesium may be in insoluble oxide phases and/or soluble phases shielded by the organic matter. In summary, we conclude that in the bituminous coals about 20% of the magnesium may be organically associated, about 25% is associated with HCl soluble carbonates such as calcite and about 25% is associated with ankerite and dolomite which are less soluble in HCl, and 30% is associated with silicates.

In the lower rank coals, 20 to 60% (average 50%) of the magnesium was leached by ammonium acetate and 20 to 30% (average: 30%) was leached by HCl. From 5 to 40% of the magnesium was leached by HF (average: 10%) from three samples. There was no nitric acid leachable magnesium in the low rank coals indicating that the nitric acid soluble phases in the bituminous coals may be diagenetic phases formed during

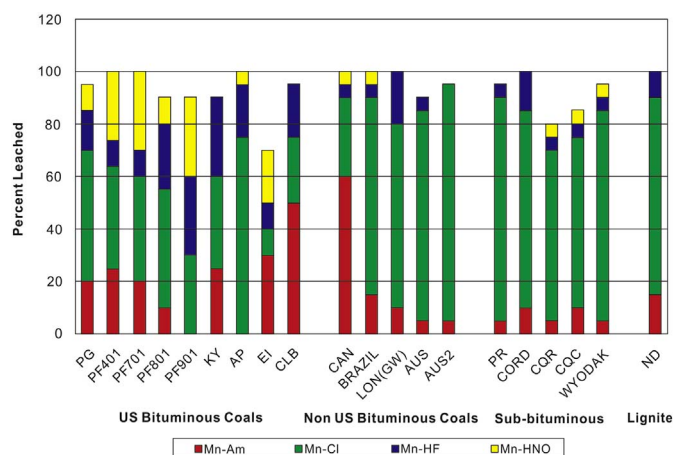


Fig. 19. Sequential leaching results for manganese.

the coalification process. The total leachable magnesium ranged from 70 to 100% (average: 85%). In contrast to the bituminous coals, there is much more ammonium acetate leachable magnesium (50% for the lower rank coals versus 10% for the bituminous coals). Because there is only a small difference in the amount of HCl leachable magnesium (carbonate associated magnesium) between the low rank coals and the bituminous coals (30 vs. 20%), we interpret the ammonium acetate leachable magnesium in the low rank coals to be primarily organically associated. In summary, for the low rank coals we interpret that about 60% of the magnesium was organically associated, 30% was associated with carbonates and 10% was percent associated with silicates.

4.18. Manganese (Mn)

The average concentration of manganese in U.S. coal is 43 ppm (Orem & Finkelman, 2003). Finkelman (Finkelman, 1994) concluded that manganese in coal is primarily found in the carbonates, especially siderite. In carbonate-poor coals the manganese may be organically bound or associated with the clays. Small amounts of manganese may be associated with pyrite (Finkelman, 1981a; Finkelman, 1981b). Swaine (Swaine, 1990) reported that organic association is the predominant mode of occurrence for manganese in low rank coals.

The selective leaching data (Fig. 19) for the high-rank coals indicates a distinct difference in the behavior of manganese between the ten North American and four non-North American coals. HCl leached about 35% (10–70%) of the manganese from the nine North American coals but more than twice that amount (80%, range of 70 to 90%) from the four non-North American coals. Ammonium acetate removed about 25% (0–60%) of the manganese from the North American coals but < 10% (5–15%) from the non-North American coals. Nitric acid removed 15% (0–35%) of the manganese from North American coals and only 5% from one of the non-North American coals. HF removed almost 20% of the manganese from North American coals but < 10% of the manganese from the non-North American coals. Virtually all of the manganese (95%, range 70 to 100%) was removed by the solvents from the high-rank coals, both North American and non-North American coals. In the low rank coals ammonium acetate extracted almost 10% (5–15%) of the manganese, HCl extracted 70% (50–85%), HF removed almost 10% of the manganese and nitric acid leached 5% of the manganese from three low rank coals. The total amount of manganese leached from the low rank coals was 90% (range 80 to 100%).

The manganese content of the five non-North American coals is 181 ppm, 75 ppm for nine North American coals and 34 ppm for the low rank coals. We interpret the leaching data to indicate that secondary carbonate mineralization contributed manganese to four of the non-North American coals. The ammonium acetate leachable manganese is probably from carbonates, but some of the manganese may also

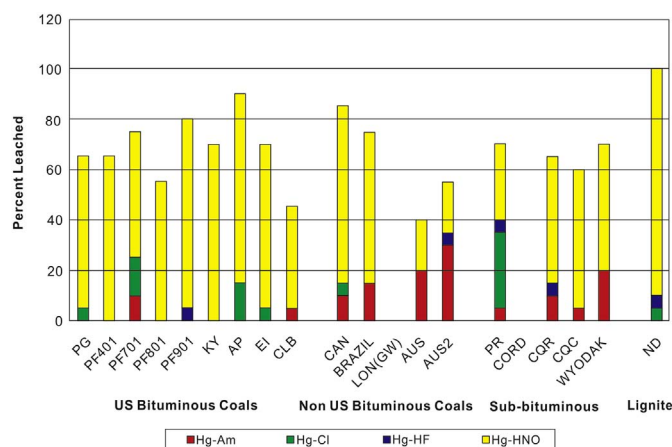


Fig. 20. Sequential leaching results for mercury.

be from ion exchange sites in clays and organics. We consider the HCl leachable Mn to be primarily from carbonates, the HF leachable Mn from clays, and the nitric acid leachable manganese from siderite.

4.19. Mercury (Hg)

Mercury released from coal through combustion has attracted considerable attention since the U.S. EPA decreed that mercury released by coal combustion may cause human health problems especially for people who eat fish that have bio-accumulated the mercury (U.S. EPA, 1997).

The average mercury content in U.S. coal is 0.17 ppm (Orem & Finkelman, 2003). (Finkelman, 1981a; Finkelman, 1981b)) concluded that although there is little direct evidence, there is strong circumstantial evidence to indicate that a significant proportion of the mercury in coal is associated with pyrite. Subsequent analysis of coal for mercury has confirmed this conclusion (Feng et al., 2001; Pan et al., 2017; Tewalt et al., 2001; Toole-O'Neil et al., 1999; Zheng et al., 2008).

The low concentrations of mercury in some samples result in a high degree of analytical uncertainty. However, the results for mercury appear to be consistent. Data from the selective leaching studies (Fig. 20) show that, on average, > 60% (range 40–75%) of the mercury was removed from 11 bituminous coals by HNO₃, but that only 25% of the mercury was removed from the two Australian coals. Ammonium acetate was not effective in removing mercury from the U.S. bituminous coals; however, it did remove 20% (10–30%) of the mercury from the four non-U.S. bituminous coals. It is possible that the non-U.S. coals were not as fresh as the U.S. coals, and that some of the sulfide minerals in the non-U.S. coals had been oxidized during shipment to the U.S. HCl leached about 5% (5–15%) of the mercury from five bituminous coal samples, and HF did not remove any of the mercury. About 70% (40–95%) of the mercury was extracted by the solvents. Some of the unleached mercury may be in shielded, fine-grained sulfides.

In the five low rank coals 45% (30–60%) of the mercury was extracted by nitric acid, about 10% (5–20%) was removed by ammonium acetate, HCl leached 30–35% of the mercury from two samples, and virtually no mercury was extracted by HF. About 70% (60–75%) of the mercury was extracted by the solvents.

It is clear that the bulk of the mercury, perhaps around 90%, is associated with sulfides likely with pyrite which is the predominant sulfide in most bituminous coal samples. There appears to be substantially less sulfide-associated mercury in the two Australian coal samples. The low rank coals had considerably less mercury (0.06 ppm) than did the bituminous coals (0.17 ppm). It is likely that sulfide mineralization added mercury during coalification. The modes of occurrence of mercury in the low rank coals are less clear than for the bituminous coals. Nevertheless, it appears that the bulk of the mercury in

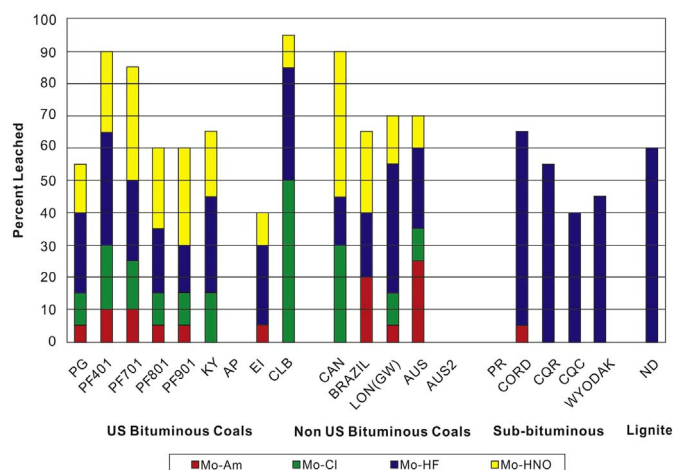


Fig. 21. Sequential leaching results for molybdenum.

these coals, perhaps as much as 75%, was associated with sulfide minerals.

4.20. Molybdenum (Mo)

The average concentration of molybdenum in U.S. coal is 3.3 ppm (Orem & Finkelman, 2003). Data in the literature do not offer any clear insights into the modes of occurrence of molybdenum (Finkelman, 1981a; Finkelman, 1981b). Molybdenum has strong chalcophile tendencies, but it is commonly found concentrated in the lighter specific gravity fractions in sink-float tests indicating an organic affinity. Swaine (Swaine, 1990) notes that the mode of occurrence of Mo in coal can be either inorganic or organic.

The selective leaching results for molybdenum (Fig. 21) are consistent with multiple modes of occurrence and are notable because they indicate that molybdenum does not have strong chalcophile tendencies in coal and because of the large difference in mode of occurrence with rank. Ammonium acetate removed < 10% (0–25%) the molybdenum from 12 bituminous coals and essentially no molybdenum from five low rank coals. HCl removed 15% (0–50%) from the bituminous coals and nothing from the low rank coals. HF removed 25% (15–40%) from the bituminous coals but 55% (40–60%) from the low rank coals. Nitric acid removed 20% (10–45%) of the molybdenum from the bituminous coal and no molybdenum from the low rank coals. About 30% of the molybdenum in the bituminous coals remained unleached as did about 45% in the low rank coals. This Mo may be associated with the organics and/or with shielded mineral grains.

It is worthwhile noting that the molybdenum concentrations in the bituminous coals (77 ppm, range 14–260) are considerably higher than in the low rank coals (23 ppm, 8–107). It thus appears that most of the molybdenum in coal may begin primarily in association with the silicates (clays) and organics. Upgrading and epigenetic mineralization would enhance the sulfide-associated molybdenum.

4.21. Nickel (Ni)

The average concentration of nickel in U.S. coals is 14 ppm (Orem & Finkelman, 2003). (Finkelman, 1981a; Finkelman, 1981b)) stated that substantial amounts of nickel in coal may be organically associated. The inorganically bound nickel may be largely associated with the sulfides. Finkelman (Finkelman, 1988) indicated that nickel in coal may also occur in clays. Finkelman (1994) notes a low level of confidence in modes of occurrence of nickel because of the lack of direct evidence and the contradictory indirect evidence.

Results from the leaching experiments (Fig. 22) indicate that about 10% of the nickel is extracted by ammonium acetate from the

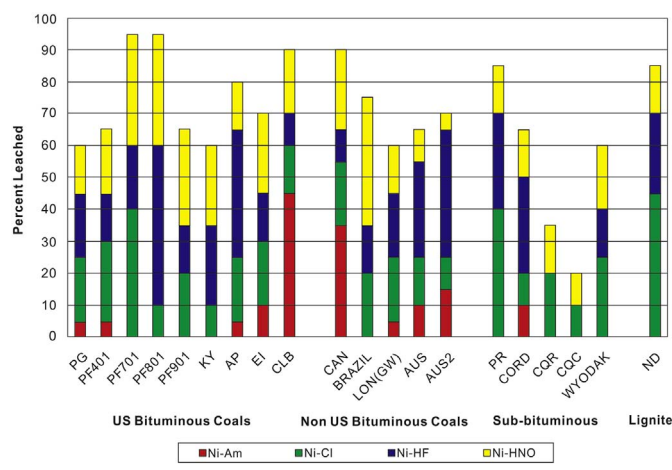


Fig. 22. Sequential leaching results for nickel.

bituminous coals with 45% and 35%, respectively being extracted from samples CLB and CAN. In the above discussion on cobalt we postulated that the nickel and cobalt in these two samples may have been associated with oxidized linnaeite group minerals. HCl removed almost 20% (range 10–40%) of the nickel from the 14 bituminous coal samples and 25% (range 10–45%) from the six low-rank coals. HF removed almost 25% (range 0–50%) of the nickel from the bituminous coal samples and about 15% (0–30%) from the six low-rank coals. Nitric acid removed about 20% (0–50%) of the nickel from the bituminous coals and 15% (10–20%) from the low rank coals. The total amount of nickel extracted was 75% (60–95%) from the bituminous coal samples but somewhat less, 60% (20–85%), from the six low-rank coals.

The mode of occurrence of nickel remains an enigma. The HCl leachable nickel may have been associated with monosulfides, sulfates, carbonates, etc. The HF leachable nickel was very likely associated with clays and the nitric acid soluble nickel was likely associated with pyrite. There is probably a portion of the nickel that is organically associated, no > 10% in the bituminous coal and, perhaps, 30% in the low-rank coals. The average amount of nickel in the bituminous coals is 22 ppm, and in the low rank coals it is 5 ppm. Thus, the postulated 30% organically associated nickel in the low rank would be about 2 ppm, essentially the same amount as the postulated 10% organically bound nickel in the bituminous coals.

4.22. Phosphorus (P)

The average phosphorus content in U.S. coal is 430 ppm (Orem & Finkelman, 2003). After noting the ubiquity of phosphorus minerals (primarily monazite, xenotime, apatite and crandallite group minerals), (Finkelman, 1981a; Finkelman, 1981b)) concluded that substantial amounts of phosphorus in many coals occur in rare earth element (REE)-phosphates and/or apatite. Swaine (Swaine, 1990), Ward et al. (Ward et al., 1996) and Dai et al. (Dai et al., 2015b) also concluded that most of the phosphate in coal is associated with minerals.

The results from the selective leaching studies (Fig. 23) indicate that nearly 85% (40–100%) of the P in the bituminous coals was leached by HCl plus HF. We interpret the phosphorus in these samples to have been extracted from the common phosphate minerals observed in coal. The leaching behavior for phosphorus is similar in the low-rank coals where HCl plus HF leached a total of 75% (25–100%). The unleached portion (15–25%) of the phosphorus may be organically bound, in insoluble phosphorus-bearing minerals, or in shielded grains.

4.23. Potassium (K)

The average concentration of potassium in U.S. coals is 0.18%

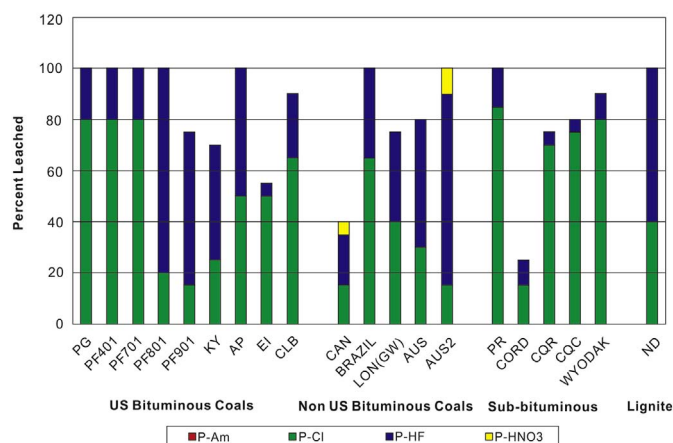


Fig. 23. Sequential leaching results for phosphorus.

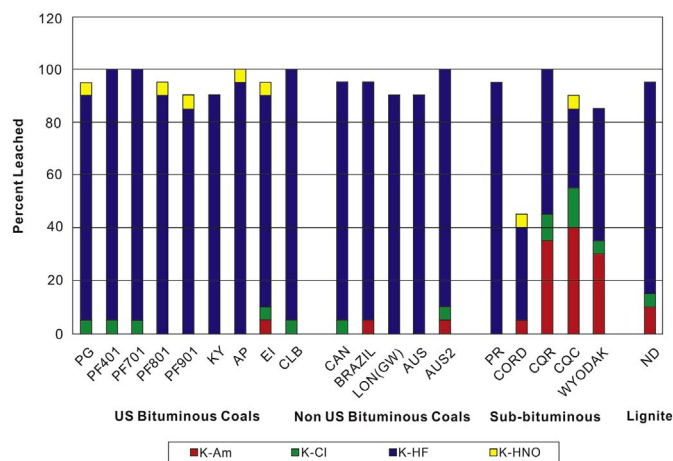


Fig. 24. Sequential leaching results for potassium.

(Orem & Finkelman, 2003). Reports in the literature indicate an almost exclusive inorganic association of potassium in coal (Finkelman, 1993a; Finkelman, 1993b; Huggins et al., 2009; Swaine, 1990).

The selective leaching behavior of potassium (Fig. 24) in the 13 bituminous coal samples is straightforward. Nearly 90% (range 60–95%) of the potassium was extracted by HF, and only small amount was extracted by the other solvents from several of the samples. Thus in the bituminous coals at least 90% of the potassium is associated with silicates.

For the low rank coals 60% of the potassium was extracted by HF (30–95%), 20% (0–40%) was leached by ammonium acetate, and 5% (0–15%) was leached by HCl. About 85% (45–100%) of the total potassium was extracted from the low rank coals.

We assume that much of the ammonium acetate soluble potassium in the low rank coals was associated with the organics or water soluble salts. Some of the potassium leached by ammonium acetate, as well as some of the potassium leached by HCl may have been in ion exchangeable sites in clays. As is the case with other elements that are commonly associated with detrital minerals, the potassium concentration is higher in the higher ash yield bituminous coals (0.56%) than in the low rank coals (0.06%).

4.24. Rare Earth Elements (REE)

Selective leaching data were obtained for yttrium (Y), cerium (Ce), lanthanum (La), lutetium (Lu), neodymium (Nd), samarium (Sm), and ytterbium (Yb). According to Orem and Finkelman (Orem & Finkelman, 2003) the average concentrations of these rare earth elements in U.S.

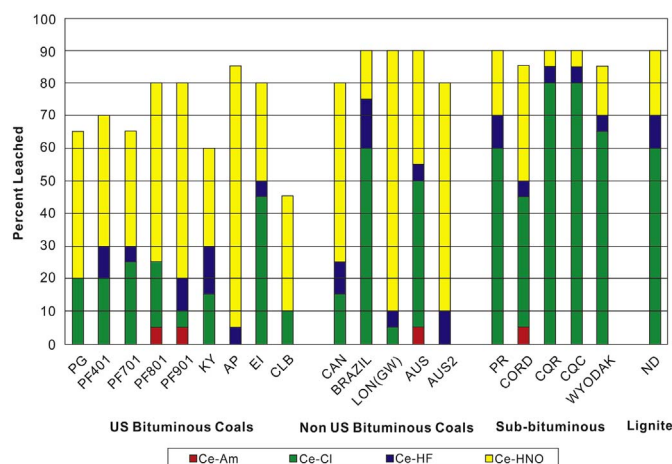


Fig. 25. Sequential leaching results for cerium.

coals are: cerium (21 ppm), lanthanum (12 ppm), lutetium (0.14 ppm), neodymium (9.5 ppm), samarium (1.7 ppm), and ytterbium (0.95 ppm). (Finkelman, 1981a; Finkelman, 1981b)) concluded that the bulk of the REE in coal occurred in the common RE-phosphates monazite and xenotime. However, Finkelman (1981a) estimated that no > 10% of the total REE (predominantly heavy-REE) in low rank coals appears to have an organic association. Swaine (Swaine, 1990) states that the REE in most coals seems to be associated with mineral matter and that in addition to REE-bearing phosphates, clays and carbonate minerals should not be ruled out as sites for the REE. Because of interest in the economic extraction, numerous papers have appeared discussing the modes of occurrence of the rare earth elements in coal, these including Seredin and Dai (Seredin & Dai, 2012), Dai et al. (Dai et al., 2016a; Dai et al., 2016b), Hower et al. (Hower et al., 2016b), and Lin et al. (Lin et al., 2017).

The leaching behavior of all six REE is broadly similar, but varies between samples. We will use cerium (Fig. 25) as a proxy for the light REE and ytterbium (Fig. 26) for the heavy REE. Essentially none of the REE was extracted by ammonium acetate. HCl extracted 20% (0–60%) of the cerium from the bituminous coal samples. In contrast, HCl extracted almost 70% (40–80%) of the cerium from the six low rank coal samples. HF extracted just about 5% (0–15%) of the cerium from the bituminous coal samples and slightly less from the low rank coals. Nitric acid extracted 45% (15–80%) of the cerium from the 14 bituminous coal samples and about 12.5% (5–35%) from the low rank coals. The total cerium extracted by the solvents was 75% (25–90%) from the

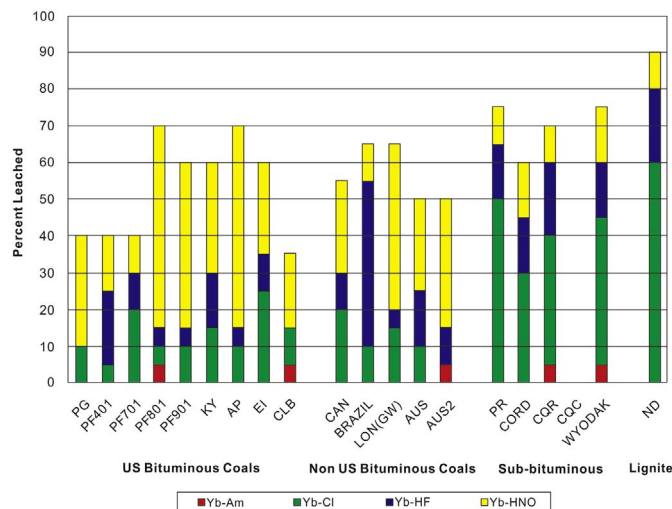


Fig. 26. Sequential leaching results for ytterbium.

bituminous coals and 90% (85–95%) from the low rank coals.

The large difference in the HCl leachable Ce between the bituminous coals and low rank coals may be due to an influx of detrital phosphates in the generally higher ash bituminous coals. The cerium concentration of the bituminous coals is about 30 ppm, and that of the low rank coals is about 7 ppm. If the difference in cerium content represents a greater proportion of detrital Ce-bearing phosphates such as monazite in the bituminous coals, then the difference in leaching behavior can be explained. Palache et al. (Palache et al., 1951) state that monazite is slowly decomposed by acids, and Sinkankas (Sinkankas, 1972) noted that monazite is only slightly attacked by warm concentrated HCl. However, the very fine grained nature of the REE phosphates in coal ($< 5 \mu\text{m}$) present an extremely large surface area to the solvents, and they may be more readily attacked by the acids than the presumably larger mineral grains used in the acid leaching experiments. The small amounts of HF leachable cerium indicate a minor cerium association with clays. However, it is possible that the HCl leachable cerium was in ion-exchange sites in the clays that resisted ammonium acetate leaching. Some of the HCl leachable cerium elements may have been associated with carbonates. The nitric acid leachable cerium is almost certainly associated with the phosphate minerals monazite, xenotime and the crandallite group. The total cerium extracted (90%) is consistent with only a small portion strongly bound to the organic matrix.

HCl extracted 10% (0–25%) of the ytterbium from the bituminous coal samples and almost 45% (30–60%) of the ytterbium from the five low rank coals (Fig. 26). HF removed about 10% (0–45%) of the ytterbium from the bituminous coals and 17% (15–20%) from the low rank coals. Nitric acid extracted 30% (10–55%) of the ytterbium from the bituminous coal samples and 12% (10–15%) from the low rank coal samples. The total ytterbium extracted was about 55% (35–70%) from the bituminous coals and 75% (60–90%) from five low rank coals. As with cerium, more ytterbium was leached by the HCl from the low rank coals and nitric acid leached more from the bituminous coals. We invoke the same explanation here as for cerium, the higher ytterbium concentrations in the bituminous coals (1.5 ppm) than in the low rank coals (0.45 ppm) likely reflects an influx of detrital Yb-bearing minerals (e.g. xenotime) that are not HCl soluble.

The lower percentage of total leachable ytterbium (75%) versus Ce (90%) is consistent with the observation by (Finkelman, 1981a; Finkelman, 1981b)) that there is a higher proportion of organically bound heavy REE than light REE. The modes of occurrence of the other REE would be similar to and generally transitional between that of cerium and ytterbium.

4.25. Rubidium (Rb)

The average concentration of rubidium in U.S. coals is 21 ppm (Orem and Finkelman (Orem & Finkelman, 2003). (Finkelman, 1981a; Finkelman, 1981b)) concluded that rubidium in coal is inorganically bound and notes that substantial amounts of rubidium may be in illite and mixed-layer clays as rubidium can readily substitute for potassium. Palmer and Filby (Palmer & Filby, 1984) stated that rubidium is clearly associated with the clays.

The selective leaching results (Fig. 27) indicated that 5% or less of the rubidium was extracted by ammonium acetate from the bituminous coals. About 15% (range 5–30%) was extracted from the low-rank coals. HCl removed about only 5% (0–5%) of the Rb from the bituminous and low rank coal samples. HF removed about 45% (10–90%) of the rubidium from the 13 bituminous coal samples and about 75% (65–85%) of the rubidium from five of the low rank coal samples. Nitric acid extracted about 40% (0–85%) of the rubidium from the bituminous coals and no rubidium from the five low rank coals. The total rubidium extracted was about 85% (40–100%) from the bituminous coals, at least 75% (30–100%) from the low rank coals.

The HF soluble rubidium was most likely associated with silicates.

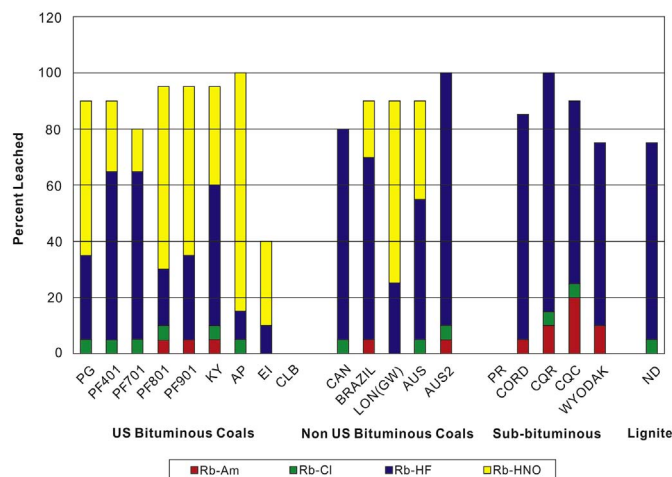


Fig. 27. Sequential leaching results for rubidium.

The surprisingly high proportion of nitric acid soluble rubidium may be due to the HF solubilizing, but not dissolving, all of the silicates. As with cesium and sodium, the nitric acid may have completed the leaching of the solubilized silicates. The leaching data would then be consistent with a dominant silicate association for rubidium.

4.26. Scandium (Sc)

The average concentration of scandium in U.S. coals is 4.2 ppm (Orem & Finkelman, 2003). (Finkelman, 1981a; Finkelman, 1981b)) noted that modes of occurrence data for scandium point to both organic and inorganic associations and recommended that more work be conducted to understand its modes of occurrence. Swaine (Swaine, 1990) concluded that there is general agreement in the literature that scandium occurs associated with the mineral matter and with the organic matter in varying proportions. Based on the negative correlation between scandium and ash Arbuzov et al. (Arbuzov et al., 2014) concluded that the scandium in Asian coals was predominantly in an organic mode of occurrence. Seredin et al. (Seredin et al., 2006) looking at scandium-bearing coals from Siberia concluded that “the nature of Sc concentration in coals of the Yakhlink field remains ambiguous” (p. 969).

The selective leaching data (Fig. 28) indicate that 25 to 80% (average 55%) of the scandium was leached by hydrofluoric acid from the both the bituminous and low rank coals. The ammonium acetate and the nitric acid essentially leached no scandium. Hydrochloric acid removed 5 to 25% (average 10%) of the scandium from the bituminous

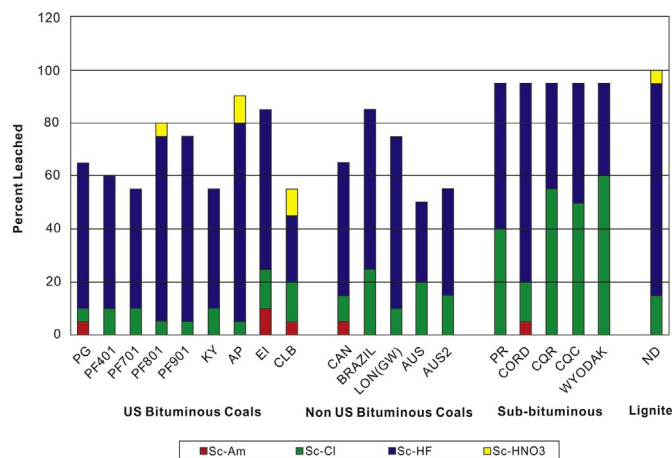


Fig. 28. Sequential leaching results for scandium.

coals and from 15 to 60% (average 40%) from the low-rank coals. The total amount of scandium leached ranged from 50 to 90% (average 70%) of the bituminous coals and 95% for the low rank coals.

We interpret these results to indicate that more than half of the scandium in bituminous and low rank coals is associated with silicate minerals, such as clays. The 30% of the scandium that was not leached from the bituminous coals was unlikely to be associated with the organics as virtually all of the scandium was leached from the low rank coals indicating little organically-bound Sc in low rank coals. The unleached scandium may be in silicates shielded by the organics or in insoluble mineral phases. The 10% of the scandium leached from the bituminous coals by the hydrochloric acid could have been organically bound, associated with carbonate minerals, or with phosphates. In contrast, 40% of the scandium was leached by HCl from the six low rank coal samples. It is possible that a substantial portion of the scandium is loosely associated with the organic matter in the low rank coals, but in up-ranking most of this scandium would more tightly bind to the organics and thus no longer be HCl soluble.

There is another distinct difference between the bituminous and the low rank coals. The bituminous coals have, on average 6 ppm scandium and the five sub-bituminous coals have a nearly uniform 1.4 ppm. This difference in concentration may be related to the difference in ash yield. The bituminous coals have an ash yield of 24.5%, whereas the six low rank coals have an ash yield of 8%. The difference in scandium concentrations can be accounted for, if the bulk of the increased mineral matter in the bituminous coals is due to the scandium-bearing silicates. This assumes that the scandium-bearing minerals are detrital and are shielded by the organics or are insoluble. If the detrital material had an average of 22 ppm scandium (the crustal average; (Mason, 1966)) the average scandium concentration of the bituminous coals would be about 5.5 ppm; close to the actual 6 ppm.

4.27. Selenium (Se)

The average concentration of selenium in U.S. coal is 2.8 ppm (Orem & Finkelman, 2003). (Finkelman, 1981a; Finkelman, 1981b)) stated that substantial amounts of selenium in coal can occur in organic complexes, in solid solution in pyrite and other sulfides, and as lead selenide (clausthalite). Dreher and Finkelman (Dreher & Finkelman, 1992) quantified the modes of occurrence of selenium in an ash-rich upper zone of a sub-bituminous Power River Basin coal. They identified seven modes of occurrence of selenium: water-soluble (22%), ion-exchangeable (21%), galena and lead selenide (2%), clays and silicates (15%), pyrite (6%), organically associated (10–20%).

In the selective leaching experiments (Fig. 29) ammonium acetate extracted about 5% (0–5%) of the Se from the bituminous coals. HCl

extracted 5% (0–35%) of the Se from the bituminous coals. HF also extracted almost 5% (0–10%) from the bituminous coals. Nitric acid extracted 50% (25–75%) of the Se from the bituminous coals. The total amount of selenium leached was 65% (35–90%) for the bituminous coals.

The ammonium acetate may be extracting loosely held organic selenium or selenium that is associated oxidized pyrite. The HCl may be extracting selenium from the clausthalite or other monosulfides. There appears to be little silicate-associated selenium. Nitric acid extracted the bulk of the selenium (50%) from the bituminous coals, possibly indicating selenium that was associated with pyrite and other sulfide and selenide minerals. Some of the non-leachable selenium may have been associated with fine-grained sulfides and selenides such as clausthalite that were shielded from the solvents by encapsulating organic matter. Some of the selenium may also have been organically associated – more in the low-rank coals than in the bituminous coals. Willett et al. (Willett et al., 2003) found lead selenides and other selenium bearing phases in several of the selective leaching residues that were examined.

There were large differences in the leaching behavior of selenium in the four low rank coals. HCl extracted 70 and 75% of the Se from two samples and only 5% from the other two samples. Nitric acid extracted 20 and 25% of the Se from two samples and no Se from the other two samples. It is difficult to draw conclusions based on the widely different leaching behavior of selenium in these low rank coals. We assume that most of the selenium in the low rank coals is organically bound with only small proportions associated with sulfide and silicate phases. As with many other elements, the concentration of Se in the bituminous coals (3.1 ppm) is higher than in the low rank coals (0.5 ppm).

4.28. Sodium (Na)

The average concentration of sodium in U.S. coals is 0.08% (Orem & Finkelman, 2003). It is generally believed that sodium in coal is primarily associated with silicates, especially clays, but in low-rank coals a substantial proportion of the sodium is organically associated (Swaine, 1990). Finkelman (Finkelman, 1991) found that in parts of the Wasatch Plateau much of the sodium was associated with the epigenetic, cleat-filling zeolite, analcime. Finkelman et al. (Finkelman et al., 1988) determined that most of the sodium in the Fort Union lignites was organically bound. Sodium in coal is particularly important because it contributes to fouling problems during coal combustion (Raask, 1985).

The selective leaching results (Fig. 30) indicate that 40% (0–70%) of the sodium in the bituminous coals was extracted by ammonium acetate and about 92% (85–95%) of the sodium from the six low-rank coals. HCl extracted 7.5% (0–35%) of the sodium from the bituminous coals and 5% from the low rank coals. HF removed almost 30%

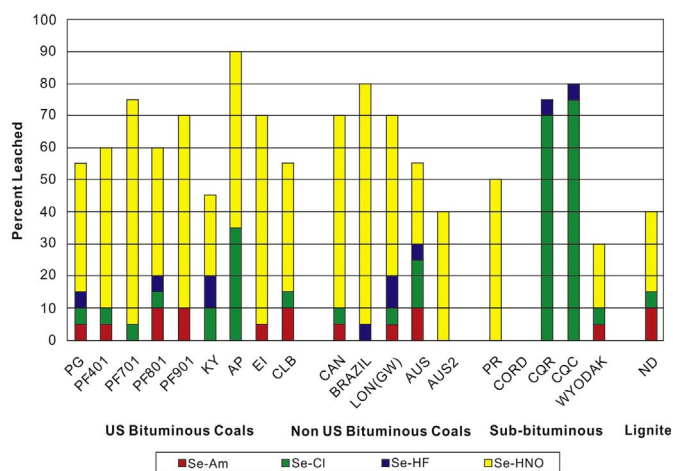


Fig. 29. Sequential leaching results for selenium.

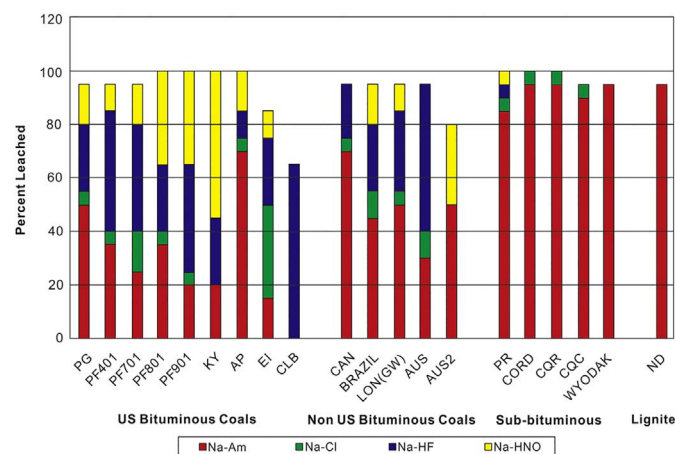


Fig. 30. Sequential leaching results for sodium.

(0–65%) of the sodium from the 14 bituminous coal samples and essentially none from the six low-rank samples. Nitric acid removed about 15% (0–55%) of the sodium from the bituminous coal samples and essentially no sodium from the six low rank coal samples. The total sodium leached was about 93% (65–100%) from the 14 bituminous coal samples and almost 98% (95–100%) from the six low rank coal samples.

Although the amounts of sodium in the bituminous coals (0.1 wt%) and the low rank coals (0.15 wt%) are similar, the modes of occurrence of sodium are quite different. The ammonium acetate leachable sodium may have been in exchange sites in clays, weakly-held organically associated sodium, sodium ions in pore water, or water soluble salts. Virtually all of the sodium in the low rank coals occurs in these forms. About 30% of the sodium in the bituminous coal samples is leached by HF indicating that this sodium may be more tightly bound in the clays. The presence of sodium in feldspars or other silicates in the low rank coals appears to be minimal, as there was almost no HF leachable sodium. Moreover, SEM characterization of coals (Finkelman, 1981a; Finkelman, 1981b) also indicates that feldspars are rare. The small amount of HCl leachable sodium may have been sodium extracted from carbonates, phosphates, or more-tightly bound sodium in clays or organics. It appears that with upranking some of the organically associated and pore-water associated sodium in low rank coals may have been adsorbed by clays in the bituminous coals.

Because it is geochemically unusual for sodium to be associated with sulfide minerals (Goldschmidt, 1954), we conclude that the HF solubilized the silicates in the bituminous coals without dissolving the silicates completely. In this interpretation, the nitric acid would have completed the leaching of the solubilized silicates. Because this leaching behavior is similar to that of cesium and rubidium, we interpret that sodium, rubidium, and cesium may be associated with the same silicate phases in bituminous coals.

4.29. Strontium (Sr)

The average concentration of strontium in U.S. coals is 130 ppm (Orem & Finkelman, 2003). (Finkelman, 1981a; Finkelman, 1981b)) concluded that strontium can have both organic and inorganic associations, and that the greater portion was organically bound. He found inorganic strontium in crandallite-group minerals and other phosphates, barite, celestite, carbonates, and clays. Swaine (Swaine, 1990) concluded that most of the strontium in low-rank coals is organically bound. He also reported strontium in calcite, goyazite and other crandallite-group minerals.

In the selective leaching procedure (Fig. 31), 15% (range 0–40%) of the strontium was extracted by ammonium acetate from the bituminous coals, and 32.5% (range 25–40%) was extracted from five sub-

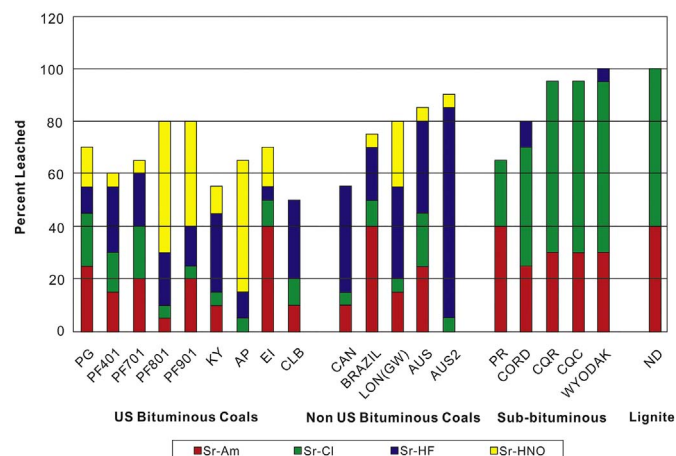


Fig. 31. Sequential leaching results for strontium.

bituminous coals. Hydrochloric acid extracted 10% (range 5–20%) from the bituminous coals and 55% (25–65%) from the low rank coals. HF extracted 25% (5–80%) of the strontium from the bituminous coals and virtually no strontium from the low rank coals. Nitric acid extracted 15% (0–50%) of the strontium from the bituminous coals and no strontium from the low rank coals. The totals for extractable strontium are 70% (50–90%) for the bituminous coals and 90% (65–100%) for the low rank coals.

It is likely that most of the ammonium acetate leachable strontium and some of the HCl leachable strontium was organically associated. According to Palache et al. (Palache et al., 1951), goyazite is only slowly soluble in acids; however, as previously discussed the small grain size of the minerals in coal would render them more susceptible to acid attack. Thus it is likely that much of the acid soluble strontium was associated with the common micrometer-sized phosphate minerals in coals.

There does appear to be a significant difference in the silicate association between the U.S. bituminous coals (20% leached by HF) and the non-U.S. bituminous coals (40% leached by HF). It should also be noted that the strontium content of the low rank coals, plus the AUS2 coal, is considerably higher (325 ppm) than the strontium content of the other 13 bituminous coals (90 ppm).

4.30. Tantalum (Ta)

The average concentration of tantalum in U.S. coals is 0.22 ppm (Orem & Finkelman, 2003). (Finkelman, 1981a; Finkelman, 1981b)) concluded that tantalum in coal is primarily associated with detrital inorganic minerals. Palmer and Filby (Palmer & Filby, 1984) suggested an association with titanium, zirconium, and phosphate minerals.

In the selective leaching experiments (Fig. 32), essentially no tantalum was removed by ammonium acetate or by HCl. HF extracted 25% (15–40%) from 12 bituminous coal samples and almost 40% (25–45%) from five low-rank coals. Nitric acid extracted about 10% (0–30%) of the tantalum from 12 bituminous coal samples and essentially none from the five low-rank coals. The total amount of tantalum extracted by the solvents was almost 40% (20–60%) for the 12 bituminous coal samples and about 45% (25–65%) from the five low-rank coals.

The selective leaching data are consistent with tantalum being associated with minerals (zircon, rutile, columbite, etc.) that are insoluble or weakly soluble in acids. In previous analysis of insoluble residues, Willett et al. (Willett et al., 2003) detected zircon in one residue and titanium oxides in all four insoluble residues that were examined. Some, if not most of the HF leachable tantalum was probably associated with clay.

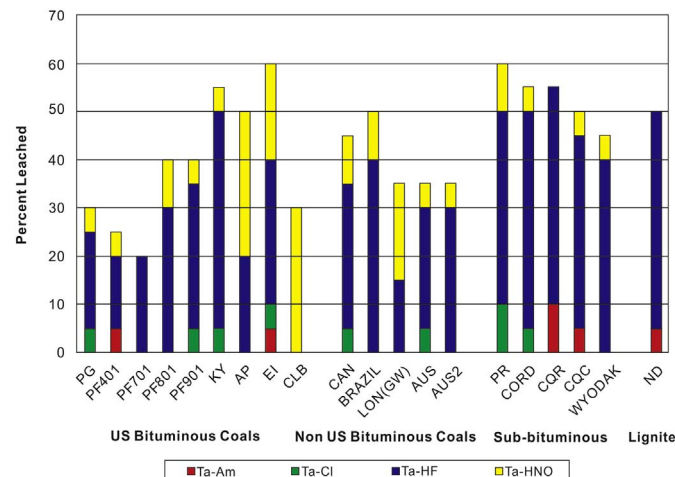


Fig. 32. Sequential leaching results for tantalum.

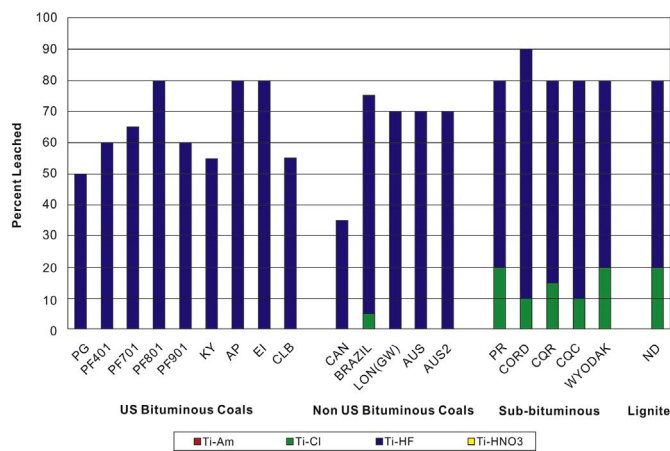


Fig. 33. Sequential leaching results for titanium.

4.31. Titanium (Ti)

The average titanium content of U.S. coal is 0.08% (Orem & Finkelman, 2003). (Finkelman, 1981a; Finkelman, 1981b)) concluded that the mode of occurrence of titanium in a specific coal may be quite complex; some Ti may be organically bound, particularly in low-rank coals. In most coals, substantial amounts of Ti occur as titanium oxides (rutile, anatase, brookite, etc.) or may be associated with the clays. Some Ti may also be found in other accessory Ti-bearing minerals. Similarly, Swaine (Swaine, 1990) concluded that the mode of occurrence of Ti in most coals is partially organic, probably dominantly so in low-rank coals, and partially inorganic, especially as rutile, anatase, other Ti-rich minerals and associated clays. Titanium oxides (rutile and anatase) are among the most common minerals observed in coal (Ward, 2002).

Both Palache et al. (1944) and (Sinkankus, (1972) state that rutile and anatase are insoluble in acid. The selective leaching data indicate that titanium is not leached by ammonium acetate or nitric acid. HCl removed 12.5% (0–20%) of the titanium from the low rank coals and essentially none from the bituminous coals. About 65% (35–80%) of the titanium is leached by HF from the bituminous coals (Fig. 33) and slightly more (70%, range 60–80%) from the low rank coals. HF extracted < 50% of the titanium from only one sample and no > 80% HF from the other samples. The total amount of titanium leached from the bituminous coals was 65% (35–80%) and 80% (80–90%) from the low rank coals.

We suggest that the HCl-leachable titanium in the low-rank coals was associated with the organic matter. A substantial portion of the HF leachable titanium was probably associated with silicates, such as clays. However, some of this titanium by HF may have been in Ti-oxides attacked by the HF. Based on previous studies showing that rutile and anatase are insoluble in acid, we suggest that the unleached titanium was largely associated with rutile and anatase grains based on the work of Willett et al. (Willett et al., 2003) who found titanium oxides in all four insoluble residues that they examined.

4.32. Tungsten (W)

The average concentration of tungsten in U.S. coals is 1.0 ppm (Orem & Finkelman, 2003). (Finkelman, 1981a; Finkelman, 1981b)) concluded that a substantial amount of tungsten in coal may be organically bound but that more detailed studies on this element would be desirable. Swaine (Swaine, 1990) cited a study indicating that tungsten is associated with carbonate minerals in Indian coals.

Ammonium acetate removed about 7.5% (0–25%) of the tungsten from the bituminous coal samples and slightly more (10%, range 0–30%) from five low-rank coals (Fig. 34). HCl extracted 10% (0–25%)

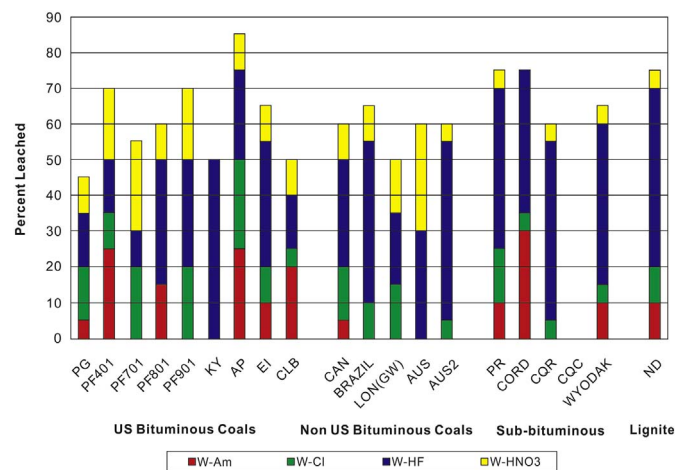


Fig. 34. Sequential leaching results for tungsten.

of the tungsten from the 14 bituminous coal samples and almost 10% (5–15%) from the low-rank coals. HF extracted about 30% (10–50%) from the bituminous coals and 45% (40–50%) from the five low rank coals. Nitric acid extracted about 15% (0–30%) of the tungsten from the bituminous coals and 5% (0–5%) for the low rank coals. The totals for tungsten leaching are 60% (45–85%) for the bituminous coals and 70% (60–75%) for the low rank coals.

Not surprisingly, the leaching behavior of tungsten parallels that of the geochemically similar molybdenum (Fig. 21). As in other rocks, these elements likely have similar modes of occurrence in coal. They appear to have a modest chalcophile tendency in the bituminous coals; however, they are strongly associated with the silicates in the lower ash low rank coals. As with molybdenum the concentration of tungsten is higher in the bituminous coals (3.6 ppm) than in the low rank coals (2.4 ppm). The 'additional' tungsten may have accompanied epigenetic sulfide mineralization. The degree of organic association is unclear.

4.33. Uranium (U)

The average concentration of uranium in U.S. coals is 2.1 ppm (Orem & Finkelman, 2003). (Finkelman, 1981a; Finkelman, 1981b)) concluded that much of the uranium in coal appears to be organically bound, but that a substantial portion may be associated with accessory minerals such as zircons and RE phosphates. (Finkelman, 1981a; Finkelman, 1981b)), Mohan et al. (Mohan et al., 1991), Dai et al. (Dai et al., 2015e) and (Hower et al., 2016a; Hower et al., 2016b)) also noted that secondary mineralization may form a diverse suite of uranium-bearing minerals. Swaine (Swaine, 1990) stated that the modes of occurrence of uranium in coal are diverse, but that organic bonding appears to be common.

Results from the leaching experiments (Fig. 35) indicate that little to no uranium is extracted by ammonium acetate. HCl removed about 10% (range 5–35%) of the uranium from the 14 bituminous coal samples and 45% (range 25–50%) from the six low-rank coals. HF removed almost 35% (range 15–55%) from the bituminous coal samples and 35% (range 30–45%) from the low rank coals. Nitric acid removed almost 15% (5–30%) of the uranium from the 14 bituminous coals and 5% from each of the low-rank coals. The total amount of uranium extracted was 60% (45–85%) from the bituminous coal samples and 85% (75–95%) from the six low-rank coals.

Based on the HF leaching data it appears that about 35% of the uranium in coals of any rank is associated with silicates, probably clays. The significantly higher proportion of HCl leachable uranium in the low rank coals is almost certainly organically associated uranium. Because it is unlikely that uranium is associated with sulfides (Goldschmidt, 1954) we interpret the nitric acid leachable uranium to have been

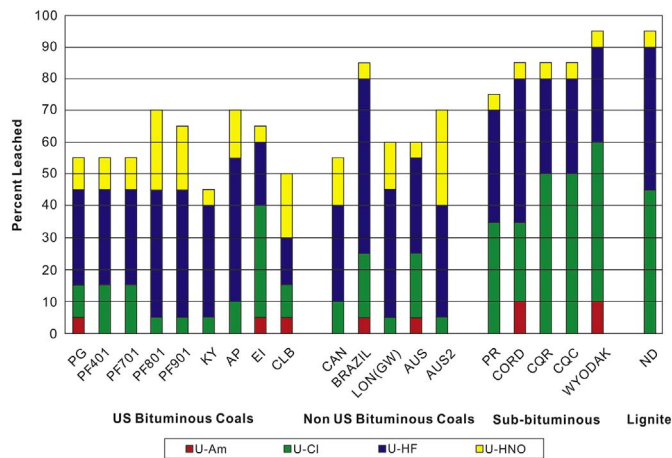


Fig. 35. Sequential leaching results for uranium.

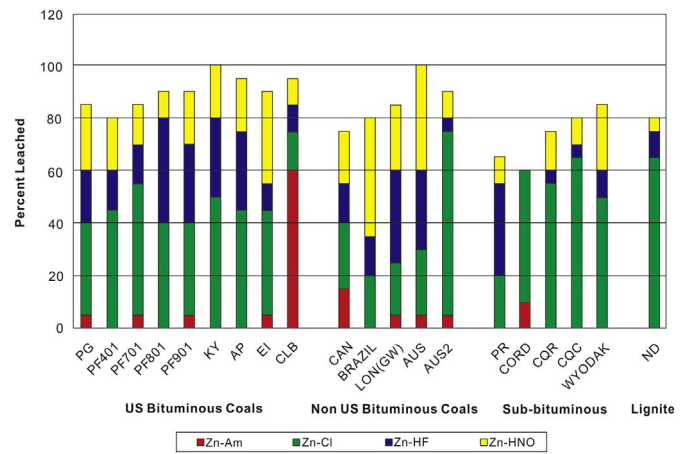


Fig. 37. Sequential leaching results for zinc.

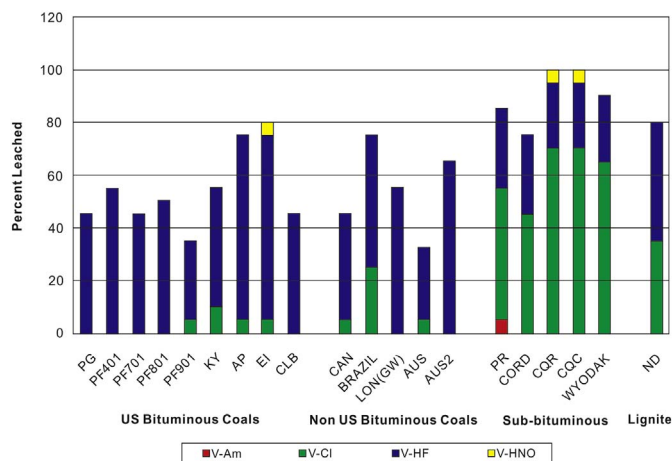


Fig. 36. Sequential leaching results for vanadium.

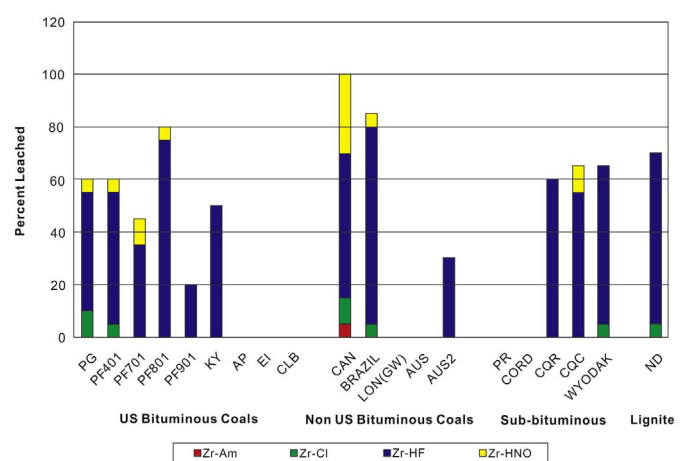


Fig. 38. Sequential leaching results for zirconium.

associated with phosphate phases. Much of the unleached uranium in the bituminous coals may be associated with insoluble phases such as zircon.

4.34. Vanadium (V)

The average vanadium concentration in U.S. coals is 22 ppm (Orem & Finkelman, 2003). According to (Finkelman, 1981a; Finkelman, 1981b) and Palmer and Filby (Palmer & Filby, 1984), vanadium is probably associated with clays and that it may also be organically associated. Swaine (Swaine, 1990) acknowledged that there are conflicting reports, but concluded that there may be a small portion of organically bound vanadium in some coals together with vanadium in clays and other minerals. Looking at superhigh-organic-sulfur coals from China Liu et al. (Liu et al., 2015) concluded that vanadium and other trace elements are mainly associated with organic matter, and to a lesser extent, associated with illite or mixed-layer illite/smectite.

In the selective leaching studies (Fig. 36) essentially no vanadium was extracted by ammonium acetate or nitric acid. Only about 5% (0–25%) of the vanadium was extracted from the 12 bituminous coals by hydrochloric acid. From 25 to 70% (average 50%) of the vanadium was extracted by HF from the bituminous coals. The total amount of vanadium extracted from the bituminous coals was 55% (30–80%).

We interpret these results to indicate that at least 50% of the vanadium in the bituminous coals was associated with the silicates, probably clays. The 45% unleached vanadium may have been in shielded or insoluble minerals or associated with the organics. We assumed that at least half of the unleached vanadium was associated with

shielded clays and the remainder may have been organically bound.

In contrast to the bituminous coals, HCl was the dominant solvent in the low rank coals removing 55% (35–70%) of the vanadium, whereas HF extracted only 30% (25–45%) of the vanadium. Ammonium acetate and nitric acid removed negligible amounts of the vanadium. The total vanadium extracted by the solvents was 90% (75–100%), which is considerably higher than what was extracted from the bituminous coals. Although the bituminous coals have a lower proportion of extractable vanadium (55%) compared to the low rank coals (90%), the vanadium content (44.9 ppm) is higher than that of the low rank coals (13.2 ppm).

The leaching behavior of vanadium is very similar to that of aluminum, beryllium, scandium and titanium. It is probable that all of these elements have significant organic association in the low rank coals. As with these other elements we hypothesize that organically bound vanadium (HCl leachable) was mobilized during the coalification process and later taken up by neogenic clays such as kaolinite.

4.35. Zinc (Zn)

The average concentration of zinc in U.S. coals is 53 ppm (Orem & Finkelman, 2003). (Finkelman, 1981a; Finkelman, 1981b) concluded that the bulk of the zinc in coal is found in pyrite, a small proportion of the zinc may occur in other sulfide minerals such as pyrite, and some zinc in low-rank coals may be organically bound. Swaine (Swaine, 1990) noted that sphalerite is the prime source of zinc in coal, but organic bonding in low-rank coals is a possibility.

Virtually no zinc was extracted by ammonium acetate with the lone

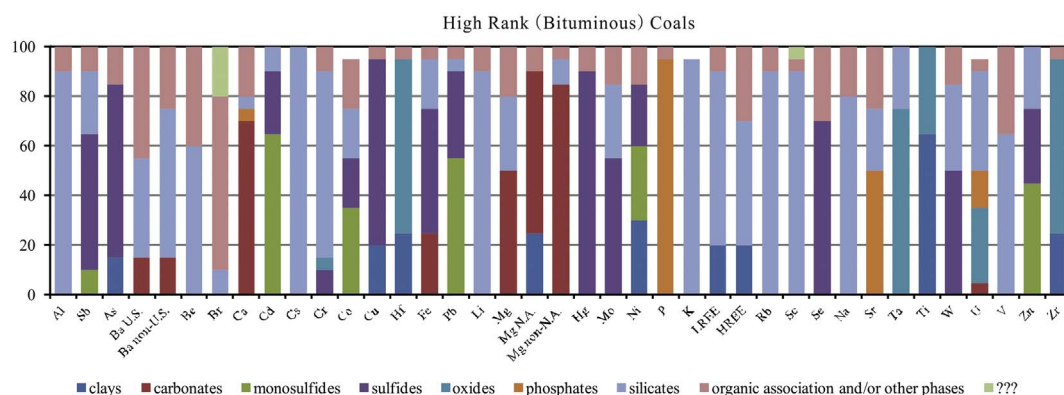


Fig. 39. Quantitative modes of occurrence of elements in high rank (bituminous) coals (x-axis, elements; y-axis, leached percentage).

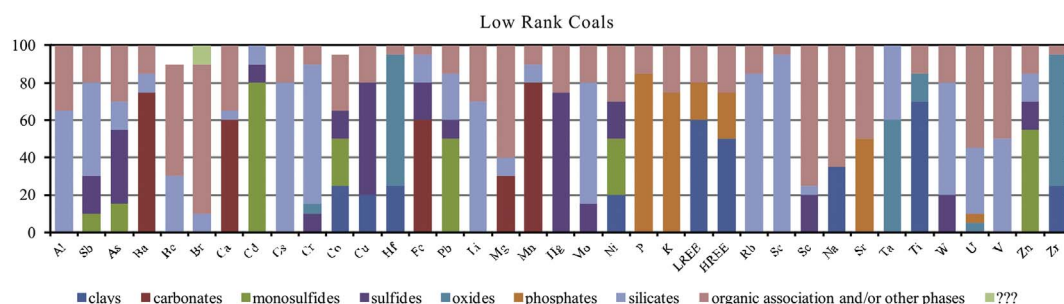


Fig. 40. Quantitative modes of occurrence of elements in low rank coals (x-axis, elements; y-axis, leached percentage).

exception of the CLB sample from which 65% of the zinc was removed. HCl extracted about 40% (range 20–70%) of the zinc from the 14 bituminous coals and 50% (20–65%) was extracted from five low-rank coals. About 20% (5–40%) of the zinc was extracted by HF from the bituminous coals and 10% (0–35%) from the low rank coals. Nitric acid extracted 25% (10–45%) of the zinc from the bituminous coals and 10% (0–25%) from the low-rank coals. The total zinc extracted was almost 90% (75–100%) for the 14 bituminous coals and 75% (60–85%) from the low-rank coals (See Fig. 37.)

Based on data for the bituminous coals in this study, we interpret the data to indicate that about 45% of the zinc occurs in sphalerite, 30% in pyrite, 25% is associated with silicates.

In the low rank coals we interpret the data to indicate about 55% of the zinc was in monosulfides, likely sphalerite, 15% of the zinc may have been in pyrite, 15% in silicates and up to 15% in organic association. As with the other chalcophile elements the concentration of zinc is higher in the bituminous coals (44 ppm) than in the low rank coals (11 ppm). This difference is probably a consequence of zinc-bearing epigenetic sulfides in the bituminous coals.

4.36. Zirconium (Zr)

The average concentration of Zr in U.S. coals is 27 ppm (Orem and Finkelman (Orem & Finkelman, 2003). (Finkelman, 1981a; Finkelman, 1981b)) concluded that the bulk of the zirconium in most high rank coals occurs as zircon, but that the mode of occurrence of zirconium in lignites is less certain. Swaine (Swaine, 1990) concluded that zircon is the main mode of occurrence of zirconium in most coals.

In the selective leaching experiments (Fig. 38), essentially no zirconium was leached by ammonium acetate, and little to no zirconium (0–10%) was removed by HCl. As with hafnium (Fig. 14), hydrofluoric acid removed 50% (20–75%) of the zirconium from all 13 coal samples and nitric acid removed about 5% (0–30%). As with hafnium, the total zirconium extracted by the solvents was about 60% (20–100%). Also like hafnium, no differences in behavior with rank were apparent.

The leaching data supports the conclusion that most of the

zirconium in coals occurs in zircons. Sinkankas (Sinkankas, 1972) stated that zircons are unaffected by acids, however, because zircons in coal are commonly only a few micrometers in size, they may be more readily attacked by acids. Zircons in coal are also more likely to be metamict which may cause them to be more acid soluble (Finkelman, 1981a; Finkelman, 1981b).

We conclude that most of the zirconium in these 13 coals is associated with zircons. We cannot rule out the presence of some zirconium in clays. The fact that there is little difference in the total zirconium leached from the nine bituminous coals (60%) and the three low-rank coals (70%) argues against any significant organic association for zirconium.

5. Conclusions

Selective leaching results from 20 coal samples have allowed us to make an initial attempt at quantifying the modes of occurrence of 42 elements. The results indicate that within a coal rank the leaching behavior of many elements are broadly similar. However, the behavior of many elements varies between bituminous and subbituminous coals (Tables 2 and 3; Figs. 39 and 40).

We recognize the limits of the selective leaching procedure, especially in trying to identify phases that are insoluble or only partially soluble. Nevertheless, we feel that the quantification of the mode of occurrence presented here are reasonable estimates for these elements in most coals. We hope that this effort will encourage others to further refine these estimates and to resolve some of the unusual leaching behaviors that we observed.

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