

Modes of occurrence of potentially hazardous elements in coal: levels of confidence

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(Received 19 April 1993; accepted in revised form 25 January 1994)

Abstract

The modes of occurrence of the potentially hazardous elements in coal will be of significance in any attempt to reduce their mobilization due to coal combustion. Antimony and selenium may be present in solid solution in pyrite, as minute accessory sulfides dispersed throughout the organic matrix, or in organic association. Because of these modes of occurrence it is anticipated that less than 50% of these elements will be routinely removed by conventional coal cleaning procedures. Arsenic and mercury occur primarily in late-stage coarse-grained pyrite therefore physical coal cleaning procedures should be successful in removing substantial proportions of these elements. Cadmium occurs in sphalerite and lead in galena. Both of these minerals exhibit a wide range of particle sizes and textural relations. Depending on the particle size and textural relations, physical coal cleaning may remove as little as 25% of these elements or as much as 75%. Manganese in bituminous coal occurs in carbonates, especially siderite. Physical coal cleaning should remove a substantial proportion of this element. More information is needed to elucidate the modes of occurrence of beryllium, chromium, cobalt, and nickel.

1. Introduction

The Clean Air Act Amendments of 1990 [1] have focused attention on 189 substances cited as potentially hazardous air pollutants. Among these substances are 11 inorganic elements: antimony, arsenic, beryllium, cadmium, chromium, cobalt, lead, manganese, mercury, nickel, and selenium. Coal combustion is an important anthropogenic source for many of these elements [2].

There are three ways to reduce the amount of the elements mobilized by coal combustion: (1) locate and mine coal with lesser concentrations of these elements, (2) remove the elements prior to combustion, and (3) remove the elements from the emissions after combustion.

The modes of occurrence of potentially hazardous elements in coal are of significance in any attempt to reduce their mobilization from combustion. The mode of occurrence refers to how the element is chemically bound and physically distributed throughout the coal. Knowledge of an element's mode of occurrence enables the

prediction of its distribution in a coal deposit, and its behavior during coal preparation and combustion.

The mode of occurrence of an element can be inferred from indirect evidence such as float–sink data, from statistical correlations with other elements or with other coal characteristics such as ash yield, from the element's geochemical characteristics, or from behavior during heating or leaching of the coal. Preferably the modes of occurrence should be determined directly, using microbeam analytical techniques or X-ray mineralogical analysis.

Unfortunately, virtually all of the available information on the modes of occurrence of elements in coal is qualitative, some appears to be inconsistent or contradictory, and much is 10 to 15 years old and was conducted on samples from mines that no longer are in operation. Among the more comprehensive discussions of the modes of occurrence of elements in coal are those by Bethell [3], Zubovic [4], Gluskoter et al. [5], Finkelman [6], Raask [7], Eskenazy [8], and Swaine [9].

This paper briefly reviews the modes of occurrence in coal for each of the 11 elements cited in the Clean Air Act amendments of 1990 [1]. A level of confidence is estimated for the most likely modes of occurrence of these elements (see discussions of individual elements and Table 1). The estimated level of confidence is a numeric value from 1 to 10, with 10 indicating the highest level of confidence and 1 indicating no confidence. This estimate is based, in large part, on whether the modes of occurrence were determined by direct or indirect methods. Another factor considered in estimating the level of confidence is how consistently the element behaved among the various studies. Thus, the estimate is a measure of the predictability an element's behavior.

The anticipated behavior of each element during coal cleaning will also be discussed. This anticipated behavior of the element will be based on its modes of occurrence and on its behavior during laboratory float–sink experiments and

Table 1

Likely modes of occurrence of 11 inorganic elements in coal and level of confidence estimate

Element	Mode of occurrence	Level of confidence
Antimony	Pyrite and accessory sulfides	4
Arsenic	Pyrite	8
Beryllium	Organic association	4
Cadmium	Sphalerite	8
Chromium	Organic or clay association	2
Cobalt	Pyrite, some in accessory sulfides	4
Lead	Galena	8
Mercury	Pyrite	6
Manganese	Carbonates, especially siderite and ankerite	8
Nickel	Unclear	2
Selenium	Organic association, pyrite and accessory sulfides, selenides	8

commercial coal cleaning studies. It should be emphasized that the estimated levels of confidence are subjective and may change as new information becomes available.

Several caveats should be considered. Firstly, although sometimes necessary, it is dangerous to generalize about an element's mode of occurrence. Each element is unique, having different modes of occurrence and offering different challenges for deciphering them. This will be evident from the discussions of the individual elements. Secondly, "It is likely that not all of a particular element in a coal will be in the mode or modes suggested. Nor will the element even occur in the suggested mode in every coal." (Finkelman [10], p. 143.) These statements are still true today.

2. Antimony (Sb)

There is relatively little information available on the modes of occurrence of Sb in coal. As with many other elements in coal, laboratory float–sink data are ambiguous. Some studies conclude that Sb is organically associated, others indicate that it exhibits an intermediate behavior, and yet others suggest that Sb is inorganically bound [6].

Antimony was partially volatilized (10–20%) in 10 coal samples that were heated to 550°C by Finkelman et al. [11]. They also noted that Sb was removed by hydrochloric acid from most bituminous coals and was removed by nitric acid from the lignites. They concluded that further work is necessary to determine the modes of occurrence of antimony.

The only Sb mineral reported from coal was crystals of ullmannite (NiSbS) found by Spencer [12] in a carbonate vein in a British coal bed. Very rare, micrometer-sized, Sb-bearing minerals (generally sulfides) have been found by use of scanning electron microscopy (SEM) on polished blocks of coal (Finkelman, unpublished data). Using an electron microprobe (EMP), Minkin [13] found small amounts of Sb in sphalerites in the Upper Freeport coal bed in Pennsylvania.

Reports on the occurrence of Sb in pyrite from coal [14] are based on bulk analyses; thus, it is possible that the Sb in their samples occurred in accessory sulfides associated with the pyrite.

Modes of occurrence. Antimony may be present in solid solution in pyrite and as minute accessory sulfides (e.g., stibnite, Sb_2S_3) dispersed throughout the organic matrix. Some Sb may be organically bound.

Level of confidence: 4. Direct evidence is lacking for the modes of occurrence of this element.

Anticipated coal cleaning behavior. In commercial coal cleaning tests, Sb displayed a wide range of behavior. Junk et al. [15] removed as much as 82% of the Sb from one coal sample, and yet in another coal no Sb was removed. Fonseca et al. [16] removed 64–81% of the Sb from one coal sample, 43–45% from a second coal, and only 5% from a third coal sample. Ford and Moses [17] removed 19–35% of the Sb from two coal samples. Based on these results and the behavior of Sb in laboratory float–sink experiments [6], it is anticipated that less than 50% of the Sb will be routinely removed by conventional coal cleaning procedures.

3. Arsenic (As)

The association of arsenic with pyrite was noted early in this century [18]. Subsequently, it was suggested that arsenic is organically associated [19, 20], is associated with clays [21], carbonates [22], and occurs as arsenopyrite [19].

The commonly reported occurrence of arsenopyrite (FeAsS) in coal appears to be a myth that has been perpetuated in the literature [23–25]. It is based largely, if not exclusively, on circumstantial evidence. Researchers noted the high concentrations of As in heavy specific gravity fractions of coal containing abundant sulfides and speculated that arsenopyrite was present. To my knowledge, the presence of arsenopyrite in coal has not been confirmed by diagnostic microbeam or X-ray diffraction procedures (except for very rare occurrences of micrometer-sized grains [26]). The most intriguing evidence for arsenopyrite is the recent X-ray absorption fine structure (XAFS) spectroscopy data of Huggins et al. [27]. They interpret the XAFS spectra for As as indicating the presence of arsenopyrite in a Pittsburgh coal sample. This was the only indication of arsenopyrite they found in about 30 coal samples analyzed.

There is abundant evidence, both direct and indirect, to support the contention that As in coal is associated with pyrite. For example, detailed microbeam studies [28, 29] have confirmed the presence of substantial amounts of As in pyrite from coal, generally in late-stage fracture-filling pyrite. White and others [30] analyzed sulfides from the United Kingdom by synchrotron radiation X-ray fluorescence. They found that nearly all the samples showed detectable As, up to 3.4 wt%. Based on the optical reflectivity of the iron sulfides, they concluded that the As was in solid solution. The XAFS data of Huggins et al. [27] and the ^{57}Fe Mossbauer data of Evans et al. [31] is consistent with As occurring in solid solution in pyrite.

Although much of the analytical data indicate an association of As with late-stage (epigenetic) cleat- and fracture-filling pyrite [32, 33], there is evidence that some As is associated with fine-grained, early-stage (sygenetic) pyrite in Czechoslovakian coals [29], a Canadian coal [34], and in the Upper Freeport coal bed, Pennsylvania [35].

Modes of occurrence. It appears that most of the As in coal is associated with pyrite. In the majority of coals studied, As is primarily associated with massive or late-stage pyrite. In some cases As is associated with fine-grained pyrite and other sulfides. There may even be some organically associated As, although this would be a minor component.

Level of confidence: 8. There is direct evidence and a substantial amount of indirect evidence.

Anticipated coal cleaning behavior. From 50% to 75% of the As should be removed from most coals by conventional coal cleaning procedures. In the commercial coal cleaning studies, about 40–95% of the As was removed [15–17, 36].

Because the As in the Upper Freeport coal bed occurs primarily in porous and pitted late-stage pyrite, the As would likely be leached easily from the waste products. Huggins et al. [27] came to a similar conclusion based on their XAFS data, which indicated that As-bearing pyrite oxidizes very rapidly and allows arsenates to be leached from coal-cleaning waste products.

4. Beryllium (Be)

Beryllium presents difficulties in determining its modes of occurrence because of its low atomic number (at. no. 4). The X-rays from Be are so soft that they cannot be detected by the conventional X-ray detectors used with the SEM, transmission electron microscope, EMP, and X-ray fluorescence spectrometry. Moreover, Be is present at relatively low concentrations (approximately 2 ppm) in US coal [37].

Abundant evidence in the literature indicates an organic affinity for Be. Few other elements are so consistently concentrated in the float fraction in laboratory float–sink experiments [6]. Moreover, the Be content of coal varies inversely with ash yield. However, Be can replace aluminum in clays and can occur in quartz.

Modes of occurrence. The available evidence indicates that Be may be bound to the organic constituents in coal. The possibility of some Be being associated with clays cannot be excluded.

Level of confidence: 4. There is no direct evidence for the mode of occurrence of Be; however, its consistency of behavior in float–sink experiments warrants a confidence level of 4.

Anticipated coal cleaning behavior. The behavior of Be in most coal cleaning tests indicates that no more than about 25% would be removed by conventional coal cleaning procedures [15, 17]. Recent data by Fonseca et al. [16] are at variance with this observation. They removed from 52% to 68% of the Be from six samples representing three coals.

5. Cadmium (Cd)

Gluskoter and Lindahl [38] convincingly demonstrated that cadmium in Illinois basin coals occurs predominantly in sphalerite (ZnS). Minkin [39] found as much as 2 wt% Cd in sphalerite from the Upper Freeport coal bed. Subsequent microbeam analytical studies [40] have detected Cd in sphalerite from numerous worldwide locations. In most compilations of analytical data there is a good correlation between Cd and zinc [37], however, Godbeer and Swaine [41] found no direct relation between Cd and zinc in low-Cd Australian coals.

Although it is generally accepted that Cd in coal occurs in solid solution in sphalerite, there are some dissenters. Kirsch et al. [42] found Cd to be associated with clays and carbonates in German coals. Bogdanov [43] suggested that Cd is associated with the “organic substance”, and Swaine [9] indicated that pyrite may contain some Cd.

Modes of occurrence. The bulk of the information on Cd in coal is consistent with its occurring in sphalerite. There may be minor amounts of Cd associated with other minerals, generally in sulfides, but in most coals this mode of occurrence would be trivial.

Level of confidence: 8. Both direct and indirect evidence is consistent with Cd occurring in sphalerite in most coals.

Anticipated coal cleaning behavior. Cadmium exhibits a wide range of behavior in coal cleaning studies. Akers and Dospoy [36] removed from 11% to 94% Cd from

various coals. Boron and Wan [44] reported that 26–50% of the Cd was removed in an evaluation of 6 commercial prep plants and in laboratory cleaning of 20 US coals. They also cite chemical coal cleaning studies in which 51–70% of the Cd was removed. Fonseca et al. [16] report Cd reductions of 40–83% in three coals. Junk et al. [15] removed 94% of the Cd from one coal sample but no Cd was removed from a second sample. Ford and Moses [17] removed 64% and 77% of the Cd from two coals and Cavallaro et al. [45] found that from 0% to 88% of the Cd was removed from the four coals that they studied.

The wide range of behavior is likely due to the different modes of occurrence of sphalerite [46]. In some coals sphalerite occurs as large ($> 100 \mu\text{m}$) crystals filling cleat and fractures. This sphalerite and the associated Cd would be relatively easy to remove during coal cleaning. In other coals, most of the sphalerite occurs as small ($< 10 \mu\text{m}$) grains enmeshed in the organic matrix. These sphalerite grains, and the Cd they contain, would be difficult to liberate during coal cleaning.

6. Chromium (Cr)

Information on the modes of occurrence of chromium in coal is inconclusive. Some reports on Cr in coal conclude that it is organically associated, others conclude that Cr has an intermediate behavior, and yet other reports find that Cr has a distinct inorganic affinity [6].

The response of Cr in coal to various solvents was examined by Finkelman et al. [11]. They concluded that the leaching behavior of Cr does not give a clear picture of its mode of occurrence.

Coals with high concentrations ($> 500 \text{ ppm}$) of Cr have been found to contain chromite (FeCrO_4) [47, 48]. Few other Cr-bearing minerals have been reported in coal.

Using XAFS spectroscopy on about 30 US coals, Huggins et al. [27] found that essentially all of the Cr is present in the +3 oxidation state. Their data indicate that there is only one significant mode of occurrence of Cr in the coals studied. They favor an organic association for Cr but acknowledge that the actual mode of occurrence has not been established.

Modes of occurrence. There are insufficient data to specify the modes of occurrence of Cr in coal. The float–sink behavior of Cr could be attributable to organic association, to association with clays, or to other fine-grained Cr-bearing minerals.

Level of confidence: 2. There is no direct evidence for the mode of occurrence of Cr in coal.

Anticipated coal cleaning behavior. Results from laboratory and commercial coal cleaning studies show a very wide range of behavior for Cr. The % reduction found by Akers and Dospoy [36] ranged from zero to more than 75%. Other studies show a similar broad range of cleanability, although the data from Fonseca et al. [16] for three coal samples show a range of only 74–82% removal. On the basis of its wide range of behavior in most coal cleaning studies it is difficult to anticipate the cleaning behavior of Cr.

7. Cobalt (Co)

In laboratory float–sink studies [6], Co has been found to concentrate in the float fractions in some samples and is, thus, inferred to have an organic association. In other studies, Co was strongly concentrated in the sink fractions and is inferred to have a strong inorganic association [6].

From 7% to 58% of the Co was leached by HCl in the 10 coal samples studied by Finkelman et al. [11], with the higher values generally coming from the low-rank coals. They suggested that some of the HCl-leached Co may be present as chelates in the coal. Virtually no Co was removed by hydrofluoric acid, indicating that Co is not associated with silicate minerals. Up to 20% of the Co was removed by nitric acid. Perhaps this Co was associated with pyrite.

Cobalt can easily substitute in the pyrite structure, this process being more efficient at high temperatures [49]. Cambel and Jarkovsky [50] found 30–50 ppm Co in pyrite concentrates from Czechoslovakian coals, and several hundred ppm Co were detected in pyrite from the Upper Freeport coal bed by ion microprobe analysis [40]. Other studies have failed to detect Co in pyrite from coal [6].

Linnaeite $[(\text{Co}, \text{Ni})_3\text{S}_4]$ and linnaeite group minerals have been reported in coals from Australia and the Pennsylvania anthracites [46].

Modes of occurrence. Cobalt in coal is probably associated with the sulfide minerals, mostly in pyrite. However, if all the Co were associated with pyrite, the pyrite would have to have several hundred ppm Co. This level of concentration of Co should have been detected analytically, and its float–sink behavior should have more clearly indicated an inorganic association. It is, therefore, likely that some Co occurs in fine-grained accessory sulfide minerals, in clays, or in organic association in low-rank coals.

Level of confidence: 4. There is still a high degree of uncertainty as to the modes of occurrence of Co.

Anticipated coal cleaning behavior. Commercial coal cleaning studies [15, 16] indicate that 50–75% of the Co can be removed from the coal. These data are consistent with the suggested modes of occurrence of Co.

8. Lead (Pb)

The information on lead is unambiguous. Brown and Swaine [51] found up to one wt% Pb in pyrite concentrates from Australian coals. They concluded that Pb commonly occurs either as sulfides or associated with sulfides. Cambel and Jarkovsky [50] also found Pb in pyrite they extracted from Czechoslovakian coals. In most laboratory float–sink experiments, Pb was concentrated in the sink fractions and was inferred to have an inorganic association [6].

Galena (PbS) has been reported to occur in many coals [3, 9, 46]. Lead selenide (PbSe, perhaps the mineral clausthalite) has been reported to be a common fine-grained constituent of coal [46]. Other Pb minerals or lead contained in other minerals appears to be quite rare [6].

Modes of occurrence. Lead occurs predominantly as sulfides or associated with sulfide minerals. Galena may be the most common form of Pb in coal, but galena can have several significantly different associations. Galena can occur as large, epigenetic crystals in cleat and fractures. It can also occur in minute grains associated with pyrite or as micrometer-sized grains dispersed in the organic matrix [6]. Lead selenide is pervasive in coal but, except for the Appalachian basin coals, it accounts for a minor portion of the Pb [46].

Level of confidence: 8. This estimate is based on direct information on lead's modes of occurrence and on its consistent behavior in coal from worldwide locations.

Anticipated coal cleaning behavior. Because of the strong inorganic affiliation of Pb it might be expected that Pb would be very efficiently removed during coal cleaning. This seems to be the case for many coal samples [15, 16, 44]. However, for many other samples the percent reduction of Pb during coal cleaning is considerably lower (< 50%) [36, 45].

It is conceivable that the difference in behavior of Pb is a reflection of the different ways in which the Pb-bearing minerals occur. Lead would be effectively removed if it occurred primarily in cleat-filling galena or in galena attached to massive pyrite. The efficiency of removal would be dramatically lower if the Pb occurred as micron-size crystals of galena or PbSe in the organic matrix.

9. Manganese (Mn)

Manganese commonly is present in coal in greater concentrations than any of the other 10 potentially hazardous air-pollutant elements. Nevertheless, the mode of occurrence is not readily apparent because few Mn minerals occur in coal. Manganese in coal generally occurs as a trace constituent substituting for iron in carbonate minerals [6].

Laboratory float–sink experiments and leaching experiments are all consistent with Mn occurring in carbonates. Small amounts of Mn may be associated with clays, pyrite, or the organic components of coal [6]. Swaine [9] suggested that, in low-rank coals, Mn may be organically bound through carboxylic acid groups. Mn has been detected by SEM–EDX analyses of siderite and ankerite grains in coals from worldwide locations [40].

Modes of occurrence. Most of the Mn in coal, especially bituminous coals, occurs in solid solution in the carbonate minerals siderite and ankerite. In low-rank coals, lignites and brown coal, a substantial part of the Mn may be organically associated.

Level of confidence: 8. Both direct and indirect information are in agreement with the modes of occurrence described above.

Anticipated coal cleaning behavior. Mn behaves largely as would be expected in commercial coal cleaning operations. Fonseca and others [16] report that 75–95% of the Mn was removed from the three coals that they studied. Cavallaro et al. [45] removed 42% of the Mn from northern Appalachian coals, 77% from southern Appalachian coals, 72% from Midwest coals, and 64% from western coals. Junk et al. [15] removed from 72% to 92% of the Mn from 4 coals and 39% from a fifth coal.

Ford and Moses [17] removed 65% and 81% of the Mn from the two coals in their study. Despite Mn reductions of less than 50% from some coal samples, it appears that Mn reductions of around 75% should be anticipated.

10. Mercury (Hg)

Mercury offers numerous challenges in determining its modes of occurrence. Mercury is present in coal in relatively low concentrations, generally less than 0.5 ppm, and because it is highly volatile, it cannot be determined in the coal ash. Because of these difficulties, there are relatively little data on the behavior and modes of occurrence of Hg in coal.

The laboratory float–sink data and analysis of minerals separated from coal indicate a clear inorganic association for Hg [6], although some authors have suggested the possibility of an organic association [52].

Finkelman et al. [11] found that Hg in coal was volatilized at temperatures as low as about 150°C. They were unable to determine the response of Hg to various solvents.

The association of Hg with pyrite, especially late-stage (epigenetic) pyrite, has been demonstrated by several workers cited in Finkelman [6]. On the basis of extensive studies of Soviet coals, Dvornikov [53, 54] proposed that Hg occurs as HgS, metallic Hg, and organometallic compounds. The coals studied by Dvornikov had up to 20 ppm Hg, so that the suggested modes of occurrence may be typical of coals that have experienced Hg mineralization [9]. Rare micrometer-sized grains of Hg-sulfides and selenides have been found in US coals [40]. Cahill and Shiley [55] found Hg in sphalerite from Illinois Basin coals.

Mercury and As appear to have similar behaviors, both in their distribution in raw coal and during coal cleaning [6]. However, the percentage of Hg removal is generally less than that of As [16], perhaps due to the occurrence of Hg in difficult-to-remove accessory sulfides and selenides.

Modes of occurrence. Much of the Hg in coal is in solid solution in pyrite. Epigenetic pyrite probably has substantially greater Hg contents than does the early-stage (syngenetic) pyrite, such as framboidal pyrite.

Level of confidence: 6. Most of the data are indirect, but there is a fairly consistent correlation in the behavior of Hg and As.

Anticipated coal cleaning behavior. The data on removal of Hg from coal indicate that 25–50% could be removed by conventional coal cleaning procedures. The range of Hg removal may be very broad. For example, in one coal sample studied by Akers and Dospoy [36] no mercury was removed, and in another, more than 75% was removed. The failure to remove Hg from the one sample with the lowest Hg content may have been due to an unusual mode of occurrence (perhaps an organic association) or to analytical problems. The data of Junk et al. [15] revealed similarly quixotic behavior of Hg; they removed 77% and 85% of the Hg from two coal samples, and found a 192% enrichment in a third sample. Cavallaro et al. [45] removed 22–48% of the Hg from four coal samples.

11. Nickel (Ni)

There is a great deal of uncertainty about the modes of occurrence of nickel in coal. Laboratory float–sink results, correlation of Ni content to ash yield, and other indirect methods indicate that Ni may be associated with both the organic and inorganic components of coal [6].

As much as 55% of the Ni was in an exchangeable form in the 10 coal samples studied by Finkelman et al. [11]. They concluded that some of the exchangeable Ni was associated with organic functional groups. They found no indication of hydrofluoric-acid- or of nitric-acid-leachable Ni, an indication that little Ni is associated with silicates or sulfides. They also found that 10–30% of the Ni was volatilized at 550°C and surmised that this Ni was organically associated.

Swaine [56] reviewed the literature on Ni in coal and concluded that there is much evidence to link Ni with the organic constituents, but there is no direct evidence as to the type of association.

There is, however, some direct evidence for inorganic associations of Ni in coal. Several nickel sulfide minerals (millerite (NiS), linnaeite (Co, Ni)₃S₄, ullmannite (NiSbS)) have been reported from coal, and traces of Ni have been reported in galena, sphalerite, pyrite, clausthalite, and other minerals in coal [6]. In lignites from the Kosovo basin, Yugoslavia, Ruppert et al. [57] found that approximately 10% of the Ni was organically associated and that most of the inorganic Ni occurred in spinels.

Modes of occurrence. The evidence indicates that, in many coals, substantial amounts of Ni may be organically bound. The inorganically bound Ni appears to be largely associated with sulfides.

Level of confidence: 2. Direct evidence for the mode of occurrence of Ni in coal is lacking, and the indirect evidence appears contradictory.

Anticipated coal cleaning behavior. It is difficult to anticipate the behavior of Ni in light of the wide range of behavior it has exhibited during coal cleaning studies. Nickel displays a greater variation in coal cleaning behavior than any of the other elements. This is supported by the wide variation in the percent reduction, both within and between the different studies. For example, Akers and Dospoy [36] removed 82% of the Ni from one coal sample and 18% from another. Cavallaro et al. [45] removed 23% and 32% of the Ni from two coal samples and 2% from two other coal samples. Junk et al. [15] found a range of 20–76% removal. This wide range in cleaning behavior may be attributable to difference in the modes of occurrence of Ni. In some samples, Ni may be predominantly associated with the organic constituents and would not be amenable to removal by physical coal cleaning procedures. In other coal samples, Ni may be associated primarily with the sulfides and could be removed during coal cleaning.

12. Selenium (Se)

Results from laboratory float–sink experiments are equivocal. In some experiments selenium is concentrated in the float fraction, in other experiments Se is

concentrated in the sink fraction, and in yet other experiments Se shows no preference [6].

Selenium from 10 coal samples, studied by Finkelman et al. [11], was largely volatilized at 550°C. However, they found that Se in these coals essentially was insoluble in five different solvents. They concluded that the combustion and leaching behavior of Se was consistent with an organic association.

Selenium can substitute readily for sulfur in many sulfide minerals. Several reports cite the occurrence of Se in pyrite extracted from coal [28, 58, 59]. Selenium also occurs in micrometer-size crystals of lead selenides, a ubiquitous accessory phase in most coals [46]. Selenium has been detected in several other sulfide minerals (especially galena) in coal [6] and in several other forms [9].

In a detailed study of selenium in coal and overburden in the Powder River basin by Dreher and Finkelman [60], it was determined that Se, present at the ppm level, occurred in at least six different forms. They found that most of the Se (70–80%) was associated with the organics, 5–10% was associated with pyrite, 1–5% was in accessory sulfides and selenides, and about 10% occurred in water-soluble and in ion-exchangeable forms.

Modes of occurrence. The data indicate that the bulk of the Se in most coals is associated with the organic constituents. A small but important part of the Se is associated with pyrite and, to a lesser extent, with accessory minerals such as clausthalite and galena.

Level of confidence: 8. The high level of confidence is justified by consistent results from different coals and from different procedures. The quantitative assessment on the Powder River basin coal also lends confidence to this interpretation.

Anticipated coal cleaning behavior. The commercial coal cleaning studies report a wide range of values for the removal of Se. These studies report that the % removal varies from zero to 80, with most values less than 50% [15–17, 36, 44]. This is consistent with the observed modes of occurrence of Se. Because as much as 80% of the Se in most coals appears to be organically bound, physical coal cleaning will not be effective in reducing the Se concentration.

13. Conclusions

A large body of information is available on the modes of occurrence of elements in coal, although much of this information is derived from indirect methods. Because of the speculative nature of the information and because many elements have several different modes of occurrence, much of the information in the literature appears to be inconsistent and contradictory. Nevertheless, for many elements in coal (Table 1) there is sufficient reliable information available from which to draw reasonable conclusions about the modes of occurrence and to predict their behavior. From information on the modes of occurrence, we can project the behavior of the element during coal cleaning and thus anticipate the degree of reduction.

There is a need for additional information on the modes of occurrence of some elements in coal, especially elements that present potential environmental hazards such as Sb, Be, Cr, and Ni.

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