

**GEOCHEMISTRY OF SELENIUM RELEASE FROM
THE ELK RIVER VALLEY COAL MINES**

by

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ABSTRACT

Elevated levels of selenium (Se) were detected downstream from the five open pit coal mines in the Elk River Valley, British Columbia. Se is an essential nutrient but, in excessive amounts, it may cause teratogenic deformities and reproductive failure in fish and birds. To provide mine operators in the Elk River Valley with the information needed to assess the risk of Se release from waste rock and plant refuse a study of Se's modes of occurrence in the strata disturbed by mining and the geochemical mechanisms of its release was conducted.

The mineralogical associations of Se were studied in 16 samples representative of the different types of material at the sites. Methods used to characterize sample mineralogy include X-ray diffraction, scanning electron microscopy, sequential extractions and heavy liquid separation. Se had both organic and inorganic associations in all lithologies tested, but sulphides, in particular pyrite, were indicated as the main Se-bearing component in the studied lithologies. The amount of organic matter in the materials appeared to play a role in determining the degree of Se enrichment in sulphides, with materials high in organics containing sulphides with less Se substitution.

Humidity cells were used to determine the rate of Se release from coal, interburden, foot wall, parting and coarse refuse. The rate of Se release was not proportional to the total amount of Se in the sample, suggesting that mineralogical factors, such as texture, pyrite liberation and porosity, determine the rate of Se oxidation. A strong positive correlation between the amount of Se and sulphate in leachate from the humidity cells, suggested that sulphide oxidation is likely the source of Se being released into tributaries of the Elk River.

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1.0 INTRODUCTION

1.1 SELENIUM IN THE ELK RIVER VALLEY

In 1995, selenium (Se) concentrations as high as 25 µg/L were detected during a water quality assessment for an effluent permit amendment at one of the five coal mines in the Elk River Valley. This was well in excess of the current Canadian water quality guideline of 1 µg/L total Se (CCME, 1999), which includes both dissolved and particulate-bound Se. This prompted a review of water quality data collected between 1984 and 1994 from the mouth of the Elk River, 65 km downstream of the coal mines. Reexamination of the data revealed that total Se had increased from 0.5 µg/L to 2.0 µg/L over that period (Wipperman and Webber, 1997). These values were the highest among those recorded at sampling sites on 30 rivers across British Columbia over the same time period. Se is an essential trace element required for the elimination of tissue damaging free radicals. However, in excessive amounts, Se may cause reproductive failure and teratogenic deformities in fish and birds. A more detailed study of Se in the Elk River and its tributaries was thus undertaken (McDonald and Strosher, 1998).

McDonald and Strosher (1998) surveyed Se levels in the water column, sediment and biota. The study indicated that Se concentrations in unfiltered water samples from waterways upstream from the mines were consistently below the 1 µg/L detection limit, while those in the major rivers downstream from the mines ranged between 2 and 20 µg/L. The highest concentrations were recorded at sampling sites closest to the mines. 92 % of the Se was in the dissolved form (McDonald and Strosher, 1998). Se levels remained relatively constant throughout the year despite a tenfold increase in stream flow during the spring, indicating that proportionally greater quantities of Se were mobilized during this period. In sediment, Se concentrations were consistently below the 5 mg/kg provincial criteria for the protection of aquatic wildlife (Nagpal et al., 1995) likely due to the fast flow of water in the Elk River and its tributaries. This limits the extent of Se bioaccumulation as it minimizes opportunities for plants and microorganisms to fix

Se from sediment. Se concentrations in algae, aquatic insects and fish tissues downstream from the mines were nonetheless 2 to 5 times greater than at the reference sites. Se levels in some of the westslope cutthroat trout caught below the Fording River mining operations exceeded the published toxic effects threshold of 8 and 12 $\mu\text{g Se/g}$ dry weight for muscle and liver respectively (McDonald and Stroscher, 1998; Lemly, 1993). Although McDonald and Stroscher's (1998) study revealed no toxicological effects in the Elk River's cutthroat trout population, there is a need to identify the source of the Se and to better understand the biogeochemical cycling of Se in this environment in order to determine the potential hazard to aquatic life.

In 1999, the Ministry of Energy and Mines conducted a comprehensive geochemical study of Se levels in all exposed strata in the coal-bearing Mist Mountain Formation at the Elkview, Line Creek, Coal Mountain, Greenhills and Fording mines (Ryan and Dittrick, 2000). Results from this study and data from earlier studies (Goodarzi, 1988; Grieve and Goodarzi, 1994) show that the lithologies closely associated with the coal, i.e. partings, hanging wall and foot wall, contain the highest amounts of Se. The data show that Se is found at levels of approximately 1.1 mg/kg in the sand- and siltstone layers between the coal seams (interburden). Coal seams contain, on average, 1.9 mg/kg Se while material immediately above and below the seams (hanging wall and foot wall) contains 4.2 mg/kg Se and bands of mineral matter in the seams (partings) 3.2 mg/kg. Estimates by Ryan and Dittrick (2000) suggest that 80% of the Se is found in the interburden, 6 to 20% in the coal and 5 to 10% in hanging wall, foot wall and parting materials.

The extraction and combustion of coal has been associated with Se mobilization in numerous instances. Specific examples include elevated Se levels detected in groundwater at a surface coal mine in Wyoming (Dreher and Finkelman, 1992) and in runoff from fly ash dumps in Texas and North Carolina (Shepard, 1987). Studies by Naftz and Rice (1988) and Dreher and Finkelman (1992), looking at the modes of occurrence of Se in coal, suggest that the bulk of it appears to be associated with the organic fraction. Se has also been shown to substitute for sulphur in sulphides

present in coals (Clarke and Sloss, 1992; White et al., 1989). When assessing Se mobilization by surface- or groundwater from coal mines, the critical factor is Se's mode of occurrence in rocks adjacent to coal seams rather than in coal seams. There have been no studies looking at the modes of occurrence of Se in these lithologies. Information about the rate of Se release from these materials is also lacking. The aim of this thesis was to address these gaps in our understanding of Se mobilization from coal-bearing geological formations in order to identify potential sources of Se to the Elk River.

This study had three main components. The first focused on sample mineralogy. Coal, parting, hanging wall, foot wall, interburden and refuse samples were characterized by means of x-ray diffraction and scanning electron microscopy, as well as by chemical analyses. The second section explored the modes of occurrence of Se in the same set of samples using a four-step sequential extraction procedure and heavy liquid separation. The latter was used to determine the relative importance of organic matter- and sulfide-associated Se since this could not be effectively achieved with the sequential extractions. Lastly, humidity cells were used to investigate the rate of Se release from coal, parting, foot wall/hanging wall, interburden and refuse over the course of a twenty-week leaching period. Together, results from these experiments were used to establish the amount of Se in each of the different fractions and to highlight potential trends in geochemical factors influencing Se release.

1.2 OBJECTIVES

The objectives of this study were to:

- Identify Se-bearing mineralogical components in the Mist Mountain Formation.
- Evaluate the rate of Se release from the different lithologies, so as to pinpoint potential sources of Se to the tributaries of the Elk River.
- Suggest possible biogeochemical mechanisms of Se mobilization.
- Provide mine operators in the Elk River Valley with information needed to assess the risk of Se release from waste rock and plant refuse.

2.0 SELENIUM IN THE ENVIRONMENT

2.1 BIOGEOCHEMICAL CYCLE OF SELENIUM

2.1.1 Chemical Properties of Selenium

J.J Brezelius discovered Se in 1818 as a residue from the oxidation of chalcopyrite in producing sulfuric acid. Atomic number 34, Se is located between sulfur and tellurium in group VIA of the periodic table and between arsenic and bromine in the fourth period. A list of the key chemical and physical properties of Se and sulphur (S) is provided in Table 2.1.

Table 2.1 Chemical Properties of Sulphur and Selenium
(Adapted from Kudriavtsev, 1974)

	S	Se
Atomic weight	32.06	78.96
Atomic number	16	34
Naturally occurring isotopes	^{32}S , ^{33}S , ^{34}S , ^{36}S ,	^{67}Se , ^{74}Se , ^{77}Se , ^{78}Se , ^{80}Se , ^{82}Se
Covalent radius	1.04	1.17
Ionic radius (Å)	1.86	1.98
Ionization potential, eV	10.36	9.75
Electron affinity, eV	2.33	4.21
Electronegativity	2.53	2.55
Oxidative states	-2, 0, +2, +3, +4, +6	-2, 0, +4, +6

There is considerable overlap of the biogeochemical cycles of S and Se due to the similarity of their physico-chemical properties. Se is readily taken up by organisms via channels intended for S (Milchunas & Lauenroth, 1984) and readily substitutes for S in sulphides. There are, however, a few important differences between Se and S chemistry that affect its occurrence and mobility. Se is less volatile than S and it does not share S's tendency to catenate, meaning that it will not form compounds like S's thiosulphate ($\text{S}_2\text{O}_3^{2-}$) (Herring, 1990). Se compounds are more easily reduced than their S analogs (Zehr and Oremland, 1987). Hence, S is more readily mobilized than Se in oxidizing environments and the co-occurrence of similar S and Se compounds can lead to the oxidation of S via the reduction of Se.

Se has four oxidation states: selenide (-2), elemental Se (0), selenite (+4) and selenate (+6), all four of which can be found in soils and sediment. The partitioning between these species is, in large part, defined by the redox conditions of the depositional environment and, to a certain extent, by microbial activity and the availability of complex-forming species (McNeal and Balistrieri, 1989). Figure 2.1 illustrates the fields of stability of predominating solid and dissolved species of Se. The area enclosed within the dashed line shows the range of Eh-pH conditions commonly found in coal swamps. Under these conditions, Se would be found in sediment as Se^0 or as Se^{-2} or in solution as Se^{+4} .

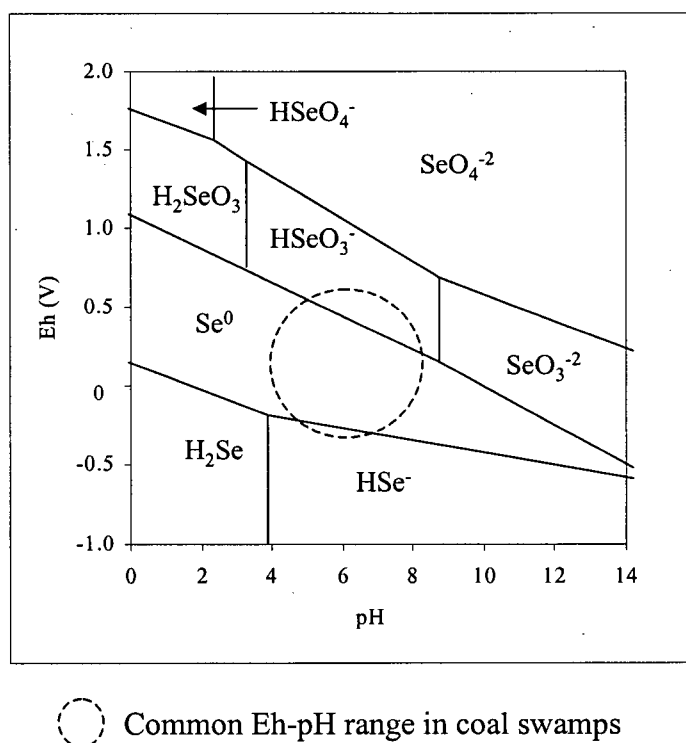


Figure 2.1 Eh-pH Diagram for Se at 25°C, 1 bar pressure and $I = 0$ for a dissolved Se activity of 10^{-6} mol/L (Adapted from Séby et al., 2001)

Se^{-2} is the most reduced form of Se and is found in compounds such as H_2Se and Fe_2Se . Due to the similarity of the ionic radii of selenide ions (1.98 Å) and sulphide ions (1.86 Å), Se^{-2} readily substitutes for S^{-2} in sulphide minerals (Fischer and Zemann, 1978). Se forms selenides with Ag,

As, Au, Bi, Cd, Co, Cu, Fe, Hg, Ni, Pb, Sb, Tl and Zn (Fischer and Zemmann, 1978). The amount of substitution varies, occurring in decreasing order in chalcopyrite (CuFeS_2), arsenopyrite (FeAsS_2), sphalerite (ZnS), pyrite (FeS_2), pyrrhotite (Fe_{1-x}S) and galena (PbS) (Lakin, 1973). The Se concentration in sulphides averages 88 mg/kg (Badalov et al., 1970), but ranges from 0 to 15 mg/kg in PbS to more than 2000 mg/kg in some CuFeS_2 samples (Fleischer, 1959). Metallic selenides are sparingly soluble (Elrashidi et al., 1987) and are not rapidly oxidized (Masscheleyn et al., 1990).

Elemental Se is allotropic and exists in either an amorphous or crystalline state (Kudriavtsev, 1974). Amorphous selenium is liquid at temperatures above 230°C . Below 31°C elemental Se is a hard and brittle glass. Naturally occurring amorphous Se is transformed into the hexagonal crystalline form at 70°C , whereas man-made amorphous Se crystallizes at 60°C . The three crystalline forms of Se are alpha-monoclinic, beta-monoclinic, and hexagonal. Both monoclinic forms are red in colour, but the alpha form consists of flat hexagonal and polygonal crystals whereas beta-monoclinic ones are needle-like or prismatic. Hexagonal selenium is grey or black and is composed of spiral Se chains. This is the most stable form of elemental Se with both alpha and beta monoclinic Se converting to the hexagonal form at temperatures above 110°C . Elemental Se is sparingly soluble and both its oxidation and reduction kinetics are slow (Herring, 1990).

In its +4 oxidation state, Se exists as crystalline Se dioxide (SeO_2), selenious acid (H_2SeO_3), or selenite (SeO_3^{2-}) salts. Se^{+4} is readily reduced to elemental Se in the presence of reducing agents or certain bacteria (Herring, 1990). When amorphous selenium is oxidized in the presence of water, H_2SeO_3 is formed. The latter is a weakly dibasic acid that frequently acts as an oxidizing agent. Se^{+4} adsorbs readily to hydrous and ferric manganese oxides (HFMO) as SeO_3^{2-} (Ballistrieri and Chao, 1987). Naturally occurring selenite salts include those formed with Ag, Ba, Be, Ca, Cd, Cu, Fe, Hg, K, Mg, Na, Ni, Pb and Zn (Kudriavtsev, 1974).

At high redox potentials, Se^{+6} predominates. Potassium and sodium selenate (SeO_4^{2-}) salts are rare, but do occur in nature (Emerick and DeMarco, 1990). They are appreciably more soluble than the corresponding sulphate compounds (Séby et al., 2001) and do not bind to HFMO as readily as selenites (Ballistrieri and Chao, 1987). Se^{+6} is thus common in aqueous environments and is readily available for uptake by plants and microorganisms. The conversion of selenates to the less stable selenites is very slow (Bar-Yosef and Meek, 1987). Selenium reacts with halogens to form gaseous halides in which Se^{+4} or Se^{+6} are found (i.e., SeF_6 , SeF_4 , SeCl_4 , SeBr_4) (Bar-Yosef and Meek, 1987). Selenium halides form acid complexes with the halogen derivatives of acids and with some of their salts.

Se occurs in several organic forms, including dimethylselenide and dimethyldiselenide, organic selenides, seleno-carbohydrates, seleno-amino acids and selenopeptides (Herring, 1990). The two methylated forms are volatile. A number of these organic compounds are synthesized in plants, while others are produced as by-products of microbial metabolic processes. Organo-selenium compounds in soil and sediment are readily available to plants (Fleming, 1962).

2.1.2 Selenium Occurrence

Taylor (1964) estimated the crustal average of Se to lie between 0.05 and 0.1 mg/kg (Table 2.2). Se concentrations of in sedimentary rocks range from below 0.1 mg/kg in sandstones and limestones to 0.6 mg/kg in shales, though concentrations as high as 100 mg/kg have been observed in some shales (Herring, 1990). Rosenfeld and Beath (1964) found concentration of Se ranging from 1 to 300 mg/kg in phosphatic rocks in the North Western United States, but did not observe a direct correlation between Se and P_2O_5 concentrations.

Table 2.2 Occurrence of Se in Various Lithologies

Material	Range (mg/kg)	Mean (mg/kg)	Reference
Crustal	0.05-0.1	-	1
Sandstones	<0.1-1.7	0.10	3
Limestone	<0.1-7.4	0.22	3
Igneous rocks	0.09-1.08	0.35	2
Shales	<0.1-12	0.53	3
Mudstones	0.4-0.6	-	4
Oil	0.01-1.4	-	4
Coal (global)	<0.1	2.15	4

¹ Taylor, 1964² Neal, 1995³ Connor and Shacklette, 1975⁴ Coleman et al., 1993

Swaine (1990) includes Se among the trace elements in coal of greatest environmental concern, along with arsenic, boron, cadmium, mercury, molybdenum and lead. It is the most enriched trace element in coal (Coleman et al., 1993; Spears and Zheng, 1999). Se can be found in coal at up to 82 times its crustal concentration (US National Committee for Geochemistry, 1980). The reduction of soluble selenate and selenite to selenide under low oxygen conditions created by the decomposition of organic matter in coal swamps is likely responsible for the high Se levels observed in coal and shales (Dale, 1996). The global average Se content of coal is 2.15 mg/kg (Coleman et al., 1993). Se concentrations in American coals average 3.3 mg/kg (Pillar et al., 1969) while those in the Mist Mountain Formation of the Elk River Valley average 1.9 mg/kg (Ryan and Dittrick, 2000). The highest reported concentration of Se in coal is 8400 mg/kg in a sample from a mine in China (Yang et al., 1983). The mode of occurrence of the Se in this sample was not specified.

Se has both organic and inorganic associations in coal (Figure 2.2). Like S, Se can be covalently bound within the molecular structure of organic material or ionically bound to its surface. Covalent bonds, such as those formed between C and Se, involve interatomic sharing of electrons, while ionic bonds, like those between Se and O in hydroxyl or carboxyl groups of organic matter, involve the complete transfer of one or more electrons from one atom to another.

Alternatively, Se may substitute for S in sulphide minerals, occur as selenides or, in the form of selenate or selenite, be bound to aluminosilicates or hydrous ferric and manganese oxides (HFMO).

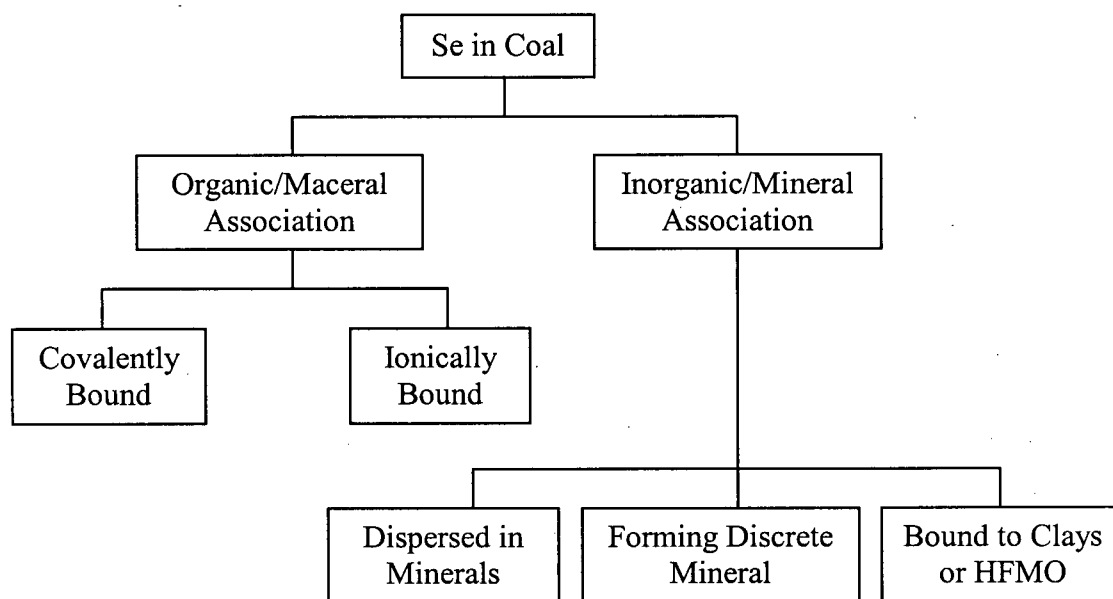


Figure 2.2 Proposed Classification Scheme for Se Occurrence in Coal
(Adapted from Dale, 1996)

2.1.2.1 Selenium Associated with Organics

Combustion experiments by Finkelman et al. (1990) showed that during ashing at 500°C, 80-95% of Se in Argonne Premium Coal samples volatilized. Combining results from high temperature ashing with those from sequential extraction and heavy liquid separation experiments, Dreher and Finkelman (1992) tried to establish the relative importance of inorganic and organic associations of Se in coal. Noting its high volatility and its low susceptibility to leaching by water or weak acids, they concluded that the bulk of the Se was associated with the organic fraction (Table 2.3). Coleman et al. (1993) reviewed data on 9000 U.S. coals and found a positive correlation between Se concentration and total S, pyritic S and organic S. In non-marine coals, Se levels correlated strongly with ash yield, suggesting that inorganic associations were of primary importance.

**Table 2.3 Distribution of Se in Coal from the Powder River Basin, Wyoming
(From Coleman et al., 1993, adapted from Dreher and Finkelman, 1992)**

Phase with which Se is associated	% of Total Se in Coal
Water soluble	0-15
Ion exchangeable	0-15
Pyrite	5-10
Other sulfides and selenides	1-5
Organics	>60

It should be noted that when using heavy liquid separation, the term “organically associated” does not necessarily imply that a chemical bond with organic matter exists. A portion of the trace elements found in the light (specific gravity $<1.5 \text{ mg/cm}^3$) organic fraction may be bound to micron-sized inorganic particles entrapped in the organic matter (Swaine, 1990; Palmer et al., 1990). In the context of this study though, the term “organically associated” will be used to designate elements or compounds covalently or ionically bound to organic matter, excluding any mineral matter that may be intimately associated with it.

Before considering how Se is associated with coal, a basic understanding of the composition of coal itself is required. The process of coalification involves a series of bio- and physico-chemical transformations that result in the progressive decrease of moisture, volatiles, oxygen and hydrogen content of organic matter deposited in the coal swamp. Coal rank is defined by the degree of coalification, increasing from peat, lignite, sub-bituminous, bituminous through to anthracite (Stach et al., 1982). Biochemical transformations, often bacterially-mediated, end at the rank of sub-bituminous coal when humic colloids have polymerized. Increased pressure and heat caused by deep post-depositional subsidence and/or tectonic activity further increases the aromaticity of the organic molecules. Coal organic matter thus consists of a complex matrix of aromatic structures with a variable number of aliphatic groups attached as side chains or as links between aromatic nuclei (Stach et al., 1982). Macerals are microscopic units in coal analogous to minerals in rocks. They lack the ordered structure of minerals and their physico-chemical

properties vary with coal rank. They are divided into three groups based on their parent material. Vitrinite generally stems from woody plant material and liptinite from spores, cuticles and resins, while inertinite forms from vegetation that has been oxidized prior to coalification. Demir and Harvey (1991) found that both S and Se tend to be enriched in vitrinite macerals. Ryan and Dittrick (2000) hypothesized that this might be due to the volatilization of Se from inertinite macerals during charring of the vegetation.

Noting Se's tendency to substitute for S, much can be deduced about the occurrence of Se in coals by looking at the information available on S. Considering first organic associations, S can be incorporated into phenolic sulphates and sulphated polysaccharides by ester bonds and into amino acids, cysteine and methionine, by carbon bonds (Casagrande and Siefert, 1977). Ester sulphate bonds are readily reduced to H_2S , but mercapto (-SH) groups persist to the bituminous stage of coalification (Saxby, 1973). A second type of organic complexing involves the formation of ionic bonds between selenate or selenite molecules and carboxylic acid groups on the surface of organic matter. For such bonds to form, the pH must be low enough that carboxyl groups will be protonated and bear a positive charge. A more detailed explanation of pH-dependent charge is provided in section 2.1.2.3. Both Se incorporated into the organic matrix and Se bound to its surface contribute to total Se during the gelification-humification stage of coalification. The importance of surface-bound Se decreases with increasing rank, since carboxylic acid groups do not persist much beyond the lignite stage (Schafer, 1984).

2.1.2.2 Selenium Associated with Sulphides

Sulphides in coals are found in a range of forms and sizes and may be of syngenetic or epigenetic origin. Studying coal samples from mines in the United Kingdom, Spears and Zheng (1999) found a strong positive correlation between pyrite content and Se, As, Mo, Sb and Tl concentrations. Pyrite is the most common sulphide in coal, but marcasite is also frequently found in them (Spears et al., 1994). The amount of pyrite in coal depends on the availability of S and Fe

and the intensity of sulphur-reducing bacterial activity. Fe is introduced to the system through the weathering of silicate minerals and the influx of Fe^{2+} and Fe^{3+} ions with groundwater. In most coals, the occurrence of siderite (Fe_2CO_3) provides evidence of iron availability (Spears et al., 1994). Casagrande and Nug (1979) suggest that the breakdown of plant and animal protein during coalification supplies the S needed for pyrite formation.

Se has been detected in pyrite grains using a number of different methods, including X-ray fluorescence (White et al., 1989), proton-induced gamma ray/X-ray emission (PIXE) microanalysis (Hickmott and Baldrige, 1995), instrumental neutron activation analysis (INAA) (Zodrow and Goodarzi, 1993) and scanning electron microscopy (SEM) (Galbreath and Brekke, 1994). Leutwein (1978) notes that sedimentary sulphides tend to contain less Se than those of magmatic origin. Magmatic sulphides form at high temperatures that favour lattice expansion and isomorphous substitution. He indicates that sedimentary sulphides contain between 10 and 20 mg/kg Se and sulphides of magmatic origin between 50 and 100 mg/kg. Wandless (1957), however, found concentrations as high as 70 mg/kg Se in British coals and Rosenfeld and Beath (1964) reported a Se concentration of 548 mg/kg in Wyoming coal pyrite concentrates, suggesting that the range proposed by Leutwein (1978) may not adequately reflect the heterogeneity of sedimentary depositional environments.

A number of studies have identified discrete Se minerals in coal, though these tend to be quite rare as Se substitutes readily for S in sulphides. Wandless (1959) and Minkin et al. (1984) found minute selenide inclusions in pyrite concentrates extracted from British and Indiana coals respectively. Pyrite samples from bituminous coal studied by Minkin et al. (1984) contained approximately 2 mg/kg Se, but electron microprobe revealed isolated points containing as much as 3000 mg/kg Se. Finkelman (1981) found clausthalite (PbSe) in Appalachian coals, while Goodarzi and Swaine (1993) documented the occurrence of both PbSe and ferroselite (FeSe_2) in coals from Western Canada. A sequential extraction experiment by Dreher and Finkelman (1992)

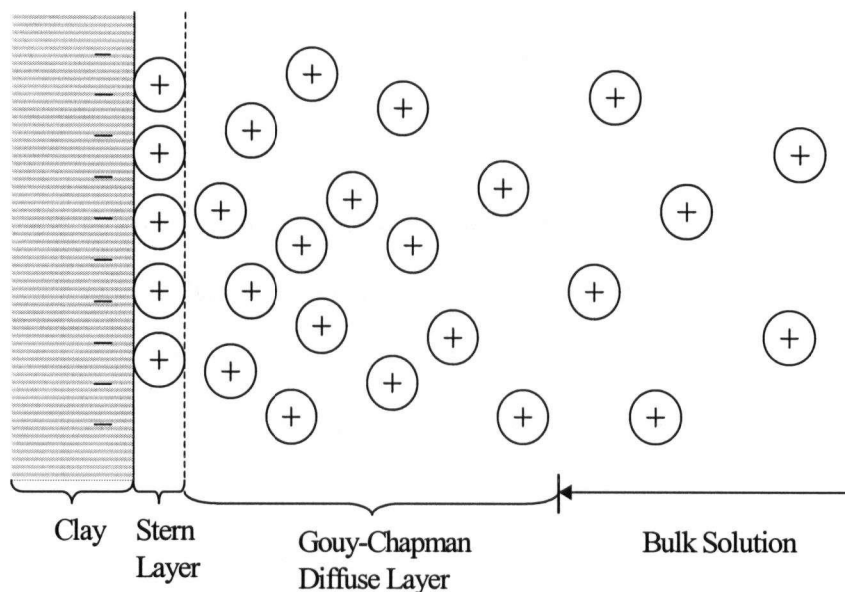
indicates that these Se minerals make only a minor contribution to total Se in coals. The oxidation of Se-bearing pyrite and selenides generates selenite, which is soluble and binds readily to clay minerals (Frost and Griffin, 1977) and HFMO (Balistrieri and Chao, 1987).

2.1.2.3 Selenium Associated with Clay Minerals

Clay minerals are the most abundant minerals in coals and associated sedimentary rock (Dale, 1996). Clay minerals are introduced into coal swamps by surface water. Those commonly found in coal include kaolinite, illite, montmorillonite, vermiculite and chlorite. They are derived from the weathering of feldspars, micas and ferromagnesian minerals and consist of different combinations of tetrahedral silica sheets and octahedral alumina sheets bound by shared O^{2-} ions occupying the vertices of the tetrahedra and octahedra (McBride, 1994). The 1:1 clays, like kaolinite, are composed of octahedral and tetrahedral sheets stacked one upon the other. In illite and montmorillonite, both 2:1 clays, an octahedral sheet is sandwiched between two tetrahedral sheets. Illite has K^+ ions trapped between the silicate layers preventing water from penetrating into the matrix and causing swelling. In montmorillonite and vermiculite the interlayer K^+ ions are replaced by hydrated Mg^{2+} ions. Both have a high specific surface area and cation exchange capacity (CEC) relative to kaolinite and illite. CEC, defined as the quantity of cations that can be reversibly adsorbed per unit weight of mineral, is generally expressed in terms of meq/100 g (McBride, 1994). Chlorite has a hydroxide sheet between the 2:1 silicate layers and is thus termed a 2:1:1 clay. The hydroxide sheet stabilizes chlorite structure impeding any swelling.

Clay minerals have two types of charge, one permanent and the other pH-dependent. The permanent charge comes from the substitution of cations of similar ionic radii but different charge. Al^{3+} substitutes for Si^{4+} in the tetrahedral layers while Mg^{2+} or Fe^{2+} replace Fe^{3+} in the octahedral layers (McBride, 1994). Though common in 2:1 clays, relatively little isomorphous substitution occurs in 1:1 clays. This type of substitution confers a negative surface charge to clay minerals. This attracts counterions and repels co-ions leading to the formation of an electric

double layer (Gouy, 1910; Chapman, 1913). According to Stern (1924), the electric double layer is composed of the Stern layer, where ions oscillate about fixed adsorption sites, and the Gouy-Chapman layer, a diffuse band of cations extending several hundred nanometers from the mineral surface. The diffuse nature of this layer results from the competition of electrostatic and diffusion forces (Figure 2.3).



**Figure 2.3 A Schematic Presentation of Cations in the Electric Double Layer
(Adapted from Yariv and Cross, 1979)**

The thickness of the Gouy-Chapman diffuse layer depends on the magnitude of the surface charge and the concentration of electrolytes in solution. Though cations are attracted to the surface, there is also a tendency for them to diffuse away from the clay surface into the bulk solution where the cation concentration is lower. The greater the ion concentration in solution, the lower the tendency of cations to diffuse away from the clay surface.

Ions in the Stern layer may form inner- or outer-sphere complexes. In inner-sphere complexes, ions form covalent bonds with hydroxyl groups on the surface of the clay mineral. Outer-sphere complexes, on the other hand, consist of hydrated ions held to the mineral surface by ionic bonds.

Selenite and selenate form different types of bonds at clay surfaces (Figure 2.4). Geering et al. (1968) suggest that selenite forms inner sphere complexes like those formed by ortho-phosphate. Binding to ligands at the surface, it becomes essentially nonexchangeable. Selenate does not adsorb specifically. Like sulfate and nitrate, selenate tends to form weak outer-sphere complexes. It is therefore easily replaced by other exchangeable anions and is more likely to be found in solution (Hayes et al., 1987).

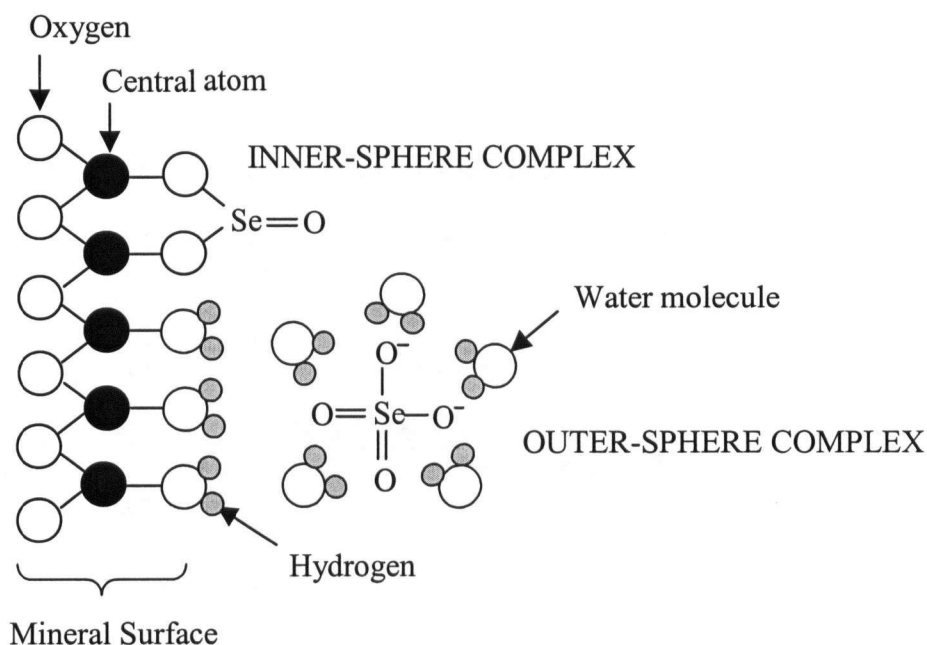


Figure 2.4 Inner- and Outer-Sphere Complexes Formed by Se Oxyanions

The second type of charge, pH-dependent charge, is of minor importance relative to the charge conferred by isomorphous substitution (Taylor, 1987). At the surface of clay minerals, unsatisfied charges on broken bonds are balanced by the adsorption of cations or anions. The point of zero charge (PZC) is the pH at which the net surface charge is zero. Below the PZC, the surface bears a positive charge and is capable of attracting anions, above it, the surface bears a negative charge (Figure 2.5). Clay minerals have PZC values between pH 2.5 and 4.5 (Förstner and Wittmann, 1979). Charge on acidic functional groups in organic matter is also pH-dependent.

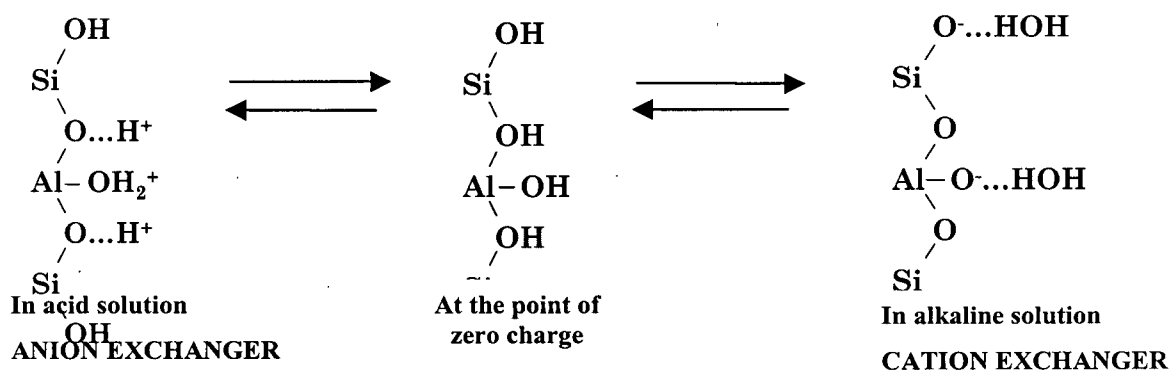


Figure 2.5 pH-Dependent Charge on Broken-Bond Aluminosilicate Surfaces
(Adapted from Yariv and Cross, 1979)

2.1.2.4 Selenium Associated with Hydrous Ferric and Manganese Oxides

Selenite adsorbs readily to hydrous ferric and manganese oxides (HFMO) (Balistrieri and Chao, 1987). HFMO are secondary oxides that generally occur as coatings on mineral surfaces or as fine discrete particles. Crystalline HFMO consist of hexagonal or cubic structures with Fe^{3+} , Mn^{4+} or Mn^{2+} in the central position surrounded by O^{2-} and/or OH^- anions. Their structure is determined by the degree to which they share corners, edges or faces. Common crystalline HFMO include goethite ($\alpha\text{-FeOOH}$), lepidocrocite ($\gamma\text{-FeOOH}$), manganite (MnOOH) and birnessite ($\text{Na}_4\text{Mn}_{14}\text{O}_{27} \cdot 9\text{H}_2\text{O}$). Due to the variability of the chemical environment in which HFMO form and their ability to incorporate foreign ions into their structure, these minerals frequently differ both in composition, crystallinity and morphology from pure specimen minerals. HFMO lacking a well-defined crystalline structure are termed "amorphous" and account for much of the HFMO in soils and sediment. They play an important role in the retention and release of contaminants such as heavy metal ions and soil nutrients due to their relatively large surface area. Many ions form covalent bonds with ligands on HFMO surfaces (Veiga et al., 1991). The surfaces of HFMO develop a limited positive or negative charge depending on variations in pH. Fe oxides have PZC values in the range of pH 7 to 9. Mn oxides tend to have a more complex mineralogical structure

than Fe oxides and have PZC values between 1.5 and 4.6 (McBride, 1995). Redox conditions, the amount of the oxide present, its degree of crystallinity and the presence of organic matter will also affect the relative importance of Mn and Fe oxides as trace element scavengers.

2.1.3 Cycling of Selenium

2.1.3.1 Major Global Fluxes

Estimates of major Se inventories from Nriagu (1990) are listed in Table 2.4. Fluxes between these compartments are illustrated in Figure 2.6. The bulk of Se is found in the lithosphere (Nriagu, 1990). Se from rocks is transferred to soil through weathering and uplift. In hot and arid areas underlain by seleniferous rocks, high Se soils are common since losses of Se through leaching are minimal (Herring, 1990). Transfers of Se from soil and sediment to water are governed by a number of factors including redox conditions and microbial activity, as well as the type of mineral and the amount of organic matter present.

Table 2.4 Major Inventories of Se (Adapted from Nriagu, 1990)

Reservoir	Se (kilotonnes)
Lithosphere	3×10^9
Soils	10^5
Fossil fuel deposits	1.4×10^5
Terrestrial biomass	70
Atmosphere (gaseous and particulate)	2
Oceans (dissolved)	2×10^5
Rivers (dissolved and particulate)	12
Shallow groundwater	0.8
Polar ice	400

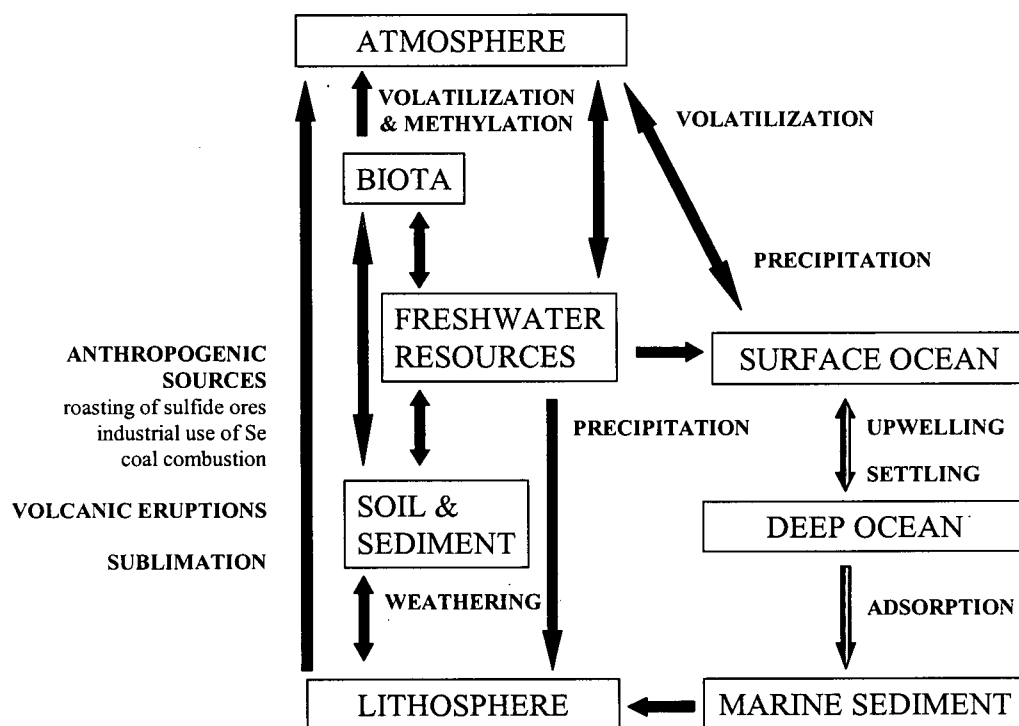


Figure 2.6 Generalized Cycle of Se (Adapted from Herring, 1990)

Se concentrations in freshwater generally range between 0.1 and 3.0 $\mu\text{g/L}$ (Lemly, 1985). Selenate and selenite account for the bulk of river-borne Se and are either dissolved or adsorbed to particulate matter (Cutter, 1989). The biogeochemical cycle of Se in soil and freshwater environments will be discussed in greater detail in Section 2.1.3.2 as it is highly relevant in identifying possible mechanisms of Se mobilization from the Mist Mountain Formation.

The average concentration of Se in sea water and freshwater is 0.2 $\mu\text{g/L}$ (Drever, 1982). Se has a short residence time in seawater as it adsorbs rapidly to sediment. Upwelling of deep water renews the supply of dissolved Se to surface waters. Selenate is the dominant form of Se in surface waters of the ocean and is assimilated by marine organisms and incorporated into particulate organic matter (Herring, 1990). The amount of Se introduced into the marine

environment through riverine inputs and rainfall is very small and consequently has virtually no effect on the overall S balance in the oceans (Herring, 1990).

Natural sources introduce between 7000 and 18 000 tonnes of Se to the atmosphere annually (Nriagu and Pacyna, 1988). About 60 to 80% of this is said to be gaseous Se of marine biogenic origin. Other natural sources of Se to the atmosphere include volcanic activity, volatilization from land plants, suspension of sea salts, sublimation and wind erosion of rocks or soils. Anthropogenic sources contribute between 1700 and 5800 tonnes of Se to the atmosphere (Nriagu and Pacyna, 1988). Se is estimated to have only a 45-day residence time in the atmosphere such that little inter-hemispheric transfer occurs (Nriagu, 1990). Removal of gaseous forms of Se from the atmosphere likely occurs by condensation onto precipitation or, in the case of particulate Se, by scavenging. Continental rain averages 0.3 to 1.1 $\mu\text{g/L}$ Se (Mosher and Duce, 1989). Haygarth et al. (1993) determined that the amount of Se deposited by precipitation is highly dependent on distance from the source.

2.1.3.2 Biogeochemical Transformations

Although Se may occur as selenate (+6), selenite (+4), elemental Se (0) and organic Se in solution, only the first two forms are found under standard conditions. Most soils are fairly well aerated, with Eh values lying between +0.3 and +0.5 volts and pH values between 3 and 9 (Sparks, 1995). It is important to note that soil is not a homogeneous media. It contains organic and mineral matter, water, air and microorganisms, all of which affect the physico-chemical properties of the soil. This, in turn, determines the speciation and sorptive capacity of metals and trace elements and thus, their mobility. Se adsorption to soil and sediment is positively correlated with organic carbon and clay content and negatively correlated with salt concentration, alkalinity and pH (Sillanpää and Jansson, 1992). Se bound to particulate matter can be transported into waterways, but when referring to mobile Se, one is generally making reference to Se in solution

(Kabata-Pendias and Pendias, 1984). Neal and Sposito (1989) identify selenite as the predominant form of Se in soils. Based on redox potentials, one would also expect selenate to be quite common in well-aerated alkaline soils, but due to its poor affinity for soil particles it is readily leached and constitutes only a minor portion of total Se.

In soil, most transformations of Se appear to be microbially mediated (Neal, 1995). There are three categories of microbially mediated transformations of Se: oxidation and reduction, immobilization and mineralization, and methylation (Doran, 1982). Most research on microbial transformations of Se has focused on microorganisms capable of rendering Se less mobile through reduction. Many fungi, bacteria and actinomycetes in soil can reduce Se oxyanions to elemental Se or to volatile or non-volatile organic compounds (Thompson-Eagle and Frankenberger, 1992). Both *Pseudomonas stutzeri* and *Thaurea selenatis* have been found to reduce selenate to selenite (Macy et al., 1992). Altschuler et al. (1983) found that *Desulfovibrio desulfuricans* and *Clostridium desulfuricans* can generate FeS_2 through the reduction of organic S compounds. These species are likely able to reduce analogous Se compounds. Nelson et al. (1996) found that co-cultures of *Desulfovibrio desulfuricans* and *Chromatium vinosum* could reduce selenate to elemental Se in a two-step process where *D. desulfuricans* reduces selenate to selenide which *C. vinosum* then oxidizes to elemental Se. Other Bacterial species able to produce elemental S and Se, are *Beggiatoa*, *Chlorobium* and *Ectothiorhodospira* (Nelson et al., 1996).

In acidic, poorly aerated soils, rich in organic matter, Se tends to be immobilized in sulphides or bound to clay minerals, HFMO or organic matter (Elrashidi et al., 1987). Oxidation of selenides proceeds slowly in most soils (Rosenfeld and Beath, 1964). In alkaline soils, Se is readily transformed by chemical or bacterial oxidation into plant-available selenate. In soils, selenite will only be reduced to elemental Se after soluble Pb^{+2} , Cu^{+1} , Cu^{+2} , Sn^{+2} and Cd^{+2} have been reduced (Elrashidi et al., 1987).

There are four processes that may participate in the transformation of elemental Se:

1. Oxidation and methylation of Se by plant roots and microorganisms
2. Oxidation of sediment through burrowing and feeding activity of benthic invertebrates
3. Chemical oxidation associated with water circulation
4. Plant photosynthesis

Once transformed into selenate or selenite, Se may be taken up by aquatic organisms or by rooted plants or it may adsorb to clay and organic carbon phase particulates. In general, as much as 90% of total Se in aquatic systems is found in the upper few centimetres of sediment (Bowie et al, 1991). The cycle is illustrated in Figure 2.7.

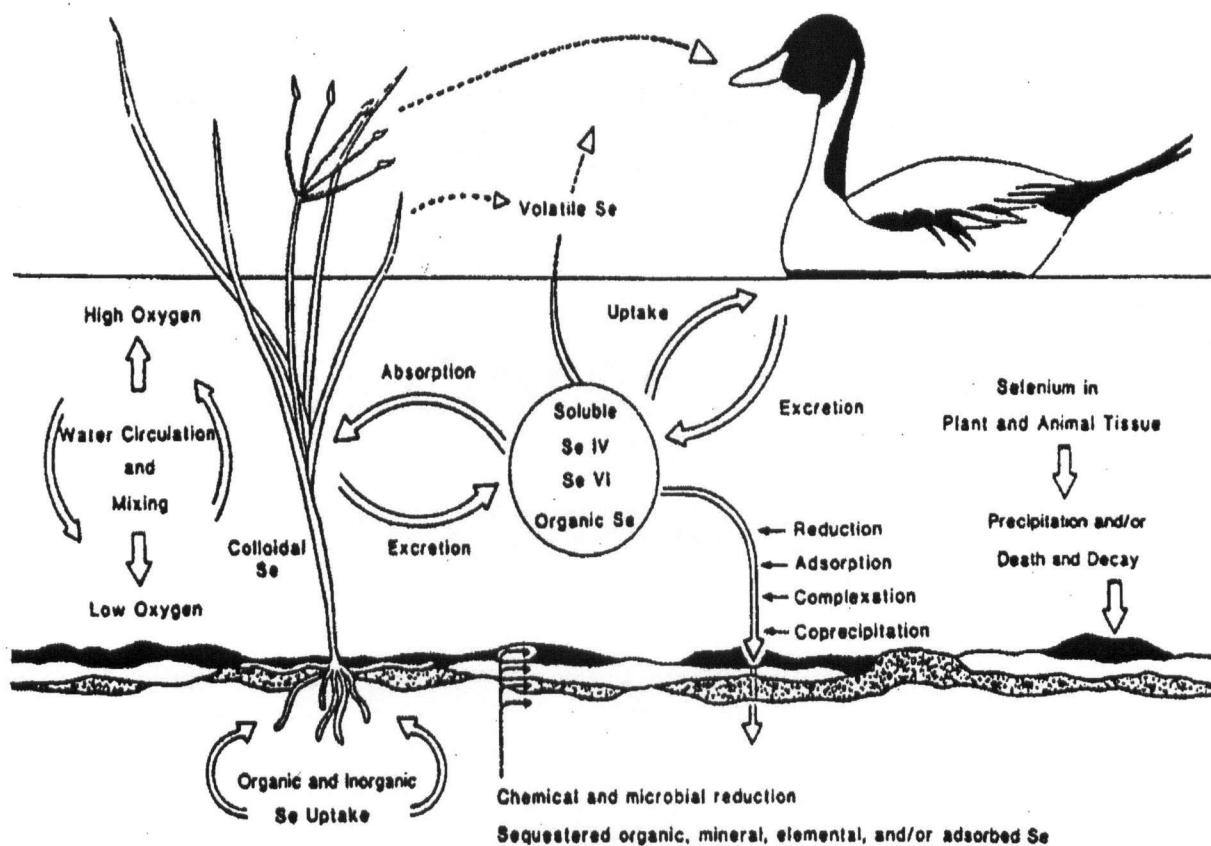


Figure 2.7 The Biogeochemical Cycle of Se in Aquatic Habitats
(From Lemly and Smith, 1990)

In the marine environment, Se may be found as elemental Se, selenate, selenite or organic Se. The latter is found in particulate form near the surface and as it sinks, it breaks down and undergoes

oxidation by opportunist species yielding selenate and selenite. Only these two forms are present in deeper waters (Cutter and Cutter, 1995). Se has a short residence time in oceans, adsorbing readily to clay sediment (Geering et al., 1968). The intensity of upwelling strongly influences the ratio of organic to inorganic Se in surface waters. Lemly and Smith (1990) found that Se, like Hg, biomagnifies i.e. it accumulates at progressively higher concentrations in successive trophic levels of a food chain placing piscivorous fish and aquatic birds at greatest risk in Se contaminated environments. They determined that Se biomagnification generally ranges from 2 to 6 times between algae and plants and invertebrates or foraging fish species.

2.3.1.3 Anthropogenic Inputs

Approximately 1500 tonnes of Se are extracted annually for commercial use through the electrolytic refining of copper, zinc and nickel ores (Herring, 1990). Se is used in the manufacture of electronic and photocopier components, glass, plastics, ceramics, paints and lubricants.

Nriagu and Pacyna (1988) studied the effects of human activity on the cycles of a number of trace elements including Se. Major sources of anthropogenic emissions to the atmosphere include coal combustion (2800 tonnes), oil combustion (800 tonnes), pyrometallurgical processes, such as Cu-Ni refining, (2100 tonnes) and municipal refuse and sewage sludge incineration (100 tonnes). Anthropogenic sources introduce between 10 and 72 tonnes of Se to aquatic ecosystems annually. Smelting, refining and steam from power generation are the primary sources of Se to aquatic ecosystems, releasing up to 20 and 30 tonnes of Se per year respectively. Manufacturing processes, sewage sludge and domestic wastewater also release Se into aquatic ecosystems. Human activity contributes approximately 73 000 tonnes of Se to terrestrial environments annually. This total excludes Se from atmospheric fallout which deposits between 1300 and 2600 tonnes of Se annually and be anthropogenic or biogenic in origin. Fly ash, the primary anthropogenic source of Se to terrestrial ecosystems, introduces up to 60 000 tonnes of Se to soils

per year. Agricultural wastes, wood wastes, urban refuse, fertilizer use and mine tailings account for the remainder of Se inputs to the environment.

Several instances of Se contamination resulting from mining activity have been documented. Se is widely distributed in the area around the Red Dog zinc mine in Alaska. Se concentrations of 9 $\mu\text{g/L}$ were found in discharge water from the mill (Brienne et al., 2000). This is almost two times greater than the EPA chronic freshwater criterion of 5 $\mu\text{g/L}$ (USEPA, 1987). High Se concentrations are also common in uranium and coal deposits in Wyoming (Naftz and Rice, 1989) and in the Western Phosphate Resource Area in Idaho (Munkers et al., 2000). Se concentrations as high as 1000 $\mu\text{g/L}$ were detected in groundwater at a uranium mine in Wyoming's Powder River basin (Naftz and Rice, 1989).

Coal mining and combustion have been particularly problematic. Groundwater samples from backfill at one of the Powder River Basin coal mines had Se concentrations between 600 and 900 $\mu\text{g/L}$ Se were detected (Dreher and Finkelman, 1992). Coals in the Powder River Basin contain, on average, 12.6 mg/kg Se (Naftz and Rice, 1989). Dreher and Finkelman (1992) attributed the elevated Se levels to the oxidation of pyrite present in the backfill of mines in the Powder River Basin. Sampling conducted in river basins of West-Central Alberta showed that Se concentrations in water samples collected immediately downstream of the Cardinal River, Gregg River and Coal Valley coal mines were up to an order of magnitude above the 1 $\mu\text{g/L}$ Canadian Council of Ministers of the Environment (CCME) guideline (Casey and Siwik, 2000). While the impact of Se on biota at many of these sites has yet to be determined, Se leached from fly ash landfills has been conclusively linked to fish kills in Martin Lake, Texas and Belews Lake, North Carolina (Shepard, 1987). More details on Se toxicity are provided in Section 2.2.1.3.

2.2 SELENIUM IN BIOTA

2.2.1 Effects of Selenium

While this study focuses on Se geochemistry the ultimate question is whether the final concentration of Se in waterways constitutes a hazard to aquatic wildlife. There is much debate, both in Canada and in the United States, as to what the fresh water criteria should be set at to adequately protect fish and bird populations. A review of the information available about Se toxicity will provide a practical framework in which to consider the implications of the results of this study.

2.2.1.1 Humans

Se was discovered to be an essential nutrient in 1957 (Schwartz and Foltz, 1957). However, its role in glutathione peroxidase, an enzyme essential for protecting cellular membranes from destruction by free radicals, was not established until 1973 (Rotruck et al., 1973). In humans, there is a very limited range over which selenium (Se) is neither toxic nor deficient, with the recommended dietary allowance for adults set at 55 μg per day (National Institute of Health, 2000). Figure 2.8 illustrates a typical dose response curve for a micronutrient with a narrow range between critically high or low levels such as Se.

Se intake occurs primarily through diet. Insufficient Se may result in nutritional muscular dystrophy, hepatic necrosis and impaired immunity. Severe nutritional Se-deficiency has been observed in two areas in China (Ge and Yang, 1993). In one case, it resulted in endemic juvenile cardiomyopathy typical of Keshan disease, and in the other it caused Kashin-Beck disease, characterized by chondrodystrophy, a disorder affecting cartilage formation. Other symptoms of Se deficiency include hemolytic anemia, hypertension, ischemic heart disease, cirrhosis and arthritis. Se deficiency has also been observed in Serbia and Croatia (Maskimovic et al., 1992) and Tibet (Moreno-Reyes et al., 1998).

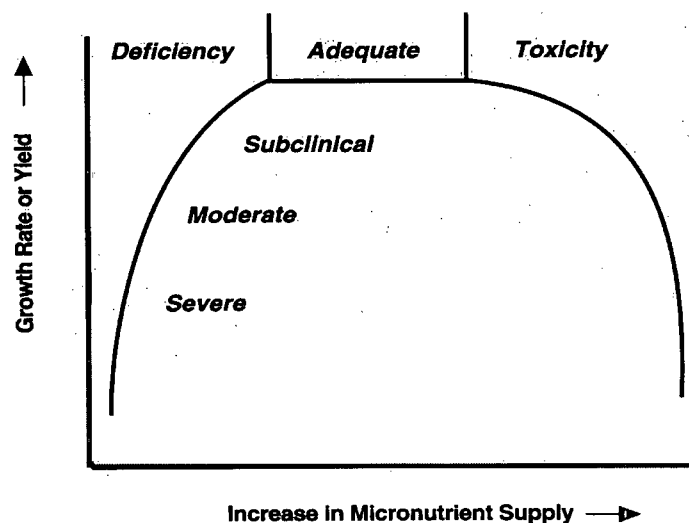


Figure 2.8 Typical Dose-Response Curve for Micronutrients (From Thornton, 1995)

Se's toxic effects were first documented by Franke and Painter (1936). Se toxicity results from its substitution for S in cysteine and methionine, S-containing amino-acids, which affects the functioning of the proteins in which they are found. Se has also been shown to reduce growth hormone production (Thorlacius-Ussing et al., 1987). Consumption of crops grown on seleniferous soils or of livestock that have grazed on high Se fodder areas may lead to selenosis, a toxic response to Se manifested by hair loss, skin lesions and nerve damage (Zheng et al., 1999). The inhalation of hydrogen selenide in occupational settings like copper refineries and self-medication of dietary supplements are, however, the primary causes of Se toxicity in humans (World Health Organization, 1986).

2.2.1.2 Livestock

Se deficient soils are far more common than Se enriched soils (Neal, 1995). In instances when livestock does not obtain the minimal daily Se requirement of 0.01 mg/kg of body weight, they should be provided with Se supplements, salt licks or injections (Wuyi et al., 1987). Failure to do so can lead to a disorder known as "white muscle disease", where calcium salts are deposited

among muscle fibers impeding muscle function. Laboratory tests and field studies indicate that decreased appetite, growth and fertility may also characterize Se deficiency.

Records of selenium toxicity in livestock date back as far back as the thirteenth century. Marco Polo described a necrotic hoof disease affecting his horses when they consumed plants generally avoided by local animals. A similar ailment observed in domestic animals in Colombia during the 16th century was also attributed to excess Se (Oldfield, 1992). Outcrops of Se-rich saline seeps in the northern Great Plains of the United States have caused problems for ranchers (Rosenfeld and Beath, 1964). In addition to hoof loss and reduced growth and reproductive performance, chronic Se intoxication in livestock may also cause hair and weight loss (Combs and Combs, 1985). Se toxicity results from the consumption of forage containing 5 to 40 mg/kg Se. High protein intake can counter the effects of excess Se by transforming it into easily excreted methylated metabolites.

2.2.1.3 Fish and Wildlife

Excess Se can pose an especially serious problem in aquatic environments as evidenced by incidents in the United States at Belews Lake, North Carolina in the late 1970s and at the Kesterson National Wildlife Refuge in California in the mid-1980s.

At Belews Lake, average Se concentrations were approximately 5 times greater than the background concentration of Se in freshwater. In some water samples, Se concentrations as high as 200 µg/L were detected (Lemly, 1985). The source of the Se was identified as fly ash from a nearby thermal power plant. The elevated Se concentrations lead to severe reproductive failure in bluegill (*Lepomis macrochirus*), green sunfish (*L. cyanellus*), largemouth bass (*Micropterus salmoides*) and flat bullhead (*Ictalurus platycephalus*) and a rapid collapse of these fish populations (Sorensen et al., 1984). Congenital malformations observed in these fish species included missing fins, protruding eyes and deformed spines and heads. Not all species were

equally affected by the high Se concentrations. Forage species, including red shiners, fathead minnows and mosquitofish, all showed a higher degree of tolerance (Lemly, 1985). Although Se levels in water eventually dropped below 1 $\mu\text{g/L}$, consumption advisories remained in place as elevated Se concentrations and teratogenic effects were still being observed up to 10 years after Se inputs from the fly ash had ceased (Lemly, 1997).

Kesterson Reservoir was constructed between 1968 and 1975 as a part of an agricultural drainage facility for the San Joaquin Valley, California. Soils in this area formed through the weathering of seleniferous Cretaceous marine sedimentary strata (Presser, 1994). The reservoir consisted of a series of 12 ponds that were to be managed as wetlands and were to be supplied with water subsurface drainage from the irrigated agricultural lands via the San Luis Drain. Problems arose in 1983 when aquatic birds nesting around the reservoir were found to have high rates of embryo deformities and mortality (Ohlendorf, et al, 1986; Ohlendorf, 1989). Water quality tests showed that water entering the ponds had Se concentrations as high as 1400 $\mu\text{g/L}$ (Presser and Barnes, 1984). By 1985, laboratory and field studies had conclusively identified Se as the agent responsible for the fish and bird deaths. Reclamation efforts were promptly undertaken; discharge to the ponds was halted in 1986 and in 1988 the ponds were dewatered and filled. Mallards were missing eyes, beaks, wings, legs and feet and showed brain, liver, heart and skeletal abnormalities. Fish populations were also affected. Mosquitofish contained up to 100 times more Se than fish of the same species in the nearby Volta Wildlife Area which received no drainage water. Invertebrates, amphibians, reptiles and mammals were also shown to have bioaccumulated Se (Ohlendorf, 1989). *Daphnia* were found to contain up to 12.4 mg Se/kg dry weight, meaning 6 to 10 times the normal background level for these organisms. Although tissues from raccoons autopsied contained from 10 to 30 times more Se than those in the Volta Wildlife Area no effects on growth or reproduction were observed. Nor were effects noted on kit foxes, coyotes, voles and shrews despite the elevated concentrations of Se in their diet.

Food is the primary exposure pathway for fish to Se, but they can also take up Se directly from the water column via their gills (Lemly, 1993). Specific manifestations of Se toxicity in fish include blindness, popeye, osteological deformities and reduced hatchability of eggs (Clark et al., 1986; Skorupa et al., 1996). In the field, reproductive failure and deformity of larvae have been reported in bluegill (*Lepomis macrochirus*) exposed to Se concentrations of 9 µg/L (Gillespie and Baumann, 1986) and malformation of late juvenile and early adult fathead minnow (*Pimephales promelas*) at concentrations of 10 µg/L (Hermanutz, 1992). In a comprehensive review of studies of Se toxicity in freshwater fish, Nagpal and Howell (2001) found LC₅₀ values to range from 5 to 126 600 µg/L. Factors found to affect Se toxicity include fish species and life stage and the form and concentration of waterborne Se. Several studies have indicated that selenite is more toxic than selenate (Niimi and LaHam, 1976; Brooke et al., 1987; Hamilton and Buhl, 1990). The lowest 96-hour LC₅₀ values for selenite and selenate reported by Nagpal and Howell (2001) were 620 µg/L and 2300 µg/L respectively. The combined effect of selenite and selenate is strictly additive (Hamilton and Buhl, 1990). The methylated forms of Se are much less toxic for the organism than selenite and selenate. However, the methylated Se derivatives have strong synergistic toxicity with other minerals such as arsenic (Jonnalagada and Prasada Rao, 1993).

Waterfowl feeding on fish from lakes, streams or wetlands with high Se concentrations are at risk of bioaccumulating Se. Lesions resulting from excess Se detected in birds include necrosis of pancreas and liver cells and atrophy of lymphoid organs, feather follicles and fat (Green and Albers, 1997). Brix et al. (2000) identify teratogenicity (embryo deformities) and chick mortality as useful endpoints for gauging the ecotoxicological effects of Se. They note that Se toxicity can also result in failure to breed and in reduced hatchability of fertile eggs and that sensitivity to Se in waterfowl varies, from relatively tolerant avocets and snowy plovers to highly sensitive mallards. Stilts and kildeer show intermediate levels of sensitivity (Brix et al., 2000).

2.2.1.4 Plants

Plants vary considerably in their capacity to survive in high Se environments. Rosenfeld and Beath (1964) divided plant species into three groups based on their capacity to accumulate Se. The first, which includes the genera *Astragalus*, *Machaeranthera*, *Haplopappus* and *Stanleya*, may contain hundreds to thousands of milligrams of Se per kilogram. In these plants, Se is generally present as water soluble methylselenocysteine, rather than as protein-bound selenomethionine (Mayland et al., 1989). In other words, these plants have metabolic pathways which ensure that Se is not incorporated into proteins. Plants in the second group accumulate between 50 and 100 mg/kg when grown on seleniferous soils (Rosenfeld and Beath, 1964), whereas those in the third group (grains, grasses and forbs) rarely accumulate more than 50 mg Se/kg (Rosenfeld and Beath, 1964). Plant tissue containing more than 5 mg/kg dry weight is considered toxic to grazing animals (Levander, 1985).

Although both selenate and selenite are available for plant uptake, selenate is the primary form taken up by plants since selenite adsorbs more strongly to clay minerals and HFMO (Brown, 1990). High soil pH decreases cation exchange capacity as hydroxide ions bind to the available sites releasing Se into the soil-solution and making it available to plants. Selenate and selenite compete with other anions, such as sulfate, phosphate, molybdate and oxalate in the soil-solution for adsorption sites on plant roots. Effects of Se on plants include reduced dry-matter yield, loss of leaf pigmentation and potentially death if concentrations in the soil-solution are very high (Girling, 1990).

2.2.2 Se Guidelines and Criteria

The EPA updated its freshwater chronic criterion for Se in 1987. In the wake of the Belews Lake and Kesterton incidents the acute criterion was set at 20 µg/L while the long-term exposure

criterion was set at 5 µg/L (USEPA, 1987). Both the acute and chronic criteria are expressed in terms of total Se and, as such, fail to identify the fraction accounted for by bioavailable species.

In British Columbia, the Ministry of Environment Lands and Parks refers to guidelines rather than to criteria, the difference being that the former only has legal ramifications once it has been used to set effluent quality standards in permits. The Canadian Council of Ministers of the Environment (CCME, 1999) set the freshwater guideline at 1 µg/L, which is five times lower than the U.S. criterion. Recently, these figures have come under scrutiny with some arguing that they may not adequately protect sensitive aquatic organisms and others that they may be overprotective, especially in lotic environments such as the Elk River Valley. The criterion for Se in drinking water in the United States is 50 µg/L (USEPA, 2001), while the Canadian guideline for drinking water is 10 µg/L (Health and Welfare Canada, 1993). There are no limits set by the USEPA, World Health Organization or Canadian government on Se intake from the consumption of fish.

Van Derveer and Canton (1997) suggested that site-specific guidelines should be developed, noting that bioaccumulation in fish may be a factor of 10 times greater in lentic systems than in lotic systems. The static nature of lentic systems allows Se to accumulate in sediment (Lemly, 1999) where one frequently finds anoxic zones rich in organic matter favouring microbial production of organic Se species. Presser et al. (1994) determined that organoselenium compounds, such as selenocysteine and selenomethionine, are much more readily bioaccumulated than inorganic forms of Se. The fact that many organisms in lentic systems have a restricted feeding range increases exposure and thus the amount of Se that bioaccumulates. Some studies stress the importance of site-specific environmental factors, such as pH and redox conditions, in determining Se speciation and its bioavailability (Bowie and Grieb, 1991; Porcella et al., 1991). It is precisely this complexity that will render it difficult to establish a framework for setting site-specific guidelines. It is necessary to consider not only the physical environment, but also how

different species utilize different niches present in the ecosystem. The USEPA is currently considering the viability of site-specific criteria related to Se concentrations in sediment and in the water column, but plans to address the issue of dietary exposure are conspicuously absent (Sappington, 1998). The generic bioaccumulation model developed by Adams et al. (2000) is perhaps more useful as it produces a criterion based on tissue values which can then be modified according to site-specific conditions. Such a model would recommend less restrictive criteria in instances where Se concentrations are high but little bioaccumulation is occurring.

Brix et al. (2000) argue that tissue based criteria provide the most effective method of assessing the risk of Se toxicity. Using logit and probit models to analyse existing laboratory and field data, they derived dose-response relationships and proposed thresholds for whole body and ovary tissue of fish of 6 to 9 and 17 mg/kg dry weight respectively. The logit and probit models are qualitative variable model estimators. In the simple probit model, the dependent variable is usually binary while in the logit model, there is a discrete choice among a small set of alternatives. Using the same approach, Brix et al. (2000) determined a bird egg threshold of 16 mg/kg dry weight and teratogenesis threshold of 26 mg/kg dry weight. This bird egg threshold is more than two times greater than the concentration found to cause chick mortality in field studies (Skorupa et al., 1996). Brix et al. (2000) suggest that this discrepancy may be due to factors other than Se bioaccumulation that were not controlled for in the field studies. There are also problems associated with tissue-based criteria; the primary one being that fish or birds of the same species living in different areas may have different levels of tolerance to Se (Van Derveer and Canton, 1997).

3.0 ENVIRONMENT OF THE ELK RIVER VALLEY

3.1 BIOPHYSICAL ENVIRONMENT

3.1.1 Geology

The Southeast Coalfields of British Columbia, located between 114° 30' and 115° 30' longitude and 49° 00' and 51° 00' latitude, are grouped into three basins: the Elk Valley, Crowsnest and Flathead coalfields. The elongated Elk Valley Coalfield lies just north of the Crowsnest Coalfield, while the Flathead Coalfield is located immediately north of the Canada-US border (Figure 3.1).

Coal deposits in the three basins are located in the Mist Mountain Formation of the Jurassic-Cretaceous Kootenay Group formed between 150 and 130 million years ago. In the Flathead Coalfield, the Mist Mountain Formation is heavily eroded. The marine Fernie Formation underlies the Kootenay Group. The lower sections of this formation consist of a series of shales, ranging from dark gray shales to brown silty shales with limestone beds while calcereous sandstone with limestone and glauconitic sandstone form the upper units. The Passage Beds, composed of interbedded shale and sandstone coarsening upwards, are the last unit deposited in this formation (Gibson, 1977).

The Morrissey Formation, with an average thickness of 40 metres, forms the base of the Kootenay Group. It is easily recognized across the Elk River Valley and contains two distinct members. The Weary Ridge member, lying immediately above the Passage Beds, is composed of quartzose, argillaceous, calcereous and ferruginous sandstone. The quartz-chert sandstone Moose Mountain member is coarser grained than that of the lower member. Minor carbonaceous shale and coal deposits occur sporadically within the Morrissey Formation. Material from tectonically active uplands was likely deposited on lower delta coastal plains draining eastward into the inland

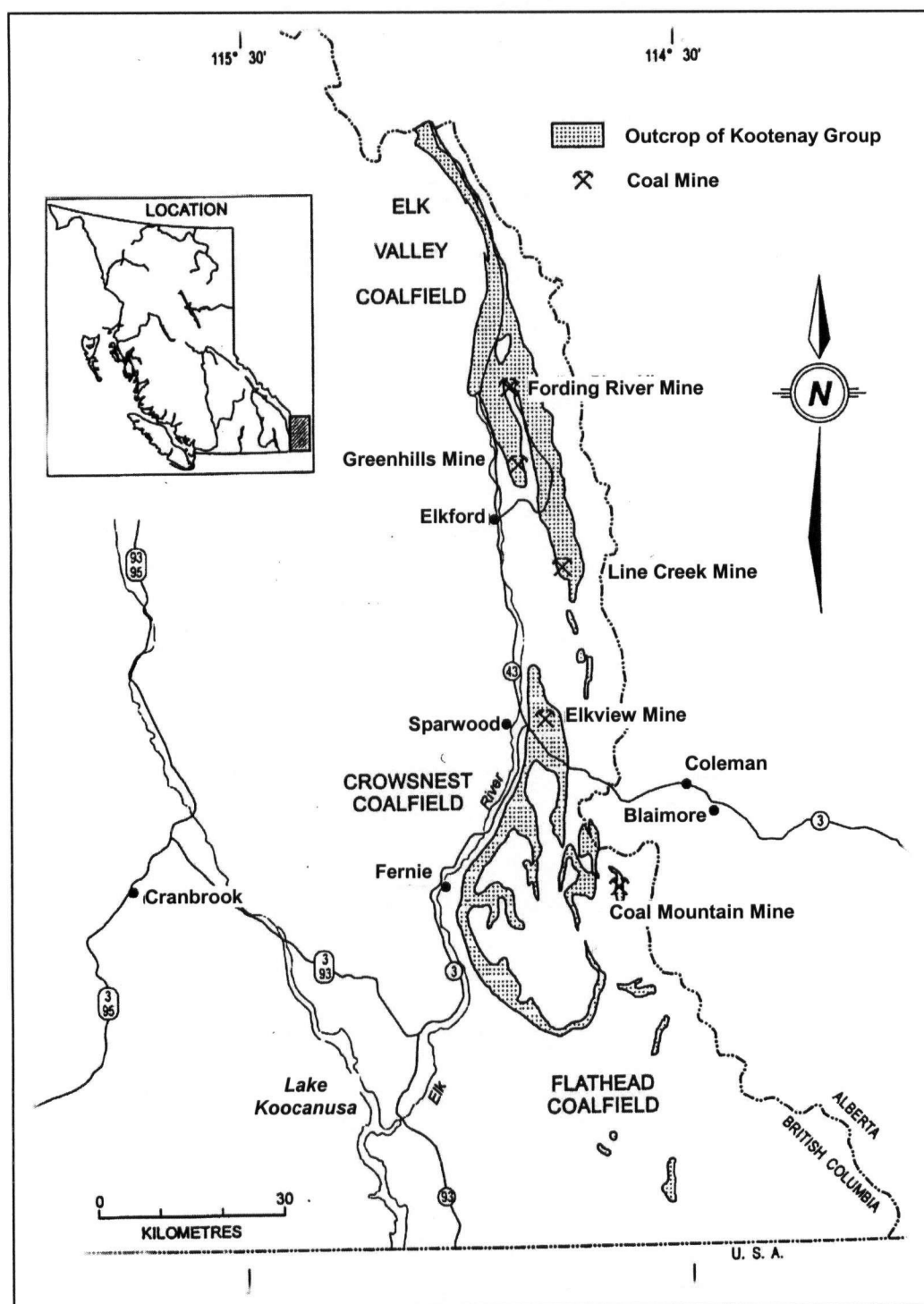


Figure 3.1 Elk Valley, Crowsnest & Flathead Coalfields of Southeastern British Columbia (Ryan and Dittrick, 2000)

Fernie Sea (Gibson, 1977). The plains were protected from direct marine influence by sand dunes that now form the Passage Beds of the Morrissey Formation (Vesey and Bustin, 2000). The Mist Mountain Formation conformably overlies the Morrissey Formation. It averages 500 metres in thickness, but ranges from 240 to almost 1000 metres. Depositional patterns typical of levee, splay, flood-basin, swamp and marsh settings suggest that material was deposited in alluvial channels and flood plains (Gibson and Hughes, 1981).

LOWER CRETACEOUS	CADOMIN FORMATION		
JURASSIC AND CRETACEOUS	KOOTENAY GROUP	ELK FORMATION	
		MIST MOUNTAIN FORMATION	
		MORRISSEY FORMATION	MOOSE MOUNTAIN MEMBER
			WEARY RIDGE MEMBER
JURASSIC	FERNIE FORMATION	PASSAGE BEDS	

Figure 3.2 Jurassic-Cretaceous Stratigraphy of the Kootenay Group (Gibson, 1977)

Coal comprises 8 to 12% of the stratigraphic thickness of the Mist Mountain Formation (Grieve, 1985). It ranks from high- to low-volatile bituminous (Smith, 1989) and has applications in coking and power generation. The main silicate minerals present in the coal are kaolinite and quartz, as in most non-marine influenced deposits (Pearson, 1980). Coals in the Mist Mountain

Formation contain between 6.5 and 33.1% ash and generally have S contents below 0.5% (Vessey and Bustin, 2000). There is a gradual shift from inertinite rich to vitrinite rich coals from the base to the top of the formation (Grieve, 1985). Siltstone, mudstone and shale of non-marine origin are interbedded with the coal. Apart from a basal coal zone within the lowermost 25 metres of the formation, there are no coal seam clusters in the stratigraphy (Gibson, 1977). Extensive tectonic activity during the Laramide Orogeny has lead to considerable deformation of the seams making it difficult to correlate seams from one mine to another (Gibson, 1979). Many coal seams are highly sheared and thickened due to folding. Thrust faults are not uncommon. Clastic sediments and thin, discontinuous humic and sapropelic coal seams in the Elk Formation overlie the Mist Mountain Formation. This constitutes the uppermost formation of the Kootenay Group. Like the Mist Mountain Formation, it is non-marine in origin (Gibson and Hughes, 1981).

3.1.2 Environmental Variables

The Elk River Valley is located in a temperate climate zone, with average highs between 19 and 25 °C during the summer months and average lows between -13 and -9 °C during the winter months. The valley receives, on average, 1095 mm of precipitation per year. Peak flow rates in the Elk River and its tributaries are generally observed in March and April as a result of snowmelt. Base flow at the 08NK005 monitoring station at Phillips Bridge on the Elk River is in the order of 20 m³/s (Wipperman and Webber, 1997). Peak flows are generally between 329 and 384 m³/s, but reached 683 m³/s in 1986. Table 3.1 lists the values of key water quality parameters measured at Phillips Bridge.

**Table 3.1 Key Parameters of Elk River Water Quality
(Data from Wipperman and Webber, 1997)**

Parameter	Range
pH	7.5 – 8.5
Alkalinity	100 - 150 mg/L CaCO ₃
Water temperature	0 – 15 °C
Non-filterable residue	0 – 1130 mg/L

MacDonald and Stroscher (1998) noted that Se concentrations in the Elk River and its tributaries remain relatively constant throughout the year. Significantly more Se is mobilized during the spring when runoff rates increase due to snowmelt. The river system can be generally characterized as fast flowing and well oxygenated.

3.2 MINING OPERATIONS

3.2.1 History

There are currently five coal mines in operation in the Elk River Valley. Their locations are illustrated in Figure 3.1. The first commercial coal mining operation in the East Kootenays went into production in 1897 at Coal Creek. By 1910, The Crow's Nest Pass Coal Company had opened mines at Michel and Morrissey and the Canadian Pacific Railroad had opened the Hosmer mine. The amount of coal produced by the mines in the Elk River Valley has varied over the years. Production peaked prior to World War I around 1,387,000 tonnes per year and decreased notably during the 1920s and early 1930s. Production began to rise again in the mid 1930s and averaged about a million tonnes until 1960. Large-scale coal mining in the Valley began in the 1960s at Elkview. Fording, Greenhills and Coal Mountain came into operation in the 1970s and Line Creek at the beginning of the 1980s. Approximately 25,000,000 tonnes of coal are produced annually in British Columbia, contributing roughly \$900,000,000 to the province's economy (Ryan, 2001). The East Kootenay coalfields are the most important coalfields in the province.

3.2.2 Current Mining Activity

All five mines are open-pit operations. Once a section has been blasted, waste is loaded into haul trucks by electric shovels and disposed of at the site's waste dumps. Cumulatively, the five mines generate approximately 140×10^6 tonnes of waste rock per year (MacDonald and Stroscher, 1998). Waste rock consists primarily of mudstone and siltstone interburden but also includes

coal from seams that are too thin or not of saleable quality. The bulk of the coal at the sites is, however, destined for sale and is transported to the crusher station to be crushed to an appropriate size for processing. At the processing plants coal is crushed and screened. It is then washed with dense-medium cyclones, spirals and flotation and dried for shipping. Due to the friable nature of coals collected from highly sheared seams, a considerable amount of fines is generated in this process. Coal Mountain and Line Creek mix coarse and fine refuse from this process, while Fording River, Greenhills and Elkview dispose of the fine refuse in tailing ponds and the coarse material in crusher reject dumps.

3.2.2.1 Fording River

Fording Coal Limited owns and operates the Fording River, Greenhills and Coal Mountain operations. Mining at Fording River began in 1971. Early mining activity at the Fording River site took place at Eagle Mountain and at a section of the property called the Greenhills Range. Henretta Ridge and Valley were mined during the 1990s. Fording River produced 8.3 Mt of coal in 1999 most of which was destined for steel production. The mine has the widest range of bituminous coals in Canada. Much of the activity planned for the next 20 years at the site focuses on Eagle Mountain, as it contains over 65% of Fording River's 515 Mt reserves but mining will continue at Henretta Ridge until 2007. In terms of waste disposal, there are spoils on both sides on Henretta Creek, around the Greenhills Range pits and on the south, east and west sides of Eagle Mountain. There are two tailings ponds on the site, with the north one currently active. Crusher reject is currently dumped at the Kilmarnock reject spoil north east of the south tailings pond. All streams on the site are directed through settling ponds before discharge into the Fording River.

3.2.2.2 Greenhills

Fording acquired Greenhills in 1992. Pits active in the 1980s include the Hawk, Falcon and Cougar pits. Cougar Pit is still active. Raven Pit was mined in the 1980s and again in the late 1990s. Greenhills has both its tailings pond and coarse refuse piles at the south end of the site. Water from the site drains into the Elk River via a series of creeks along the western side of the site. Some drains in Greenhills Creek, a tributary of the Fording River. Greenhills produced 5.0 Mt of coal in 1999. The mine has approximately 128 Mt of reserves and generates both metallurgical and thermal coals.

3.2.2.3 Coal Mountain

Small-scale mining started at Coal Mountain in 1908, largely as underground operations. Open pit mining on Coal Mountain started in the 1940s in Pit 34. Most of the waste from both Pit 3, mined in the 1970s, and Pit 51, mined in the 1980s, was dumped over the mountain's western flank. Waste from the currently active Pits 7, 34 and 37 is dumped to the east in the Corbin Creek drainage. A rock drain was created over Corbin Creek in the 1990s. The site has no tailing impoundment. Fines are dried, mixed with coarse refuse and dumped on Middle Mountain, northwest of the crushing plant. Water from the site drains into Corbin Creek, which connects with Michel Creek, a tributary of the Elk River. The mine produced 2.1 Mt of medium-volatile thermal and soft coking coals in 1999. Reserves on this site are estimated to be in the order of 35 Mt of cleaned coal and will be extracted over the course of the next 14 years. This will come from one main coal horizon. This seam, known as the Mammoth seam, varies in thickness from 1 m up to 200 m due to its extreme structural character.

3.2.2.4 Elkview

The Elkview mine, owned by Teck-Cominco Corporation, has been in operation since 1969. The first pits dug were the Harmer Knob and Adit 29 pits. Mining in the Harmer, Baldy, Camp 8, A40

and A40C pits started in the 1970s. Waste was trucked to the Erickson Dump, which now forms a rock drain over Erickson Creek, and into mined out areas. The South, A40FW and Adit 29 East pits were started in the 1980s. In the 1990s, mining continued in some of these areas and started in the Elk, Natal West and Indigo pits. The waste rock from Elk pit has been trucked to the Bodie dump since 1996. Currently, waste from Natal West is hauled to the Erickson dump and waste from the Indigo pit to another area draining into Erickson Creek. The mine has a tailing impoundment located on the western edge of the property where it borders the Elk River. The coarse refuse dumps are found just north of the tailings pond. Some water drains directly into the Elk River via creeks along the western side of the property, but some first flows into Erickson or Michel creeks. Teck acquired the property from Westar Mining Limited in 1992. The mine now produces approximately 5 million tonnes of metallurgical coal annually. At current extraction rates, mine life is estimated to be more than 40 years.

3.2.2.5 Line Creek

Line Creek is a 50:50 joint venture owned by Luscar Limited and Consol Energy Canada Limited. It has been operation since 1981. The mine has an annual production capacity of 3.5 million tonnes of coal. Thermal coal accounts for approximately one-fifth of the total production. Seams vary from 2 to 15 meters in thickness. The first section of the property to be mined was the Line Creek Ridge (South Pit/North Pit). Having trended northward over the last two decades, mining in this area continues. Work in the Mine Services Areas (MSA) North, MSA West Pits and North Horseshoe Ridge Pits started in 1992, 1993 and 1994 respectively. There are rock dumps adjacent to the pits. Line Creek has no tailings impoundment. Instead, fines are dried, mixed with the coarse refuse. All water from the site drains via Line Creek that flows into the Fording River.

Land reclamation at the coal mines is carried out towards a designated land use objective. In the Elk Valley emphasis is placed on reclaiming mined lands primarily for moderate yield forestry and wildlife habitat. Reclamation is carried out in a progressive manner as the mines develop. When possible, pits are backfilled with waste from adjacent pits. Prior to revegetation, waste rock dumps are resloped. Topsoil is generally not used at the coal mines since the waste rock is broken down to a fine, soil-like texture during recontouring. Most areas are seeded with a grass-legume forage mix, but selected areas are planted with deciduous trees and conifers.

3.3 SELENIUM DISTRIBUTION

3.3.1 Biota and Sediment of the Elk River and Tributaries

Attention was first drawn to the Se issue in the Elk River Valley in 1995 during an effluent permit amendment when Se levels of 25 µg/L were detected in surface water downstream from one of the coal mines. Further sampling (Figure 3.3) showed that Se concentrations in water of some of the mine affected tributaries were 5 to 10 times greater than the provincial guideline, set at 2 µg/L as of August 2001 (Nagpal, 2001). Seepage from waste dumps contained up to 542 µg/L Se. Remarkably, concentrations in sediment, algae, insects and fish were only 2 to 5 times higher than at reference sites (MacDonald and Strosher, 1998). The situation nonetheless warranted further investigation as Se levels in Westslope cutthroat trout tissues were as much as two times greater than the respective toxic effects thresholds for muscle and liver of 8 and 12 mg/kg Se dry weight (MacDonald and Strosher, 1998). Though the study produced no evidence of deformities or increased mortality in cutthroat trout caught downstream of the mines, serious teratogenic effects could have occurred (Lemly and Smith, 1987, Lemly, 1997). Two of the 17 fish analyzed in the MacDonald and Strosher study had very high Se levels (64 and 81 mg/kg Se dry weight) in their eggs.

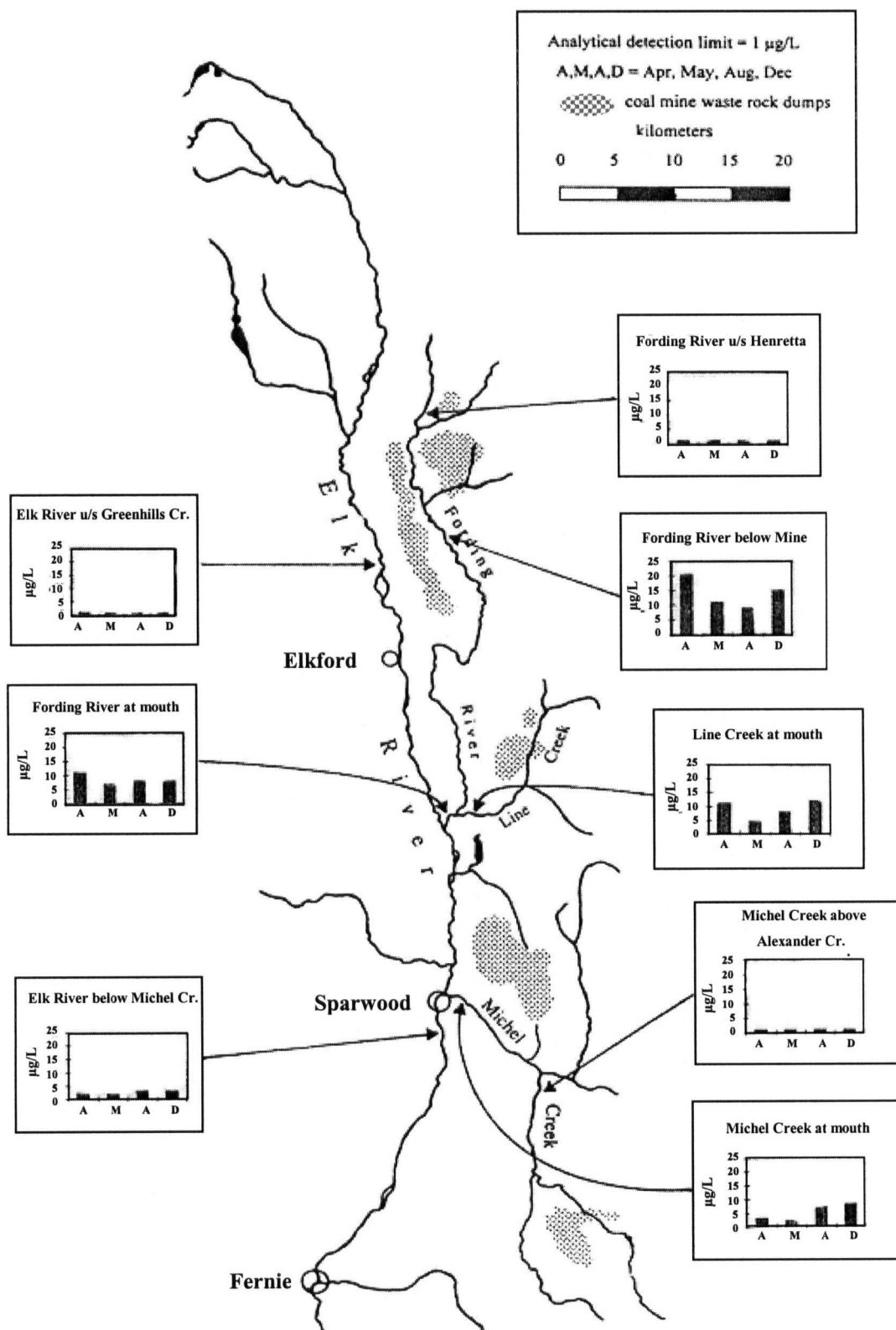


Figure 3.3 Total Se in Tributaries of the Elk River (from McDonald and Stroscher, 1998)

The remaining eggs contained between 8 and 25 mg/kg Se dry weight. Lemly (1997) determined that the occurrence of teratogenic effects increases significantly at Se concentrations greater than 10 mg/kg dry weight in eggs. However, McDonald and Stroscher's (1998) study showed that even at Se concentrations of 80 mg/kg in egg, no decrease in survivorship was observed suggesting that the Elk River's Westslope cutthroat trout may have a relatively elevated tolerance to Se. In order to conclusively establish if Se has any adverse effect on biota in the Elk River watershed, a comprehensive study has been undertaken by the five coal mines. This study, conducted by EVS Environment Consultants, will include long term monitoring of the cutthroat trout populations and an investigation of possible Se bioaccumulation in aquatic birds. Studies focussing on Se mobility will complement those addressing potential ecotoxicity. They will help clarify whether species in the Elk River Valley have a naturally high tolerance for Se or if environmental conditions, such as temperature, pH, flow rate, sediment composition and the amount and type of particulate matter suspended in the water column, affect complexation and speciation and render the Se less bioavailable.

3.3.2 Selenium in the Mist Mountain Formation

Until the recent study by Ryan and Dittrick (2000) from the British Columbia Ministry of Energy and Mines, relatively little data on Se occurrence in the province's coals were available. Coal samples collected from the Mist Mountain Formation at the Fording River and Coal Mountain operations (Goodarzi, 1987; Goodarzi 1988, Goodarzi and Swaine, 1993) had an average Se content of 1.36 mg/kg. Ryan and Dittrick (2000) sampled all accessible strata of the Mist Mountain Formation at the five mines in the Elk River Valley. Samples from waste piles and tailings ponds were also collected. Samples of 4 to 5 kg were obtained for each stratum by chipping material from the pit walls at regular intervals. Partings in coal seams, consisting generally of carbonaceous mudstone, were sampled separately, as were the hanging wall and foot wall of seams where there was a distinct band of carbonaceous mudstone between the seam and

the rock between the seams, termed interburden. Figure 3.4 illustrates the position of hanging wall, foot wall, parting material and interburden relative to the coal seams.

There was no major stratigraphic control of Se concentration in coal seams (Ryan and Dittirck, 2000). A weak trend of increasing Se concentration was observed moving upward in the Mist Mountain Formation. Due to the extensive folding it is not possible to correlate Se levels in strata at the different mines. Average concentrations of Se in the different lithologies are presented in Table 3.2. The average Se content of Mist Mountain coals (1.9 mg/kg) is below the global average of 2.15 mg/kg for coals. Average Se concentrations in interburden ranged from 1.1 mg/kg for coarser grained material to 3.2 mg/kg for mudstones with coal stringers. The highest concentrations were observed in samples collected from transitional zone between coal and interburden (Ryan and Dittirck, 2000).

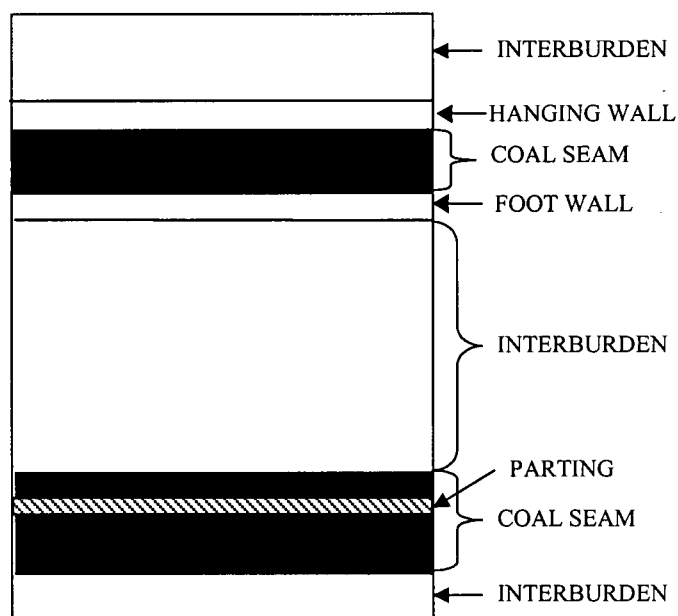


Figure 3.4 Cross-section of Pit Wall Illustrating the Different Types of Material Sampled

**Table 3.2 Average Se in Different Lithologies of the Mist Mountain Formation
(From Ryan and Dittrick, 2000)**

Lithothology	Se concentration (mg/kg)	Number of samples
Coal	1.9	107
Hanging wall	4.2	21
Foot wall	4.2	21
Partings	3.2	23
Coarse breaker refuse	2.8	24
Interburden	1.1	130

Se concentrations in the hanging wall and footwall were more than twice the levels found in the coal seams. Partings also contained relatively elevated Se levels. It is interesting to note that refuse material contains less Se than the hanging wall, foot wall and parting samples. Based on the Se content of these materials and the relative amount of them present at the sites, Ryan and Dittrick (2000) estimated that 80% of the Se is found in the interburden, while 6 to 20% is in the coal and 5 to 10% in the hanging wall, foot wall and parting material. Ryan and Dittrick (2000) also collected samples from the Fernie Shale, which underlies the Mist Mountain Formation and is exposed at a number of locations. It was thought that it might contain relatively high concentrations of Se since it formed at the margins of the Fernie Sea, however, Se concentrations in samples from the Fernie Shale averaged only 1.1 mg/kg Se.

Ryan and Dittrick (2000) analyzed incremental samples from two coal seams to determine to what extent Se concentrations varies within seams. Se and ash concentrations were closely correlated in the cross-section of these seams. Float sink data obtained by Ryan and Dittrick (2000) for hanging wall and footwall samples indicate that Se concentrations in ash, consisting of sulphides, clays and HFMO, are slightly higher than those in organic matter. The same authors suggest that adsorption to clays is not the primary mode of occurrence of Se in coal mineral matter since a poor correlation between Se concentrations and the $\text{Al}_2\text{O}_3/\text{SiO}_2$ ratio was obtained.

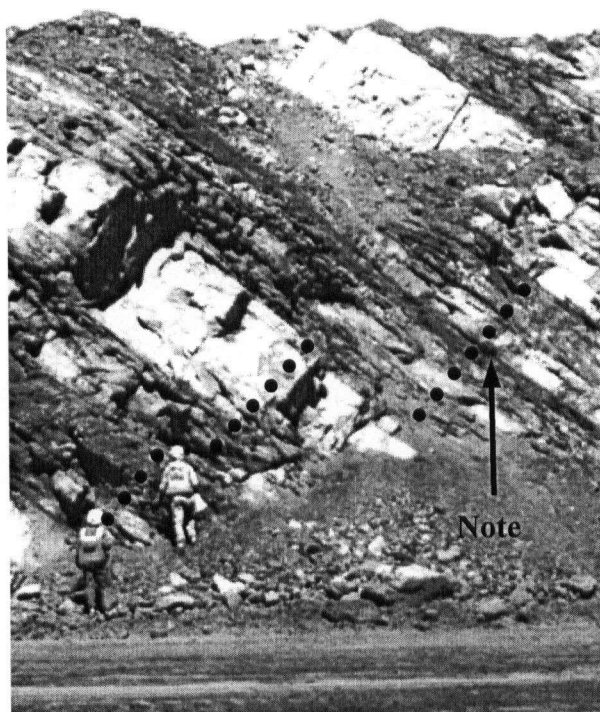
Se content also correlates weakly with organic S. At higher ash concentrations, the Se/organic S ratio increases, highlighting the importance of Se associated with the inorganic fraction.

To date, no study has been conducted to determine the main Se-bearing minerals in the Mist Mountain Formation or the geochemical mechanisms by which it is mobilized.

4.0 METHOD DEVELOPMENT AND PROCEDURES

4.1 SAMPLING

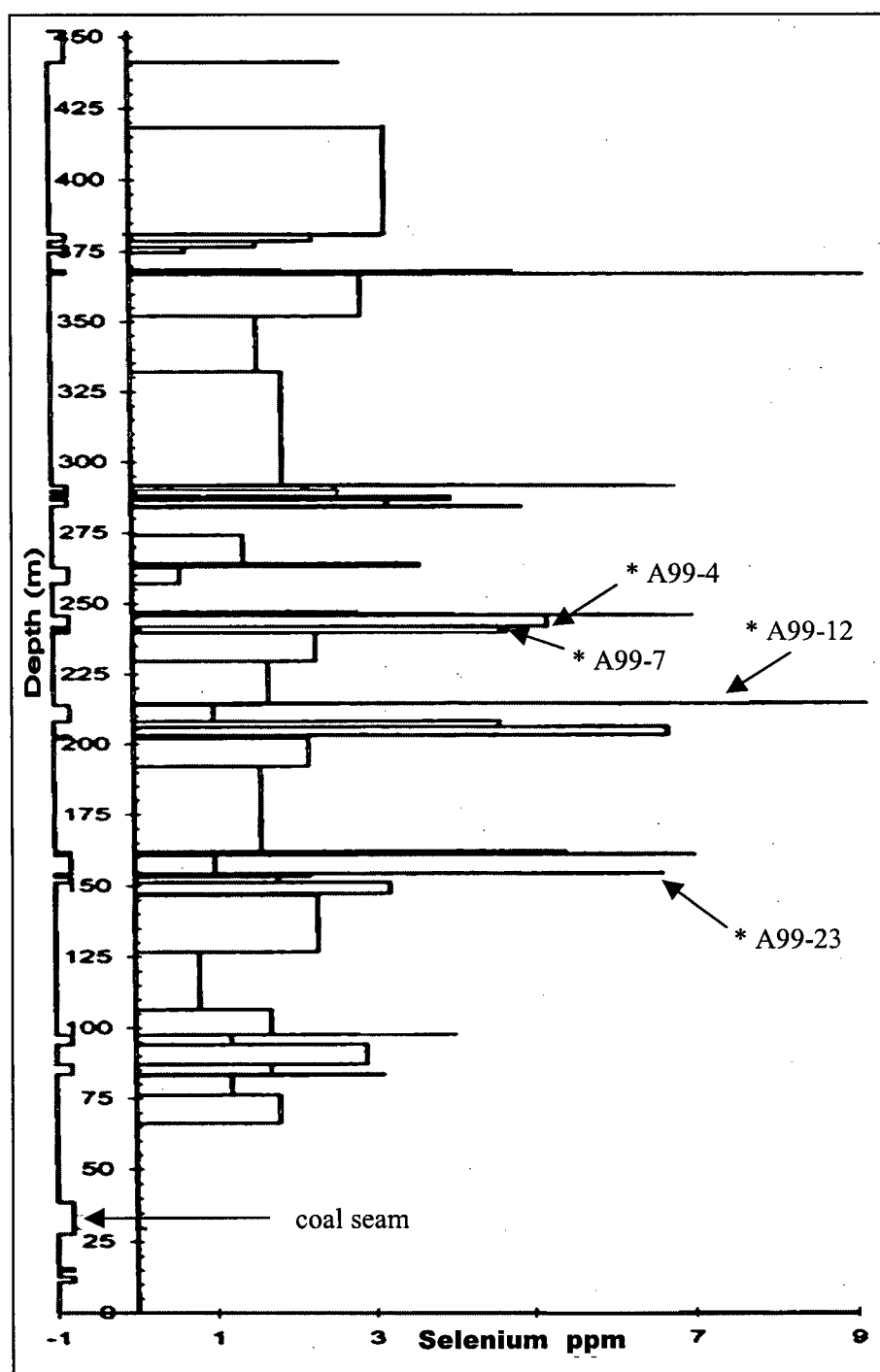
Sampling for this study was conducted in conjunction with a team of geologists from the British Columbia Ministry of Energy and Mines who have been studying Se occurrence in the Mist Mountain Formation (Ryan and Dittrick, 2000). Samples were collected from the pit walls of the five coal mines in the Elk River Valley. An effort was made to sample the entire cross-section of the Mist Mountain Formation at each of the sites, however some strata were not accessible. Chipping material from the pit walls at regular intervals in the cross-section of each stratum 1 to 5 kg samples were obtained (Figure 4.1).



• • • • Denotes line of sampling

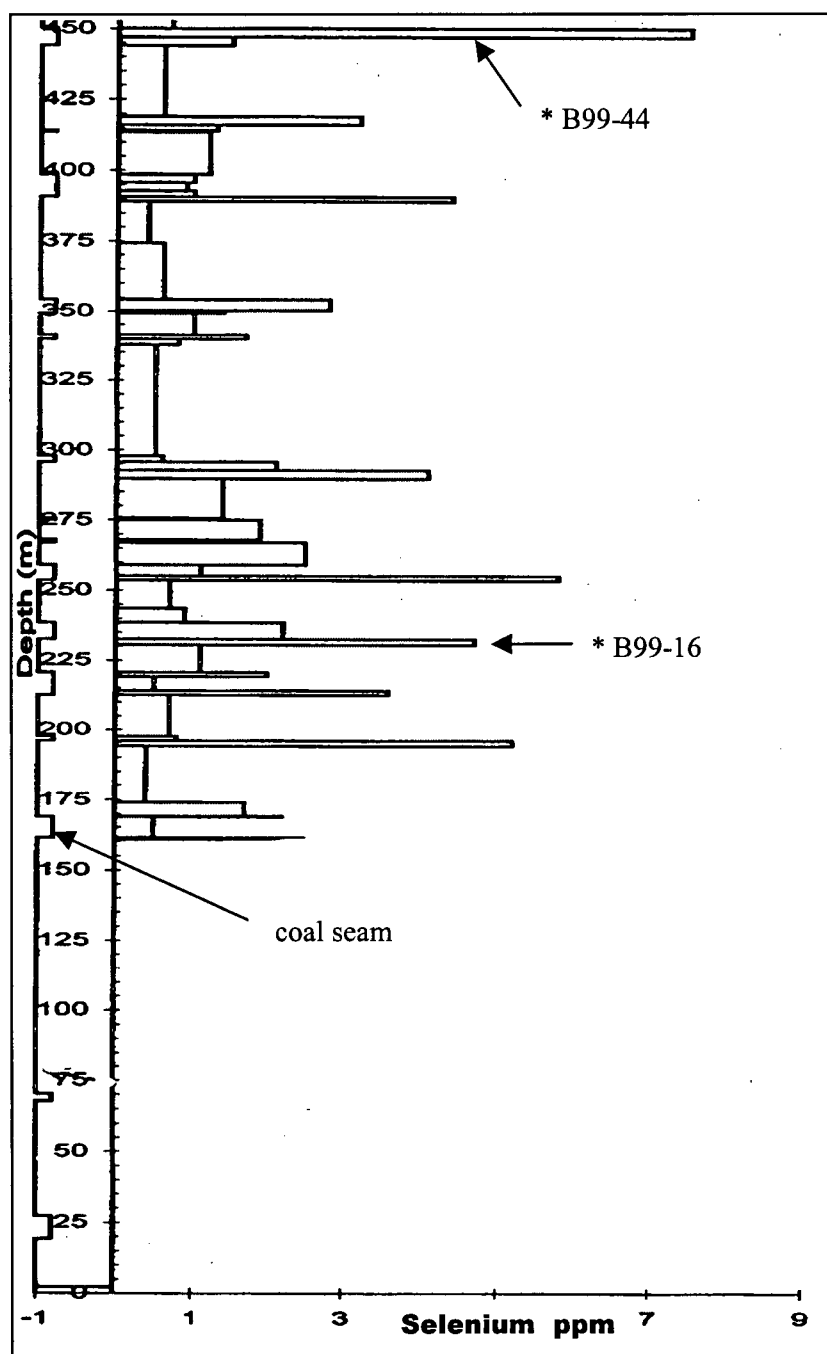
Note: Small coal seam sampled separately

Figure 4.1 Sample Collection from Pit Walls



* Samples used in this study

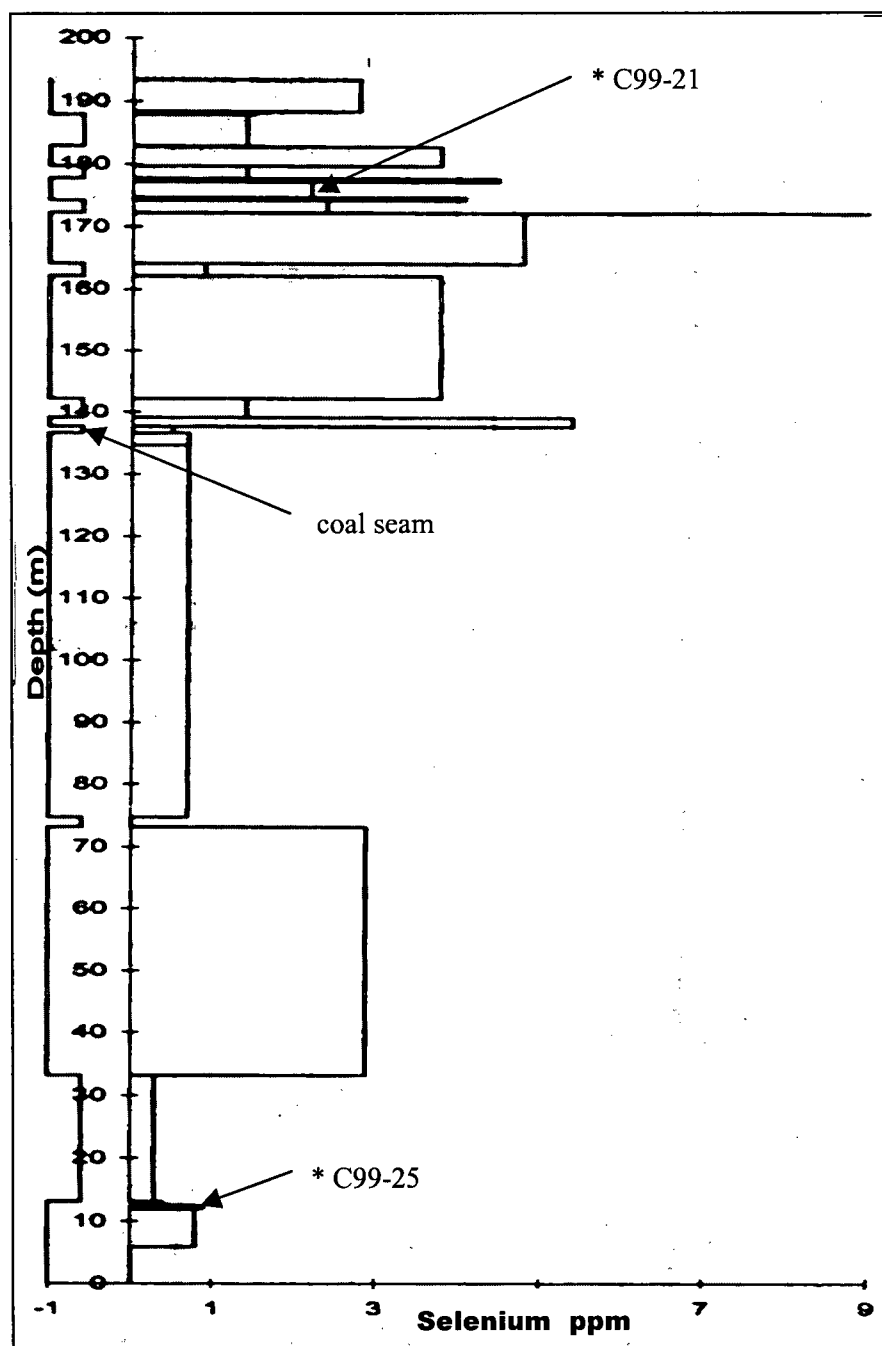
Figure 4.2 Stratigraphic Section of the Mist Mountain Formation at Mine A Illustrating Variations in Se Concentration with Depth (From Ryan and Dittrick, 2000)



* Samples used in this study

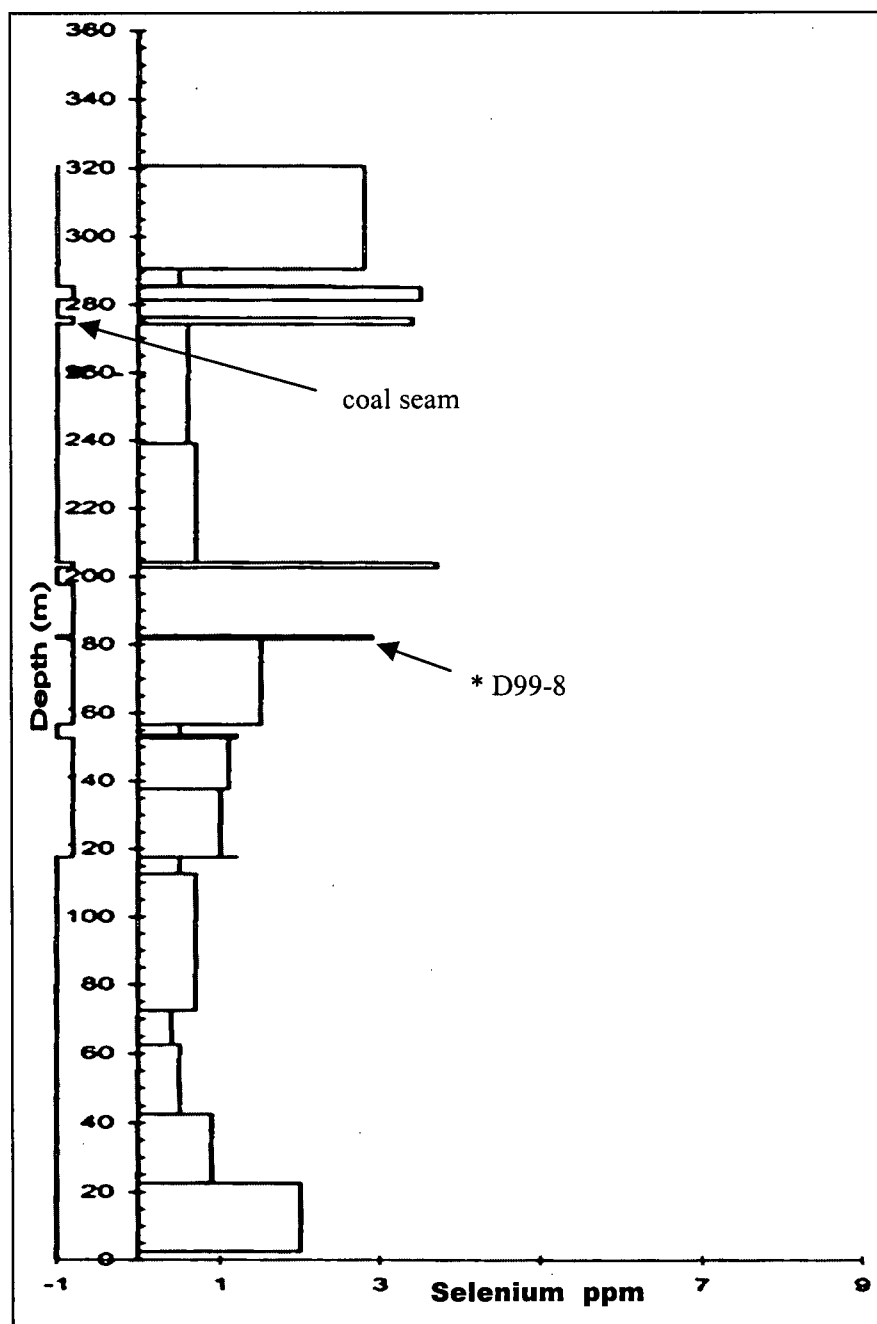
NOTE: B99-62 is located above the top stratum in this figure

Figure 4.3 Stratigraphic Section of the Mist Mountain Formation at Mine B Illustrating Variations in Se Concentration with Depth (From Ryan and Dittrick, 2000)



* Samples used in this study

Figure 4.4 Stratigraphic Section of the Mist Mountain Formation at Mine C Illustrating Variations in Se Concentration with Depth (From Ryan and Dittrick, 2000)



* Samples used in this study

Figure 4.5 Stratigraphic Section of the Mist Mountain Formation at Mine D Illustrating Variations in Se Concentration with Depth (From Ryan and Dittrick, 2000)

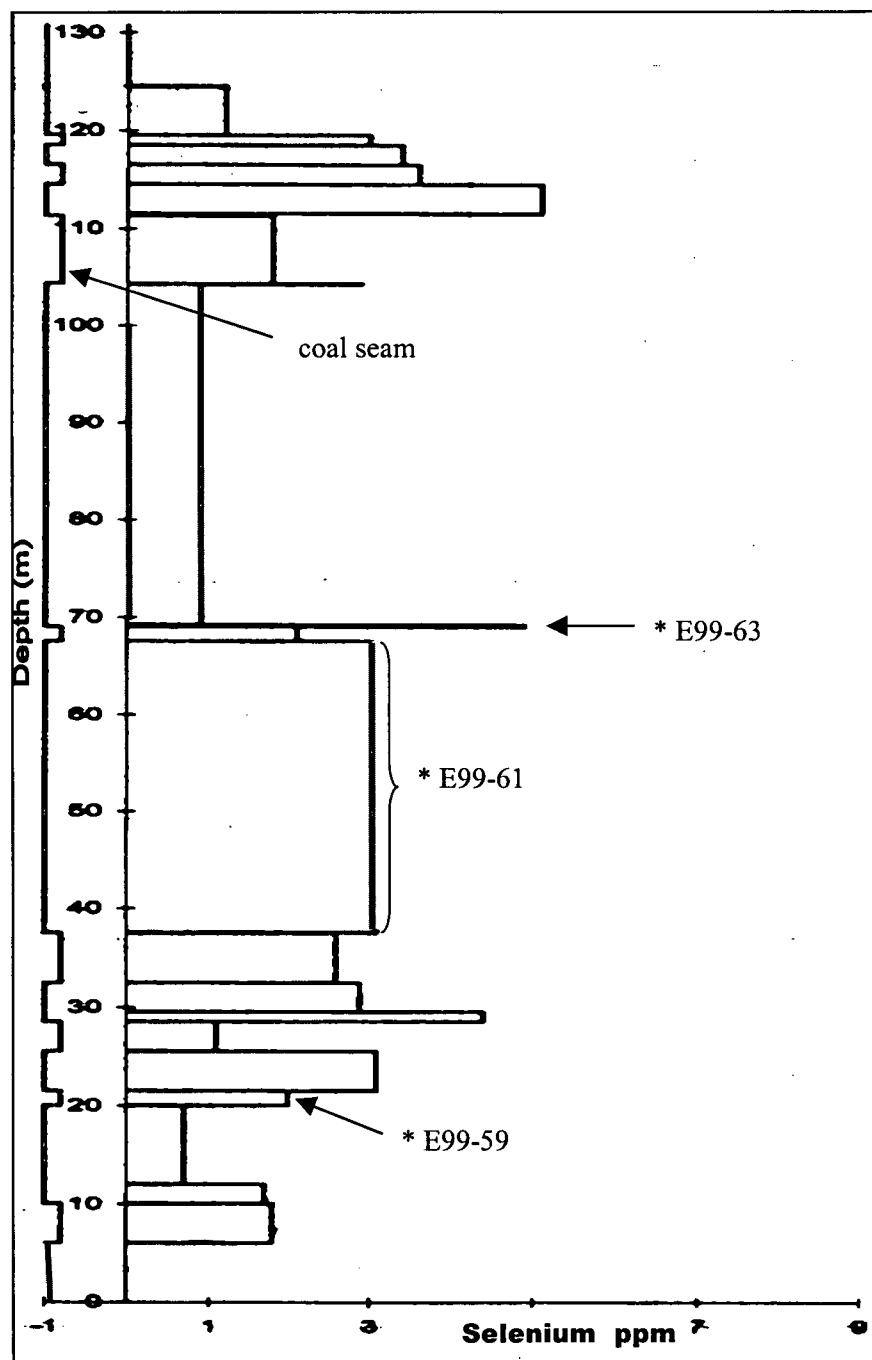


Figure 4.6 Stratigraphic Section of the Mist Mountain Formation at Mine E (East Pit) Illustrating Variations in Se Concentration with Depth (From Ryan and Dittrick, 2000)

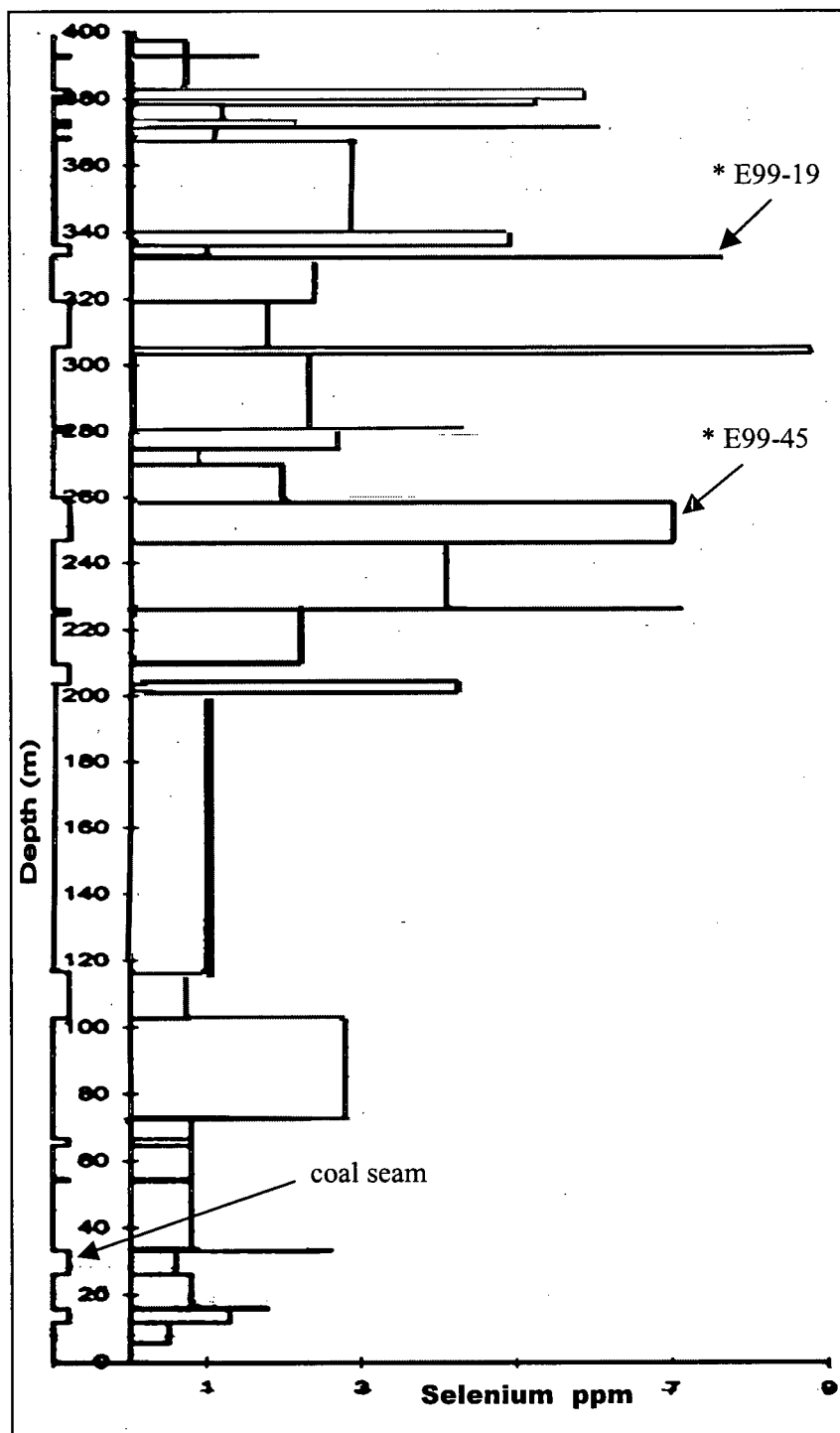


Figure 4.7 Stratigraphic Section of the Mist Mountain Formation at Mine E (West Pit) Illustrating Variations in Se Concentration with Depth (From Ryan and Dittrick, 2000)

Hanging wall and foot wall of seams where there was a distinct band of carbonaceous mudstone between the seam and the interburden were sampled separately. Partings in coal seams were also sampled separately. All 375 samples were collected and labeled using an A to E code to designate from which of the five mines the samples originated. The mines are not identified by their names to respect the confidentiality agreement signed at the outset of this work. The samples were then crushed in a cone crusher to a top size of approximately 50 mm and split so as to provide material for both this study and Ryan and Dittrick's (2000). Results from the latter study are graphically represented in Figures 4.2 to 4.7. The depth is reported in meters from the base of the Mist Mountain Formation. Samples in which Se concentrations were below the analytical detection limit are represented in the graphic at the limit value that ranged from 0.2 to 0.8 mg/kg, depending on interferences during analyses.

4.2 SAMPLE SELECTION AND PREPARATION

It was not financially feasible to run a complete element analysis on all of the samples collected before selecting material for the static and kinetic tests. Instead, 16 pit wall samples representing the different lithologies were chosen based on the Se concentrations determined by Ryan and Dittrick (2000) (Table 4.1). Materials with relatively high Se concentrations were selected to ensure that the amount of Se in leachate would exceed the analytical detection limit and allow for a comparison between the different materials. Mineralogical analyses, sequential extractions, heavy liquid separation, and scanning electron microscopy (SEM) were used to investigate the mineralogical associations of Se in these samples. Sample preparation is outlined in Figure 4.8. Material pulverized below 200 mesh (0.074 mm) was used for all tests other than SEM and the humidity cell tests. Humidity cells were used to model the rate of Se release from 1 kg samples following procedures developed to predict acid rock drainage rates (Lawrence, 1990).

Table 4.1 Samples Included in the Geochemical and Kinetic Tests

Sample Number	Type of Material	Description	Se ** (mg/kg)
A99-4	Coal	Coal	5.2
A99-7	Parting	Multiple partings	4.9
A99-12	Hanging wall	Carbonaceous mudstone	8.0
A99-23*	Parting	Carbonaceous mudstone	7.0
B99-16	Foot wall	Mudstone with coal	5.8
B99-44*	Coal	Coal	7.5
B99-62	Hanging wall	Coal, silstone, mudstone	2.2
CREF*	Refuse	Plant refuse	3.5
C99-21	Hanging wall	Coal (w/ elemental S)	1.8
C99-25	Foot wall	Mudstone	<0.5
D99-8	Parting	Parting	2.9
E99-19*	Foot wall	Mixed coal & mudstone	8.4
E99-45	Hanging wall	Mudstone & coal	7.1
E99-59	Coal	Coal	2.6
E99-61*	Interburden	Mudstone	3.1
E99-63	Parting	Carbonaceous mudstone	4.9

* Samples selected for the humidity cell tests

** Se values obtained from Ryan and Dittrick (2000)

Samples selected for the humidity cell tests represent the main categories of material in the waste piles or exposed along the pit walls. These include coal, interburden, carbonaceous mudrocks closely associated with the coal seams (partings, hanging wall, foot wall) and plant refuse. All materials used in the humidity cell tests were crushed with a disc crusher and passed through a 3 mesh sieve (6.3 mm). In general, approximately 1 kg of each of these samples remained after the two 1 kg humidity cells were set up in duplicate. This material, once pulverized to below 200 mesh in a planetary pulverizer, was used for mineralogical analyses, sequential extractions, heavy liquid separation, and SEM. These tests were run on the eight samples used in the humidity cell experiments and on eight additional samples selected based on lithological characteristics and Se content. About 500 g of each of the additional eight samples were pulverized to below 200 mesh using the planetary pulverizer. Samples were stored at room temperature in polyethylene bags.

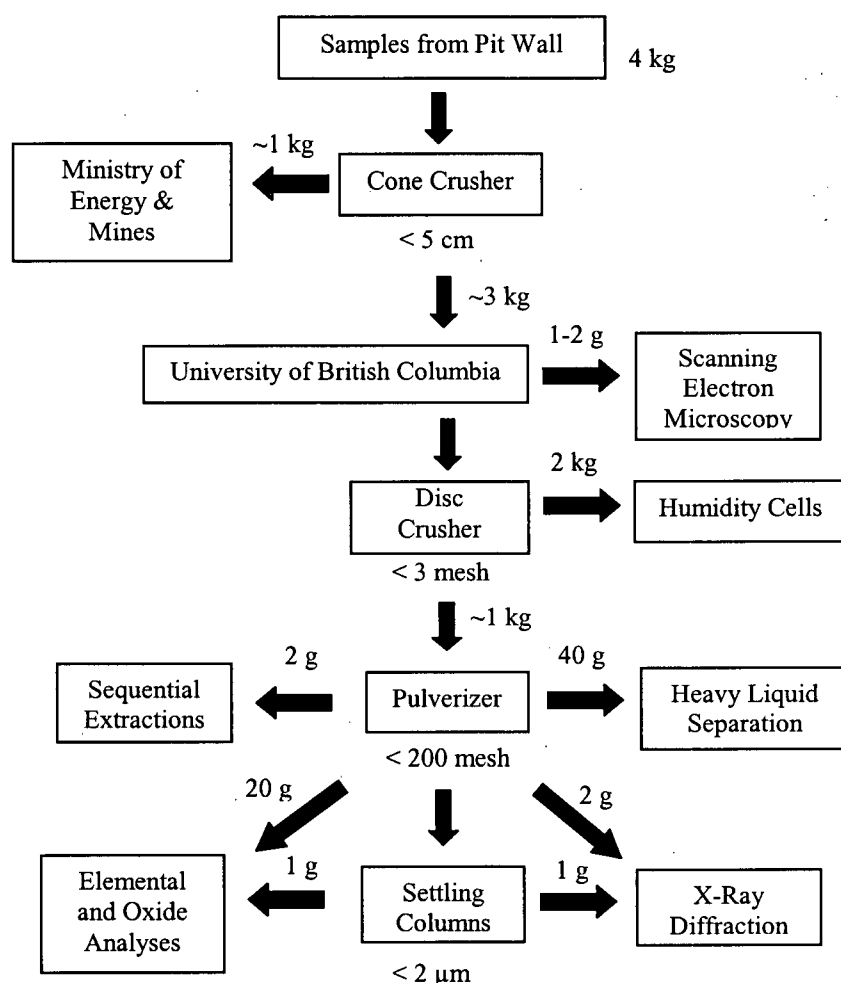


Figure 4.8 Sample preparation

4.3 MINERALOGY

4.3.1 Qualitative Mineralogy

4.3.1.1 X-Ray Diffraction

The X-ray diffraction spectra of the 16 selected samples were analyzed using a D5000 Diffractometer at the Department of Earth and Ocean Sciences of the University of British Columbia. Approximately 2 g of each of the <200 mesh samples were ground with a mortar and pestle to ensure that the grains would be finer than 2 μm. Approximately 0.4 g of sample were then mixed with 2 to 3 mL of distilled water in a glass test tube and placed in an ultrasonic bath

for 2 to 3 minutes for dispersion of the suspension. The mixture was then pipetted onto a glass slide, coating it evenly. The same procedure was used to prepare slides with the $<2 \mu\text{m}$ fraction extracted from the <200 mesh fraction. The intention of was to concentrate the clay minerals. The $<2 \mu\text{m}$ particles were separated from the bulk of the sample using sedimentation. This procedure was repeated five times to guarantee efficient removal of the $<2 \mu\text{m}$ fraction. The settling velocity of the $<2 \mu\text{m}$ particles in 500 mL graduated cylinders filled with distilled water was calculated by equation 4.1 (Stoke's Law).

$$V_d = \frac{D^2(\rho - \rho_0) * g}{18n} \quad \text{Equation 4.1}$$

V_d : velocity of sedimentation
 ρ : particle density (g/cm^3)
 ρ_0 : fluid density (g/cm^3)
 n : viscosity of water (g/cm/s)
 g : gravitational acceleration constant (980 cm/s)
 D : particle diameter (cm)

The diffracted x-ray detector attached to the goniometer scanned at a speed of $2^\circ(2\theta)/\text{min}$ from 2 to 33 degrees of 2θ . This range of 2θ was broad enough to detect the main diffracted peaks of minerals typically found in coals i.e. quartz, clay minerals and carbonates. Tables 4.2 and 4.3 summarize results from the x-ray diffraction analyses.

The diffractograms for the $<2 \mu\text{m}$ and $<200 \mu\text{m}$ fractions of the 5 samples included in Table 4.3 are found in Appendix 1 (Figures A1.1 through A1.10). A strong quartz peak was observed in all samples except in the $<2 \mu\text{m}$ fraction of B99-44, a high Se coal with the highest kaolinite content. In the $<2 \mu\text{m}$ fraction, kaolinite contents were higher than those in the coarse fraction. Illite was enriched only in the $<2 \mu\text{m}$ fraction of the mudstone interburden sample (E99-61). Carbonates were detected in only three samples. E99-61 was the only sample in which carbonates were detected in the $<2 \mu\text{m}$ fraction. Calcite, ankerite and siderite, the most common carbonates in coals, were found in trace quantities in the three samples.

Table 4.2 Minerals in <200 mesh Fraction Determined by X-Ray Diffraction

	Type of Material	Quartz	Kaolinite	Illite	Calcite	Ankerite	Siderite
A99-4	Coal	+++	+	+	ND	ND	ND
A99-7	Parting	+++	+	+	ND	ND	ND
A99-12	Hanging wall	+++	+	+	ND	ND	ND
A99-23	Parting	+++	+	+	ND	ND	ND
B99-16	Foot wall	+++	+	+	ND	ND	ND
B99-44	Coal	+++	+++	+	ND	ND	ND
B99-62	Hanging wall	+++	+	+	ND	ND	ND
CREF	Refuse	+++	+	+	Tr	Tr	Tr
C99-21	Hanging wall	+++	+	+	Tr	Tr	Tr
C99-25	Foot wall	+++	+	+	ND	ND	ND
D99-8	Parting	+++	+	+	ND	ND	ND
E99-19	Foot wall	+++	+	+	ND	ND	ND
E99-45	Hanging wall	+++	+	+	ND	ND	ND
E99-59	Coal	+++	+	+	ND	ND	ND
E99-61	Interburden	+++	+	+	Tr	Tr	Tr
E99-63	Parting	+++	+	+	ND	ND	ND

+: Amount present (estimated by relative X-ray diffractogram peak height)

ND: Not detected

Tr: Trace

Table 4.3 Minerals in <2 μ m Fraction of Samples Selected for 20-Week Humidity Cell Tests Determined by X-Ray Diffraction

	Type of Material	Quartz	Kaolinite	Illite	Calcite	Ankerite	Siderite
A99-23	Parting	+++	+	+	ND	ND	ND
B99-44	Coal	++	+++	+	ND	ND	ND
CREF	Refuse	+++	++	+	ND	ND	ND
E99-19	Foot Wall	+++	++	+	ND	ND	ND
E99-61	Interburden	+++	++	++	Tr	Tr	Tr

+: Amount present (estimated by relative X-ray diffractogram peak height)

ND: Not detected

Tr: Trace

4.3.1.2 Scanning Electron Microscopy

Scanning electron microscopy (SEM) was used to investigate the occurrence of selenides and sulphides. A SEM image is produced by scanning an electron beam across the surface of a sample. Characteristic fluorescent X-rays produced by a Philips XS 30 SEM were detected using

a Princeton Gamma-Tech energy-dispersive spectrometer (EDS) equipped with a Li-Si detector. The X-rays were generated from a volume of $1\ \mu\text{m}^3$.

Four pieces of A99-11, B99-44 and E99-19 weighing approximately 2 g each were selected for SEM analysis. They were mounted in an epoxy resin, allowed to harden under ambient conditions and polished. The polished sections were coated with a conductive layer of carbon.

Sample A99-11, with a Se content of 10 mg/kg, was from a massive pyrite inclusion in a coal seam at Mine A. B99-44 was a coal with 8.8 mg/kg Se and E99-19 was a foot wall sample with 8.4 mg/kg Se and both have pyrite visible on their surfaces. It was assumed that samples consisting of or containing pyrite would be most likely to host selenides or Se in solid solution with sulphides given the similarity between S and Se geochemistry. These samples have the highest Se concentrations among those collected for this study, but the probability of detecting Se at 10 mg/kg is low. Reed (1995) notes that detection limit for SEM-EDS is generally around 0.1% i.e. two orders of magnitude greater than the concentrations found in the selected samples. Taking this into account, two methods were tested. For A99-11, a 10 minute line scan with 15 000 counts per second was used. A typical count time is 100 seconds (Reed, 1995). A longer count time was chosen to scan as large an area as possible and integrating the signal thereby maximizing the chance of detecting Se. For the other two samples, 8 to 10 sections of pyrite ($5\ \mu\text{m}$ by $6\ \mu\text{m}$) were scanned in an attempt to obtain an average for those areas. This was repeated for two mounts of each sample. No selenium was detected in the three materials analyzed.

4.3.2 Chemical Analyses

The 16 selected samples were pulverized prior to analysis for Se, total S, sulphides, total organic carbon (TOC) and trace elements by ACME Analytical Laboratories in Vancouver, British Columbia.

ACME conducted Se analyses using ICP-MS, which has a detection limit of 0.1 mg/kg. An aqua regia digestion i.e. a 3:1 ratio of nitric to hydrochloric acid, was used to solubilize the sample. Results from the ICP-MS analysis of 1 g samples were compared with those obtained by Ryan and Dittrick (2000). Since there was poor agreement between the two sets of results (Table 4.4), a second set of samples was sent to ACME for analysis. To minimize sampling error, 15 g of each sample were then analyzed. This time, Se values differed from Ryan and Dittrick's (2000) by less than 35% (1 mg/kg) for all but 3 samples (Table 4.4). To provide a third measure of the accuracy of ACME's analyses, a set of eight samples was sent to Analytical Laboratories Services (ALS) Limited, Vancouver, British Columbia, where Se analysis was conducted using hydride generation atomic absorption spectrometry (HG-AAS) following EPA Method 7742 (USEPA, 1994). Samples were digested using a 1:1 ratio of nitric acid and hydrochloric acid as specified in EPA Method 3051 (USEPA, 1986).

Se values obtained using the different analytical methods varied by more than 70% for B99-44 and CREF (Table 4.4). The difference between the Se values was below 15% for A99-7, B99-62, E99-45 and E99-63. The percent difference ranged from 20% to 50% for the remainder of the samples. Dale (1996) reviewed analytical techniques for trace elements in coal. For Se, he recommended using INAA or HG-AAS to obtain accurate results. Without interference, the detection limit of INAA is 0.1 mg/kg and its precision is estimated to be 5% (Coleman et al., 1993). Disadvantages of INAA include its high cost and the length of time required to obtain results. HG-AAS also has a detection limit of 0.1 mg/kg for Se in solids. The main drawback associated with HG-AAS is the need to digest the sample, which may result in serious losses of Se through volatilization (Raptis et al., 1983; Verlinden, 1982; Welz, et al., 1984).

Table 4.4 Interlaboratory Comparison of Se Values Expressed in mg/kg

	ACME ICP-MS 1 g sample	ACME ICP-MS 15 g sample	ALS HG-AAS 1 g sample	INAA* 10 g sample	Average	Standard Deviation
A99-4	5.9	5.2	3.4	5.2	4.9	1.1
A99-7	4.1	4.5	n/a	4.9	4.5	0.4
A99-12	6.4	6.7	n/a	8.0	7.0	0.9
A99-23	5.8	6.1	4.8	7.0	5.9	0.9
B99-16	5.4	5.0	3.4	5.8	4.9	1.1
B99-44	4.0	16.6	7.0	7.5	8.8	5.4
B99-62	2.2	2.3	n/a	2.2	2.2	0.1
CREF	11.8**	3.6	3.2	3.5	3.4	0.2
C99-21	2.4	2.5	n/a	1.8	2.2	0.4
C99-25	0.7	0.9	n/a	<0.5	0.8	0.3
D99-8	2.2	2.2	n/a	2.9**	2.2	0.0
E99-19	10.0	10.4	5.5	7.7	8.4	2.3
E99-59	1.5	1.7	1.4	2.6	1.8	0.5
E99-45	7.2	7.7	n/a	7.1	7.3	0.3
E99-61	3.3	3.2	2.3**	3.1	3.0	0.1
E99-63	4.2	4.1	n/a	4.9	4.4	0.4

n/a: not analyzed

* INAA data from Ryan and Dittrick (2000)

** These anomolous results were excluded from the average based on criteria specified by Dean and Dixon (1951) described in the section below

In recent years, ICP-MS has gained acceptance as an analytical method for Se (Ting et al., 1989; McCurdy et al., 1993; Menegario and Gine, 2000). When using ICP-MS to measure Se concentrations, signal interference from Cu, Ni, Co, precious metals and hydride-forming elements may pose a problem (Dale, 1996; D'Ulivo, 1997) and like HG-AAS, ICP-MS requires sample digestion. Ryan and Dittrick (2000) analyzed 19 samples using both ICP-MS and INAA and found that the two methods yielded similar results. Ryan and Dittrick (2000) calculated the average Se value for the 19 samples tested and found it to be slightly higher when using ICP-MS (3.4 mg/kg) rather than INAA (2.7 mg/kg) indicating that losses to volatilization were minimal.

Average Se values obtained by the different analytical methods are compiled in Table 4.4. In order to eliminate the effect of anomalously high or low values on the estimate of Se content, a Quotient Test, as described by Dean and Dixon (1951), was used. The difference between a

questionable value and its nearest neighbour is calculated and then divided by the difference between the highest and lowest values of the set. If the ratio, Q , exceeds the Rejection Quotient, $Q_{0.90}$, the value may be rejected with 90% confidence i.e. the value has a 10 % likelihood of rejection in a normally distributed population. The $Q_{0.90}$ values used are those published by Dean and Dixon (1951) of 0.94 and 0.76 for $n=3$ and $n=4$ respectively (where n = number of samples analyzed). Based on this criteria three values were excluded and the average recalculated using the remaining values. All four available Se values were included in the average calculated for B99-44 despite a difference of as much as 74 % (8 mg/kg) between the highest and next highest values. The wide range of Se values for B99-44 is taken as an indication of greater overall variability making it less likely that a notably high or low value occurs only as a product of chance.

Total S, sulphide, total C, TOC and ash concentrations were determined by ACME Analytical Laboratories, Vancouver and results are recorded in Table 4.5. Total S was determined with a CS-244 LECO analyser by ASTM Method D4239 (ASTM, 2001). A 0.1 g sample was leached with 15% HCl at 70°C for 1 hour, washed and then solution dried in a furnace at 200°C for 3 hours. Sulphide content was determined by placing evaporation residues in a furnace at 800°C for 1 hour and using a LECO analyser to measure the S remaining (Sobek et al., 1978). This method was selected over the Sobek method, which calculates sulphides as the difference between S remaining after leaching the sample with 40% HCl and organic S, eliminated by leaching the sample with 12.5% HNO₃. While the organic S measurements obtained by the 15% HCl and 12.5% HNO₃ leaches are fairly similar, the Sobek method's 1 hour leach with 40% HCl does not extract as much of the organic S as sample ignition at 800°C (Leong, 2001, pers. com.). The ASTM method used thus provides a more conservative estimate of sulphides.

Table 4.5 Selenium, Sulphur, Sulphides, Carbon and Ash Analyses

Sample Number	Type of Material	Se (mg/kg)	Total S (%)	Sulphides (%)	Organic S (%)	Total C (%)	TOC (%)	Ash (%)
A99-4	Coal	4.9	1.05	0.84	0.21	59.7	59.4	31.9
A99-7	Parting	4.5	0.32	0.26	0.07	24.9	23.9	67.2
A99-12	Hanging wall	7.0	0.43	0.42	0.02	24.3	24.0	69.5
A99-23	Parting	5.9	0.12	0.07	0.05	5.83	4.68	88.8
B99-16	Foot wall	4.9	0.45	0.31	0.14	21.9	18.8	69.2
B99-44	Coal	8.8	0.60	0.12	0.48	75.0	70.3	12.2
B99-62	Hanging wall	2.2	0.62	0.53	0.09	56.2	56.0	32.3
CREF	Refuse	3.4	0.18	0.05	0.13	18.6	12.5	71.6
C99-21	Hanging wall	2.5	0.48	0.37	0.11	54.8	54.3	37.0
C99-25	Foot wall	0.8	0.18	0.17	0.01	41.1	41.0	54.2
D99-8	Parting	2.2	0.23	0.22	0.01	28.0	27.9	64.3
E99-19	Foot wall	8.4	0.60	0.43	0.17	45.3	42.1	47.1
E99-45	Hanging wall	7.3	0.19	0.18	0.01	14.8	14.7	79.6
E99-59	Coal	1.8	0.40	0.34	0.06	46.9	46.1	47.0
E99-61	Interburden	3.2	0.17	0.03	0.14	4.66	3.99	89.9
E99-63	Parting	4.4	0.16	0.15	0.02	7.08	6.85	87.8

Table 4.6 Oxide Concentrations Expressed as a Percentage of Total Sample Weight

	A99-4	A99-7	A99-12	A99-23	B99-16	B99-44	B99-62	CREF	C99-21	C99-25	D99-8	E99-19	E99-45	E99-59	E99-61	E99-63
SiO ₂	18.8	44.4	46.2	65.8	53.4	7.18	21.1	51.4	24.2	45.3	42.3	32.1	57.4	29.4	65.2	62.0
Al ₂ O ₃	7.69	12.7	14.9	15.2	11.7	3.06	5.91	14.8	6.86	5.75	15.9	8.41	15.4	10.8	11.9	17.1
Fe ₂ O ₃	2.08	5.52	1.49	1.39	1.15	0.27	0.78	2.24	0.84	0.25	0.91	0.88	0.84	1.17	2.47	1.82
MgO	0.28	1.12	0.83	0.75	0.77	0.28	0.58	0.85	0.73	0.22	0.48	0.35	0.64	0.40	1.78	1.03
CaO	0.40	0.26	0.50	0.72	0.75	1.29	0.69	1.14	1.16	0.11	0.22	0.32	0.35	0.19	3.28	0.14
Na ₂ O	0.02	0.08	0.11	0.05	0.03	<0.01	0.06	0.05	0.06	0.08	0.19	0.02	0.09	0.05	0.06	0.12
K ₂ O	0.75	1.92	2.95	2.77	2.3	0.52	0.86	1.77	0.98	0.82	1.77	1.38	2.40	1.20	2.36	2.96
TiO ₂	0.40	0.63	0.65	0.74	0.65	0.15	0.27	0.77	0.37	0.58	0.74	0.4	0.70	0.54	0.65	0.79
P ₂ O ₅	0.11	0.05	0.3	0.61	0.21	0.19	0.16	0.22	0.22	0.01	0.03	0.12	0.25	0.06	0.31	0.06
MnO	0.04	0.03	0.01	<0.01	<0.01	<0.01	0.01	0.01	0.01	<0.01	<0.01	<0.01	<0.01	0.01	0.03	0.01
LOI*	69.2	33.0	31.8	11.6	28.9	87.1	68.8	26.4	64.0	46.8	37.2	55.8	21.6	55.9	11.6	13.6
Total	99.8	99.7	99.7	99.7	99.9	100	99.2	99.7	99.4	99.9	99.8	99.7	99.7	99.8	99.6	99.7

* LOI: Loss on ignition

Table 4.7 Trace Element Concentrations Expressed in mg/kg

	A99-4	A99-7	A99-12	A99-23	B99-16	B99-44	B99-62	CREF	C99-21	C99-25	D99-8	E99-19	E99-45	E99-59	E99-61	E99-63
Cr	27	68	116	82	82	14	55	75	41	41	27	62	144	34	96	123
Ba	394	633	556	1730	633	158	340	673	339	297	537	378	934	415	711	791
Ni	<20	21	44	55	83	<20	<20	160	<20	<20	<20	<20	30	<20	<20	57
Sr	95	134	140	378	118	148	196	152	107	58	113	107	159	105	71	159
Zr	55	103	120	116	149	28	66	118	105	134	150	133	135	90	159	138
Y	15	25	35	30	26	<10	120	26	19	41	28	14	28	18	195	23
Nb	<10	19	22	<10	<10	<10	18	<10	19	12	26	<10	24	<10	<10	19
Sc	7	13	15	12	10	3	16	11	9	9	14	7	13	9	30	14

Table 4.8 Oxide Concentrations in the <2 μm Fraction Expressed as a Percentage of Total Sample Weight

	A99-23	B99-44	CREF	E99-19	E99-61
SiO ₂	52.9	9.47	44.8	29.0	53.6
Al ₂ O ₃	19.9	4.91	17.9	10.6	19.6
Fe ₂ O ₃	1.51	0.48	1.63	1.55	2.53
MgO	0.88	0.34	0.66	0.44	1.40
CaO	0.44	1.13	0.58	0.34	1.72
Na ₂ O	0.08	0.04	0.08	0.09	0.11
K ₂ O	3.15	0.44	2.20	1.54	3.54
TiO ₂	0.71	0.19	0.77	0.42	0.76
P ₂ O ₅	0.51	0.09	0.24	0.19	0.40
MnO	0.01	<0.01	0.01	0.01	0.02
LOI*	19.5	83.0	31.0	55.0	16.0
Total	99.6	100	99.8	99.1	99.7

* LOI: Loss on ignition

Table 4.9 Trace Element Concentrations in the <2 μm Fraction Expressed in mg/kg

	A99-23	B99-44	CREF	E99-19	E99-61
Cr	82	14	75	62	96
Ba	1730	158	673	378	711
Ni	55	<20	160	<20	<20
Sr	378	148	152	107	71
Zr	116	28	118	133	159
Y	30	<10	26	14	195
Nb	<10	<10	<10	<10	<10
Sc	12	3	11	7	30

Table 4.10 Se Concentrations in the <2 μm Fraction Compared with Se Concentrations in the Whole Sample

	Se in <2 μm Fraction (mg/kg)	Se in Whole Sample (mg/kg)	% Total Weight in <2 μm Fraction	% D _{Se} in <2 μm Fraction
A99-23	7.3	5.9	2.2	2.7
B99-44	20.6	8.8	2.3	5.4
CREF	4.2	3.4	4.1	5.1
E99-19	11.9	8.4	2.8	3.9
E99-61	2.8	3.2	3.7	3.2

Total carbon in the sample was measured using the CS-244 LECO analyser after transforming all carbon species in the sample into CO_2 by combustion in an induced furnace at 2000°C . Inorganic carbon was also determined using the CS-244 LECO analyser, but in this case, the sample was first leached in a boiling water bath for 1 hour with 5 mL HNO_3 and 5 mL of 50% HF, washed and dried at 200°C for 3 hours. TOC was calculated by subtracting inorganic carbon from total carbon as specified by ASTM Method D5291 (ASTM, 2001).

Ash was determined according to the ASTM D3174-00 Standard Test Method for Ash in the Analysis Sample of Coal and Coke from Coal (ASTM, 2001). A sample of 1 g was heated from room temperature to 750°C over an hour and kept at this temperature for two additional hours. The combustion residue was then weighed.

Trace element and oxide concentrations were determined using Inductively Coupled Plasma Optical Emission Spectroscopy (ICP-OES). The 0.2 g samples were melted with LiBO_2 to transform all silicates into glass and digested with aqua regia. The concentrations of major oxides (SiO_2 , Al_2O_3 , Fe_2O_3 , CaO , MgO , Na_2O , K_2O , MnO , TiO_2 , P_2O_5 , Cr_2O_3) are listed in Table 4.6 for the whole samples and in Table 4.8 for the $<2\ \mu\text{m}$ fraction. Detection limits for these oxides ranged from 0.001 to 0.04%. Trace element concentrations are compiled in Tables 4.7 and 4.9 for the whole samples and $<2\ \mu\text{m}$ fractions. Se concentrations in the $<2\ \mu\text{m}$ fractions are compared with those in the whole samples in Table 4.10. As and Pb concentrations were measured by ALS Limited, Vancouver using ICP-MS and were found to be below their respective detection limits of 200 and 100 mg/kg in all 16 samples.

4.3.3 Quantitative Mineralogy

Percentages of major mineral components were calculated using data from the chemical analyses of major oxides (Table 4.11) and qualitative information on sample mineralogy obtained by

XRD (Tables 4.2 and 4.3). The most common mineralogical formulas for the minerals were obtained from Deer (1993) (Appendix 1). Assuming that illite is the only K-bearing phase, K_2O

Table 4.11 Percentages of the Major Mineral Components

	Type of Material	% Illite	% Kaolinite	% Quartz	% Carbonate	% Sulphide	% Total
A99-4	Coal	5.71	11.3	4.02	0.71	0.84	22.6
A99-7	Parting	14.6	10.6	12.3	0.46	0.26	38.3
A99-12	Hanging wall	22.5	3.96	11.3	0.89	0.42	39.0
A99-23	Parting	21.1	6.97	20.4	1.28	0.07	49.8
B99-16	Foot wall	17.5	3.15	16.9	1.34	0.31	39.2
B99-44	Coal	3.96	1.84	1.30	2.30	0.12	9.5
B99-62	Hanging wall	6.55	5.30	5.98	1.23	0.53	19.6
CREF	Refuse	13.5	17.9	14.6	2.03	0.05	48.1
C99-21	Hanging wall	7.46	6.37	6.81	2.07	0.37	23.1
C99-25	Foot wall	6.24	5.35	17.4	0.20	0.17	29.4
D99-8	Parting	13.5	20.8	9.77	0.39	0.22	44.6
E99-19	Foot wall	10.5	5.65	9.36	0.57	0.43	26.5
E99-45	Hanging wall	18.3	12.0	16.6	0.62	0.18	47.6
E99-59	Coal	9.14	14.2	6.92	0.34	0.34	31.0
E99-61	Interburden	18.0	3.01	22.3	5.85	0.03	49.1
E99-63	Parting	22.5	9.64	17.5	0.25	0.15	50.0

concentrations were used to calculate the illite content of the samples, that ranged from 3.9 % (B99-44) to 22.5% (A99-12) (Table 4.8). Kaolinite content was calculated based on the difference between total Al_2O_3 in the sample and Al_2O_3 in illite. The percent of kaolinite in the 16 selected samples ranges from 1.8 to 20.8% (Table 4.11). Quartz content was calculated by subtracting SiO_2 in illite and kaolinite from total SiO_2 . The results show that the quartz content ranged from 1.3 % (B99-44) to 22.3 % (E99-61) (Table 4.11). To obtain a rough estimate of the carbonate content of the sample, all CaO was assumed to be present in calcite ($CaCO_3$). Some CaO was likely present as ankerite ($Ca_{1.05}(Fe_{0.48},Mg_{0.45},Mn_{0.04})(CO_3)_2$) and/or siderite ($FeCO_3$). Subtracting Fe in sulphides from total Fe in the samples shows that iron sources other than pyrite, on average, account for 0.7% of total Fe mass. These include siderite, HFMO, Fe complexed by organic matter and Fe in the silicates.

4.4 SEQUENTIAL EXTRACTIONS

Single and sequential extractions are usually used to establish which mineralogical component or components bear heavy metals or trace elements in soils, sediment or rocks. This can also provide indirect information about metal bioavailability and the potential for mobilization by surface- or groundwater. As no universally accepted methodology currently exists, the Standards, Measurements and Testing Program of the European Commission has tried to establish a definitive procedure and create a database allowing for quality control and comparison between different materials (Ure et al., 1993; Quevauviller et al., 1994). There is, however, still much debate concerning the efficiency and specificity of extractants. The fractions are thus defined operationally by the reagent employed, the extraction sequence, the time, temperature and nature of contact and the sample to extractant ratio. Table 4.12 provides an overview of commonly used sequential extraction methods for most trace elements. Only the procedure developed by Chao and Sanzalone (1989) was designed specifically for Se. Figure 4.9 illustrates the four-part sequential extraction procedure used in this study. Details on extractant selection are provided in Sections 4.4.1 through 4.4.4.

All solutions were prepared using de-ionized water obtained from a MILLI-Q water purification system. Extractions were performed in 250 ml Erlenmeyer flasks washed with 10% HNO_3 and rinsed with de-ionized water. After each extraction, samples were filtered through 0.45 μm millipore filters. A volume of 2 ml of 1:1 HNO_3 was added to the filtered solution to prevent the formation of insoluble metal complexes. Solids collected on filter paper were air dried and weighed after each extraction. Filtrates were sent to ALS Limited for Se and metal analysis by HG-AAS and ICP-MS respectively. Residues collected after the KClO_3/HCl extraction were sent to ACME Limited for Se analysis by ICP-MS.

Table 4.12 Summary of Selected Sequential Extraction Procedures Presented in Literature (Adapted from Hall et al., 1996)

Exchangeable	Adsorbed, Carbonates	Mn Oxides	Soluble Organics	Amorphous Fe oxides	Crystalline Fe oxides	Sulphides & Organics	Residual	Reference
		0.1 M $\text{NH}_2\text{OH} \cdot \text{HCl}$ in 0.01 M HNO_3		0.25 M $\text{NH}_2\text{OH} \cdot \text{HCl}$ / 0.25 M HCl	Citrate-dithionate buffer	$\text{KClO}_3\text{-HCl}$ / HNO_3	HF-HNO_3	Chao and Theobald (1976)
1 M MgCl_2 at pH 7	1 M NaOAc at pH 5			0.04 M $\text{NH}_2\text{OH} \cdot \text{HCl}$ in 25% HOAc		$\text{H}_2\text{O}_2\text{-HNO}_3$	HF-HClO_4	Tessier et al. (1979)
		0.1 M $\text{NH}_2\text{OH} \cdot \text{HCl}$ pH 2.5	NaOCl pH 9.5	0.175 M $(\text{NH}_4)_2\text{C}_2\text{O}_4$ in 0.1 M $\text{H}_2\text{C}_2\text{O}_4$	Citrate-dithionate buffer		$\text{HClO}_4\text{-HNO}_3$	Hoffman and Fletcher (1979)
1 M HOAc		0.1 M $\text{NH}_2\text{OH} \cdot \text{HCl}$ in 0.01 M HNO_3		0.25 M $\text{NH}_2\text{OH} \cdot \text{HCl}$ in 25% HOAc		$\text{H}_2\text{O}_2 / \text{NH}_4\text{Oac}$ in 6% HNO_3	$\text{HF-HNO}_3\text{-HCl}$	Filipek and Theobald (1981)
		0.1 M $\text{NH}_2\text{OH} \cdot \text{HCl}$	NaOCl	0.25 M $\text{NH}_2\text{OH} \cdot \text{HCl}$ / 0.25 M HClO	1.0 M $\text{NH}_2\text{OH} \cdot \text{HCl}$ in 25% HOAc		HNO_3	Bogle and Nichol (1981)
1 M HOAc at pH 4.5		0.1 M $\text{NH}_2\text{OH} \cdot \text{HCl}$ pH 2.5		0.175 M $(\text{NH}_4)_2\text{C}_2\text{O}_4$ in 0.1 M $\text{H}_2\text{C}_2\text{O}_4$	0.175 M $(\text{NH}_4)_2\text{C}_2\text{O}_4$ in 0.1 M $\text{H}_2\text{C}_2\text{O}_4$		$\text{HF-HNO}_3\text{-HCl}$	Cardoso Fonseca and Martin (1986)
0.1 M KH_2PO_4					4 M HCl	$\text{KClO}_3\text{-HCl}$	$\text{HF-HClO}_4\text{-HNO}_3$	Chao and Sanzolone (1989)
1 M HOAc at pH 4.5			0.25 M $\text{NH}_2\text{OH} \cdot \text{HCl}$			35% H_2O_2		Ure et al. (1993)
1 M NaOAc at pH 5				0.25 M $\text{NH}_2\text{OH} \cdot \text{HCl}$ in 0.25 M HCl	0.25 M $\text{NH}_2\text{OH} \cdot \text{HCl}$ in 25% HCl	$\text{KClO}_3\text{-HCl}$ / HNO_3	$\text{HF-HClO}_4\text{-HNO}_3$	Hall et al. (1996)

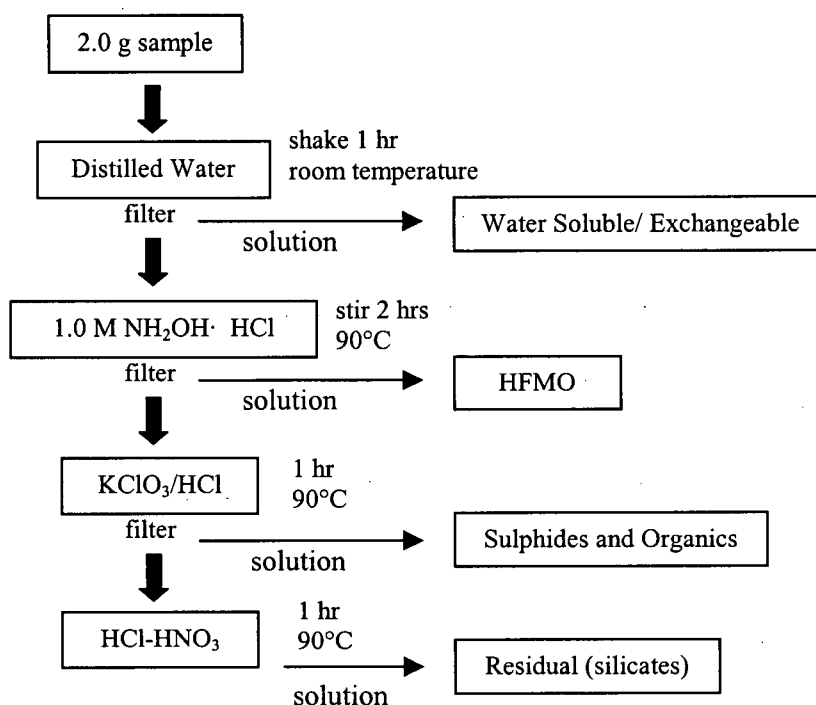


Figure 4.9 Sequential Extraction Procedure

Se concentrations were measured by HG-AAS by ALS Limited using a Perkin Elmer model 2380 HVAK atomic absorption spectrophotometer. This instrument generally has a detection limit of 0.5 µg/L for Se in solution. Se volatilisation and signal interference from matrix components, such as chlorides, sulfates, phosphates and iron may increase the detection limit. One sample from each batch was selected for quality control of the analytical procedure. In instances when results from the replicates differed from the original analyses, they did so by less than 2%. The Se concentration in the distilled water with which the cells were leached was below the detection limit of 0.5 µg/L. Metal concentrations in solution were measured by ALS Limited using Thermo Janell Ash Model ICAP61 and Thermo Janell Ash IRIS ICP-OES instruments. The procedure followed corresponds to EPA Method 6010B (USEPA, 1996).

4.4.1 Extraction Method for Exchangeable Selenium

The first set of extractions targeted exchangeable Se, or more precisely, Se oxyanions held to the

surface of clays, HFMO or organic matter through electrostatic attraction. Four extractants were tested to determine their relative efficiency in removing exchangeable Se from E99-22, a foot wall sample containing 7.1 mg/kg Se.

The extractants tested were:

- 0.05 M ethylenediamine-tetraacetic acid (EDTA)
- 1.0 M magnesium chloride (MgCl_2)
- 1.0 M sodium acetate ($\text{CH}_3\text{COONH}_4$, abbreviated NaOAc)
- 0.1 M potassium dihydrogenase phosphate (KH_2PO_4)
- Distilled water

To test the extractants, 2 g of pulverized sample were placed in an Erlenmeyer flask with 100 ml of solution. The mixture was shaken for 1 hour and passed through a 0.45 μm millipore filter. The filtrate was sent to ALS Limited for Se analysis. Se concentrations in the leachate were consistently above the detection limit (Table 4.13).

The sample to solution ratio used was recommended by Chao and Sanzolone (1989) and Hall et al. (1996). A low solid to extractant ratio could yield a solution with a Se concentration below the detection limit, while a high ratio could lead to incomplete extraction. In order to determine the effect of an increase in the solid:solution ratio on the amount of Se extracted, 4 g were mixed with 100 ml of KH_2PO_4 . The percent of total Se extracted from the 2 g and the 4 g samples using KH_2PO_4 were identical (Table 4.13), confirming that there was enough KH_2PO_4 present in 100 ml of the KH_2PO_4 solution to extract all of the exchangeable Se in 2 g of this sample. Most procedures reviewed used a centrifuge to separate the supernatant from the solid portion of the sample. However, since filtration is simpler and has been shown to be as effective as centrifugal methods (Quevauviller et al., 1996) this approach was used for these experiments.

EDTA, a chelating agent, was of interest because it has been used to determine the amount of bioavailable metals in soils, sediment and biological tissues (Quevauviller et al., 1996). EDTA

extracted 20% of total Se from E99-22 i.e. 3 to 4 times more Se than the other solutions (Table 4.13), suggesting that it may have been removing Se from other mineral phases. MgCl_2 and NaOAc, on the other hand, are frequently used in sequential extraction procedures (Table 4.12). Extracting 6.1 and 7.8% of total Se respectively, MgCl_2 and NaOAc provided a more conservative estimate of exchangeable Se than EDTA. KH_2PO_4 , an extractant used in several Se-specific extraction procedures (Ballistrieri and Chao, 1987; Chao and Sanzolone, 1989; Martens and Suarez, 1997), removed approximately the same amount of Se as distilled water (Table 4.13).

Table 4.13 Se Extracted from Sample E99-22 (Foot Wall) Expressed in $\mu\text{g/L}$

	Se Extracted			
	Blank ($\mu\text{g/L}$)	E99-22 ($\mu\text{g/L}$)	E99-22 Replicate ($\mu\text{g/L}$)	Average % of Total
MgCl_2 (1.0 mol/l)	1.9	8.2	9.2	6.1
EDTA (0.05 mol/l)	0.7	36.0*	20.0*	19.7
NaOAc (1.0 mol/l)	0.7	10.6	11.6	7.8
KH_2PO_4 (0.1 mol/l)	0.7	7.9	7.6	5.5
KH_2PO_4 (0.1 mol/l)**	0.7	16.3	15.3	5.5
Distilled water	<0.5	6.1	7.8	4.9

* Total Se was measured as a precipitate had formed prior to arrival of the samples at ASL

** 4 g of sample were used instead of 2 g as for the other samples

Reagents such as NaOAc, MgCl_2 and KH_2PO_4 release adsorbed Se anions into solution replacing them with acetate, chloride and phosphate anions. Distilled water extracts only marginally less than the other three solutions. This suggests that the Se being removed by these extractants is primarily in the form of salts, possibly the products of sulphide oxidation. Distilled water was selected as it enabled a comparison between the sequential extraction and humidity cell results. Lacking significant ionic potential, distilled water does not remove ions through an exchange process. The fraction is therefore more accurately termed water soluble and will be referred to as such in the text.

In the initial round of tests, the goal was to assess the relative strength of the different extractants rather than to determine an optimal extraction time so a 1 hour extraction time was used (Dold, 1999). Extractions periods of 0.5, 1, 2 and 4 hours were tested to select a final extraction time that would maximize Se removal and minimize Se re-adsorption. Maximum Se removal occurred after 2 hours (Table 4.14). However, the 2 hour extraction removed less Se than the 1 hour extractions in the initial round of tests (Table 4.13). The difference between the three 1 hour extractions (Tables 4.13 and 4.14) was greater than the difference between the least and most effective extractions in the time trial, suggesting that a 1 hour extraction would provide as accurate a measure of water soluble Se as the 2 hour extraction.

Table 4.14 Results from Time Trials for the Extraction of the Water Soluble Phase from Sample E99-22 (Foot Wall)

Extraction Time (hours)	Se Extracted	
	$\mu\text{g/L}$	% of Total Se
0.5	4.3	2.4
1	4.8	2.7
2	5.9	3.3
4	5.1	2.9

4.4.2 Extraction Method for HFMO Associated Selenium

Reagents that have been used to extract metals and trace elements associated with amorphous and crystalline HFMO include: citrate-dithionate buffer (CDB), ammonium oxalate in oxalic acid ($(\text{NH}_4)_2\text{C}_2\text{O}_4$ in $\text{H}_2\text{C}_2\text{O}_4$), HCl and hydroxyl ammonium chloride ($\text{NH}_2\text{OH} \cdot \text{HCl}$) in 25% acetic acid (Table 4.9). Hall et al. (1996) note that CDB is often highly contaminated and may yield sulphides precipitates to which trace elements may adsorb. They also note though it dissolves Fe-rich layer silicates, it does not effectively dissolve hematite or goethite. Ammonium oxalate in oxalic acid, known as Tamm's reagent, is not effective on samples with a high organic matter content (Hall et al., 1996), making it unsuitable for use with the hanging wall, foot wall and coal samples in this study. HCl effectively dissolves HFMO, but it may partially attack sulphides (Hall

et al., 1996). For the reasons listed above, CDB, Tamm's reagent and HCl were not given further consideration.

To roughly assess the effectiveness of $\text{NH}_2\text{OH} \cdot \text{HCl}$, a 2 g sample of limonite sample (from the Carajan Region of the Brazilian Amazon) was dissolved in 100 ml of a 1.0 M $\text{NH}_2\text{OH} \cdot \text{HCl}$ in an Erlenmeyer flask in a 90°C water bath. Approximately 80% of the sample was dissolved. Tessier et al. (1979) investigated the specificity of $\text{NH}_2\text{OH} \cdot \text{HCl}$ measuring both the sulphur and carbon content of the solids before and after the extraction. Both remained constant indicating that neither sulphur in sulphides or in organic material was affected by the extractant. Taking the limonite test and Tessier et al.'s (1979) results as grounds to assume that $\text{NH}_2\text{OH} \cdot \text{HCl}$ was sufficiently selective, the concentration and contact time were then selected.

Hall et al. (1996) removed first amorphous HFMO from soil and till samples, using an extraction with 0.25 M $\text{NH}_2\text{OH} \cdot \text{HCl}$ lasting 2 hours, and then crystalline HFMO, with a 3 hour extraction with 1.0 M $\text{NH}_2\text{OH} \cdot \text{HCl}$. Tessier et al. (1979) employed a single 6 hour long extraction with 0.04 M $\text{NH}_2\text{OH} \cdot \text{HCl}$. Since we sought to remove Se from both amorphous and crystalline HFMO with a single extraction, a 1.0 M $\text{NH}_2\text{OH} \cdot \text{HCl}$ solution was used. 2 g of E99-22 crushed to <200 mesh and mixed with 100 ml of solution for time trials of 1, 2, 4 and 8 hours. Matrix interference made it impossible to detect Se in filtrate from these extractions. As much as 5% of total Se could have been extracted from the samples without being detected if the concentration were just below the 10 µg/L detection limit. If all Fe in the samples not accounted for by pyrite were in the form of HFMO, the mass of iron and manganese oxides contained in the 16 selected samples would range from 0 to 6% of the total. Making this assumption, HFMO account for on average only 1%. In order to determine whether signal interference would pose a problem for all analyses of Se in $\text{NH}_2\text{OH} \cdot \text{HCl}$ or if no Se was associated with HFMO in E99-22, three other samples, B99-25, B99-44 and CREF, were tested and the contact time set at 3 hours following the procedure developed by Hall et al. (1996). These samples were selected on the basis of their Fe_2O_3 contents

which ranged from 0.27 to 2.24 %. There was less signal interference and 6.5, 4.4 and 4.8% of total Se was found to be associated with HFMO in B99-25 (a coal sample containing 3.1 mg/kg Se), B99-44 and CREF respectively.

Based on the results of the exploratory tests, 100 mL of 1.0 M $\text{NH}_2\text{OH} \cdot \text{HCl}$ in 25% acetic acid were used to extract the Se associated with amorphous and crystalline HFMO from the 16 selected samples. For the $\text{NH}_2\text{OH} \cdot \text{HCl}$ extraction, the flasks were sealed with a piece of paraffin film, placed in a 90°C water bath and stirred constantly with a magnetic stirring rod for 3 hours.

4.4.3 Extraction Method for Sulphide and Organic Matter Associated Se

Chao and Sanzolone (1977) found KClO_3 combined with HCl to be the most effective method to extract trace elements associated with sulphides and organic matter. Chao and Sanzolone (1989) use KClO_3/HCl in their procedure developed to extract Se. Hydrogen peroxide (H_2O_2) has also been used to extract trace elements associated with the sulphide/organic fraction (Tessier et al., 1979; Filipek and Theobald, 1981; Ure et al., 1993).

A pyrite sample from Zacatelas, Mexico (Ward's Natural Science Establishment Incorporated, catalogue reference number 46 E 6445) and the organic fraction of B99-44 collected via heavy liquid separation (see Section 4.5) were used to test the relative efficiency of KClO_3/HCl and H_2O_2 . A 100 ml volume of KClO_3/HCl digested 95% of the 0.1 g pyrite sample in an hour at room temperature, while the same volume of 35% H_2O_2 dissolved only 75% of the pyrite under the same conditions. KClO_3/HCl and 35% H_2O_2 displayed similar efficiency in destroying organic matter, with the former reducing the mass of the 2 g sample of organic matter from B99-44 by 69% and the latter by 76%. 10% H_2O_2 dissolved 39% of a 0.1 g of pyrite suggesting that one might be able to first use a low concentration H_2O_2 wash to remove organics, however, this proved unfeasible when 10% H_2O_2 failed to digest more than 37% of a 2 g sample of organic matter from B99-44.

The time trials confirmed that KClO_3/HCl was more effective than H_2O_2 in targeting the combined sulphide/organic fraction, with optimal Se extraction occurring after 1 hour (Table 4.15). For the KClO_3/HCl extraction, a modified version of Hall et al.'s (1996) procedure was used. A volume of 40 mL of concentrated HCl was gradually added to Erlenmeyer flasks containing 2 g of sample and 2 g of KClO_3 . The flasks were covered and the mixture stirred continuously with a magnetic stirring rod. At the end of the extraction, the samples were topped up to 100 ml with de-ionized water.

Table 4.15 Results from Time Trials for the Extraction of the Sulphide and Organic Matter Associated Se from Sample E99-22 (Foot Wall) with KClO_3/HCl and H_2O_2

Extractant	Extraction Time (hours)	Se Extracted	
		$\mu\text{g/L}$	% of Total Se
35% H_2O_2	1	250	65.6
	2	270	73.7
	4	240	60.5
	8	350	50.3
KClO_3/HCl	0.25	150	84.3
	0.5	140	78.7
	1	150	84.3
	1.5	140	78.7

4.4.4 Extraction Method for Selenium in Silicates

The final digestion, extracting Se from the silicate lattice, was conducted by ACME Analytical. The solid residue from the sequential extractions was fused using LiBO_2 and digested using aqua regia. Most procedures also use HF (Table 4.12) to ensure complete dissolution of organic material. The sum of the Se extracted from the four fractions differed little from the Se totals (see Section 5.2) indicating that the aqua regia digestion was sufficiently rigorous.

4.5 HEAVY LIQUID SEPARATION

Heavy liquid separation was used to determine if the Se was concentrated in the organics or in the sulphides. Eight samples were split into three density fractions (Figure 4.10). A mixture of

perchloroethylene and methylene bromide with a density of 1.6 g/cm^3 was used for the first separation. About 20 g of sample ground to <200 mesh were mixed with 300 ml of the heavy liquid in a glass separator and left over night.

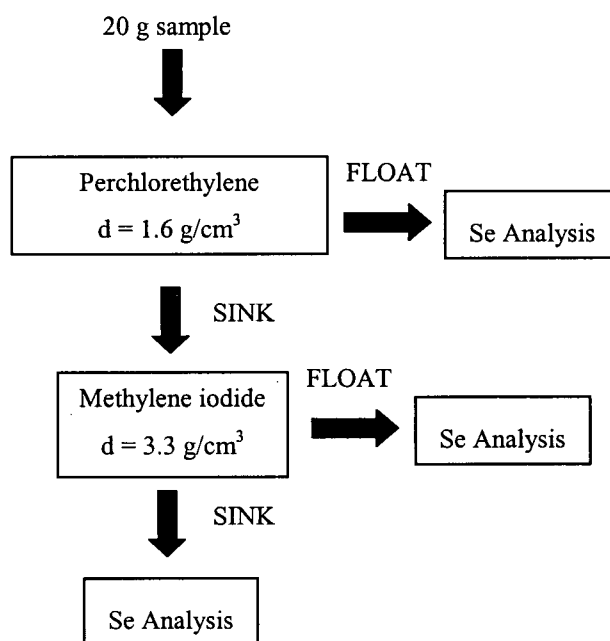


Figure 4.10 Heavy Liquid Separation Procedure

The sink fraction was collected, rinsed with methanol and mixed with methylene iodide with a density of 3.3 g/cm^3 . The float fraction from the first separation, as well as the float and sink fractions from the methylene iodide separation were air dried and weighed. All samples were sent to ACME Analytical Laboratories for Se analysis (refer to section 4.3 for details concerning the analytical method). Replicates were run for each of the samples. Due to the fine particle size, in a few cases distinct float/sink fractions were not generated. In such instances, approximately half of the material was categorized as light and the remainder as heavy.

4.7 HUMIDITY CELLS

Two bench-top cells were mounted for each of the five materials selected for the 20-week humidity cell tests in the Surface Chemistry Laboratory in the Department of Mining and Mineral

Process Engineering. Samples included in the humidity cell tests are listed in Table 4.16. These samples were selected to represent the major classes of material being handled at the sites. Materials relatively high in Se were selected to ensure that Se concentrations in leachate would be above the detection limit.

Table 4.16 Samples Included in the Humidity Cell Tests

	Designation in Tables	Se Content (mg/kg)
E99-61	Interburden	3.2
CREF	Refuse	3.4
A99-23	Parting	5.9
B99-44	Coal	8.8
E99-19	Foot wall	8.4

The humidity cells tests were run following ASTM procedure D5744-96 (White and Sorini, 1997). The 30 cm high and 10 cm wide cells were made of Plexiglass pipe. A hole for air supply was drilled into the side of the pipe, 1 cm from the base of the cells as illustrated in Figure 4.11. A perforated acrylic plate supported the sample above the air feed. Another hole was drilled into the center of the humidity cell cover through which to add distilled water for the leaches and to allow air to escape. A final hole was drilled into the bottom of the cell to drain the leachate.

A plastic connector piece, to which tubing was connected, was screwed into each of these holes. Three pieces of plastic coated window mesh were placed at the bottom of each of the cells to minimize the loss of fines during the weekly leaches. 1 kg of sample crushed to below 6.3 mm (1/4 inch) was loaded into each of the cells. The material was thoroughly mixed before being placed in the cell to ensure that the fines would be even distributed throughout the cells.

Before putting the covers on the cells, a circular piece of absorbent cloth was placed on top of the material to distribute water evenly during the leaching step. The humidity cells were then placed on a metal stand (Figure 4.12) and operated following a cycle of 3 days of moist air, 3 days of dry air and a 1-hour leach on the seventh day using 500 mL distilled water.

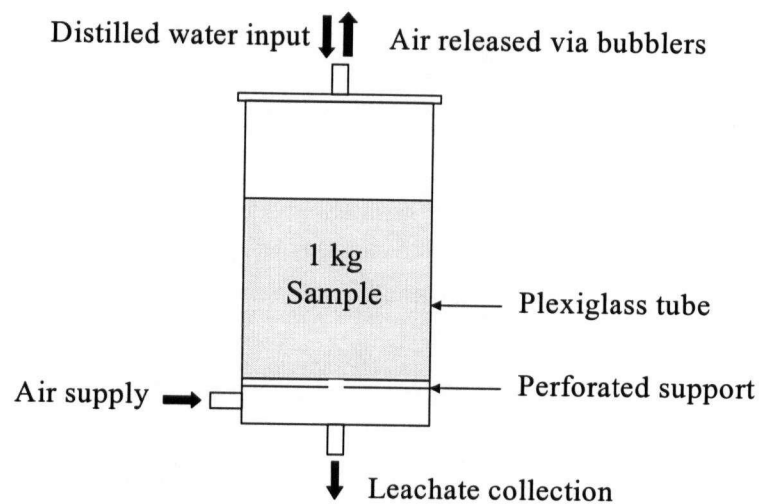


Figure 4.11 Humidity Cell Diagram



Figure 4.12 Humidity Cells in Operation

(1/4 inch) was loaded into each of the cells. The material was thoroughly mixed before being placed in the cell to ensure that the fines would be even distributed throughout the cells.

Before putting the covers on the cells, a circular piece of absorbent cloth was placed on top of the material to distribute water evenly during the leaching step. The humidity cells were then placed on a metal stand (Figure 4.12) and operated following a cycle of 3 days of moist air, 3 days of dry air and a 1-hour leach on the seventh day using 500 mL distilled water.

After each of the weekly leaches, the connector on top of the cell was screwed back in and the stopper on the tube connected to the air supply was re-opened. Moist air from a humidifier was passed through the cells for the first three days following each leach and dry air for the next three. Water in the humidifier was kept between 26 and 28°C. A single hose supplied air to the cells. Airflow through the cells was maintained at approximately 0.5 litres per minute using an airflow regulator. The cells were connected to the air hose by plastic T-connectors. The uniformity of airflow was monitored using “bubblers”. These consisted of 100 mL vials containing 50 mL of water capped with a rubber stopper fitted with two glass tubes, one long and the other short. The rubber outflow tubes connected to the top of the humidity cells were attached to the glass tube extending into the water forcing the air to escape through the vial as bubbles. As noted by Frostad et al. (2000), material in the cells connected closest to the tube supplying air to the system tended to dry faster than material in the cells attached at the end of the air supply hose. Less carbonaceous materials also tended to dry faster. Since dry materials received increased airflow, screw clamps were installed on the inlet hose of all the cells to allow airflow to each cell to be regulated independently.

The ASTM Procedure (White and Sorini, 1997) requires a minimum test duration of 20 weeks, while Price (1997) recommends a minimum of 40 weeks. In this case, Se concentrations in the leachate from these columns reached relatively constant levels as early as the fourth week, with

the notable exception of the parting material, such that it was feasible to stop the tests after 20 weeks.

The pH and Eh of the leachate were measured in all samples immediately after filtering. The potential meter was equipped with Ag-AgCl electrodes filled with saturated KCl. In order to transform the potential obtained by the calomel electrode into $E_{S.H.E}$ (standard hydrogen electrode), 199.0 mV were added to the potential readings (Light, 1972). Leachate from the humidity cell tests was analyzed by ALS Limited, Vancouver for Se every week and for dissolved metals sulphates, total inorganic carbon (TIC), total organic carbon (TOC), alkalinity and acidity every second week.

As with samples from the sequential extractions, 2 ml of 1:1 HNO_3 were added to the solutions to prevent the formation of insoluble metal complexes during transport of the solution to the analytical lab. To prevent the growth of bacteria, 2 ml of 1:1 H_2SO_4 were added to samples sent for TIC and TOC analysis. Se in humidity cell leachate was determined using HG-AAS and total metals by ICP-OES.

Total alkalinity was measured using a colorimetric method adapted from EPA Method 310.2 (USEPA, 1979). Methyl orange was mixed with a weak buffer solution acid at pH 3.1 and added to the sample in a fixed amount. Since methylorange has a pH range similar to that of the equivalence point for total alkalinity, the loss of colour corresponds to the amount of alkaline species present. The change in colour is measured with a COBAS FARA II spectrophotometer and compared against a standard curve. Acidity was determined following American Public Health Association (APHA) Method 2310 (APHA, 1998) that called for potentiometric titration of a sample aliquot with a standard solution of NaOH to pH 8.3. Though it is expressed in milliequivalents $CaCO_3$ per litre, all acidic species are measured.

ALS Limited analyzed TIC and TOC with a Shimazu TOC Analyzer model TOC-5000A. The analysis was carried out using procedures adapted from APHA Method 5310 (APHA, 1998). Total carbon was measured using a LECO analyzer that converted organic carbon to CO₂ by combustion at 980°C. A second carbon analyzer was used to convert inorganic carbon to CO₂ by acidification with phosphoric acid at 200°C. The amount of CO₂ produced, proportional to the amount of carbon in the sample, was measured with an infrared detector. TOC, representing the carbon fraction covalently bonded in organic molecules was obtained by subtracting TIC from total carbon.

Sulphate concentrations were determined by APHA Method 4500-SO₄ (APHA, 1998). Sulphate ions are converted to aluminum sulphate suspension in which turbidity was measured using a COBAS FARA II spectrophotometer. The reference method for Sulphite is 4500-SO₃ B Iodometric Method (APHA, 1998). An acidified sample containing sulphite is titrated with a standardized potassium iodide-iodate titrant. Free iodine, liberated by the iodide-iodate reagent, reacts with SO₃. The titration endpoint is signaled by the blue color obtained when the first excess iodine reacts with the starch indicator. At the end of the 20-week period, the material from the cells was crushed to <200 mesh and sent to ACME Limited, Vancouver for Se analysis.

5.0 RESULTS AND DISCUSSION

Based on the methodology applied to 16 samples representative of the different lithologies of the Mist Mountain Formation this chapter aims to answer three main questions:

1. In which mineralogical associations is Se found?
2. From which materials is Se being released and how fast is this occurring?
3. What geochemical mechanisms are involved in Se mobilization?

5.1 CORRELATION OF SELENIUM CONCENTRATIONS WITH SAMPLE MINERALOGY

In order to establish the predominant Se-bearing phases in waste rock from the mining operations, the correlation between concentrations of Se and TOC, organic S, sulphides and trace elements reported in Table 4.5 was assessed. Pearson's correlation coefficient, r , was used as a measure of the strength of the linear relationship between variables. It is calculated using equation 5.1.

$$r = \frac{\sum (X_i - \bar{X})(Y_i - \bar{Y})}{\sqrt{\sum (X_i - \bar{X})^2 \sum (Y_i - \bar{Y})^2}} \quad \text{Equation 5.1}$$

The statistical significance of the correlations was determined using the Student t-test with the level of significance set at $\alpha=0.05$. The relationship was said to be significant when $P<0.05$. P is the probability of obtaining, by chance, a value equal to or more extreme than that observed.

None of the trace elements found in the 16 samples studied (Table 4.5) are well correlated with Se (Table 5.1). These elements are not expected to form Se-bearing minerals, but based on knowledge of their modes of occurrence correlations with Se might have indicated whether Se was found primarily in organic or inorganic associations. As and Pb were not included in this table as concentrations were below the detection limit for all samples tested. Se concentrations also correlate poorly with carbonates ($r = -0.018$), kaolinite ($r = -0.340$) and illite ($r = 0.228$).

Table 5.1 Correlation Coefficients for Se versus Various Trace Elements

	r^*
Ba	0.160
Ni	-0.014
Sr	0.109
Zr	-0.206
Y	-0.369
Nb	-0.118
Sc	-0.180

* In cases where concentrations were below the detection limit, values half that of the limit were assigned

A correlation between Se and TOC would be expected if organic matter were the main Se-bearing component. However, no correlation was observed between Se and TOC (Figure 5.1), suggesting that organic associations are not of primary importance in the 16 selected samples. An equally poor correlation is noted between organic S and TOC (Figure 5.2). Coleman et al. (1993) and Chou (1990) report a positive correlation between organic S and TOC in U.S. coals. The relationship of organic S with TOC may be less consistent in materials other than coal. Looking at only the 7 high TOC samples (TOC >40%) in Figures 5.1 and 5.2, one finds that both Se and organic S correlate well with TOC ($r = 0.832$ and 0.814 respectively). But because there is a positive correlation between sulphides and TOC (Figure 5.3), the correlation between organic S and TOC may simply reflect an increase in Se associated with sulphides rather than an increase in the amount of Se substituting for organic S. Indeed, studies of coals from British Columbia and the U.S. have shown a positive correlation between TOC and pyritic S (Wandless, 1959; Coleman, 1993), likely resulting from the microbial reduction of sulphate to sulphides occurring in low O_2 environments like coal swamps (Spears et al., 1994).

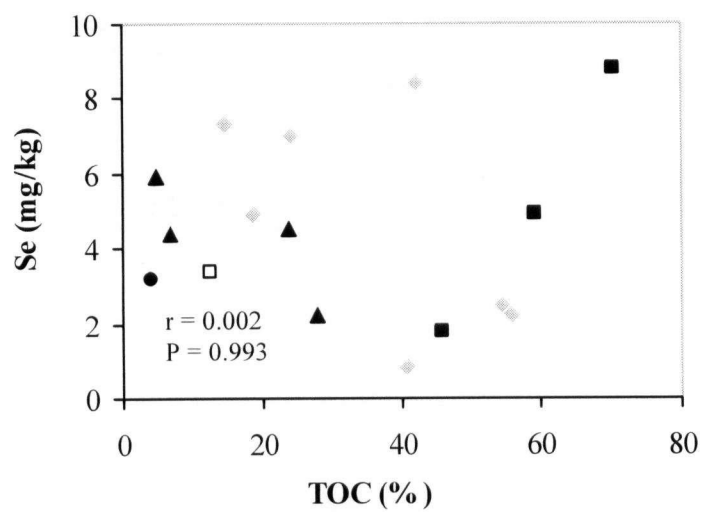


Figure 5.1 Concentration of Se versus Concentration of TOC

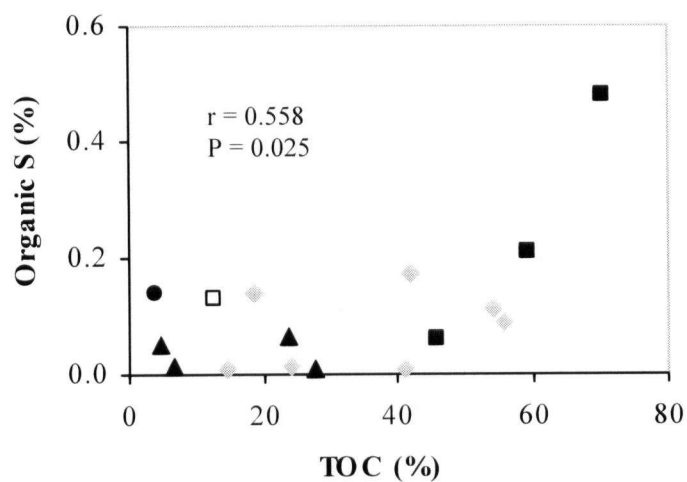


Figure 5.2 Concentration of Organic S versus Concentration of TOC

□ refuse ■ coal ▲ parting ● interburden ◆ hanging wall/foot wall

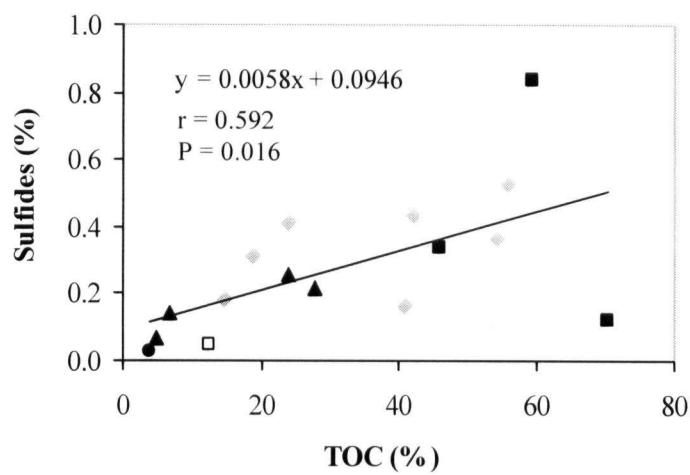


Figure 5.3 Concentration of Sulphides versus Concentration of TOC

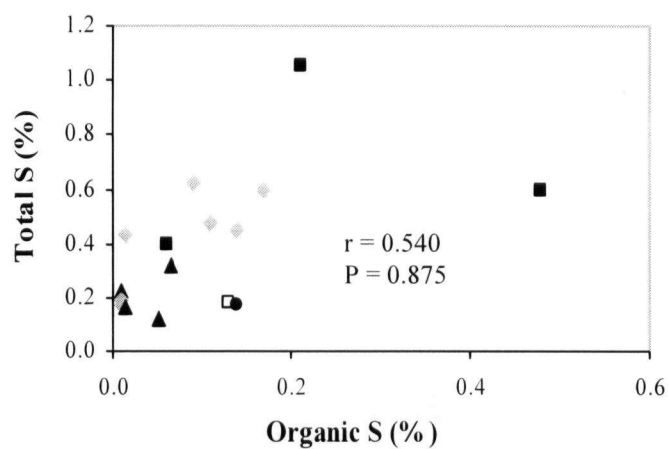


Figure 5.4 Concentration of Total Sulphur versus Concentration of Organic Sulphur

□ refuse ■ coal ▲ parting ● interburden ◆ hanging wall/foot wall

Holuszko et al. (1992) report an average total S content of 0.57 % for metallurgical and thermal coals of southeastern British Columbia. S contents of materials included in this study range from 0.40 to 0.83 %. While organic S shows no evident association with total S (Figure 5.4), sulphides and total S in the 16 samples are highly correlated (Figure 5.5) because sulphides account for, on average, 70% of total S (Table 4.5). In three samples, B99-44 (coal), C-REF (refuse) and E99-61 (interburden), sulphide content is below 30% of total S (Table 4.3). Pyritic S was identified as a major contributor to total S in lignite from Spain (Monterroso and Macias, 1998) and in bituminous coals from the U.K. (Spears et al., 1994) suggesting that the sulphide/total S ratio in B99-44, C-REF and E99-61 is abnormally low.

Sulphides are known to be important Se-bearing minerals (Fleischer, 1959; Lakin, 1973; Wedepohl, 1978; White et al., 1989; Hickmott and Baldrige, 1995). Figure 5.6 though, shows no link between Se and sulphides. Organic matter can influence the Se content of sulphides in two ways:

1. By drawing from the pool labile Se in the coal swamp (Price and Shieh, 1979)
2. By decreasing the redox potential in the depositional environment (Brown et al., 2000)

In the first case, organic matter competes directly with sulphides for available Se. In the second, it creates a more reducing environment. This, in turn, leads to an increase in the ratio of Se to S incorporated into diagenetic pyrite as Se is more readily reduced than S (Zehr and Oremland, 1987). In order to distinguish between the effects of sulphides and TOC on Se levels, Se was plotted against sulphides/TOC ratio (Figure 5.7). By dividing sulphides by TOC, all 16 samples can be compared as if they contain a fixed amount of TOC. In this way, a sample with a high Se concentration related to its high TOC content can be distinguished from a sample with high Se, but low TOC. Se levels in 11 of the 16 samples showed a high degree of correlation ($r = 0.916$)

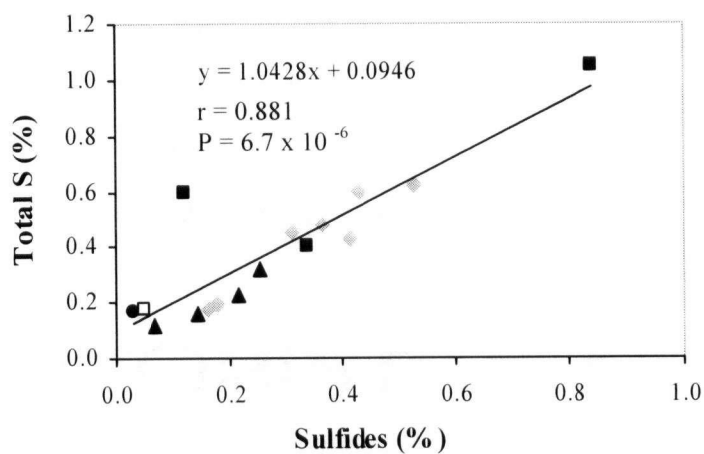


Figure 5.5 Concentration of Total Sulphur versus Concentration of Sulphides

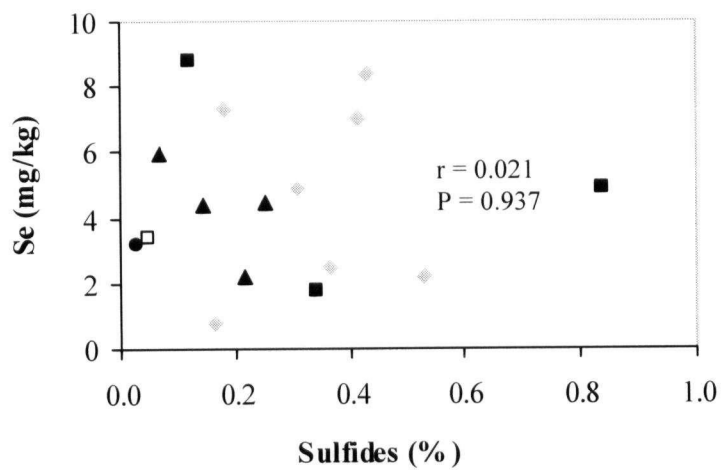
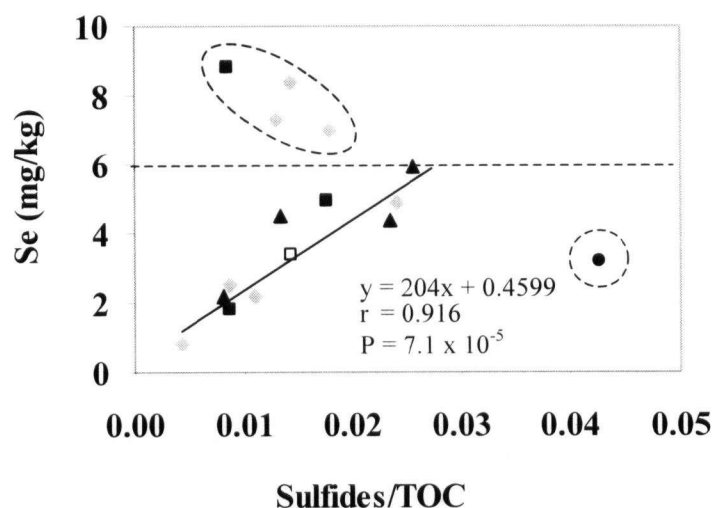


Figure 5.6 Concentration of Se versus Concentration of Sulphides

□ refuse ■ coal ▲ parting ● interburden ◆ hanging wall/foot wall



Note: Excluded from linear regression and calculation of the correlation coefficient

□ refuse ■ coal ▲ parting ● interburden ◐ hanging wall/foot wall

Figure 5.7 **Concentration of Se versus Concentration of Sulphides Normalized for TOC**

with the sulphide/TOC ratio. Only the interburden sample and four samples with Se contents greater than 6 mg/kg Se did not fit this trend. The interburden sample was excluded from the linear regression on the grounds that it was the only sample in this study deposited in an environment geochemically distinct from a coal swamp. Eh and pH in this environment were likely higher than those found in coal swamps or transitional environments (Casagrande et al., 1977) which would affect Se speciation and binding. Four other samples were excluded from the linear regression: A99-12 and E99-45, hanging wall samples with 7.0 and 7.3 mg/kg Se, E99-19, a foot wall sample with 8.4 mg/kg Se and B99-44, a coal with 8.8 mg/kg Se. Se concentrations in A99-12, E99-19 and E99-45 were almost two times greater than the average values for hanging wall and foot wall material in the Mist Mountain Formation (Table 4.3). B99-44 contained almost four times as much Se as the average coal in the formation. Se in these samples likely has an atypical mode of occurrence, suggesting the presence of selenides or high Se sulphides, and for

atypical mode of occurrence, suggesting the presence of selenides or high Se sulphides, and for this reason do not provide a fair linear correlation between Se and the sulphide/TOC ratio. No selenides were detected in these samples by microanalysis with SEM, but this cannot be considered conclusive as samples with Se concentrations as low as 10 mg/kg are usually unsuitable for SEM-EDS analysis. Galbreath and Brekke (1994) and Katrinak and Benson (1995) were able to detect Se in coal pyrite using SEM, but proton-induced X-ray emission (PIXE) may be more effective for samples with low Se concentrations (Hickmott and Baldrige, 1995). Clausthalite and ferroselite have been found in coals from Western Canada (Goodarzi and Swaine, 1993).

The study of correlations between Se and other elements shows that Se is not found in a single, dominant geochemical association. Rather, Se concentrations seem to be controlled by an interaction between sulphides and organic matter resulting from direct competition for Se or from indirect effects on redox conditions in the depositional environment.

5.2 SEQUENTIAL EXTRACTIONS

Results from the four-step sequential extractions are presented in Table 5.2. The amount of Se in leachate and residue is reported as a percentage of the total amount of Se extracted from the 16 samples. Actual Se concentrations in the leachate and in the solid residue are found in Table A3.1 of Appendix 3. Percentages were calculated using average Se concentrations from the duplicates. Concentrations were below the 3 µg/L detection limit in the leachate collected from half of the $\text{NH}_2\text{OH} \cdot \text{HCl}$ extractions targeting HFMO-associated Se. For these samples, the Se concentration was assumed to be half the detection limit i.e. 1.5 µg/L when calculating the percentages. The magnitude of the variation in the Se concentrations found in the duplicates is presented in Table A.3.2 in Appendix 3. The sum of the Se extracted from the four fractions correlates well with the concentrations of Se measured in the head samples ($r = 0.954$) (see Table A.3.3 in Appendix 3).

Figure 5.8, a graphical representation of the results in Table 5.2, illustrates that the bulk of the Se in the 16 samples is associated with sulphides and organics. This fraction contains between 60.7% and 83.7% of total Se. Water soluble Se accounts for between 2.4 % and 21.3 % of total Se. Between 1.0 % and 10.6 % of total Se is associated with HFMO. The residual fraction, consisting essentially of silicates, contributes between 5.9% and 24.7 % to the total Se. No lithology-related trend in Se distribution was observed. For instance, in the case of water soluble Se both the maximum and minimum values are accounted for by foot wall samples. On average, the water soluble, HFMO-associated, sulphide/organic-associated and residual Se account for 8 %, 4 %, 73 % and 15 % of total Se respectively.

Table 5.2 Amount of Se in Sequential Extraction Leachate and Residue as a Percent of the Total Amount of Se Extracted

		Amount of Se Extracted (% of Total Se in Sample)			
		Water	HFMO	Sulphides & Organics	Residual
A99-4	Coal	7.9	3.0	68.0	21.1
A99-7	Parting	2.5	3.1	77.3	17.1
A99-12	Hanging wall	5.8	3.2	79.1	11.9
A99-23	Parting	6.0	2.6	83.7	7.7
B99-16	Foot wall	21.3	3.3	59.6	15.8
B99-44	Coal	4.7	1.4	79.6	14.3
B99-62	Hanging wall	6.7	7.9	60.7	24.7
CREF	Refuse	4.8	3.9	81.3	10.0
C99-21	Hanging wall	8.4	3.4	74.5	13.7
C99-25	Foot wall	4.8	8.9	74.4	11.9
D99-8	Parting	9.8	3.6	67.6	19.0
E99-19	Foot wall	2.4	1.0	79.3	17.3
E99-45	Hanging wall	18.1	1.0	72.9	8.0
E99-59	Coal	2.9	10.6	66.9	19.6
E99-61	Interburden	8.9	7.5	62.1	21.5
E99-63	Parting	10.8	4.5	78.8	5.9

ICP-MS analyses were conducted to determine the concentrations of 30 elements in the water soluble, HFMO and organic/sulphide fractions of 8 of the 16 samples. Results from these analyses are compiled in Tables A3.3 through A3.5 in Appendix 3. Of the 30 elements, less than half were present in concentrations above the detection limit. Those with concentrations above

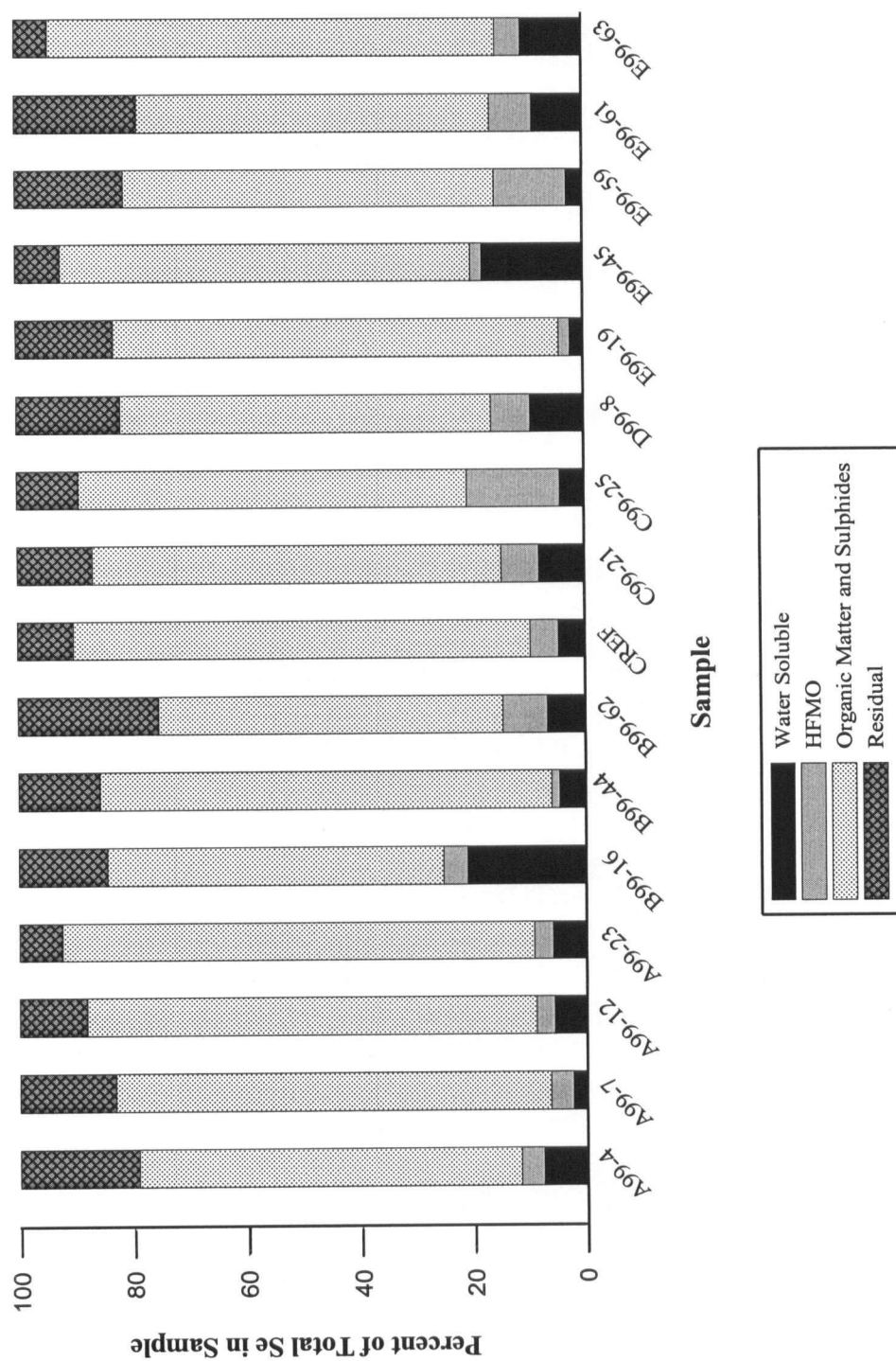


Figure 5.8 Percent of Total Se Accounted for by Se in the Water Soluble, HFMO, Sulphides/Organic Matter and Residual Fractions

Table 5.3 Correlation Coefficients Relating Se and Other Elements in Leachate from the Water Soluble, HFMO and Sulfide/Organic Matter Fractions of A99-4, A99-23, B99-16, B99-44, CREF, E99-19, E99-59 and E99-61

	Water	HFMO	Sulphides & Organics
Aluminium	*	0.15	-0.42
Barium	0.04	-0.04	-0.31
Calcium	-0.03	-0.28	-0.0003
Chromium	*	-0.22	*
Copper	*	0.47	-0.40
Iron	*	-0.14	-0.37
Magnesium	0.07	-0.27	-0.08
Manganese	*	-0.09	*
Phosphorous	*	0.20	*
Potassium	0.17	0.40	-0.09
Silicon	0.08	0.18	-0.48
Strontium	-0.12	-0.27	*
Titanium	*	*	0.89
Zinc	*	0.65	-0.63

* Concentrations consistently below the detection limit

the detection limit were compared with Se (Table 5.3). Among these, only Ti in the sulphide/organic fraction showed a strong correlation with Se. Organic associations are the dominant mode of Ti occurrence in coals (McIntyre et al., 1985; Miller and Given, 1987). The strong correlation between Se and Ti is thus due to their respective modes of occurrence i.e. associated with organic matter or sulphides and not a geochemical interaction between them. Correlations between Zn and Se in leachate from the HFMO and Sulphide/Organic fraction also seem to be relevant, but they are not statistically significant. Data in Table A3.2 in Appendix 3 shows that a few extreme values bias the r value in a situation where there is otherwise little correlation between the two sets of values.

The correlations between Se solubilized by the water extraction and TOC, sulphide and Se concentrations in the solids and are weak (Table 5.4). Were a significant amount of Se ionically bound to the surface of organic matter, there should have been a correlation between Se in the

water soluble fraction and the amount TOC in the material. This was not the case in the 16 samples included in this study. A link between water soluble Se and sulphide concentrations

Table 5.4 Correlation Coefficients Relating TOC, Sulphides and Se in the Solids and Se Solubilized by Water for 16 Samples

	r
TOC	- 0.345
Sulphide	0.056
Se	0.075

seemed more probable given that Chang and Berner (1999) determined sulphide oxidation to be the primary source of S released in the process of coal weathering. The absence of such a trend could be accounted for by variations in sulphide liberation or the attenuation of sulphide oxidation by the accumulation of HFMO on exposed surfaces (Goldhaber, 1983; Nicholson et al., 1990) particularly in the case of selenite which adsorbs readily to HFMO (Ballistrieri and Chao, 1987). Alternatively, the release of selenide/sulphide oxidation products may be affected by interactions with organic ligands. The lack of a correlation between total Se and water soluble Se confirms that the rate of oxidation varies as a function of the form in which Se occurs in the material or of other mineralogical factors.

Se has been shown to adsorb onto HFMO, particularly in the form of selenite (Ballistrieri and Chao, 1989). With PZC values between pH 7 and 9 (Förstner and Wittmann, 1979), HFMO could potentially release Se adsorbed to pH-dependent charges since the pH measured in surface water in the Elk River falls within that range. On average though, HFMO account for only 1.3 % of sample mass in the 16 samples herein studied, such that HFMO-associated Se would not be expected to account for a large portion of total Se in the lithologies of the Mist Mountain Formation or of the Se being released into the Elk River.

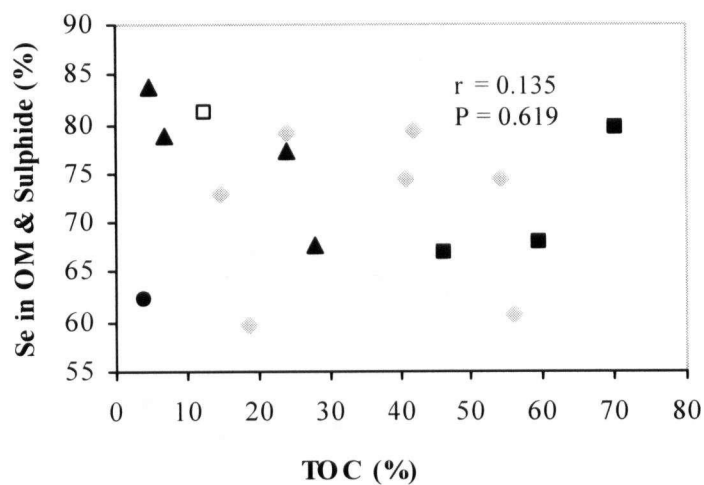


Figure 5.9 Percent of Sulphide/Organic Associated Se versus TOC Concentration in Solids

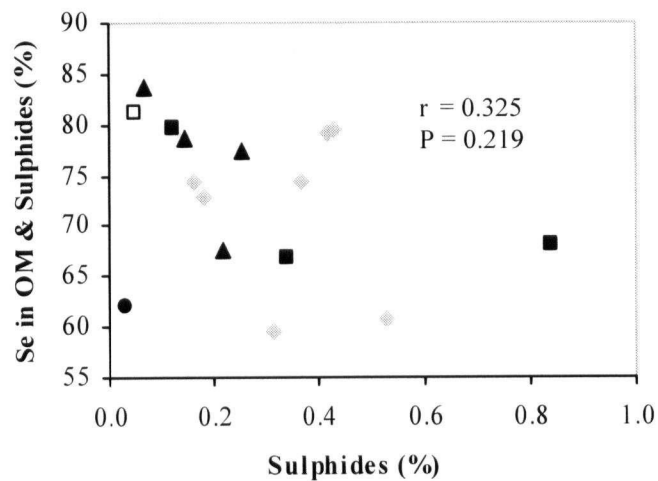


Figure 5.10 Percent of Sulphide/Organic Associated Se versus Sulphide Concentration in Solids

□ refuse ■ coal ▲ parting ● interburden ◆ hanging wall/foot wall

The KClO_3/HCl extraction showed that the Sulphide/Organic fraction accounted for the bulk of the Se. Se in the Sulphide/Organic fraction, while not immediately available, constitutes a reservoir for long term Se release. Since KClO_3/HCl did not selectively attack sulphides or organic matter, it was necessary to use indirect means of estimating the relative contribution of these two fractions. To evaluate the relative contributions of sulphide- and organic-associated Se to the total amount of Se in the Sulphide/Organic fraction, the percent of total Se extracted by KClO_3/HCl was plotted against the sulphide and TOC contents of the solids (Figures 5.9 and 5.10). Neither of these plots yielded a strong correlation, suggesting that the amount of Se associated with organics and sulphides varies. Price and Shieh (1979) and Casagrande and Nug (1979) studied the relationship between organic and inorganic forms of S and found that H_2S from the microbial reduction of SO_4^{2-} could react with Fe to form pyrite or with organic matter to be incorporated into coal (Figure 5.11).

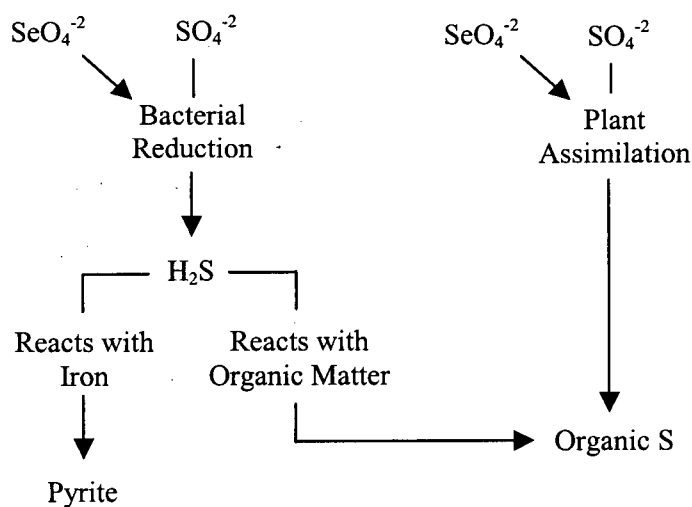


Figure 5.11 Incorporation of Sulphur in Coal (From Price and Shieh, 1979)

Organic matter and sulphides would thus be competing for labile Se. A brief look at S biogeochemistry in coal swamps provides some insight into the variability of Se associations. In early coal diagenesis, ferric iron is reduced to ferrous iron, which reacts with hydrogen sulfide produced by sulphur reducing bacteria to form iron monosulfide (Casagrande et al., 1977; Given

and Miller, 1985). Iron monosulfide is later transformed by reaction with elemental sulfur into pyrite. Organic S, on the other hand, is incorporated into coal by the reaction of reduced sulfur species with the premaceral humic substances formed by bacterial decomposition of the peat (Chou, 1990; Brueechert and Pratt, 1996). Organic S compounds formed in peat are mostly thiols and sulfides, which gradually convert to thiophenes with increasing coal maturation. Given the similarity between the biogeochemical properties of S and Se, this is expected to substitute for S in such compounds and undergoing analogous transformations.

The residual fraction is greater than expected given that the literature cites organic and sulphidic associations as being of primary importance. On average, Se in the residual fraction accounts for 15% of total Se. The high Se content of the residual fraction may also be a result of incomplete extraction of Se in the organic fraction. Se in the silicate matrix is highly resistant to weathering.

5.3 HEAVY LIQUID SEPARATION

Heavy liquid separation was used to determine the amount of Se associated with material of low, medium and high density. Se concentrations in the three density fractions for each sample and the percent distribution are listed in Table 5.6.

Table 5.5 Se Concentrations and Percent Distribution in the Different Density Fractions

	Light (<1.6 g/cm ³)		Medium (1.6-2.9 g/cm ³)		Heavy (>2.9 g/cm ³)	
	[Se] (mg/kg)	% Distribution	[Se] (mg/kg)	% Distribution	[Se] (mg/kg)	% Distribution
A99-4	4.2	39	5.3	43	19	18
A99-23	*	0	4.8	75	4.9	25
B99-16	*	0	4.1	44	8.6	56
B99-44	11	62	8.1	17	12	21
CREF	*	0	3.1	100	*	0
E99-19	7.3	39	7.2	50	12	12
E99-59	1.2	43	0.8	15	2.9	41
E99-61	*	0	2.7	100	*	0

*No material in these fractions

The light fraction consists mainly of organic material. In samples A99-23, B99-16, CREF and E99-61 no light fraction ($<1.6 \text{ g/cm}^3$) floated in the heavy liquid. These samples contain relatively little TOC. The other four samples all contain high TOC. Neither B99-44, nor E99-19, produced a distinct light fraction in the separation funnel during the separation. Instead, it was possible only to split the material into two equal parts by volume, designating one light and the other heavy. Noting that all three fractions contain similar amounts of Se, it is possible that the organic and mineral particles were not liberated and remained mixed to a greater or lesser extent in all three fractions. However, calculated total Se concentrations from the summation of the amount of Se in the different fractions do correlate well with the total Se concentrations analyzed ($r = 0.925$).

The average Se content of the intermediate density fraction (1.6 to 2.9 g/cm^3) density fraction was 4.5 mg/kg . This fraction is rich in clays. The relatively high concentration of Se in the intermediate density fractions suggest that clay minerals, as well as carbonates might still have pyrite associated with them, given that little Se was found to be associated with these minerals in the sequential extractions. Fine pyrite ($<20 \text{ }\mu\text{m}$) has been found to be associated even with clean coal (Frankie and Hower, 1985). The $<2 \text{ }\mu\text{m}$ fraction contains, on average 42% more Se. The enrichment of Se in the $<2 \text{ }\mu\text{m}$ fraction could be indicative of an association with fine pyrite or with clay minerals.

The heavy fraction is enriched in sulphides and other heavy minerals such as HFMO and siderite. A clean separation of sulphide was not possible due to lack of liberation. However, all heavy products do show higher Se than the other fractions, indicating that part of Se is associated with heavy minerals. The correlation between sulphide and Se concentrations in the $>2.9 \text{ g/cm}^3$ density fraction was calculated. The correlation coefficient of 0.69 indicates that sulphides account for a significant portion of Se in this fraction. A99-4, the sample containing the highest level of sulphides (0.84%) also had the highest concentration of Se in the heavy fraction. In this instance, a clean split was obtained for the duplicates. Assuming that all the Se in the heavy fraction is

found in sulphides, the Se content of sulphide in this material is approximately 19 mg/kg. This falls within the 10 to 30 mg/kg range of Se concentrations in pyrite in coals reported by Leutwein (1978).

The heavy liquid separations demonstrate that both organic and inorganic modes of occurrence are important for Se. The relative amount of Se in these fractions varies from one lithology to another. However, the heavy fraction contains up to four times more Se than the light fraction, suggesting that sulphide-associated Se may make an important contribution to total Se.

5.4 HUMIDITY CELL TESTS

The humidity cells tests were used to assess the rate of Se release from five different types of material: interburden (E99-61), parting (A99-23), refuse (CREF), coal (B99-44) and foot wall (E99-19). Duplicate cells were mounted for each of the materials. Once a week for 20 weeks the cells were leached with distilled water. The leachate was analysed for Se, metals, sulphate, alkalinity, TOC and TIC. Results from these analyses are compiled in Tables A4.1 through A4.10 of Appendix 4. The volume of leachate collected and its Eh and pH values are also recorded in these tables. Leachate pH varied from 4.99 to 8.57 and averaged 6.61. No particular trend was noted in pH variation. Average leachate Eh was 425.6 mV, but it ranged from 309 to 540 mV indicating highly oxidizing conditions. Under these conditions, most of the Se would be found as Se (IV) or Se (VI) (Figure 2.1).

Se concentrations in leachate from the 10 cells can be compared in Table 5.6 or in Figure 5.12. Although the volume of leachate collected from the different cells remained fairly constant, in some instances the amount varied by as much as 10%. To facilitate a comparison of Se release from the five materials, a graph of the mass of weekly Se release (in μg) was prepared (Figure 5.13). In the first leach (week 0), the cells containing coal released most Se, 80 μg , and the

Table 5.6 Se Concentrations in $\mu\text{g/L}$ in Humidity Cell Leachate in 20-Week Test

Week	E99-61A	E99-61B	A99-23A	A99-23B	CREF-A	CREF-B	B99-44A	B99-44B	E99-19A	E99-19B
	Interburden		Parting		Refuse		Coal		Footwall	
0	5.5	3.8	15.5	17.2	13.1	10.7	66.4	96.0	21.5	24.6
1	5.1	5.7	46.0	54.0	25.8	28.1	82.3	96.8	66.8	73.2
2	4.7	5.2	51.0	44.6	16.9	12.5	49.0	40.5	38.3	34.3
3	3.5	3.6	16.7	12.7	5.4	5.0	10.9	8.4	3.1	3.2
4	4.4	5.3	29.0	30.5	6.4	7.4	10.3	9.6	2.9	3.3
5	3.5	3.8	15.4	18.3	7.2	6.4	15.2	10.8	3.9	4.7
6	3.6	4.0	16.7	20.2	7.5	6.9	11.9	12.4	3.5	3.9
7	3.5	3.3	16.8	15.6	6.2	6.5	9.2	6.8	3.4	3.7
8	3.7	3.7	9.6	15.4	6.4	5.6	9.9	7.3	3.1	3.2
9	3.6	3.7	16.8	15.5	5.3	5.1	11.3	9.1	3.0	3.1
10	3.8	4.7	23.7	19.8	7.4	6.5	11.6	8.3	3.1	3.3
11	4.3	5.2	28.7	23.4	8.0	8.0	8.7	10.1	3.8	3.9
12	4.3	5.1	29.5	30.2	6.5	7.5	10.0	10.8	3.4	3.5
13	4.5	5.2	26.3	25.8	7.1	6.9	11.0	7.1	2.8	3.4
14	4.0	4.5	21.6	21.0	7.9	7.4	10.1	9.8	3.3	3.9
15	4.3	4.9	31.7	21.6	8.3	6.5	8.5	9.5	3.3	3.4
16	5.4	5.5	23.7	23.0	9.3	7.8	9.8	9.4	3.5	3.4
17	4.4	3.9	19.8	21.0	6.4	6.5	8.1	7.1	3.3	2.9
18	4.4	6.7	20.0	20.5	7.2	5.9	6.5	6.0	2.5	2.9
19	3.4	3.3	20.3	18.5	6.9	6.7	6.6	5.4	2.1	2.0
20	2.6	3.4	15.8	16.1	4.2	4.7	5.5	5.3	2.3	2.3

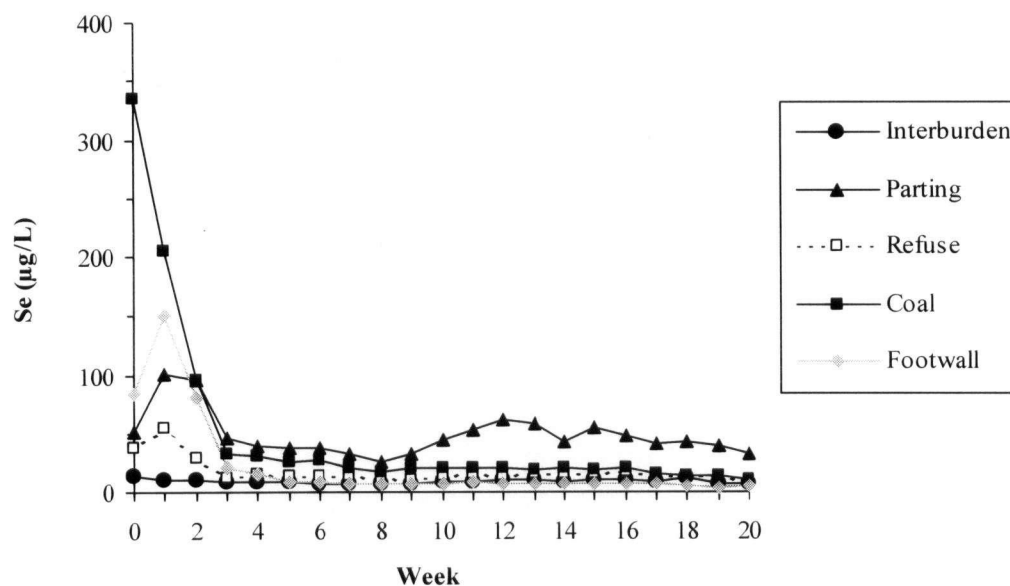


Figure 5.12 Se Concentration in Humidity Cell Leachate in $\mu\text{g/L}$ in 20-Week Test

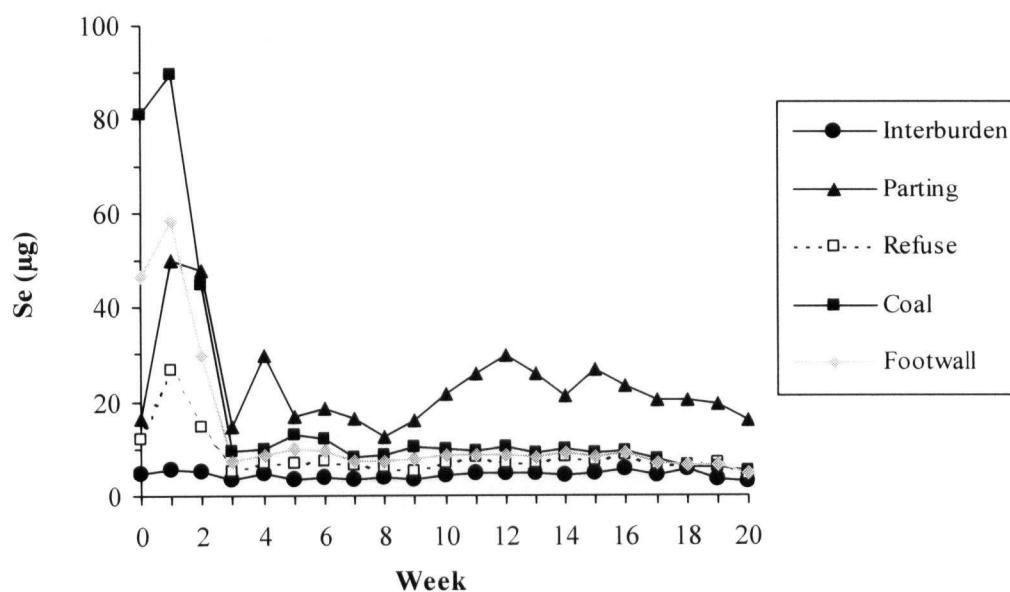


Figure 5.13 Amount of Se in Humidity Cell Leachate in μg in 20-Week Test

interburden containing cells the least amount of Se, 10 μg . The footwall released just over half as much Se as the coal, while the parting and refuse released less than a quarter of that amount. Se release from the coal, foot wall and refuse samples rose after the first week, but by the third week decreased to around 0.01 mg and stabilized. Se levels in leachate from the parting cells also peaked before the third week, but did not stabilize. Amounts of Se leached from the parting material appeared to taper off somewhat after week 12, but remained higher than those from other cells. Se release from the interburden samples remained constant around 0.01 mg through the 20-week period. The peaks observed in the first three weeks result from either:

1. The release of Se oxyanions adsorbed to clay minerals.
2. The removal of sulphide or selenide oxidation products.

The distilled water used to leach the cells had an average pH of 6.5. The dominant clay minerals in the Mist Mountain Formation, illite and kaolinite, have PZC values of 2.8 and 4.6 respectively (Förstner and Wittmann, 1979) such that neither selenate nor selenite will remain adsorbed to their surfaces. If this were the source of the Se mobilized during the first three weeks, there should be a positive correlation between Se release and clay mineral content, but no such correlation is observed. A positive correlation is observed between peak Se release and sulphide content (Figure 5.14), suggesting that sulphides are the source of the Se.

Peak release from the foot wall sample is low considering the fact that it contains almost four times as much sulphides as any of the other materials. Mineralogical factors such as grain size, degree of liberation, type of sulphide, neutralizing potential and trace element content affect the rate of sulphide oxidation (Lawrence and Day, 1997) and likely account for the differences observed in the rate of Se mobilization.

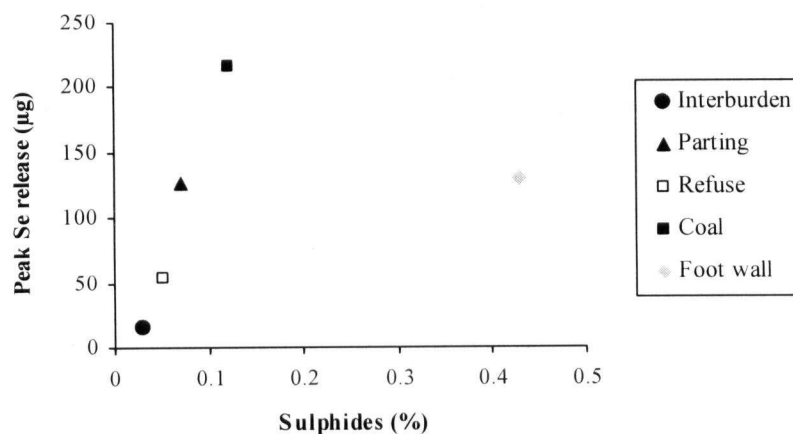


Figure 5.14 Peak Se Release from the Humidity Cells versus Sulphide Content

SO_4^{-2} concentrations in the leachate were measured every second week, providing a larger data set with which to assess the role of sulphide oxidation in Se mobilization. Average SO_4^{-2} concentrations were calculated for the duplicates. There is no overall correlation between Se and SO_4^{-2} concentrations when average SO_4^{-2} concentrations from all five materials were plotted against average respective Se concentrations in a single graph (Figure 5.15). A significant correlation between the concentrations Se and SO_4^{-2} results though, when the different materials are considered individually (Figures 5.16 through 5.20). This is a critical finding since it provides a much stronger case for sulphides as the main source of water soluble Se, than the peak release data. The correlation is strongest for the coal, interburden and foot wall samples. With $r = 0.559$ and a bi-modal distribution, the correlation between Se and SO_4^{-2} for the parting sample is considerably weaker than for the other types of material. The lack of a correlation between Se and SO_4^{-2} concentrations in leachate from this sample and the erratic release of Se from the parting humidity cells may be due to any one of the factors affecting oxidation rates, such as texture, porosity and the degree of liberation.

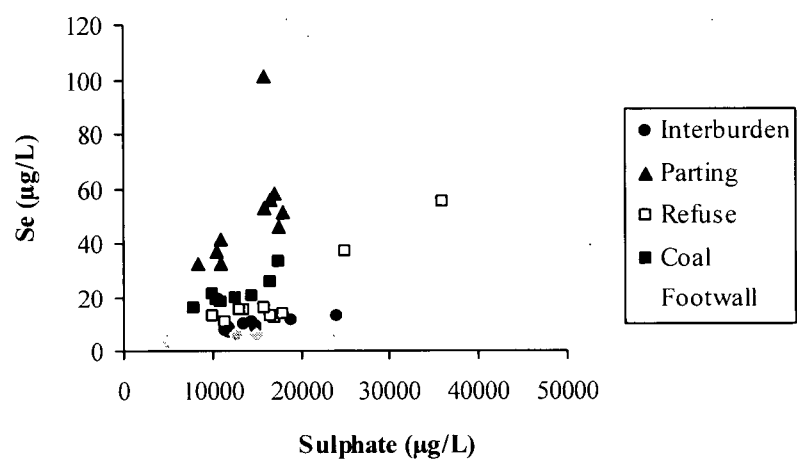


Figure 5.15 Se versus Sulphate Concentrations in Leachate from the Five Humidity Cells

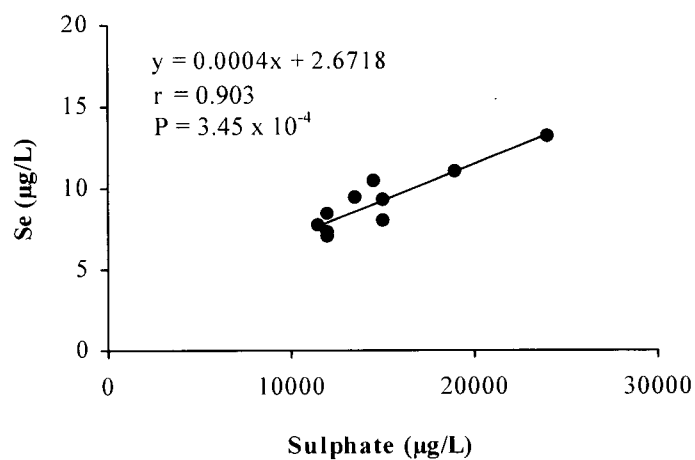


Figure 5.16 Se versus Sulphate Concentrations in Leachate from the E99-61 (Interburden) Humidity Cells

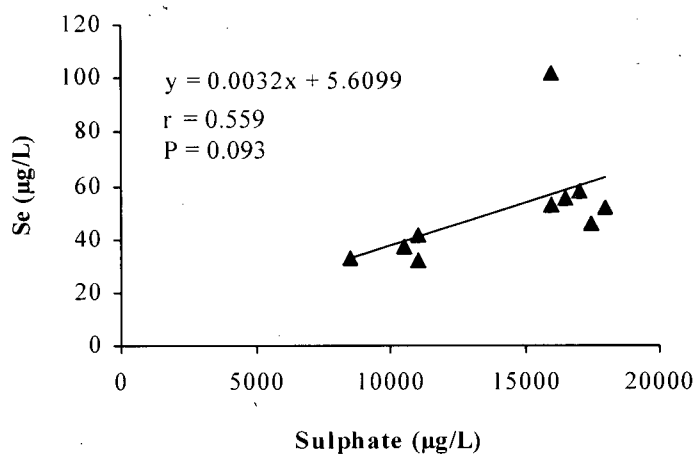


Figure 5.17 Se versus Sulphate Concentrations in Leachate from the A99-23 (Parting) Humidity Cells

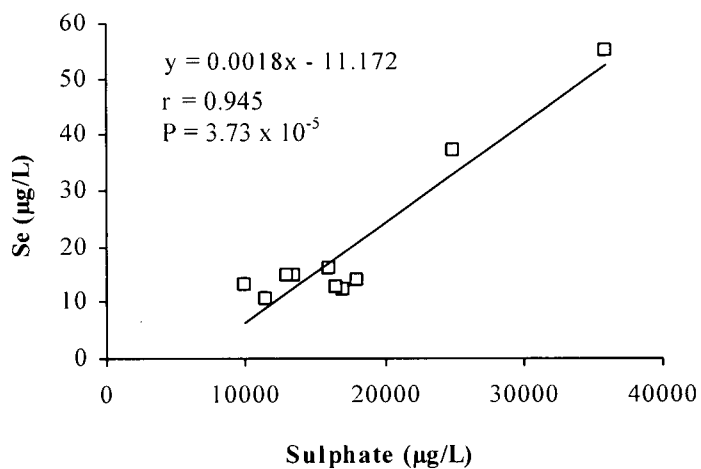


Figure 5.18 Se versus Sulphate Concentrations in Leachate from the CREF (Refuse) Humidity Cells

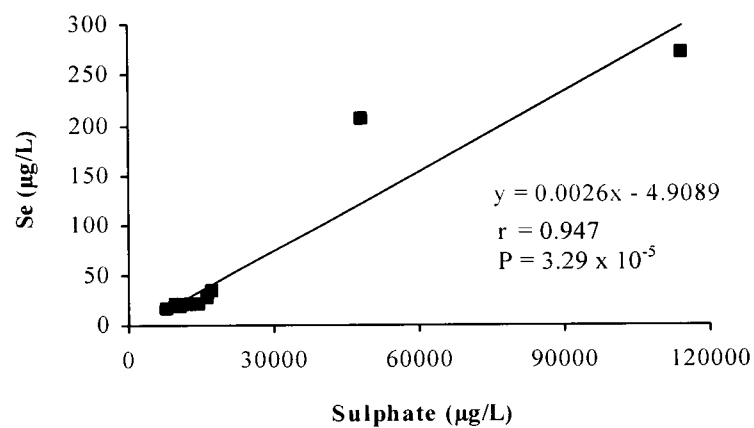


Figure 5.19 Se versus Sulphate Concentrations in Leachate from the B99-44 (Coal) Humidity Cells

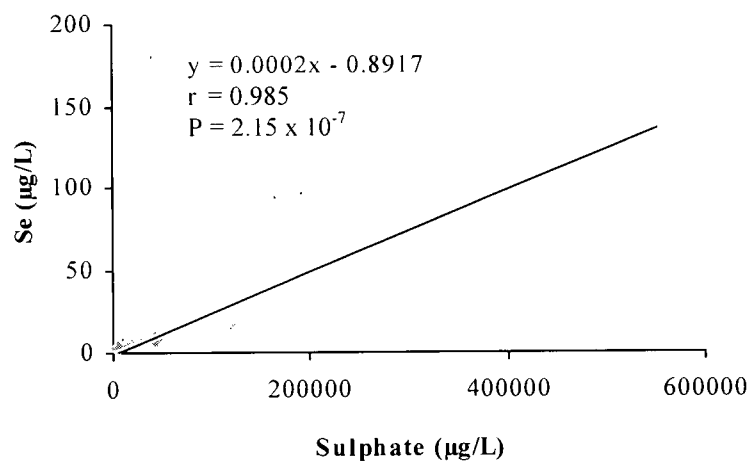


Figure 5.20 Se versus Sulphate Concentrations in Leachate from the E99-19 (Foot Wall) Humidity Cells

Sample to sample variation in the ratio of Se to SO_4^{2-} release appears to stem from the ratio of Se to sulphides in the solids (Table 5.7). Samples with a high Se to sulphides ratio tend to show a more pronounced decline in the Se to SO_4^{2-} ratio in leachate i.e. they consistently release more Se. Given the low sulphide concentration in the interburden sample, its Se/Sulphide could be drastically inflated by even a slight error in the measurement of sulphides.

Table 5.7 Se to Sulphide Ratios in the Materials Used for the Humidity Cell Tests

	Type of Material	Se/Sulphide Ratio in Solids	Slope of Se versus Sulphate in Humidity Cell Leachate Plots
A99-23	Parting	0.008	0.0032
B99-44	Coal	0.007	0.0026
CREF	Refuse	0.007	0.0018
E99-19	Foot Wall	0.002	0.0002
E99-61	Interburden	0.011	0.0004

* Calculated from data in Table 4.5

The multi-element analyses of the leachate provided no evidence of other mineralogical associations contributing to or affecting Se release. Two thirds of the elements included in the ICP-OES scan were consistently below the detection limit (Table A4.1 to A4.10 in Appendix 4). K, Li, Zn, Cu and Fe were above the detection limit in some of the samples. Elements consistently above the detection limit in all the samples were Ba, Ca, Mg, Se and Si. Of these, only Ca concentrations showed any correlation with Se and this was more likely the result of the gradual dissolution of CaCO_3 than of the release of Se associated with Ca.

Se showed no correlation with TIC or TOC concentrations in leachate. Dibenzothiophene, a polycyclic aromatic compound, is frequently used as a model of organic S-containing molecules the macromolecular coal matrix (Van Afferden et al., 1993). When oxidized, this compound releases S as sulfinic acid (Kargi, 1987), meaning that if S were being released primarily as a result of the oxidation of organic matter a correlation between S and TOC concentration should

be observed. Noting that the rate of sulphide oxidation is up to three orders of magnitude greater than that of organic matter in coal (Chang and Berner, 1999), the lack of a correlation between TOC and Se in leachate is not unexpected.

Having identified sulphides as a probable source of labile Se, due note should be given to the chemistry involved. The oxidation of sulphides and analogous Se compounds would occur as described in Appendix 6. At neutral pH, the reaction generates water soluble selenate. Selenite, if present, would be expected to adsorb readily to the $\text{Fe}(\text{OH})_3$ produced (Ballistreri and Chao, 1987). The next issue to address is the rate of Se release. A significant amount (20 to 76 %) of the total amount of Se released from the humidity cells during the 20-week period is released in the first three weeks (Table 5.8). After this, Se release occurs at a regular rate (Figure 5.13) with all samples releasing between 0.04 and 0.36 % of their total Se per week (Figure 5.21). Table 5.9 presents these results in both net and relative terms.

Table 5.8 Peak Se Release in the First 3 Weeks as a Percent of Total Se Release from the Humidity Cells in 20 Weeks

	Type of Material	Peak Se/Total Se Extracted (%)
A99-23	Parting	26
B99-44	Coal	59
CREF	Refuse	34
E99-19	Foot wall	76
E99-61	Interburden	20

Table 5.9 Weekly Se Release after the First 3 Weeks in μg and as a Percent of Total Se in the Head Samples

	Weekly Se Release	
	$\mu\text{g}/\text{kg}$	Percent of Total Se in the Sample
A99-23	21	0.36
B99-44	9	0.10
CREF	7	0.20
E99-19	3	0.04
E99-61	4	0.13

Acid-generation potential (AP) and neutralization potential (NP) are commonly used to predict the risk of acid rock drainage (Lawrence and Day, 1997). Although coals of the Mist Mountain Formation have low sulphide contents (Holuszko et al., 1992), the neutralization potential ratio (NP/AP) could conceivably affect the rate of S and Se mobilization. The AP and NP of the five materials used in the humidity cell tests were calculated using the formulas presented in Lawrence and Scheske (1997) (Appendix 5). For the purpose of the NP calculations, calcite was assumed to be the only carbonate mineral present. Given that siderite does not contribute to NP, the calculated value may be somewhat inflated due to the assumption about all CaO being accounted for by calcite. Relative reactivity values used in determining NP were obtained from Kwong (1993). AP was calculated based on the amount of sulphidic S in each of the materials.

Table 5.10 NP and AP Values and Neutralization Potential Ratios of the Five Materials Included in the Humidity Cell Tests

	NP (kg CaCO ₃ /tonne)	AP (kg CaCO ₃ /tonne)	NP/AP
A99-23	15.2	2.2	6.9
B99-44	23.3	3.8	6.2
CREF	22.9	1.6	14.7
E99-19	7.0	13.4	0.5
E99-61	60.6	0.9	64.7

There is poor correlation between the neutralization potential ratios and the net weekly Se release from the humidity cells ($r = -0.335$). If the ratio of neutralizing to acid-producing material exercised a dominant control on the rate of Se release, low NP/AP ratios should be associated with high Se release rates. However, the foot wall (E99-19) had the lowest NP/AP ratio and the lowest weekly Se release rate and the parting (A99-23) released more than twice as much Se per week as the coal (B99-44), though they had very similar NP/AP ratios.

The parting (A99-23) released most Se over the course of the 20-week period (Figure 5.22). It contains less Se than the coal (B99-44) and the foot wall (E99-19) and only a sixth of the sulphides found in the foot wall. This suggests that the degree of liberation of sulphides from.

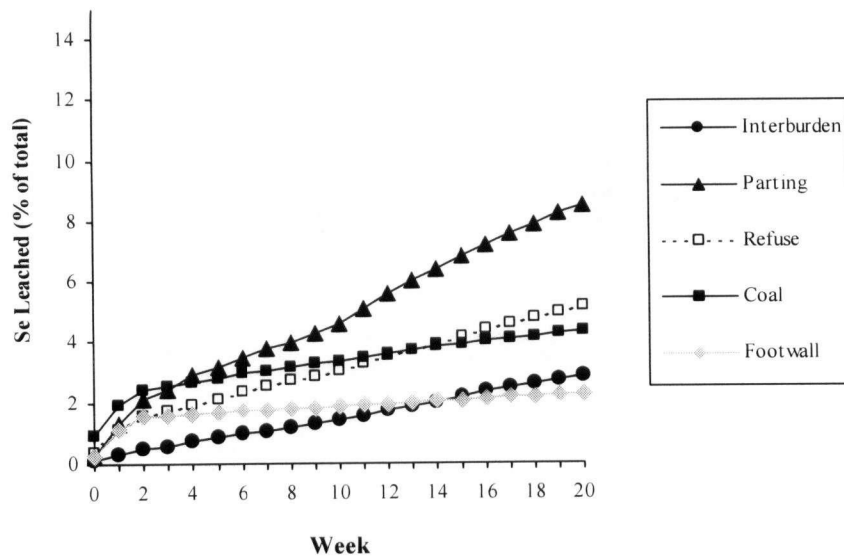


Figure 5.21 Percent of Se Extracted from the 20-week Humidity Cell Tests

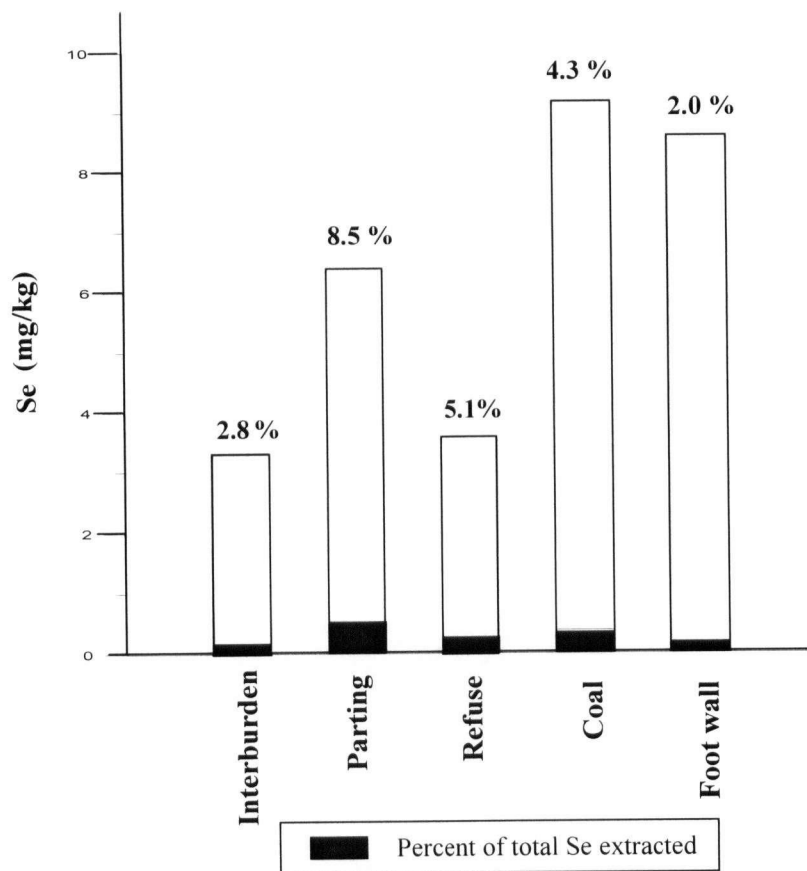


Figure 5.22 Percent of Total Se Extracted During the 20-week Humidity Cell Tests

other mineralogical components may play a role in determining long-term rates of Se release. Chen et al. (1999) demonstrated that a coating of organic compounds may passivate sulphide oxidation. Organic compounds could be responsible for slowing Se release from the foot wall and the coal (B99-44) which both contain significantly more TOC than the parting (A99-23). Goldhaber (1983) and Nicholson et al., (1990) showed that the build up HFMO on sulphide surfaces may have a similar effect, while Sharmasarkar and Vance (2001) suggest that HFMO may slow Se release, adsorbing the oxyanions. This does not appear to be occurring in this instance as A99-23 has more HFMO-associated Se than E99-19 and B99-44.

Although the humidity cell tests have provided useful information, it is important to understand the limitations of this type of test. Correlation between humidity cells and run off from test plots in the field tends to be weak (Frostad et al., 2000). Factors that may contribute to this include:

1. Artificial grain size distribution

Reducing grain size to below 6.3 mm for the humidity cell tests exposes a substantially greater surface area of the material to oxidative weathering than would be exposed in waste rock. Price (1997) notes that grinding and crushing may make the minerals more susceptible to oxidation as this process may expose soluble base cations and hydroxides.

2. Flushing frequency

The dry air/moist air regime used in humidity cell tests is far more regular and intense than drying and wetting cycles in mine spoils (Lapakko, 1994).

3. Degree of wetting

The water flush is meant to remove all of the oxidation products accumulated during the week. Due to channelling of runoff, complete wetting and flushing is not achieved in waste rock piles which generates further discrepancy between laboratory and field tests.

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4. Operating humidity cell tests at room temperature

Temperatures in the laboratory are generally greater than those in the field, which may lead to increased rates of chemical and biological reactions.

Though it is clear that humidity cells accelerate the weathering process, it is not clear by how much. Using results from such tests to model geochemical processes in mine spoils is difficult due to the heterogeneous nature of waste rock and the high degree of variability in field conditions (Paktunc, 1999). Differences between the percent of total Se extracted using a 1-hour shake flask extraction in the sequential extraction with distilled water with peak Se extraction from the humidity cells (Table 5.11) emphasize the importance of particle size on leaching rates and illustrate the problems of "scaling up" results even in a controlled environment with relatively homogeneous samples. In the case of the sequential extractions, material crushed to below 200 mesh was used while material below 3 mesh was used for the humidity cell tests. The shake flask leach removes as much as 15 times more Se than the humidity cells do because of the relatively large amount of exposed surface area which increases reactivity.

Table 5.11 Percent of Water Soluble Se in the Sequential Extraction Compared with Percent of Total Se Represented by Peak Extraction from the Humidity Cells

	Water Soluble Se in Sequential Extraction (%)	Peak Se Extraction from Humidity Cells (%)
A99-23	6.0	2.2
B99-44	4.7	2.6
CREF	4.8	1.7
E99-19	2.4	1.7
E99-61	8.9	0.6

Lastly, the relatively short duration of humidity cell tests was of concern since waste rock at the mine is continuously subject to oxidative weathering. It was particularly problematic in this instance because Se release rates showed no sign of slowing by the end of the 20-week period. However, due to both time and budget limitations it was not possible to extend the duration of the tests.

In summary, the humidity cell tests show that:

1. Se is being released from all materials, with the parting (A99-23) exhibiting the highest weekly release rate at 21 µg/week and the interburden (E99-61) the lowest at 4 µg/week.
2. Se release, as a function of total Se content of the head samples, is within the same order of magnitude for all five lithologies tested.
3. Sulphide oxidation appears to be the main geochemical mechanism driving Se release.
4. Se release is poorly correlated with the neutralization potential ratios of the five lithologies tested. Organic material may decrease the rate of sulphide oxidation thereby reducing Se mobilization. Further tests will be required to evaluate the role of TOC in regulating Se release and to determine to what extent the rate of Se release is affected by other mineralogical factors, such as grain size, degree of liberation, type of sulphide, and trace element content.

6.0 CONCLUSIONS

This research project was undertaken to determine the source or sources of Se being mobilized by surface- or groundwater from the five open-pit coal-mining operations in the Elk River Valley, as well as the rate and geochemistry of its release.

The following conclusions were made regarding mineralogical associations of Se in the Mist Mountain Formation:

- Se is associated with both organic and inorganic components in the 16 samples representing the main lithologies in the coal-bearing stratigraphic section.
- Water soluble Se accounts for approximately 10% of total Se, though values range from 3% to 21%. Less than 5% of the Se is found in association with HFMO. Se incorporated into the silicate structure accounts for, on average, 15% of total Se and between 60% and 84% the Se is found in association with sulphides and organic material.
- The oxide analyses reveal no correlation between Se and clay mineral concentrations. Se is, however, the medium density fraction contained between 0.8 and 8.1 mg/kg Se, and the <2 μm fraction contained, on average, 42% more Se. These findings suggest that clay minerals contain Se but do not make a consistent contribution to the amount of total Se.
- The amount of Se associated with the organics and sulphides varies, reflecting a high degree of heterogeneity in the depositional environments.
- The ratio of sulphides to TOC is well correlated with the amount of Se in materials closely associated with coal seams containing less than 6 mg/kg Se. The amount of organic matter present may affect the incorporation of Se into sulphides by modifying redox conditions or it may compete with sulphides for available Se.

In seeking to pinpoint potential sources of Se to the tributaries of the Elk River, the magnitude and rate of Se release from different lithologies were investigated. Listed below are the most important findings with regard to this topic:

- Se was released, in order of decreasing magnitude, from parting, coal, refuse, foot wall interburden.
- All samples, other than the interburden, exhibited a peak in Se release in the first three leaches likely resulting from the removal of oxidation products. Peak release accounted for between 20 % and 76 % of total Se leached. It correlates poorly with the amount of Se in the water soluble phase of the sequential extractions highlighting difficulties of scaling-up results even within a controlled laboratory environment.
- After the first three weeks, weekly Se release rates stabilized between 3 and 21 $\mu\text{g/L}$.
- The amount of Se leached from each of the different materials on a weekly basis does not correlate well with total Se content. The parting material, containing 5.9 mg/kg Se, released most Se, 21 $\mu\text{g/kg/week}$. The coal, which contained 8.8 mg/kg Se, released 9 $\mu\text{g/kg/week}$ and the foot wall, with 8.4 mg/kg Se, released only 3 $\mu\text{g/kg/week}$. The interburden, which contained 3.0 mg/kg Se, released 4 $\mu\text{g/kg/week}$ while the refuse, which contained 3.4 mg/kg Se, released 7 $\mu\text{g/kg/week}$.
- The rate of Se release from these materials was also poorly correlated with sulphide content. The foot wall sample contained most sulphides, but released least Se suggesting that mineralogical factors play an important role in determining the magnitude of Se release.
- Se release from the humidity cells with parting material fluctuated more than Se release from the other cells. A larger number of parting samples would have to be analyzed to

determine if this is a function of the form in which Se is present in this particular sample or Se is as readily released from other parting samples with similar mineralogical characteristics.

- The rate of Se release from the humidity cells did not level off at the end of the 20-week test period. It is unlikely that Se release would continue at the same rate indefinitely since a portion of the Se in all of the materials is found in unliberated sulphides, within the silicate structure, and in slow-weathering organics. Humidity cell tests would have to be run over a much longer period to confirm this.
- The percent of total Se leached in the 20-week period, varied from 2.2 % for the foot wall to 8.3 % for the parting.

The main conclusions regarding possible biogeochemical mechanisms of Se mobilization were:

- No correlation was found between Se and TOC or concentrations of the other 30 elements measured in the humidity cell leachate indicating that the Se being removed did not stem from the organic matrix or a mineral association with any one of those elements.
- The only statistically significant correlation was observed between Se and sulphate concentrations in leachate from the humidity cells containing interburden, foot wall, coal and refuse. This strongly suggests that sulphides are the primary source of Se being mobilized by runoff from the mine sites.
- The correlation between peak Se release from the humidity cells and sulphide content provides further evidence of sulphide oxidation as a source of Se. Selenides have slower oxidation kinetics than sulphides, but when present, they would likely make a contribution to Se being leached from the samples. However, no selenides were identified in this study.

- Given that the rate of Se release was poorly correlated with sulphide content, mineralogical factors, such as texture, porosity and sulphide liberation, clearly play an important role in governing the access of air and water to the Se in the material and hence the rate of Se mobilization.

Since the 1970s, an estimated 2.5 billion tonnes of rock have been extracted in the Elk River Valley. Exposing this amount of rock to air and water, creates a significant potential for continued Se mobilization though the coals and associated materials, on average, contain only 0.57% total S. Further study will be required to determine the magnitude of Se release under field conditions.

In order to assess the risk presented by Se release from waste rock and plant refuse, it is necessary to evaluate information on both Se geochemistry and bioavailability. If the high Se concentrations in the Elk River and its tributaries prove to have an adverse effect on biota, information on Se occurrence and mobilization would play an important role in adopting an effective remediation strategy. Given that Se is so widely distributed in the Mist Mountain Formation and that it is being mobilized from all types of rock, it would not be practical to try to isolate material from which Se is leaching. Instead, abatement measures would have to focus on diverting water away from the spoil piles and pits or on treating runoff.

7.0 RECOMMENDATIONS

This project addresses some of the fundamental questions about the modes of occurrence of Se in coal bearing geological units and its mobilization. To improve the understanding of the geochemistry of Se release from lithologies in the Mist Mountain Formation and to better evaluate the risks, the following work is recommended:

- Conduct longer term humidity cell tests or set up field plots to establish if Se rates eventually level off or if Se release continues until most or all of it has been released.
- Perform a Se mass balance to establish if some spoils are releasing more Se than others. This would involve estimating the amount of Se in waste rock based on results from Ryan and Dittrick (2000) and determining if there is any correlation with the amount of Se in runoff, calculated using data from Se monitoring stations on the rivers and streams running from the mines to the Elk River and flow rates in these waterways.
- Study the form in which sulphides occur in the different materials at the sites to determine how it affects reactivity.
- Obtain more information on the effect of Se speciation and complexation with dissolved organic matter and sediment on its bioavailability and the process of bioaccumulation.
- Test the reliability of the correlation between Se content and the sulphide/TOC ratio to determine whether it could be used to rapidly estimate Se concentrations in lithologies of similar coal-bearing depositional environments.
- Investigate the importance of selenides in the Mist Mountain Formation using microprobe analysis.

- Study Se abatement methods and their applicability. These include:
 1. Chemical or wetland-based remediation systems designed to precipitate Se oxyanions with sulphides (Lin et al., 2000; Labrenz et al., 2000)
 2. The use of ferrous iron amendments to immobilize Se with hydrous ferric oxides (Manning and Bureau, 1995; Qui et al., 2000)
 3. The addition of gypsum to precipitate calcium selenate dihydrate (Brienne et al., 2000)
 4. Phytoremediation through volatilization (Lin et al., 2000) or harvesting (Banuelos et al., 1998).

8.0 ABBREVIATIONS

AP	Acid-Producing Potential
APHA	American Public Health Association
ASTM	American Society for Testing and Materials
BEF	Biospheric Enrichment Factor
CCME	Canadian Council for Metals in the Environment
CDB	Citrate Dithionate Buffer
EDS	Energy-Dispersive Spectrometer
EDTA	Ethylenediamine-Tetraacetic Acid
HG-AAS	Hydride Generation Atomic Absorption Spectroscopy
HFMO	Hydrous Ferric and Manganese Oxides
ICP-MS	Inductively Coupled Plasma Mass Spectroscopy
ICP-OES	Inductively Coupled Plasma Optical Emission Spectroscopy
INAA	Instrumental Neutron Activation Analysis
NP	Neutralization Potential
PIXE	Proton-Induced Gamma-ray/X-ray Emission
PZC	Point of Zero Charge
SEM	Scanning Electron Microscopy
TIC	Total Inorganic Carbon
TOC	Total Organic Carbon
USEPA/EPA	United States Environmental Protection Agency
XRD	X-Ray Diffraction

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10.0 APPENDICES

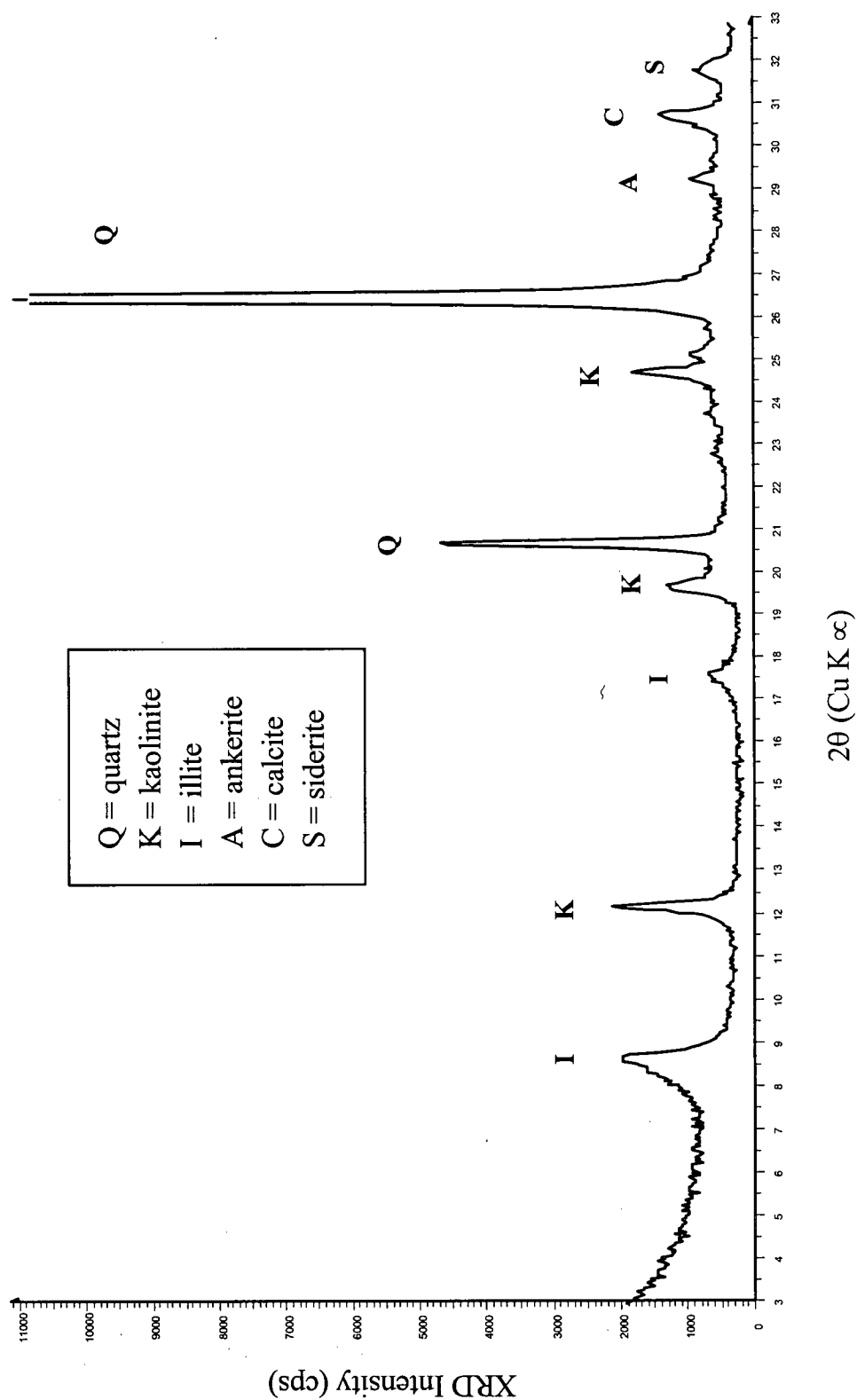
10.1 APPENDIX 1 X-Ray Diffractograms for the <2 μm and <200 μm Fractions of 5 SamplesFigure A1.1 X-Ray Diffractogram for the <200 μm Fraction of the Interburden Sample E99-61

Figure A1.3 X-Ray Diffractogram for the <200 μm Fraction of the Parting Sample A99-23

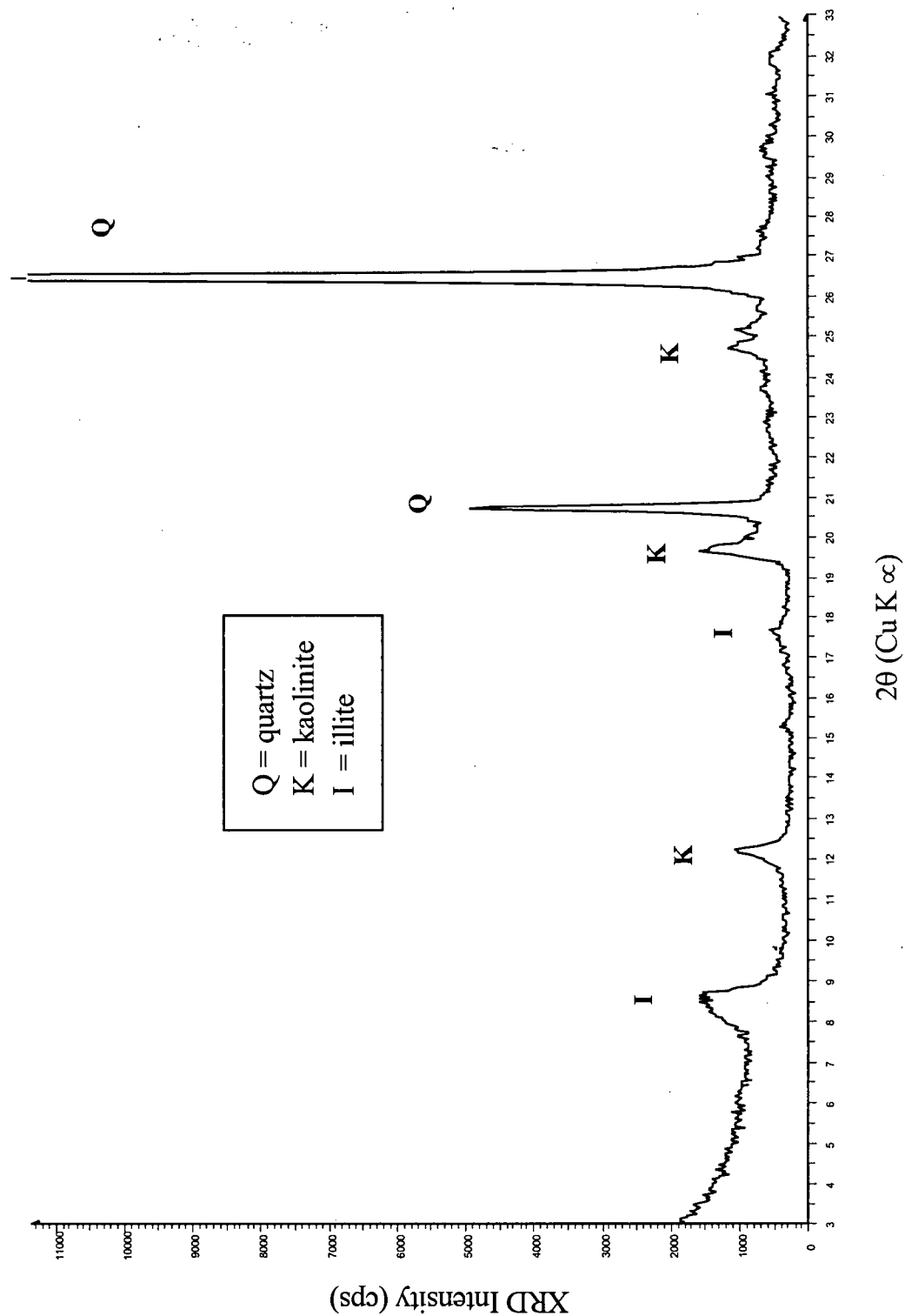


Figure A1.4 X-Ray Diffractogram for the <2 μm Fraction of the Parting Sample A99-23

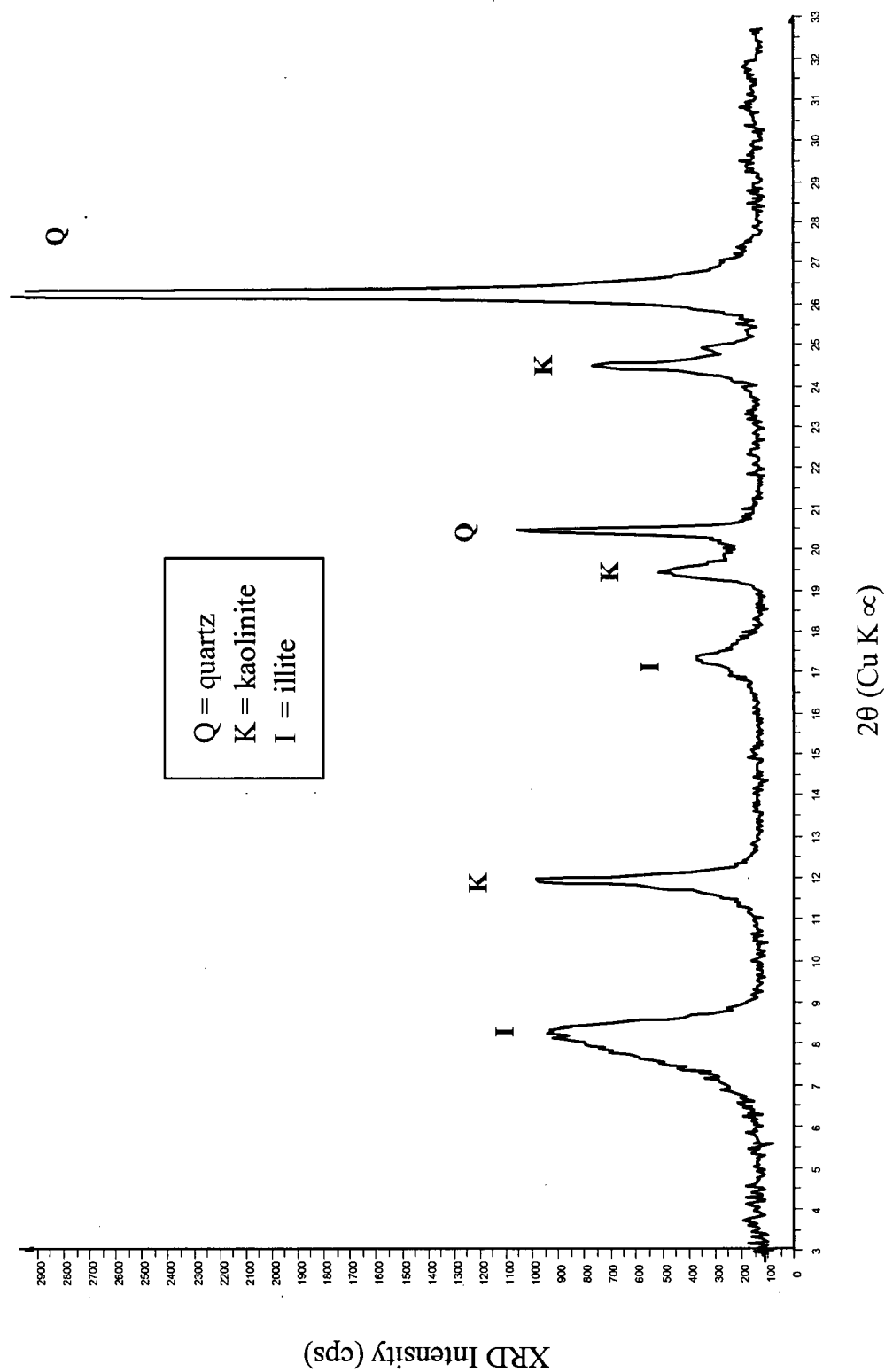


Figure A1.5 X-Ray Diffractogram for the <200 μm Fraction of the Refuse Sample CREF

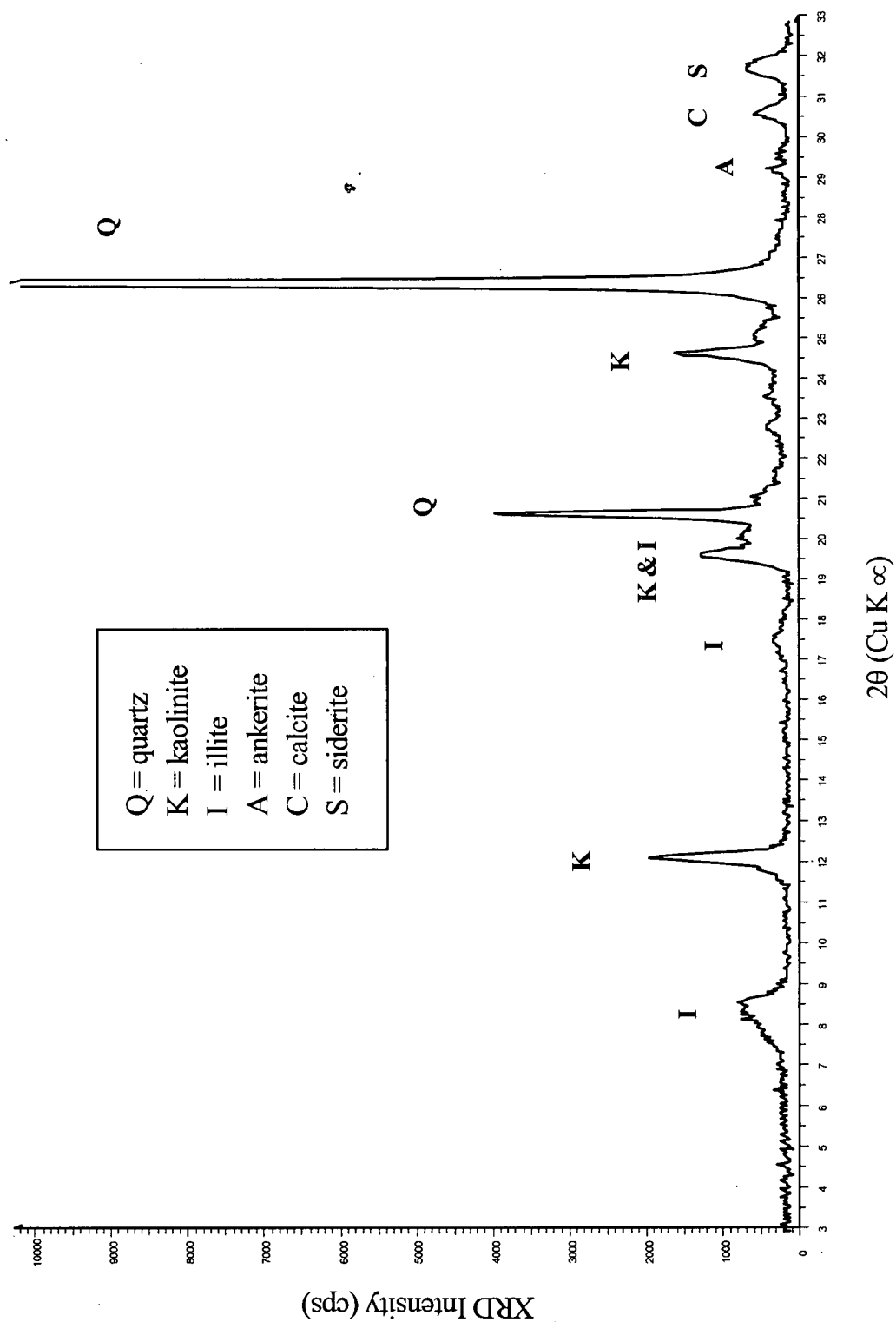


Figure A1.6 X-Ray Diffractogram for the <2 μm Fraction of the Refuse Sample CREF

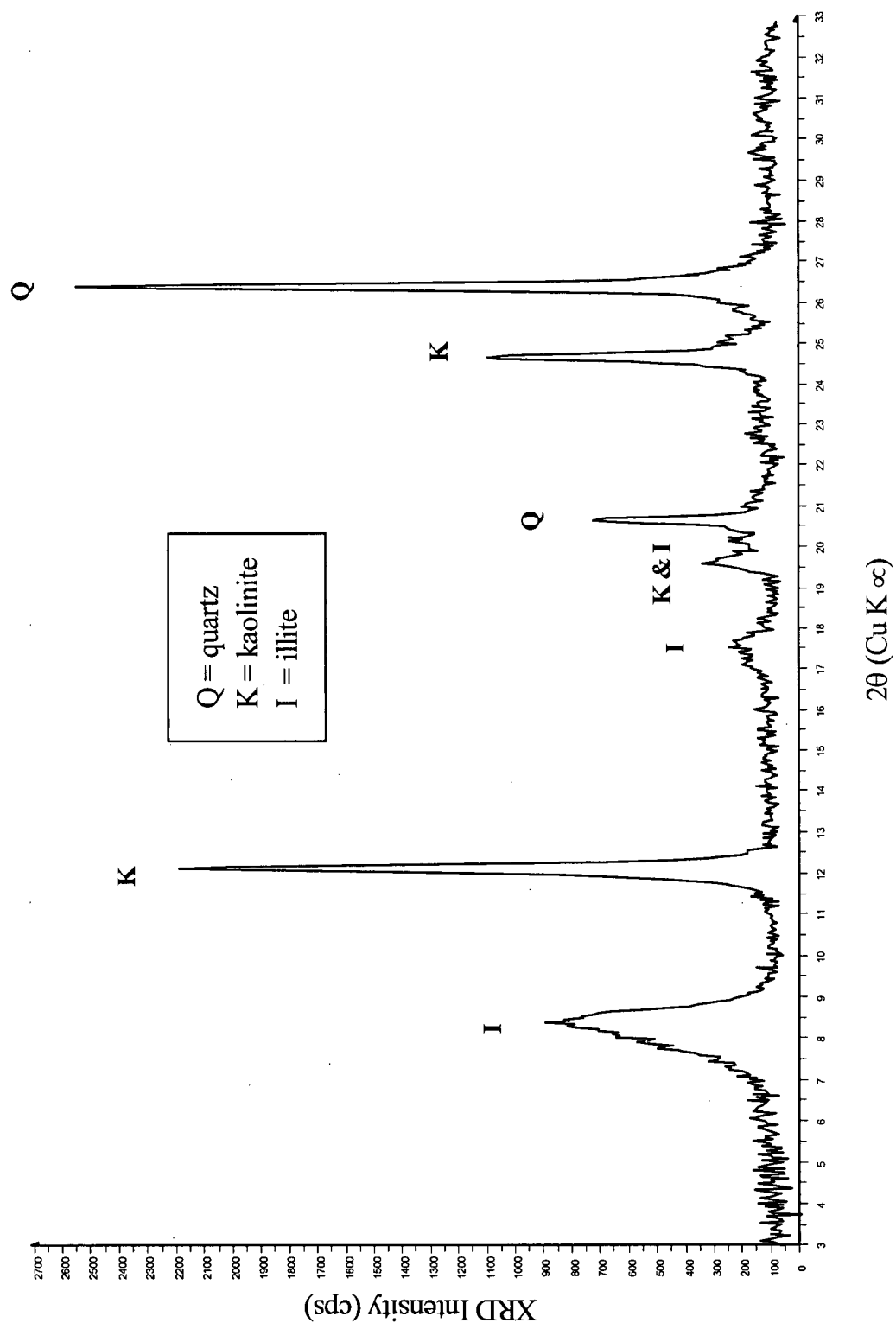


Figure A1.7 X-Ray Diffractogram for the <200 μm Fraction of the Coal Sample B99-44

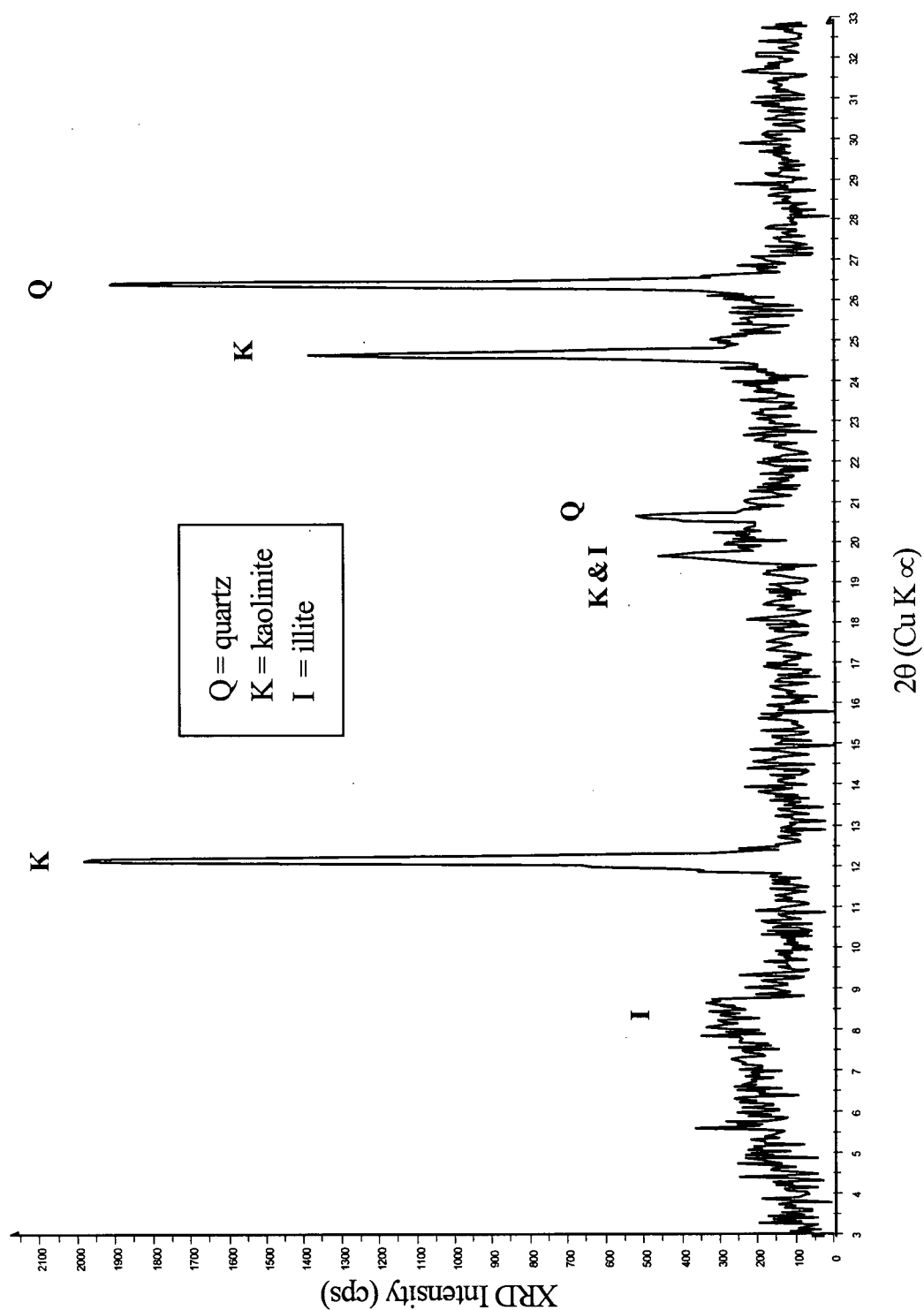


Figure A1.8 X-Ray Diffractogram for the <2 μm Fraction of the Coal Sample B99-44

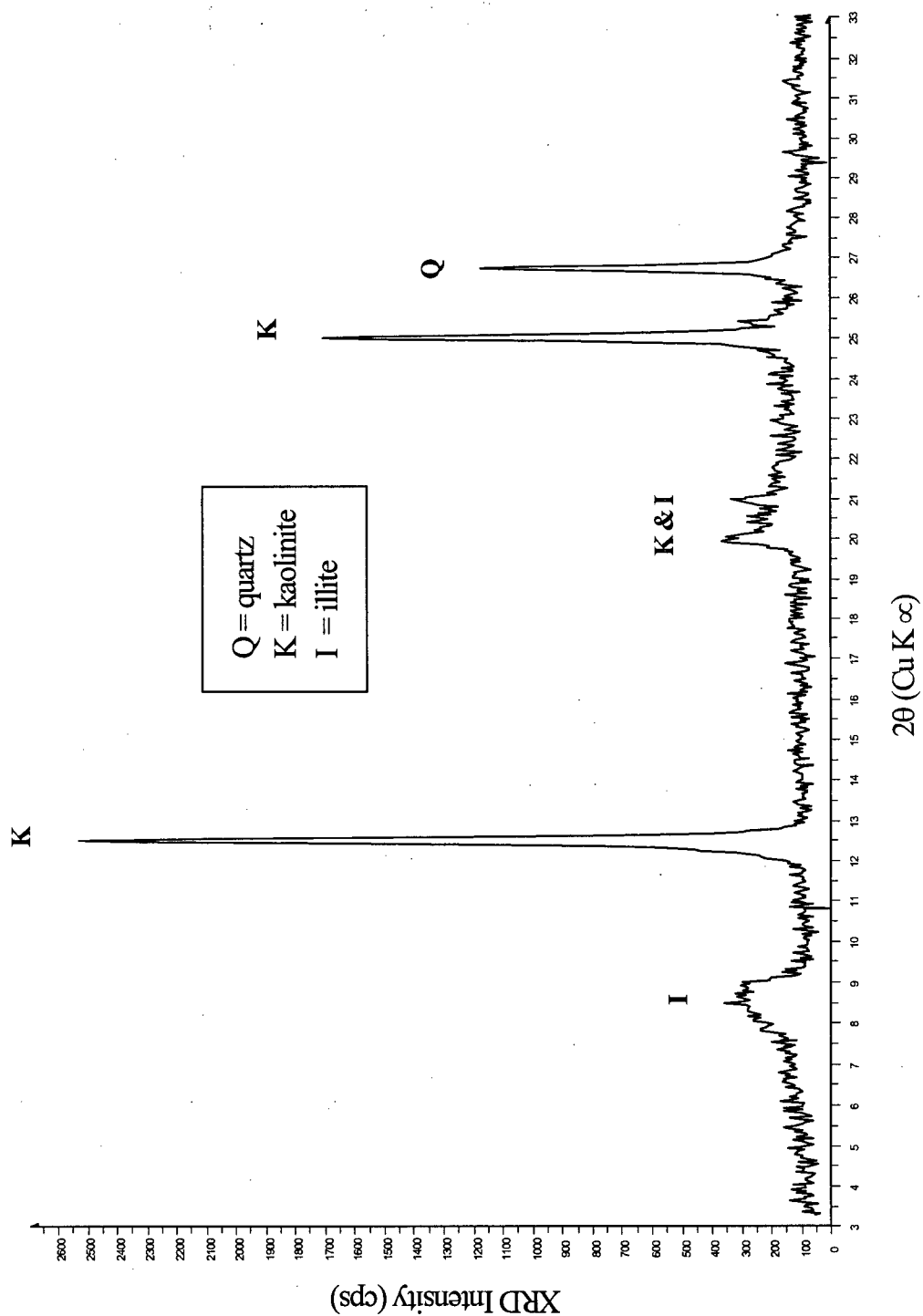


Figure A1.9 X-Ray Diffractogram for the <200 μm Fraction of the Foot Wall Sample E99-19

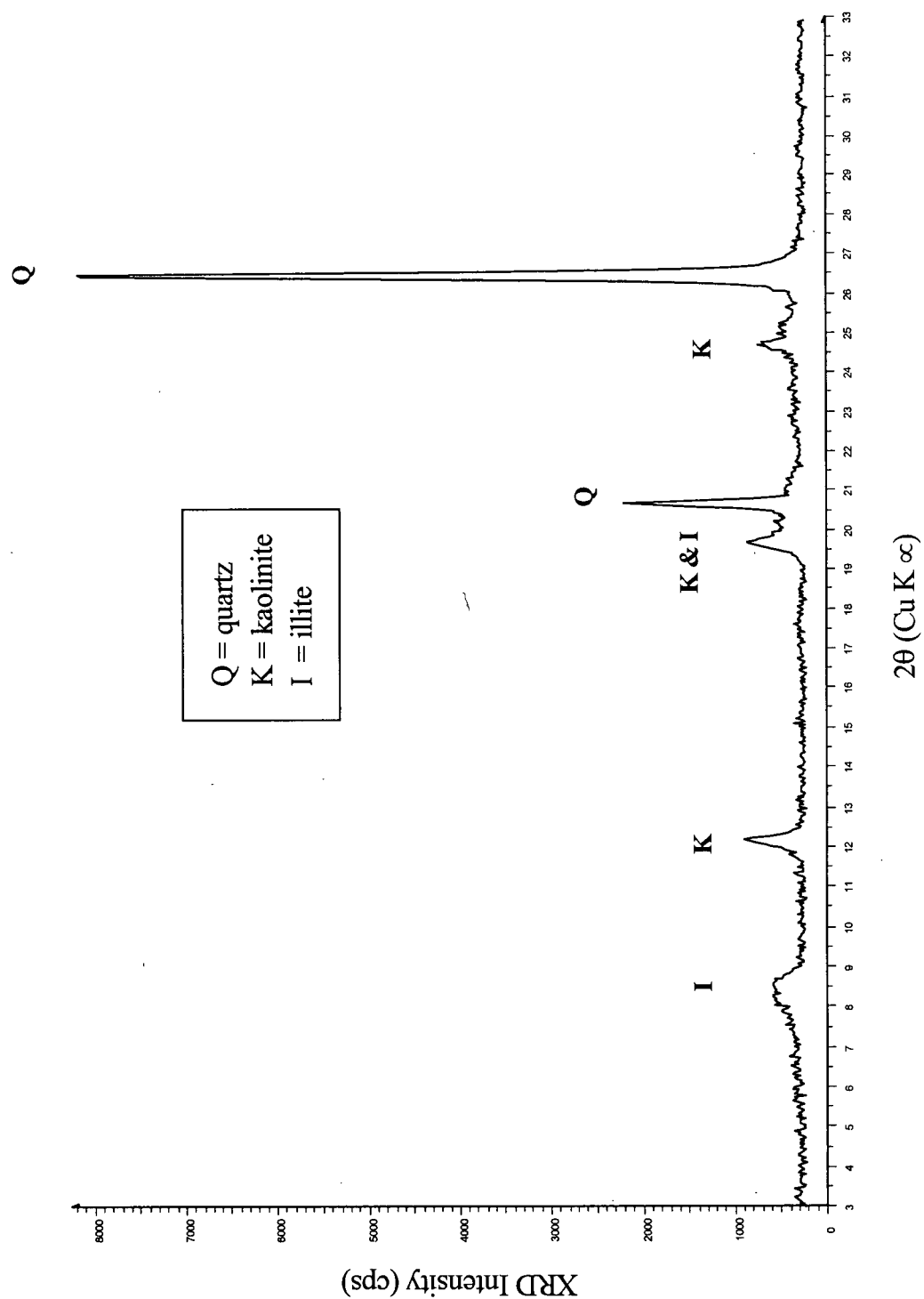
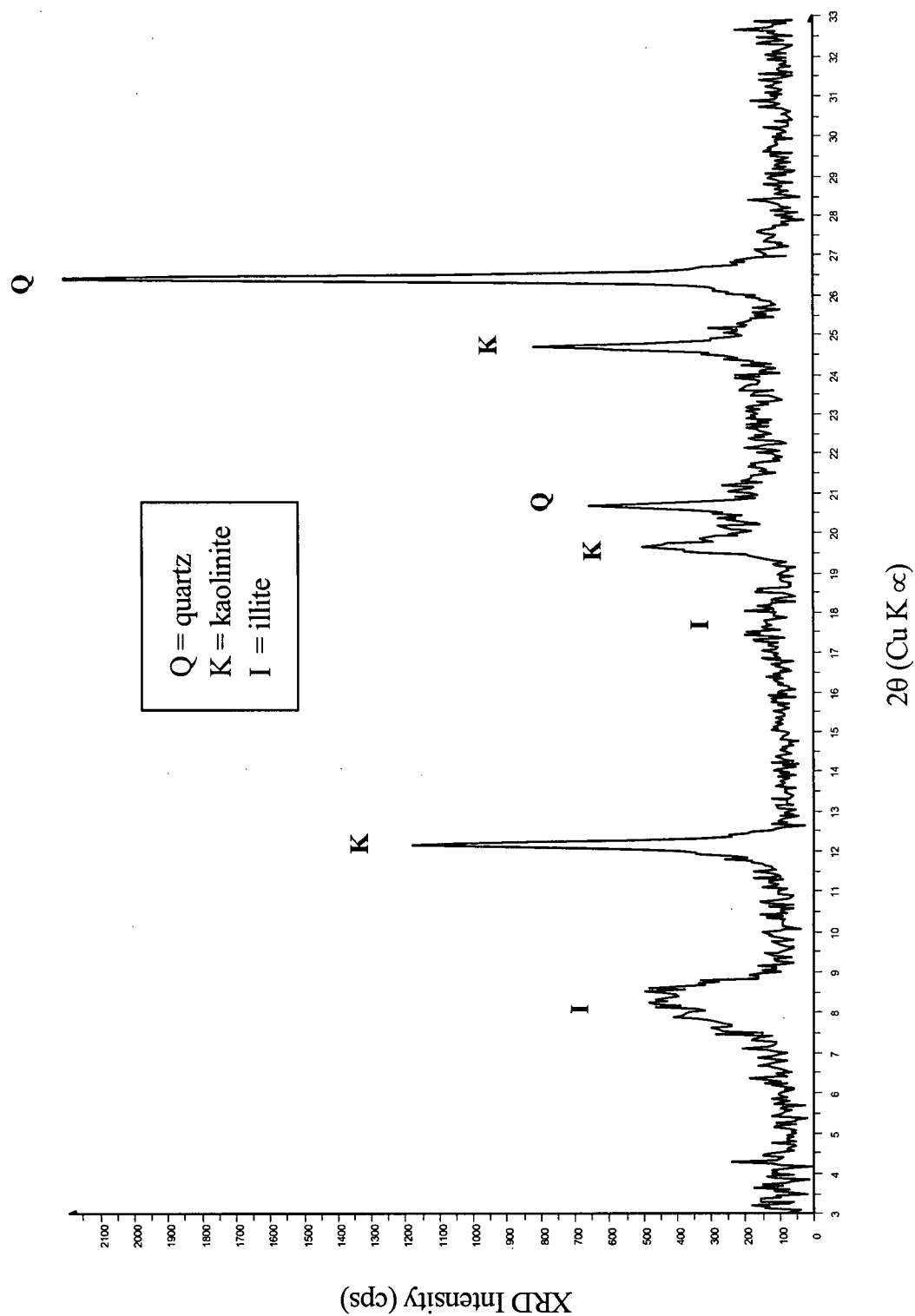


Figure A1.10 X-Ray Diffractogram for the <2 μm Fraction of the Foot Wall Sample E99-



10.2 APPENDIX 2 Calculation of the Percent of Total Sample Mass Accounted for by Major Mineral Components

Table A2.1 Formulas Used to Calculate the Percent of Total Mass Accounted for by Major Mineral Components

Mineral	Chemical Formula*	Molecular Mass (g/mol)
Calcite	CaCO_3	100.1
Ankerite	$\text{Ca}_{1.05}(\text{Fe}_{0.48}, \text{Mg}_{0.45}, \text{Mn}_{0.04})(\text{CO}_3)_2$	202.0
Siderite	FeCO_3	115.8
Kaolinite	$\text{Al}_2\text{Si}_2\text{O}_5(\text{OH})_4$	270.2
Illite	$\text{K}_{1.0-1.5}\text{Al}_4(\text{Si}_{6.5-7.0}\text{Al}_{1.0-1.5}\text{O}_{20})(\text{OH})_4$	448.3
Quartz	SiO_2	60.1

* From Deer (1993)

$$\% \text{K}_{\text{sample}} = \frac{n \cdot \text{atomic weight K}}{\text{molecular weight Illite}} \cdot \% \text{Illite}$$

$$\% \text{Al}_{\text{sample}} = \left(\frac{n \cdot \text{atomic weight Al}}{\text{molecular weight Illite}} \cdot \% \text{Illite} \right) + \left(\frac{n \cdot \text{atomic weight Al}}{\text{molecular weight Kaolinite}} \cdot \% \text{Kaolinite} \right)$$

$$\% \text{Si}_{\text{sample}} = \left(\frac{n \cdot \text{atomic weight Si}}{\text{molecular weight Illite}} \cdot \% \text{Illite} \right) + \left(\frac{n \cdot \text{atomic weight Si}}{\text{molecular weight Kaolinite}} \cdot \% \text{Kaolinite} \right) + \frac{n \cdot \text{atomic weight Si}}{\text{molecular weight Quartz}} \cdot \% \text{Quartz}$$

$$\% \text{Ca}_{\text{sample}} = \frac{n \cdot \text{atomic weight Ca}}{\text{molecular weight Calcite}} \cdot \% \text{Calcite}$$

Although XRD detected the presence of calcite, ankerite and siderite in only 4 of the 16 samples it is likely that most of the samples contain at least a small fraction of these carbonate minerals. Due the fact that the Fe in pyrite and HFMO could not be distinguished from the Fe in siderite or ankerite it was not possible to calculate the content of carbonates using the same approach as the one used to determine the amount of quartz, illite and kaolinite present in the sample. In order to obtain a rough quantitative estimate of the contribution of carbonates to the samples, it was assumed that all of the carbonates present were in the form of calcite.

10.3 APPENDIX 3 Raw Data from the Sequential Extractions

Table A3.1 Se Concentrations in Leachate and Solid Residue Collected from the Sequential Extractions

	Se Extracted ($\mu\text{g/L}$)			Se Remaining (mg/kg)
	Water Soluble	HFMO	Sulphides and Organics	Residual
A99-4A	6.0	3.0	49.0	0.8
A99-4B	5.9	<3.0	54.0	0.8
A99-7A	2.1	<3.0	68.0	0.7
A99-7B	2.3	<3.0	68.0	0.8
A99-12A	7.1	4.0	98.0	0.7
A99-12B	7.4	4.0	101.0	0.8
A99-23A	6.4	<3.0	89.0	0.4
A99-23B	6.1	4.0	86.0	0.4
B99-16A	17.0	3.0	55.0	0.3
B99-16B	18.0	4.0	43.0	1.0
B99-44A	11.5	<3.0	180.0	1.4
B99-44B	12.0	<3.0	220.0	2.2
B99-62A	3.2	<3.0	27.0	0.6
B99-62B	2.8	<3.0	27.0	0.5
CREFA	3.2	<3.0	59.0	0.3
CREFB	3.5	<3.0	55.0	0.4
C99-21A	4.4	5.0	32.0	0.3
C99-21B	2.9	4.0	33.0	0.3
C99-25A	0.7	<3.0	12.0	0.1
C99-25B	0.9	<3.0	13.0	0.1
D99-8A	4.4	<3.0	27.0	0.4
D99-8B	3.9	<3.0	30.0	0.4
E99-19A	3.8	<3.0	122.0	1.2
E99-19B	3.6	4.0	125.0	1.5
E99-45A	27.0	6.0	108.0	0.6
E99-45B	27.0	6.0	110.0	0.6
E99-59A	0.8	<3.0	17.0	0.2
E99-59B	1.0	<3.0	24.0	0.4
E99-61A	5.3	<3.0	36.0	0.3
E99-61B	5.4	<3.0	39.0	1.0
E99-63A	10.2	4.0	126.0	0.5
E99-63B	19.0	8.0	86.0	0.3

Table A3.2 Variation Between Se Concentrations in Extractant and Residue Duplicates

	Average Variation (% of mean)	Range of Variation (% of mean)
Water Soluble	4	0-60
HFMO	12	0-91
Sulphides and Organics	21	0-100
Residual	2	0-34

Table A3.3 Measured Se Concentrations in Head Samples versus Total Se Calculated From the Sequential Extraction Results

	Measured Se Concentration (mg/kg)	Average Calculated Se Concentration (mg/kg)
A99-4	4.9	3.8
A99-7	4.5	4.3
A99-12	7.0	6.3
A99-23	5.9	5.3
B99-16	4.9	4.2
B99-44	8.8	12.4
B99-62	2.2	2.1
CREF	3.4	3.4
C99-21	2.2	2.3
C99-25	0.8	0.8
D99-8	2.2	2.0
E99-19	8.4	7.9
E99-59	1.8	7.7
E99-45	7.3	1.4
E99-61	3.0	2.8
E99-63	4.4	6.7

Table A3.4 Concentrations of Trace Elements Associated with the HFMO Phase in µg/L

	A99-4		A99-23		B99-16		B99-44		CREF		E99-19		E99-59		E99-61	
	A	B	A	B	A	B	A	B	A	B	A	B	A	B	A	B
Al	9000	7000	48000	44000	20000	21000	<2000	4000	36000	31000	9000	9000	13000	14000	14000	15000
Sb	<1000	<1000	<1000	<1000	<1000	<1000	<1000	<1000	<1000	<1000	<1000	<1000	<1000	<1000	<1000	<1000
As	<1000	<1000	<1000	<1000	<1000	<1000	<1000	<1000	<1000	<1000	<1000	<1000	<1000	<1000	<1000	<1000
Ba	1230	1080	4010	3980	3430	3260	<100	370	3330	2970	980	1050	3330	3850	5130	5360
Be	<30	<30	<30	<30	<30	<30	<30	<30	<30	<30	<30	<30	<30	<30	<30	<30
Bi	<1000	<1000	<1000	<1000	<1000	<1000	<1000	<1000	<1000	<1000	<1000	<1000	<1000	<1000	<1000	<1000
B	<500	<500	<500	<500	<500	<500	<500	<500	<500	<500	<500	<500	<500	<500	<500	<500
Cd	<50	<50	<50	<50	<50	<50	<50	<50	<50	<50	<50	<50	<50	<50	<50	<50
Ca	45 300	45 300	38 100	<50	101 000	101 000	99 800	170 000	196 000	151 000	132 000	38 900	43 700	20 100	23 600	382 000
Cr	70	70	160	140	160	170	25	25	340	250	60	70	110	130	470	480
Co	50	<50	70	60	100	90	<50	<50	50	<50	<50	<50	<50	<50	<50	<50
Cu	650	400	1230	1140	740	720	80	70	520	440	560	430	350	330	350	170
Fe	290 000	236 000	85 000	67 400	65 700	58 800	11 800	10 900	216 000	176 000	36 400	30 400	77100	81 700	132 000	116 000
Pb	<300	<300	<300	<300	<300	<300	<300	<300	<300	<300	<300	<300	<300	<300	<300	<300
Li	<100	<100	<100	<100	<100	<100	<100	<100	<100	<100	<100	<100	<100	<100	<100	<100
Mg	9200	7300	13100	10300	30500	30 200	20300	23400	47 300	40 700	4500	5000	10 400	11 800	106 000	106 000
Mn	6230	4810	310	240	560	520	50	60	1810	1460	490	510	910	1020	2660	2470
Mo	<200	<200	<200	<200	<200	<200	<200	<200	<200	<200	<200	<200	<200	<200	<200	<200
Ni	<300	<300	<300	<300	<300	<300	<300	<300	2100	1600	<300	<300	<300	<300	<300	<300
P	9000	8000	39000	41000	17000	16000	14000	17000	14000	12000	5000	4000	4000	4000	17000	18000
K	<10 000	<10 000	31 000	32 000	19 000	20 000	<10 000	<10 000	22 000	18 000	<10 000	<10 000	13 000	12 000	17 000	15 000
Se	3	1.5	1.5	4	3	4	1.5	1.5	1.5	1.5	1.5	4	1.5	1.5	1.5	39
Si	5000	3700	30 700	27 300	16 800	16 300	1500	1300	24 700	20 400	4900	4400	7900	7900	9300	2100
Ag	<50	<50	<50	<50	<50	<50	<50	<50	<50	<50	<50	<50	<50	<50	<50	<50
Na	<10 000	<10 000	<10 000	<10 000	<10 000	<10 000	<10 000	<10 000	<10 000	<10 000	<10 000	<10 000	<10 000	<10 000	<10 000	<10 000
Sr	60	50	260	260	180	180	280	300	260	230	110	120	120	140	660	690
Th	<30 000	<30 000	<30 000	<30 000	<30 000	<30 000	<30 000	<30 000	<30 000	<30 000	<30 000	<30 000	<30 000	<30 000	<30 000	<30 000
Sn	<200	<200	<200	<200	<200	<200	<200	<200	<200	<200	<200	<200	<200	<200	<200	<200
Ti	<50	<50	<50	<50	<50	<50	<50	<50	<50	<50	<50	<50	<50	<50	<50	<50
V	<200	<200	<200	<200	200	200	<200	<200	300	200	<200	<200	<200	<200	300	<200
Zn	750	640	1080	920	1560	1430	170	200	670	480	1300	1250	240	240	190	190

Table A3.5 Trace Elements Associated with the Sulphide/Organic Phase in µg/L

	A99-4		A99-23		B99-16		B99-44		CREF		E99-19		E99-59		E99-61	
	A	B	A	B	A	B	A	B	A	B	A	B	A	B	A	B
Al	3000	3000	7000	8000	4000	4000	<2000	2000	13000	13000	3000	3000	7000	6000	8000	9000
Sb	<2000	<2000	<2000	<2000	<2000	<2000	<2000	<2000	<2000	<2000	<2000	<2000	<2000	<2000	<2000	<2000
As	<2000	<2000	<2000	<2000	<2000	<2000	<2000	<2000	<2000	<2000	<2000	<2000	<2000	<2000	<2000	<2000
Ba	200	200	300	300	100	100	<100	100	200	200	100	200	100	100	300	400
Be	<50	<50	<50	<50	<50	<50	<50	<50	<50	<50	<50	<50	<50	<50	<50	<50
Bi	<1000	<1000	<1000	<1000	<1000	<1000	<1000	<1000	<1000	<1000	<1000	<1000	<1000	<1000	<1000	<1000
B	<1000	<1000	<1000	<1000	<1000	<1000	<1000	<1000	<1000	<1000	<1000	<1000	<1000	<1000	<1000	<1000
Cd	<100	<100	<100	<100	<100	<100	<100	<100	<100	<100	<100	<100	<100	<100	<100	<100
Ca	7500	7500	3800	<50	9200	2500	3500	11700	10600	6300	9400	3300	5100	3700	2900	22000
Cr	<100	<100	<100	<100	<100	<100	<100	<100	100	<100	<100	<100	<100	<100	100	100
Co	<100	<100	<100	<100	<100	<100	<100	<100	<100	<100	<100	<100	<100	<100	<100	100
Cu	600	400	1100	1400	400	400	300	300	600	800	400	500	1500	1500	300	500
Fe	34100	39800	6600	19400	7500	8200	1700	4500	21300	41000	16400	22400	4300	8200	82500	112000
Pb	<500	<500	500	600	<500	<500	<500	<500	<500	<500	<500	<500	<500	<500	<500	<500
Li	<100	<100	<100	<100	<100	<100	<100	<100	<100	<100	<100	<100	<100	<100	<100	100
Mg	<100	<100	<100	300	<100	100	<100	<100	300	500	<100	50	200	200	1000	1500
Mn	160	170	<50	70	<50	<50	<50	<50	240	380	<50	<50	60	87	135	<5
Mo	<300	<300	<300	<300	<300	<300	<300	<300	<300	<300	<300	<300	<300	<300	<300	<300
Ni	<500	<500	<500	<500	<500	<500	<500	<500	<500	<500	<500	<500	<500	<500	<500	<500
P	<300	<300	<300	<300	<300	<300	<300	<300	<300	<300	<300	<300	<300	<3000	6000	7000
K	<2000	<2000	7.8×10^6	5.7×10^6	6.8×10^6	6.3×10^6	<2000	<2000	7.6×10^6	6.3×10^6	7.8×10^6	5.0×10^6	7.8×10^6	7.2×10^6	6.8×10^6	6.5×10^6
Se	49	54	89	86	55	43	180	220	59	55	122	125	17	24	36	39
Si	900	1100	1700	2300	1900	1700	600	800	2600	4200	1300	1700	1800	2000	2200	2100
Ag	<100	<100	<100	<100	<100	<100	<100	<100	<100	<100	<100	<100	<100	<100	<100	100
Na	<20 000	<20 000	<20 000	<20 000	<20 000	<20 000	<20 000	<20 000	<20 000	<20 000	<20 000	<20 000	<20 000	<20 000	<20 000	<20 000
Sr	<50	<50	<50	<50	<50	<50	<50	<50	<50	<50	<50	<50	<50	<50	<50	<50
Th	<2000	<2000	<2000	<2000	<2000	<2000	<2000	<2000	<2000	<2000	<2000	<2000	<2000	<2000	<2000	<2000
Sn	<300	<300	<300	<300	<300	<300	<300	<300	<300	<300	<300	<300	<300	<300	<300	<300
Ti	100	100	100	100	200	200	900	200	300	300	300	300	100	100	100	<100
V	<300	<300	<300	<300	<300	<300	<300	<300	<300	<300	<300	<300	<300	<300	<300	<300
Zn	1280	1440	3300	3510	2180	2170	240	310	2390	2830	670	880	1930	1840	3020	3620

10.4 APPENDIX 4 Raw Data from the Humidity Cell Tests

Table A4.1 Analysis of Leachate from the E99<61A (Interburden) Humidity Cell

	wash 1	wash 2	wash 3	wash 4	wash 5	wash 6	wash 7	wash 8	wash 9	wash 10	wash 11
Week	0	1	2	3	4	5	6	7	8	9	10
Eh	382.6	334.5	382.4	376.2	340.1	412.0	383.3	428.6	377.3	390.2	390.2
pH	6.80	6.89	7.20	6.13	6.00	6.23	5.98	5.75	5.87	6.17	6.17
Vol. (mL)	346	508	505	477	486	487	488	484	516	497	497
Dissolved Anions											
Acid.*	1000	1000		1000		1000		1000		6000	
Alk.**	25000	34000		23000		28000		30000		30000	
SO ₄ ²⁻	28000	23000		17000		12000		14000		13000	
Dissolved Metals											
Al	<200	<200		<200		<200		<200		<200	
Sb	<200	<200		<200		<200		<200		<200	
As	<200	<200		<200		<200		<200		<200	
Ba	400	190		130		110		110		80	
Be	<5	<5		<5		<5		<5		<5	
Bi	<100	<100		<100		<100		<100		<100	
Bo	<100	<100		<100		<100		<100		<100	
Cd	<10	<10		<10		<10		<10		<10	
Ca	11 200	16 000		8210		20 500		20 900		14 000	
Cr	<10	<10		<10		<10		<10		<10	
Co	<10	<10		<10		<10		<10		<10	
Cu	<10	10		<10		<10		<10		<10	
Fe	<30	<30		<30		<30		<30		<30	
Pb	<50	<50		<50		<50		<50		<50	
Li	50	50		30		30		20		20	
Mg	4200	6400		3700		8000		8500		6000	
Mn	11	15		7		16		16		12	
Mo	<30	40		40		<30		<30		<30	
Ni	70	<50		<50		<50		<50		<50	
P	<300	<300		<300		<300		<300		<300	
K	7000	33000		4000		3000		3000		3000	
Se	16	10	9	7	8	7	7	7	7	7	8
Si	790	1070		890		880		1080		980	
Ag	<10	20		<10		<10		<10		<10	
Na	2000	<2000		<2000		<2000		<2000		<2000	
Sr	79	83		48		95		92		59	
Th	<200	<200		<200		<200		<200		<200	
Sn	<30	<30		<30		<30		<30		<30	
Ti	<10	<10		<10		<10		<10		<10	
V	<30	<30		<30		<30		<30		<30	
Zn	<5	8		<5		5		9		<5	
Organic Parameters											
TIC	600	3100		1600		1000		1100		1600	
TOC	7500	4100		3600		1500		1500		5300	

NOTE: All concentrations expressed in µg/L

Table A4.1 Continued

	wash 12	wash 13	wash 14	wash 15	wash 16	wash 17	wash 18	wash 19	wash 20	wash 21
Week	11	12	13	14	15	16	17	18	19	20
Eh	453.4	396.3	400.1	490.4	466.8	399.6	415.9	521.4	456.8	444.1
pH	7.02	7.27	5.94	8.47	7.10	6.76	8.17	8.27	8.06	7.14
Vol. (mL)	517	480	450	512	483	490	494	491	506	442
Dissolved Anions										
Acid.	<1000		6000		<1000		3000			
Alk.	23 000		23 000		24 000		31 000			
SO ₄ ^{2<}	15 000		15 000		13 000		12 000			
Dissolved Metals										
Al	<200		<200		<200		<200			
Sb	<200		<200		<200		<200			
As	<200		<200		<200		<200			
Ba	80		90		80		90			
Be	<5		<5		<5		<5			
Bi	<100		<100		<100		<100			
Bo	<100		<100		<100		<100			
Cd	<10		<10		<10		<10			
Ca	9740		9240		9280		9900			
Cr	<10		<10		<10		<10			
Co	<10		<10		<10		<10			
Cu	<10		<10		<10		<10			
Fe	<30		<30		<30		<30			
Pb	<50		<50		<50		<50			
Li	10		10		10		10			
Mg	4000		4700		4100		4300			
Mn	7		6		7		7			
Mo	<30		<30		<30		<30			
Ni	<50		<50		<50		<50			
P	<300		<300		<300		<300			
K	2000		2000		<2000		2000			
Se	8	8	10	8	9	11	9	9	7	6
Si	850		1030		1050		1030			
Ag	<10		<10		<10		<10			
Na	<2000		<2000		<2000		<2000			
Sr	46		47		50		51			
Th	<200		<200		<200		<200			
Sn	<30		<30		<30		<30			
Ti	<10		<10		<10		<10			
V	<30		<30		<30		<30			
Zn	<5		<5		<5		<5			
Organic Parameters										
TIC	1700		1500		2100		<500			
TOC	1200		1600		1200		1000			

NOTE: All concentrations expressed in µg/L

Table A4.2 Analysis of Leachate from the E99<61B (Interburden) Humidity Cell

	wash 1	wash 2	wash 3	wash 4	wash 5	wash 6	wash 7	wash 8	wash 9	wash 10	wash 11
Week	0	1	2	3	4	5	6	7	8	9	10
Eh	341.9	470.2	470.9	340.1	418.4	394.5	404.7	408.0	386.4	410.1	504.1
pH	6.76	6.95	7.35	6.28	6.65	6.45	6.12	5.97	5.51	6.30	7.61
Vol. (mL)	365	477	480	482	505	457	508	494	470	498	496
Dissolved Anions											
Acid.*	2000	2000		1000		1000		1000		6000	
Alk.**	23 000	26 000		30 000		28 000		30 000		37 000	
SO ₄ ²⁻	20 000	15 000		13 000		11 000		10 000		11 000	
Dissolved Metals											
Al	<200	<200		<200		<200		<200		<200	
Sb	<200	<200		<200		<200		<200		<200	
As	<200	<200		<200		<200		<200		<200	
Ba	310	240		150		150		190		140	
Be	<5	<5		<5		<5		<5		<5	
Bi	<100	<100		<100		<100		<100		<100	
Bo	<100	<100		<100		<100		<100		<100	
Cd	<10	<10		<10		<10		<10		<10	
Ca	10 500	15 700		9470		13 000		23 000		16 600	
Cr	<10	<10		<10		<10		<10		<10	
Co	<10	<10		<10		<10		<10		<10	
Cu	10	30		<10		<10		<10		<10	
Fe	70	170		<30		<30		<30		<30	
Pb	<50	<50		<50		<50		<50		<50	
Li	40	40		30		30		30		20	
Mg	3200	5900		4000		5400		9100		6900	
Mn	12	12		5		8		14		13	
Mo	<30	50		50		30		<30		<30	
Ni	<50	<50		<50		<50		<50		<50	
P	<300	<300		<300		<300		<300		<300	
K	7000	5000		5000		4000		3000		3000	
Se	10	12	11	9	9	8	8	7	8	7	10
Si	690	1040		1090		990		1190		1170	
Ag	<10	<10		<10		<10		<10		<10	
Na	3000	<2000		<2000		<2000		<2000		<2000	
Sr	65	82		60		70		110		78	
Th	<200	<200		<200		<200		<200		<200	
Sn	<30	<30		<30		<30		<30		<30	
Ti	<10	<10		<10		<10		<10		<10	
V	<30	<30		<30		<30		<30		<30	
Zn	7	215		<5		<5		<5		47	
Organic Parameters											
TIC	1200	<500		1900		1600		900		1200	
TOC	5700	5500		2100		1400		1600		5300	

NOTE: All concentrations expressed in µg/L

Table A4.2 Continued

	wash 12	wash 13	wash 14	wash 15	wash 16	wash 17	wash 18	wash 19	wash 20	wash 21
Week	11	12	13	14	15	16	17	18	19	20
Eh	411.4	398.8	410.5	450.6	445.7	414.7	445.2	455.6	480.7	438.2
pH	7.33	8.27	7.70	8.43	7.60	7.80	8.17	8.15	6.76	7.39
Vol. (mL)	496	483	469	480	494	497	490	479	490	496
Dissolved Anions										
Acid.	<1000		4000		1000		1000			
Alk.	30 000		25 000		30 000		30 000			
SO ₄ ²⁻	15 000		14 000		14 000		12 000			
Dissolved Metals										
Al	<200		<200		200		<200			
Sb	<200		<200		<200		<200			
As	<200		<200		<200		<200			
Ba	120		110		140		130			
Be	<5		<5		<5		<5			
Bi	<100		<100		<100		<100			
Bo	<100		<100		<100		<100			
Cd	<10		<10		<10		<10			
Ca	12800		9990		10700		10200			
Cr	<10		<10		<10		<10			
Co	<10		<10		<10		<10			
Cu	<10		<10		10		<10			
Fe	<30		<30		<30		<30			
Pb	<50		<50		<50		<50			
Li	20		10		20		<10			
Mg	5200		4800		4600		4400			
Mn	9		7		6		6			
Mo	30		<30		<30		<30			
Ni	<50		<50		<50		<50			
P	<300		<300		<300		<300			
K	3000		2000		2000		<2000			
Se	10	9	11	9	10	11	8	14	7	7
Si	1040		1090		1290		1070			
Ag	<10		<10		<10		<10			
Na	<2000		<2000		<2000		<2000			
Sr	62		51		61		52			
Th	<200		<200		<200		<200			
Sn	<30		<30		<30		<30			
Ti	<10		<10		<10		<10			
V	<30		<30		<30		<30			
Zn	<5		<5		<5		<5			
Organic Parameters										
TIC	2000		2000		900		2200			
TOC	1200		1500		1600		900			

NOTE: All concentrations expressed in µg/L

Table A4.3 Analysis of Leachate from the A99<23A (Parting) Humidity Cell

	wash 1	wash 2	wash 3	wash 4	wash 5	wash 6	wash 7	wash 8	wash 9	wash 10	wash 11
Week	0	1	2	3	4	5	6	7	8	9	10
Eh	456.2	332.6	350.2	399.0	347.0	374.3	397.5	417.5	382.1	423.8	436.6
pH	6.40	6.58	6.82	6.20	5.87	6.87	7.01	5.40	5.51	5.51	5.74
Vol. (mL)	322	495	510	490	475	452	476	512	495	492	484
Dissolved Anions											
Acid.*	2000	2000		2000		2000		2000		3000	
Alk.**	11 000	9000		10 000		9000		9000		3000	
SO ₄ ²⁻	18 000	16 000		17 000		10 000		10 000		9000	
Dissolved Metals											
Al	<200	<200		<200		<200		<200		<200	
Sb	<200	<200		<200		<200		<200		<200	
As	<200	<200		<200		<200		<200		<200	
Ba	310	100		80		80		100		70	
Be	<5	<5		<5		<5		<5		<5	
Bi	<100	<100		<100		<100		<100		<100	
Bo	<100	<100		<100		<100		<100		<100	
Cd	<10	<10		<10		<10		<10		<10	
Ca	5780	5330		4600		8960		12 400		13 000	
Cr	<10	<10		<10		<10		<10		<10	
Co	10	<10		<10		<10		<10		10	
Cu	<10	<10		<10		<10		20		20	
Fe	<30	30		<30		<30		<30		<30	
Pb	<50	<50		<50		<50		<50		<50	
Li	70	50		40		30		40		40	
Mg	1400	1400		1100		2200		3300		3400	
Mn	12	<5		<5		<5		<5		6	
Mo	80	240		150		30		<30		<30	
Ni	<50	<50		<50		<50		<50		<50	
P	<300	<300		<300		<300		<300		<300	
K	8000	17 000		5000		6000		5000		4000	
Se	48	93	100	46	38	34	35	33	19	34	49
Si	800	1330		1660		1550		2620		2880	
Ag	<10	<10		<10		<10		<10		<10	
Na	4000	<2000		<2000		<2000		<2000		<2000	
Sr	16	14		11		18		24		23	
Th	<200	<200		<200		<200		<200		<200	
Sn	<30	<30		<30		<30		<30		<30	
Ti	<10	<10		<10		<10		<10		<10	
V	<30	<30		<30		<30		<30		<30	
Zn	50	23		8		21		41		47	
Organic Parameters											
TIC	700	600		1000		<500		<500		<500	
TOC	6300	5500		1800		1900		1700		2500	

NOTE: All concentrations expressed in µg/L

Table A4.3 Continued

	wash 12	wash 13	wash 14	wash 15	wash 16	wash 17	wash 18	wash 19	wash 20	wash 21
Week	11	12	13	14	15	16	17	18	19	20
Eh	423.3	423.0	417.5	450.8	474.1	448.2	509.5	487.0	540.5	439.9
pH	6.37	6.19	6.24	7.40	6.43	6.37	6.18	6.50	6.08	5.59
Vol. (mL)	486	483	445	470	481	484	507	475	495	493
Dissolved Anions										
Acid.	2000		2000		2000		2000			
Alk.	2000		1000		2000		1000			
SO ₄ ²⁻	18 000		18 000		20 000		12 000			
Dissolved Metals										
Al	<200		<200		<200		<200			
Sb	<200		<200		<200		<200			
As	<200		<200		<200		<200			
Ba	70		70		60		50			
Be	<5		<5		<5		<5			
Bi	<100		<100		<100		<100			
Bo	<100		<100		<100		<100			
Cd	<10		<10		<10		<10			
Ca	13 800		9640		9330		5570			
Cr	<10		<10		<10		<10			
Co	20		20		20		10			
Cu	<10		10		20		20			
Fe	<30		<30		<30		<30			
Pb	<50		<50		<50		<50			
Li	40		20		30		20			
Mg	3700		2900		2600		1600			
Mn	7		7		8		6			
Mo	<30		<30		<30		<30			
Ni	<50		<50		<50		<50			
P	<300		<300		<300		<300			
K	4000		4000		4000		<2000			
Se	59	46	59	46	66	49	39	42	41	32
Si	3330		3210		3940		2820			
Ag	<10		<10		<10		<10			
Na	<2000		<2000		<2000		<2000			
Sr	27		20		21		12			
Th	<200		<200		<200		<200			
Sn	<30		<30		<30		<30			
Ti	<10		<10		<10		<10			
V	<30		<30		<30		<30			
Zn	95		80		89		72			
Organic Parameters										
TIC	<500		2100		<500		<500			
TOC	1400		1500		1400		1100			

NOTE: All concentrations expressed in µg/L

Table A4.4 Analysis of Leachate from the A99<23B (Parting) Humidity Cell

	wash 1	wash 2	wash 3	wash 4	wash 5	wash 6	wash 7	wash 8	wash 9	wash 10	wash 11
Week	0	1	2	3	4	5	6	7	8	9	10
Eh	460.5	408.7	344.7	368.5	352.7	415.7	398.9	425.8	378.2	393.4	489.2
pH	7.02	6.51	6.60	6.14	6.05	6.55	6.82	5.70	5.26	5.10	6.12
Vol. (mL)	313	491	495	405	484	461	493	490	480	496	494
Dissolved Anions											
Acid.*	2000	2000		1000		2000		3000		<1000	
Alk.**	10 000	6000		7000		7000		8000		1000	
SO ₄ ²⁻	18 000	16 000		18 000		11 000		12 000		8000	
Dissolved Metals											
Al	<200	<200		<200		<200		<200		<200	
Sb	<200	<200		<200		<200		<200		<200	
As	<200	<200		<200		<200		<200		<200	
Ba	340	130		90		60		80		100	
Be	<5	<5		<5		<5		<5		<5	
Bi	<100	<100		<100		<100		<100		<100	
Bo	<100	<100		<100		<100		<100		<100	
Cd	<10	<10		<10		<10		<10		<10	
Ca	8070	7730		4750		3790		6370		10600	
Cr	<10	<10		<10		<10		<10		<10	
Co	<10	<10		<10		<10		<10		<10	
Cu	10	<10		<10		<10		<10		<10	
Fe	<30	<30		<30		<30		<30		<30	
Pb	<50	<50		<50		<50		<50		<50	
Li	80	70		40		20		30		30	
Mg	1900	1900		1100		900		1700		2700	
Mn	24	6		<5		<5		<5		<5	
Mo	90	280		140		90		50		<30	
Ni	<50	<50		<50		<50		<50		<50	
P	<300	<300		<300		<300		<300		<300	
K	8000	6000		5000		5000		5000		5000	
Se	55	110	90	46	42	39.7	41	32	32	31	40
Si	1010	1220		1340		1610		2320		2300	
Ag	<10	<10		<10		<10		<10		<10	
Na	6000	3000		<2000		<2000		<2000		<2000	
Sr	21	19		11		8		14		21	
Th	<200	<200		<200		<200		<200		<200	
Sn	<30	<30		<30		<30		<30		<30	
Ti	<10	<10		<10		<10		<10		<10	
V	<30	<30		<30		<30		<30		<30	
Zn	82	45		19		9		20		47	
Organic Parameters											
TIC	<500	<500		700		800		500		<500	
TOC	7100	3600		2500		1400		1500		2400	

NOTE: All concentrations expressed in µg/L

Table A4.4 Continued

	wash 12	wash 13	wash 14	wash 15	wash 16	wash 17	wash 18	wash 19	wash 20	wash 21
Week	11	12	13	14	15	16	17	18	19	20
Eh	428.3	405.6	418.1	465.7	480.7	442.1	548.9	497.0	529.0	442.7
pH	6.75	6.84	5.96	7.58	6.40	6.22	6.41	6.10	6.45	5.62
Vol. (mL)	508	480	453	511	479	500	478	488	501	489
Dissolved Anions										
Acid.	2000		4000		1000		2000			
Alk.	2000		2000		2000		2000			
SO ₄ ²⁻	14 000		16 000		13 000		10 000			
Dissolved Metals										
Al	<200		<200		<200		<200			
Sb	<200		<200		<200		<200			
As	<200		<200		<200		<200			
Ba	70		80		70		60			
Be	<5		<5		<5		<5			
Bi	<100		<100		<100		<100			
Bo	<100		<100		<100		<100			
Cd	<10		<10		<10		<10			
Ca	8470		10000		7570		6840			
Cr	<10		<10		<10		<10			
Co	<10		<10		<10		<10			
Cu	10		<10		10		<10			
Fe	<30		<30		<30		<30			
Pb	<50		<50		<50		<50			
Li	20		20		20		20			
Mg	2100		2800		2000		1900			
Mn	<5		5		<5		<5			
Mo	<30		<30		<30		<30			
Ni	<50		<50		<50		<50			
P	<300		<300		<300		<300			
K	4000		5000		4000		3000			
Se	46	41	57	41	45	46	44	42	37	33
Si	2030		3440		2780		2560			
Ag	<10		<10		<10		<10			
Na	<2000		<2000		<2000		<2000			
Sr	18		22		18		16			
Th	<200		<200		<200		<200			
Sn	<30		<30		<30		<30			
Ti	<10		<10		<10		<10			
V	<30		<30		<30		<30			
Zn	39		54		46		55			
Organic Parameters										
TIC	<500		<500		<500		<500			
TOC	1400		1400		1400		1000			

NOTE: All concentrations expressed in µg/L

Table A4.5 Analysis of Leachate from the CREFA (Refuse) Humidity Cell

	wash 1	wash 2	wash 3	wash 4	wash 5	wash 6	wash 7	wash 8	wash 9	wash 10	wash 11
Week	0	1	2	3	4	5	6	7	8	9	10
Eh	441.0	328.8	383.3	354.8	409.9	361.4	371.2	393.3	370.9	310.1	415.0
pH	6.81	6.96	7.03	5.98	6.33	6.88	7.27	6.35	6.01	6.98	7.44
Vol. (mL)	336	469	497	482	490	479	500	499	493	481	492
Dissolved Anions											
Acid.*	000	2000		1000		<1000		2000		4000	
Alk.**	26 000	25 000		27 000		35 000		39 000		26 000	
SO ₄ ²⁻	24 000	32 000		16 000		18 000		15 000		11 000	
Dissolved Metals											
Al	<200	<200		<200		<200		<200		<200	
Sb	<200	<200		<200		<200		<200		<200	
As	<200	<200		<200		<200		<200		<200	
Ba	160	80		130		90		120		130	
Be	<5	<5		<5		<5		<5		<5	
Bi	<100	<100		<100		<100		<100		<100	
Bo	<100	<100		<100		<100		<100		<100	
Cd	<10	<10		<10		<10		<10		<10	
Ca	12 200	21 800		17 600		14 300		15 100		17 600	
Cr	<10	<10		<10		<10		<10		<10	
Co	<10	<10		<10		<10		<10		<10	
Cu	<10	<10		<10		<10		<10		<10	
Fe	<30	<30		<30		<30		<30		<30	
Pb	<50	<50		<50		<50		<50		<50	
Li	<10	<10		<10		<10		<10		<10	
Mg	3400	5500		5100		4600		5300		5900	
Mn	7	7		<5		<5		<5		<5	
Mo	<30	50		<30		<30		<30		<30	
Ni	<50	<50		<50		<50		<50		<50	
P	<300	<300		<300		<300		<300		<300	
K	3000	3000		<2000		<2000		<2000		<2000	
Se	39	55	34	11	15	15	15	13	13	11	34
Si	490	580		530		540		610		530	
Ag	<10	<10		<10		<10		<10		<10	
Na	<2000	<2000		<2000		<2000		<2000		<2000	
Sr	39	40		42		37		41		46	
Th	<200	<200		<200		<200		<200		<200	
Sn	<30	<30		<30		<30		<30		<30	
Ti	<10	<10		<10		<10		<10		<10	
V	<30	<30		<30		<30		<30		<30	
Zn	<5	6		<5		<5		<5		5	
Organic Parameters											
TIC	1000	1900		1800		2200		<500		3000	
TOC	5800	4900		1200		1300		4300		2500	

NOTE: All concentrations expressed in µg/L

Table A4.5 Continued

	wash 12	wash 13	wash 14	wash 15	wash 16	wash 17	wash 18	wash 19	wash 20	wash 21
Week	11	12	13	14	15	16	17	18	19	20
Eh	403.1	397.3	401.5	433.6	447.4	415.8	515.7	482.7	492.7	467.0
pH	6.92	7.97	7.69	8.57	7.31	7.71	7.74	7.63	7.69	7.27
Vol. (mL)	500	502	442	466	491	489	490	478	494	464
Dissolved Anions										
Acid.	<1000		3000		<1000		2000			
Alk.	36 000		26 000		44 000		34 000			
SO ₄ ²⁻	16 000		14 000		14 000		10 000			
Dissolved Metals										
Al	<200		<200		<200		<200			
Sb	<200		<200		<200		<200			
As	<200		<200		<200		<200			
Ba	110		90		140		130			
Be	<5		<5		<5		<5			
Bi	<100		<100		<100		<100			
Bo	<100		<100		<100		<100			
Cd	<10		<10		<10		<10			
Ca	13400		9870		14000		10000			
Cr	<10		<10		<10		<10			
Co	<10		<10		<10		<10			
Cu	<10		<10		<10		<10			
Fe	<30		<30		<30		<30			
Pb	<50		<50		<50		<50			
Li	<10		<10		10		<10			
Mg	4700		4400		6100		4100			
Mn	<5		<5		<5		<5			
Mo	<30		<30		<30		<30			
Ni	<50		<50		<50		<50			
P	<300		<300		<300		<300			
K	<2000		<2000		<2000		<2000			
Se	16	17	16	170	17	19	13	15	14	9
Si	450		420		600		380			
Ag	<10		<10		<10		<10			
Na	<2000		<2000		<2000		<2000			
Sr	38		29		46		32			
Th	<200		<200		<200		<200			
Sn	<30		<30		<30		<30			
Ti	<10		<10		<10		<10			
V	<30		<30		<30		<30			
Zn	<5		<5		<5		<5			
Organic Parameters										
TIC	2500		1200		2800		2100			
TOC	1200		1400		1300		1200			

NOTE: All concentrations expressed in µg/L

Table A4.6 Analysis of Leachate from the CREFB (Refuse) Humidity Cell

	wash 1	wash 2	wash 3	wash 4	wash 5	wash 6	wash 7	wash 8	wash 9	wash 10	wash 11
Week	0	1	2	3	4	5	6	7	8	9	10
Eh	453.6	322.0	366.0	361.4	393.2	381.5	370.9	399.1	369.5	308.9	453.2
pH	6.87	7.01	6.90	6.18	6.73	7.09	7.24	6.43	6.20	6.80	7.54
Vol. (mL)	305	510	499	480	491	499	490	493	494	488	500
Dissolved Anions											
Acid.*	2000	1000		1000		<1000		2000		3000	
Alk.**	26 000	30 000		25 000		32 000		53 000		50 000	
SO ₄ ²⁻	26 000	40 000		18 000		18 000		18 000		12 000	
Dissolved Metals											
Al	<200	<200		<200		<200		<200		<200	
Sb	<200	<200		<200		<200		<200		<200	
As	<200	<200		<200		<200		<200		<200	
Ba	200	100		140		80		140		120	
Be	<5	<5		<5		<5		<5		<5	
Bi	<100	<100		<100		<100		<100		<100	
Bo	<100	<100		<100		<100		<100		<100	
Cd	<10	<10		<10		<10		<10		<10	
Ca	15 400	17 100		17 400		13 100		21 700		17 700	
Cr	<10	<10		<10		<10		<10		<10	
Co	<10	<10		<10		<10		<10		<10	
Cu	10	<10		<10		<10		<10		<10	
Fe	<30	<30		<30		<30		<30		<30	
Pb	<50	<50		<50		<50		<50		<50	
Li	<10	<10		<10		<10		10		10	
Mg	3500	5000		5000		4300		7000		6200	
Mn	13	<5		<5		<5		<5		<5	
Mo	<30	50		<30		<30		<30		<30	
Ni	<50	<50		<50		<50		<50		<50	
P	<300	<300		<300		<300		<300		<300	
K	4000	2000		<2000		<2000		<2000		<2000	
Se	35	55	25	14	17	13	14	13	11	10	32
Si	500	530		490		470		690		480	
Ag	<10	<10		<10		<10		<10		<10	
Na	<2000	<2000		<2000		<2000		<2000		<2000	
Sr	38	46		38		30		47		41	
Th	<200	<200		<200		<200		<200		<200	
Sn	<30	<30		<30		<30		<30		<30	
Ti	<10	<10		<10		<10		<10		<10	
V	<30	<30		<30		<30		<30		<30	
Zn	<5	<5		<5		<5		<5		10	
Organic Parameters											
TIC	1400	2600		-		2800		<500		800	
TOC	7200	3500		1400		1200		2100		2800	

NOTE: All concentrations expressed in µg/L

Table A4.6 Continued

	wash 12	wash 13	wash 14	wash 15	wash 16	wash 17	wash 18	wash 19	wash 20	wash 21
Week	11	12	13	14	15	16	17	18	19	20
Eh	397.5	392.5	393.8	421.1	445.5	501.1	492.3	478.9	470.2	449.1
pH	6.62	7.96	7.52	8.26	7.44	7.68	7.69	7.92	7.88	7.48
Vol. (mL)	502	498	490	492	502	487	501	494	482	499
Dissolved Anions										
Acid.	<1000		2000		1000		1000			
Alk.	32 000		33 000		30 000		31 000			
SO ₄ ²⁻	16 000		13 000		12 000		10 000			
Dissolved Metals										
Al	<200		<200		<200		<200			
Sb	<200		<200		<200		<200			
As	<200		<200		<200		<200			
Ba	80		90		100		90			
Be	<5		<5		<5		<5			
Bi	<100		<100		<100		<100			
Bo	<100		<100		<100		<100			
Cd	<10		<10		<10		<10			
Ca	12 100		11 400		9680		10 800			
Cr	<10		<10		<10		<10			
Co	<10		<10		<10		<10			
Cu	<10		10		<10		<10			
Fe	<30		<30		<30		<30			
Pb	<50		<50		<50		<50			
Li	<10		<10		<10		<10			
Mg	4400		4900		4200		4700			
Mn	<5		<5		<5		<5			
Mo	<30		<30		<30		<30			
Ni	<50		<50		<50		<50			
P	<300		<300		<300		<300			
K	<2000		<2000		<2000		<2000			
Se	16	15	14	150	13	16	13	12	14	9
Si	380		420		420		390			
Ag	<10		<10		<10		<10			
Na	<2000		<2000		<2000		<2000			
Sr	31		30		30		31			
Th	<200		<200		<200		<200			
Sn	<30		<30		<30		<30			
Ti	<10		<10		<10		<10			
V	<30		<30		<30		<30			
Zn	<5		<5		<5		<5			
Organic Parameters										
TIC	2800		2700		2300		2500			
TOC	2000		1900		1900		1100			

NOTE: All concentrations expressed in µg/L

Table A4.7 Analysis of Leachate from the B99<44A (Coal) Humidity Cell

	wash 1	wash 2	wash 3	wash 4	wash 5	wash 6	wash 7	wash 8	wash 9	wash 10	wash 11
Week	0	1	2	3	4	5	6	7	8	9	10
Eh	475.2	334.4	495.4	426.7	385.7	381.7	403.3	412.2	375.0	403.8	429.1
pH	7.01	6.05	3.83	5.42	6.62	7.31	4.99	5.49	6.07	5.35	7.06
Vol. (mL)	246	433	445	475	492	498	425	361	490	495	485
Dissolved Anions											
Acid.*	3000	2000		2000		2000		2000		1000	
Alk.**	6000	3000		2000		2000		2000		1000	
SO ₄ ²⁻	95 000	77 000		23 000		17 000		12 000		10 000	
Dissolved Metals											
Al	<200	<200		<200		<200		<200		<200	
Sb	<200	<200		<200		<200		<200		<200	
As	<200	<200		<200		<200		<200		<200	
Ba	30	10		<10		<10		<10		<10	
Be	<5	<5		<5		<5		<5		<5	
Bi	<100	<100		<100		<100		<100		<100	
Bo	<100	<100		<100		<100		<100		<100	
Cd	<10	<10		<10		<10		<10		<10	
Ca	28 500	23 900		6060		4380		3690		3250	
Cr	<10	<10		<10		<10		<10		<10	
Co	<10	<10		<10		<10		<10		<10	
Cu	20	<10		10		10		10		<10	
Fe	70	<30		<30		50		30		40	
Pb	<50	<50		<50		<50		<50		<50	
Li	<10	<10		<10		<10		<10		<10	
Mg	13 700	11 700		3000		2100		1900		1600	
Mn	19	7		<5		<5		<5		<5	
Mo	<30	<30		<30		<30		<30		<30	
Ni	<50	<50		<50		<50		<50		<50	
P	<300	<300		<300		<300		<300		<300	
K	<2000	<2000		<2000		<2000		<2000		<2000	
Se	270	190	110	40	32	31	28	25	20	23	56
Si	740	1290		1120		990		560		650	
Ag	<10	<10		<10		<10		<10		<10	
Na	<2000	<2000		<2000		<2000		<2000		<2000	
Sr	40	31		9		6		5		<5	
Th	<200	<200		<200		<200		<200		<200	
Sn	<30	<30		<30		<30		<30		<30	
Ti	<10	<10		<10		<10		<10		<10	
V	<30	<30		<30		<30		<30		<30	
Zn	52	11		<5		6		<5		6	
Organic Parameters											
TIC	<500	<500		<500		<500		500		1300	
TOC	12 000	8300		6100		7700		6400		6500	

NOTE: All concentrations expressed in µg/L

Table A4.7 Continued

	wash 12	wash 13	wash 14	wash 15	wash 16	wash 17	wash 18	wash 19	wash 20	wash 21
Week	11	12	13	14	15	16	17	18	19	20
Eh	437.2	390.6	500.4	496.8	496.8	465.7	449.5	415.8	461.5	445.9
pH	6.68	6.47	7.09	6.81	6.81	6.46	6.11	6.76	6.96	5.30
Vol.	436	478	478	480	499	465	479	466	472	480
Dissolved Anions										
Acid.	1000		2000		1000		2000			
Alk.	2000		<1000		1000		2000			
SO ₄ ²⁻	14 000		11 000		11 000		8000			
Dissolved Metals										
Al	<200		<200		<200		<200			
Sb	<200		<200		<200		<200			
As	<200		<200		<200		<200			
Ba	<10		<10		<10		<10			
Be	<5		<5		<5		<5			
Bi	<100		<100		<100		<100			
Bo	<100		<100		<100		<100			
Cd	<10		<10		<10		<10			
Ca	3310		2910		2610		2420			
Cr	<10		<10		<10		<10			
Co	<10		<10		<10		<10			
Cu	<10		<10		10		50			
Fe	<30		30		<30		<30			
Pb	<50		<50		<50		<50			
Li	<10		<10		<10		<10			
Mg	1600		1600		1300		1200			
Mn	<5		<5		<5		<5			
Mo	<30		<30		<30		<30			
Ni	<50		<50		<50		<50			
P	<300		<300		<300		<300			
K	<2000		<2000		<2000		<2000			
Se	20	21	23	21	17	21	17	14	14	11
Si	490		500		450		370			
Ag	10		10		<10		<10			
Na	<2000		<2000		<2000		<2000			
Sr	<5		<5		<5		<5			
Th	<200		<200		<200		<200			
Sn	<30		<30		<30		<30			
Ti	<10		<10		<10		<10			
V	<30		<30		<30		<30			
Zn	<5		<5		<5		8			
Organic Parameters										
TIC	<500		<500		<500		<500			
TOC	5000		5600		5300		3900			

NOTE: All concentrations expressed in µg/L

Table A4.8 Analysis of Leachate from the B99<44B (Coal) Humidity Cell

	wash 1	wash 2	wash 3	wash 4	wash 5	wash 6	wash 7	wash 8	wash 9	wash 10	wash 11
Week	0	1	2	3	4	5	6	7	8	9	10
Eh	475.8	483.4	410.8	385.7	345.1	394.0	388.4	463.6	388.6	468.5	448.9
pH	6.97	5.43	5.58	6.62	3.42	7.12	5.38	5.81	6.02	6.26	6.62
Vol. (mL)	240	440	505	445	482	505	494	475	502	481	487
Dissolved Anions											
Acid.*	2000	2000		3000		2000		2000		5000	
Alk.**	6000	3000		2000		1000		1000		2000	
SO ₄ ^{2<}	134 000	20 000		12 000		16 000		13 000		10 000	
Dissolved Metals											
Al	<200	<200		<200		<200		<200		<200	
Sb	<200	<200		<200		<200		<200		<200	
As	<200	<200		<200		<200		<200		<200	
Ba	50	10		<10		<10		<10		<10	
Be	<5	<5		<5		<5		<5		<5	
Bi	<100	<100		<100		<100		<100		<100	
Bo	<100	<100		<100		<100		<100		<100	
Cd	<10	<10		<10		<10		<10		<10	
Ca	37 400	22 500		3710		3890		3510		3140	
Cr	<10	<10		<10		<10		<10		<10	
Co	<10	<10		<10		<10		<10		<10	
Cu	30	10		<10		10		10		20	
Fe	210	<30		60		40		80		50	
Pb	<50	<50		<50		<50		<50		<50	
Li	<10	<10		<10		<10		<10		<10	
Mg	17 300	10 900		1800		1900		1800		1500	
Mn	16	7		<5		<5		<5		<5	
Mo	<30	<30		<30		<30		<30		<30	
Ni	<50	<50		<50		<50		<50		<50	
P	<300	<300		<300		<300		<300		<300	
K	2000	<2000		<2000		<2000		<2000		<2000	
Se	400	220	80.1	26	29	21	25	14	15	19	46
Si	1010	1830		1190		860		720		530	
Ag	<10	<10		<10		<10		<10		<10	
Na	<2000	<2000		<2000		<2000		<2000		<2000	
Sr	49	29		6		6		<5		<5	
Th	<200	<200		<200		<200		<200		<200	
Sn	<30	<30		<30		<30		<30		<30	
Ti	<10	<10		<10		<10		<10		<10	
V	<30	<30		<30		<30		<30		<30	
Zn	174	19		6		<5		<5		6	
Organic Parameters											
TIC	<500	<500		<500		<500		<500		<500	
TOC	15 400	9000		9100		6800		8800		5200	

NOTE: All concentrations expressed in µg/L

Table A4.8 Continued

	wash 12	wash 13	wash 14	wash 15	wash 16	wash 17	Wash 18	wash 19	wash 20	wash 21
Week	11	12	13	14	15	16	17	18	19	20
Eh	483.5	436.5	509.8	509.8	495.6	446.4	451.7	476.0	499.8	465.8
pH	6.45	5.70	6.67	6.67	5.95	6.62	6.55	6.37	6.69	5.67
Vol. (mL)	479	540	470	490	500	494	506	496	464	492
Dissolved Anions										
Acid.	1000		2000		2000		2000			
Alk.	2000		1000		2000		2000			
SO ₄ ²⁻	15 000		10 000		11 000		8000			
Dissolved Metals										
Al	<200		<200		<200		<200			
Sb	<200		<200		<200		<200			
As	<200		<200		<200		<200			
Ba	<10		<10		<10		<10			
Be	<5		<5		<5		<5			
Bi	<100		<100		<100		<100			
Bo	<100		<100		<100		<100			
Cd	<10		<10		<10		<10			
Ca	3580		2450		2580		2050			
Cr	<10		<10		<10		<10			
Co	<10		<10		<10		<10			
Cu	<10		<10		10		20			
Fe	40		<30		30		<30			
Pb	<50		<50		<50		<50			
Li	<10		<10		<10		<10			
Mg	1700		1300		1200		1000			
Mn	<5		<5		<5		<5			
Mo	<30		<30		<30		<30			
Ni	<50		<50		<50		<50			
P	<300		<300		<300		<300			
K	2000		<2000		<2000		<2000			
Se	21	20	15	20	19	19	14	12	12	11
Si	580		480		540		420			
Ag	<10		<10		<10		<10			
Na	<2000		<2000		<2000		<2000			
Sr	5		<5		<5		<5			
Th	<200		<200		<200		<200			
Sn	<30		<30		<30		<30			
Ti	<10		<10		<10		<10			
V	<30		<30		<30		<30			
Zn	<5		<5		<5		11			
Organic Parameters										
TIC	<500		<500		<500		<500			
TOC	4900		4500		5300		4000			

NOTE: All concentrations expressed in µg/L

Table A4.9 Analysis of Leachate from the E99<19A (Foot Wall) Humidity Cell

	wash 1	wash 2	wash 3	wash 4	wash 5	wash 6	wash 7	wash 8	wash 9	wash 10	wash 11
Week	0	1	2	3	4	5	6	7	8	9	10
Eh	478.0	367.2	447.8	460.6	377.3	394.0	417.2	412.0	387.7	354.2	469.5
pH	6.68	5.51	6.96	5.01	5.75	5.95	5.80	6.10	6.30	6.02	6.00
Vol. (mL)	272	445	425	500	427	480	473	495	504	493	503
Dissolved Anions											
Acid.*	3000	2000		3000		1000		1000		4000	
Alk.**	6000	7000		<1000		2000		1000		2000	
SO ₄ ²⁻	368 000	577 000		129 000		44 000		24 000		20 000	
Dissolved Metals											
Al	<200	<200		<200		<200		<200		<200	
Sb	<200	<200		<200		<200		<200		<200	
As	<200	<200		<200		<200		<200		<200	
Ba	80	30		40		40		30		20	
Be	<5	<5		<5		<5		<5		<5	
Bi	<100	<100		<100		<100		<100		<100	
Bo	<100	<100		<100		<100		<100		<100	
Cd	10	<10		<10		<10		<10		<10	
Ca	110 000	144 000		36 800		11 800		6760		5570	
Cr	<10	<10		<10		<10		<10		<10	
Co	10	<10		<10		<10		<10		<10	
Cu	30	<10		10		<10		<10		<10	
Fe	280	<30		230		<30		<30		<30	
Pb	<50	<50		<50		<50		<50		<50	
Li	10	20		10		10		<10		<10	
Mg	29 000	47 800		10 200		4200		2600		2100	
Mn	112	131		26		10		6		<5	
Mo	<30	<30		<30		<30		<30		<30	
Ni	<50	<50		<50		<50		<50		<50	
P	<300	<300		<300		<300		<300		<300	
K	3000	3000		2000		<2000		<2000		<2000	
Se	270	150	90	17	13	8	8	7	6	6	6
Si	740	2410		2700		2210		1920		1580	
Ag	<10	<10		<10		<10		<10		<10	
Na	<2000	<2000		<2000		<2000		<2000		<2000	
Sr	145	219		64		25		15		12	
Th	<200	<200		<200		<200		<200		<200	
Sn	<30	<30		<30		<30		<30		<30	
Ti	<10	<10		<10		<10		<10		<10	
V	<30	<30		<30		<30		<30		<30	
Zn	653	329		87		34		21		18	
Organic Parameters											
TIC	<500	<500		<500		<500		<500		<500	
TOC	6600	4600		2200		2200		2600		2400	

NOTE: All concentrations expressed in µg/L

Table A4.9 Continued

	wash 12	wash 13	wash 14	wash 15	wash 16	wash 17	wash 18	wash 19	wash 20	wash 21
Week	11	12	13	14	15	16	17	18	19	20
Eh	411.3	414.6	417.6	456.7	458.9	454.3	510.7	505.8	477.8	455.5
pH	6.84	6.45	6.44	7.68	6.61	6.75	6.16	6.37	6.25	6.50
Vol. (mL)	504	490	486	478	500	493	477	490	487	495
Dissolved Anions										
Acid.	2000		2000		2000		2000			
Alk.	2000		1000		2000		1000			
SO ₄ ²⁻	23 000		16 000		15 000		10 000			
Dissolved Metals										
Al	<200		<200		<200		<200			
Sb	<200		<200		<200		<200			
As	<200		<200		<200		<200			
Ba	20		20		20		<10			
Be	<5		<5		<5		<5			
Bi	<100		<100		<100		<100			
Bo	<100		<100		<100		<100			
Cd	<10		<10		<10		<10			
Ca	5510		3620		3630		2800			
Cr	<10		<10		<10		<10			
Co	<10		<10		<10		<10			
Cu	<10		<10		<10		<10			
Fe	<30		<30		<30		<30			
Pb	<50		<50		<50		<50			
Li	<10		<10		<10		<10			
Mg	2000		1400		1300		1000			
Mn	6		7		<5		<5			
Mo	<30		<30		<30		<30			
Ni	<50		<50		<50		<50			
P	<300		<300		<300		<300			
K	<2000		<2000		<2000		<2000			
Se	7.6	7	5	8	6.5	7	7	5	4	5
Si	1410		1290		1540		1190			
Ag	<10		<10		<10		<10			
Na	<2000		<2000		<2000		<2000			
Sr	13		9		10		9			
Th	<200		<200		<200		<200			
Sn	<30		<30		<30		<30			
Ti	<10		<10		<10		<10			
V	<30		<30		<30		<30			
Zn	19		14		13		13			
Organic Parameters										
TIC	<500		<500		<500		<500			
TOC	1700		1700		1800		1500			

NOTE: All concentrations expressed in µg/L

Table A4.10 Analysis of Leachate from the E99<19B (Foot Wall) Humidity Cell

	wash 1	wash 2	wash 3	wash 4	wash 5	wash 6	wash 7	wash 8	wash 9	wash 10	wash 11
Week	0	1	2	3	4	5	6	7	8	9	10
Eh	376.8	363.0	454.9	412.3	367.3	390.0	389.4	407.4	393.7	351.9	461.5
pH	6.77	5.41	6.83	5.20	5.86	5.93	5.29	5.87	6.20	5.72	6.23
Vol. (mL)	280	488	490	510	484	484	494	495	499	495	494
Dissolved Anions											
Acid.*	2000	2000		2000		1000		1000		7000	
Alk.**	6000	7000		2000		<1000		1000		1000	
SO ₄ ²⁻	395000	525000		114 000		42 000		24 000		-	
Dissolved Metals											
Al	<200	<200		<200		<200		<200		<200	
Sb	<200	<200		<200		<200		<200		<200	
As	<200	<200		<200		<200		<200		<200	
Ba	60	30		30		30		20		20	
Be	<5	<5		<5		<5		<5		<5	
Bi	<100	<100		<100		<100		<100		<100	
Bo	<100	<100		<100		<100		<100		<100	
Cd	<10	<10		<10		<10		<10		<10	
Ca	107000	148000		29500		11100		6330		5320	
Cr	<10	<10		<10		<10		<10		<10	
Co	<10	<10		<10		<10		<10		<10	
Cu	30	<10		<10		<10		<10		<10	
Fe	110	<30		<30		<30		<30		<30	
Pb	<50	<50		<50		<50		<50		<50	
Li	10	20		10		10		<10		<10	
Mg	28800	52200		10100		4000		2400		1900	
Mn	105	115		31		12		7		6	
Mo	<30	<30		<30		<30		<30		<30	
Ni	<50	<50		<50		<50		<50		<50	
P	<300	<300		<300		<300		<300		<300	
K	3000	3000		<2000		2000		<2000		3000	
Se	88	150	70	25	17	10	8	8	6	6	7
Si	600	2500		2220		2010		1610		1430	
Ag	<10	<10		<10		<10		<10		<10	
Na	<2000	<2000		<2000		<2000		<2000		<2000	
Sr	148	223		52		23		14		11	
Th	<200	<200		<200		<200		<200		<200	
Sn	<30	<30		<30		<30		<30		<30	
Ti	<10	<10		<10		<10		<10		<10	
V	<30	<30		<30		<30		<30		<30	
Zn	616	345		79		33		20		18	
Organic Parameters											
TIC	<500	<500		<500		<500		<500		<500	
TOC	6300	2800		1500		2200		2100		<500	

NOTE: All concentrations expressed in µg/L

Table A4.10 Continued

	wash 12	wash 13	wash 14	wash 15	wash 16	wash 17	wash 18	wash 19	wash 20	wash 21
Week	11	12	13	14	15	16	17	18	19	20
Eh	413.0	410.0	410.6	440.1	485.5	434.3	532.2	508.8	446.0	461.7
pH	6.59	6.37	6.08	7.55	6.46	7.12	6.30	6.39	6.11	5.91
Vol. (mL)	496	500	407	492	490	489	486	489	482	499
Dissolved Anions										
Acid.	1000		1000		1000		2000			
Alk.	2000		1000		2000		2000			
SO ₄ ²⁻	22 000		23 000		14 000		9000			
Dissolved Metals										
Al	<200		<200		<200		<200			
Sb	<200		<200		<200		<200			
As	<200		<200		<200		<200			
Ba	20		20		20		<10			
Be	<5		<5		<5		<5			
Bi	<100		<100		<100		<100			
Bo	<100		<100		<100		<100			
Cd	<10		<10		<10		<10			
Ca	5170		6510		3310		2440			
Cr	<10		<10		<10		<10			
Co	<10		<10		<10		<10			
Cu	<10		<10		<10		<10			
Fe	<30		<30		<30		<30			
Pb	<50		<50		<50		<50			
Li	<10		<10		<10		<10			
Mg	1800		1900		1100		900			
Mn	6		7		<5		<5			
Mo	<30		<30		<30		<30			
Ni	<50		<50		<50		<50			
P	<300		<300		<300		<300			
K	<2000		<2000		<2000		<2000			
Se	8	8	8	8	7	7	6	6	4	4
Si	1290		1260		1430		1030			
Ag	<10		<10		<10		<10			
Na	<2000		<2000		<2000		<2000			
Sr	12		15		9		<5			
Th	<200		<200		<200		<200			
Sn	<30		<30		<30		<30			
Ti	<10		<10		<10		<10			
V	<30		<30		<30		<30			
Zn	17		19		12		11			
Organic Parameters										
TIC	<500		<500		<500		<500			
TOC	1800		2400		1900		1400			

NOTE: All concentrations expressed in µg/L

10.5 APPENDIX 5 Calculation Acid-Generation and Neutralization Potential

Acid-generation potential (AP) and neutralization potential (NP) are commonly used to predict the risk of acid rock drainage (Lawrence and Day, 1997). AP is a function of the amount of sulphides present in the material, NP is determined by the amount of acid-consuming minerals present in the material. Both AP and NP are expressed in terms of CaCO_3 equivalents/tonne of material.

Each mole of S produces 2H^+ , which can be neutralized by 1 mole of CaCO_3 . 1 g of S is therefore equivalent to 3.125 g of CaCO_3 and the acid generating potential of a given material can be determined using the following equation (Lawrence and Day, 1997):

$$\text{AP} = \% \text{ sulphide} \cdot 31.25$$

The contributions of the main mineral components (calcite, kaolinite, illite, quartz) to NP were calculated using the following formula from Lawrence and Scheske (1997):

$$\text{NP}_{\text{contribution}} = \frac{\% \text{ weight of mineral}}{100} \cdot \frac{1000 \text{ kg}}{1 \text{ tonne}} \cdot \frac{\text{molecular weight of calcite}}{\text{molecular weight of mineral}} \cdot \text{relative reactivity}$$

Relative reactivity rates were obtained from Kwong (1993) (Table A10.1), while mineral molecular weights were calculated based on chemical formulas from Deer (1993) (Table A2.1). All carbonates were assumed to be in the form of calcite. NP was calculated by summing the contributions of calcite, kaolinite, illite and quartz.

Table A5 .1 Relative Reactivity of Minerals at pH 5 (From Lawrence and Scheske, 1997)

Mineral Group	Typical Minerals	Relative Reactivity at pH 5
Dissolving	calcite, dolomite, magnesite, aragonite, brucite	1.00
Fast weathering	anorthite, olivine, garnet, diopside, wollastonite, jadeite, nepheline, leucite, spodumene	0.60
Intermediate weathering	epidote, zoisite, enstatite, hedenbergite, augite, hypersthene, hornblende, tremolite, actinolite, serpentine, chrysotile, talc, chlorite, biotite	0.40
Slow weathering	plagioclase feldspars, kaolinite, vermiculite, montmorillonite, gibbsite	0.02
Very slow weathering	K-feldspars, illite	0.01
Inert	quartz, rutile, zircon	0.004

A NP/AP ratio greater than 4:1 is indicative of an extremely low risk of acid-generation (Price, 1997). Materials with a NP/AP ratio between 2 and 4 are unlikely to generate acid, but could do so if sulphides were preferentially exposed along fracture planes or if they contained extremely reactive sulphides with insufficiently reactive NP minerals. The likelihood of acid-generation increases as the NP/AP ratio decreases, with a ratio of 1:1 or lower signalling a high risk of acid-generation.