Chapter 17

Dissolution chemistry of inorganic selenium in alkaline mine soils

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Abstract

Selenium (Se) is a natural geological constituent in many mining areas of the western United States. While Se is an essential micronutrient for humans and animals, its low toxicity threshold poses health concerns. Oxidative exposure of Se in excavated mine soils leads to increased concentrations of selenite ($Se^{IV}O_3^{2-}$) and selenate ($Se^{VI}O_4^{2-}$) species, which can potentially enter the food chain. To ascertain the geochemical processes contributing to Se bioavailability, we examined Se dissolution, speciation, fractionation, adsorption, and solid phases in coal and uranium mine soils from Wyoming. The soils were alkaline in nature, and majority (86%) of the labile Se remained in the exchange phase. Despite 49% of total Se levels identified in siliceous minerals, the exchangeable Se exceeded the critical toxicity limit in $>60\%$ samples. Se^{VI} and Se^{IV} were the dominant species in aqueous and exchangeable fractions, respectively. Se^{VI} was the major Se species that dissolved under alkaline condition. Se^{IV} was primarily related to ligand exchange or complexation processes. Mine soils adsorbed up to 99% of Se^{IV} and 95% of Se^{VI}, and the relative sorption was on an average six-fold higher for Se^{IV}. Occurrence of oxides and oxyhydroxides of Ca, Mn, and Fe in soil resulted in greater Se retention, which was mostly augmented in presence of Fe-minerals. The soil solutions were undersaturated with respect to Se solid phases, thereby suggesting that Se precipitation would less likely prevail. $CaSeO_3 \cdot 2H_2O$ and $CaSeO_4$ were the only Se^{IV} and Se^{VI} solids in the vicinity of the saturation equilibrium line. Fe_2O_3, $CuFe_2O_4$, $ZnFe_2O_4$, $CuFeO_2$, $FeOOH$, Fe_3O_4, $CaFe_2O_4$, $MgFe_2O_4$, $Al(OH)_3$, Al_2O_3, CuO, and $Cu_4(SO_4)(OH)_6$ were the primary saturated mineral phases, and could potentially bind Se. These results are germane to Se chemistry of earth materials under pedochemical weathering.

17.1. Introduction

Selenium (Se) occurs indigenously within geological materials associated with coal and uranium (U) mining areas of the western United States (Valkovic, 1983; Boon, 1989). While Se is an essential micronutrient for humans and animals, its low toxicity thresholds (as related to 0.5 and 5 mg Se/kg soil and vegetation, respectively) pose potential concern for land use (Rosenfeld and Beath, 1964; Lakin, 1972; Maas, 1998; Vance, 2000). This is critical as animal grazing is the primary post-reclamation land use practice in many mining areas of the western United States. Revegetation of mine backfill materials high in Se may result in plants that contain elevated level of Se. Seleniferous mine land environments and areas impacted by mine drainage waters may, therefore, be problematic to wildlife and domestic grazing animals that consume vegetation containing greater than 5 mg kg^{-1} Se for extended periods of time (NRC, 1976; Vance, 2000). During mining operations, excavated soils and subsurface materials are exposed to oxidative conditions, thereby elevating the potential levels of bioavailable selenite ($Se^{IV}O_3^{2-}$) and selenate ($Se^{VI}O_4^{2-}$) species, which ultimately could enter the food chain via grazing by wildlife and domestic animals. Se related mortality in waterfowls, shorebirds, migratory and aquatic birds have been well documented (Ohlendorf, 1989).

The bioavailability of Se is dependent on the presence of different soil Se species including selenide (Se^{2-}), elemental Se (Se^0), selenite ($Se^{IV}O_3^{2-}$) and selenate ($Se^{IV}O_4^{2-}$); both $Se^{IV}O_3^{2-}$ and $Se^{VI}O_4^{2-}$ are the predominant Se species in oxidized and alkaline environments (Elrashidi et al., 1987; Jayaweera and Biggar, 1996). Details on the natural occurrence and geochemistry of Se in various seleniferous environments other than mines have been reviewed by McNeal and Balistrieri (1989) and Mayland et al. (1989). There are numerous reports on Se geochemistry in diverse terrestrial systems such as alluvial soils (Neal et al., 1987), biogenic particles and sediments (Cutter, 1985), oil shale (Spackman et al., 1990), goethite (Balistrieri and Chao, 1987), kaolinite (Bar-Yosef and Meek, 1987), montmorillonite (Goldberg and Glaubig, 1988), groundwaters (Vance et al., 1998), and agricultural and forest soils (Pezzarossa et al., 1999). Siddique et al. (2005) studied agricultural drainage waters that were amended with rice straw and reported that Se^{VI} could be reduced by bacteria to Se^{IV} and Se^0. Vegetative and microbial remediation of Se from agricultural drainage water was discussed within several recently published studies (Lin et al., 2002; Gao et al., 2003; Bañuelos et al., 2004).

Limited information exists on the geochemical behavior and bioavailability of Se in alkaline mine soils. Blaylock et al. (1995) assessed

$Se^{IV}O_3^{2-}$ sorption by coal mine soils using various equilibrium models. Their study found that mine soils could sorb $> 90\%$ of the added Se, and that the initial mass (IM) model was a better predictor of Se sorption than Freundlich and Langmuir isotherms. In a field study that assessed plant and soil Se at a reclaimed U mine site, Sharmasarkar and Vance (2002a) observed that grass, forbs, and shrub type vegetation accumulated high level (10–1000 mg kg^{-1}) of Se. Lovett (2005) evaluated the chemistry and mitigation of Se in coal-mine drainage waters and observed this system had ''a far more substantial biochemistry than traditional mine drainage contaminants'' thereby facilitating the release of Se back into solution. For Se in coal-mine drainage waters from Canada and Alaska, Sobolewski (2005) suggested that in-situ treatments and phyto techniques were the most feasible remediation approaches. Cummings (2000) suggested the possible use of microbial reduction of Se for the reclamation of mine spoil leachates.

Several areas within the western United States have overburden geological materials that contain Se. Mine soils within these areas are potential sites for environmental Se problems if not managed correctly because Se toxicity can occur when Se is present even at low levels. To determine the prospective of Se transfer through the food chain and possible development of biological (e.g., plant and microbial) remediation techniques, it is important to understand the chemistry related to Se bioavailability. Therefore, the objectives of this study were to assess geochemical processes causing Se dissolution and speciation chemistry of solution Se in alkaline mine soils. This information could be utilized for developing mine land reclamation strategies.

17.2. Materials and methods

17.2.1. Soil sampling

Soil samples were collected from coal and U mine sites located within the Powder River Basin of eastern Wyoming (Fig. 17.1). The taxonomy of the native soils within the contiguous areas of the mine sites were comprised of Ustic Torrifluvents, Ustic Haplargids, Ustic Torriorthents, Ustic Calciargids, Mesic Haplargids, Ustic Torrpsamments, Ustic Paleargids, Ustic Haplocambids, Typic Haplocambids, and Typic Torriorthent. In Wyoming, high levels of Se occur naturally within several regions known as super toxic (Rosenfeld and Beath, 1964).

We were interested in specific mine sites that contained high Se indicator plants within their surrounding native areas. The sites consisted of
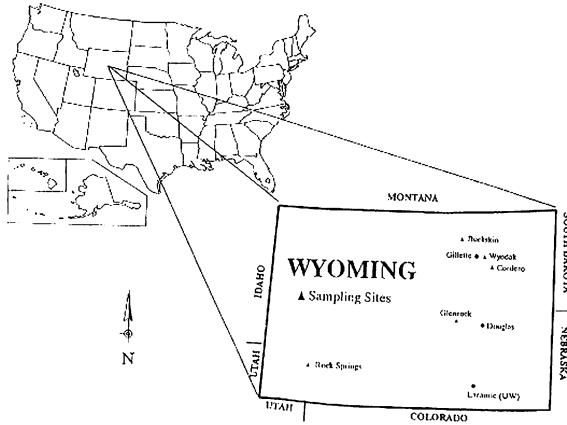
Figure 17.1. Mine soil-sampling areas in Wyoming.

Table 17.1. Physicochemical properties of mine soils

pH	EC (dS m^{-1})	Sand (%)	Clay (%)	Organic carbon (%)	Sulfate (mg kg^{-1})	Total Se (mg kg^{-1})	Fe (g kg^{-1})	Mn (g kg^{-1})	Ca (g kg^{-1})
7.3–8.5	0.3–10	3–84	8–59	0.1–7	48–2940	0.24–26	1.3–4.1	0.05–0.19	0.9–15

overburden materials collected from both coal and U mine pits, which were deeper than the depths of our soil-sampling cores. Vegetation at the sites was primarily reseeded plant species; however, some native species were also evident and resulted from dispersion of soils that contained native plant seeds. The native areas surrounding the sites were slightly undulating with a predominance of bare soil, scattered grasses, forbs, and shrubs. No trees existed in the dry, harsh landscape associated with our study sites. Soil moisture was greatest in sampling site located in depressions, particularly during late spring and early summer due to accumulation of snowmelt and rainfall. However, during the time of sampling (e.g., June and July) there were no noticeable differences in the moisture status of the different sampling sites.

Sixty soil samples (0–200 cm depth) were collected from the different mine sites. The samples were of contrasting nature to ensure diversity within the mine environment. Soils had alkaline pH levels, moderate to high-salt contents, low organic carbon levels, and a predominance of sand particle-sized materials (Table 17.1). These soils were enriched in kaolinite, smectite, illite, Fe, Mn, Ca, and high levels of sulfate. The soil Se concentrations were generally above the toxic level.

17.2.2. Analytical techniques

Soils were air-dried, finely ground (<0.25 mm), and stored at room temperature in polyethene bags following established processing and analytical protocols for mine soil materials (Spackman et al., 1994). Inorganic Se (Se_i) was analyzed after extraction with deionized water (DW), 0.1% $CaCl_2$ background electrolyte in hot water (HW), ammonium bicarbonate–diethylenetriamine pentaacetic acid at pH 7.6 (AB), 0.01 M NaOH at pH 11.6 (OH), and 1 M KH_2PO_4 at pH 4.7 (PO). These dissolution agents cover a wide array of pH, and some of these extractants have been reported to be significant predictors of soil–plant Se correlations under field conditions (Pasch and Vance, 1995). In a study of Se isotopes in agricultural drainage sediments, Herbel et al. (2002) also utilized NaOH extraction to assess soluble Se. Total Se (Se_T) was determined in mixed acid (15.8 M HNO_3 + 11.7 M $HClO_4$ + 28.9 M HF) digests. Net inorganic Se ($Se^{IV}O_3^{2-}$ + $Se^{VI}O_4^{2-}$) was determined with atomic absorption spectrophotometry—hydride generation (AAS-HG) after an HCl reduction step. Solution $Se^{IV}O_3^{2-}$ concentrations were measured prior to the reduction process, and then subtracted from the net Se values to obtain $Se^{VI}O_4^{2-}$ concentrations. Extraction protocol was based on correspondence of soil Se with plant availability (Orso et al., 1993; Spackman et al., 1994; Sharmasarkar and Vance, 1995).

The fractional partitioning technique of Chao and Sanzolone (1989) was followed by dissolving soil Se sequentially using 0.25 M KCl, 1 M KH_2PO_4, 4 M HCl, $KClO_3$ + 12 M HCl, and mixed acid (15.8 M HNO_3 + 11.7 M $HClO_4$ + 28.9 M HF). There was occasional modification based on the standard methodologies for Se in mine soils (Spackman et al., 1994). For example, 1 M KH_2PO_4 (pH 4.7) was used instead of 0.1 M KH_2PO_4, as Se extracted by the former has been reported to correspond more closely to plant-available Se (Orso et al., 1993). Each fraction was then analyzed for Se by AAS-HG.

Soil organic carbon and particle size distributions were analyzed by the Walkley-Black method (Nelson and Sommers, 1982) and the pipette method (Gee and Bauder, 1986), respectively. The pH, electrical conductivity (EC), and soluble sulfate (SO_4^{2-}) were determined in saturated paste extracts. Crystalline Fe, Mn, and Ca were determined using citrate–dithionite buffer (Holmgren, 1967) method.

Se sorption experiments were conducted using a range of 0–2.5 ppm Se. Aqueous extracts of selected samples containing high Se levels were analyzed for dissolved ions by inductively coupled plasma mass spectroscopy (ICP-MS) and ion chromatography (IC) for estimating solution and solid phases using a geological equilibration model PHREEQC

(Parkhurst and Appelo, 1999). All experiments were conducted in trip-
licate at room temperature ($23 \pm 1^{\circ}C$), and statistical evaluations were
conducted using Minitab (1992).

17.3. Results and discussion

17.3.1. Dissolution and speciation

Total dissolved inorganic Se in different extracts and the relative distri-
bution of bioavailable selenate (Se^{VI}) and selenite (Se^{IV}) in these fractions
are shown in Fig. 17.2. Concentrations of Se in the various extracts
followed the order: PO > OH > AB > HWDW. On a relative scale, PO and
OH dissolved up to 56 and 30% of Se_i, respectively, as compared to only
3–7% by water and AB. More than 50% of the total soluble Se was
in inorganic form. On an absolute scale, DW, HW, AB, OH, and PO
extracted 67, 50, 57, 68, and 52% of Se_t, respectively, with $r = 0.80$–0.99
($p < 0.01$). About 70% of DW and OH extractable Se fractions were
inorganic in nature. Selenium dissolved by PO and OH in $> 60\%$ of our
samples exceeded the Wyoming Department of Environmental Quality
critical limit of 0.3–0.8 mg kg^{-1} for mine soils (Vance et al., 1998). The
Se^{VI} concentrations were greater in OH, DW, and HW solutions as
compared to PO and AB solutions. The OH-DW-HW fractions con-
tained equiproportional (nearly 30% each) fraction of Se^{VI}, albeit with
an occurrence of a very low level ($< 5\%$) of Se^{IV}. Conversely, AB and PO
extracts together contained $> 90\%$ Se^{IV} species. Thus, Se^{VI} may be
inferred as the major species to be released under aqueous or alkaline
dissolution conditions, whereas, Se^{IV} would be primarily solvated
by ligand exchange or complexation phenomena during pedochemical
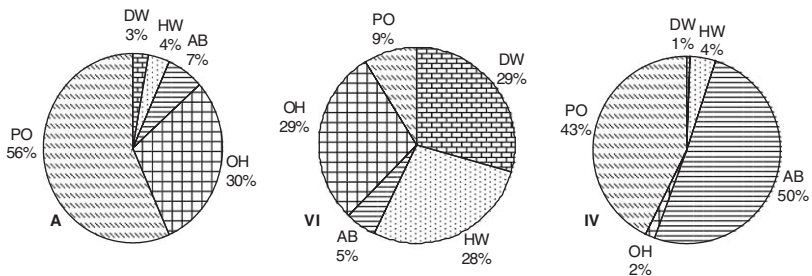processes.

Figure 17.2. Selenium dissolution and speciation in mine soils: (A) dissolved Se as % total
Se; (VI) bioavailable selenate (Se^{VI}); and (IV) bioavailable selenite (Se^{IV}).

A correlation matrix indicated dissolved Se_i and anionic Se (IV and VI) species in various extracts were linearly related within the $p < 0.01$ probability level. Selenium concentrations in PO, AB, and HW extracts resulted in better correlations ($r0.90$) with Se in the OH extracts. The r-values corresponding to Se^{VI} were always higher in HW than DW solutions. Even greater r-values were observed for Se^{IV} in AB solutions when correlated with SE^{VI} in OH and Se^{IV} in PO solutions. Correlation coefficients for DW-extractable Se were lower than other solvents, even though they were significant at the $p < 0.01$ level. These correlations are statistical validations of thermodynamic reactions among the Se species, for example, oxidation of Se^{IV} to Se^{VI} (Elrashidi et al., 1989). Such correlations also validate the importance of various Se extraction methods; for example, a linear correlation ($r = 0.98$, $p < 0.01$) between Se fractions in DI and HW extracts suggested that HW extractable inorganic Se could be readily dissolved by soil moisture present in pore spaces. Thus, statistical correlations may be used as indicators of plausible geochemical processes.

Our findings for Se bioavailability in mine soils were consistent with Se reported in other ecosystem studies. Martens and Suarez (1998) reported that Se^{IV} and Se^{VI} species were dominant in phosphate and aqueous extracts, respectively. Conceptually, the Se^{VI} species extracted by distilled-deionized and/or hot water is thought to be loosely bound to the soil particles and hence brought into solution by solubilization or low thermal energy processes. In contrast to the inner-sphere complexation of Se^{IV}, bonding of Se^{VI} is considered to occur mainly through diffuse-ion swarm association and outer-sphere complexation (Sposito, 1989). The relatively lower strength of Se^{VI} stems from its electrostatic nature of bonding as compared with the more stable nature of combined ionic and covalent bonds involving Se^{IV}. Subsequently, the stabilization energy (heat of bond formation) for Se^{VI} bonding is larger than that for Se^{VI}. The hydroxyl ions (OH^-) in the hot water extract can substitute for nonspecifically adsorbed $Se^{VI}O_4^{2-}$ that is weakly bound in outer-sphere complexes. This is also consistent with thermodynamic predictions regarding $Se^{VI}O_4^{2-}$ solubility (Elrashidi et al., 1987, 1989). Phosphate can solubilize specifically adsorbed Se^{IV} species by means of anionic competition and/or ligand exchange mechanisms (Parfitt, 1978). The Se^{IV} species are generally present as inner-sphere complexes associated with clay minerals such as kaolinite and montmorillonite (Bar-Yosef and Meek, 1987). Extraction with AB-DTPA, a strong chelating ligand, can result in metal cation complexes that release Se compounds, thereby solubilizing Se^{IV} species. However, the predominance of a particular species does not exclude the occurrence of other species in solution in relatively

lower concentrations. Thus, $Se^{VI}O_4^{2-}$ was also detected in KH_2PO_4 and AB-DTPA extracts, as well as $Se^{VI}O_4^{2-}$ was determined in the other extracts.

17.3.2. Sequential fractionation

Results of sequential fractionation of Se are illustrated in Fig. 17.3. Fractions included Se components that were aqueous (AQ; 0.25 M KCl), exchangeable (EX; 1 M KH_2PO_4), associated with amorphous and carbonate materials (AC; 4 M HCl), sulfide and humic bound (SH; $KClO_3$ + 12 M HCl), and structured into siliceous minerals (SI; 15.8 M HNO_3 + 11.7 M $HClO_4$ + 28.9 M HF). Aqueous and exchangeable fractions are available for leaching and plant uptake, whereas the acid extractable fraction may be conditionally available. The last two fractions are weathered with time and pedochemical changes.

Our samples indicated Se distributions in fractions followed the order AQ < EX < AC < SH < SI. There was a greater abundance of sulfide-humic bound and siliceous Se. The sum of all the five fractions (0.24–1.45 mg kg^{-1}) was very close to the total soil Se (0.26–1.55 mg kg^{-1}). We were able to recover > 95% of the total soil Se by fractional partitioning technique ($r = 0.99$ at $p < 0.001$). Se^{VI} and Se^{IV} were the dominant species in AQ and EX, respectively. Fraction AQ would primarily correspond to the nonspecifically adsorbed Se formed through outer-sphere complexation. Since this interaction is a weak-bond force, chloride (from 0.25 M KCl) can easily provide the dissolution energy for SeO_4^{2-} and bring it into solution by means of anion exchange and mass action mechanisms. Selenium in fraction EX would be specifically adsorbed on exchange sites of oxides (e.g., goethite (Balistrieri and Chao, 1987)) and clay minerals (kaolinite and montmorillonite (Bar-Yosef and Meek, 1987)). This interaction is a strong-field innersphere complex. Phosphate (1 M KH_2PO_4) would solubilize SeO_3^{2-} by means of anionic competition or ligand exchange mechanisms (Parfitt, 1978).

Fraction AC would correspond to Se associated with amorphous materials (Rajan and Watkinson, 1976) and carbonates (Goldberg and Glaubig, 1988), which would be solubilized by HCl (4 M) through hydrolysis and dissolution mechanisms. The Se in this fraction would be subjected to sudden chemical changes in the soil environments; for example, decrease in redox potential or pH (during acid leaching process) might enhance the solubilization of Se in fraction AC. Thus, Se in fraction AC would be only conditionally available. Both Se^{IV} and Se^{VI} were evenly distributed in this fraction.
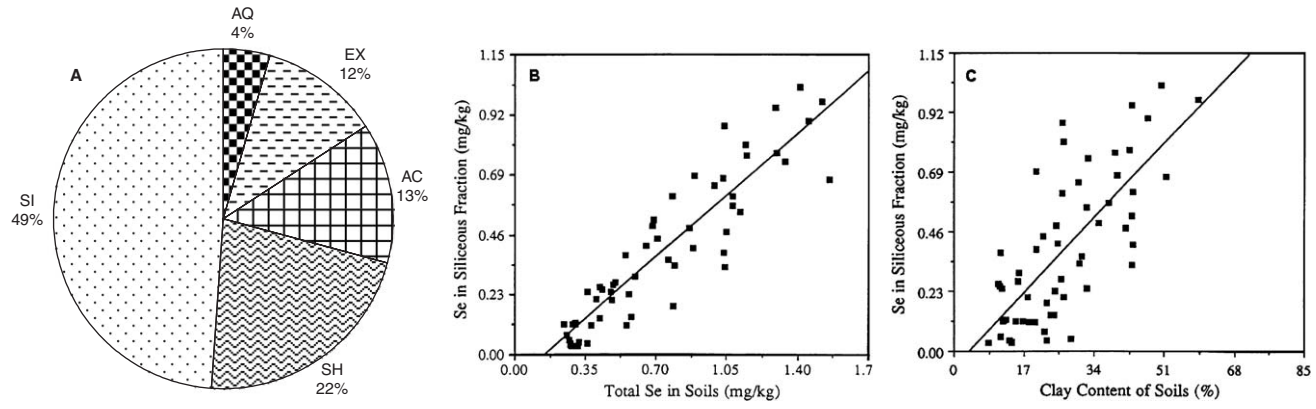
Figure 17.3.   Fractional partitioning of mine soil Se: (A) % distribution; and correlations of siliceous Se with (B) total Se and (C) clay content.

Selenium could also be released from its association with sulfides (Coleman and Delevaux, 1957; Hawley and Nichol, 1959) and organic matter (Rosenfeld and Beath, 1964) during oxidative weathering (fraction SH). Associations of Se with resistant sulfide minerals (e.g., pyrites) could be due to the comparable ionic radii of Se^{-II} and S^{-II} ($r_{Se-2} = 0.191$ nm, and $r_{S-2} = 0.184$ nm; Weast, 1985). Combination of $KClO_3$ and $12\,M$ HCl acts as a strong oxidant that can dissolve such materials, which otherwise may not be easily attacked by $4\,M$ HCl.

Fraction SI corresponds to highly resistant Se in layer lattices of siliceous minerals. The SI component contained the largest fraction of Se, which increased linearly by 68% with proportional increases in total soil Se content ($r = 0.91$ at $p < 0.001$, Fig. 17.3b). The siliceous Se was also directly correlated with clay content of soils ($r = 0.74$ at $p < 0.001$, Fig. 17.3c), thereby suggesting the presence of Se in silicate minerals. Though there have been no mineralogical studies done to identify Se in the clay lattice, Chao and Sanzolone (1989) observed that Se "compounds may occur in accessory minerals imbedded within the silicate matrices". The Se in SI fraction increased linearly with total Se ($r = 0.91$ at $p < 0.001$) and clay content ($r = 0.74$ at $p < 0.001$) of the soils. This suggested possible presence of Se within the silicate minerals.

Total soil Se increased with increasing clay content ($r = 0.81$ at $p < 0.001$), while the reverse was observed with sand content ($r = -0.69$ at $p < 0.001$). This suggested a probable association of Se with clay (Bar-Yosef and Meek, 1987; Mayland et al., 1989). Our finding conformed to Chao and Sanzolone (1989) who studied altogether different types of soils (soils from Hawaii and certain reference sample materials from U.S. Geological survey, namely, GXR 5).

Selenium speciation data (e.g., Se^{IV} and Se^{VI}) for SH and SI fractions were not conclusive. This could be due to any drastic changes in the oxidation states of the Se species caused by the strong oxidative reagents. Similar changes in oxidation status during sequential extraction of Se were also reported by Neal et al. (1987). Selenium in these two fractions could be transformed into simpler available forms through weathering and pedochemical changes.

17.3.3. Adsorption

High adsorption coefficients ($K10$ kg/10 g) suggested the mine soils could retain significant amounts of both Se^{IV} and Se^{VI} species, and that Se^{IV} adsorption was on an average six-fold higher than that for Se^{VI} (Fig. 17.4). Overall, the soils adsorbed 40–99% of the added Se^{IV} and
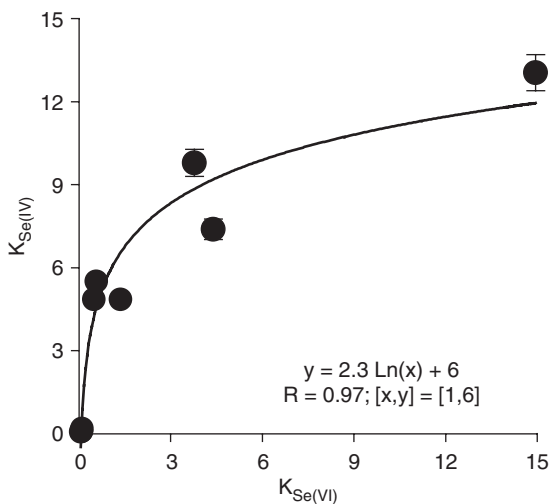
Figure 17.4. Relative adsorption of Se[IV] and Se[VI] by mine soils.

30–95% of added Se[VI], and the relative sorption was always higher for Se[IV]. The large magnitude of sorbate to sorbent ratio suggested a possible multilayer sorption mechanism. This was verified by applying various sorption isotherm models to the data. The poorest fit ($r = 0.01$–0.56) was observed with the Langmuir monolayer model. In using the Langmuir model, the energy of adsorbed molecules is assumed to be uniform, which is possible only for an intrinsically homogeneous surface. Based on this assumption, intra- and inter-molecular forces of attraction or repulsion should be zero, which is unlikely in a heterogeneous mine soil system. Hence, it is not unexpected that $> 90\%$ of our data did not conform to the Langmuir model.

In contrast with the Langmuir model, multilayer Temkin and Freundlich models fit the Se[VI] and Se[IV] data for 60–100% of the mine soils at varying degree of correlations within the significance level of $p < 0.01$. The best conformation was noticed for the Initial Mass model, which was fitted to both Se species for all of our samples with high correlation ($r = 0.99$–1.00). We already reported various model fittings elsewhere (Sharmasarkar and Vance, 2002b), and therefore, presented here only a relevant synopsis. The continued sorptive loading suggested that at low Se concentrations sorption sites on mine soil particles were probably never saturated. This was consistent with our observation of undersaturated soil conditions as described below.

In a study with SeO_3^{2-}, Blaylock et al. (1995) concluded that the IM isotherm was able to describe Se sorption behavior better than Freundlich and Langmuir isotherms. However, it should be realized that the model fitting would be ecosystem specific. For example, Singh et al. (1981) reported conformity of Se sorption to the Langmuir isotherm in Indian agricultural soils. In a study with oil shales, Spackman et al. (1990) concluded that both Langmuir and Freundlich isotherms described SeO_3^{2-} adsorption, with data fitting best with the Freundlich model. Freundlich fitting of Se sorption was reported by Fio et al. (1991), who observed that $Se^{VI}O_4^{2-}$ was not retained by alluvial soils, whereas $Se^{IV}O_3^{2-}$ was rapidly adsorbed and conformed to the Freundlich model under alkaline soil conditions. Greater sorption capacity of Se^{IV} than Se^{VI} was also reported in other types of soils by Balistrieri and Chao (1987). Application of the Temkin model to Se sorption is a new approach; this isotherm was used by Sanyal et al. (1993) to evaluate phosphate sorption by acid soils.

In contrast to the inner-sphere complexation of $Se^{IV}O_3^{2-}$, sorption of $Se^{VI}O_4^{2-}$ is considered to occur mainly through diffuse-ion swarm association and outer-sphere complexation (Sposito, 1989). Relatively lower sorption strength of the Se^{VI} species is due to its electrostatic nature of bonding as compared to the more stable coupling of ionic and covalent bonds for Se^{IV} species. The stabilization energy of bond formation for Se^{IV} sorption is subsequently higher than that for Se^{VI} sorption.

Adsorption parameters were multivariate functions of chemical and physical properties of the mine soils. For example, amounts of both Se species in PO were directly related to Freundlich K values. The correlation was more significant for Se^{IV}, which could be attributed to Se^{IV} being the predominant Se species in PO, as we have noted earlier. Both phosphate and SeO_3^{2-} adsorb principally as inner-sphere complexes via ligand exchange mechanism (Sposito, 1989), and so, their mutual relationship is not unusual. Similar correlations were also observed between Se_t and K values for both Se species. These relationships are important because Se in PO has been reported to be an indicator of plant Se uptake in mine environment (Sharmasarkar and Vance, 1995).

Presence of oxides or oxyhydroxides of Ca, Mn and Fe also would result in greater Se retention in the mine soils. This was evident from direct correlations of these dissolved metals with Se sorption parameter such as Freundlich-n, which was also a function of electrical conductivity, clay content, and specific surface area. Also, complexes of these metals with Se would control Se solid phases and their dissolution under pedochemical changes. Se sorption increased with increasing metal concentrations, with the effect of metals being in the order of $Fe > MnCa$.
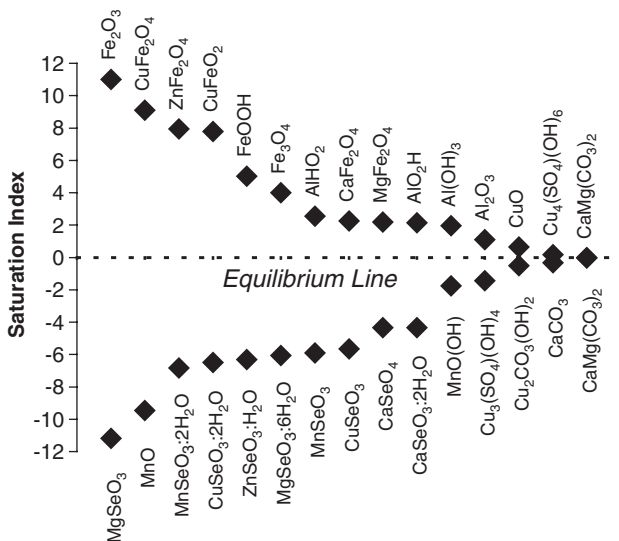
Figure 17.5. Saturation equilibrium of mineral solid phases in mine soils.

The functional relationships with soil properties could be used as predictors of Se loads and bioavailability in mine environments.

17.3.4. Solid phases

Although dissolved Se levels surpassed the Se contaminant threshold, mineral saturation index values in these mine soils indicated they were undersaturated with respect to various Se solid phases (Fig. 17.5). This observation suggests that Se availability in these mine soils is less likely to be controlled by a precipitation mechanism; rather, desorption—adsorption equilibrium would plausibly control solution Se concentrations. Solution phase computation by the geochemical modeling predicted the predominance of $[>SeO_3]^0$ and $[>SeO_4]^0$ over corresponding metal complexes of Se^{IV} and Se^{VI}. Detailed review of the data indicated that $CaSeO_3 \cdot 2H_2O$ and $CaSeO_4$ were the closest Se^{IV} and Se^{VI} solids to the saturation equilibrium line. These solid phases, therefore, have the future potential for partially controlling the solution Se chemistry if the saturation equilibria are reached through long-term pedochemical weathering.

The supersaturated solid phases in our mine soils included Hematite (Fe_2O_3), Ferrite–Cu ($CuFe_2O_4$), Ferrite–Zn ($ZnFe_2O_4$), Delafossite ($CuFeO_2$), Goethite ($FeOOH$), Magnetite (Fe_3O_4), Diaspore ($AlHO_2$),

Ferrite–Ca ($CaFe_2O_4$), Ferrite–Mg ($MgFe_2O_4$), Boehmite (AlO_2H), Gibbsite ($Al(OH)_3$), Corundum (Al_2O_3), Tenorite (CuO), and Brochantite ($Cu_4(SO_4)(OH)_6$), with Dolomite ($CaMg(CO_3)_2$) on the equilibrium line. These Fe, Cu, Zn, Al, Ca, and Mg-based minerals would play important roles in solution phase chemistry and subsequently impact the bond strength of inner- or outer- sphere complexes of Se species during its sorption or desorption processes.

17.4. Conclusion—Physicochemical and environmental significance

Our data indicate Se^{IV} was the dominant Se species in AB and PO extracts, whereas Se^{VI} was the major Se species in the DW, HW, and OH extracts. Conceptually, the Se^{VI} extracted by DI and HW extracts are loosely bound to the soil particles and hence brought into solution by mass action mechanisms or low-thermal energy. The hydroxyl ions (OH^-) in the NaOH extract can substitute for non-specifically adsorbed selenate that is weakly bound in outer-sphere complexes. This is consistent with thermodynamic predictions on Se solubility (Elrashidi et al., 1987). Phosphate can solubilize specifically adsorbed $Se^{IV}O_3^{2-}$ by means of anionic competition or ligand exchange mechanisms (Parfitt, 1978); SeO_3^{2-} is present as an inner-sphere complex associated with clay minerals such as kaolinite and montmorillonite (Bar-Yosef and Meek, 1987). The AB extracts, being a strong chelating ligand, can form complexes with metal cations associated with Se compounds, thereby solubilize Se oxyanions. It should be realized that the predominance of a particular species does not exclude the occurrence of other species in solution in relatively lower concentrations. Thus, both Se^{IV} and Se^{VI} species were detected in all the extracts. From a thermodynamic stand-point, SeO_3^{2-} remains stable within a pE + pH range of 7.5–14.5, and above this value $Se^{VI}O_4^{2-}$ predominates in soil solutions (Elrashidi et al., 1989); thus, occurrence of these two Se species is probable in coal mine environments where mining activity exposes soils to atmospheric oxidative conditions.

The plausibility of multilayer sorption suggested that at low Se concentrations the sorption sites were probably never saturated. Subsequently, it was not unusual to observe $> 90\%$ sorption for both Se species. Differences in the sorption mechanisms for $Se^{IV}O_3^{2-}$ and $Se^{VI}O_4^{2-}$ can be attributed to the structural difference of the two Se species, both of which are formed from the same cationic and anionic counterparts, i.e., Se and O with respective electronic configurations of $[Ar]3d^{10}4s^24p^4$ and $[He]2s^22p^4$. Applying the concepts of the valence shell electron pair repulsion theory and hybridization, structures of SeO_3^{2-} and SeO_4^{2-} can be concluded to be

distorted pyramidal (Se is sp^2) and tetrahedral (Se is sp^3), respectively. There are three-bond pairs (BP) and one lone pair (LP) of electrons in the valence shell of SeO_3^{2-}, whereas, SeO_4^{2-} valence shell contains four-bond pairs only with no lone pairs at all. The distortions in structure are caused by the BP–BP and BP–LP repulsions. In SeO_3^{2-}, the hybridized Se possesses 33.3% *s*-character as compared to 25% *s* in SeO_4^{2-}. However, the *p*-character of Se is much higher in SeO_4^{2-} (75%) in comparison to SeO_3^{2-} (66.7%).

Owing to undersaturated soil conditions with respect to various Se solid phases, albeit with high levels of phosphate-extractable Se surpassing the Wyoming Department of Environmental Quality critical limits, sorption–desorption processes appeared to be the more plausible mechanism governing mine Se immobilization chemistry. The mine soils were rich in siliceous Se fraction. The aqueous Se was dependent on the exchangeable fraction, which was again directly related to the acid extractable Se. In aqueous and exchange phases, Se^{VI} and Se^{IV} were the respective major species, whereas, both Se species were distributed almost evenly in acid extractable fraction. Aqueous Se^{VI} and exchangeable Se^{IV} were also functions of exchangeable Se^{IV} and acid extractable Se^{IV}, respectively.

The results of this study also indicated that Se must be present in the structure of clay minerals. Statistical analysis indicated that there were several significant functional correlations between different partitioning and speciation parameters. These relationships indicate a possibility of the geochemical processes that may occur with time. Solution-phase Se extraction and subsequent speciation provide a means of evaluating the distribution of different Se components in various soluble forms. This information is also important for examining the mutual relationships among Se forms and species, which can be useful in understanding the solubility and toxicity behavior of Se in coal mine environments. For future research, we recommend mineralogical studies that investigate Se in soil minerals.

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