## Table 45. Background Pore-Water Chemistry Assumed for SSL MINTEQ Modeling Effort[a]

| Parameter | Concentration (mg/L) |
|---|---|
| Aluminum | 0.2 |
| Bromine | 0.3. |
| Calcium | 48 |
| Carbonate | 187 |
| Chlorine | 15 |
| Iron (+3) | 0.2 |
| Magnesium | 14 |
| Manganese (+2) | 0.04 |
| Nitrate | 1 |
| Phosphate | 0.09 |
| Potassium | 2.9[b] |
| Sodium | 22 |
| Sulfate | 25 |

[a] Median values from STORET database as reported in U.S. EPA (1992a).
[b] Median values from STORET database; personal communication from J. Allison, Allison Geosciences.

### 5.4.3. Assumptions and Limitations.

The SSL MINTEQ modeling effort incorporates several basic simplifying assumptions. In addition, the applicability and accuracy of the model results are subject to limitations. Some of the more significant assumptions and limitations are described below.

- **The system is assumed to be at equilibrium.** This assumption is inherent in geochemical aqueous speciation models because the fundamental equations of mass action and mass balance are equilibrium based. Therefore, any possible influence of adsorption (or desorption) rate limits is not considered.

This assumption is conservative. Because the model is being used to simulate metal desorption from the solid substrate, if equilibrium conditions are not met, the desorption reaction will be incomplete and the metal concentration in pore water will be less than predicted by the model.

- **Redox potential is not considered.** The redox potential of the system is not considered due to the difficulty in obtaining reliable field measurements of oxidation reduction potential (Eh), which are needed to determine a realistic frequency distribution of this parameter. Furthermore, the geochemistry of redox-sensitive species is poorly understood. Reactions involving redox species are often biologically mediated and the concentrations of redox species are not as likely to reflect thermodynamic equilibrium as other inorganic constituents.

To provide a conservative estimate of metal mobility, all environmentally viable oxidation states are modeled separately for the redox-sensitive metals; the most conservative was selected for defining SSL metal $K_d$ values. The redox-sensitive

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constituents that make up the background chemistry are represented only by the oxidation state that most enhances metal mobility (U.S. EPA, 1992a).

- **Potential sorbent surfaces are limited.** Only metal adsorption to FeOx and solid organic matter is considered in the system. It is recognized that numerous other natural sorbents exist (e.g., clay and carbonate minerals); however, thermodynamic databases describing metal adsorption to these surfaces are not available and the potential for adsorption to such surfaces is not considered. This assumption is conservative and will underpredict sorption for soils with significant amounts of such sorption sites.

- **The available thermodynamic database is limiting.** As metal behavior increases in complexity, thermodynamic data become more rare. The lack of complete thermodynamic data requires simplification to the defined system. This simplification may be **conservative or nonconservative** in terms of metal mobility.

- **Metal competition is not considered.** Model simulations were performed for systems comprised of only one metal (i.e., the potential for competition between multiple metals for available sorbent surface sites was not considered). Generally, the competition of multiple metals for available sorption sites results in higher dissolved metal concentrations than would exist in the absence of competition. Consequently, this assumption is **nonconservative** but is significant only at metal concentrations much higher than the SSLs.

Other assumptions and limitations associated with this modeling effort are discussed in RTI (1994).

### 5.4.4 Results and Discussion.

MINTEQ model results indicate that metal mobility is most affected by changes in pH. Based on this observation and because iron oxide content is not routinely measured in site characterization efforts, pH-dependent $K_d$s for metals were developed for SSL application by fixing iron oxide at its medium value and fraction organic carbon at 0.002. For arsenic (+3), chromium (+6), selenium, and thallium, the empirical pH-dependent $K_d$s were used.

Table 46 shows the SSL $K_d$ values at high, medium, and low subsurface pH conditions. Figure 11 plots MINTEQ-derived metal $K_d$ values over this pH range. Figure 10 shows the same for the empirically derived metal $K_d$s. These results are discussed below by metal and compared with measured values. See RTI (1994) for more information. pH-dependent values are not available for antimony, cyanide, and vanadium. The estimated $K_d$ values shown in Table 46 for antimony and vanadium are reported by Baes et al. (1984) and the $K_d$ value for cyanide is obtained from SCDM.

**Arsenic.** $K_d$ values developed using the empirical equation for arsenic (+3) range from 25 to 31 L/kg for pH values of 4.9 to 8.0, respectively. These values correlate fairly well with the range of measured values reported by Battelle (1989)—5.86 to 19.4 L/kg. They are slightly above the range reported by Baes and Sharp (1983) for arsenic (+3) (1.0-8.3). The estimated $K_d$ values for arsenic (+3) do not correlate well with the value of 200 L/kg presented by Baes et al. (1984). Oxidation state is not specified in Baes et al. (1984), and the difference between the empirical-derived $K_d$ values presented here and the value presented by Baes et al. (1984) may reflect differences in oxidation states (arsenic (+3) is the most mobile species).
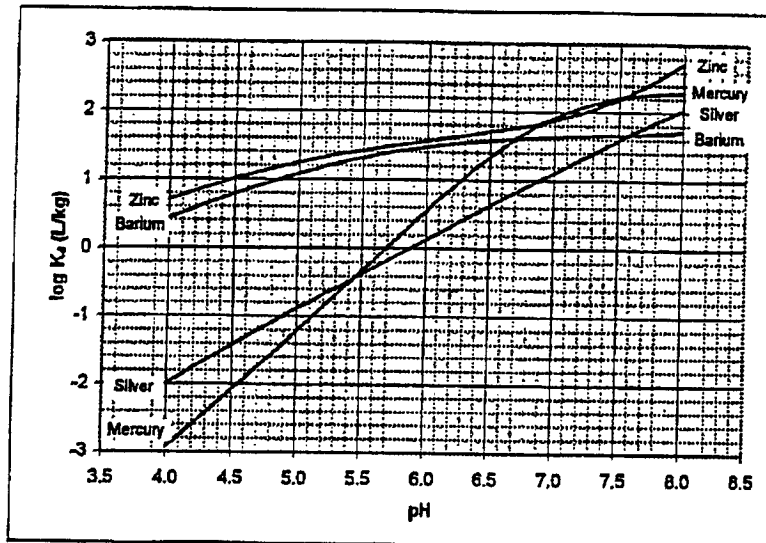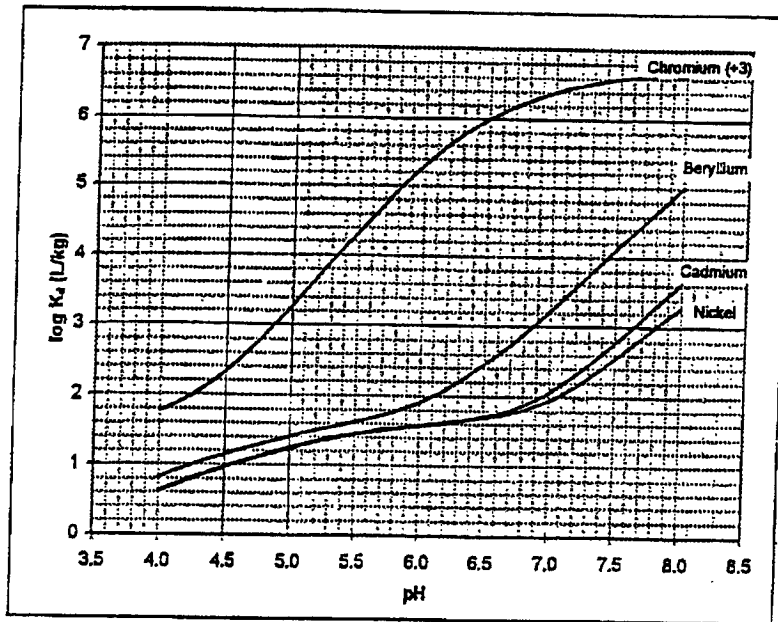
Note: Conditions depicted are medium iron oxide content (0.31 wt %)
and organic matter of 0.2 wt %.

Figure 11. Metal Kd as a function of pH.

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# Table 46. Estimated Inorganic $K_d$ Values for SSL Application

| Metal | Estimated $K_d$ (L/kg) | | |
|---|---|---|---|
| | pH = 4.9 | pH = 6.8 | pH = 8.0 |
| Antimony[a] | | 4.5E+01 | |
| Arsenic (+3)[b] | 2.5E+01 | 2.9E+01 | 3.1E+01 |
| Barium | 1.1E+01 | 4.1E+01 | 5.2E+01 |
| Beryllium | 2.3E+01 | 7.9E+02 | 1.0E+05 |
| Cadmium | 1.5E+01 | 7.5E+01 | 4.3E+03 |
| Chromium (+3) | 1.2E+03 | 1.8E+06 | 4.3E+06 |
| Chromium (+6)[b] | 3.1E+01 | 1.9E+01 | 1.4E+01 |
| Cyanide[c] | | 9.9E+00 | |
| Mercury (+2) | 4.0E-02 | 5.2E+01 | 2.0E+02 |
| Nickel | 1.6E+01 | 6.5E+01 | 1.9E+03 |
| Selenium[b] | 1.8E+01 | 5.0E+00 | 2.2E+00 |
| Silver | 1.0E-01 | 8.3E+00 | 1.1E+02 |
| Thallium[b] | 4.4E+01 | 7.1E+01 | 9.6E+01 |
| Vanadium[a] | | 1.0E+03 | |
| Zinc | 1.6E+01 | 6.2E+01 | 5.3E+02 |

[a] Geometric mean measured value from Baes et al., 1984 (pH-dependent values not available).
[b] Determined using an empirical pH-dependent relationship (Figure 10).
[c] SCDM = Superfund Chemical Data Matrix (pH-dependent values not available).

**Barium.** For ground water pH conditions, MINTEQ-estimated $K_d$ values for barium range from 11 to 52 L/kg. This range correlates well with the value of 60 L/kg reported by Baes et al. (1984). Battelle (1989) reports a range in $K_d$ values from 530 to 16,000 L/kg for a pH range of 5 to 9. The model-predicted $K_d$ values for barium are several orders of magnitude less than the measured values, possibly due to the lower sorptive potential of iron oxide, used as the modeled sorbent, relative to clay, a sorbent present in the experimental systems reported by Battelle (1989).

**Beryllium.** The $K_d$ values estimated for beryllium range from 23 to 100,000 L/kg for the conditions studied. AECL (1990) reports medians of observed values for $K_d$ ranging from 250 L/kg for sand to 3,000 L/kg for organic matter. Baes et al. (1984) report a value of 650 L/kg. Battelle (1989) reports a range of $K_d$ values from 70 L/kg for sand to 8,000 L/kg for clay. MINTEQ results for medium ground water pH (i.e., a value of 6.8) yields a $K_d$ value of 790 L/kg. Hence, there is reasonable agreement between the MINTEQ-predicted $K_d$ values and values reported in the literature.

**Cadmium.** For the three pH conditions, MINTEQ $K_d$ values for cadmium range from 15 to 4,300 L/kg, with a value of 75 at a pH of 6.8. The range in experimentally determined $K_d$ values for cadmium is as follows: 1.26 to 26.8 L/kg (Baes et al., 1983), 32 to 50 L/kg (Coughtrey et al., 1985), 14.9 to 567 L/kg (Battelle, 1989), and 2.7 to 17,000 L/kg (AECL, 1990). Thus the MINTEQ estimates are generally within the range of measured values.

**Chromium (+3).** MINTEQ-estimated $K_d$ values for chromium (+3) range from 1,200 to 4,300,000 L/kg. Battelle (1989) reports a range of $K_d$ values of 168 to 3,600 L/kg, orders of

magnitude lower than the MINTEQ values. This difference may reflect the measurements of mixed systems comprised of both chromium (+3) and (+6). The incorporation of chromium (+6) would tend to lower the $K_d$. Because the model-predicted values may overpredict sorption, the user should exercise care in the use of these values. Values for chromium (+6) should be used where speciation is mixed or uncertain.

**Chromium (+6).** Chromium (+6) $K_d$ values estimated using the empirical pH-dependent adsorption relationship range from 31 to 14 L/kg for pH values of 4.9 to 8.0. Battelle (1989) reports a range of 16.8 to 360 L/kg for chromium (+6) and Baes and Sharp (1983) report a range of 1.2 to 1,800. The predicted chromium (+6) $K_d$ values thus generally agree with the lower end of the range of measured values and the average measured values (37) reported by Baes and Sharp (1983). These values represent conservative estimates of mobility the more toxic of the chromium species.

**Mercury (+2).** MINTEQ-estimated $K_d$ values for mercury (+2) range from 0.04 to 200 L/kg. These model-predicted estimates are less than the measured range of 322 to 5,280 L/kg reported by Battelle (1989). This difference may reflect the limited thermodynamic database with respect to mercury and/or that only the divalent oxidation state is considered in the simulation. Allison (1993) reviewed the model results in comparison to the measured values reported by Battelle (1989) and found reasonable agreement between the two sets of data, given the uncertainty associated with laboratory measurements and model precision.

**Nickel.** MINTEQ-estimated $K_d$ values for nickel range from 16 to 1,900 L/kg. These values agree well with measured values of approximately 20 L/kg (mean) and 12.2 to 650 L/kg, reported by Coughtrey et al. (1985) and Battelle (1989), respectively. These values also agree well with the value of 150 L/kg reported by Baes et al. (1984). However, the predicted values are at the low end of the range reported by the AECL (1990)—60 to 4,700 L/kg.

**Selenium.** Empirically derived $K_d$ values for selenium range from 2.2 to 18 L/kg for pH values of 8.0 to 4.9. The range in experimentally determined $K_d$ values for selenium is as follows: less than 9 L/kg (Coughtrey et al., 1985), 5.9 to 14.9 L/kg (Battelle, 1989), and 150 to 1,800 L/kg (AECL, 1990). Baes et al. (1984) reported a value of 300 L/kg. Although they are significantly below the values presented by the AECL (1990) and Baes et al. (1984), the MINTEQ-predicted $K_d$ values correlate well with the values reported by Coughtrey et al. (1985) and Battelle (1989).

**Silver.** The $K_d$ values estimated for silver range from 0.10 to 110 L/kg for the conditions studied. The range in experimentally determined $K_d$ values for silver is as follows: 2.7 to 33,000 L/kg (AECL, 1990), 10 to 1,000 L/kg (Baes et al., 1984), 50 L/kg (Coughtrey et al., 1985), and 0.4 to 40 L/kg (Battelle, 1989). The model-predicted $K_d$ values agree well with the values reported by Coughtrey et al. (1985) and Battelle (1989) but are at the lower end of the ranges reported by AECL (1990) and Baes et al. (1984).

**Thallium.** Empirically derived $K_d$ values for thallium range from 44 to 96 L/kg for pH values of 4.9 to 8.0. Generally, these values are about an order of magnitude greater than those reported by Battelle (1989)—0.0 to 0.8 L/kg - but are well below the value predicted by Baes et al. (1984).

**Zinc.** MINTEQ-estimated $K_d$ values for zinc range from 16 to 530 L/kg. These estimated $K_d$ values are within the range of measured $K_d$ values reported by the AECL (1990) (0.1 to 100,000 L/kg) and Baes et al. (1984) (0.1 to 8,000 L/kg). Coughtrey et al. (1985) reported a $K_d$ value for zinc of greater than or equal to 20 L/kg.

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**5.4.5 Analysis of Peer-Review Comments.** A peer review was conducted of the model assumptions and inputs used to estimate $K_d$ values for SSL application. This review identified several issues of concern, including:

- The charge balance exceeds an acceptable margin of difference (5 percent) in most of the simulations. A variance in excess of 5 percent may indicate that the model problem is not correctly chemically poised and therefore the results may not be chemically meaningful.

- The model should not allow sulfate to adsorb to the iron oxide. Sulfate is a weakly outer-sphere adsorbing species and, by including the adsorption reaction, sulfate is removed from the aqueous phase at pH values less than 7 and is prevented from participating in precipitation reaction at these pH values.

- Modeled $K_d$ values for barium and zinc could not be reproduced for all studied conditions.

A technical analysis of these concerns indicated that, although these comments were based on true observations about the model results, these factors do not compromise the validity of the MINTEQ results in this application. This technical analysis is provided in Appendix M.