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ADSORPTION OF OXYANIONS BY SPENT WESTERN OIL SHALE: II SELENITE
Adsorption of Oxyanions by Spent Western Oil Shale:

II. Selenite

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Running Heads: Selenite Adsorption by Spent Western Oil Shale
The adsorption and desorption of selenite by processed Green River Formation oil shales was examined. The selenite adsorption data could be quantitatively described by both the Freundlich and Langmuir isotherms. However, greater $R^2$ values were obtained for the Freundlich isotherms. Further, selenite adsorption was not a function of oil extraction process. The adsorption of selenite by the processed oil shales was irreversible. Upon dilution of the equilibrium systems additional selenite removal from solution occurred. A thermochemical analysis of the adsorption and desorption equilibrium solutions indicated that the solutions were undersaturated with respect to a number of metal selenite solids. This indicates that precipitation processes are not influencing selenite behavior. However, not all selenite minerals were examined in the evaluation due to the lack of thermochemical data. An insufficient equilibration period for the adsorption study or the alteration of processed oil shale solids as a result of hydration reactions may also have hastened the additional removal of selenite during the desorption studies.

Introduction

The chemical characteristics of leachates and aqueous extracts from processed Green River Formation oil shales have been extensively examined (Saether and Runnells 1981; Flansway and Wagenet 1981; Stollenwerk and Runnells 1981; Esmaili and others 1985; Reddy and Lindsay 1986; Reddy and others 1986; Stark and Redente 1986; Essington 1988a). However, the processes that distribute elements between
processed oil shale solid and solution phases have not been adequately characterized for elements of well established environmental concern. Heat-induced mineralogical alterations that occur during the retorting of oil shale results in a suite of minerals, principally alkaline earth oxides and silicates. These minerals buffer the pH of retorted oil shale leachates above 11. Under these pH conditions elements exhibiting anionic character, such as fluorine, molybdenum, boron, selenium, and arsenic, may be highly soluble and mobile.

The behavior of anions and oxyanions in processed oil shale systems has only been critically examined to a limited extent. Fluoride concentrations in processed oil shale leachates and aqueous extracts have been shown to be controlled by the precipitation of fluorite (CaF$_2$) (Saether and Runnells 1980; Stollenwerk and Runnells 1981; Essington 1988a). Similarly, dissolved molybdenum and boron may be controlled by the dissolution of powellite (CaMoO$_4$) and borosilicates, respectively (Stollenwerk and Runnells 1981). Recent examinations of arsenate adsorption behavior (Spackman and others 1988) indicated that arsenate adsorption could be characterized by Freundlich adsorption isotherms. However, attempts to desorb arsenate from the processed oil shale solids by diluting the equilibrating solutions resulted in additional adsorption. Thermochemical evaluations indicated that the adsorption-desorption solutions were supersaturated with respect to a number of alkaline-earth arsenates. This suggests arsenate solid-phase precipitation and explains the additional removal of arsenate from solution.

Selenium can exist in the environment as Se(-II) [selenide], Se (0) [elemental], SE (IV) [selenite], Se (VI) [selenate], and as organic
compounds. Under the redox and pH conditions prevalent in processed oil shale leachates, selenium is predicted to exist as selenite (\(\text{SeO}_3^{2-}\)) (Elrashidi and others 1987). Further, selenite solids are highly soluble, indicating that soluble selenite concentrations may be controlled by adsorption reactions. Unfortunately, the adsorption behavior of selenium by processed oil shales has not been examined, and has been examined to only a limited extent in soil and single mineral phase systems (Hingston and others 1968; Gearing and others 1968; Hamdy and Gissel-Nielsen 1977; Bowden and others 1980; Singh and others 1981; Balistrieri and Chao 1987; Neal and others 1987a and b). Adsorption of selenium by processed oil shales is perhaps analogous to adsorption by Fe-oxides, because of the formation of Fe-oxides during retorting (Essington and Spackman 1986; Essington and others 1987). Selenite adsorption by Fe-oxides is pH-dependent, decreasing with increasing pH. Thus, processes that result in the reduction of pH in processed oil shale leachates, such as recarbonation and the oxidation of reduced sulfur, may also result in greater selenite attenuation.

Although, in general, the concentrations of selenium in processed oil shale leachates are at or below detectable levels (Sollenwerk and Runnells 1981; Stark and Redente 1986; Essington and others 1987) there exists the need to understand the processes that partition selenium between processed oil shale solid and leachate phases. The purpose of this study was to examine selenite partitioning in processed oil shale batch equilibrations. The data were evaluated with various adsorption isotherm models and solubility relationships to provide an indication of the processes controlling soluble selenite concentrations.
Materials and Methods

Green River Formation oil shale from the Piceance Creek Basin was obtained from the Exxon Colony Oil Shale Mine near Parachute, CO. The oil shale was retorted using the Paraho process operated in the indirect and direct heating modes and combusted in an inclined fluid bed. Four processed oil shale samples were used in the adsorption isotherm studies: indirectly heated (IH), directly heated (DH1 and DH2), and combusted (CS). Retorting and combustion parameters used to produce the processed oil shale samples, as well as the basic chemical and physical characteristics of the processed oil shales, are presented by Spackman and others (1988).

Adsorption isotherms were performed by combining 200-ml of a Na₂SeO₃ solution and 20-g of air-dried processed oil shale in a 250-ml polypropylene centrifuge bottle. These bottles were capped, shaken, immediately placed on a floor shaker, and equilibrated for 48 hours at ambient temperatures (23°-25°C). Literature sources indicate considerable variability in the time required to reach selenite adsorption equilibria. A review of the pertinent literature by Neal and others (1987a) indicated that selenite adsorption experiments have been conducted with contact times ranging from 1 to 72 hours. Kinetic experiments by Balistrieri and Chao (1987), Bar-Yosef and Meek (1987), and Neal and others (1987a) indicated that selenite adsorption by goethite, soils, and kaolinite was essentially complete after 2, 2, and 35 hours, respectively. Based on these previous studies, selenite adsorption by the processed oil shale samples was assumed to be complete after a 48-hour equilibration period.
Duplicate samples were run at initial selenium concentrations of approximately 20, 40, 80, and 160 mg L⁻¹. Duplicate blanks were also run for each spent oil shale sample. The adsorption samples and blanks were centrifuged with a Beckman J-6B centrifuge (JS-4.2 swing bucket rotor) operated at 2560 g (maximum radius) to obtain clear supernatant solutions. The pH of the equilibrium solutions was determined before sampling for chemical analysis. The concentration of selenium in the equilibrium solutions was determined by extracting a 20-mL aliquot for chemical analysis. The extract was split into two subsamples. One subsample was acidified to pH 2 with nitric acid and analyzed for selenium, aluminum, barium, calcium, iron, potassium, lithium, magnesium, sodium, silicon, and strontium by inductively coupled argon plasma spectrometry (ICAP). Extracts with selenium concentrations below ICAP detectable levels were reanalyzed by graphite furnace atomic absorption spectroscopy. The unacidified subsample was analyzed by ion chromatography for fluoride, chloride, nitrate, phosphate, and sulfate and by coulometry for inorganic carbon. The concentrations of selenium in the initial solutions were also determined by ICAP. The concentration of selenite (assuming selenite-selenium equals total selenium) in solution following the 48-hour adsorption equilibration, expressed in mmol L⁻¹, was labeled $C_e$. The amount of selenite adsorbed per mass of processed oil shale solid ($x/m$) was calculated from the amount of selenite removed from solution, and was expressed in mmol kg⁻¹.

Desorption isotherms were performed by replacing the 20-mL aliquot extracted for adsorption analysis with 20-mL deionized - distilled water. The processed oil shale was resuspended and the centrifuge
bottles placed on a floor shaker. The desorption samples were reequilibrated for 48 hours at ambient temperatures (23°C-25°C). The samples were then centrifuged and a 20-μL aliquot removed for chemical analysis, resulting in a new $C_e$. A new $x/m$ value was calculated, taking into account the mass of selenite removed from the system in the 20-μL aliquot for adsorption isotherm sampling. The desorption sequence was repeated, resulting in two desorption data points for every adsorption isotherm data point.

The adsorption data was quantitatively characterized using the Freundlich, Langmuir, and partitioning isotherms. These adsorption models have been reviewed by Voice and Weber (1983). Total selenite concentration was used to construct the adsorption isotherms and coefficients of determination values ($R^2$) were used to establish goodness of fit characteristics. The Langmuir isotherm equation can be expressed as:

$$\frac{C_e}{x/m} = \frac{1}{K_L b} + \frac{C_e}{b}$$

where $x/m$ and $C_e$ are as previously defined, $K_L$ is a constant related to the bonding strength, and $b$ is the maximum amount of adsorbate that can be adsorbed assuming a complete monomolecular layer. The adsorption data are said to conform to the Langmuir isotherm model when a $C_e/x/m$ vs. $C_e$ plot of the data is linear. The Freundlich isotherm equation is expressed as:

$$\log(x/m) = \frac{1}{n} \log C_e + \log K_F$$
where $x/m$ and $C_e$ are as previously defined, and $K_F$ and $1/n$ are constants that correspond to solid surface characteristics. Adsorption data are said to conform to the Freundlich isotherm when a log($x/m$) vs. log($C_e$) plot of the data is linear. In general, solute adsorption that is described by either the Langmuir or Freundlich equation indicates a high relative affinity of the solute for the adsorbing surface. Further, this affinity decreases as surface coverage increases. If the solute has equal affinities for solid and solution phases, then adsorption may be described by a simple partitioning isotherm:

$$\frac{x}{m} = K_p C_e$$  \hspace{1cm} (3)

The Freundlich and Langmuir adsorption constants ($K_L$, $b$, $K_F$, and $1/n$) are determined by regression analysis. The partitioning isotherm constant is determined separately for each system by dividing $x/m$ by $C_e$.

The analytical concentration data from the adsorption and desorption experiments were also evaluated to determine the stability of metal selenite solids. The observation that data from the batch adsorption isotherm experiments can be quantified by a particular adsorption isotherm model does not indicate that adsorption processes are controlling solution concentrations. However, solution undersaturation with respect to possible selenite solids is further evidence in support of adsorption as controlling soluble selenite concentrations. The geochemical code GEOCHEM (Sposito and Mattigod 1980) was used to calculate the distribution and activities of elements in the batch adsorption and desorption solutions. Selenite and free
metal cation activities were used to calculate ion activity product (IAP) values for comparison to the solubility product constants ($K_{sp}$) of metal selenites. For a given metal selenite solid, a calculated IAP equal to the $K_{sp}$ would indicate solution saturation with respect to the solid. Undersaturated and supersaturated conditions are suggested when IAP<$K_{sp}$ and IAP>$K_{sp}$, respectively. For convenience, the saturation index [$SI = \log(IAP/K_{sp})$] is used to illustrate the status of a solution with respect to a given solid phase. Positive SI values indicate supersaturation, negative SI values indicate undersaturation, and zero SI values indicate saturation.

Results and Discussion

The selenite adsorption data were consistently described by the Freundlich equation (Table 1). With the exception of the IH sample, the Freundlich $R^2$ values were greater than the corresponding Langmuir $R^2$ values. The adsorption of selenite could not be described using the simple partitioning isotherm (Table 2). The partitioning constant ($K_p$) decreased with increasing selenium concentration, indicative of a decreasing affinity of selenite for the processed oil shale solids with increasing surface coverage. Relative differences in the adsorption isotherms as a function of processed oil shale type are illustrated in a Freundlich plot of the data (Figure 1). Although processed oil shale type appears to influence selenite adsorption, least-squares mean test analysis of the Freundlich adsorption isotherms (Table 1) indicates that the isotherms are not significantly different.
The observation that selenite adsorption was independent of processed oil shale type is not consistent with literature observations or with the chemical and physical characteristics of the solids. Spackman and others (1988) found that the Freundlich adsorption isotherms describing arsenate adsorption by IH, DH1, and DH2 were not significantly different. However, the Freundlich adsorption isotherm for arsenate adsorption by CS was significantly different from the isotherms describing arsenate adsorption by IH, DH1, and DH2. The CS processed oil shale was observed to have greater affinity for arsenate, which was attributed to the elevated specific surface area and Fe-oxide content of the CS sample with respect to the other processed oil shale samples. Iron-oxides are also thought to control the adsorption behavior of selenite by complex mineral assemblages (Geering and others 1968; Rai and others 1984). Thus, the adsorption of selenite by CS should be significantly greater than selenite adsorption by the other processed oil shale samples. The CS sample was found to have a slightly greater affinity for selenite (suggested by the $K_F$ values), however, the affinities were statistically similar.

The desorbability of selenite from solids has been examined as a function of solid type, displacing anion, and changing pH conditions. Rai and others (1984), in a review of the pertinent literature, noted selenite to be irreversibly adsorbed by goethite, partially reversibly adsorbed by hydrous alumina, and reversibly adsorbed by gibbsite. Singh and others (1981) were able to partially displace soil adsorbed selenite with sulfate and phosphate. These authors, however, did not examine selenite behavior upon dilution of the equilibrating solutions. Selenite adsorption by goethite was found to be completely reversible.
with respect to changes in pH (Balistreri and Chao 1987). In general, retention of selenium by the processed oil shale solids was irreversible (Figures 2 through 5). Dilution of the lowest selenium concentration DHI system resulted in additional selenium in the solution phase (Figure 3). This may be a result of the dissolution processed oil-shale-borne selenium-bearing minerals dissolving. However, blanks (no selenium added) contained below detectable levels of selenium. For the remaining systems, however, dilution of the processed oil shale equilibrium solutions did not result in the release of selenium to solution. Indeed, upon dilution of the solution phase, additional selenium removal from the solution phase was observed.

The additional removal of selenium upon dilution suggests that adsorption may not be the only process influencing the removal of selenium by processed oil shale. Spackman and others (1988) observed the additional removal of arsenate by processed oil shale solids upon dilution of the solution phase. A thermochemical analysis indicated that the equilibrating solutions were supersaturated with respect to a number of metal arsenates. It was concluded that the precipitation of metal arsenates was occurring and influencing soluble arsenate concentrations. Further, at short reaction times adsorption processes controlled soluble arsenate concentrations, and as reaction time increased precipitation reactions began to influence soluble arsenate.

A thermochemical analysis of the selenium adsorption and desorption solutions indicates that the solutions are undersaturated with respect to a number of metal selenites. Saturation index values were highly negative for the solids examined. However, only a limited number of selenium solids were examined in the evaluation due to the limited
number of elements quantified in the solutions. Further, solubility product constants are known for only a relative few metal selenites (Essington 1988b). Maximum and minimum saturation index values for metal selenites for all adsorption and desorption equilibrium solutions are shown in Table 3. The largest predicted SI values were noted for CaSeO$_3$·2H$_2$O(s). These values indicate that the adsorption and desorption isotherm equilibrium solutions were undersaturated with respect to CaSeO$_3$·2H$_2$O(s). All other solids examined showed even more negative SI values.

Similarities between selenite and arsenate desorbability from processed oil shales (Spackman and others 1988) suggests these species to be influenced by the same processes. However, the highly negative SI values calculated for metal selenites indicates that precipitation reactions may not influence soluble selenite. Unfortunately, the selenite minerals examined in the thermochemical analysis are thought to represent only a small sampling of the selenite minerals that may precipitate. The lack of thermochemical and analytical data prevent additional analysis. Additional removal of selenite from the processed oil shale solutions upon dilution may also indicate that adsorption equilibrium was not attained, or that basic mineralogical alterations that occur during the hydration of processed oil shales may be creating new adsorption surfaces. Although a kinetic study was not performed, a review of the pertinent literature indicates that the 48-hour equilibration period was more than adequate for selenite adsorption. Mineralogical alterations that may result from processed oil shale hydration (Essington, unpublished data) did not influence arsenate adsorption by processed oil shales (Boardman and others 1985; Spackman
1 and others 1988). Thus, it is not anticipated that these mineralological
2 alterations would significantly influence selenite adsorption. However,
3 weathered processed oil shale solids are currently being characterized
4 to assess changes in chemical and physical properties that may result
5 from hydration.
Conclusions

The adsorption of selenite by processed oil shales was examined as a function of oil extraction process. The adsorption data were quantitatively characterized by Freundlich adsorption isotherms. The data were also described by Langmuir adsorption isotherms. However, regression analysis indicated that the Freundlich isotherm provided consistently greater (more significant) $R^2$ values over the range of selenite concentrations examined. Least-squares mean test of the Freundlich isotherms indicated that processed oil shale type did not influence selenite adsorption. Selenite adsorption by the processed oil shale solids was found to be irreversible. Following dilution of the equilibrium systems, selenite removal from solutions continued. This was consistent with the behavior of arsenate in these same processed oil shale systems. The additional removal of selenite from solution upon dilution could not be attributed to the precipitation of metal selenites. An examination of saturation index values indicated that the equilibrium solutions were highly undersaturated with respect to metal selenites. However, the list of selenite solids examined was not all-inclusive due to the lack of thermochemical data.

Acknowledgements

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References


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Figure 5. Freundlich Plot of Selenite Adsorption/Desorption by CS
| Processed Oil Shale | Freundlich | | | | | | Langmuir | | | |
|---------------------|------------|-----|-----|-----|-----|-----|-----|
|                     | $K_F$      | $1/n$ | $R^2$ | $K_L$ | $b$  | $R^2$ |
| IH                  | 0.13       | 0.43a | 0.968* | 3150  | 0.0097 | 0.973* |
| DH1                 | 0.12       | 0.33a | 0.994** | 9270  | 0.0135 | 0.973* |
| DH2                 | 0.70       | 0.39a | 0.983* | 1200  | 0.0147 | 0.960* |
| CS                  | 1.58       | 0.56a | 0.989* | 8580  | 0.0249 | 0.854 |

† $C_e$ and $x/m$ expressed in mmol L$^{-1}$ and mmol kg$^{-1}$, respectively

* Significance at the 5% level

** Significance at the 1% level

* Pairs of Freundlich parameters followed by the same letter represent insignificantly different isotherms ($P=0.05$)
Table 2. Partitioning Isotherm Constants ($K_p$)

<table>
<thead>
<tr>
<th>Se IN</th>
<th>IN</th>
<th>DH1</th>
<th>DH2</th>
<th>CS</th>
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<td>246.4</td>
<td>15.01</td>
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<td>40</td>
<td>13.89</td>
<td>93.97</td>
<td>14.76</td>
<td>171.3</td>
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<td>80</td>
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<td>9.03</td>
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<td>12.45</td>
<td>6.71</td>
<td>62.32</td>
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† Initial selenium concentration in mgL\(^{-1}\)
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<th>Min</th>
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<td>-12.38</td>
<td>-15.16</td>
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† Values taken from Reddy and Drever (1987) unless noted otherwise
* Naumov and others (1974)
§ Neal and others (1987a)
† Essington (1988b)
# Below detectable levels of magnesium

Table 3. Maximum and Minimum Saturation Index Values (log (IAP/K)) for Selenite Minerals in Adsorption and Desorption Equilibrium Solutions
Figure 1. Selenite Adsorption by IH, DH1, DH2, and CS
Adsorption

Desorption
-1.8
-1.9
-2
-2.1
-2.2
-2.3
-2.4
-2.5
-2.6
-2.7
-2.8
-2.9
-5.5
-5
-4.5
-4
-3.5
-3
-2.5

log x/m, mmole kg⁻¹

log C₀, mmole L⁻¹

- Adsorption
- Desorption
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