# Selenite and Selenate Determination in Surface Coal Mine Backfill Ground Water[1]

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**Abstract:** A majority of Wyoming's public water supplies are based on ground water resources. It is necessary, therefore, to protect these resources from contamination by pollutants (e.g., selenium), which can be harmful to human health. Dissolved selenium (Se) in ground water may contain different species, including selenite ($SeO_3^{2-}$), selenate ($SeO_4^{2-}$), organic Se, and Se ion pairs (e.g., $MgSeO_4^{\circ}$, $CaSeO_4^{\circ}$). For an understanding of the toxicity potential of Se, it is necessary to know the concentrations of $SeO_3^{2-}$ and $SeO_4^{2-}$, as well as total Se content in ground water. The hydride generation atomic absorption spectrometry (HGAAS) method of Se analysis requires oxidation of organic matter, which destroys the natural distribution of Se. Ion chromatography (IC) can determine $SeO_3^{2-}$ and $SeO_4^{2-}$ concentrations, but other common anions (e.g., $SO_4^{2-}$) will interfere with $SeO_3^{2-}$ and $SeO_4^{2-}$ measurements. The objective of this study was to determine $SeO_3^{2-}$ and $SeO_4^{2-}$ concentrations to evaluate the chemical speciation of Se in ground water. Both $SeO_3^{2-}$ and $SeO_4^{2-}$ from ground water samples were adsorbed onto copper oxide (CuO) at pH 5.5 and subsequently desorbed with NaOH solution at pH 12.5. Extracted $SeO_3^{2-}$ and $SeO_4^{2-}$ were determined using HGAAS and IC. From the $SeO_3^{2-}$ and $SeO_4^{2-}$ measurements, Se speciation in ground water was calculated. Results showed that dissolved Se concentrations in ground water ranged from 22 to 151 $\mu$g/L. Selenium speciation suggested that ground water consisted primarily of $SeO_4^{2-}$ ion (33 to 66%), $SeO_3^{2-}$ ion (6 to 38%), organic Se (14 to 23%), and Se ion pairs (9 to 18%) (e.g., $MgSeO_4^{\circ}$, $CaSeO_4^{\circ}$, $Na_2SeO_4^{\circ}$). These results also show that mobility of dissolved Se will depend on the chemical form in which Se is present in the ground water.

**Additional Key Words:** dissolved selenium, selenite, selenate, ionic species, toxicity, ion pairs, mobility.

## Introduction

Selenium (Se) is a required micronutrient for animals and humans. The essentiality of Se for plants is not clearly understood. However, excessive Se can be toxic to plants, animals, and humans (Lakin, 1972). The total dissolved Se concentration in drinking water is federally regulated not to exceed 0.01 mg/L (USEPA, 1986). The primary source of Se in nature is volcanic emanations and metallic sulfides associated with igneous activity. Secondary sources are biological pools in which Se has bioaccumulated (NAS, 1974). In general, shales have the highest concentrations of Se and are the primary sources of high-Se soils in the Great Plains and Rocky Mountain foothills in the United Sates (Lakin, 1961). Although approximately 50 Se minerals are known, Se is commonly associated with heavy metal (e.g., Cu, Pb, Ni) sulfides. Additionally, recent studies have shown that organic Se species are present in soils (Abrams et al., 1990; Fio and Fujii, 1990).

During surface coal mining, overburden materials are brought to the earth's surface where they are exposed to oxidizing conditions. The oxidizing conditions decrease the stability of the Se containing sulfides and organic matter, thereby increasing dissolved Se concentration in backfill materials. An increase in the dissolved Se concentration in backfill materials can potentially enhance Se mobility into adjacent ground water. Dissolved Se concentrations ranging from 3 to 330 $\mu$g/L have been detected in shallow post-mining ground water from coal mines in the Powder River Basin, Wyoming (Martin et al., 1988; Naftz and Rice, 1989). It has been estimated that 70% of Wyoming 's population uses ground water as their source of drinking water (Canter, 1987 ). Thus, any contamination of ground water could lead to public health problems.

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The chemistry of Se in surface coal mine backfill ground water environments is complex because it can exist in different oxidation states, for example: Se (4+) includes $SeO_3^{2-}$, $HSeO_3^-$, $H_2SeO_3^0$, $CaSeO_3^0$, and $MgSeO_3^0$; Se (6+) includes $SeO_4^{2-}$, $HSeO_4^-$, $H_2SeO_4^0$, $CaSeO_4^0$, and $MgSeO_4^0$; Se (2- ) includes $Se^{2-}$, $HSe^-$, $H_2Se^0$, $CaSe^0$, and $MgSe^0$. Additionally, complexation with other metals, adsorption, precipitation reactions, and biological interactions can further complicate chemistry of Se. Thermodynamic calculations show that Se (2-) species should be found in reducing environments, Se (4+) species in moderately oxidizing environments, and Se (6+) species in oxidizing environments (Elrashidi et al., 1987). The measurement of individual Se species (e.g., $SeO_3^{2-}$ and $SeO_4^{2-}$) in ground water is important, especially considering that the different Se species vary in their potential toxicity. For example, Page and Bingham (1986) reported that $SeO_4^{2-}$ is more toxic to plants than $SeO_3^{2-}$. Additionally, the range between Se toxicity and deficiency in plants, animals, and humans is narrow. Knowing the concentration of $SeO_3^{2-}$ and $SeO_4^{2-}$ in ground water is also useful in predicting the mobility of Se in ground water because $SeO_4^{2-}$ is more mobile than $SeO_3^{2-}$. This difference in mobility is due, in part, to the strong adsorption of $SeO_3^{2-}$ by oxides (Balistrieri and Chao, 1987).

The most commonly used method for Se speciation is hydride generation-atomic absorption spectrometry (HGAAS) (Presser and Barnes, 1984; Cutter, 1985). The HGAAS method will measure Se as total Se and Se (4+), from which Se (6+) and organic Se can be determined by difference or by altering the pretreatment steps. The HGAAS method can detect $1 \mu g/L$ of Se in aqueous solutions. However, the concentration of Se (4+) and Se (6+) may be different from that of individual $SeO_3^{2-}$ and $SeO_4^{2-}$ ionic species because Se (4+) and Se (6+) also includes solution complexes and ion pairs. Another drawback of HGAAS is that it requires oxidation of organic matter. These HGAAS procedures, however, cannot separate Se into individual species. Ion chromatography (IC) method can directly measure the concentration of $SeO_3^{2-}$ and $SeO_4^{2-}$ simultaneously in aqueous solutions. However, the detection limit is not as low as HGAAS. Additionally, ground water commonly contains other anions, that can affect IC measurements. For example, carbonate peak interferes with $SeO_3^{2-}$ (Murayama et al., 1988) and sulfate peak overlaps with $SeO_4^{2-}$ (Hoover and Yager, 1984).

Roden and Tallman (1982) found that passing ground water samples through a column of XAD-8 resin at pH 1.6-1.8 can remove organic compounds without altering Se (4+) and Se (6+) chemistry. Fio and Fujii (1990) extended this technique and separated Se in soil solutions into Se (4+), Se (6+), and organic Se. They further isolated the dissolved organic matter and presented evidence for hydrophobic organic Se in soil solutions. Commonly, the XAD-8 resin will retain organic compounds while inorganic forms of Se (4+) and Se (6+) passes through the column. However, other Se species (e.g., $CaSeO_3^0$, $MgSeO_4^0$ ) may also pass through the exchange column. Although these methods are useful for laboratory characterization of soil and aquatic solutions, they are not practical for field applications. Our objective was to measure $SeO_3^{2-}$ and $SeO_4^{2-}$concentrations and examine the chemical speciation of Se in surface coal mine backfill ground water systems.

## Material and Methods

### Collection and Chemical Analyses of Ground Water Samples

Three ground water samples were collected from reclaimed coal mine sites in the Powder River Basin, Wyoming. Wells were pumped at approximately 1.2 gallons per minute with a submersible, positive displacement pump until pH, specific conductance, and temperature were stable (± 10%). More details regarding the collection of ground water samples are reported by See et al. (1995). Ground water samples were filtered through 0.45 $\mu$ fiber glass filters and were analyzed for cations and anions.

Ground water pH was measured using an Orion combination electrode, Eh using an Orion platinum (Pt) electrode with a $Ag/AgCl_2$ reference electrode, and dissolved organic carbon (DOC) with a Shumadzu Carbon Analyzer. Concentrations of $SO_4^{2-}$, $Cl^-$, $F^-$, and $NO_3^-$ were measured using IC (Dionex, Sunnyvale, CA). Cations and anions in the acidified samples were measured with inductively coupled plasma optical emission spectrophotometry (ICP-OES) and concentrations of Na and K were measured with Atomic Emission Spectrophotometry (AES). The speciation of Se in ground water samples was determined with IC. Complete details regarding the procedures involved in Se speciation with IC are published elsewhere (Blaylock and James, 1993).

A Perkin-Elmer model 5000 atomic absorption spectrometer equipped with a VGA-76 hydride generation system was used to determined Se species by the selective digestion procedure of Fio and Fujii (1990), with few modifications. The concentration of Se (4+) in samples was determined by generating $H_2Se$ using $NaBH_4$ (0.6% (w/v) $NaBH_4$; 0.5% (w/v) NaOH), and 7 M HCl (undigested). Another aliquot of sample was heated for 20 min. at 85°C with 7M HCl to reduce Se (6+) to Se (4+). The concentration of Se in this solution is considered as the sum of Se (6+) and Se (4+) (digested). Difference between the concentration of Se in digested and undigested samples is assumed as Se (6+) concentration. The total Se concentration in samples was determined by oxidizing organic matter with $H_2O_2$ for 20 min at 85°C and then digested with 7M HCl for another 20 min. at 85°C (Workman and Soltanpour, 1980). The difference between total Se and digested Se concentrations was identified as the concentration of organic Se.

Selection of CuO

Ground water samples collected from the Power River Basin, Wyoming had dissolved $SO_4^{2-}$ concentration as high as 11,000 mg/L. Such high $SO_4^{2-}$ concentrations can interfere in the speciation of Se with IC. Initially, $BaCl_2$ and $Ba(OH)_2$ solutions were used to precipitate $SO_4^{2-}$ from aqueous solutions; however, in addition to $SO_4^{2-}$, $SeO_3^{2-}$ and $SeO_4^{2-}$ were also precipitated. Later, $Cu^{2+}$ (cupric) was selected to precipitate $SO_4^{2-}$ from aqueous solutions. The $Cu^{2+}$ was selected because $Cu^{2+}$-$SeO_3^{2-}$ and $SeO_4^{2-}$ solution species are not significant in aqueous solutions, and because $Cu^{2+}$-$SeO_3^{2-}$ and $SeO_4^{2-}$ solid phases are highly soluble in aqueous solutions (Elrashidi et al., 1987).

Initially, $CuCl_2$ solution was added to aqueous solutions containing $SO_4^{2-}$, $SeO_3^{2-}$, and $SeO_4^{2-}$ and $SO_4^{2-}$ was precipitated as hydroxy sulfate by adding NaOH to the solutions. This procedure appeared to work for some samples. However on further investigation, addition of $CuCl_2$ and NaOH was found to be ineffective in removing $SO_4^{2-}$. In some $CuCl_2$ solutions, increasing the pH by adding NaOH precipitated CuO (tenorite). Excessive $Cu^{2+}$ in solutions slowly lowered the pH to around 6.0 through hydrolysis reactions. At this point, we could not detect $SeO_3^{2-}$ and $SeO_4^{2-}$ in solutions; when solution pH was increased to 12, $SeO_3^{2-}$ and $SeO_4^{2-}$ were detected in solutions. These results suggested that CuO selectively adsorbed $SeO_3^{2-}$ and $SeO_4^{2-}$, in the presence of $SO_4^{2-}$, at low pH, and desorbed of Se at high pH. More details regarding the factors affecting adsorption and desorption of $SeO_4^{2-}$ and $SeO_3^{2-}$ by CuO are reported by Reddy et al. (1995).

Extraction of $SeO_3^{2-}$ and $SeO_4^{2-}$ from Ground Water Samples with CuO

Two 100 mL samples from three ground water solutions were used in these studies. One sample was acidified to pH 5.5 with concentrated HCl. The other sample was spiked with approximately 2 mg/L of standard $SeO_3^{2-}$ and $SeO_4^{2-}$ and then acidified to pH of 5.5 with concentrated HCl. The concentration of Se (4+), Se (6+), and organic Se in these samples was determined with HGAAS following the selective digestion procedure described above. Twenty mL of the spiked and unspiked ground water samples were transferred into 50 mL centrifuge tubes containing of 0.6 g of CuO. After reacting for 4 hours, tubes were centrifuged and the supernatant was separated from the CuO by decantation. Twenty mL of NaOH solution (pH 12.5) was added to each centrifuge tube to desorb Se species from the CuO. These solutions were reacted overnight and then centrifuged. The concentration of $SeO_3^{2-}$ and $SeO_4^{2-}$ in the supernatant solutions was determined using both HGAAS and IC.

## Results and Discussion

Extraction of $SeO_3^{2-}$ and $SeO_4^{2-}$ from Ground Water Samples with CuO

The partial chemical composition of ground water samples used in this study are presented in Table 1. The pH ranged between 5.5 and 7.1. Total Se concentrations were between 22 and 151 $\mu$g/L and As, Cd, Cr, Pb, and Zn concentrations were all less than 0.001 mg/L. High concentration of $SO_4^{2-}$ (2,960 - 11,300 mg/L) in ground water samples prevented direct determination of $SeO_3^{2-}$ and $SeO_4^{2-}$ with IC.

**Table 1. Partial chemical data of ground water samples from reclaimed coal mine sites in the Powder River Basin, Wyoming. Units are in mg/L unless otherwise indicated.**

| Sample | pH | Eh (mV) | Ca | Mg | Na | K | $SO_4^{2-}$ | $Cl^-$ | DOC | Se (μg/L) |
|---|---|---|---|---|---|---|---|---|---|---|
| SP2 | 5.5 | 450 | 470 | 693 | 339 | 18 | 4,980 | 46 | 14 | 22 |
| SP4 | 7.1 | 360 | 427 | 2,080 | 1,180 | 38 | 11,300 | 340 | 88 | 151 |
| CA649B | 6.3 | 400 | 545 | 391 | 347 | 33 | 2,960 | 65 | 87 | 107 |

Dissolved Se speciation in spiked and unspiked samples, as determined by HGAAS, is summarized in Table 2. These results show that approximately 38 to 49% of the dissolved Se in the ground water samples was Se (4+). Similarly, the Se (6+) concentration ranged between 39 and 50% of the dissolved Se. Organic Se was found between 13 and 23% of the dissolved Se.

**Table 2. Selenium speciation of ground water samples determined with HGAAS. Units are in μg/L.**

| Sample | Se (4+) | Se (6+) | Organic Se | Total Se |
|---|---|---|---|---|
| SP2 unspiked | 8 | 9 | 5 | 22 |
| SP2 spiked | 1,809 | 1,781 | 104 | 3,694 |
| SP4 unspiked | 10 | 110 | 31 | 151 |
| SP4 spiked | 1,789 | 1,967 | 134 | 3,890 |
| CA649B unspiked | 7 | 85 | 15 | 107 |
| CA649B spiked | 1,848 | 1,927 | 112 | 3,887 |

The $SeO_3^{2-}$ and $SeO_4^{2-}$ concentrations in ground water samples recovered with CuO are presented in Table 3. These results show that 96 to 98% of $SeO_3^{2-}$ in ground water samples was recovered, suggesting that Se (4+) in these samples is dominated by $SeO_3^{2-}$ ion. High concentration of $SO_4^{2-}$ in ground water did not affect the recovery of $SeO_3^{2-}$ by the CuO.

**Table 3. Determination of $SeO_3^{2-}$ and $SeO_4^{2-}$ in ground water samples extracted with CuO. Units are in μg/L. Numbers in parentheses represent the percent recovery**

| Sample | IC† | | | | HGAAS† | | | |
|---|---|---|---|---|---|---|---|---|
| | Unspiked | | Spiked | | Unspiked | | Spiked | |
| | $SeO_3^{2-}$ | $SeO_4^{2-}$ | $SeO_3^{2-}$ | $SeO_4^{2-}$ | $SeO_3^{2-}$ | $SeO_4^{2-}$ | $SeO_3^{2-}$ | $SeO_4^{2-}$ |
| SP2 | ND‡ | ND | 1,820<br>(100) | 1,640<br>(92) | 8<br>(100) | 7<br>(77) | 1,780<br>(98) | 1,520<br>(85) |
| SP4 | ND | ND | 1,750<br>(98) | 1,500<br>(76) | 9<br>(90) | 87<br>(79) | 1,720<br>(96) | 1,450<br>(73) |
| CA649B | ND | ND | 1,800<br>(97) | 1,710<br>(88) | 7<br>(100) | 70<br>(83) | 1,770<br>(96) | 1,650<br>(85) |
| | | Mean | (98) | (85) | (96) | (79) | (96) | (81) |

†Ion Chromatography (IC) and Hydride Generation Atomic Absorption Spectrometry (HGAAS)
‡Not Detected.

However, the recovery rate for $SeO_4^{2-}$ ranged between 79 and 85%. This lower recovery rate could be due to: (1) high concentration of $SO_4^{2-}$, which may compete for adsorption sites on CuO and (2) other Se species such as $MgSeO_4^0$ or $CaSeO_4^0$ may be present in the ground water samples, which may not be adsorbed by the CuO. Several studies have reported that $SeO_4^{2-}$ and $SO_4^{2-}$ behave similarly for adsorption on goethite and soils (Hayes et al., 1987; Neal and Sposito, 1989). Balistrieri and Chao (1987), based on the relationship between the intrinsic constant and the protonation constant, suggested that $SeO_4^{2-}$ and $SO_4^{2-}$ binding on goethite would be similar. To determine the effect of $SO_4^{2-}$ concentration on the adsorption of $SeO_4^{2-}$ on CuO, different concentrations of $SO_4^{2-}$ (0, 100, 300, 700, 1200, 2200 mg/L) were added to solutions containing 0.6 g of CuO and approximately 1.0 mg/L of $SeO_4^{2-}$. After reacting for 4 hours, supernatant solutions were analyzed for $SeO_4^{2-}$ by HGAAS. Results from this experiment suggested that $SO_4^{2-}$ had little or no effect on the adsorption of $SeO_4^{2-}$ by the CuO. A possible explanation is that zero point of charge (ZPC) for CuO occurs at pH of 9.5 than the ZPC of goethite, which occurs at pH between 6 and 7.

Yates and Healy (1975) examined anion adsorption on ferric and chromic oxides. They observed a significant difference between these two oxides for the adsorption of $PO_4^{3-}$, $SO_4^{2-}$, and $NO_3^-$. If $SO_4^{2-}$ and $SeO_4^{2-}$ behave similarly or compete for adsorption sites on CuO, one would expect low recovery or no recovery of $SeO_4^{2-}$, especially with ground water samples having a very high $SO_4^{2-}$ and $SeO_4^{2-}$ ratio. For example, sample SP4 has a total Se concentration of 151 $\mu$g/L compared to 11,300 mg/L of $SO_4^{2-}$($SO_4^{2-}$:total Se = 74,000:1) and 79% of the $SeO_4^{2-}$ was recovered with CuO from the unspiked sample. Over all, results of this study suggested that $SeO_4^{2-}$ has a high affinity for CuO even in the presence of $SO_4^{2-}$.

Magnesium concentrations in the ground water are high compared to $Ca^{2+}$, $Na^+$, and $K^+$. It may be possible that Mg forms a $MgSeO_4^0$ ion pair in solution. To test this hypothesis, 1 mg/L of $SeO_4^{2-}$ was reacted with different concentrations of $Mg^{2+}$ (400, 700, 1000, 1500, and 2,000 mg/L). Each solution was reacted for 0.5 hour and samples were injected into the IC to determine $SeO_4^{2-}$ concentration. Most ion pairs will dissociate in the IC column and be detected. Only strong ion pairs will pass through the IC column undetected. Therefore, if $MgSeO_4^0$ is a strong ion pair, it will pass through the IC column and the measured $SeO_4^{2-}$ concentration will decrease. Data obtained from this experiment are plotted in Figure 1. When no $Mg^{2+}$ was added to the solutions, we recovered 1 mg/L of $SeO_4^{2-}$. As $Mg^{2+}$ concentration increased to 2,000 mg/L, measured $SeO_4^{2-}$ concentration in solutions decreased from 1.0 to 0.75 mg/L, suggesting that Se (6+) in solution probably consisted of the $MgSeO_4^0$ ion pair. The observed 79 to 85% recovery for $SeO_4^{2-}$ in ground water samples may therefore be attributed to the presence

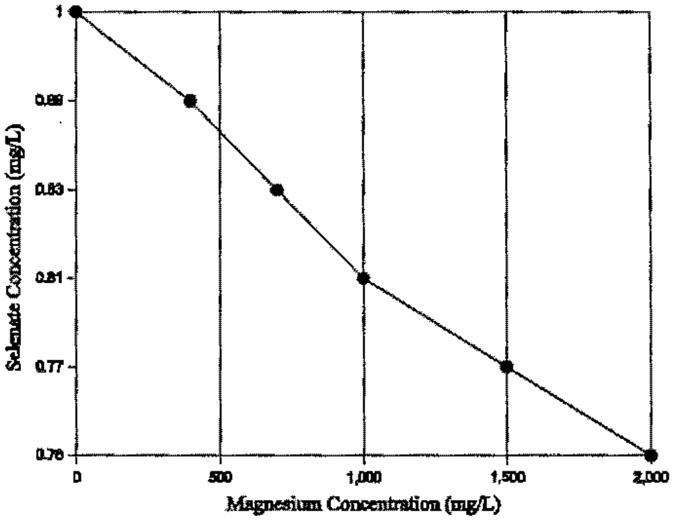

Figure 1. The effect of $Mg^{2+}$ concentration on $SeO_4^{2-}$ concentration in aqueous solutions

of $MgSeO_4^0$ as well as other Se ion pairs (e.g., $CaSeO_4^{\circ}$, $Na_2SeO_4^{\circ}$ ) because strongly bonded neutral species may not be adsorbed by the oxides (Reddy and Gloss, 1993).

Speciation of dissolved Se concentration in unspiked ground water samples, based on the extraction of $SeO_3^{2-}$ and $SeO_4^{2-}$ by CuO, is presented in Table 5. For SP2, dissolved Se was dominated by $SeO_3^{2-}$ (36%) and $SeO_4^{2-}$ (32%) followed by organic Se (23%) and Se ion pairs (9%). For remaining samples (SP4 and CA649B), dissolved Se was dominated by $SeO_4^{2-}$ (57 to 65%) followed by organic Se (14 to 23%), $MgSeO_4^0$ (11 to 18%), and $SeO_3^{2-}$ (6%). The CuO method described in this study to extract $SeO_4^{2-}$ and $SeO_3^{2-}$ from ground water in the presence of other anions is simple and effective. Another important aspect of this method is that CuO could be used in the field to extract both $SeO_3^{2-}$ and $SeO_4^{2-}$ ionic species from ground water and later these species could be desorbed and determined with HGAAS and/or IC.

**Table 5. Selenium speciation in ground water samples collected from the reclaimed coal mine sites from the Powder River Basin, Wyoming. Units are in μg/L. Values in parentheses are percent of total Se**

| Sample/Species | SP2 | SP4 | CA649B |
|---|---|---|---|
| $SeO_3^{2-}$ | 8 (38) | 9 (6) | 7 (6) |
| $SeO_4^{2-}$ | 7 (33) | 87 (56) | 70 (66) |
| Organic Se | 5 (23) | 31 (20) | 15 (14) |
| Ion pairs | 2 (9) | 29 (18) | 15 (14) |
| Total | 24 (100) | 156 (100) | 107 (100) |

The State of Wyoming class III ground water standard for total dissolved Se for livestock drinking is 50 μg/L (Wyoming Department of Environmental Quality, 1993). Out of three ground water samples, two exceeded this limit (SP4 and CA649B), based on total dissolved Se. However, the Gillette Area Ground Water Monitoring Organization reported a general decline in dissolved Se concentrations in ground water from the Powder River Basin (Hydro Engineering, 1991 and 1992). Chemical speciation for these two samples indicate total dissolved Se was dominated by $SeO_4^{2-}$ ion, followed by organic Se and ion pairs ($MgSeO_4^0$, $CaSeO_4^0$, $Na_2SeO_4^0$). The $SeO_4^{2-}$ ion is shown to be more toxic to plants than the $SeO_3^{2-}$ ion (Page and Bingham, 1986). Studies by Dreher and Finkelman (1992) suggested reduction of $SeO_4^{2-}$ to $SeO_3^{2-}$ in surface coal mine overburden materials in the Powder River Basin, Wyoming due to microbial processes. Recently, Blaylock et al. (1994) also observed a similar process in surface coal mine backfill materials from Powder River Basin, Wyoming. These workers attributed the reduction of $SeO_4^{2-}$ in surface coal mine backfill materials to both chemical and microbiological reduction processes. Thus, a general decline in the concentration of dissolved Se in ground water of Powder River Basin, Wyoming could be due to both chemical and biological reduction processes of $SeO_4^{2-}$.

The remaining two forms of dissolved Se (organic Se and Se ion pairs) comprised 27 to 38% of total dissolved Se in ground water samples (SP4 and CA649B), which are either below or slightly above the State of Wyoming class III ground water standard of 50 μg/L. Currently, bioavailability and toxicity of organic Se species in soils and ground water are not well understood. Commonly, ion pairs such as, $MgSeO_4^0$, $CaSeO_4^0$, $Na_2SeO_4^0$ are not adsorbed by the oxide surface (Reddy and Gloss, 1993) or they participate in chemical reactions, unless they are dissociated. For example, data from the IC study suggested that the $MgSeO_4^0$ ion pair once formed is difficult to dissociate in aqueous solutions, even at pH 10. This ion pair moves readily along with the pore water through the column. Overall, results in this study show that the determination of $SeO_4^{2-}$ and $SeO_3^{2-}$ ionic species and chemical speciation of Se are important in assessing Se toxicity and mobility in ground water environments.

## Conclusions

Currently, speciation of dissolved Se concentration in ground water is not well understood. This is due, in part, to the fact that this element is regulated as total Se and the EPA approved analysis is HGAAS, which cannot determine individual Se species (Oppenheimer et al., 1985). However, determination of individual Se species is important for understanding both the Se toxicity potential and the mobility of Se in ground water systems. Adsorption phenomena of $SeO_3^{2-}$ and $SeO_4^{2-}$ by CuO at different pH's provided an approach to separate ionic Se species in ground water samples. CuO has a strong affinity for both $SeO_3^{2-}$ and $SeO_4^{2-}$ species in the presence of other anions including $SO_4^{2-}$. Both $SeO_3^{2-}$ and $SeO_4^{2-}$ were adsorbed onto the surface of CuO at pH 5.5 and later desorbed by raising the pH of the solution to 12.5. The $SeO_3^{2-}$ and $SeO_4^{2-}$ concentrations in the Se solutions were determined with both HGAAS and IC.

The results suggested that dissolved Se in ground water samples consisted of $SeO_4^{2-}$, organic Se, Se ion pairs, and $SeO_3^{2-}$. To determine low concentrations ($\mu$g/L levels) of $SeO_3^{2-}$ and $SeO_4^{2-}$ in solutions, extraction with CuO followed by HGAAS will be useful due to the lower detection limit of this analytical method. For Se, ground waters examined in this study were dominated by $SeO_4^{2-}$ion. Earlier studies involving Se in Powder River Basin, Wyoming area suggested that $SeO_4^{2-}$ may attenuate naturally through chemical and biological reduction processes. Further research is required to understand the behavior and predominance of organic Se species and Se ion pairs in surface coal mine backfill ground water environments and their toxicity to plants, animals, and human.

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# ROLE OF NATURAL ORGANIC SOLUTES ON THE SORPTION OF SELENIUM BY COAL MINE BACKFILL-CORE SAMPLES FROM THE POWDER RIVER BASIN, WYOMING[1]

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**Abstract:** Concentrations of dissolved selenium (Se) as large as 330 $\mu g\ L^{-1}$ have been detected in water samples from backfill aquifers in the southern Powder River Basin (PRB) of northeastern Wyoming. During surface coal mining, rock material overlying the coal is redistributed in relation to its original stratigraphic position; exposure of the previously buried material to surface oxidizing conditions decreases the stability of sulfides and organic matter containing Se, increasing Se concentrations in associated ground waters. Ground-water and backfill-core samples were collected from three sites located at two active mines in the PRB. Dissolved organic carbon (DOC) in the ground-water samples was dominated by the acid fraction (sum of hydrophobic and hydrophilic acids) at 38 to 84% of the DOC; the neutral fraction (sum of hydrophobic and hydrophilic neutrals) ranged from 10 to 55% and the base fraction (sum of hydrophobic and hydrophilic bases) was generally less than 10%. Three sorption experiments were conducted to investigate selenite sorption on backfill-core samples. Selenite concentrations in these experiments ranged from 0 to 11 mg $kg^{-1}$ in backfill-core samples. The first experiment determined the selenite sorption capacity of the backfill-core samples with selenite in distilled-deionized water as a background solution. In the second experiment, selenite in 0.1 M $CaCl_2$ was used as a background solution. In the third experiment, hydrophobic and hydrophilic acid fractions, isolated and concentrated from ground-water samples, were added to the selenite background solutions. Results of the three experiments indicated that the backfill-core samples have a high sorption capacity for Se (generally, greater than 90% of the added Se) and can sorb as much as 99 % of Se added as selenite. Selenium sorption increased in most samples when 0.1 M $CaCl_2$ was used as a background solution compared to distilled-deionized water background solution. The increase in selenite removal might have been caused by precipitation reactions or by an increase in positively charged surfaces caused by calcium sorption, or both. A substantial decrease in selenite sorption rates occurred in the presence of individual organic-solute fractions. Hydrophilic acids caused the largest decrease in Se sorption by the backfill-core samples.

**Additional Key Words:** Selenium Geochemistry; Coal Mines; Sorption/Competition; Dissolved Organic Carbon; Mobility; Powder River Basin, Wyoming.

## Introduction

Studies have shown that the chemistry of selenium (Se) in coal overburden materials can be affected by mining and reclamation operations (Dreher and Finkelman, 1992). Exposure of previously buried material to surface oxidizing conditions can decrease the stability of Se-containing sulfides and organic matter. The oxidation of such compounds can transform reduced and less mobile Se species such as selenide ($Se^{2-}$) and elemental selenium ($Se^0$) into oxidized Se species, selenite ($SeO_3^{2-}$) and selenate ($SeO_4^{2-}$), which are more soluble in alkaline and oxidizing ground waters (Naftz and Rice, 1989). Concentrations of Se, ranging from 3.4 $\mu g\ L^{-1}$ (Martin et al., 1988) to 330 $\mu g\ L^{-1}$ (Naftz and Rice, 1989), have been detected in shallow post-mining ground waters from coal mines in the PRB of northeastern Wyoming. Currently, the Wyoming Class I (domestic), II (agricultural), and III (livestock) ground-water standards for total Se are 10, 50 and 50 $\mu g\ L^{-1}$ (Wyoming Department of Environmental Quality, 1993). The ground-water contribution to surface water flow may provide a mechanism to transport Se from ground-water environments to surface-water resources. Surface-water Se concentrations ranging from 2 to 13 $\mu g\ L^{-1}$ have been reported to cause reproductive problems in aquatic birds (Skorupa and Ohlendorf, 1991).

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