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

Katta J. Reddy*, Zhonghua Zhang, and George F. Vance[2]

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., $MgSeO_4^{\cdot}$, $CaSeO_4^{\cdot}$). 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 μg/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., $MgSeO_4^{\cdot}$, $CaSeO_4^{\cdot}$, $Na_2SeO_4^{\cdot}$). 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 μg/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 1μg/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 μ 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 μg/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 (100)	1,640 (92)	8 (100)	7 (77)	1,780 (98)	1,520 (85)
SP4	ND	ND	1,750 (98)	1,500 (76)	9 (90)	87 (79)	1,720 (96)	1,450 (73)
CA649B	ND	ND	1,800 (97)	1,710 (88)	7 (100)	70 (83)	1,770 (96)	1,650 (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 μg/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

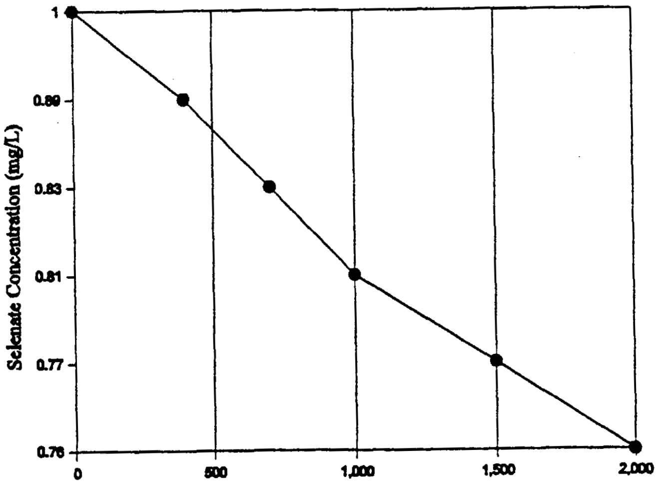

Figure 1. The effect of Mg^{2+} concentration on SeO_4^{2-} concentration in aqueous solutions

of $MgSeO_4^0$ as well as other Se ion pairs (e.g., $CaSeO_4^0$, $Na_2SeO_4^0$) 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 $\mu g/L$. 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 $\mu g/L$ (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 $\mu g/L$. 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 (μg/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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