

Immobilization of Se(VI) in mine drainage by permeable reactive barriers: column performance

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Received 15 May 2006; accepted 10 August 2007

Editorial handling by R. Fuge

Available online 15 January 2008

Abstract

The potential for immobilization of Se in mine drainage water using a permeable reactive barrier was investigated by a column study, in which the reactive components were zero valent Fe, municipal leaf compost, sawdust, and wood chips. These components were mixed with silica sand and gravel. Trace amounts of creek sediment were added to serve as a source of anaerobic bacteria. The influent concentration (40 mg L^{-1}) of SeO_4^{2-} decreased to less than 2 mg L^{-1} within one week and to less than 0.014 mg L^{-1} within 1 month during passage through the column. In the column, the concentrations of SO_4^{2-} also were reduced from 620 to 220 mg L^{-1} . After 2 months, cell populations of SO_4^{2-} -reducing bacteria, estimated using the MPN method, were in the range of 10^6 – 10^7 cells g^{-1} . Isotopic analysis of S showed $\delta^{34}\text{S} = -9.19\text{‰}$ for the input solution, and $\delta^{34}\text{S} = -4.69\text{‰}$ for the output solution. This change in isotopic ratio is attributed to the preferential utilization of $^{32}\text{SO}_4^{2-}$ over $^{34}\text{SO}_4^{2-}$ by SO_4 -reducing bacteria in the column. Geochemical calculations indicate that SeO_4^{2-} is stable in the influent water, and that conditions within the column favour reduction of SeO_4^{2-} to metallic Se or SeO_3^{2-} , and the reduction of SO_4^{2-} to S^{2-} .

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1. Introduction

Selenium is both toxic and an essential element that occurs naturally mainly by substitution for S in sulfides such as chalcopyrite (Goldschmidt, 1958). Release of Se by anthropogenic disturbances, including mining, agricultural activities and industrial waste disposal, can lead to contamination

of aquifers and then deterioration of groundwater resources. Canadian, Japanese, and United States drinking-water limits for Se are 0.01, 0.01, and 0.05 mg L^{-1} , respectively. Contamination of groundwater with Se causes damage to ecological systems, including plants, microorganisms, animals, and humans, through accumulation in the food chain. Carcinogenic and mutagenic effects have been reported due to the consumption of excess Se (Lawrence, 1991).

Permeable reactive barrier (PRB) systems can be used to provide passive treatment of contaminated

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groundwater (Blowes et al., 2000; Scherer et al., 2000; Naftz et al., 2002). A wide variety of reactive materials has been developed for use in PRBs: e.g., zero valent Fe (ZVI) for remediation of chlorinated hydrocarbons and heavy metals, oxides like slag for treatment of As and PO_4^{3-} , surfactant-modified zeolites for adsorption of anions, ion-exchange resins for species such as B, and organic C to promote microbially mediated contaminant removal reactions. Reaction processes primarily include sorption, precipitation, chemical oxidation–reduction reactions, and microbiologically mediated reactions. The present study, using ZVI and natural C sources as reactive materials, suitable for application in a PRB, assesses the potential for immobilization of Se. Recently Zhang et al. (2001) have reported that zero valent Fe would be an effective agent to remove Se from Se-contaminated drainage water, and that most co-existing anions did not significantly inhibit the removal of SeO_4^{2-} , except for PO_4^{3-} under aerobic conditions. Zero valent Fe was included in this study to further promote reduction and removal reactions and to provide a source of H_2 to optimize bacterially mediated reduction reactions. Laboratory tests were conducted using mine drainage water derived from the vicinity of the Phosphoria Formation overburden, near Soda Springs, Idaho, USA. This water was spiked with elevated concentrations of SeO_4^{2-} to assess Se removal within a limited time period, and to provide a sufficient concentration of the reaction products for mineralogical study. These tests were used to determine the rate and extent of Se attenuation, the mechanisms of Se removal, the stability of Se-bearing mineral precipitates, the role of bacterial species in Se attenuation, and to estimate the potential duration of reactivity to provide projections of barrier longevity. The use of water derived from an existing mine site provides an indication of whether other dissolved, potentially competing constituents, interact with the reactive materials to form precipitates and decrease reactivity or permeability.

2. Experimental

2.1. Column experiments

Groundwater from the field site was collected in sealed glass containers without a head space and was shipped refrigerated at 4 °C to the laboratory. The composition of the water was determined by inductively coupled plasma atomic emission spectroscopy (ICP-AES), with the exception of pH which was determined using an electrode and meter (Table 1). The input solution for the column experiments was prepared by spiking this mine drainage water with Na_2SeO_4 to increase the Se concentration to 40 mg L^{-1} .

The column was constructed of acrylic, and was 40 cm in length, 7.5 cm in inner diameter, and approximately 1700 mL in internal volume. There were two influent ports on the base of the column, one to provide the input solution, and the second to allow flushing of the end-plate and for collection of samples of influent water. Two similar ports were located at the top of the column for discharge of the effluent solution and for sample collection. In addition, 15 equally spaced sampling ports were installed along the length of the column.

The bottom layer (3.8 cm) and top layer (2.0 cm) of the column packing consisted of 100% silica sand (0.6–0.8 mm in diameter) as a nonreactive material. The middle reactive layer was composed of 10 (v/v)% zero valent granular Fe (ZVI), 30 (v/v)% silica sand, 20 (v/v)% gravel, and 40 (v/v)% organic C material. The organic C material consisted of 50 (v/v)% compost leaf mulch, 25 (v/v)% wood chips, 25 (v/v)% sawdust, and trace amounts of limestone. The ZVI was obtained from a commercial supplier (iron aggregate ETI-CC-1004; Connelly-GPM, Inc., Chicago). The Fe grains were elongate in shape with a maximum length of 7 mm and 2.4 mm width. The maximum width is consistent with the grain size of a medium to coarse sand.

The central portion of the column was filled with reactive material, approximately 100 g at a time.

Table 1
Water chemistry of original mine drainage (all concentrations in mg L^{-1} except for pH)

| Al | As | B | Ba | Ca | Cd | Co | Cr | Cu | Fe | K | Li | Mg | Mn | Mo |
|--------|--------|-------|--------|-----|--------|----------------|--------|-------|-------|--------|--------|-------|--------|-------|
| <0.37 | <0.084 | 0.029 | 0.049 | 236 | <0.005 | <0.009 | <0.004 | 0.01 | <0.03 | 1.82 | <0.004 | 69.2 | <0.001 | 0.029 |
| Na | Ni | P | Pb | S | Se | SiO_2 | Sn | Sr | Ti | Tl | V | Zn | pH | |
| <0.014 | <0.014 | <0.16 | <0.068 | 231 | 2.24 | 9.16 | <0.055 | 0.529 | 0.007 | <0.074 | 0.015 | 0.019 | 7.57 | |

Table 2

Gravimetric and modeled physical characteristics of the present column during the conservative test

| Porosity | | Dispersion (cm ² h ⁻¹) | Dispersivity (cm) | Velocity (cm h ⁻¹) | | Flow rate (pv d ⁻¹) | | Pore volume (cm ³) | | Residence time (d) | |
|-------------------|-------------------|--|----------------------|-----------------------------------|--------------------|---------------------------------|--------------------|-----------------------------------|--------------------|--------------------|--------------------|
| 0.37 ^a | 0.39 ^b | 15.33 ^b | 16.23 ^b | 0.978 ^a | 0.944 ^b | 1.564 ^a | 1.452 ^b | 662.47 ^a | 688.7 ^b | 0.639 ^a | 0.688 ^b |

^a Average gravimetric calculations.^b Calculated from CXTFIT (Parker and van Genuchten, 1984).

Around 1.5 g in wet weight of anaerobic creek sediment was also added between each addition of reactive material to provide a source of SO₄-reducing bacteria. The creek sediment was collected from Laurel Creek near the University of Waterloo in February, 2003. Iron and silica sand were dry when placed in the column. Based on the difference between the dry mass of the column and its water-saturated mass, the gravimetrically estimated water-filled void space or pore volume of the column was 662.47 mL, and the calculated gravimetric porosity of the column was approximately 0.37 (Table 2). The exact porosity is unavailable due to trace amounts of moisture in the creek sediment.

Prior to initiating the column experiment, the column was placed in an anaerobic glove box (COY, Ltd., US), filled with 5% H₂ and 95% N₂. The column was flushed with CO₂ gas for 6 h and then saturated for 48 h with 1000 mg L⁻¹ (as sulfate) of CaSO₄ solution containing 5% Na-lactate to serve as an initial electron donor for microbial metabolism.

A conservative tracer test, with 70 mg L⁻¹ KBr solution, was performed to determine the flow and transport characteristics of the packed solids. The computer code CXTFIX (Parker and van Genuchten, 1984), a one-dimensional, non-linear, least squares, inversion program, was used to determine the porosity, pore volume, velocity, and dispersion coefficient of the permeable mixture, from effluent concentration data (Table 2). Evaluation of the results of the conservative tracer test indicated that flow through the column is consistent with that expected for a relatively uniform porous medium. After the tracer experiment, the column was eluted with several pore volumes (4 days) with CaCO₃-saturated water to displace the tracer solution. The pore volume was estimated to be 688.7 cm³ by the conservative tracer test. This value is in good agreement with the value obtained by the gravimetric method.

The spiked test water containing Se(VI) was pumped from an input container to the column

using a high-precision peristaltic pump for 60 days. The daily measurements of effluent volume indicated an average flow rate of 0.144 L day⁻¹, corresponding to 0.217 pore volumes per day. This flow rate corresponds to an average linear groundwater velocity of 3.26 cm day⁻¹, and a residence time of 4.77 days. The effluent from the column passed through a glass sample cell prior to its discharge to a waste container.

Water samples were collected using 60 mL syringes to minimize exposure of water to the atmosphere. For collection of samples of input solution, water was pumped through the input valves directly to a polyethylene syringe. For collection of water from the sampling ports, a glass syringe was attached directly to the appropriate port, such that it filled at the same rate that water was being introduced to the column (approximately 6.01 mL h⁻¹).

For each sample, 5.0 mL of unfiltered water were used for the measurement of Eh and pH. The remaining water was passed through a 0.45 µm filter for the measurement of alkalinity, and for the determination of the concentrations of major cations, anions, and other species. For analysis of major cations, the filtered water was acidified to pH < 2 with HNO₃. Alkalinity, Eh and pH were measured immediately following the collection of the samples. Alkalinity was measured in the laboratory using a Hach™ digital titrator (Titration Method 2320 B; American Public Health Association (APHA), 1992). Eh (Oxidation–Reduction Potential Method 2580 B; APHA) and pH (Electronic Method 4500-H⁺ B; APHA) determinations were made in the laboratory using Orion Pt and Orion Ross electrodes, respectively, immediately after the sample had been collected in the syringe. Total Se was determined by hydride generation/atomic absorption spectrometry (HG AAS, 3500-Se C; APHA, 1992), ICP AES (EPA Method 200.7), and by Inductively Coupled Plasma Mass Spectrometry (ICP-MS) for low concentrations. The detection limits for Se were reported to be

$2 \mu\text{g L}^{-1}$ using HG-AAS, $200 \mu\text{g L}^{-1}$ using ICP-AES and $2 \mu\text{g L}^{-1}$ using ICP-MS. Concentrations of Al, B, Ba, Cd, Co, Cr, Cu, Fe, Mn, Mo, Ni, Pb, S, Si, Sr, Ti, Tl, V, Zn, Ca, Na, and Mg were determined using ICP-AES. Sulfate, Cl^- , NO_3^- , NO_2^- , and F^- were determined by ion chromatography. Concentrations of carbonate were calculated using the geochemical speciation program MINTEQA2 on the basis of the alkalinity and pH.

2.2. Geochemical calculations and SEM observation

Geochemical calculations were performed with MINTEQA2, a geochemical equilibrium speciation model for dilute aqueous solutions (Allison et al., 1990). The database was modified to agree with the WATEQ4F database (Ball and Nordstrom, 1991). Geochemical calculations were based on the measured concentrations of dissolved constituents. The measured pH and Eh values were used in all speciation calculations. Hydrogen sulfide gas concentrations were not measured during this experiment. In similar experiments, evaluating zero valent Fe as a reactive media component, H_2S concentrations typically were near or below the analytical detection limit.

Scanning electron microscopy and electron dispersive X-ray analysis (SEM-EDX) was performed on Au/C-coated grain mounts using a LEO 1530 SEM-EDX, to observe the morphology and elemental distributions of Se-bearing grains. Accelerated voltage was 10 kV.

2.3. Microbiological enumerations

Microbiological enumerations were conducted on 10 samples, which were extracted from different levels of the column immediately after the termination of the experiment. For SO_4 -reducing bacteria, a modified Postgate medium was used (Postgate, 1984; Benner et al., 2000). For Se-reducing bacteria, the medium was prepared following the method described by Oremland et al. (2004). For each sample, 1 g of column material was diluted successively to a final dilution of 10^{10} . Samples were incubated in an anaerobic glove box at room temperature for 30 days. Positive readings were shown by the occurrence of black precipitates attributable to the formation of Fe sulfides for SO_4 -reducing bacteria, and to metallic Se and FeSe^- for Se-reducing bacteria. The most probable number (MPN) technique (Postgate, 1984) was used to evaluate the number of SO_4 -

reducing bacteria and Se-reducing bacteria in each sample.

3. Results and discussion

Bacterially-mediated reactions occurring in the column resulted in a decrease in pH, a decrease in Eh and the production of alkalinity. The generally lower pH in the output solution suggests the formation of acids by decomposition of organic substances (Fig. 1). Alkalinity was always higher in

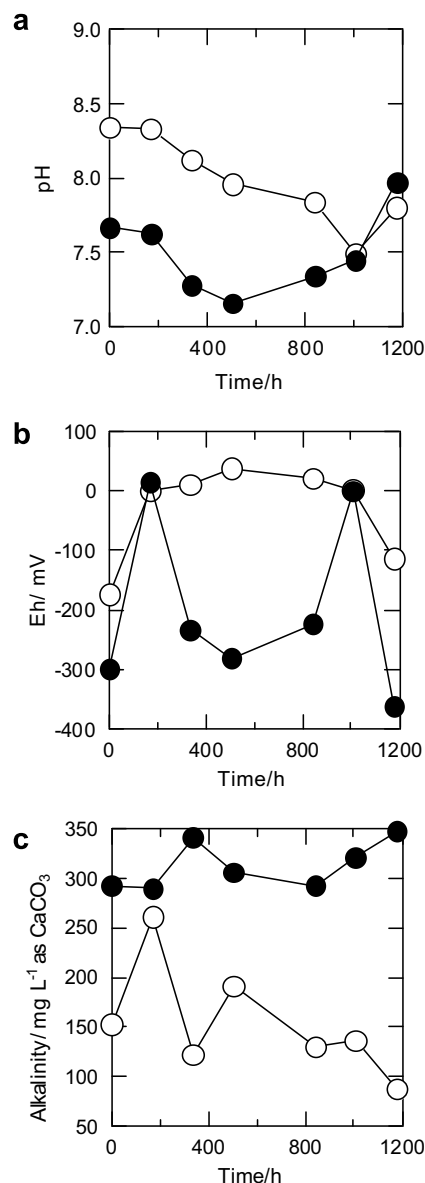


Fig. 1. Time courses of (a) pH, (b) Eh, (c) alkalinity in input and output water during the column experiment. One pore volume requires 114 h of flow.

the output solution than in the input solution, with an initial increase in alkalinity of 150 mg L^{-1} and an increase of more than 250 mg L^{-1} at the conclusion of the experiment. These trends, which are consistent with previous reports (Hulshof et al., 2003),

are attributed to the activity of SO_4 -reducing bacteria.

Concentrations of dissolved Se declined from approximately 40 mg L^{-1} in the column input to consistently less than 0.002 mg L^{-1} , which is the

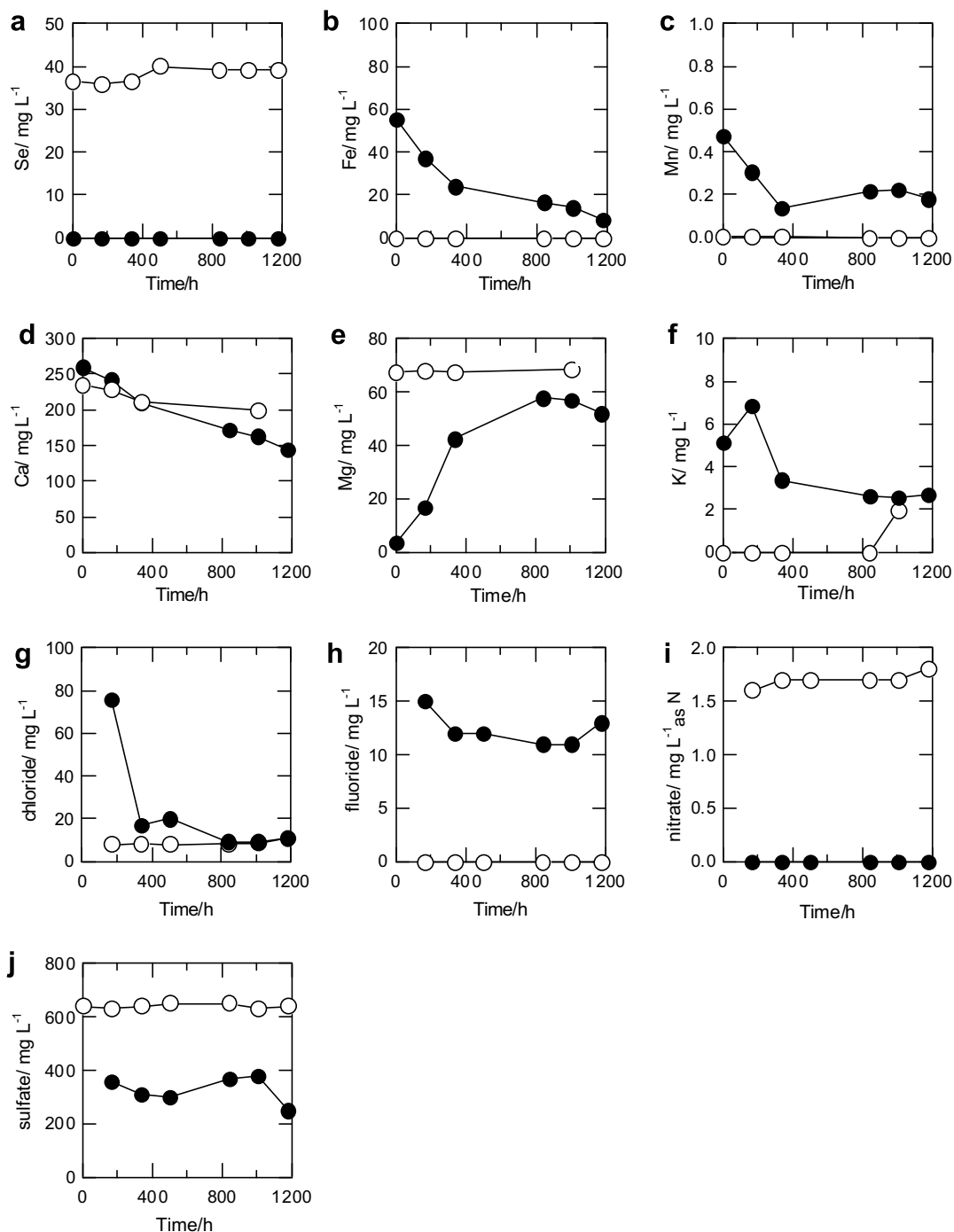


Fig. 2. Time courses of (a) Se, (b) Fe, (c) Mn, (d) Ca, (e) Mg, (f) K, (g) Cl^- , (h) F^- , (i) NO_3^- and (j) SO_4^{2-} concentrations in input and output water during the column experiment.

detection limit by ICP-MS. These low concentrations were obtained at the initial sampling of the effluent water at 168 h, and this rate of removal

was sustained throughout the 1200 h of the experiment (Fig. 2). The initial concentrations of dissolved Fe were 0.03 mg L^{-1} in the column input and

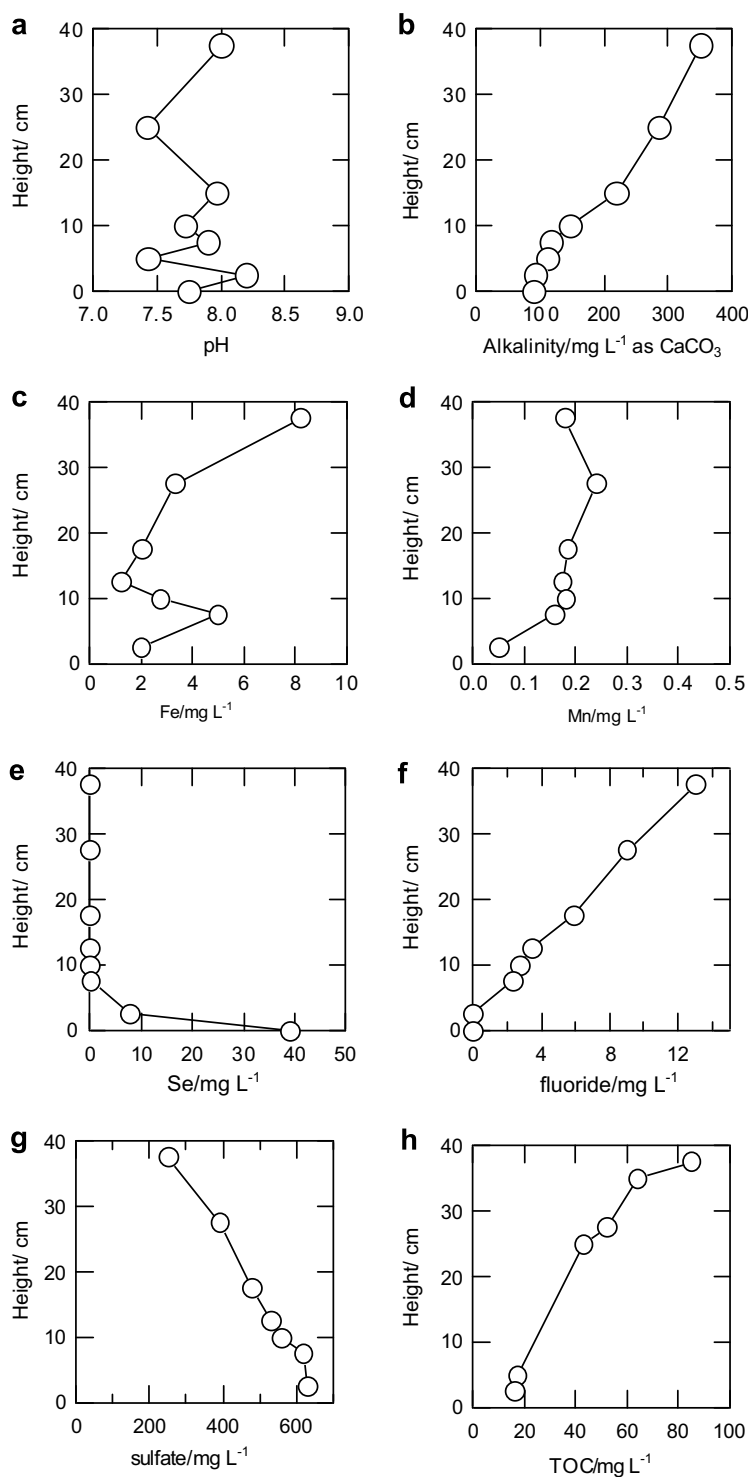


Fig. 3. Column profiles of (a) pH, (b) alkalinity, (c) Fe, (d) Mn, (e) Se, (f) F^{-} , (g) SO_4^{2-} , (h) TOC in output water after 1200 h.

55.2 mg L⁻¹ in the output; as the experiment progressed, the output concentration declined to 8.2 mg L⁻¹ in the final sampling (Fig. 2). The Fe is likely derived from the reductive dissolution of Fe oxides that surround the ZVI grains in the column mixture. Concentrations of dissolved Mn and K also increased, suggesting that these elements might be released from the leaf compost used as one of the components of the reactive mixture (Fig. 2). The release of Mn(II) through the reduction of Mn oxides in contact with organic substances in anoxic environments is well documented (Stone and Morgan, 1984). Concentrations of dissolved Ca were conservative throughout the experiment (Fig. 2). Concentrations of dissolved Mg initially declined but later increased to near the influent concentrations (Fig. 2). Ion exchange reactions may also have affected the concentrations of these cations.

The Cl concentration in the column output, initially exceeded that of the input, then declined rapidly from 76 to <10 mg L⁻¹ near the end of the experiment (Fig. 2). The high Cl concentrations are probably derived from the leaf compost portion of the reactive material. In contrast, F was continuously released from the column components at concentrations between 10 and 15 mg L⁻¹ (Fig. 2). This F likely originated from the organic matter, including the creek sediments, or from the gravel used in the experiments. Nitrate was completely removed from approximately 1.5 mg L⁻¹ as N in the column input to less than the analytical detection limit (0.25 mg L⁻¹) as a result of the reduction to NO₂⁻ and N₂ under the anoxic conditions prevailing in the column (Fig. 2). Sulfate was continuously removed by microbiologically mediated reduction in the column (Fig. 2). Input concentrations of

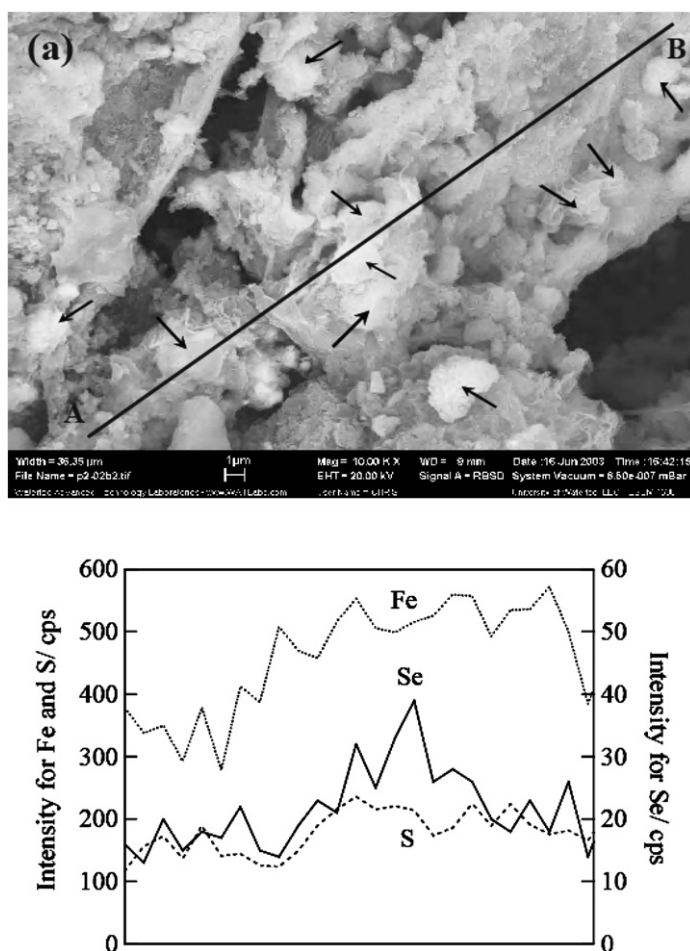
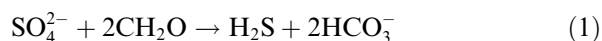


Fig. 4. (a) SEM image of Fe-sulfide precipitates on zero valent Fe and (b) EDX analysis along a transect A–B in (a). In (a) the arrows indicate newly precipitated particles. Horizontal bar indicates 1 μ m.

>600 mg L⁻¹ SO₄ declined to <400 mg L⁻¹ over the course of the experiment. The difference between input and output SO₄²⁻ concentrations was 250–400 mg L⁻¹. On the basis of residence time (4.77 days), the apparent rate of SO₄²⁻ reduction is 62.5–100 mg L⁻¹ day⁻¹ (0.0265–0.0425 mmol h⁻¹). This rate is similar to those observed in column experiments conducted by Waybrant et al. (2002), who evaluated the treatment of acid mine drainage using mixtures of organic C sources.

The pH varied from 7.4 to 8.2, independent of the length of the column (Fig. 3). Alkalinity increased from <100 mg L⁻¹ (as CaCO₃) at the base of the column to 350 mg L⁻¹ at the output end (Fig. 3). This increase is likely caused by the production of HCO₃⁻ through microbial decomposition of organic substances by SO₄²⁻-reducing bacteria through the reaction:



The increase in alkalinity is consistent with changes in concentrations of Se, Fe and SO₄. Concentrations of dissolved Se declined from 40 mg L⁻¹ at the base of the column to below the analytical detection limit (0.025 mg L⁻¹) within 8 cm into the column (Fig. 3). Concentrations of Fe increased within 8 cm from the column bottom, decreased at 8–12 cm above the bottom, and increased again at >12 cm above the bottom (Fig. 3). The SO₄ concentrations in the interval from the base of the column to 8 cm did not change markedly (Fig. 3), but from 8 cm to 40 cm, the concentration decreased from >600 to <250 mg L⁻¹.

Mineralogical study confirmed the presence of sulfide-bearing precipitates within the column materials. Fig. 4 shows an SEM image of biogenic Fe-sulfide framboidal aggregates collected 2.5–5.0 cm from the base of the column, near the interface between the reactive material and the sand layer. The individual framboids were 1–2 μm in diameter as shown with arrows in Fig. 4a. The elemental distribution of Fe, S and Se along transect A–B in Fig. 4a indicate that Se concentrations correlate strongly with Fe. This correlation suggests that S may be partly replaced with Se in the Fe sulfide (FeS).

The results of the microbiological enumeration indicated that SO₄-reducing bacteria were abundant within the column (Fig. 5). The cell density of viable SO₄-reducing bacteria ranged from 10⁵ to 10⁶ cultured cells per gram of column materials. These counts are on the same order of magnitude as were observed for a column experiment that promoted

bacterial SO₄²⁻ reduction using organic C as a reactive material (Waybrant et al., 2002).

Isotopic analysis of O and S showed δ¹⁸O = -11.98‰ and δ³⁴S = -9.19‰ for the input solution, and δ¹⁸O = -8.44‰ and δ³⁴S = -4.69‰ for the output solution, indicating that ³²S and ¹⁶O were preferentially consumed in the column. That is, the SO₄-reducing bacteria preferentially reduced ³²SO₄²⁻ over ³⁴SO₄²⁻ to precipitate sulfides inside the column. Se-reducing bacteria were not detected in any sample. Stolz and Oremland (1999) have indicated that Se-reducing bacteria reduce Se(VI) and Se(IV) to Se(0), not to Se(II). An X-ray photoelectron spectroscopic examination of the precipitates derived from the column experiment indicated that much of the Se accumulated in the reaction products is in the Se(II) state.

After 1200 h, the concentrations of Mn, Ca, Mg, and K were almost constant independent of the column length. Fluoride concentrations consistently increased upward along the length of the column (Fig. 3), possibly due to release from gravel or the compost materials, which were evenly distributed

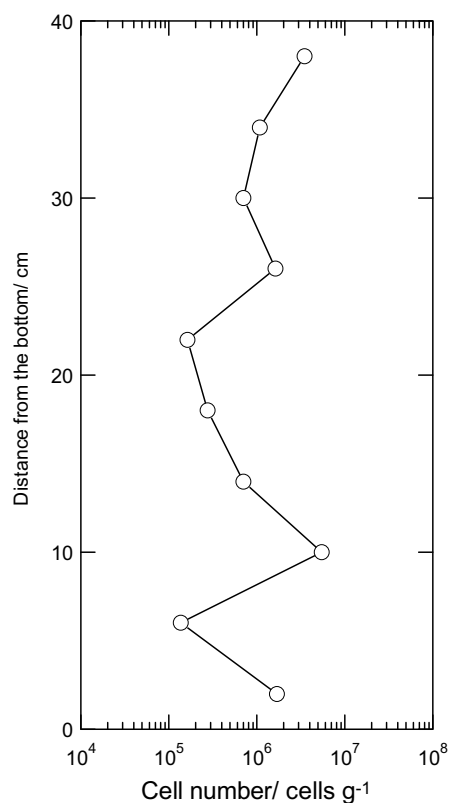


Fig. 5. Distributions of SO₄-reducing bacteria in column contents by MPN methods.

in the column. Total dissolved organic C concentrations increased towards the top of column (Fig. 3), likely because of microbiological decomposition of organic materials. Distribution of Cl^- concentrations showed a large increase from 7 to 34 mg L^{-1} in the central portion of the column.

Saturation index (SI) values calculated for selected minerals indicated that the output water is supersaturated with respect to carbonate minerals (Fig. 6). The SI for dolomite was close to zero initially, and increased with time. This increase is coincident with the decrease in the difference between input and output Mg concentrations (Fig. 2). The output water is supersaturated with respect to pyrite, Fe monosulfide, mackinawite and elemental S (Fig. 6). The output water is also supersaturated with respect to ferroselite (FeSe_2), FeSe and metallic Se (hexagonal and amorphous types) (Fig. 6).

The column water is supersaturated with respect to the carbonate minerals calcite, dolomite and siderite at every sampling port along the column

(Fig. 7). The SI for siderite approached 0 at the 10 cm level, and gradually became more supersaturated with increasing column length. The water was supersaturated with respect to pyrite at all sampling ports and the SI values indicate near equilibrium conditions with respect to Fe monosulfide, mackinawite and S at all sampling ports (Fig. 7). Saturation indices calculated for the Se-bearing minerals indicate supersaturation with respect to ferroselite (FeSe_2), FeSe and metallic Se (hexagonal and amorphous types) at all of the sampling ports. These saturation indices indicate that conditions within the column favour the precipitation of Fe, S and Se as reduced secondary precipitates within the column. These observations, coupled with the abundance of SO_4 -reducing bacteria, the change in the isotopic ratios of $\delta^{18}\text{O-SO}_4$ and $\delta^{34}\text{S-SO}_4$, and the formation of secondary Fe-sulfide precipitates, indicate that the mechanism of removal is reduction and precipitation of reduced secondary Fe-, S- and Se-bearing phases.

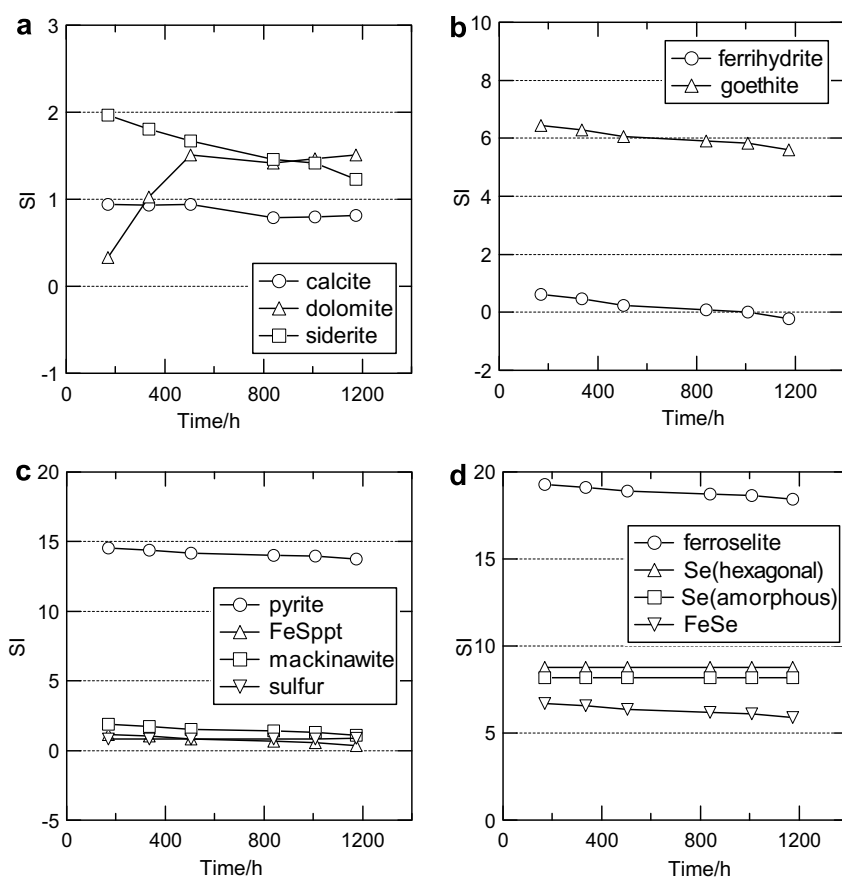


Fig. 6. Changes in selected saturation indices as calculated by MINTEQA2 versus time. (a) calcite/dolomite/siderite, (b) ferrihydrite/goethite, (c) pyrite/FeS ppt/mackinawite/sulfur, (d) ferroselite (FeSe_2)/Se (hexagonal)/Se (amorphous)/FeSe.

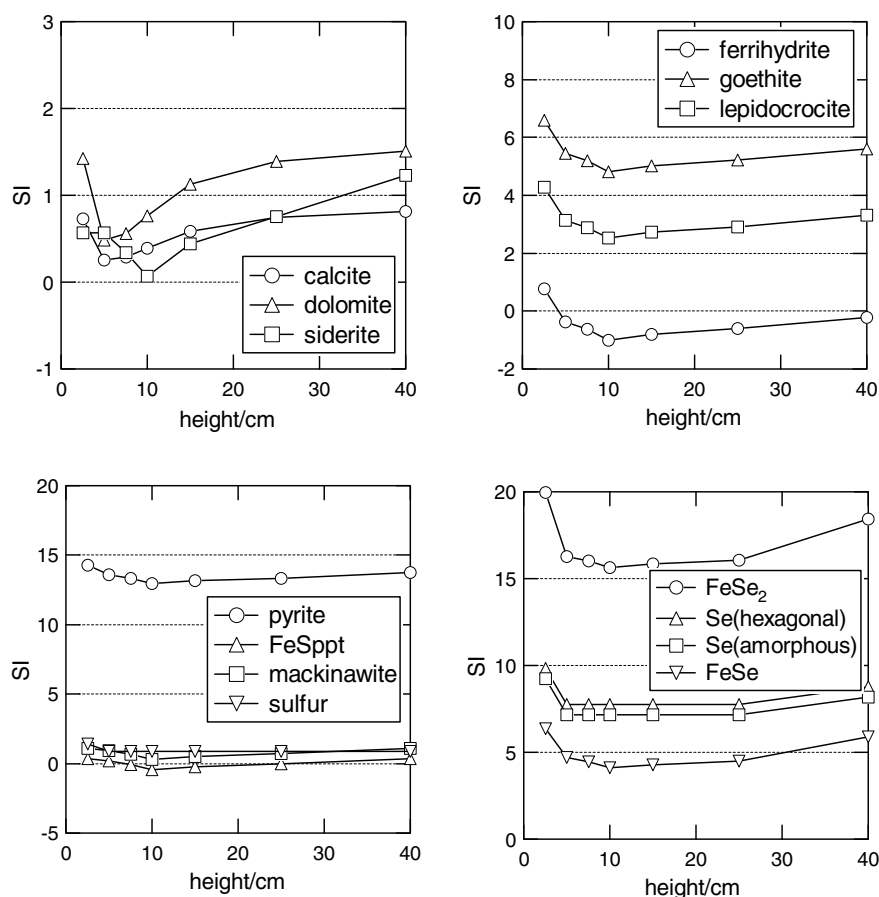


Fig. 7. Changes in selected saturation indices as calculated by MINTEQA2 *versus* column height. (a) calcite/dolomite/siderite, (b) ferrihydrite/goethite, (c) pyrite/FeS ppt/mackinawite/sulfur, (d) ferroselite (FeSe₂)/Se (hexagonal)/Se (amorphous)/FeSe.

The total mass of Se introduced to the column during the experiments for 60 days was calculated to be 0.215 g. Assuming that all of the immobilized Se in the column was accumulated in the section interval within 3 cm of the column base, the removal capacity, which is defined as the amount of removed Se per unit gram of reactive material, is calculated to be more than 3.6 mg-Se g⁻¹-reactive materials. Considering a plume with an average velocity of 20 m a⁻¹ and a Se concentration of 2 mg L⁻¹, 4 mg of Se would flow through each 1 cm² every year. Based on the removal capacity of the reactive materials, 40 mg of Se would be accumulated in 13.07 g of reactive materials for 10 a. Given that the average density of reactive materials is 0.636 g cm⁻³, a 20.55 cm³ volume of reactive materials would be required to treat 2 mg L⁻¹ of Se for 10 a. The present column contains 1546.8 cm³ of reactive materials, indicating that 2 mg L⁻¹ Se can be treated annually for 75 a.

Acknowledgements

This work was conducted at the University of Waterloo, and partly at the CANMET Biotechnology Laboratory. We thank the Japan Society of the Promotion of Science (JSPS), the Canada Research Chair program, the Canadian Water Network, and the NSERC discovery grant program for financial support, to Dr. R.S. Oremland at of the US Geological Survey for discussion on the isotopic effect of sulfate-reducing bacteria and Se-reducing bacteria, to L.G. Groza, J.G. Bain, M.R. Gunsinger, D. Smyth and C.J. Hanton-Fong at the University of Waterloo for technical support, and to Dr. J.L. Jambor and an anonymous reviewer for helpful and meaningful comments.

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