

Biogeochemistry of permeable reactive barriers for arsenic and selenium remediation

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Introduction

Contamination of groundwater by arsenic (As) and selenium (Se) arises from the natural weathering of geologic materials, but can be exacerbated by mining activities. Column experiments were conducted to evaluate treatment of oxic groundwater containing As and Se using permeable reactive barriers (PRBs). Three columns were packed with varied mixtures of granular iron filings (GIF) from two separate suppliers (a and b), organic carbon (OC) and silica sand. An input solution containing 2 mg L⁻¹ As(V) and 0.8 mg L⁻¹ Se(VI) was passed through the 0.3 m long columns for 325 days.

ID	GIF-a	GIF-b	OC	Sand
C1	50			50
C2		50		50
C3	25		25	50

Table 1: Composition of columns given as volume percentages.

Water chemistry was monitored over time, and solid-phase samples were collected at the conclusion of the experiment. Reaction products were examined by field emission-scanning electron microscopy-energy dispersive spectroscopy (FE-SEM-EDS). Solid-phase As and Se speciation was investigated by X-ray absorption near edge structure (XANES) spectroscopy. Microbial ecology was assessed by tag encoded FLX amplicon pyrosequencing (TEFAP) of the bacterial 16S rRNA gene.

Results and Conclusions

Effective removal of As and Se was observed for all columns. Effluent concentrations of As and Se concentrations were generally < 2 µg L⁻¹ for C1 and C2. Treatment improved over time for C3, with effluent As concentrations decreasing to < 2 µg L⁻¹ after 120 days and Se concentrations remaining < 30 µg L⁻¹ after this time. Examination by FE-SEM-EDS revealed the common presence of discrete As-bearing phases in C1 and C2. Results of XANES analysis indicate that As(V) and As(III) occurred in differing proportions within C1 and C2, whereas As predominantly exhibited a reduced oxidation state in C3. Solid-phase Se was consistently present in a reduced oxidation state in all columns. The microbial community within C3 exhibited the greatest phylogenetic and metabolic diversity. However, sulfate reducers were common to all columns, even in the absence of OC in C1 and C2. Results of this study demonstrate that As and Se removal by PRBs may result from various biogeochemical processes. Understanding these processes is critical for assessing long-term treatment performance and the potential stability of reaction products.

Crystal chemical constraints on element distribution in oxides

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Spinel

The oxide spinel structure, one of the first to be determined by x-ray diffraction, is based on a unit cell of 32 oxygens, which are (nearly) cubic-close-packed when viewed along the cube diagonals {1,2}. For stoichiometric spinels in the space group Fd3m, half the possible octahedral interstices (B) and one-quarter of the possible tetrahedral interstices (A) are occupied by cations, yielding the nominal formula AB₂O₄. Spinel may be normal or inverse, depending on whether the B cations are restricted to the octahedral sites or are split between the sites. The spinel structure is extraordinarily flexible; this stems from the fact that (1) the entire oxygen framework can expand *and* (2) the position of oxygens shared by tetrahedral and octahedral sites can shift along (111); the latter causes a puckering of the oxygen planes. This shift is measured by the *u* parameter, which ideally is 0.25, but can be either larger or smaller depending on the relative sizes of the tetrahedral and octahedral cations. The ideal spinel would contain cations having ionic radii of 0.0315 nm (tetrahedral) and 0.0575 nm (octahedral), but in fact at least 30 different cations, with valences ranging from +1 to +6 and ionic radii ranging from 0.026 to 0.103 nm, can form **major** components of spinels. As a great many trace elements have properties falling within these limits, the ability of spinels to host such elements is quite large.

Rhombohedral Oxides

The rhombohedral oxides, exemplified by hematite or corundum (A₂O₃) and ilmenite ABO₃, crystallize in space groups $R\bar{3}c$ and $R\bar{3}$ respectively. Oxygen forms planes parallel to (111) of the rhombohedral cell [(0001) of the equivalent hexagonal cell]; these planes are stacked in (nearly) hexagonal-close-packing, with 18 potential octahedral cation sites per 18 oxygens. Typically 2/3 of those sites are occupied by cations, most often as the couples 3⁺-3⁺ or 2⁺-4⁺ (as in hematite and ilmenite respectively). In hematite, oxygen layers alternate with cation layers, while in ilmenite the sequence of layers is O-Fe-O-Ti, thus leading to the lower symmetry. Again, however, at least 30 different cations with valences from +1 to +5, and ionic radii ranging from 0.039 to 0.095 nm (although the majority are 0.06-0.075 nm) can form **major** components in the rhombohedral oxides. If the flexibility of the rhombohedral phases is not quite so great as that of spinels, their capacity to host many trace elements is still large.

Conclusions

In view of the great flexibility of the spinel and rhombohedral oxide structures, a more appropriate title for this abstract might well be “Lack of crystal chemical constraints...”

[1] Waychunas (1991) *Reviews in Mineralogy*. **Volume 25**, 11-68.

[2] Lindsley (1969) *Reviews in Mineralogy*. **Volume 3**, L1-L60.