

***In situ* remediation of Arsenic in groundwater**

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Dissolved arsenic (As) concentrations in groundwater pumped by municipal wells in many areas of the United States exceed the new 10 µg/L US Environmental Protection Agency drinking-water standard. A potentially cost-effective alternative to traditional above-ground treatment is to lower As concentrations within the aquifer by increasing As sorption through *in situ* alteration of the geochemical environment. The effectiveness of *in situ* remediation will be tested by using cross-flow field experiments at a site in Carson Valley, Nevada. Reducing conditions are dominant in this aquifer; sediments are gray in color, groundwater contains <1 mg/L O₂, and As concentrations are about 30 µg/L as As(III). Groundwater will be pumped to the surface and modified by addition of 7 mg/L Fe(II), 6 mg/L O₂, and HCl to a pH of 5.5. The modified groundwater will be injected into a well that is up-gradient from a monitor well. Oxidation of Fe(II) and precipitation of hydrous ferric oxide (HFO) are expected to decrease arsenic concentrations by adsorption and coprecipitation.

Prior to the field experiments, a laboratory column experiment was conducted to quantify the significant reactions in this system and provide guidance for the field experiments. Sediment from a core collected from the aquifer was packed under a N₂ atmosphere into a column 30.5 cm long by 2.54 cm inside diameter. An eluent solution similar to the proposed field injectate was eluted through the column and breakthrough of constituents monitored for 150 pore volumes.

At the influent end of the column, Fe(II) was rapidly oxidized. Precipitation of HFO was evident by the reddish brown color that developed in the sediment. Concentrations of Fe(II) in leachate never exceeded the detection limit of 0.01 mg/L. There was no indication of plugging of sediment pores by HFO based on flow rates. Arsenic concentrations in the leachate decreased rapidly from 30 µg/L to 8 µg/L during the first 10 pore volumes. After this time, As concentrations stabilized between 7 and 8 µg/L for the duration of the experiment. These results indicate that *in situ* remediation in this aquifer could successfully decrease As concentrations to levels below the drinking water standard.

Reductive dissolution of PbO₂(plattnerite) and MnO₂(pyrolusite) by biofluid constituents

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Chlorine, used to disinfect water, oxidizes Pb²⁺(aq) into suspended PbO₂(plattnerite) particles. MnO₂(pyrolusite) may occur naturally in some source waters. Suspended particles in drinking water come into contact with skin, are ingested, and are inhaled as fine aqueous aerosols. Reductive dissolution by biofluid constituents follows the rate equation $d[M^{2+}(aq)]/dt = k'A_{MO_2}[Reductant]$, where A_{MO_2} is the area loading (m²L⁻¹). k (L·m⁻²·s⁻¹) has been measured for the following reductants at pH 6.5:

	k(PbO₂)	k(MnO₂)	k(PbO₂)/k(MnO₂)
L-Cysteine	1.6x10 ⁻²	1.1x10 ⁻³	15
Ascorbic acid	1.4x10 ⁻²	3.8x10 ⁻²	0.37
Uric acid	9.9x10 ⁻³	1.2x10 ⁻²	0.83
Glutathione	8.1x10 ⁻³	2.0x10 ⁻⁴	41
Sialic acid	1.4x10 ⁻⁵	2.4x10 ⁻⁷	58
L-Cystine	1.8x10 ⁻⁶	3.0x10 ⁻⁶	0.60
Urocanic acid	3.1x10 ⁻⁷	4.8x10 ⁻⁸	6.5

L-cysteine and glutathione both possess a free thiol group, and yield reductive dissolution rates with PbO₂ that are substantially higher than rates with MnO₂. L-cysteine is an amino acid residue, while glutathione is an important nucleophile in blood. Glutathione, ascorbic acid, and uric acid are the most important reductants in blood and respiratory tract fluids.

Sialic acid also yields reductive dissolution rates with PbO₂ that are higher than rates with MnO₂. N-Acetyl-D-galactosaminitol (not shown above) has a structure similar to sialic acid, but lacks the α-ketoacid moiety. It serves as the core of many mucins, molecules that coat respiratory and digestive tracts. PbO₂ reductive dissolution rates by sialic acid and N-acetyl-D-galactosaminitol are quite similar. Urocanic acid is a component of sweat.

Actual biofluids contain a mix of low-, medium-, and high-molecular weight biochemicals. In addition to the chemical effects examined here, physiochemical effects are probably also important in determining reductive dissolution rates.