

The Removal of Arsenic from Groundwater Using Permeable Reactive Barriers (PRBs)

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PRBs are engineered systems that provide passive interception and in situ treatment of contaminated groundwater. Within the past decade, PRBs have been applied for the control and remediation of a range of organic and inorganic contaminants in groundwater. In recent laboratory batch and dynamic column tests, a selection of reactive materials that effectively attenuate dissolved arsenic in groundwater to low levels (<0.01 mg/L) have been identified. Basic oxygen furnace (BOF) slag promotes the oxidation of As(III) to As(V), which is subsequently sorbed to the BOF surface. Activated alumina also removes arsenic by the sorption of both As(III) and As(V). Zero-valent iron (ZVI) reduces As(V) to As(III), which is subsequently removed from solution by co-precipitation. In groundwater containing sulfate, ZVI and mixtures containing organic carbon can promote sulfate reduction and the subsequent precipitation of sparingly soluble arsenic and other metal sulfides. The laboratory tests have been conducted using neutral and low pH groundwater, with arsenic concentrations of as much as 4 mg/L. Groundwater chemistry, contaminant flux, the required duration for treatment, and costs for materials and installation will influence the selection of specific media for field-scale PRBs.

Blowes et al. (1999ab) provide detailed documentation of the installation and performance of a zero-valent iron PRB that was installed at Elizabeth City, NC, to remediate chromium (VI) and several chlorinated solvents in groundwater. The PRB was installed in 1996 in co-operation with the United States Environmental Protection Agency and the United States Coast Guard. The PRB was installed in a continuous trench approximately 46 m long, 7 m deep and 0.6 m in thickness in the direction of groundwater flow. Influent concentrations of Cr(VI) have been as high as 5 mg/L, but removal of chromium to non-detectable levels (<0.0025 mg/L) has been achieved since installation of the PRB. In fact, Cr(VI) was not detected in multi-level monitors approximately 0.01 m into the zero-valent iron zone during the first three years of monitoring. Eh conditions were strongly reducing and pH increased from approximately 6.5 up-gradient to between 9 and 11 within the PRB. Laboratory investigations indicated the removal mechanism for Cr(VI) was abiotic and was achieved by reduction to Cr(III) and the precipitation as Cr(III) oxyhydroxide or co-precipitation with iron oxyhydroxide

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minerals on the iron-grain surfaces (Blowes et al., 1997). Concentrations of alkalinity, calcium, magnesium and manganese also decreased as groundwater migrated through the wall. Geochemical and reactive transport modelling suggested that the precipitation of secondary carbonate minerals was responsible for these observed decreases in concentrations, and that the secondary precipitates may contribute to declining hydraulic conductivity and reactivity of the zero-valent iron with time. Reactive-transport modelling estimated that the porosity of the entry zone of the PRB may decrease from the initial 0.5 to 0.36 after 20 years (Blowes and Mayer, 1999b).

Pilot and full-scale PRB systems have also been installed to treat technetium (Tc(VII)), uranium (U(VI)) and molybdenum (Mo(VI)) in groundwater (Blowes et al., 2000; Naftz et al., 2000). Zero-valent iron has achieved reductive precipitation of these electroactive metals. The removal of other electroactive metals such as arsenic and selenium from groundwater using reactive materials has been evaluated at the laboratory scale, but to our knowledge, no field-scale PRBs have yet been evaluated.

In typical groundwater environments, arsenic may be present in both the As(III) and As(V) states. As(III) is generally more mobile in water than As(V), and has higher toxicity (Korte and Fernando, 1991). McCrae (1999) and McCrae et al. (1999) observed rapid removal of arsenic from water in static batch tests using zero-valent iron. For arsenic, As(V) concentrations decreased from 1 to less than 0.018 mg/L in a two-hour period. Similar removal was observed for As(III) and As(V)/As(III) mixtures. In a column containing 10 wt. % iron in silica sand, McCrae et al. (1999) observed the removal of approximately 0.5 mg/L of both As(III) and As(V) in simulated groundwater. Effluent concentration of total As was less than 0.018 mg/L for more than 320 pore volumes.

McCrae (1999) examined zero-valent iron from the batch experiments using energy dispersive x-ray (EDX) analysis and x-ray photoelectron spectroscopy. Arsenic was found associated with the grain surfaces, and with a secondary precipitate coating the grains. Both As(III) and As(V) were identified, but a higher ratio of As(III) to As(V) than in the initial solution suggested that reductive precipitation, possibly as a co-precipitate with iron, had occurred. These results are consistent with Su and Puls (2001), who experienced greater difficulty in liberating As(III) and As(V) from zero-valent iron as initial reaction time between arsenic-rich water and zero-valent iron increased.

Subsequent testing performed at the University of Waterloo since 1999 has demonstrated the removal of as much as 15 mg/L total arsenic in groundwater from industrial and mine sites using reactive mixtures. Arsenic concentrations in the effluent of the columns have typically been less than 0.002 mg/L. The reactivity of the iron and mixtures indicates that PRBs designed to function for years to more than ten years could be constructed at these sites. Arsenic removal is enhanced where there is sulfate present in the groundwater and sulfate-reducing conditions develop within the PRB. The formation of stable and sparingly soluble, arsenic sulfide minerals are favored under these conditions.

In addition to evaluating the performance of zero-valent iron, McCrae et al. (1999) found columns containing 10% BOF (Basic Oxygen Furnace) slag and 20% activated alumina

in agricultural limestone and silica sand mixtures attenuated the transport of arsenic in synthetic groundwater containing 0.5 mg/L of both As(III) and As(V). The attenuation mechanism for these materials is sorption. The subsequent laboratory tests using BOF slag also attenuated the advance of arsenic through treatment columns, but concentrations of arsenic of several to several tens of micrograms per liter were generally present in the effluent. Thus, the potential applicability of specific reactive materials would need to be evaluated with respect to specific remedial objectives.

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