The Removal of Arsenic from Groundwater Using Permeable Reactive Materials

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Abstract

The use of permeable reactive barriers (PRB) for the treatment of contaminated groundwater is gaining interest as an alternative to conventional (pump and treat) methods. Laboratory experiments investigating the potential for treatment of arsenic contaminated groundwater through the use of potential reactive barrier materials have been in progress since October 2000. For this investigation, arsenic contaminated groundwater collected from a mine located in Ontario, Canada, is continuously passed through two laboratory columns, one containing 100% zero valent iron and the other a mixture containing 20% zero valent iron. During the experiments, the influent groundwater has contained between 9 and 15 mg/L of dissolved arsenic. The AsIII:AsV ratio of the groundwater input varies from dominantly AsIII to dominantly AsV. Flow through the columns (0.2 to 0.4 pore volumes/day; [PV/day] or 25 to 65 m/a) is several times the groundwater velocity measured at the mine site (10-40 m/a). Results indicate that both reactive mixtures are capable of removing the dissolved arsenic to below current Canadian interim guideline concentration of 0.025 mg/L and the new U.S. EPA maximum contaminant level of 0.01 mg/L for more than 200 pore volumes. After treating 200 PV of water containing an average of 12 mg/L As, concentrations exceeding 0.1 mg/L of As migrate less than 5 cm into the reactive material. Concentrations exceeding 0.05 mg/L have not moved more than 12 cm into the reactive material. The position of the reaction front has been immobile for approximately 2 years. Current results suggest almost a 2:1 mass ratio of As removed vs. reactive material consumed. These results indicate rapid removal of the dissolved As and a negligible decrease in the reactivity since the start of the experiment. Under field conditions, (e.g. a 1 m thick *in situ* PRB installation), this represents the potential for several years or decades of treatment.

INTRODUCTION

The conventional approach for groundwater remediation is to pump the groundwater and treat it at surface. Research conducted at a mine site in northern Ontario indicates movement of dissolved As in a confined aquifer adjacent to the tailings area. The movement of As in the aquifer may be attenuated partly by natural processes, including adsorption and reductive precipitation (Ross et al., 1999). These mechanisms are, however, not expected to prevent off-site migration of As. *In situ* permeable reactive barriers, installed in the path of the As-bearing groundwater, are being evaluated as an alternative method for preventing off-site migration of the As (McRae et al., 1999b). The University of Waterloo holds several international patents, dating back to 1994, for the use of zero valent iron in *in situ* permeable reactive barrier installations for the treatment of electroactive metals contained in groundwater (Canadian Pat. # 2,062,204; U.S. Pat. # 5,514,279).

This paper describes some of the findings of recent investigations, conducted by University of Waterloo researchers, into the remediation of As-bearing water using permeable reactive materials. The paper also describes an ongoing laboratory investigation that has two objectives. One objective is to evaluate and compare the As treatment performance of a reactive mixture containing 20% zero valent iron (20Fe) to a reactive medium composed 100% of zero valent iron (100Fe). Mixtures containing less than 100% zero valent iron have the potential to

provide effective As removal, but at lower cost than a 100% Fe reactive medium.

Competition for the reactive properties of the zero valent iron by groundwater components other than As may hinder or improve the performance of zero valent iron as a reactive medium at contaminated sites. The second objective is to evaluate the performance of both reactive mixtures for the treatment of groundwater at a mine site.

BACKGROUND

The ingestion of arsenic may lead to serious health effects (Dhar et al., 1997). Arsenic is a redox sensitive metal that occurs in groundwater in two valence states, arsenite (AsIII) and arsenate (AsV). In its reduced form, As^0, arsenic is insoluble. Under the reducing and neutral to acidic pH conditions typical of most natural groundwaters, As(III), generally in the form H_3AsO_3 (arsenious acid), is dominant. Under more oxidizing conditions, As(V) is dominant in forms including H_3AsO_4, $H_2AsO_4^-$, $HAsO_4^{2-}$ and AsO_4^{3-} (Farrell, et al., 2001; Hug et al., 2001) Under neutral pH conditions, arsenite is more mobile than arsenate in groundwater. In a reduced state, arsenic may form sparingly soluble precipitates such as As_2S_3 or FeAsS, and may be co-precipitated with ferric hydroxides.

Due to its sensitivity to redox conditions, one option to control the mobility of arsenic is to manipulate the redox conditions of groundwater. Zero valent iron is a strong reductant, and has been found suitable for reducing the oxidized form of many dissolved metals (Blowes et al., 1997; Gu et al., 1998; McRae et al., 1999b; Blowes et al., 2000; Morrison et al., 2001; Su & Puls, 2001). McRae (1999a,b) conducted a set of laboratory batch and column experiments evaluating the potential for the treatment of As bearing water with mixtures containing zero valent iron.

The laboratory batch and column experiments initiated by McRae in 1996 indicated that reactive mixtures containing zero valent iron remove dissolved As from water containing 1 to 1.8 mg/L of As (1:1 ratio of AsIII to AsV) to less than 0.018 mg/L. Removal occurred primarily during the first 2 hours of the experiment, with treatment to below 0.05 mg/L within 3 hours. Analysis of reactive materials from the batch experiments by energy dispersive X-ray analysis (EDX) and X-ray photoelectron spectroscopy (XPS) suggests that the As(III) and As(V) were removed from solution by adsorption and also by coprecipitation with goethite (FeOOH) at the surface of the iron particles, after reduction of As(V) to As(III) by the zero valent iron (McRae, 1999a). In the column experiments, water containing approximately 1 to 1.6 mg/L As (1:1 molar ratio of As(III) to As(V)) has been treated to below 0.05 mg/L (total As) for more than 1200 pore volumes (Figure 1).

EXPERIMENTAL PROCEDURE

The laboratory columns investigating the removal of As from groundwater under flowing conditions were initiated by Spink (2001) in October 2000. The experiment consists of two Plexiglas™ columns packed with permeable reactive material, through which As-bearing (7-16 mg/L As) groundwater collected from an aquifer at a mine site in northern Ontario is pumped continuously. Two permeable reactive materials are being evaluated: one composed 100% of zero valent iron (100Fe) and the other a mixture containing 20% zero valent iron (20Fe).

The columns (5 cm in diameter and 41.8 cm long) were filled with the reactive media, and were operated in an upflow manner. Input water was pumped into both columns from one source, and at the same flux. However, because of differences in the packing density and the porosity of the two reactive media, the pore volume (PV) of the 20Fe column is only 56% of the 100Fe column PV. Hence, the velocity in the 20Fe column is roughly double that in the 100Fe column. The porewater flow in the columns is 3 to 5 times more rapid than groundwater flow velocities at the mine site. At this velocity, total residence time is 3 days in the 20Fe column and 5.5 days in the 100Fe column.

The groundwater used in the experiments contains moderate levels of several dissolved species including SO_4, Cl, Ca, Mg and Fe, a condition not present in the testing conducted by

McRae (1999). Table 1 describes the major ion chemistry of the input water, which was fairly consistent during the experiment. The combined interaction of these species with the zero valent iron is not well known. Favourable or adverse effects on the performance of the zero valent iron in its treatment of As-bearing groundwater or in the permeability of the reactive materials should become evident from these experiments.

Table 1. Typical chemistry of input water for the column experiments. Concentrations are in mg/L.

Parameter	Value
pH	7.2
Eh (mV)	329
CO_3	62
As_{Tot}	10
SO_4	562
Ca	99
Fe	0.4
K	22
Mg	64
Mn	0.4
Na	133
Si	3
Zn	0.1
Cl	73

The input water was collected monthly from piezometers installed at the mine site. Previous research at the mine (Ross, *et al*., 1999; Stichbury *et al.*, 2000) indicates that 50-90% of the total As in freshly collected groundwater from this site is in the As(III) valence. Typically the As ratio in the input water started as dominantly (>50%) As(III) and oxidized almost completely to As(V) by the end of each month, with <10% decrease in the total As, due to precipitation in the sample container. Recently, efforts have been made to better preserve the natural As(III):As(V) ratio in the input water during the month that it is pumped into the columns.

Sampling ports installed at 2-3 cm intervals along the length of the column facilitated profile measurement of porewater chemistry at regular intervals during the experiment. Influent and effluent water samples were also collected for analysis. Samples were collected and immediately analysed for pH, Eh and alkalinity, while additional sample was collected and filtered to 0.45 µm. Cation samples were acidified. A suite of cations was analysed by inductively coupled plasma-optical emission spectrometry (ICP-OES) and separate As samples were analysed by hydride generation and atomic absorption (HG-AA) at the University of Waterloo or by graphite furnace atomic absorption (GF-AA) at Philip Analytical Laboratories in Mississauga.

RESULTS

Figures 2 and 3 illustrate the treatment of As in the 20Fe and 100Fe columns, respectively. Arsenic contained in the groundwater is removed at similar rates, if not faster, in the column with the mixture containing 20% zero valent iron. Note that the residence time in this column is less than in the 100Fe column. In both cases, however, the majority of As removal, occurs within the first 5 cm travel distance into the reactive material. In this distance, input As concentrations of 7 to 16 mg/L decrease to ~1 mg/L. Over the next 5 cm travel distance in the columns the As concentration decreases further to values below detection limits, which were between 5 and 20 ppb depending on the laboratory and analysis procedure used. For the duration of the experiment, effluent As concentrations have remained below 0.01 mg/L (Figure 4).

After more than 113 PV of flow in the 100Fe column and more than 207 PV in the 20 Fe column, water containing As concentrations above the maximum drinking water limit has progressed only ~11 cm distance into the reactive material. As a result, the rate of movement of As through the columns cannot be quantified. A conservative estimate can be based on the assumption that the treatment capacity of the column, up to the observed As removal front, has been consumed.

With this assumption, the 20Fe mixture treats more than 18 pore volumes of water per centimeter of column length, and the 100Fe treats more than 10 pore volumes of water per

centimeter of column length. Noting that the PV of the 20Fe column is only 56% that of the 100Fe column, similar volumes of water are treated (10 PV normalized to the 100Fe column).

These calculations should be considered conservative, however, because the position of the As front has been stable for tens to hundreds of pore volumes of treatment. If we instead assume the treatment capacity of the reactive material in the first 11 cm of column length has not been consumed, these performance figures should improve moderately with continued operation of the columns.

If these observations are extended to the mine site from which the water was collected, a typical 1 m thick PRB intersecting a plume of As-bearing groundwater moving at 40 m/a, has the potential to treat groundwater for several decades. These estimates are dependent on As concentrations in the water.

SUMMARY

Porewater, containing 7-16 mg/L As, collected from the aquifer at a mine site, has been treated to less than 0.01 mg/L As in laboratory column experiments operated at flow rates several times greater than the groundwater velocity at the mine site. Two reactive mixtures are being evaluated in the column experiments. Current results, with the treatment of 113 to 207 pore volumes of water, suggest that an effective barrier can be constructed of either reactive material. The fact that similar treatment is observed in both columns, but with the 20Fe column having a higher flow velocity, suggests that the As removal mechanism is equally, if not more efficient with the 20Fe mixture than with the 100Fe mixture.

With continued operation of the columns, estimates of the potential longevity of the reactive materials will be improved. An evaluation of the mechanisms responsible for As removal in both columns will be conducted at a later stage in the experiment, when the columns can be disassembled for examination.

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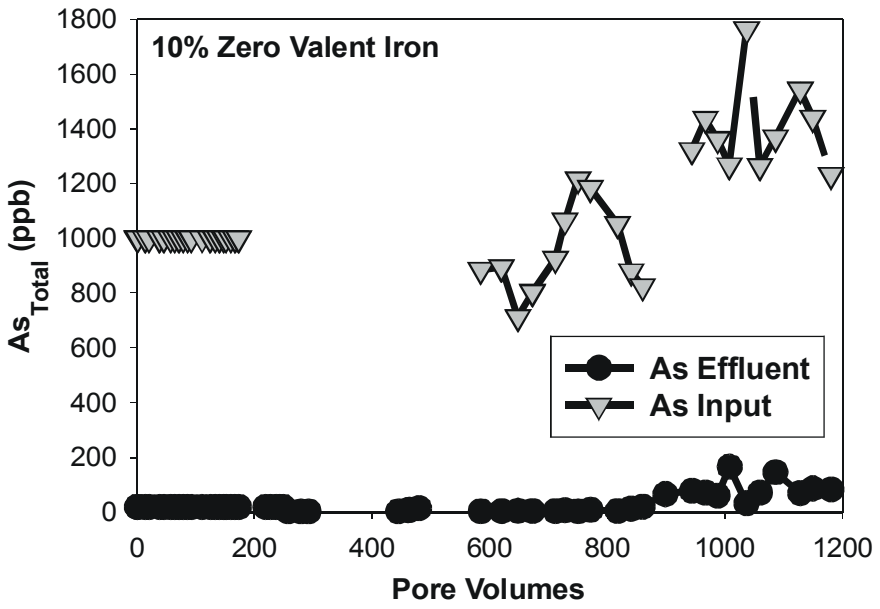

Figure 1. Removal of As from water containing 1 to 1.8 mg/L As (after McRae, 1999a)

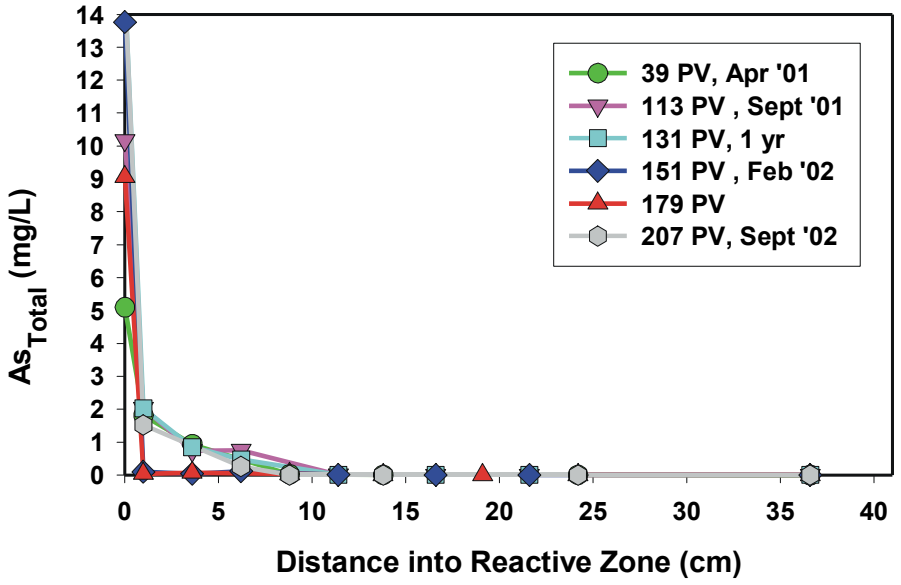

Figure 2. Arsenic concentration profile in the 20% Fe column at selected times.

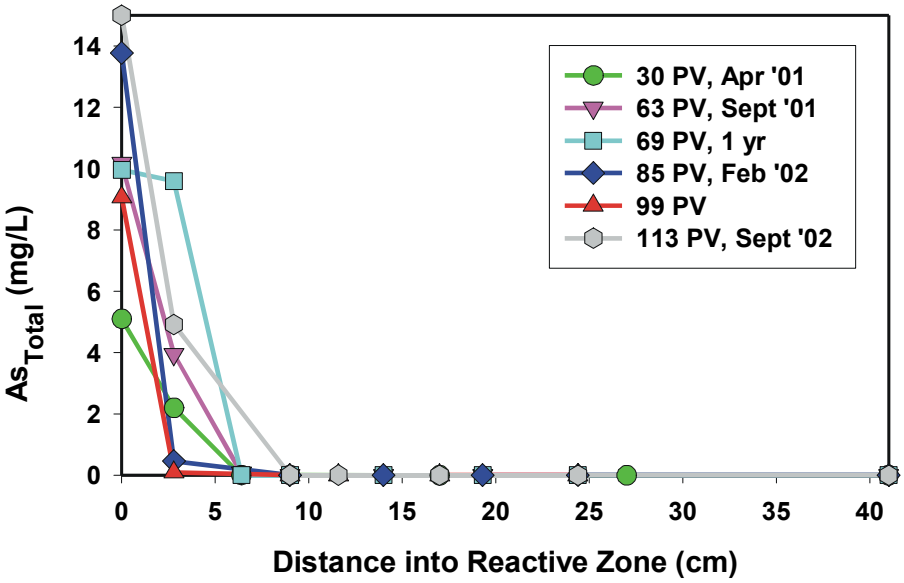

Figure 3. Arsenic concentration profile in the 100% Fe column at selected times.

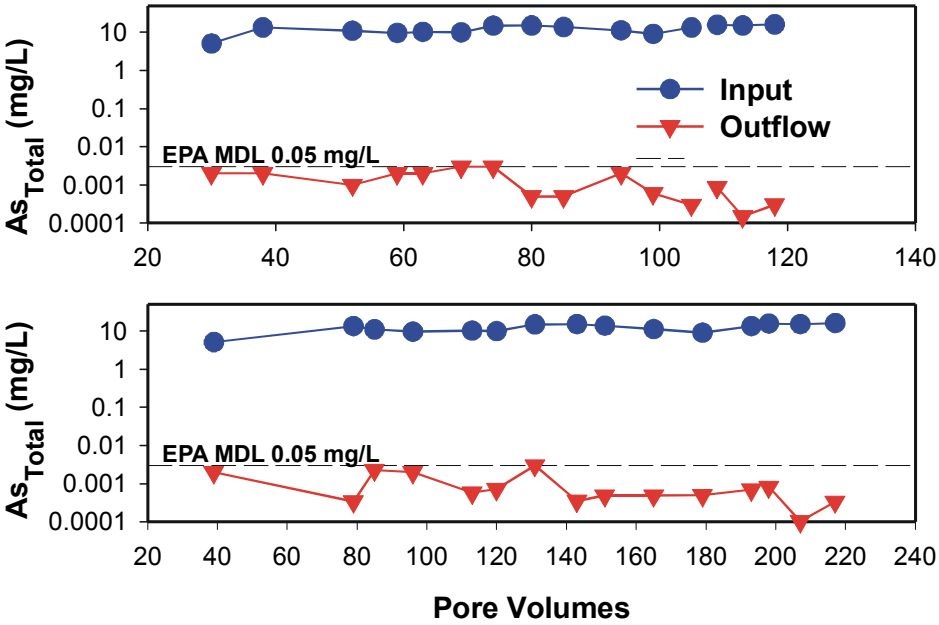

Figure 4. Input and effluent As(tot) concentrations for both columns vs. pore volumes of water treated.