

## **Permeable Reactive Barriers for In-Situ Treatment of Arsenic-Contaminated Groundwater**

**Jeff Bain** (jbain@uwaterloo.ca), David Blowes, David Smyth and \*Carol Ptacek  
(University of Waterloo, Waterloo, Canada)

(\* also Environment Canada, Burlington, Canada)

John Wilkens (DuPont Engineering Research and Technology, Wilmington, DE)

Ralph Ludwig (US Environmental Protection Agency)

**ABSTRACT:** Many areas around the world are under increasing pressure to protect local inhabitants from arsenic in groundwater. Arsenic (As) is a toxic metal that commonly occurs in groundwater as a result of natural processes and anthropogenic activities. Laboratory and field research has shown that permeable reactive barriers (PRBs) containing a variety of materials can treat As contaminated groundwater. Since 2002 we have been evaluating the performance of several PRBs installed at industrial sites in Canada and USA for the treatment of As-contaminated groundwater. The sites where these PRBs are located include a mine tailings facility, fertilizer and chemical manufacturing sites, a thermal-electric power generation facility and an electrical transmission site. The reactive material in these PRBs includes mixtures based on zero valent iron (ZVI) filings with or without an organic carbon (OC) source such as wood chips or compost or alternatively, basic oxygen furnace slag (BOFS). Removal of As to below drinking water limits (currently 0.05 mg/L Canada; 0.01 mg/L mandate in USA effective January 23, 2006) has been observed in all of these PRBs. The PRBs range from test scale a few meters long to 600 m long. Although the reactive materials in each PRB (except BOFS) are similar, there is significant diversity in the groundwater geochemistry and flow conditions encountered by each of the PRBs. Despite this diversity, groundwater geochemical monitoring at these sites indicates that two or more years after installation, removal of As is still occurring in all of the PRBs, and there is no indication that the level of treatment is diminishing.

### **INTRODUCTION**

Permeable reactive barriers are gradually being accepted as a remedial alternative for some groundwater contamination problems, including arsenic contaminated groundwater. A PRB consists of a trench filled with reactive materials placed in the pathway of contaminated groundwater. The reactive materials are selected based on their contaminant-removal and permeability properties. As contaminants flow through the reactive materials, they are degraded, precipitated or adsorbed to the reactive material, thus removing the contaminant from solution. Ideally, the reactive material will have a long lifetime of reactivity and will remove and retain the contaminants permanently.

Laboratory studies have proven several materials to be effective for the removal of As from groundwater. Zero valent iron has been evaluated in batch studies and in laboratory and field columns (Blowes et al., 1997; Gu et al., 1999; McRae et al., 1999; Farrell et al., 2001; Su and Puls, 2001; Nikolaidis et al., 2003) for removing Fe, U, Cr, As and other metals from contaminated groundwater. In these studies, As was removed from solution

by several different mechanisms, including coprecipitation with iron oxyhydroxides and green rust and adsorption to iron oxide surfaces. In a column study, Bain et al. (2003) evaluated the performance of a mixture of zero valent iron plus organic carbon, for the removal of As from sulfate-bearing mine-water. In that study, the proposed mechanisms of As removal are the same, with additional removal by As-sulfide precipitation, following sulfate reduction. Laboratory investigations conducted by the University of Waterloo (UW) and by DuPont indicate that basic oxygen furnace slag (BOFS) is also effective for the treatment of As contaminated water. BOFS is a waste product from the manufacturing of steel. The mechanisms of As removal from groundwater by BOFS are not well defined at this time. Due to the high surface area of iron oxides and the abundance of calcium in the BOFS, removal is presumed to be a combination of adsorption removal of arsenate and potentially the precipitation of calcium arsenate minerals.

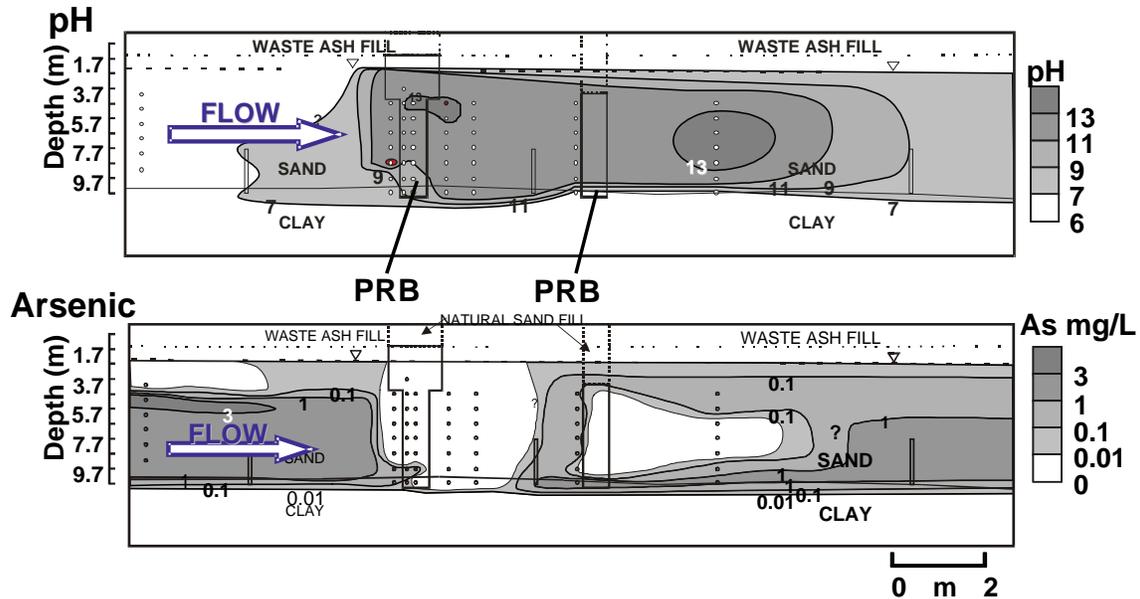
Under field site conditions, variables such as the nature of the groundwater flow system in and around the PRB, as well as ambient geochemical conditions affect the performance of the PRBs. In this paper, we describe our investigation of four PRBs, installed at industrial sites in 2002 for treatment of As in groundwater. Two of these PRBs contain mixtures of zero valent iron and organic carbon, and the other two contains BOFS. To our knowledge these are the first field-site installations of PRBs using these materials for the treatment of groundwater As.

## **METHODS**

To facilitate monitoring of the geochemistry within and up/downgradient, piezometers were installed at close spacing vertically and in the direction of flow (see Figures) in each of the PRBs. Detailed groundwater chemistry, including field measurements of pH, Eh, alkalinity, As speciation and sample collection for analysis of dissolved metals and cations was done annually. Where possible, cores of the reactive material were collected near the piezometers for mineralogical analysis. The mechanisms responsible for As removal from the water are under investigation by means of sequential chemical extractions, geochemical modelling with MINTEQA2 (Allison et al., 1990) and mineralogical examination by SEM, x-ray fluorescence spectroscopy and synchrotron x-ray absorption spectroscopy. This information will support our evaluation of the long-term stability of the removed As and about the longevity of the reactive materials.

## **RESULTS AND DISCUSSION**

**Full-Scale Basic Oxygen Furnace Slag PRB.** In-house studies conducted by E.I. DuPont de Nemours and Company confirmed that As in groundwater at one of their industrial sites could be treated with BOFS. On the basis of these results, in June 2002 DuPont installed a full-scale (600 m long x 11.3 m deep) PRB composed of BOFS for the treatment of As-contaminated groundwater at an industrial site in East Chicago, Indiana. The installation consists of two parallel 76 cm wide PRBs, separated ~4.5 m in the direction of flow. Parallel PRBs were installed to minimize the potential of As transporting untreated past the PRBs. The PRBs were installed in a vacant part of the property using a trenching machine, which operated from a bench, excavated ~3 m below grade. The PRB is installed from the base of a fill layer at the site (1.5 m) to a depth of 11.3 m, including 0.7 m penetration into a clay aquitard (Figure 1). The aquifer consists of aeolian fine sand. Groundwater at the site flows at approximately 5-10 m/yr, and between 20 and 40 pore



**FIGURE 1. Vertical cross-section of pH and As (mg/L) across the mid-line of the full-scale basic oxygen furnace slag (BOFS) PRB. Data are from 1 year after installation.**

volumes of water flowed through the PRB as of July 2005. The average residence time for water in each of the PRBs is about five weeks.

Groundwater at the site is contaminated with 1-3 mg/L of As, predominantly as arsenite (As(III)). The groundwater is neutral-pH and slightly aerobic (Eh ~50 mV). Other dissolved constituents in the groundwater include zinc ( $\leq 34$  mg/L) and lead ( $\leq 8$  mg/L), which are believed to be infiltrating downward from the surface fill layer, as the concentrations are highest near the water table. Dissolved sulfate concentrations range up to 4000 mg/L and are most concentrated at the base of the aquifer.

The pH of water that passes through the barriers increases from near neutral to  $>12$  in the BOFS. The high pH conditions result from the dissolution of lime (CaO) and portlandite (Ca(OH)<sub>2</sub>) contained in the BOFS. As of July 2005, water distinctly influenced by the PRBs (pH=8) migrated to approximately 8 m downgradient of the PRBs, while pH 12 water was at half this distance, indicating moderate retardation of the high pH plume. The pH of water in contact with the BOFS is diminishing as the alkaline materials are depleted. The advance of this high pH water in the aquifer is being monitored.

Dissolved As concentrations decrease sharply from 1-3 mg/L upgradient of the PRB to below detectable values ( $< 0.002$  to  $0.02$  ppb) in the aquifer sand immediately upgradient of the PRB and within the BOFS. A zone of water with  $< 0.05$  mg/L As has developed between the two barriers and extends ~2.5 m downgradient of the first PRB in July 2005. A similar zone of treated water containing 0.06-0.25 mg/L of As extends ~2.3 m past the downgradient PRB (herein called the second PRB). Monitoring wells situated at ~6.5 m downgradient of the second PRB first showed evidence of treated water (As  $< 1$  mg/L) arriving in July 2005.

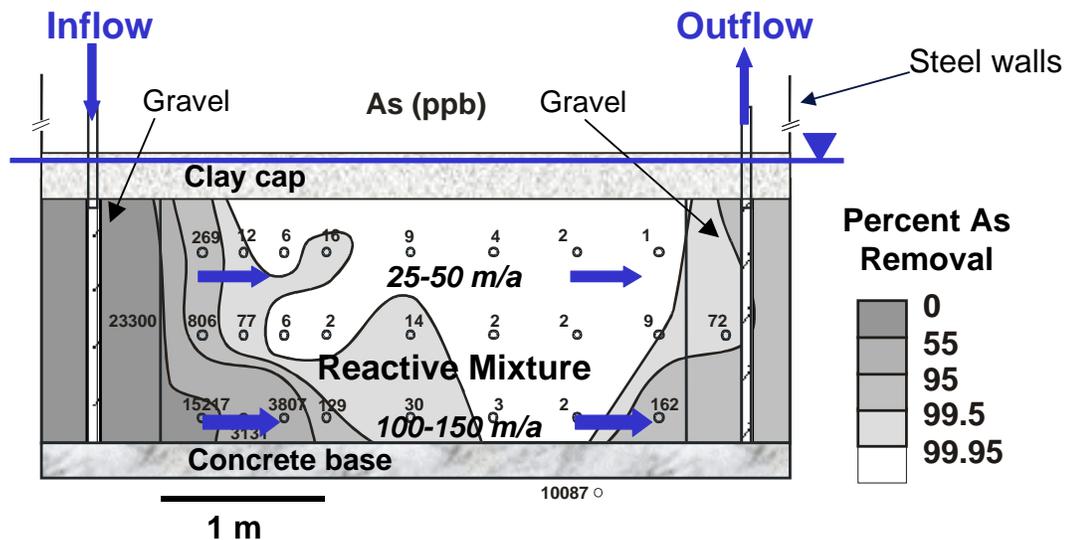
A preliminary interpretation of the As treatment mechanisms at the site is presented here. Dissolved As is removed from groundwater as it enters the zone where BOFS is

present. The removal process begins in the natural materials upgradient of the first detail piezometer bundle (~0.5 m upgradient of the PRB). These upgradient sands accumulated ~150 mg/kg of As, as of June 2004. Selective extraction results indicate that the As in this zone is associated with secondary amorphous iron hydroxides similar to ferrihydrite ( $\text{Fe}(\text{OH})_3$ ), probably due to coprecipitation. The precipitation of As-bearing iron oxides is induced by the sharp increase in pH conditions in the sand adjacent to the PRB, where trace amounts of BOFS are present. This is supported by a strong decrease in the concentration of dissolved Fe (from  $> 50$  to  $< 0.1$  mg/L) and MINTEQA2 calculations, which indicate that the water is slightly supersaturated with respect to ferrihydrite in the front part of the treatment zone. Selective extraction results indicate that As is retained in other ways as well, including association with weak-acid (pH 5) soluble phases and by adsorption to mineral surfaces. The As is also associated with a currently unidentified residual phase that is soluble in aqua regia. The precipitation of discrete As-bearing minerals is not indicated by the MINTEQA2 calculations, although the water is near equilibrium with respect to Ca-arsenate ( $\text{Ca}_3(\text{AsO}_4)_2 \cdot 6\text{H}_2\text{O}$ ) in a few samples from the PRB. In addition to the precipitation of As-bearing phases, the potential for gypsum and calcite precipitation in the PRB materials exists due to alkalinity and sulfate in the groundwater and the availability of Ca in the slag. The PRB is being monitored for evidence of degraded reactive or hydraulic performance due to accumulation of these materials.

A few centimeters into the PRB (100% BOFS) the slag accumulated ~70 mg/kg of As, as of June 2004. In these areas, the extraction results suggest that the As is primarily associated with weakly crystalline iron oxide surfaces and aqua regia soluble solids, with lesser amounts that are adsorbed or soluble in weak acid. The nature of the As-bearing phases continues to be investigated. Dissolved lead and zinc are also removed from the groundwater as it progresses through the PRB. Lead concentrations decrease from  $\leq 8$  mg/L to below detection (0.05 mg/L). Zinc concentrations decrease from  $\leq 38$  mg/L to below detection (0.009 mg/L). The mechanisms of Pb and Zn removal are being evaluated. The adsorption of heavy metal cations to iron (hydr-) oxide surfaces and the precipitation of hydroxide phases may be responsible for the removal of Pb and Zn.

**Mine Tailings Pilot Scale Iron Filing-OC PRB.** A gold mine tailings impoundment in Canada is the site of a pilot scale PRB installation. At this site, neutral pH tailings porewater contains elevated concentrations of dissolved As. Based on the successful laboratory results of Bain et al. (2003), a homogeneous mixture of zero valent iron filings (Connelly GPM Inc.), locally available wood waste (coniferous tree bark and wood chips) and gravel was installed in an enclosed sheet-piling cell, in a convenient part of the tailings impoundment. Enclosing the system isolates it from the ambient tailings, so that geochemical and flow conditions can be controlled. The installation was done in July 2002. The PRB mixture is intended to promote As-sulfide precipitation following bacterially mediated sulfate reduction, in addition to providing an environment where As may be adsorbed or coprecipitated. Locally available organic material was used, rather than attempting to optimize the organic material for sulfate reduction. Adsorption of the dissolved As onto the surfaces of the iron filings and coprecipitation with secondary coatings on the iron are also expected to remove As.

The base of the cell is poured concrete. Because the installation has four walls and a base, flow is constrained to be horizontal through the use of inflow and outflow pumps, at opposite ends of the PRB. The reactive material forms a unit that is 1.5 m vertical thickness (below the water table), 2 m wide and 3.5 m in the direction of flow (Figure 2). The purpose of this installation is to evaluate the performance of the reactive mixture under flow-controlled, normal to stressed operational conditions. Neutral pH tailings water containing 20-25 mg/L of As, ten times the average groundwater concentration, is continuously pumped into the PRB. Arsenite (AsIII) is the dominant valence of As in the water. No other dissolved metals are at levels of concern. Sulfate concentrations in the water are around 500 mg/L. Inflow and outflow pumping rates are balanced to maintain linear velocities that range between 2 and 10 times average site groundwater velocities. The PRB was not pumped between December and May most years due to freezing conditions. As of February 2006, more than 75 pore volumes of flow have been treated, with residence times ranging from 7 to 14 days.



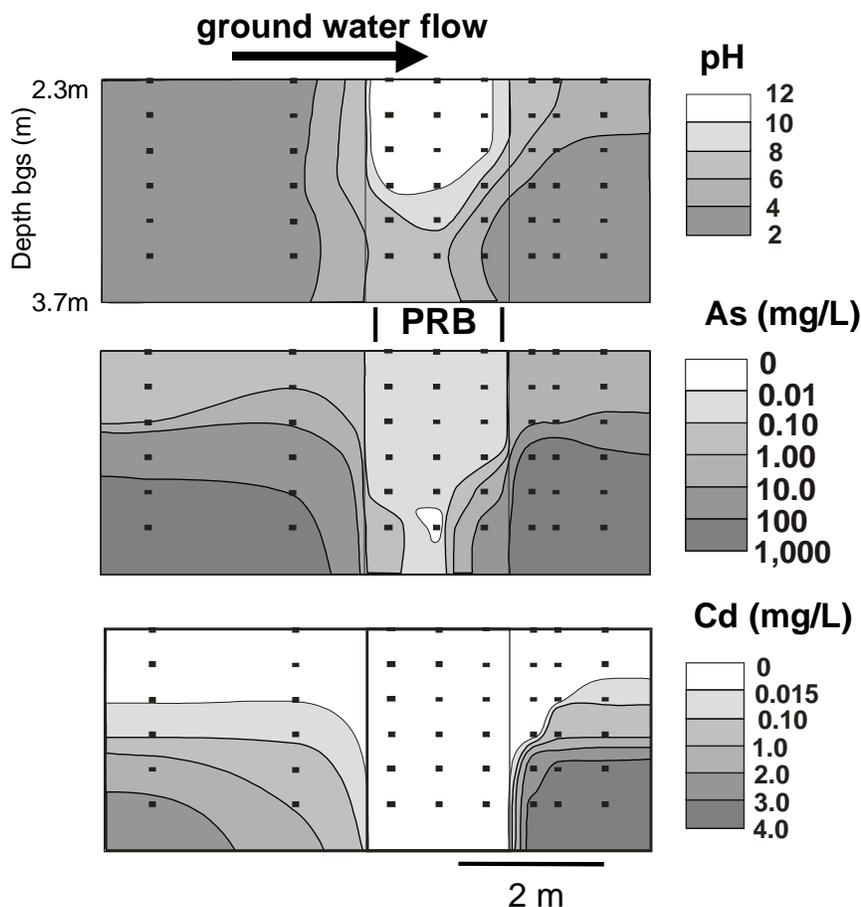
**FIGURE 2.** Vertical cross-section of As (ppb) within the pilot scale iron filings + organic carbon PRB installed below the water table in a gold mine tailings impoundment. Data are from 2 years after installation. The four vertical walls of the PRB are steel sheet pilings. Non-reactive gravel inflow and outflow zones define the opposite ends of the system.

Over more than three seasons of operation, groundwater containing 15-25 mg/L of dissolved As has successfully been treated to < 0.01 mg/L in the PRB. The degree of As removal is consistent throughout the PRB, however, heterogeneities in the flow system through the PRB complicate the interpretation. Groundwater tracer tests using dissolved bromide indicate that water flows most rapidly through the base of the PRB cell and is slow flowing near the water table. The tracer information is supported by borehole dilution technique estimates of groundwater velocity. The reasons for the flow heterogeneity are thought to be a result of increased percentage of gravel and iron the deeper materials, due to separation during emplacement, and preferential flow along the cement-mixture contact.

The water pumped into the PRB rises from pH 7.4 to pH 9.5 and the Eh of the system becomes very reduced due to the reduction of water as the iron filings corrode. Recognizing the complexity in the flow system in the PRB cell, the removal of As occurs relatively quickly, showing a gradual decrease in As concentrations to < 0.01 mg/L over 1.5 m of travel distance in the fastest flowing part of the PRB. Based on our interpretation of flow in the PRB mixture, this correlates to approximately six days residence time required for this degree of As treatment. In the figure, it is evident that elevated As concentrations (> 1 mg/L) occur at several of the points downgradient of where As has already been removed. In these areas, inward seepage of As-bearing groundwater from the tailings adjacent to the PRB is suspected. This is supported by the reoccurrence of other components of tailings water (Ca, Cl, SO<sub>4</sub>) in these positions in the PRB. Short-circuiting of flow along the cement base and along the sheet piling walls is also suspected to occur. This allows water to travel from the inflow end of the PRB to the outflow end in less than one day, with minimal contact with the reactive materials. These specific mechanisms would not be encountered in non-pilot scale applications of the technology because a concrete base and sheet piling walls would likely not be used. Given that the treatment is occurring at As concentrations and groundwater velocities that are higher than are expected at the site, the reactive mixture being used is promising for full-scale application. The PRB is being monitored for evidence of degraded reactive or hydraulic performance due to accumulation of secondary phases or degradation of the reactive materials.

The mechanisms of As removal are being evaluated. Analyses indicate that the solids in the deepest parts of the PRB, within 1 m of the input zone contain up to 0.76 wt% As. A decrease in dissolved SO<sub>4</sub> concentrations, complimented by isotopic enrichment of <sup>34</sup>S in the dissolved SO<sub>4</sub>, as well as detectable amounts of dissolved H<sub>2</sub>S support the conclusion that bacterially mediated sulfate reduction is occurring. Selective extraction analysis and additional XANES work and mineralogy are being done to gain insight into the As removal mechanisms.

**Phosphate fertilizer site, pilot scale iron filing-limestone-OC PRB.** Water at this site differs distinctly from the other two sites. Here, sulfuric acid was used in the production of fertilizer. The groundwater at the site has low pH values (2-4) and high concentrations of dissolved As (depth-specifically up to several hundred mg/L), as well as elevated concentrations of Fe, Cd and Pb. A reactive mixture consisting of zero valent iron filings, compost and gravel was installed in an excavated trench. Five percent by volume limestone gravel was added to the mixture to improve pH conditions for sulfate reducing bacteria. The trench was held open during construction using guar gum biopolymer, which was displaced out of the trench during placement of the reactive mixture. The PRB is 8.2 m wide (across flow), extends 2.3 m below the water table and is 1.8 m in the direction of flow (Figure 3). The PRB was installed in the fall of 2002 and has been monitored by UW and the U.S. EPA. In this document we will highlight how the reactive materials perform in comparison to the pilot scale PRB at the gold mine. Ludwig et al., (abstract, this volume), presents additional information about the site, the installation and monitoring results.



**FIGURE 3. Vertical cross-section of pH, As and Cd within the pilot scale iron filings + organic carbon + limestone PRB installed at the fertilizer manufacturing facility. Data are from 18 months after installation.**

This pilot scale PRB has been operating for more than three years. This PRB is similar in composition to the one described for the gold mine, except that it contains limestone to neutralize the acidity of the groundwater entering the PRB, to increase the potential for bacterially mediated sulfate reduction to occur. Sulfate reduction brings with it the potential to remove dissolved As, Fe, and heavy metals (Pb, Cd) from the groundwater in the form of sulfide minerals. The removal of Fe(II) from solution will reduce the acid-generating potential of this water in the receiving water body, while the alkalinity generated during sulfate reduction will improve the low pH conditions prevalent at this site.

The PRB is situated in a part of the property where groundwater flow is very slow and the residence time for porewater in the PRB is approximately 5 months. Approximately 6 pore volumes of water have gone through the PRB as of February 2006. Upon entering the PRB, groundwater As concentrations decrease from values  $\leq 126$  mg/L to  $< 0.04$  mg/L. The concentration of dissolved Pb  $\sim 3$  mg/L to  $< 0.01$  mg/L and dissolved Cd concentrations decrease from  $\sim 2$  mg/L to  $< 0.003$  mg/L. As was noted in the gold mine pilot scale PRB, decreased  $\text{SO}_4$  concentrations, the presence of dissolved  $\text{H}_2\text{S}$  and

enriched  $^{34}\text{S}$  values in the sulfate and a viable population of sulfate reducing bacteria support the interpretation that sulfate reduction followed by metal sulfide precipitation is occurring and could be responsible for the removal of metals from the water. The alkalinity also increases significantly, but evidence that this is a result of sulfate reduction rather than limestone dissolution is not currently available. A plume of clean water is starting to develop downgradient of the PRB, although evidence of this progress is complicated by high concentrations of metals downgradient of the PRB and slow groundwater velocities.

**Power Distribution Site BOFS PRB.** An electrical distribution station in Ontario, Canada is the site of a BOFS PRB system. The system was installed in the fall of 2002. Groundwater containing up to 0.4 mg/L As is directed into a concrete chamber that contains 2 m<sup>3</sup> of a 50% BOFS, 50% gravel mix. Other dissolved components of the water are at dilute levels. The residence time for water in this chamber is approximately one day. Within the chamber, dissolved As concentrations decrease to < 5 ppb. Due to the high lime/portlandite content of the BOFS, the pH of effluent is near 12. To manage the high pH effluent, a 20 m<sup>2</sup> collection bed containing a ~75 cm layer of peat, wood chips and gravel was constructed. Laboratory batch testing suggested that peat would be an effective remediation for the high pH water because the natural decay of peat releases organic acids (e.g. humic and fulvic acids). Effluent from the BOFS chamber is distributed through PVC tile drain into the peat layer. The drainage is collected in a continuous polyethylene liner that underlies the peat. Since it was installed in Sept. 2003, the peat layer has been effective in lowering the pH to between 6 and 7.

## **SUMMARY**

The effective removal of As in groundwater under highly different geochemical conditions attests to the viability of mixtures based on zero valent iron and organic carbon. Both As(III) and As(V) are effectively treated. In the iron filing + OC PRBs there is supporting evidence of the precipitation of sulfide minerals, potentially as a primary mechanism of As removal. In the mine site PRB, complete removal of As from high concentrations (averaging 20 mg/L) has been observed for more than three years and more than 70 PV of flow. The PRB operating conditions are more extreme (higher groundwater velocity and higher concentrations) than would be encountered in a full-scale PRB installation at the site. At the fertilizer site, acidic pH conditions in the incoming water are neutralized by limestone that was included in the mixture. As a result, conditions favourable for the removal of As, Cd and Pb are generated inside of the PRB. Low groundwater flow velocities in the PRB location allow very high concentrations of dissolved As to be removed from the groundwater. Additional efforts are under way to determine the significance of As removal by adsorption onto and coprecipitation with secondary phases that probably are forming on the surfaces of the zero valent iron. The two BOFS installations, one with high concentrations of dissolved As, Pb, Zn, and SO<sub>4</sub> and the other with only As at 0.4 mg/L as the concern demonstrate complete removal of As from the water for more than two years. In the latter case, the high pH effluent was managed using a peat drain; in the former, observations of the conditions are continuing. In all of the PRBs, there is no evidence to date for degrading hydraulic properties or As-removing ability, but observations for this are continuing.

## ACKNOWLEDGMENTS

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## REFERENCES

- Allison, J.D., D.S. Brown, and K.J. Novo-Gradac. 1990. MINTEQA2/PRODEFA2, A *Geochemical Assessment Model for Environmental Systems*. Version 3.0 User's Manual. U.S. EPA.
- Bain, J.G., L. Spink, D.W. Blowes, and D.J.A. Smyth. 2003. "The removal of arsenic from groundwater using permeable reactive materials." In: *Proceedings of Sudbury 2003, Mining and the Environment III*. May 25-28, 2003, Sudbury, ON, pp. 468-474.
- Blowes, D.W., C.J. Ptacek and J.L. Jambor. 1997. "In-situ remediation of Cr(VI)-contaminated groundwater using permeable reactive walls: Laboratory studies." In: *Env. Sci. Tech.* 31(12): 3348-3357.
- Farrell, J., J. Wang, P. O'Day, and M. Conklin. 2001. "Electrochemical and spectroscopic study of arsenate removal from water using zero-valent iron media." In: *Env. Sci. Tech.* 5(10): 2026-2032.
- Gu, B., L. Liang, M.J. Dickey, X. Yin, and S. Dai, S. 1998. "Reductive precipitation of uranium(VI) by zero-valent iron." In: *Env. Sci. Tech.* 32(21): 3366-3373.
- McRae, C.W.T., D.W. Blowes, and C.J. Ptacek. 1999. "In-situ removal of arsenic from groundwater using permeable reactive barriers: A laboratory study." In: *Sudbury '99 - Mining and the Environment II*. Edited by D. Goldsack, N. Belzile, P. Yearwood, and G. Hall. September 13-17, 1999, Sudbury, Ontario, Canada. 601-609.
- Nikolaidis, N.P., G.M. Dobbs, and L.A. Lackovic. 2003. "Arsenic removal by zero-valent iron: field, laboratory and modeling studies." In: *Water Research*. 37: 1417-1425.
- Su, C., and R.W. Puls. 2001. "Arsenate and arsenite removal by zerovalent iron: kinetics, redox transformation, and implications for in situ groundwater remediation." In: *Env. Sci. Tech.* 35(7): 1487-1492.