IRON FOUNDRY SLAGS FOR REMOVING ARSENIC FROM WATER

by

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Summary:

This paper describes findings from leach testing, total element analyses, and kinetic
batch tests conducted to evaluate the feasibility of using iron foundry slag (an
industrial byproduct of iron casting) as a reactive material in permeable reactive
barriers used to remove arsenic (As) from groundwater. Tests were conducted on
four slags from foundries in Wisconsin using solutions containing arsenite (As-III)
and arsenate (As-V) having initial total As concentrations ranging from 100-2500
μg/L. Comparative tests were also conducted on zero valent iron (ZVI) and sand as a
non-reactive control. Water leach testing and total elemental analyses suggested that
leaching from slags is not appreciably different from ZVI, at least in the context of
environmental regulations in Wisconsin. For the same liquid-to-solid ratio, As
removal was slower with slag than ZVI. Arsenic removal rates also varied
considerably from slag to slag, and did not depend on the quantity of iron in the slag.
The removal rate typically decreased with increasing concentration, and was slower
for As-III than As-V. Computations made using the rate coefficients measured in this
study suggest that a common 1-m-thick PRB containing iron foundry slag could
effectively treat groundwater contaminated with As-III or As-V at a concentration of
1000 μg/L, although other factors such as slag heterogeneity and competition with
other species might influence effectiveness in a field setting.
Related Publications:

Related Publications:

Metz, S. and Benson, C. (2007), Iron Foundry Slags as Permeable Reactive Barriers
Materials for Removing Arsenic from Groundwater, Proceedings, GeoDenver,
American Society of Civil Engineers, in press.

Key Words: arsenic, groundwater, permeable reactive barrier, iron, slag, beneficial
use

INTRODUCTION

Contamination of groundwater by arsenic (As) from natural and anthropogenic sources has become a significant issue because studies have shown that long-term ingestion of As via drinking water has serious impacts on health (Dhar et al. 1997, Mehang and Rahman 2003). The US Environmental Protection Agency (USEPA) also reports that As is the second most common contaminant of concern at Superfund sites (USEPA 2002). Natural sources of As in groundwater are also common, and in some cases are being aggravated by oxidation of bedrock in response to pumping of groundwater (Schreiber et al. 2000, Gotkowitz et al. 2004).

Contacting As-contaminated groundwater with zero-valent iron (ZVI) particles (e.g., using a permeable reactive barrier, or PRB, containing ZVI particles) has been shown to be an effective method for removing As from groundwater (Blowes et al. 2000, Su and Puls 2001, Nikolaidis et al. 2003, Leupin et al. 2005). However, world-demand for iron has driven up the cost and reduced the availability of ZVI. Consequently, there is interest in finding less costly, but effective, reactive materials that can be used to remove As from groundwater. Low-cost materials that improve sustainability, such as industrial byproducts, are particularly attractive (Lee and Benson 2004, Lee et al. 2004).

A recent case history by Wilkens et al. (2003) has shown that a PRB containing crushed steel slag (a byproduct of steel production) has been effective in removing As from groundwater at a site in Gary, Indiana, USA. Laboratory-experiments conducted with steel slags by McRae et al. (1999) and Ahn et al. (2003) have demonstrated similar effectiveness. Mechanisms thought to be responsible for As removal include sorption to metal oxides on the slag surface or precipitation of insoluble compounds (e.g. Ca-As compounds) (McRae et al. 1999, Ahn et al. 2003).

Iron foundry slag is a material similar to steel slag that is a byproduct of iron casting. Iron foundry slag is landfilled in large quantities by industrialized nations that produce cast iron products. Consequently, iron foundry slags can be obtained for little or no cost, and finding beneficial uses for iron slags improves sustainability. This paper describes findings from kinetic batch tests conducted to evaluate the feasibility of using iron foundry slags to remove As from groundwater. Tests were conducted on slags from four foundries in Wisconsin using solutions containing arsenite (As-III) and arsenate (As-V) having initial total As concentrations ranging between 100 and 2500 μg/L. Leach testing was also conducted to evaluate the potential for unintended impacts to groundwater.

MATERIALS

Control Materials

ZVI from Peerless Metal Powders, Inc. (Detroit, MI, USA) and a clean medium sand were used as control materials. The ZVI was used as a well-defined granular reactive material known to be effective in removing As from water (Su and Puls 2001). The sand was used as a non-reactive granular material. Physical properties of the ZVI are summarized in Table 1.

Table 1. Physical properties of ZVI and slags.

Material	USCS Classification	Specific Gravity	Surface Area (m²/g)	Hydraulic Conductivity[a] (m/s)	% Iron[b]
ZVI	SP	6.85	0.96	2.4×10^{-3}	100
ARC	SW	2.73	0.098	8.0×10^{-4}	20
MAN	SW	2.50	0.10	1.5×10^{-3}	19
MTG	SP	3.11	0.15	2.4×10^{-4}	0.68
SHN	SW	3.04	0.089	1.6×10^{-3}	7.5

[a]measured following ASTM D 2434, [b]determined by X-ray fluorescence spectroscopy.

Slag

Iron foundry slags were collected from four foundries in Wisconsin noted as ARC, MAN, MTG, and SHN. The slags arrived unprocessed in large pieces ranging from 50 to 500 mm and were crushed using a mechanical crusher until they passed a US No. 4 sieve (4.75 mm). Some of the slags contained molten metal that could not be crushed. These pieces were excluded. Particle size distributions for the crushed slags and the ZVI are shown in Fig. 1. The slags have similar particle size distributions that have the convex shape characteristic of crushed materials. The slags are also coarser and more broadly graded than the ZVI.
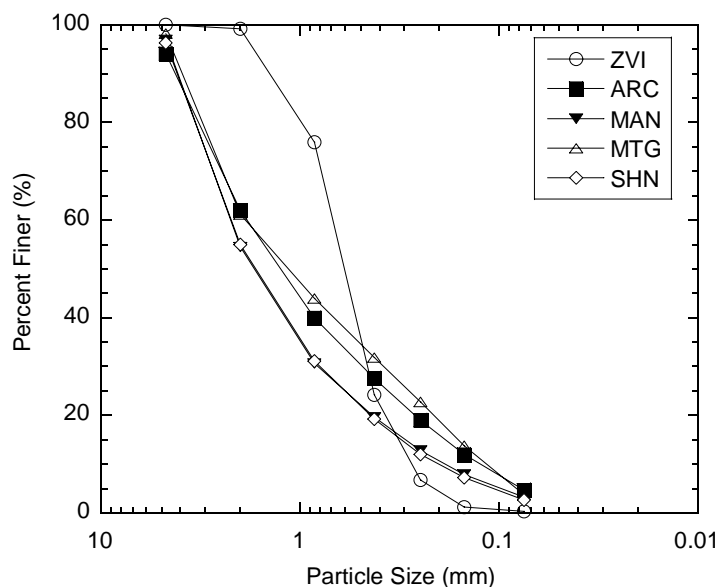

Fig. 1. Particle size distributions of slag and ZVI.

Physical properties of the slags are summarized in Table 1. The slags classify as poorly or well-graded sands in the Unified Soil Classification System (USCS) and have hydraulic conductivities on the order of 10^{-4} to 10^{-3} m/s. Two of the slags have specific gravities exceeding 3.0, which reflects the presence of heavier elements (e.g., metals) not typically found in abundance in soil minerals. Iron (Fe) content of the slags ranges from < 1% to 20%.

METHODS

Water Leach Testing and Total Elemental Analysis

Total elemental analyses (TEAs) and water leach testing (WLT) were conducted on each slag following USEPA Method 3050 (TEA) and ASTM D 3987 (WLT) as stipulated in the Wisconsin Administrative Code (WAC) for industrial byproducts used beneficially in lieu of landfilling (Wisconsin 2004). As required by the WAC, WLTs were conducted for aluminum (Al), antimony (Sb), arsenic (As), barium (Ba), beryllium (Be), cadmium (Cd), chromium (Cr), copper (Cu), cyanide (CN⁻), fluoride (F⁻), iron (Fe), lead (Pb), manganese (Mn), mercury (Hg), nickel (Ni), selenium (Se), sulfate (SO_4^{2-}), thallium (Tl), and zinc (Zn). TEAs were conducted for Sb, As, Ba, Be, Cr, Pb, and Tl.

Batch Kinetic Tests

Batch kinetic tests were conducted on each of the slags, the ZVI, and the sand. Solid (10.00 ± 0.02 g of slag, ZVI, or sand) was added to a 120 mL polyethylene bottle along with 100.0 ± 0.5 mL of deionized water. The bottle was then spiked with 0.1 to 0.2 mL of As stock solution to achieve a target As-III or As-V concentration of approximately 100, 500, 1000 or 2500 μg/L. The stock solutions were prepared with deionized water and reagent-grade $NaAsO_2$ (LabChem, Pittsburgh, PA, USA) or reagent-grade $Na_2HAsO_4 \cdot 7H_2O$ (J.T. Baker, Phillipsburg, NJ, USA). For each set of batch tests, at least two control samples were prepared without solids following the same method to determine the actual initial concentration.

After spiking, the bottles were immediately placed in a tumbler rotating at 30 rpm. Bottles were removed from the tumbler approximately 1 min before the designated end time and were mixed by hand during transfer from the tumbler to the bench. Samples to be collected within 2 min of spiking were mixed by hand for the duration of the experiment. At the designated end time, each sample was opened and filtered using a 0.2 μm syringe filter. A portion of the filtrate (50 mL) was collected, preserved with 0.5 mL of trace-metal grade nitric acid (Fisher Scientific, Toronto, Ontario, Canada), and refrigerated at 4.0 °C prior to analysis. Another 25 mL was tested immediately for pH, redox potential (Eh), and electric conductivity.

Rate coefficients were determined by fitting first-order and second-order rate expressions to the batch test data using non-linear least squares regression implemented with the Solver package in Microsoft EXCEL. The first-order expression is:

$$C_t = C_0 \exp(-\lambda_1 t) \tag{1}$$

where C_t is the concentration at time t, C_0 is the initial concentration (average of concentrations from samples without solid) and λ_1 is the first order rate coefficient. The second-order expression is:

$$C_t = \frac{C_0}{1 + \lambda_2 C_0 t} \tag{2}$$

where λ_2 is the second-order rate coefficient.

Analytical Methods

Metals analyses for the WLTs and the TEAs were conducted at the Wisconsin State Laboratory of Hygiene (Madison, WI). WLT samples were digested according to USEPA Method 3010 and then analyzed by inductively coupled plasma-mass spectrometry (ICP-MS) following USEPA Method 6020. Solutions from the TEAs were analyzed for metals by inductively coupled plasma-atomic emission spectrometry (ICP-AES) following USEPA Method 6010.

Analyses for CN^- and Hg were conducted by CT Laboratories (Baraboo, WI). Flow injection automated colorimetry with off-line distillation was used for the CN^- analyses following USEPA Method 9012A. Cold-vapor atomic adsorption was used for the Hg analyses following USEPA Method 7470.

Analyses for F^- and SO_4^{2-} were conducted in-house by high-performance liquid chromatography (HPLC) following USEPA Method 9056 with a modification for HPLC. Total As concentrations for the batch kinetic tests were determined in-house by ICP-AES following USEPA Method 6010. The arsenic detection limit was less than 6 μg/L.

RESULTS

Reuse Evaluation

Solid-phase concentrations from the TEAs are summarized in Table 2 along with maximum permissible concentrations (MPCs) stipulated in Section NR 538 of the WAC for beneficial use applications below the groundwater table. Concentrations exceeding MPCs are shown in bold. MPCs were exceeded for As, Be, and Cr for each of the slags as well as the ZVI. In fact, ZVI has some of the highest solid-phase concentrations for these elements. The MPC for Tl was also exceeded for MTG slag, but for none of the other slags or the ZVI.

Table 2. Solid-phase concentrations from total elemental analyses. Maximum concentrations stipulated in the Wisconsin Administrative Code for reuse applications below the groundwater table are shown in parentheses.

Reactive Material	Solid-Phase Concentration (mg/kg)						
	Sb (6.3)	As (0.042)	Ba (1100)	Be (0.014)	Cr (14.5)	Pb (50)	Tl (1.5)
ZVI	<2.0	**11**	20	**5.5**	**530**	41	<1.5
ARC	<2.0	**11**	20	**0.6**	**110**	5.5	<1.5
MAN	<2.0	**1.1**	28	**0.7**	**77**	3.4	<1.5
MTG	<2.0	**<0.8**	750	**9.0**	**28**	0.3	**7.4**
SHN	<2.0	**3.2**	320	**3.6**	**150**	3.2	<1.5

Note: "< X.Y" indicates that concentration is below the detection limit (X.Y mg/kg).

For the WLTs, only Mn was had a concentration above the MPC (25 μg/L) and only for one slag (ARC – 99 μg/L). The other 18 contaminants of concern were always below MPCs (Al<1500 μg/L, As<5 μg/L, Ba<400 μg/L, Be<0.4 μg/L, Cd<0.5 μg/L, Cr<10 μg/L, Cu<130 μg/L, CN$^-$<40 μg/L, F$^-$<800 μg/L, Fe<150 μg/L, Pb<1.5 μg/L, Hg<0.2 μg/L, Ni<20 μg/L, Se<10 μg/L, Sb<1.2 μg/L, SO$_4^{2-}$ <125,000 μg/L, Tl<0.4 μg/L, and Zn<2500 μg/L).

The similarity of the findings for the iron foundry slags and ZVI suggests that slags used in PRBs should pose no greater risk for unintended groundwater contamination than ZVI, at least in the context of the criteria stipulated in the WAC. The higher liquid-phase Mn concentration for ARC slag is believed to be insignificant, as the Mn criterion is based on aesthetics rather than toxicity. The solid-phase Tl concentration for MTG slag is also believed to be insignificant because the solid-phase MPC was exceeded modestly and the liquid-phase Tl concentration from the WLT on MTG slag was below the detection limit (0.4 μg/L). However, more detailed study on the leaching behavior of slags is needed before a definitive conclusion can be made regarding the risks of unintended groundwater impacts. A study on the leaching properties of iron foundry slags currently is being conducted by the authors.

Slag Type and Reaction Order

Total As concentrations are shown as a function of time in Fig. 2 for batch tests conducted with a 100 μg/L As-V solution and the four slags. Comparative data are also shown for ZVI and for sand (non-reactive control). Trends obtained from other test series were similar to those shown in Fig. 3 regardless of As speciation or initial As concentration.

The solid lines shown in Fig. 3 correspond to fits of the first-order rate expression (Eq. 1). In general, similar fits were obtained using the first-order and second-order (Eq. 2) expressions, even though the mean square error typically was slightly higher for first-order fits compared to second-order fits (with only four exceptions, the difference between the mean absolute errors for the two fits was within a factor of 2.2). Because the first-order expression is simpler and provided a reasonable fit, first-order rate coefficients are used herein.

As shown in Fig. 2, the removal rate was always lower for the slags than ZVI. Also, essentially no removal was obtained for the sand, as expected. Slower removal was expected for the slags relative to ZVI, even if the intrinsic reactivity of the materials was the same, because the coarser slags have lower surface area than ZVI for the same amount of mass. The curves in Fig. 2 also show that the removal rate for the slags does not depend on the Fe content. For example, MAN slag, which had the second highest Fe content of the four slags that were tested, had the lowest rate of removal. In contrast, the highest rate of removal was obtained for the MTG slag, which has the lowest Fe content. This may indicate that different mechanisms are responsible for removal of As using ZVI and slag. Ahn et al. (2003) suggest that precipitation of relatively insoluble Ca-As compounds may be responsible for As removal using crushed steel slags. A similar mechanism may be occurring for iron foundry slags, which have appreciable Ca content due to the limestone or dolomite that is added as a fluxing agent to the molten iron.
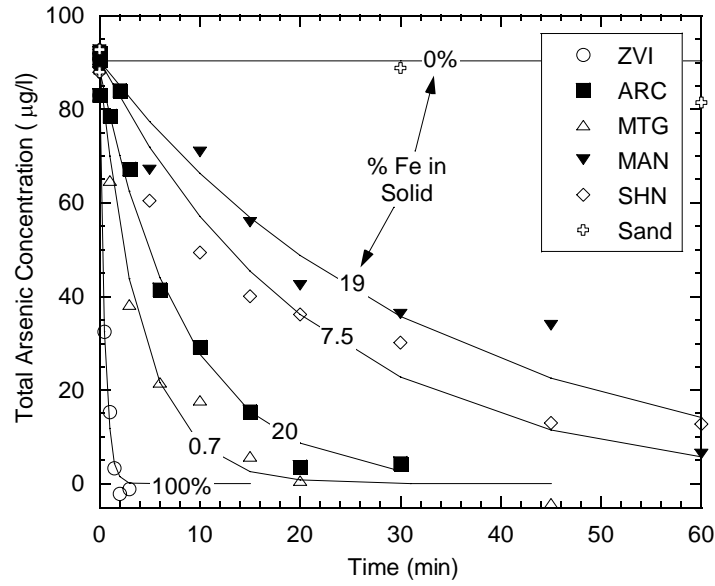
Fig. 2. **Total arsenic removal for batch tests conducted with 100 μg/L As-V solution using slag, ZVI, or sand as the reactive material.**
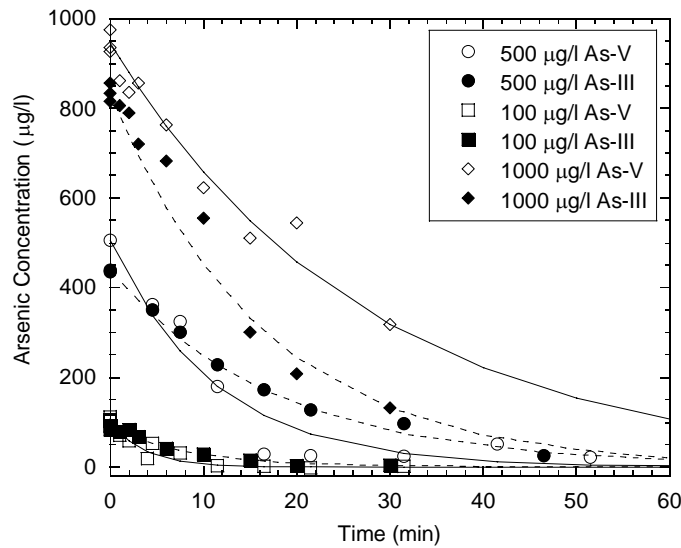

Fig. 3. **As-III and As-V removal as a function of time using ARC slag for target initial concentrations of 100, 500, and 1000 μg/L. Solid lines are fits for As-V and dashed lines are fits for As-III.**

Initial Concentration and Speciation

The effect of As speciation and concentration is illustrated in Fig. 3 for ARC slag. The rate of removal is slightly faster for As-V than As-III for initial concentrations of 100 and 500 μg/L, whereas As-III is removed faster than As-V at 1000 μg/L. The rate of removal also appears to be affected by concentration, with slower removal at higher concentration for both As-III and As-V.

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The effect of initial concentration on As-V removal for all tests is shown in Fig. 4 in terms of normalized removal rate coefficients. The rate coefficient corresponding to an initial concentration of 100 μg/L was used for normalization for each slag. The removal rate coefficient decreases with increasing concentration for each slag, indicating slower removal as the concentration increases (Fig. 4). The effect of initial concentration on the rate coefficient is more significant for slags that are more reactive. For example, the rate coefficient for MTG slag, which is the most reactive (Fig. 2), is very sensitive to initial concentration, whereas the rate coefficient for the least reactive MAN slag is much less sensitive to concentration. The dependence on concentration also suggests that the removal reaction is not truly first order with respect to arsenic concentration. The removal reaction probably also depends on the availability of reactive materials (Fe, Ca, etc.) in the slag.
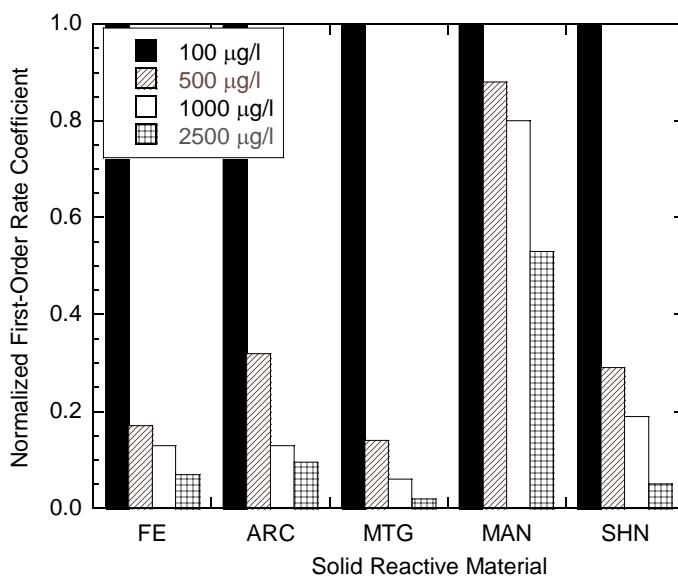
Fig. 4. Normalized As-V removal rate coefficients for initial concentrations of 100, 500, 1000, and 2500 μg/L.

The general effect of speciation is shown in Fig. 5, which shows first-order rate coefficients for As-III (λ_{III}) vs. those for As-V (λ_V) for tests conducted under similar conditions (e.g., the same slag and target initial concentration). In general, the rate coefficients are lower for As-III compared to As-V, with the difference between the rate coefficients increasing as the rate coefficients increase. There are some exceptions to this trend for lower rate coefficients. Whether these exceptions are real deviations is unclear, as they may also be due to heterogeneity in the slag samples or differences in initial concentration used in the batch test (initial As-III concentrations tended to be at least 10% lower than the initial As-V concentrations).
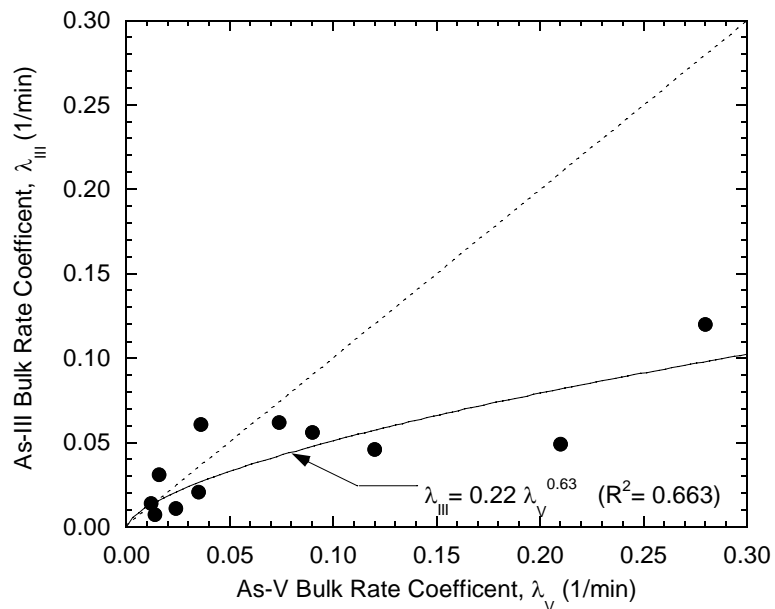
Fig. 5. Rate coefficients for As-III vs. those for As-V for tests conducted under similar conditions (target initial concentration and type of slag).

PRACTICAL IMPLICATIONS

Required thicknesses of PRBs containing iron slag for a typical field scenario were estimated using the data from the batch tests. Computations were made using the steady-state solution in Lee and Benson (2004) without dispersion. The seepage velocity was assumed to be 1 m/d and the influent concentration was assumed to be 1000 μg/L. The PRB was required to reduce the effluent concentration to 10 μg/L.

Rate coefficients obtained from the batch tests were adjusted to the liquid-to-solid ratio expected in an actual PRB assuming that the reactivity could be scaled by the surface area of the reactive material as described in Lee and Benson (2004). The porosities used in these computations were based on porosities achieved in column tests where slag was placed in lifts and gently tapped to simulate the procedure that might occur in the field. Rate coefficients obtained from batch tests with As-III solutions were used in the analysis to represent conditions where the removal rate is slower. The required PRB thicknesses are summarized in Table 3 along with the input parameters used in the analysis. In all cases, the required thickness is very small (< 7 mm) and is much less than the typical thickness of the reactive zone in PRBs (≈ 1 m).

An important consideration when using slag as a PRB material is the potential effects of heterogeneity. Unlike manufactured materials, slag is an industrial byproduct and the properties vary as manufacturing operations change. Even in a given lot of slag, the properties can vary from particle to particle. This is illustrated in the scanning electron micrographs (SEMs) shown in Fig. 6, which correspond to two particles from a single sample of slag used in this study. Despite coming from the same sample, the slags have very different surface properties, and

therefore may have different reactivity. These heterogeneities may also be responsible for the greater scatter in the data obtained with slags relative to ZVI (e.g., see Figs. 2 and 3).

Table 3. Required thickness of PRB to reduce As-III concentration from 1000 µg/L to 10 µg/L for a seepage velocity of 1 m/d.

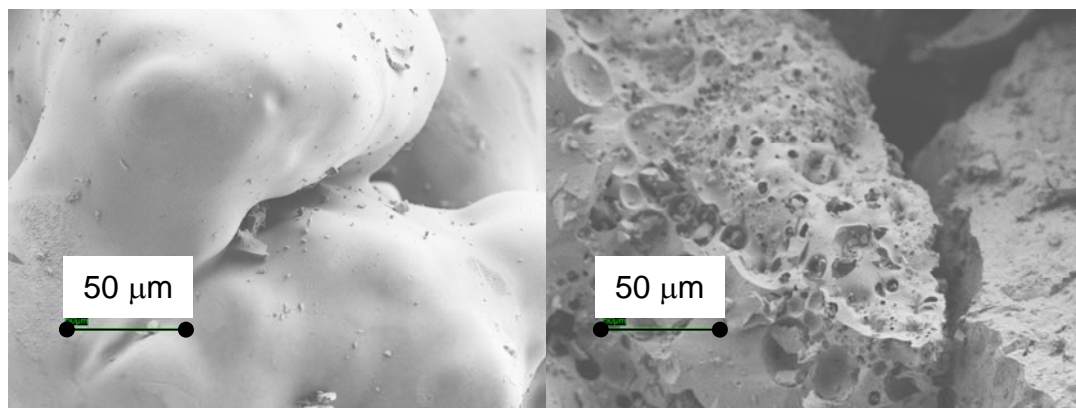| Material	Batch Rate Coefficient (1/min)	Porosity	Field Rate Coefficient (1/min)	Required PRB Thickness (mm)
ZVI	0.89	0.63	36	0.089
ARC	0.062	0.35	3.1	1.0
MAN	0.014	0.41	0.50	6.5
MTG	0.062	0.35	3.6	0.88
SHN	0.011	0.41	0.46	6.9

Fig. 6. SEMs of two particles of slag from the same sample.

SUMMARY AND RECOMMENDATIONS

The findings of this study suggest that slags from iron foundries may be effective low-cost reactive media for PRBs used to remove arsenic from groundwater. Iron foundry slags may not be as reactive as conventional ZVI, but do have sufficient reactivity so that PRBs having a reactive zone of typical thickness (< 1 m) could be constructed to effectively remove arsenic. However, the reactivity of the iron slags was evaluated under a limited set of idealized conditions, and more study is needed to demonstrate the generality of the findings. For example, column testing is needed to verify that the reactivity observed in the batch tests is realized under flow-through conditions at lower liquid-to-solid ratios. Additional factors that may be important in the field also need to be studied, such as the effects of other dissolved ions, pH, and dissolved oxygen content on the removal efficiency. The importance of slag heterogeneity, longevity of the reactivity, and the mechanisms controlling removal also need to be evaluated. Research on these issues is currently being undertaken by the authors.

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