Removal of Arsenic from Leachate of Tailing using Laboratory-synthesized Zerovalent Iron

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Feasibility of laboratory-synthesized zerovalent iron was investigated to remove arsenic from leachates of tailings taken from an Au-Ag abandoned mine. The tailings were seriously contaminated with arsenic, and its potential adverse effect on the ecosystems around the mine seems to be significantly high. Long-term column experiments were conducted for about 3.5 months to evaluate the effectiveness of the synthesized zerovalent iron for removal of arsenic. Over than 95% removal efficiency of As was observed in the zerovalent iron mediated tests. In addition, the XRD data suggest that the corrosion products of ZVI were identified magnetite, maghemite, goethite, and lepidocrocite, all of which support Fe(II) oxidation as an intermediate step in the zerovalent iron corrosion process. The results indicate that arsenic can be removed from the tailing-leachate by the mechanism of coprecipitation and/or adsorption onto those iron oxides formed from ZVI corrosion.

Key words: *arsenic, tailing-leachate, zerovalent iron*

Until recently, more than one thousand of metal-mining operations have been closed in Republic of Korea, most of which have been left unmanaged. Amounts of contaminated tailings remain near the mining sites, and the tailings contain several toxic contaminants, such as arsenic (As) and heavy metals, which are known to have a high potential for the deterioration of the surrounding ecosystems. Arsenic and heavy metal contamination of the agricultural soils and crops surrounding these areas has recently been identified as one of the most serious environmental problems facing South Korea [Kim et al., 1998; Jung and Thornton, 1996]. It has been reported that some gold mine tailings in South Korea have extremely acidic to neutral pH values, and contain high levels of arsenic and other heavy metals [Min et al., 1997]. Among various hazardous contaminants included in tailings, in

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Abbreviations: AAA-GF, Atomic Adsorption Spectrometric-Graphite Furnace; ICP-MS, Inductive Coupled Mass Spectrometry; XRD, X-Ray Diffraction; ZVI, Zerovalent Iron.

particular, As has been one of the elements of public concern due to its highly toxic and carcinogenic properties with regard to human beings, animals, and plants. The presence of As in groundwater and soil can pose a significant threat to human and ecological systems. In many areas of the world, soils have been contaminated with As by human activities such as mining, smelting, landfilling of industrial wastes, disposal of chemical warfare agents, and agriculture [Azcue et al., 1994; Schneider and Johnson, 1999] Arsenic-bearing tailings, resulting from gold-mining operations, are of a great concern because of their potential as sources of environmental contamination. Elevated concentrations of arsenic in surface waters and groundwaters around mine-tailing dumps, produced by the dissolution of sulfide minerals such as arsenopyrite (FeAsS), have been commonly reported [Williams, 2001]. On the other hand, As may be retained by its adsorption onto clays and metal oxides, particularly those of Fe, Al and Mn [Smedely and Kinniburgh, 2002]. Generally, there is a good correlation between extractable Fe and As in soils and sediments around As-enriched area [Fox and Doner, 2002]. However, the adsorbed As is released from clays and

oxides by reductive desorption or reductive dissolution under reducing conditions, resulting in adverse effects on the surrounding environment [Smedely and Kinniburgh, 2002].

There has been a great interest in the remediation of certain organic and inorganic contaminants using zerovalent iron as a permeable reactive barrier medium [Chunming and Robert, 2001]. The ZVI has been used to effectively destroy numerous chlorinated hydrocarbon compounds via reductive dehalogenation [Chunming and Robert, 2001; Johnson et al., 1996; Robert et al., 1996]. The oxidation of the ZVI surface is a spontaneous corrosion reactions that forms Fe(II) and Fe(III) and can act as an electron donor causing reduction of dissolved ions [Manning et al., 2002]. Inorganic contaminants which are electrochemically reduced during ZVI corrosion include Cr(VI) [Blowes et al., 1997; Pratt et al., 1997], U(VI) [Gu et al., 1998], and Pb(II) [Ponder et al., 2000]. A recent study has shown that dissolved As(V) does not participate in the electrochemical oxidation reaction of ZVI [Farrell et al., 2001]. Rather, water molecules are the primary oxidant of the ZVI surface (water reduction) and that Fe(II) is the initial oxidation product:

$$Fe^0 + 2H_2O \rightarrow Fe^{2+} + H_2 + 2OH^- \qquad (1)$$
$$2Fe^0 + O_2 + 2H_2O \rightarrow 2Fe^{2+} + 4OH^- \qquad (2)$$

The Fe(II) formed at the corroding ZVI surface reacts with OH⁻ to form ferrous hydroxides (Fe(OH)₂) followed by oxidation to an Fe(II)/Fe(III) mixed phase such as magnetite over the course hours to days [Farrell et al., 2001; Manning et al., 2002; Schwertmann and Taylor, 1989; Schwertmann and Cornell, 2000]. This time-dependent process results in a gradient going from magnetite near the ZVI surface to maghemite [Farrell et al., 2001; Manning et al., 2002].

The objectives of this study were to evaluate the applicability and feasibility of the laboratory-synthesized ZVI for As removal from tailing-leachate using a relatively long-term column experiments. In addition, the transformation of the ZVI within the duration of treatment was elucidated by identification of corrosion products of ZVI using x-ray diffraction (XRD) and scanning electron microscopy analyses.

Materials and Methods

Physicochemical characterization of tailing samples. For this study, As-contaminated tailing samples were collected from the Songcheon mine located in Gangneung, Gangwondo. The mine was actively operated from 1939 to 1943, and its target elements were Au, Ag, and Mo. The tailing samples were air-dried and pretreated using #10 sieve to characterize physicochemical properties, such as bulk and particle densities, porosity, particle size distribution, hydraulic conductivity, average linear velocity, and initial pH. ICP-MS (Agilent 7500CE, USA) and AAS-GF (Perkin-Elmer 5100PC, USA) were used for determination of As concentration in tailings before and after the ZVI treatment. In addition to physicochemical analyses, main mineral constituents of the tailing samples used were measured by XRD (SIEMENS D5005 Diffractometer, CuKα: 40 kV and 35 mA). The 2θ range and the scanning speed were 3°~90° and 0.02°/sec, respectively. Through the XRD analysis, the primary sulfide minerals dominant in tailing samples were identified. The secondary minerals formed from the oxidation or alterations of the primary sulfides were characterized as well.

Synthesis of ZVI. The ZVI was synthesized using the method described previously [Lowry and Johnson, 2004; Wang and Zhang, 1997]. Into 1 l of a 30% (volume) MeOH/deionized water solution was dissolved 20 g of FeSO₄·7H₂O. While stirring, 10 ml of 5 N NaOH aqueous solution was added dropwise to the dissolved iron solution, yielding a pH of 6.1. Next, 50 ml of a 2.1 M NaBH₄ aqueous solution was added at a rate ~0.5 ml s⁻¹. This is approximately 2.9 times the stoichiometric amount of NaBH₄ required to reduce all the dissolved Fe²⁺ in solution to ZVI. A fine black precipitate formed instantly upon addition of NaBH₄ and remained in solution throughout the process. The mixture was stirred for 20 min before being centrifuged in plastic centrifuge tubes for 5 min at 3500 rpm to separate the solids. The supernatant was discarded and the remaining solids were rinsed with MeOH twice to remove any excess salt. The nanoscale ZVI particles were then dried in a 100°C oven for 4 h under nitrogen gas (N₂). Once dry, the particles remained in the oven for a minimum of 8 h to cool and allow oxygen to slowly bleed into the oven. This passivated the iron surface slightly and prevented the highly reactive iron particles from spontaneously igniting. The iron particles were dried in particles were finely ground and stored in sealed serum bottles until use.

Experimental setup. Long-term (~3.5 months) experiments were carried out using the column (27 × 30 mm) apparatus shown in Fig. 1. Two sets of tests were designed and conducted to evaluate the applicability of the laboratory-synthesized ZVI for removal of As from the tailing-leachate. One was conducted as the control test without ZVI to quantify the original concentrations of As leached from the tailing. The other was made with ZVI to elucidate the efficacy of ZVI for removal of As from the tailing-leachate. All the tests and analyses were performed in triplicate, and the results were displayed with error bars
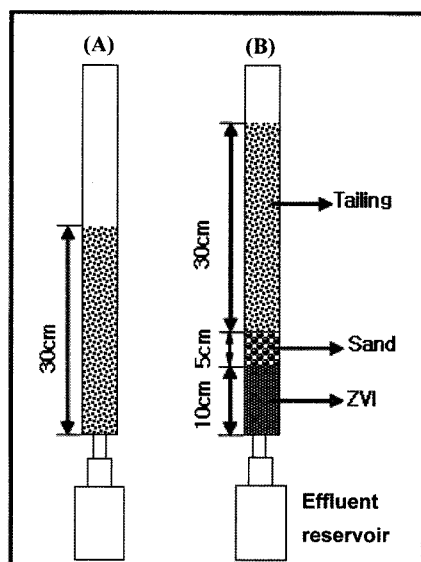
Fig. 1. Schematic diagrams showing experimental apparatus for (A) control test without ZVI and (B) removal test with ZVI.

Fig. 2. X-ray diffraction patterns of tailing samples (Q: quartz, M: mica, F: feldspar, P: pyrite, S: scorodite).

expressed as mean ± standard deviation. In order to simulate lixiviation of As from the tailing in natural environments, synthetic precipitation leaching procedure (SPLP) method proposed by USEPA was applied [USEPA, 2004]. The SPLP method was originally designed to determine the mobility of inorganic contaminants present in liquids, soils, and wastes. In this study, the extraction fluid employed was a pH 4.2 solution made by addition of nitric acid into distilled water. The SPLP method was implemented by pouring continuously the extraction solution from the top of columns containing tailings. The overflow of the extraction solution was prevented using peristaltic pump, and a constant hydraulic head was maintained during the period of experiments. The As concentrations in the effluents were periodically measured, and they were quantitatively compared between the control and the treatment tests without and with ZVI, respectively. All the concentrations of As in effluents were analyzed using the same instruments mentioned above.

Solid-phase analyses of ZVI corrosion products. In order to indentify the types of ZVI corrosion products, the ZVI samples before and after treatment were analyzed by the same XRD analysis mentioned previously, but CoKα radiation was used because normally CuKα radiation is less suitable due to its strong absorption of Fe rich phases leading to loss of X-ray intensity and a high background [Schwertmann and Cornell, 1997]. Together with the XRD analysis for the ZVI samples, the fresh and reacted ZVI samples were analyzed by scanning electron microscopy (Philips XL30 S FEG, Netherlands) to observe a morphological change in ZVI through treatment.
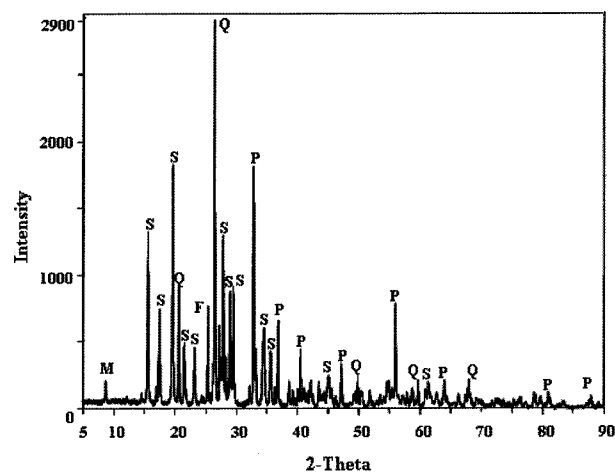
Results and Discussion

Characteristics of tailing samples used. The bulk and particle densities of the tailings used were measured 1.90 g cm^{-3} and 2.99 g cm^{-3}, respectively, rendering its porosity of 36.5. The soil texture was silt loam having the composition of 10.7% sand, 69.3% silt, and 20.0% clay, and its average particle size was 22.0 μm. The hydraulic conductivity and average linear (seepage) velocity were observed 4.6 × 10^{-5} cm s^{-1} and 7.8 × 10^{-5} cm s^{-1}, respectively, and the hydraulic properties of the tailings correspond to be typical to silt soils. The initial pH values of the tailings were measured 1.9 ± 0.5, and the extremely low pH indicates that the tailings have experienced the significant weathering and/or oxidation so far. The extremely acidic pH value is a crucial factor to bring about a variety of detrimental effects of the tailing on the surrounding environments, such as soil, surface and/or ground waters, and crops. The results of chemical analyses for As in initial tailing samples reveal that the tailings are seriously contaminated with As (data not shown).

The main mineral constituents examined by XRD analyses are shown in Fig. 2. Because the samples were tailings, dominant minerals detected by XRD were not common rock forming minerals, rather were primary sulfide ore minerals and their secondary products generated by oxidation. Pyrite (FeS$_2$) and scorodite (FeAsO$_4$ · 2H$_2$O) were identified as predominant primary and secondary minerals, respectively. Even though chemical analyses show a high As concentration in tailings, arsenopyrite (FeAsS) known as a representative As-bearing ore mineral was not detected in the XRD analyses. It is likely that the amount of arsenopyrite was very small and/or it was depleted through weathering (oxidation) due to the
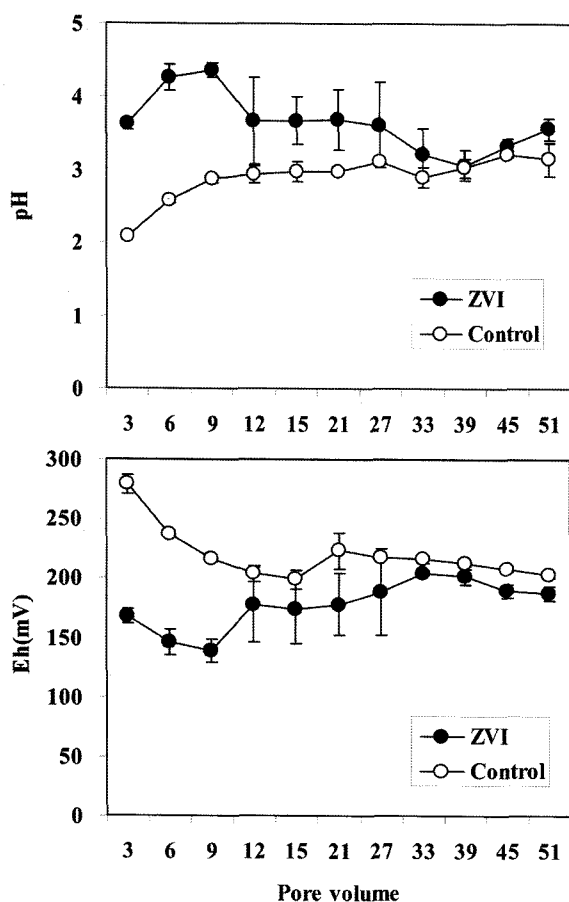
Fig. 3. Variations in pH (A) and Eh (B) during the experiment. Error bars are standard deviations of triplicates.

Fig. 4. X-ray diffraction analysis of the ZVI corrosion products. Major peaks are due to zerovalent iron (Fe⁰), magnetite (Fe_3O_4) (Mn), maghemite (γ-Fe_2O_3) (Mh), goethite (α-FeOOH), and lepidocrocite (γ-FeOOH).

exposure of tailings to surface environments for a long while after the mining operation was ceased, and it is confirmed by detection of predominant peaks of scorodite including As. The large amount of scorodite attributes to the source of contaminants such as As.

Variation of pH and Eh. The variation in pH and Eh values over the experiment is shown in Fig. 3. Even though the initial pH of the tailing was extremely low (~1.9), the pH values in the control test without ZVI increased gradually throughout the experiment (Fig. 3A), since the influent of a higher pH value was continuously introduced from the top of the column based on the SPLP method. On the contrary, the overall pH in the ZVI test was observed much higher than that in the control test, resulting from the production of hydroxide ions through the oxidation of ZVI, as previously shown in Equations (1) and (2). In particular, the pH in the ZVI test appeared to be highest in the initial stage of the experiment, and then decreased gradually over the duration of the experiment. It seems to be caused by the fact that the rate of the ZVI oxidation generating the hydroxide ions decreased gradually as the experiment proceeded, since
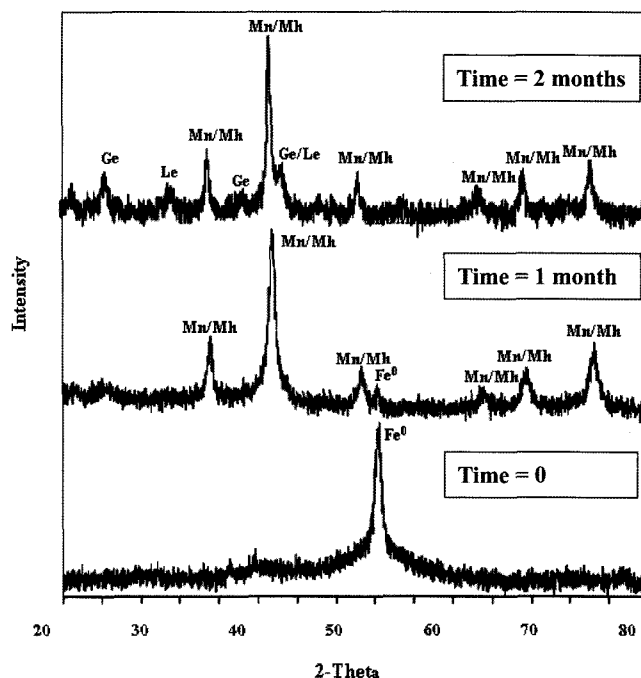
the corrosion products of the ZVI coated the surface of fresh (unreacted) ZVI. The phenomena may give an adverse effect on the removal of contaminants due to decrease in the activity of the ZVI surface. The Eh in the ZVI test was measured much lower than that in the control test (Fig. 3B), since the reducing environment created in the ZVI test due to the ZVI oxidation (Equations (1) and (2)). However, it is not likely that the strict reducing environment was created in the ZVI test, since the Eh values showed the range of 130-200 mV. Similarly to the pH variations, the Eh values in the ZVI test approached to those in the control test with time, resulting from the decrease in the activity of ZVI surface due to the coating effect of the ZVI corrosion products, as mentioned before. The lower Eh environment plays a crucial role in extracting As through change in the As speciation from As(V) to As(III), since As(III) is considered to be more mobile than As(V) in the environment. The gradual decrease in the Eh within the control test can be contributed to the continuous oxidation of sulfur ore minerals, such as pyrite (FeS_2) and arsenopyrite (FeAsS), included in the tailings.

Identification of corrosion products of ZVI. Analysis of ZVI by XRD indicates the presence of magnetite, goethite, and maghemite after the treatment with tailing effluents (Fig. 4). The initial (t = 0) sample gave only Fe⁰ XRD peak intensities and confirmed the existence of ZVI
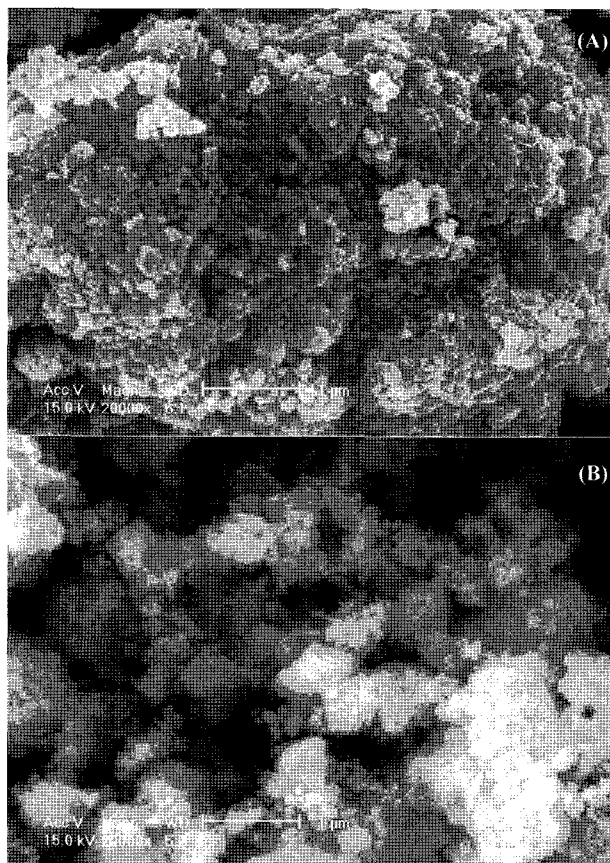
Fig. 5. SEM images of ZVI before (A) and after reaction with the tailing-leachate for 2 months (B).

Fig. 6. Variation in the accumulative amount of As during the experiment. Error bars are standard deviations of triplicates.

without other iron products. After one month, the intensities of ZVI XRD peak were declined and those of ZVI corrosion products such as magnetite (Fe_3O_4) and maghemite (γ-Fe_2O_3) were strengthened. Because magnetite and maghemite are isostructural and were effectively indistinguishable by the XRD data, either or both oxides may be present. The XRD data of samples obtained after 2 month treatment show absence of Fe^0 peaks and new peaks correspondent to those of goethite (α-FeOOH) and lepidocrocite (γ-FeOOH) in addition to the peaks of magnetite and maghemite. These XRD analytical data are consistent with the results by numerous researchers [Gu *et al.*, 1999; Manning *et al.*, 2002; Schwertmann and Taylor, 1989. As mentioned previously, the Fe(II) formed at the corroding ZVI surface reacts with OH⁻ to form ferrous hydroxides [$Fe(OH)_2$)] followed by oxidation to an Fe(II)/Fe(III) mixed phase such as magnetite over the course hours to days [Farrell *et al.*, 2001; Schwertmann and Taylor, 1989; Schwertmann and Cornell, 2000]. This time-dependent process results in a gradient going from magnetite near the ZVI surface to maghemite [Farrell *et al.*, 2001; Manning *et al.*, 2002]. Consequently, those ZVI corrosion products detected by XRD analyses indicate
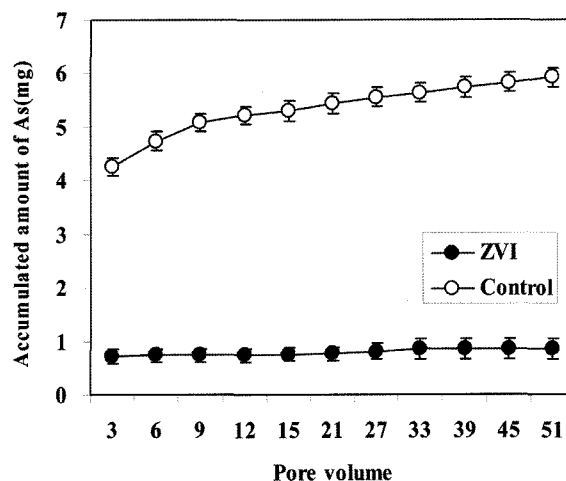
Fe(II) oxidation as an intermediate step in the ZVI corrosion process.

The SEM data of ZVI before and after treatment are presented in Fig. 5. The SEM image elucidates nanoscale particles of the synthesized ZVI in a range of 10-100 nm (Fig. 5A). Aggregation of particles of the iron was observed after 2 months treatment of ZVI with the tailing-leachates (Fig. 5B), suggesting that the formation of ZVI corrosion products, as confirmed by the XRD analyses. From the view of implementation, this aggregation may bring out a decrease in the flow rate of the tailing-leachate to be treated, and finally reduce the efficacy of whole operation system. Therefore, the promising strategy for prevention of the aggregation of iron particles should be deliberated for a practical implementation.

Removal of As by ZVI. The accumulative amounts of As according to the pore volume of effluents are shown in Fig. 6. Globally, a significant removal of As was observed in the test with ZVI, and the removal efficiency of As approached to over than 95% for about only 6 pore volume of the effluents. The As amount of the effluents in the control test was gradually increased throughout the experiment due to continuous leaching from the tailing. However, the increasing rate of As was significantly higher in the early stage of the experiment (until 9 pore volume), and then decreased gradually. It is likely that the more weakly bound fractions of As were lixiviated early, and then leaching of strongly bound fractions was initiated. On the contrary, the small amount of As was detected in the effluents of the ZVI test over the period of the experiment, suggesting that As was effectively removed by ZVI during the experiment. The mechanism of As removal involves surface precipitation or adsorption

onto iron oxides which are corrosion products of ZVI. When the laboratory synthesized ZVI is corroded to Fe(II) and/or Fe(III) oxides, such as magnetite, maghemite, goethite, and lepidocrocite, As is removed from the leaching solution of tailings by copreicipitation with them. In addition to coprecipitation, those iron oxides can adsorb and remove As from the tailing-leachate as well.

This study confirms that the laboratory synthesized ZVI is effective in removing As from the tailing-leachate. Not only can ZVI treat chlorinated solvents-contaminated water, but it also can immobilize a variety of inorganic cations and anions including metallic elements and As. The ability to treat media contaminated with mixed contaminants and the availability of ZVI at a reasonable cost make it a promising material for in situ remediation of tailing-leachates or acid rock drainage generated from the abandoned mines. The aqueous corrosion of ZVI is mediated by the layer of oxides that forms at the iron-water interface, and the porous nature of oxide films on iron may allow adequate and continuous coprecipitation and/or adsorption of As over the time of operation in the area. Consequently, the formation of the iron oxide sorbent and the potential to remove As makes ZVI a particularly prominent candidate for treatment of water with elevated levels of As.

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