Laboratory Comparison of Four Iron-Based Filter Materials for Water Treatment of Trace Element Contaminants

Barry J. Allred[1*], Brian C. Tost[2]

ABSTRACT: A laboratory investigation provided preliminary comparison of trace element contaminant water treatment capabilities for four iron-based filter materials. The iron-based filter materials tested were zero-valent iron (ZVI), porous iron composite (PIC), sulfur modified iron (SMI), and iron oxide/hydroxide (IOH). Two types of trace element contaminant solutions were tested, one combined As, Cr, and Se (added as AsO_4^{3-}, CrO_4^{2-}, and SeO_4^{2-}, respectively), while the second combined Cd^{2+}, Cu^{2+}, and Pb^{2+}. The laboratory investigation included saturated falling-head hydraulic conductivity tests, contaminant removal–desorption/dissolution batch tests, and low-to-high flow rate saturated solute transport column tests. Hydraulic conductivity test results indicate that all four iron-based filter materials have sufficient water flow capacity as indicated by saturated hydraulic conductivity values greater than 1×10^{-2} cm/s. Essentially, 100% of each trace element (As, Cd, Cr, Cu, Pb, and Se) was removed by SMI during the contaminant removal portion of the batch tests and during the column tests, while IOH exhibited good removal of each trace element except Se. Results from the contaminant removal portion of the batch tests and from the column tests showed ZVI and PIC were effective in treating Cd, Cr, Cu, and Pb. With the exception of Se adsorption/precipitation onto IOH, the desorption/dissolution portion of the batch tests showed that once As, Cd, Cr, Cu, Pb, or Se are adsorbed/precipitated onto ZVI, PIC, SMI, or IOH particle surfaces, these trace elements are then not readily desorbed or dissolved back into solution. *Water Environ. Res.*, **86**, 2221 (2014).

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Introduction

Natural processes along with agricultural, mining, and manufacturing activities can result in the environmental release of trace element contaminants, which degrade ground and surface waters (Sparks, 2003). Often, more than one trace element contaminant is found to be present in these degraded waters. Arsenic (As), chromium (Cr), and/or selenium (Se) are often found together in leachate at waste disposal sites that store fly ash from coal-burning power plants (Daniels and Das, 2006; Huggins et al., 2007; Shah et al., 2007); agricultural drainage water discharge in the San Joaquin Valley, California (Ong and Tanji, 1993; Ong et al., 1995; Ong et al., 1997); groundwater beneath chromated copper arsenate (CCA) wood treatment facilities or landfills where discarded CCA-treated wood is deposited (Guan et al., 2011; Khaodhair et al., 2000; Moghaddam and Mulligan, 2008); surface runoff and shallow groundwater recharge to streams within areas with wildfire-affected soils (Wolf et al., 2010); and coalbed methane production waters (McBeth et al., 2003). Cadmium (Cd), copper (Cu), and/or lead (Pb) are commonly present together in industrial wastewaters such as acid mine drainage (U.S. Environmental Protection Agency, 1994); textile factory effluents (Manzoor et al., 2006); effluent discharge from paint manufacturing plants (Gondal and Hussain, 2007); and metal plating facility effluents (Vilar et al., 2009).

Consequently, previous investigations show that degraded natural waters and industrial effluents often contain a combination of As, Cr, and/or Se trace element contaminants. Within natural waters and industrial effluents, As, Cr, and Se are commonly found in soluble oxyanion forms such as arsenate ($H_nAsO_4^{3-n}$), arsenite ($H_nAsO_3^{3-n}$), chromate ($HCrO_4^-$ or CrO_4^{2-}), selenate ($HSeO_4^-$ or SeO_4^{2-}), and selenite ($H_nSeO_3^{2-n}$) (Fetter, 1993; Moore and Ramamoorthy, 1984). Likewise, scientific literature also indicates that degraded natural waters and industrial effluents often contain a combination of Cd, Cu, and Pb. Within soils and ground/surface waters, Cd, Cu, and Pb are commonly present as divalent cations (i.e., Cd^{2+}, Cu^{2+}, and Pb^{2+}) and various metal hydroxide ions (Fetter, 1993; Moore and Ramamoorthy, 1984).

As a result of environmental and health concerns, effective treatment options are therefore needed to remove multiple trace element contaminants from already degraded natural waters or from industrial effluents. Filtration systems could be a viable treatment option. There are a wide range of potential filter systems that could be used for remediation of trace element contaminants, including permeable reactive barriers for contaminated groundwater plumes, large fluidized bed filters for municipal or industrial water treatment, filter cartridges for agricultural drainage pipe discharge, and so forth. The type of porous, chemically-reactive material that is incorporated into a filter system for trace element contaminant removal will be critical for effective water treatment, and in this regard, iron-based materials could be promising.

Iron-based materials, such as elemental iron (i.e., zero-valent iron) and iron oxides/hydroxides, have been evaluated for water

[1*] USDA/ARS—Soil Drainage Research Unit, 590 Woody Hayes Drive, Room 234, Columbus, OH 43210, U.S.A.; e-mail: Barry.Allred@ars.usda.gov.

[2] Ohio State University, School of Earth Sciences, 275 Mendenhall Laboratory, Columbus, Ohio.

Table 1—Iron-based filter material chemical and physical properties.[a]

Filter material	pH	Orp[b] Mv	Particle density g/cm³	Particle size distribution % by weight			
				Course sand size 2.0–4.75 mm	Medium sand size 0.43–2.0 mm	Fine sand size 0.075–0.43 mm	Silt/clay size <0.075 mm
ZVI	10.35	−592	7.03	0.01	73.58	25.92	0.49
PIC	10.14	−538	7.13	0.00	23.50	76.48	0.02
SMI	6.75	−660	5.93	0.12	21.11	78.71	0.06
IOH	8.18	26	3.62	0.04	97.87	2.05	0.04

[a] Values of pH and ORP represent a three replicate average obtained from 1:2 by weight slurry mixtures of filter material to deionized water at ambient laboratory temperatures of 20 to 25 °C.

[b] ORP = oxidation/reduction potential.

treatment of trace element contaminants. Zero-valent iron (ZVI) has been used within permeable reactive barriers to remove trace element contaminants from ground water (Henderson and Demond, 2007). Iron oxides/hydroxides (IOH) have been used by municipalities and in the home for filtration water treatment of trace element contaminants, particularly arsenic (Dennis, 2010; State of Maine, Dept. of Health and Human Services—Drinking Water Program, 2010). The mechanisms by which ZVI removes trace element contaminants from water are complex and can include either individually or in combination; electro-chemical reduction in association with iron oxidation (Ponder et al., 2000; Puls et al., 1999; Yoon et al., 2011; Zhang et al., 2005, Zhang et al., 2011), chemical precipitation (Lackovic et al., 2000; Puls et al., 1999; Sasaki et al., 2009), and inner-sphere or outer-sphere surface complexation on iron corrosion products (iron oxides/hydroxides) (Melitas et al., 2002; Ponder et al., 2000; Yoon et al., 2011; Zhang et al., 2005, Zhang et al., 2011). The mechanisms by which IOH removes trace element contaminants from water are likewise complex and can include either individually or in combination; electrochemical reduction in association with oxidation of ferrous iron to ferric iron (Kendelewicz et al., 2000); and inner-sphere or outer-sphere surface complexation on IOH particles (Jang et al., 2006; Kendelewicz et al., 2000; Khaodhair et al., 2000; Mostafa et al., 2011; Tuutijärvi et al., 2010). Two recently developed iron-based materials, porous iron composite (PIC) and sulfur modified iron (SMI), may also have filter treatment potential for waters contaminated with trace elements. The trace element removal mechanisms for PIC and SMI have not yet been identified, but might be similar to ZVI and IOH trace element contaminant removal mechanisms.

To date, there has been little direct trace element filter treatment comparison of ZVI versus IOH and, especially, ZVI or IOH versus PIC or SMI. Consequently, for the purpose of providing a preliminary comparison of ZVI, PIC, SMI, and IOH in regard to trace element contaminant filter treatment potential, a laboratory investigation was carried out with hydraulic conductivity tests, batch tests, and solute transport column tests. Previous discussions have indicated that degraded natural waters and industrial effluents often contain a combination of As, Cr, or Se trace elements or a combination of Cd, Cu, and Pb trace elements; therefore, two types of solutions were used in the batch and column tests: one with As, Cr, and Se species combined together and a second with Cd, Cu, and Pb species combined together. The stated research objective was, therefore, to conduct a preliminary laboratory comparison of

ZVI, PIC, SMI, and IOH filter materials with respect to hydraulic flow efficiency and trace element contaminant water treatment capability.

Materials and Methods

Iron-Based Water Filtration Products. Four iron-based water filtration products were evaluated in this investigation. The first product, zero-valent iron, designated as ZVI, was obtained from Connelly-GPM, Inc. (Chicago, Illinois; Product Name: CC-1190; http://www.connellygpm.com), and can be described as a ground iron aggregate consisting of shavings from cast iron borings. The second product, porous iron composite, designated as PIC, was obtained from North American Höganäs, Inc. (Hollsopple, Pennsylvania; Product Name: Cleanit LC; http://www.hoganas.com/nah), and is manufactured with high purity elemental iron powder to which functional additives are mixed. The mixture was then processed through powder metallurgical technologies to achieve an iron composite media with high internal porosity (specific surface ~10.0 m²/g) where functional groups are evenly distributed in either free or partially alloyed forms. The third product, sulfur modified iron, designated as SMI, was obtained from SMI_PS, Inc. (Lincoln, California; Pete@smiwater.com), and can be described as a hydrogen-reduced, high surface area iron powder that has been additionally modified through chemical reaction with pure sulfur to produce sulfur/iron compound surface coatings on the iron particles. The fourth product, an iron oxide/hydroxide, designated as IOH, is manufactured by LANXESS AG (Leverkusen, Germany; Product Name: Bayoxide E33; http://lanxess.com), and can be described as a synthetic, high surface area (~150 m²/g) goethite (chemical formula α-FeOOH). To improve hydraulic flow efficiency (i.e., increase hydraulic conductivity), fine-grained particles passing through a 100-mesh sieve (particle size <0.15 mm) were removed from the ZVI, PIC, SMI, and IOH filter materials that were tested in this investigation.

Properties of the ZVI, PIC, SMI, and IOH filter materials are provided in Table 1. The pH and oxidation/reduction potential (ORP) were measured on 1:2 by weight slurry mixtures of filter material to deionized water. All pH values were determined using an Oakton (Vernon Hills, Illinois) pHTestr 10 BNC. Oxidation/reduction potential was measured with a YSI Inc. (Yellow Springs, Ohio) EcoSense pH100 Meter and a YSI Inc., 115-1 ORP Probe. Table 1 shows that, with respect to pH, the ZVI and PIC slurries were strongly alkaline (>10), the IOH slurry was moderately alkaline (8 to 10), and the SMI slurry was

near neutral (6 to 8). The ZVI, PIC, and SMI had ORP values less than −500 mV, indicating that ZVI, PIC, and SMI would likely produce very low redox conditions within a filter treatment system environment. The low ORP values for the water slurries with ZVI, PIC, and SMI were expected, because Eh-pH diagrams for iron/water systems indicate that elemental iron is stable only under very low Eh (low ORP) conditions (Takeno, 2005).

Iron-based filter material specific gravity values were determined in a rigorous manner using American Society for Testing and Materials procedures (Wray, 1986). The particle density testing method uses Archimedes principle, and once the weight of an iron-based filter material amount was measured along with its displaced water volume, the particle density of the iron-based filter material was then easily calculated. The laboratory-measured particle density of IOH was 3.62 g/cm^3, which was much lower than the particle density values of 7.03, 7.13, and 5.93 g/cm^3 that were obtained, respectively, for ZVI, PIC, and SMI. The cast iron shavings or scrap metal used as feedstock for producing ZVI, PIC, and SMI are composed predominantly of iron, although small but significant quantities of other constituents, such as carbon, silicon, manganese, and others, are also present. Furthermore, PIC and SMI particle surfaces have attached functional groups or sulfur compounds containing not only iron but other constituents as well. Consequently, it could be expected that the particle density of ZVI (7.03 g/cm^3), PIC (7.13 g/cm^3), and SMI (5.93 g/cm^3) differed from that of elemental iron (7.87 g/cm^3). Table 1 particle size data, based on mechanical sieving methods (Wray, 1986) and a particle size classification from Perloff and Baron (1976) shows that the 100-mesh sieved ZVI and IOH materials were predominantly composed of medium sand sized particles, while the 100-mesh sieved PIC and SMI materials were predominantly composed of fine sand sized particles.

Test Solutions. The hydraulic conductivity test solution contained 1361 ppm (0.01 mole/L) of dissolved calcium sulfate (CaSO$_4$). The solution used in Stage 1 of the arsenic-chromium-selenium (As-Cr-Se) batch tests contained 50 ppm As, 50 ppm Cr, and 50 ppm Se. The solution used in the As-Cr-Se column tests contained 25 ppm As, 25 ppm Cr, and 25 ppm Se. For the As-Cr-Se batch and column test solutions, As was initially added as the arsenate oxyanion, AsO_4^{3-}, by dissolving potassium arsenate monobasic (KH$_2$AsO$_4$); Cr was initially added as the chromate oxyanion, CrO_4^{2-}, by dissolving potassium chromate (K$_2$CrO$_4$); and Se was initially added as the selenate oxyanion, SeO_4^{2-}, by dissolving potassium selenate (K$_2$SeO$_4$). The solution used in Stage 1 of the cadmium-copper-lead (Cd-Cu-Pb) batch tests contained 50 ppm Cd, 50 ppm Cu, and 50 ppm Pb. The solution used in the Cd-Cu-Pb column tests contained 25 ppm Cd, 25 ppm Cu, and 25 ppm Pb. For the Cd-Cu-Pb batch and column test solutions, Cd was initially added as a divalent cation, Cd^{2+}, by dissolving cadmium chloride (CdCl$_2$); Cu was initially added as the divalent cation, Cu^{2+}, by dissolving copper chloride dihydrate (CuCl$_2$·2H$_2$O); and Pb was initially added as the divalent cation, Pb^{2+}, by dissolving lead chloride (PbCl$_2$). Ultrapure deionized water was used as the extraction solution during Stage 2 of all batch tests. The extraction solution used during Stage 3 of the As-Cr-Se batch tests contained 1743 ppm (0.01 mole/L) dissolved potassium sulfate (K$_2$SO$_4$). The extraction solution used during Stage 3 of the Cd-Cu-Pb batch tests contained 1110 ppm (0.01 mole/L) dissolved calcium chloride (CaCl$_2$). The hydraulic conductivity, As-Cr-Se batch test, and

As-Cr-Se column test solutions had had pH values near neutral (6 to 8), while the Cd-Cu-Pb batch test, Cd-Cu-Pb column test, ultrapure deionized water, K$_2$SO$_4$ batch test extraction, and CaCl$_2$ batch test extraction solutions were moderately acidic (4 to 6). The ORP values for all test solutions ranged from 100 to 300 mV.

Saturated Falling-Head Hydraulic Conductivity Tests. Saturated hydraulic conductivity is the porous media property governing the rate at which water flows through a filter material (e.g., ZVI, PIC, SMI, or IOH) under saturated conditions. To be practical for water treatment use from a hydraulic standpoint, a filter material must have a sufficiently high saturated hydraulic conductivity, at least equal and preferably much greater than 1.0 × 10^{-3} cm/s, which is a stormwater sand filter design criteria (Barr Engineering Co., 2001; Blick et al., 2004; Claytor and Schueler, 1996). Standard falling-head hydraulic conductivity tests (Freeze and Cherry, 1979; Todd, 1980) were used for saturated hydraulic conductivity measurement. Saturated falling-head hydraulic conductivity tests were carried out on 100-mesh sieved ZVI, PIC, SMI, and IOH filter materials at ambient laboratory temperatures ranging from 20 to 25 °C. Hydraulic conductivity measurements were obtained from two separately packed columns for each individual filter material. The packed ZVI, PIC, SMI, or IOH filter material columns were 152 mm in length, 41 mm in diameter, and were saturated with 0.01 mole/L CaSO$_4$ solution 24 hours prior to hydraulic conductivity measurement.

Contaminant Removal–Desorption/Dissolution Batch Tests. The three-stage contaminant removal–desorption/dissolution batch tests were carried out for two purposes: (1) to provide an initial assessment of the potential trace element removal capabilities of ZVI, PIC, SMI, and IOH to decide if further testing was warranted for any of these filter materials (Stage 1 of tests); and (2) to determine if the trace element contaminants that adsorbed or precipitated onto ZVI, PIC, SMI, or IOH particle surfaces could be then readily desorbed or dissolved back into solution via washing with water (Stage 2 of tests) or an electrolyte solution (Stage 3 of tests). The ZVI, PIC, SMI, and IOH filter materials were rinsed with distilled water prior to beginning the contaminant removal–desorption/dissolution batch tests. Batch tests were carried out at ambient laboratory temperatures ranging from 20 to 25 °C. Repeatability of results for the batch tests was confirmed by conducting two replicate batch tests for each combination of filter material (or no filter material [NFM]) and As-Cr-Se or Cd-Cu-Pb solution used in Stage 1.

For the first stage of each filter material batch test, 5 g (dry weight) of filter material (100-mesh sieved) and 40 g of either As-Cr-Se or Cd-Cu-Pb batch test solution were combined in a 50-mL polypropylene centrifuge tube (BD Biosciences, Bedford, Massachusetts). The filter material and As-Cr-Se or Cd-Cu-Pb solution were thoroughly mixed by placing the centrifuge tube on a laboratory rotator (Mini LabRoller Rotator, Labnet International, Inc., Woodbridge, New Jersey) operated at 20 rpm. The first stage of each batch test was then stopped after 24 hours of mixing. Procedures for the control batch tests (NFM) were the same, with only As-Cr-Se or Cd-Cu-Pb solution (40 g), but no added filter material. All batch test centrifuge tubes containing filter material (or NFM) and solution were then centrifuged (Beckman Model TJ-6 Centrifuge, Beckman Coulter, Inc., Fullerton, California) at 2500 rpm (800 g) for 15 minutes to

Table 2—Saturated solute transport column test information.

Column test number	Filter material	Test solution	Column dry bulk packing density g/cm³	Column pore volume cm³	Average low flow rate, - Flux -, and (Contact time) mL/h - mL/cm²•h - (minutes)
1	NFM[a]	25 mg/L As, Cr, Se	NA	NA	47.88 - NA - (NA)
2	ZVI	25 mg/L As, Cr, Se	3.23	160.84	51.29 - 2.56 - (188.15)
3	PIC	25 mg/L As, Se, Cr	2.04	214.35	55.22 - 2.76 - (232.90)
4	SMI	25 mg/L As, Cr, Se	2.06	196.16	51.76 - 2.58 - (227.39)
5	IOH	25 mg/L As, Cr, Se	0.52	256.87	51.83 - 2.59 - (297.36)
6	NFM[a]	25 mg/L Cd, Cu, Pb	NA	NA	49.36 - NA
7	ZVI	25 mg/L Cd, Cu, Pb	2.73	184.00	52.61 - 2.62 - (209.85)
8	PIC	25 mg/L Cd, Cu, Pb	2.03	215.01	54.07 - 2.69 - (238.59)
9	SMI	25 mg/L Cd, Cu, Pb	2.06	195.86	53.23 - 2.65 - (220.77)
10	IOH	25 mg/L Cd, Cu, Pb	0.51	258.07	60.01 - 3.00 - (258.03)

[a] NFM = notation for "no filter material" (empty column).
NA = not applicable.

separate the filter material from the solution. The Stage 1 supernatant solution was then decanted into a clean 50-mL polypropylene centrifuge tube.

For the second stage of each batch test, once the Stage 1 supernatant had been removed, 40 g of ultrapure deionized water only was added to the original centrifuge tubes, which had either 5 g of filter material or were empty (NFM—control tests). As with the first stage, the centrifuge tubes with filter material (or NFM) and the added ultrapure deionized water were placed on a laboratory rotator and mixed for 24 hours and then centrifuged for 15 minutes. Next, the Stage 2 supernatant was decanted into a clean 50-mL centrifuge tube.

For the third stage of each batch test, once the Stage 2 supernatant had been removed, 40 g of 0.01 mole/L K_2SO_4 solution or 0.01 mole/L $CaCl_2$ solution were added to the original centrifuge tubes, which again had either 5 g of iron-based filter material or were empty (NFM— control tests). The K_2SO_4 solution was added only to those original centrifuge tubes with filter material (or NFM) that were exposed to the As-Cr-Se solution during the first stage of the batch tests. The $CaCl_2$ solution was added to those original centrifuge tubes with filter material (or NFM) that were exposed to the Cd-Cu-Pb solution during the first stage of the desorption/dissolution batch tests. As with the first and second stages, the centrifuge tubes with filter material (or NFM) and either K_2SO_4 or $CaCl_2$ solution were placed on a laboratory rotator and mixed for 24 hours, then centrifuged for 15 minutes, followed by decanting of the Stage 3 supernatant into a clean 50-mL centrifuge tube. Concentrations of As, Cr, and Se or Cd, Cu, and Pb were measured for the supernatant solutions from the first, second, and third stages of the contaminant removal–desorption/dissolution batch tests using inductively coupled plasma (ICP) methods.

Low-to-High Flow Rate Saturated Solute Transport Column Tests. By allowing control of solution flux and the filter material to solution contact time, saturated solute transport column tests can help better evaluate the likely trace element contaminant (As, Cd, Cr, Cu, Pb, Se) removal behavior of 100-mesh sieved ZVI, PIC, SMI, or IOH filter materials within an actual filter treatment system. For these column tests, continuously operated variable flow rate peristaltic pumps (Model 3384 and Model 3386, Control Company, Friendswood, Texas) delivered the initial influent trace element contaminant solution to the bottom inlet of a vertically oriented Teflon

permeameter containing a packed filter material (or empty-NFM) column. Ambient laboratory temperatures during testing ranged from 20 to 25 °C. Filter material columns contained within the Teflon permeameters had a diameter of 51 mm and a length of 150 mm. Effluent exiting the permeameter was collected over time in glass containers. Plastic laboratory tubing was used to deliver solution between the influent supply container, peristaltic pump, permeameter, and effluent sample container. Every other effluent sample (one out of two) was centrifuged to separate out any filter material present and then analyzed for As, Cr, and Se or Cd, Cu, and Pb using ICP methods. Direct pH measurements were obtained for those effluent samples (one out of two) not analyzed for trace element contaminants.

Table 2 provides information on the 10 saturated solute transport column tests conducted during this study. The column test information provided in Table 2 includes type of filter material (or NFM), contaminant test solution (As-Cr-Se or Cd-Cu-Pb), filter material packing density, column pore volume, flow rate, flux, contact time, and effluent amount. Column tests 1 through 5 were carried out with the As-Cr-Se column test solution, while column tests 6 through 10 were conducted with the Cd-Cu-Pb column test solution. Column tests 1 and 6 were carried out with empty columns that contained NFM. These empty column tests were conducted for baseline comparison purposes to quantify the amounts of trace element contaminants lost by the experimental apparatus and procedures. Because trace element contaminant adsorption on experimental apparatus is likely to be greatest under low flow rate conditions, column tests 1 and 6 were therefore carried out at one relatively low flow rate of approximately 50 mL/h. Column tests 2 through 5 and 7 through 10 were conducted with the Teflon permeameters packed with ZVI, PIC, SMI, or IOH filter materials. These filter material column tests (2 through 5 and 7 through 10) were carried out in two flow rate steps, with an initial longer duration lower flow rate (∼45 to 60 mL/h) followed by a shorter duration much higher flow rate (>1500 mL/h). By conducting the filter material column tests (2 through 5 and 7 through 10) with both low and high flow rates, insight was gained on the water filter treatment contact time needed for effective removal of trace element contaminants. The duration for each of the 10 column tests ranged from 6 to 8 days; and for the ZVI, PIC, SMI, and IOH filter material column tests, the

Table 2—(Extended)

Low flow rate effluent amount L and (# pore volumes)	Average high flow rate, - Flux -, and (Contact time) mL/h - mL/cm²•h - (minutes)	High flow rate effluent amount L and (# pore volumes)	Total effluent amount L and (# pore volumes)
8.85 (NA)	NA - NA - (NA)	NA (NA)	8.85 (NA)
8.59 (53.40)	2550.31 - 127.33 - (3.78)	1.81 (11.23)	10.40 (64.63)
9.19 (42.90)	1722.89 - 86.02 - (7.46)	2.05 (9.54)	11.24 (52.44)
8.62 (43.94)	1538.79 - 76.83 - (7.65)	1.96 (9.97)	10.58 (53.91)
8.63 (33.58)	2615.34 - 130.57 - (5.89)	1.85 (7.21)	10.48 (40.79)
9.18 (NA)	NA - NA - (NA)	NA (NA)	9.18 (NA)
8.55 (46.49)	6173.00 - 308.19 - (1.79)	2.54 (13.80)	11.09 (60.29)
9.03 (42.00)	4059.10 - 202.65 - (3.18)	2.37 (11.01)	11.40 (53.01)
7.72 (39.42)	3477.95 - 173.64 - (3.38)	2.09 (10.66)	9.81 (50.08)
8.48 (32.88)	3533.57 - 176.42 - (4.38)	2.45 (9.51)	10.93 (42.39)

total amount of As-Cr-Se or Cd-Cu-Pb solution flushed through the column during testing ranged from 40 to 65 pore volumes.

Trace Element Analysis Methods for Batch and Column Tests. Concentrations of As, Cd, Cr, Cu, Pb, and Se within batch test supernatant and column test effluent were measured using ICP methods (American Public Health Association et al., 1998) using a Perkin-Elmer (Waltham, Massachusetts) Optima 3300 DV ICP-OES Spectrometer. Trace element contaminant detection limits for this ICP method are As: 0.061 ppm, Cd: 0.001 ppm, Cr: 0.003 ppm, Cu: 0.001 ppm, Pb: 0.016 ppm, and Se: 0.054 ppm.

Results and Discussion

Saturated Falling-Head Hydraulic Conductivity Test Results. Saturated hydraulic conductivity measurements are provided in Table 3 for the 100-mesh sieved ZVI, PIC, SMI, and IOH filter materials. Filter material packing densities for the saturated falling-head hydraulic conductivity tests are also provided in Table 3. There was a wide range in filter material packing densities, from an average of only 0.52 g/cm³ for IOH to 3.04 gm/cm³ for ZVI. The IOH particles have an extremely large amount of internal porosity. A measured specific surface of ~150 m²/g for IOH (personal communication with product distributor), provides evidence of the large amount of internal porosity present. Consequently, air-filled pores comprise a large percentage of the overall volume for any dry IOH particle. Therefore, the dry packing density of IOH is very low for the hydraulic conductivity tests and solute transport column tests.

All measured saturated hydraulic conductivity measurements for the four iron-based filter materials were at least an order of magnitude greater than the previously discussed 1.0×10^{-3} cm/s hydraulic conductivity criterion used for stormwater sand filters (Barr Engineering Company, 2001; Blick et al., 2004; Claytor and Schueler, 1996). Hydraulic conductivity tends to have a strong, positive correlation with average particle size (Freeze and Cherry, 1979). The lowest two-test average hydraulic conductivity values were exhibited by PIC (1.80×10^{-2} cm/s) and SMI (1.73×10^{-2} cm/s), and these results are probably due in large part to PIC and SMI having a much greater amount of fine sand sized particles (>75%, Table 1) compared to ZVI or IOH, which were composed mostly of medium sand sized particles. The highest average hydraulic conductivity was obtained with IOH (9.75×10^{-2} cm/s), which has the greatest amount of medium sand sized particles (>95%, Table 1). Consequently, the overall results for the saturated falling-head hydraulic conductivity tests indicate that 100-mesh sieved ZVI, PIC, SMI, and IOH all have sufficient hydraulic conductivity for use in filter treatment of water.

Contaminant Removal–Desorption/Dissolution Batch Tests. Results of the contaminant removal–desorption/dissolution batch tests are shown in Tables 4 and 5. The Stage 2 and Stage 3 percentage desorbed/dissolved values represent the percentage of a trace element desorbed/dissolved during Stage 2 or Stage 3 relative to the total amount of the trace element that was originally removed during Stage 1. The control (NFM) contaminant removal–desorption/dissolution batch tests results indicate that experimental equipment and procedures do not account for substantial trace element contaminant removal during Stage 1 or substantial trace element contaminant desorption/dissolution during either Stage 2 or Stage 3.

There was effectively 100% removal of As, Cr, and Se during Stage 1 of the As-Cr-Se batch tests conducted with SMI (Table 4). Essentially 100% of As, ~98% of Cr, and ~33% of Se were removed by IOH during Stage 1 of the As-Cr-Se batch tests. Both ZVI and PIC removed nearly 80% of the Cr during Stage 1 of the batch tests, but neither were particularly effective in removing As or Se. Consequently, the results for Stage 1 of the As-Cr-Se batch tests (Table 4) indicate, in a preliminary manner, that SMI may work best for mixed As, Cr, and Se removal, followed closely by IOH (good As and Cr removal), then ZVI and PIC (good Cr removal only).

Table 3—Iron-based filter material hydraulic conductivities and associated packing densities.

Filter material	Test number	Column dry bulk packing density G/cm³	Saturated hydraulic conductivity cm/s
ZVI	1	3.00	3.89×10^{-2}
	2	3.08	1.73×10^{-2}
PIC	1	2.22	1.28×10^{-2}
	2	2.13	2.32×10^{-2}
SMI	1	1.98	2.15×10^{-2}
	2	1.97	1.30×10^{-2}
IOH	1	0.51	1.03×10^{-1}
	2	0.52	9.20×10^{-2}

Table 4—Contaminant removal-desorption/dissolution batch test results for As-Cr-Se solution[a].

Batch test	Stage 1 – percent and (amount) of trace element removal[b] % - (mg)			Stage 2 - percent and amount of trace element desorption/ dissolution with ultrapure water[b] % - (mg)			Stage 3 - percent and amount of trace element desorption/ dissolution with 0.01 mole/L K_2SO_4 solution[b] % - (mg)		
	As	Cr	Se	As	Cr	Se	As	Cr	Se
NFM[c] 1	1.5 (0.030)	1.9 (0.038)	4.0 (0.079)	0.0 (0.000)	0.0 (0.000)	0.0 (0.000)	0.0 (0.000)	0.0 (0.000)	0.0 (0.000)
NFM[c] 2	1.8 (0.037)	1.3 (0.025)	3.9 (0.077)	0.0 (0.000)	0.0 (0.000)	0.0 (0.000)	0.0 (0.000)	0.0 (0.000)	0.0 (0.000)
ZVI 1	25.5 (0.510)	83.0 (1.659)	20.6 (0.411)	5.7 (0.029)	8.3 (0.137)	0.0 (0.000)	0.0 (0.000)	0.0 (0.000)	0.0 (0.000)
ZVI 2	28.2 (0.563)	82.7 (1.654)	22.6 (0.451)	6.7 (0.037)	7.5 (0.125)	0.0 (0.000)	0.0 (0.000)	0.0 (0.000)	0.0 (0.000)
PIC 1	35.6 (0.712)	79.2 (1.584)	21.6 (0.432)	3.9 (0.028)	0.0 (0.000)	0.0 (0.000)	0.0 (0.000)	0.0 (0.000)	0.0 (0.000)
PIC 2	35.3 (0.706)	78.2 (1.564)	22.1 (0.411)	4.5 (0.032)	0.0 (0.000)	0.0 (0.000)	0.0 (0.000)	0.0 (0.000)	0.0 (0.000)
SMI 1	100.0 (2.000)	100.0 (2.000)	100.0 (2.000)	0.0 (0.000)	0.0 (0.000)	0.0 (0.000)	0.0 (0.000)	0.0 (0.000)	0.0 (0.000)
SMI 2	100.0 (2.000)	100.0 (2.000)	100.0 (2.000)	0.0 (0.000)	0.0 (0.000)	0.0 (0.000)	0.0 (0.000)	0.0 (0.000)	0.0 (0.000)
IOH 1	100.0 (2.000)	97.9 (1.958)	32.5 (0.650)	0.0 (0.000)	0.0 (0.000)	8.0 (0.052)	0.0 (0.000)	2.6 (0.051)	66.0 (0.429)
IOH 2	100.0 (2.000)	97.9 (1.958)	32.5 (0.651)	0.0 (0.000)	0.0 (0.000)	8.6 (0.056)	0.0 (0.000)	2.8 (0.054)	72.9 (0.475)

[a] Initial Stage 1 concentration of As = 50 ppm, Cr = 50 ppm, and Se = 50 ppm.
[b] Stage 1 percent and amount values for trace element removal equaling 100.0% and 2.000 mg, respectively, is a general indication that the batch test supernatant solution collected at the completion of Stage 1 had a trace element concentration below the detection limit. Stage 2 or Stage 3 percent and amount values for trace element desorption/dissolution equaling 0.0% and 0.000 mg, respectively, is a general indication that the batch test supernatant solution collected at the completion of Stage 2 or Stage 3 had a trace element concentration below the detection limit.
[c] NFM = no filter material.

Results from Stage 1 of the Cd-Cu-Pb batch tests (Table 5) show that ZVI, PIC, SMI, or IOH removed at least 90% of Cd, Cu, and Pb. The ZVI, PIC, SMI, and IOH materials, therefore, all have promise regarding water treatment of Cd, Cu, and Pb. Consequently, the overall Stage 1 batch test results (Tables 4 and 5) indicate that further investigation of ZVI, PIC, SMI, and IOH as potential filter materials is warranted using saturated solute transport column tests. Furthermore, these Stage 1 batch test results also imply that ZVI, PIC, SMI, and IOH could possibly be used in large mixing reactors to clean industrial effluents containing multiple trace element contaminants.

Tables 4 and 5 indicate that proportionally little of the As, Cd, Cr, Cu, Pb, and Se originally adsorbed or precipitated onto ZVI, PIC, SMI, or IOH particle surfaces during Stage 1 were then desorbed/dissolved back into solution during the Stage 2 wash with ultrapure deionized water. During Stage 3, electrolyte solutions were used to potentially displace trace elements that were electrostatically attached to ZVI, PIC, SMI, and IOH particle surfaces. A fairly high concentration (0.01 mole/L) of K_2SO_4 was used for the electrolyte wash in the As-Cr-Se batch tests, and a fairly high concentration (0.01 mole/L) of $CaCl_2$ was used for the electrolyte wash in the Cd-Cu-Pb batch tests. The K_2SO_4 and $CaCl_2$ compounds were chosen in part so that the Stage 3 extraction solutions would contain anions and cations commonly found in natural waters. The molar amount of sulfate (SO_4^{2-}) added during Stage 3 was 10 to 15 times greater than the molar amounts the of As, Cr, or Se oxyanions introduced during Stage 1 of the As-Cr-Se batch tests, and due to chemical mass

Table 5—Contaminant removal-desorption/dissolution batch test results for Cd-Cu-Pb solution[a].

Batch test	Stage 1—Percent and (amount) of trace element removal[b] % - (mg)			Stage 2—Percent and amount of trace element desorption/ dissolution with ultrapure water[b] % - (mg)			Stage 3—Percent and amount of trace element desorption/ dissolution with 0.01 mole/L $CaCl_2$ solution[b] % - (mg)		
	Cd	Cu	Pb	Cd	Cu	Pb	Cd	Cu	Pb
NFM[c] 3	3.8 (0.076)	2.2 (0.044)	2.6 (0.051)	0.0 (0.000)	0.0 (0.000)	0.0 (0.000)	0.0 (0.000)	0.0 (0.000)	0.0 (0.000)
NFM[c] 4	3.3 (0.066)	1.7 (0.033)	2.2 (0.045)	0.0 (0.000)	0.0 (0.000)	0.0 (0.000)	0.0 (0.000)	0.0 (0.000)	0.0 (0.000)
ZVI 3	91.5 (1.829)	98.8 (1.975)	99.9 (1.998)	1.4 (0.026)	0.0 (0.000)	0.0 (0.000)	0.0 (0.000)	0.0 (0.000)	0.0 (0.000)
ZVI 4	91.7 (1.833)	98.8 (1.975)	100.0 (2.000)	1.6 (0.029)	0.0 (0.000)	0.0 (0.000)	0.0 (0.000)	0.0 (0.000)	0.0 (0.000)
PIC 3	99.3 (1.986)	100.0 (2.000)	100.0 (2.000)	0.0 (0.000)	0.0 (0.000)	0.0 (0.000)	0.0 (0.000)	0.0 (0.000)	0.0 (0.000)
PIC 4	99.6 (1.992)	100.0 (2.000)	100.0 (2.000)	0.0 (0.000)	0.0 (0.000)	0.0 (0.000)	0.0 (0.000)	0.0 (0.000)	0.0 (0.000)
SMI 3	100.0 (2.000)	100.0 (2.000)	100.0 (2.000)	0.0 (0.000)	0.0 (0.000)	0.0 (0.000)	0.0 (0.000)	0.0 (0.000)	0.0 (0.000)
SMI 4	100.0 (2.000)	100.0 (2.000)	100.0 (2.000)	0.0 (0.000)	0.0 (0.000)	0.0 (0.000)	0.0 (0.000)	0.0 (0.000)	0.0 (0.000)
IOH 3	100.0 (2.000)	100.0 (2.000)	100.0 (2.000)	0.0 (0.000)	0.0 (0.000)	0.0 (0.000)	0.0 (0.000)	0.0 (0.000)	0.0 (0.000)
IOH 4	100.0 (2.000)	100.0 (2.000)	100.0 (2.000)	0.0 (0.000)	0.0 (0.000)	0.0 (0.000)	0.0 (0.000)	0.0 (0.000)	0.0 (0.000)

[a] Initial Stage 1 concentration of Cd = 50 ppm, Cu = 50 ppm, and Pb = 50 ppm.
[b] Stage 1 percent and amount values for trace element removal equaling 100.0% and 2.000 mg, respectively, is a general indication that the batch test supernatant solution collected at the completion of Stage 1 had a trace element concentration below the detection limit. Stage 2 or Stage 3 percent and amount values for trace element desorption/dissolution equaling 0.0% and 0.000 mg, respectively, is a general indication that the batch test supernatant solution collected at the completion of Stage 2 or Stage 3 had a trace element concentration below the detection limit.
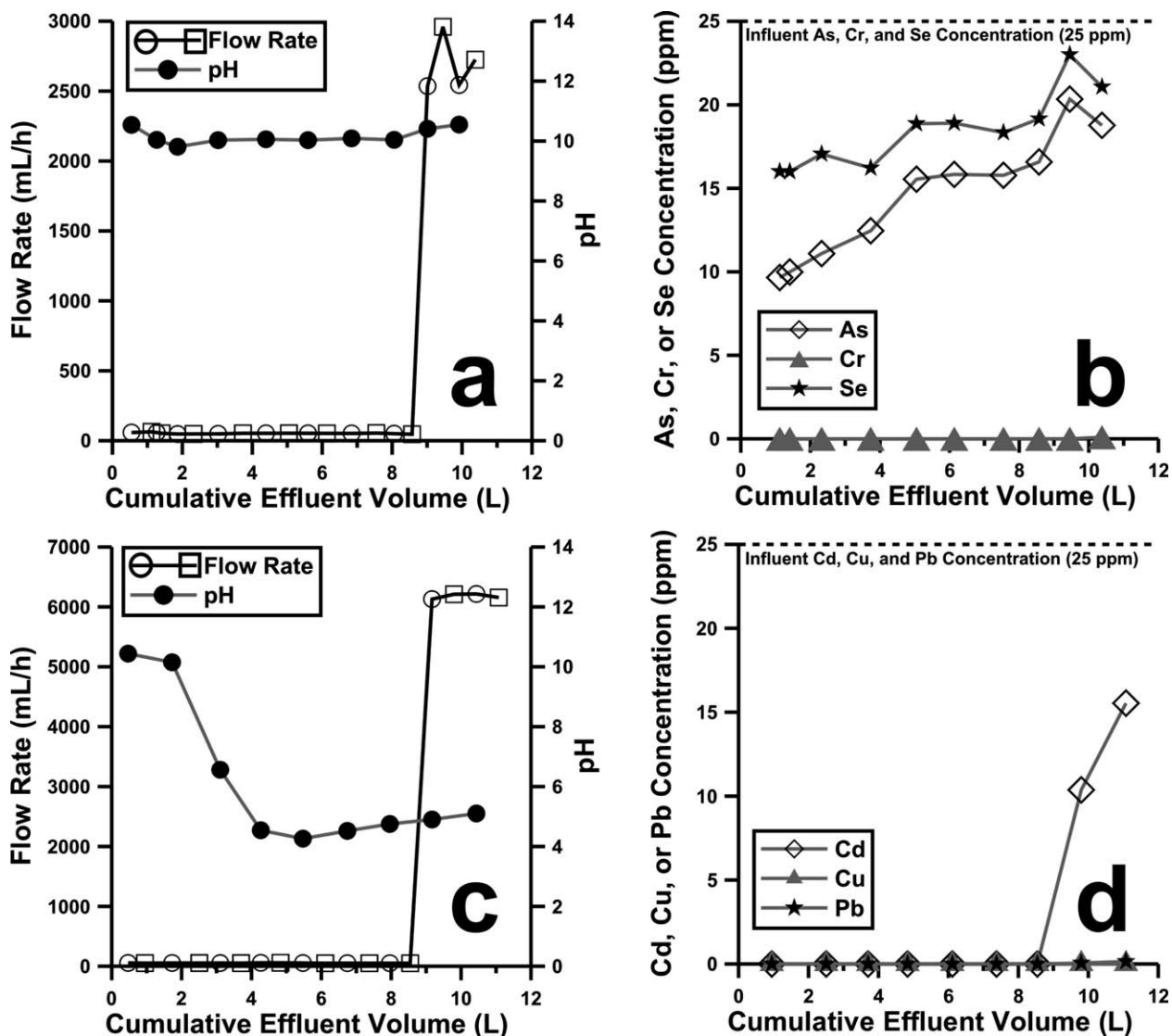[c] NFM = no filter material.

Figure 1—Representative column test results: (a) flow rate and pH for As-Cr-Se ZVI column test 2—flow rate open circle symbols denote pH measurement samples and open square symbols denote contaminant measurement samples; (b) measured contaminant concentrations for As-Cr-Se ZVI column test 2; (c) flow rate and pH for Cd-Cu-Pb ZVI column test 7—flow rate open circle symbols denote pH measurement samples and open square symbols denote contaminant measurement samples; and (d) measured contaminant concentrations for Cd-Cu-Pb ZVI column test 7.

action considerations, it was expected that SO_4^{2-} could in turn displace significant amounts of any As, Cr, or Se oxyanions that had been electrostatically adsorbed by the iron-based filter materials. Likewise, the molar amount of divalent calcium cations (Ca^{2+}) added during Stage 3 was 10 to 40 times greater than the molar amounts the of divalent Cd, Cu, or Pb cations (Cd^{2+}, Cu^{2+}, or Pb^{2+}) introduced during Stage 1 of the Cd-Cu-Pb batch tests, and again due to chemical mass action considerations, it was expected that Ca^{2+} could in turn displace significant amounts of any Cd^{2+}, Cu^{2+}, or Pb^{2+} that had been electrostatically adsorbed by the iron-based filter materials. With one exception, Stage 3 results showed very little desorption/ dissolution of the trace element contaminants. The exception being desorption of Se from the IOH filter material, which implies that Se is adsorbed onto IOH particle surfaces via a

relatively weak electrostatic interaction. Generally, with the one exception just noted, the Tables 4 and 5 show that once As, Cd, Cr, Cu, Pb, or Se are adsorbed or precipitated onto ZVI, PIC, SMI, or IOH particle surfaces, these trace elements tend to remain fixed and not readily desorbed or dissolved back into solution.

Low-to-High Flow Rate Saturated Solute Transport Column Test Results. As previously mentioned, these column tests allow control of solution flux and the filter material to solution contact time; therefore facilitating better assessment of the likely trace element contaminant water treatment capabilities of iron-based filter materials within an actual water filter treatment system. As representative examples of graphed column test data obtained during this study, Figure 1 shows flow rates, effluent pH values, and effluent trace element

Table 6—Column test results for As-Cr-Se solution.

Column test	Filter material	Low flow rate pH Results Average pH	High flow rate pH Results Average pH
1	NFM[c]	6.15	NA
2	ZVI	10.08	10.48
3	PIC	10.33	10.55
4	SMI	3.80	5.95
5	IOH	7.98	8.28
		Start (s) and finish (f) pH	**Start (s) and finish (f) pH**
1	NFM[c]	6.31 (s) 6.41 (f)	NA (s) NA (f)
2	ZVI	10.54 (s) 10.04 (f)	10.41 (s) 10.55 (f)
3	PIC	10.19 (s) 10.46 (f)	10.58 (s) 10.51 (f)
4	SMI	4.33 (s) 3.77 (f)	5.79 (s) 6.10 (f)
5	IOH	8.02 (s) 8.06 (f)	8.21 (s) 8.34 (f)
		Std. dev. of pH	**Range of pH**
1	NFM[c]	0.14	NA
2	ZVI	0.20	0.14
3	PIC	0.11	0.07
4	SMI	0.24	0.31
5	IOH	0.16	0.13

[a] Initial concentration of As = 25 ppm, Cr = 25 ppm, and Se = 25 ppm.
[b] ND = not detected; NA = not applicable.
[c] NFM = no filter material.

contaminant concentration values for the two column tests carried out with ZVI. Effluent pH and effluent trace element contaminant concentration results for all 10 column tests are more concisely compiled in Tables 6 and 7.

Table 6 shows that the effluent pH for the As-Cr-Se SMI column test 4 was generally acidic (<6), while the As-Cr-Se NFM column test 1 effluent pH was near neutral (6 to 8). The As-Cr-Se IOH column test 5 effluent had a pH near 8, and the

Table 7—Column test results for Cd-Cu-Pb solution.

Column test	Filter material	Low flow rate pH results Average pH	High flow rate pH results Average pH
6	NFM[c]	4.84	NA
7	ZVI	6.46	5.00
8	PIC	8.47	6.37
9	SMI	4.16	5.30
10	IOH	7.91	7.41
		Start (s) and finish (f) pH	**Start (s) and finish (f) pH**
6	NFM[c]	4.45 (s) 4.63 (f)	NA (s) NA (f)
7	ZVI	10.44 (s) 4.75 (f)	4.90 (s) 5.10 (f)
8	PIC	10.62 (s) 6.28 (f)	7.15 (s) 5.59 (f)
9	SMI	3.65 (s) 4.36 (f)	5.29 (s) 5.31 (f)
10	IOH	7.95 (s) 8.06 (f)	7.58 (s) 7.23 (f)
		Std. dev. of pH	**Range of pH**
6	NFM[c]	0.20	NA
7	ZVI	2.73	0.20
8	PIC	1.85	1.56
9	SMI	0.25	0.02
10	IOH	0.11	0.35

[a] Initial concentration of Cd = 25 ppm, Cu = 25 ppm, and Pb = 25 ppm.
[b] ND = not detected; NA = not applicable.
[c] NFM = no filter material.

Table 6—(Extended)

Low flow rate effluent concentration[a] ppm			High flow rate effluent concentration[a] ppm		
Average effluent concentration[b]			Average effluent concentration[b]		
As	Cr	Se	As	Cr	Se
21.93	24.31	22.77	NA	NA	NA
13.37	ND	17.57	19.55	0.05	22.04
11.73	ND	15.78	14.93	ND	17.33
ND	ND	ND	ND	ND	ND
0.05	ND	18.23	0.04	6.03	27.40
Start (s) and finish (f) effluent concentrations[b]			Start (s) and finish (f) effluent concentration[b]		
As	Cr	Se	As	Cr	Se
22.1 (s) 21.7 (f)	24.4 (s) 24.1 (f)	22.9 (s) 22.5 (f)	NA (s) NA (f)	NA (s) NA (f)	NA (s) NA (f)
9.66 (s) 16.6 (f)	ND (s) ND (f)	16.0 (s) 19.3 (f)	20.3 (s) 18.8 (f)	ND (s) 0.09 (f)	23.0 (s) 21.1 (f)
10.0 (s) 12.9 (f)	ND (s) ND (f)	17.0 (s) 15.2 (f)	16.7 (s) 13.1 (f)	ND (s) ND (f)	19.7 (s) 14.9 (f)
ND (s) ND (f)	ND (s) ND (f)	ND (s) ND (f)	ND (s) ND (f)	ND (s) ND (f)	ND (s) ND (f)
0.08 (s) 0.06 (f)	ND (s) ND (f)	ND (s) 27.9 (f)	0.04 (s) 0.03 (f)	2.67 (s) 9.38 (f)	28.7 (s) 26.1 (f)
Std. dev. of effluent concentration[b]			Range of effluent concentration[b]		
As	Cr	Se	As	Cr	Se
0.13	0.11	0.12	NA	NA	NA
2.88	NA	1.39	1.57	0.09	1.93
1.16	NA	1.01	3.58	NA	4.82
NA	NA	NA	NA	NA	NA
0.02	NA	11.57	0.01	6.71	2.57

effluent pH values for the As-Cr-Se ZVI and PIC column tests 2 and 3 were strongly alkaline (>10). With the influent As-Cr-Se column test solution having a near neutral pH of 6.46, it is apparent that ZVI, PIC, SMI, and IOH can significantly affect the pH of this particular contaminated water. Consequently, additional water treatment in conjunction with ZVI, PIC, SMI, and IOH may be required if the release of alkaline or acidic waters into the environment is a potential problem.

Table 7—(Extended)

Low flow rate effluent concentration[a] ppm			High flow rate effluent concentration[a] ppm		
Average effluent concentration[b]			Average effluent concentration[b]		
Cd	Cu	Pb	Cd	Cu	Pb
25.84	23.33	24.25	NA	NA	NA
ND	ND	ND	12.96	ND	0.10
ND	ND	ND	2.61	ND	ND
ND	ND	ND	ND	ND	ND
ND	ND	ND	8.30	ND	ND
Start (s) and finish (f) effluent concentrations[b]			Start (s) and finish (f) effluent concentration[b]		
Cd	Cu	Pb	Cd	Cu	Pb
26.3 (s) 25.1 (f)	23.8 (s) 22.3 (f)	24.9 (s) 22.9 (f)	NA (s) NA (f)	NA (s) NA (f)	NA (s) NA (f)
ND (s) ND (f)	ND (s) ND (f)	ND (s) ND (f)	10.4 (s) 15.5 (f)	ND (s) ND (f)	0.05 (s) 0.15 (f)
ND (s) ND (f)	ND (s) ND (f)	ND (s) ND (f)	ND (s) 5.21 (f)	ND (s) ND (f)	ND (s) ND (f)
ND (s) ND (f)	ND (s) ND (f)	ND (s) ND (f)	ND (s) ND (f)	ND (s) ND (f)	ND (s) ND (f)
ND (s) ND (f)	ND (s) ND (f)	ND (s) ND (f)	ND (s) 16.6 (f)	ND (s) ND (f)	ND (s) ND (f)
Std. dev. of effluent concentration[b]			Range of effluent concentration[b]		
Cd	Cu	Pb	Cd	Cu	Pb
0.42	0.47	0.61	NA	NA	NA
NA	NA	NA	5.17	NA	0.09
NA	NA	NA	5.21	NA	NA
NA	NA	NA	NA	NA	NA
NA	NA	NA	16.60	NA	NA

The Table 6 average effluent contaminant levels for As-Cr-Se NFM column test 1 indicates that column test equipment and procedures alone can remove ~12% of As, ~3% of Cr, and ~9% of Se, and these results need to be taken into account when analyzing the As-Cr-Se column test results for ZVI, PIC, SMI, and IOH. The most effective contaminant removal for the As-Cr-Se column tests was exhibited by the SMI filter material. For the As-Cr-Se SMI column test 4, regardless of whether flow rate was low (52 mL/h—227-minute contact time, Table 2) or high (1539 mL/h—8 minute contact time, Table 2), there was no As, Cr, or Se detected in the effluent. The IOH filter material effectively removed As and Cr, but not Se at both low flow rate (52 mL/h—297-minute contact time, Table 2) and high flow rate (2615 mL/h—6-minute contact time, Table 2). The ZVI and PIC filter materials, at both low and high flow rates, worked very well removing Cr; however, they were not exceedingly good at removing As and Se. Low trace element effluent concentrations obtained at high flow rates are an indication of not just effective contaminant removal (>60% reduction, Table 6), but also a relatively fast reaction rate needing only a 4 to 8 minutes of contact time (Table 2) for trace element removal of Cr by ZVI; Cr by PIC; As, Cr, and Se by SMI; and As and Cr by IOH.

At test completion, the effluent pH for the Cd-Cu-Pb ZVI, PIC, and SMI column tests 7, 8, and 9 had acidic pH values (<6) of 5.10, 5.59, and 5.31, respectively (Table 7), which were similar to the acidic 4.96 pH value of the influent Cd-Cu-Pb column test solution. The final effluent pH for the Cd-Cu-Pb IOH column test 10 had a value of 7.23 indicating that IOH may have the beneficial attribute of being able to neutralize the acidic pH present in certain heavy metal contaminated waters. The Table 7 effluent contaminant levels for Cd-Cu-Pb NFM column test 6 indicates that column test equipment and procedures removed only ~−3% of Cd, ~7% of Cu, and ~3% of Pb, which would not be considered substantially large contaminant losses. For both low and high flow rates, Table 7 shows that ZVI, PIC, SMI, and IOH removed basically all of the Cu and Pb from the influent Cd-Cu-Pb column test solution. All Cd (at least below detection limits) was removed by ZVI, PIC, SMI, and IOH at low flow rates; however, only SMI removed all Cd at high flow rates. These results imply that the chemical reactions between all four iron-based filter materials and the Cu or Pb species appear to occur quite rapidly, based on essentially all Cu and Pb being removed during high flow rates when filter material to solution contact times within the column were only 2 to 4 minutes (Table 2 and Table 7). The chemical reaction between SMI and Cd species also occurs quite rapidly, based on essentially all Cd being removed during high flow rates when SMI to solution contact time within the column was only ~3 minutes (Table 2 and Table 7). Overall, Figure 1d and Table 7 indicate that ZVI, PIC, SMI, and IOH all exhibit promise, to a greater or lesser extent, for Cd, Cu, and Pb water treatment.

The high pH values (>8) related to ZVI and PIC found in Table 1 (chemical and physical properties) and Table 6 (As-Cr-Se saturated solute transport column test results) may reflect a chemical reaction between iron and water, such as $Fe^0 + 2H_2O = Fe^{2+} + H_2 + 2OH^-$, which produces ferrous iron, hydrogen gas, and hydroxyl anions (Kamolpornwijit and Liang, 2006). If this reaction is common with ZVI and PIC, then the production of hydroxyl anions would tend to cause a significant pH increase, thereby accounting for some of the high pH results obtained with ZVI and PIC. The very low effluent pH (<6) values for the

SMI As-Cr-Se column test may result from oxidation of the sulfur/iron compounds present in SMI. In a manner similar to the processes that cause acid mine drainage, the oxidation of these sulfur/iron compounds generates hydrogen cations, H^+, in turn producing low pH in the SMI As-Cr-Se column test effluent. There are a number of possible trace element removal mechanisms with respect to ZVI, PIC, SMI, and IOH. These removal mechanisms could include precipitation of iron-arsenate/arsenite, iron-chromate, and iron-selenate/selenite compounds; chemisorption of trace element oxyanions or cations at functional group sites present on ZVI, PIC, SMI, or IOH particle surfaces; electrostatic attraction of trace element oxyanions or cations to charged exchange sites present on ZVI, PIC, SMI, or IOH particle surfaces (dependent on point of zero charge); and oxidation/reduction reactions in which iron is oxidized and trace element species are reduced to forms readily precipitated or adsorbed (McBride, 1994; Sparks, 2003; Stumm and Morgan, 1981). The relative importance of these removal mechanisms with respect to each combination of iron-based filter material (ZVI, PIC, SMI, IOH) and trace element contaminant (As, Cd, Cr, Cu, Pb, or Se) is at present not clearly known and is a topic for further investigation.

Summary, Conclusions, and Future Research Degraded natural waters and industrial effluents often contain mixtures of trace element contaminants such As, Cr, and Se or Cd, Cu, and Pb. Granular iron-based materials like ZVI, PIC, SMI, and IOH have potential use in filter systems for treatment of waters contaminated with trace element contaminants. This research has shown that ZVI, PIC, SMI, and IOH all have a saturated hydraulic conductivity greater 1×10^{-2} cm, which is more than sufficient from an hydraulic standpoint for use as water treatment filter materials. Batch and column test results indicate that SMI can treat waters containing As, Cd, Cr, Cu, Pb, and Se; IOH can remove As, Cd, Cr, Cu, and Pb; while ZVI and PIC can be fairly effective in treating Cd, Cr, Cu, and Pb. With the exception of Se adsorption/precipitation onto IOH, Stage 2 and 3 of the batch tests also showed that once As, Cd, Cr, Cu, Pb, or Se are adsorbed/precipitated onto ZVI, PIC, SMI, or IOH particle surfaces, these trace elements are then not readily desorbed or dissolved back into solution. The column test results additionally indicate that for many filter material (ZVI, PIC, SMI, or IOH) and trace element contaminant (As, Cd, Cr, Cu, Pb, or Se) combinations, the contact time needed for effective trace element contaminant removal is oftentimes fairly short (<10 minutes).

Consequently, ZVI, PIC, SMI, and IOH, to a greater or lesser extent, all exhibit promise as filter materials for use in water treatment of As, Cd, Cr, Cu, Pb, or Se trace element contaminants. The research results, on the whole, further imply that ZVI, PIC, SMI, and IOH could be used in a wide variety of trace element contaminant water treatment filter systems, with some possible examples including permeable reactive barriers for contaminated groundwater plumes, large fluidized bed filters for municipal or industrial water treatment, filter cartridges for agricultural drainage pipe discharge, and so forth. In addition, the batch test results also imply that ZVI, PIC, SMI, and IOH could potentially be used in large mixing reactors to clean industrial effluents containing multiple trace element contaminants.

However, these results are quite preliminary. More laboratory testing of ZVI, PIC, SMI, and IOH is needed with respect to

determining the minimum contact time needed for effective trace element contaminant removal, measurement of the maximum capacity for trace element contaminant removal per unit weight of filter material, and development of adsorption isotherms to gain insight on trace element removal mechanisms. These laboratory studies should then be followed by large-scale field studies to fully evaluate the performance of ZVI, PIC, SMI, or IOH within an actual filter treatment used for trace element contaminant water treatment.

Authors' Note

The use of manufacturer/developer/marketer names are for informational purposes only and does not imply endorsement by the authors or their organizations.

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