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

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ABSTRACT

A laboratory investigation was conducted to evaluate four iron-based filter materials for trace element contaminant water treatment. The iron-based filter materials evaluated were zero valent iron (ZVI), porous iron composite (PIC), sulfur modified iron (SMI), and iron oxide/hydroxide (IOH). Only filter material retained on a 100 mesh sieve (> 0.15 mm) was used for testing. Tested trace element contaminant solutions combined As, Cr, and Se (added as $\text{AsO}_4^{3-}$, $\text{CrO}_4^{2-}$, and $\text{SeO}_4^{2-}$, respectively) or combined Cd$^{2+}$, Cu$^{2+}$, and Pb$^{2+}$. The laboratory investigation included saturated falling-head hydraulic conductivity tests, contaminant removal 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 $1 \times 10^{-2}$ cm/s. Essentially 100% of each trace element contaminant (As, Cd, Cr, Cu, Pb, and Se) was removed by SMI during batch and column tests, while IOH exhibited good removal of each trace element except Se. The combined batch and column test results showed ZVI and PIC were most capable of treating Cd, Cr, Cu, and Pb. Consequently, ZVI, PIC, SMI, and IOH all have substantial potential for trace element contaminant water treatment.

Keywords: Trace Elements, Iron-Based Filter Materials, Water Treatment
1. Introduction

Natural process along with agricultural, mining, and manufacturing activities can result in the environmental release of trace element contaminants which degrade surface and ground waters [1]. Often, more than one trace element contaminant is found to be present in these degraded waters. For example, waste disposal sites for fly ash generated by coal-burning power plants can leach arsenic and selenium into the environment [2-4]. High levels of both arsenic and selenium can also be found in evaporation ponds that collect agricultural drainage waters in the San Joaquin Valley in California, U.S.A [5-7]. Chromated copper arsenate (CCA) wood treatment facilities or landfills where discarded CCA treated wood is deposited can pose arsenic, chromium, and copper contamination risks to underlying ground waters [8-10]. Mobile, leachable forms of arsenic, chromium, and selenium are found in wildfire affected soils [11]. Acid mine drainage from mining locations can lead to heavy metal pollution of surface waters. As a case in point, during the early 1980's, acid mine drainage from the Yak tunnel at the California Gulch mining site in Colorado, U.S.A. discharged a combined total of 210 tons per year of cadmium, copper, iron, lead, manganese, and zinc into California Gulch, which is a tributary to Arkansas River [12].

This study focused on the trace element contaminants; arsenic (As), cadmium (Cd), chromium (Cr), copper (Cu), lead (Pb), and selenium (Se). The most mobile types of As found in the environment are forms of arsenate ($\text{H}_n\text{AsO}_4^{3-n}$) and arsenite ($\text{H}_n\text{AsO}_3^{3-n}$) [13,14]. With regard to Cr in natural waters, the chromate forms, $\text{HCrO}_4^-$ and $\text{CrO}_4^{2-}$, are some of the most common mobile species [13,14]. The environmentally mobile types of Se are forms of selenate ($\text{HSeO}_4^-$ and $\text{SeO}_4^{2-}$) and selenite ($\text{H}_n\text{SeO}_3^{2-n}$) [13]. Within soils, surface waters, and ground
waters, mobile Cd, Cu, and Pb are often present as divalent cations (i.e. Cd\(^{2+}\), Cu\(^{2+}\), and Pb\(^{2+}\)) [13,14].

Iron-based materials, such as elemental iron (i.e. zero-valent iron) and iron oxides/hydroxides, have been evaluated for water treatment of trace element contaminants. Zero-valent iron (ZVI) has been employed within permeable reactive barriers to remove trace element contaminants from ground water [15]. Iron oxides/hydroxides (IOH) have been used by municipalities and in the home for filtration water treatment of trace element contaminants, particularly arsenic [16,17]. The mechanisms by which ZVI removes trace element contaminants from water are complex, and depending on the contaminant species involved, can include either individually or in combination; electrochemical reduction in association with iron oxidation [18-22], chemical precipitation [18, 23, 24], and inner-sphere or outer-sphere surface complexation on iron corrosion products (iron oxides/hydroxides) [19-22,25]. The mechanisms by which IOH removes trace element contaminants from water are likewise complex, and again depending on the contaminant species involved, can include either individually or in combination; electrochemical reduction in association with oxidation of ferrous iron to ferric iron [26] and inner-sphere or outer-sphere surface complexation on IOH particles [8, 26-29]. 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. Research on PIC and SMI water treatment capabilities have to date been very limited. The trace element contaminant removal mechanisms for PIC and SMI have not yet been identified, but are likely similar to the ZVI and IOH trace element contaminant removal mechanisms.

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 saturated falling-head
hydraulic conductivity tests, contaminant removal batch tests, and low-to-high flow rate
saturated solute transport column tests. In accordance with previous studies indicating the
common occurrence of mixed trace element contaminant release into the environment [2-12],
solutions with As, Cr, and Se species combined together and solutions with Cd, Cu, and Pb
species combined together were both utilized in the batch tests and the column tests. The stated
research objective was therefore to conduct a preliminary laboratory comparison of zero-valent
iron, porous iron composite, sulfur modified iron, and iron oxide/hydroxide filter materials with
respect to hydraulic efficiency and mixed trace element contaminant water treatment capabilities.

2. Materials and methods

2.1. 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), and can be described as a ground iron aggregate comprised
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), and is manufactured with high purity elemental iron powder to which
functional additives are mixed. The mixture was then is processed through powder metallurgical
technologies to achieve an iron composite media with high internal porosity 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. (Walnut Creek, California),
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), and can be described as a synthetic, high surface area goethite (Chemical Formula - α-FeOOH). To improve 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. Table 1 shows that, with respect to pH, the ZVI and PIC slurries were strongly alkaline (> 10), the IOH slurry was moderately alkaline (8 - 10), and the SMI slurry was near neutral (6 - 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 laboratory measured specific gravity [30] of IOH was 3.62 g/cm³, which was much lower than the specific gravity values of 7.03, 7.13, and 5.95 g/cm³ that were obtained, respectively, for ZVI, PIC, and SMI. Table 1 particle size analysis data, based on mechanical sieving methods [30] and a particle size classification from Perloff and Baron [31], shows that the 100 mesh sieved ZVI and IOH filter materials were predominantly comprised of medium sand sized particles, while the 100 mesh sieved PIC and SMI filter materials were predominantly comprised of fine sand sized particles.

2.2. Test solutions

The constituent and chemical properties of the test solutions used in this study are provided in Table 2. The hydraulic conductivity test solution, the As-Cr-Se batch test solution,
and the As-Cr-Se column test solution all had pH values near neutral, while the Cd-Cu-Pb batch
test solution and the Cd-Cu-Pb column test solution were strongly acidic. The ORP values were
well above zero for all test solutions. For the As-Cr-Se batch and column test solutions, arsenic
(As) was initially added as the oxyanion, AsO$_4^{3-}$, chromium (Cr) was initially added as the
oxyanion, CrO$_4^{2-}$, and Se was initially added as the oxyanion SeO$_4^{2-}$; however, once solution
equilibrium was achieved, As was likely present in some form of arsenate (H$_n$AsO$_4^{3-n}$) or
arsenite (H$_n$AsO$_3^{3-n}$), Cr was likely present in some form of chromate (HCrO$_4^-$ or CrO$_4^{2-}$), and Se
was likely present in some form of selenate (HSeO$_4^-$ or SeO$_4^{2-}$) or selenite (H$_n$SeO$_5^{2-n}$) [32]. For
the Cd-Cu-Pb batch and column test solutions, cadmium (Cd), copper (Cu), and lead (Pb), were
likely present as divalent cations, Cd$^{2+}$, Cu$^{2+}$, and Pb$^{2+}$ [32]. Trace element concentrations for
the batch tests (50 ppm for each contaminant) and column tests (25 ppm for each contaminant)
would be considered quite high for degraded surface and ground waters [1,13,14], and as a
consequence, serve to provide a rigorous assessment of iron-based filter material water treatment
capabilities.

2.3. 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 to and preferably much greater
than 1.0 x 10$^{-3}$ cm/s, which is a stormwater sand filter design criteria [33-35]. Standard falling-
head hydraulic conductivity tests [36,37] were employed 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. For each individual filter material, duplicate saturated falling-head hydraulic conductivity tests were conducted so as to make certain that results were consistent. That is, 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 15.2 cm in length, 4.1 cm in diameter, and were saturated with 0.01 mole/L CaSO₄ solution 24 hours prior to hydraulic conductivity measurement.

2.4. Contaminant removal batch tests

Contaminant removal batch tests were carried out with ZVI, PIC, SMI, and IOH at ambient laboratory temperatures ranging from 20° to 25°C. Control batch tests without filter material, designated NFM, were also carried out to quantify contaminant amounts adsorbed by the experimental apparatus. These contaminant removal batch tests were conducted to provide a preliminary assessment of the potential contaminant removal capabilities of ZVI, PIC, SMI, and IOH, and in turn decide if further saturated solute transport column testing was warranted for any of these filter materials. The repeatability of results for trace element contaminant removal was confirmed by conducting a set of three batch test replicates for each combination of filter material (or NFM) and As-Cr-Se or Cd-Cu-Pb batch test solution. One batch test within each three replicate set was chosen for measurement of pH and ORP within the reaction vessel immediately after batch test completion.

In each filter material batch test, 5 g of filter material and 40 g of either As-Cr-Se or Cd-Cu-Pb batch test solution (see Table 2) were combined in a 50 mL polypropylene centrifuge tube (BD Biosciences, Bedford, Massachusetts). The filter material and batch test solution 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. Each batch
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 batch test solution (40 g), but no filter material, added to the centrifuge tube.

Once pH and ORP values were obtained for one batch test within each three replicate set, 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 in order to separate the filter material from the solution. The supernatant solution was then decanted into a second 50 mL polypropylene centrifuge. This process of separating solution from filter material was done for the purpose of discontinuing chemical reactions between the filter material and test solution upon batch test completion. Batch test pH and ORP were measured with equipment previously described (Table 1).

Concentrations of As, Cr, and Se or Cd, Cu, and Pb present within the batch test supernatant solutions were measured using inductively coupled plasma (ICP) methods [38] 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.

2.5. Low-to-high flow rate saturated solute transport column tests

By allowing control of solution flux and the filter material to solution exposure time, saturated solute transport column tests can help better evaluate the likely trace element contaminant (As, Cd, Cr, Cu, Pb, Se) removal behavior of ZVI, PIC, SMI, or IOH filter materials within an actual water 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) column. Ambient laboratory temperatures during testing ranged from 20° to 25° C. Filter material columns contained within the Teflon permeameters had a diameter of 5.1 cm and a length of 15.0 cm. Effluent exiting the permeameter was collected over time in glass containers. Excepting a small amount of flexible 5 mm ID silicon tubing (Catalog Number 3364, Control Company, Friendswood, Texas) threaded through the peristaltic pump, 6 mm ID Tygon (Saint-Gobain Performance Plastics, Akron, Ohio) R-3603 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 remove any filter material present and then analyzed for As, Cr, and Se or Cd, Cu, Pb using previously described inductively coupled plasma methods [38]. Direct pH measurements were obtained for those effluent samples not analyzed for trace element contaminants (again, one out of every two samples).

Table 3 provides information on the ten saturated solute transport column tests conducted during this study. The column test information provided in Table 3 includes filter material (or no filter material), contaminant solution, 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 (Table 2), while column tests 6 through 10 were conducted with the Cd-Cu-Pb column test solution (Table 2). Column tests 1 and 6 were carried out with empty columns that contained no filter material (NFM). These empty column tests were conducted for baseline comparison purposes in order to quantify the amounts of trace element contaminants lost by the experimental apparatus and procedures. Since 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.

3. Results and discussion

3.1. Saturated falling-head hydraulic conductivity results.

Saturated hydraulic conductivity measurements are provided in Table 4 for the 100 mesh sieved zero valent iron (ZVI), porous iron composite (PIC), sulfur modified iron (SMI), and iron oxide/hydroxide (IOH) filter materials. Filter material packing densities for the saturated falling-head hydraulic conductivity tests are also provided in Table 4. There was a wide range in filter material packing densities, from an average of 0.52 g/cm$^3$ for IOH to 3.04 gm/cm$^3$ for ZVI. All measured saturated hydraulic conductivity measurements for the four iron-based filter materials were at least and order of magnitude greater than the previously discussed 1.0 x 10$^{-3}$ cm/s hydraulic conductivity criterion used for stormwater sand filters [33-35]. The lowest two-test average hydraulic conductivity values were exhibited by PIC (1.80 x 10$^{-2}$ cm/s) and SMI (1.73 x 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%) than the other two iron-based filter materials. By far the highest average hydraulic conductivity was obtained with IOH (9.75 x 10$^{-2}$ cm/s) and is likely the result, at least in part, of IOH having a much greater amount of medium sand sized
particles (> 95%) than the other iron-based filter materials tested. Consequently, overall results for the saturated falling-head hydraulic conductivity tests generally indicate that ZVI, PIC, SMI, and IOH all have sufficient hydraulic conductivity for use in water filter treatment.

3.2. Contaminant removal batch test results.

Results for the contaminant removal batch tests are provided in Table 5 and Table 6. The pH values, ORP (oxidation/reduction potential) values, and trace element contaminant concentrations for the As-Cr-Se (arsenic-chromium-selenium) batch tests are shown in Table 5. Again, for the As-Cr-Se batch test solution, 50 ppm of As was originally added as the oxyanion, AsO$_4^{3-}$ (arsenate), 50 ppm of Cr was added as the oxyanion, CrO$_4^{2-}$ (chromate), and 50 ppm of Se was added as the oxyanion, SeO$_4^{2-}$ (selenate). The pH, ORP, and trace element contaminant concentrations for the Cd-Cu-Pb (cadmium-copper-lead) batch tests are shown in Table 6. For the Cd-Cu-Pb batch test solution, Cd (50 ppm), Cu (50 ppm), and Pb (50 ppm) were again likely initially present as divalent cations, Cd$^{2+}$, Cu$^{2+}$, and Pb$^{2+}$.

Table 5 shows that the As-Cr-Se NFM (control - no filter material) and SMI batch tests had near neutral pH (6 - 8), while the As-Cr-Se batch tests with ZVI, PIC, and IOH had alkaline pH values (> 8). Positive ORP values were measured for the As-Cr-Se NFM, PIC, and IOH batch tests. The As-Cr-Se batch tests with ZVI and SMI had negative ORP values, indicating that reducing conditions were present during these batch tests. Based on initial and final contaminant levels, the As-Cr-Se NFM batch tests indicate that batch test equipment and procedures alone remove ~11% of As, ~1% of Cr, and 11% of Se, which in turn must be taken into account when analyzing the As-Cr-Se batch test results for ZVI, PIC, SMI, and IOH. There was complete 100% removal of As, Cr, and Se during the As-Cr-Se batch tests conducted with SMI, at least below detection limits, which were 0.061 ppm for As, 0.003 ppm for Cr, and 0.054...
ppm for Se. Near 100% of As, ~96% of Cr, and ~52% of Se were removed during the As-Cr-Se batch tests with IOH. The As-Cr-Se batch tests with ZVI had averaged ~41% As removal, ~83% Cr removal, and ~43% Se removal. The results for the As-Cr-Se batch tests with PIC (~23% As removal, ~9% Cr removal, and ~18% Se removal) were only modestly better than results obtained with the As-Cr-Se NFM batch tests. Consequently, the As-Cr-Se batch tests results provided in Table 5 indicate, in a preliminary manner, that SMI may work best for mixed As, Cr, and Se removal, followed closely by IOH, then ZVI, and finally PIC.

Table 6 shows that the Cd-Cu-Pb NFM (control - no filter material), PIC, and SMI batch tests had moderately acidic pH (4 - 6), while the Cd-Cu-Pb IOH batch test pH was near neutral (6 - 8), and Cd-Cu-Pb ZVI batch test pH was strongly alkaline (> 10). Positive ORP values were measured for the Cd-Cu-Pb NFM and IOH batch tests. The Cd-Cu-Pb batch tests with ZVI, PIC, and SMI had negative ORP values, indicating that reducing conditions were present during testing. Based on initial and final contaminant levels, the Cd-Cu-Pb NFM batch test results show that batch test equipment and procedures remove ~14% of Cd, ~10% of Cu, and ~3% of Pb. The Cd-Cu-Pb batch tests with ZVI, PIC, SMI, or IOH all had near 100% removal of Cd, Cu, and Pb (detection limits: 0.001 ppm for Cd, 0.001 ppm for Cu, and 0.016 ppm for Pb).

Therefore, even taking into account contaminant losses due to batch test equipment and procedures, Table 6 shows that ZVI, PIC, SMI, and IOH all have promise for water treatment of Cd, Cu, and Pb. Preliminarily, these batch test results indicated that further investigation of ZVI, PIC, SMI, and IOH with saturated solute transport column tests was warranted in order to better assess the trace element contaminant water treatment effectiveness and efficiency of these four iron-based filter materials.
3.3. 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 exposure 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. Representative column tests results are displayed in Fig. 1. The compiled effluent pH and effluent contaminant concentration results for all ten column tests are provided in Tables 7 and 8. The influent concentration for each trace element contaminant was 25 ppm for the As-Cr-Se column tests and the Cd-Cu-Pb column tests. The likely initial form (species) of the trace element contaminants has already been discussed.

Table 7 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 - 8). The As-Cr-Se IOH column test 5 effluent had near neutral to moderately alkaline pH (6 - 10), and the 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 impact this contaminated water’s pH. Consequently, additional water treatment in conjunction with ZVI, PIC, SMI, and IOH may be required, if the release of alkaline or acid waters into the environment is a potential problem.

The Table 7 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 (227 min contact time) or high (8 min contact time),
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 and high flow rates (297 and 6 min contact time, respectively).
The ZVI and PIC filter materials, at both high and low flow rates, worked very well removing
Cr; however, they were not particularly good at removing As and Se. The chemical reactions
between the iron-based filter materials and the As, Cr, or Se species present appear to occur quite
rapidly, as was inferred based on the last low flow rate effluent contaminant concentration values
being generally similar in magnitude to the high flow rate contaminant concentration values (Fig.
1b and Table 7). Furthermore, the Table 7 results indicate that with regard to waters containing a
mixture of As, Cr, and Se, the contaminant removal effectiveness of ZVI, PIC, SMI, and IOH is
determined primarily by the amount of contaminants over time to which these iron-based filter
materials have been exposed.

By 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, which were similar 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 8 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 8 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, with regard to waters containing a mixture of Cd, Cu,
and Pb, the chemical reactions between all iron-based filter materials and Cu or Pb species appear to occur quite rapidly, chemical reactions between SMI and Cd species also occur quite rapidly, but chemical reactions seem to be slower between Cd species and either ZVI, PIC, or IOH. Overall, Fig. 1d and Table 8 indicate that ZVI, PIC, SMI, and IOH all exhibit promise for removal of Cd, Cu, and Pb when these heavy metal trace elements are present together in contaminated waters.

4. Conclusions

A laboratory study that included saturated falling-head hydraulic conductivity tests, contaminant removal batch tests, and low-to-high flow rate saturated solute transport column tests was conducted to evaluate the capabilities of four iron-based filter materials to remove trace element contaminants from waters containing either arsenic, chromium, and selenium (As-Cr-Se) or cadmium, copper, and lead (Cd-Cu-Pb). Sulfur modified iron (SMI) was found to completely remove As, Cd, Cr, Cu, Se, and Pb (at least below detection limits). An iron oxide/hydroxide (IOH) was especially effective in removing As, Cd, Cr, Cu, and Pb, but not Se. Potential advantages for using IOH compared to the other three iron-based filter materials include its very high hydraulic conductivity and the release of treated waters that are not extremely acidic or alkaline. The zero valent iron (ZVI) and porous iron composite (PIC) filter materials generally worked quite well removing Cd, Cr, Cu, and Pb. These results are preliminary, and more laboratory and field research is certainly needed to fully evaluate these four iron-based materials for filter treatment of waters contaminated with mixtures of trace elements.

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.
References


Table 1
Iron-based filter material chemical and physical properties.\textsuperscript{a}

<table>
<thead>
<tr>
<th>Filter Material</th>
<th>pH\textsuperscript{b}</th>
<th>ORP\textsuperscript{c}</th>
<th>Specific Gravity</th>
<th>Particle Size Distribution % by wt.</th>
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<td></td>
<td>mV</td>
<td>g/cm\textsuperscript{3}</td>
<td></td>
<td>Course Sand Size 2.0-4.75 mm</td>
</tr>
<tr>
<td>ZVI</td>
<td>10.35</td>
<td>-592</td>
<td>7.03</td>
<td>0.01</td>
</tr>
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<td>PIC</td>
<td>10.14</td>
<td>-538</td>
<td>7.13</td>
<td>0.00</td>
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<td>SMI</td>
<td>6.75</td>
<td>-660</td>
<td>5.93</td>
<td>0.12</td>
</tr>
<tr>
<td>IOH</td>
<td>8.18</td>
<td>26</td>
<td>3.62</td>
<td>0.04</td>
</tr>
</tbody>
</table>

\textsuperscript{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\textdegree C to 25\textdegree C.

\textsuperscript{b} pH was determined using an Oakton (Vernon Hills, Illinois) pHTestr 10 BNC.

\textsuperscript{c} ORP is oxidation/reduction potential measured with a YSI Inc. (Yellow Springs, Ohio), EcoSense pH100 Meter and an YSI Inc., 115-1 ORP Probe.
Table 2
Test solution constituents and chemical properties.

<table>
<thead>
<tr>
<th>Solution</th>
<th>Contaminant Concentrations ppm</th>
<th>Added Chemical Compound Concentrations ppm</th>
<th>Solution Chemical Properties</th>
</tr>
</thead>
<tbody>
<tr>
<td>Hydraulic Conductivity Test Solution</td>
<td>As - 50</td>
<td>CaSO$_4$ - 1361 (0.01 mole/L)</td>
<td>pH 7.03, ORP 193 mV</td>
</tr>
<tr>
<td>As-Cr-Se Batch Test Solution</td>
<td>Cr - 50</td>
<td>K$_2$AsO$_4$ - 120</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Se - 50</td>
<td>K$_2$CrO$_4$ - 187</td>
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</tr>
<tr>
<td></td>
<td></td>
<td>K$_2$SeO$_4$ - 140</td>
<td></td>
</tr>
<tr>
<td>Cd-Cu-Pb Batch Test Solution</td>
<td>Cd - 50</td>
<td>CdCl$_2$ - 82</td>
<td>pH 4.48, ORP 238 mV</td>
</tr>
<tr>
<td></td>
<td>Cu - 50</td>
<td>CuCl$_2$*2H$_2$O - 134</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Pb - 50</td>
<td>PbCl$_2$ - 67</td>
<td></td>
</tr>
<tr>
<td>As-Cr-Se Column Test Solution</td>
<td>As - 25</td>
<td>K$_2$AsO$_4$ - 60</td>
<td>pH 6.46, ORP 187 mV</td>
</tr>
<tr>
<td></td>
<td>Cr - 25</td>
<td>K$_2$CrO$_4$ - 93</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Se - 25</td>
<td>K$_2$SeO$_4$ - 70</td>
<td></td>
</tr>
<tr>
<td>Cd-Cu-Pb Column Test Solution</td>
<td>Cd - 25</td>
<td>CdCl$_2$ - 41</td>
<td>pH 4.96, ORP 255 mV</td>
</tr>
<tr>
<td></td>
<td>Cu - 25</td>
<td>CuCl$_2$*2H$_2$O - 67</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Pb - 25</td>
<td>PbCl$_2$ - 34</td>
<td></td>
</tr>
<tr>
<td>Column Test Number</td>
<td>Filter Material</td>
<td>Test Solution</td>
<td>Column Dry Bulk Packing Density (g/cm³)</td>
</tr>
<tr>
<td>-------------------</td>
<td>----------------</td>
<td>---------------</td>
<td>------------------------------------------</td>
</tr>
<tr>
<td>1</td>
<td>Empty Column (NFM&lt;sup&gt;a&lt;/sup&gt;)</td>
<td>25 mg/L As, Cr, Se</td>
<td>NA</td>
</tr>
<tr>
<td>2</td>
<td>ZVI</td>
<td>25 mg/L As, Cr, Se</td>
<td>3.23</td>
</tr>
<tr>
<td>3</td>
<td>PIC</td>
<td>25 mg/L As, Se, Cr</td>
<td>2.04</td>
</tr>
<tr>
<td>4</td>
<td>SMI</td>
<td>25 mg/L As, Cr, Se</td>
<td>2.06</td>
</tr>
<tr>
<td>5</td>
<td>IOH</td>
<td>25 mg/L As, Cr, Se</td>
<td>0.52</td>
</tr>
<tr>
<td>6</td>
<td>Empty Column (NFM&lt;sup&gt;a&lt;/sup&gt;)</td>
<td>25 mg/L Cd, Cu, Pb</td>
<td>NA</td>
</tr>
<tr>
<td>7</td>
<td>ZVI</td>
<td>25 mg/L Cd, Cu, Pb</td>
<td>2.73</td>
</tr>
<tr>
<td>8</td>
<td>PIC</td>
<td>25 mg/L Cd, Cu, Pb</td>
<td>2.03</td>
</tr>
<tr>
<td>9</td>
<td>SMI</td>
<td>25 mg/L Cd, Cu, Pb</td>
<td>2.06</td>
</tr>
<tr>
<td>10</td>
<td>IOH</td>
<td>25 mg/L Cd, Cu, Pb</td>
<td>0.51</td>
</tr>
</tbody>
</table>

<sup>a</sup> NFM is the notation for “no filter material”.
Table 4
Iron-based filter material hydraulic conductivities and associated packing densities.

<table>
<thead>
<tr>
<th>Filter Material</th>
<th>Test Number</th>
<th>Column Dry Bulk Packing Density g/cm³</th>
<th>Saturated Hydraulic Conductivity cm/s</th>
</tr>
</thead>
<tbody>
<tr>
<td>ZVI</td>
<td>1</td>
<td>3.00</td>
<td>3.89 x 10⁻²</td>
</tr>
<tr>
<td></td>
<td>2</td>
<td>3.08</td>
<td>1.73 x 10⁻²</td>
</tr>
<tr>
<td>PIC</td>
<td>1</td>
<td>2.22</td>
<td>1.28 x 10⁻²</td>
</tr>
<tr>
<td></td>
<td>2</td>
<td>2.13</td>
<td>2.32 x 10⁻²</td>
</tr>
<tr>
<td>SMI</td>
<td>1</td>
<td>1.98</td>
<td>2.15 x 10⁻²</td>
</tr>
<tr>
<td></td>
<td>2</td>
<td>1.97</td>
<td>1.30 x 10⁻²</td>
</tr>
<tr>
<td>IOH</td>
<td>1</td>
<td>0.51</td>
<td>1.03 x 10⁻¹</td>
</tr>
<tr>
<td></td>
<td>2</td>
<td>0.52</td>
<td>9.20 x 10⁻²</td>
</tr>
</tbody>
</table>
### Table 5
Batch test results for As-Cr-Se solution.

<table>
<thead>
<tr>
<th>Filter Material</th>
<th>Final Test Conditions</th>
<th>Final Contaminant Solution Concentration&lt;sup&gt;a&lt;/sup&gt; and (Standard Deviation&lt;sup&gt;b&lt;/sup&gt;) ppm</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>pH</td>
<td>ORP&lt;sup&gt;c&lt;/sup&gt;</td>
</tr>
<tr>
<td></td>
<td></td>
<td>mV</td>
</tr>
<tr>
<td>NFM&lt;sup&gt;d&lt;/sup&gt;</td>
<td>6.37</td>
<td>150</td>
</tr>
<tr>
<td>ZVI</td>
<td>10.31</td>
<td>-186</td>
</tr>
<tr>
<td>PIC</td>
<td>8.17</td>
<td>72</td>
</tr>
<tr>
<td>SMI</td>
<td>6.35</td>
<td>-150</td>
</tr>
<tr>
<td>IOH</td>
<td>8.10</td>
<td>155</td>
</tr>
</tbody>
</table>

<sup>a</sup> Initial concentration of As = 50 ppm, Cr = 50 ppm, and Se = 50 ppm.

<sup>b</sup> Based on three batch test replicates. ND = not detected. NA = not applicable.

<sup>c</sup> ORP is oxidation/reduction potential.

<sup>d</sup> NFM is the notation for “no filter material.”
### Table 6
Batch test results for Cd-Cu-Pb solution.

<table>
<thead>
<tr>
<th>Filter Material</th>
<th>Final Test Conditions</th>
<th>Final Contaminant Solution Concentration&lt;sup&gt;a&lt;/sup&gt; Average&lt;sup&gt;b&lt;/sup&gt; and (Standard Deviation&lt;sup&gt;b&lt;/sup&gt;) ppm</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>pH</td>
<td>ORP&lt;sup&gt;c&lt;/sup&gt;</td>
<td>Cd</td>
</tr>
<tr>
<td></td>
<td></td>
<td>mV</td>
<td></td>
</tr>
<tr>
<td>NFM&lt;sup&gt;d&lt;/sup&gt;</td>
<td>4.85</td>
<td>245</td>
<td>43.16 (3.99)</td>
</tr>
<tr>
<td>ZVI</td>
<td>10.21</td>
<td>-117</td>
<td>0.55 (0.48)</td>
</tr>
<tr>
<td>PIC</td>
<td>5.99</td>
<td>-190</td>
<td>ND (NA)</td>
</tr>
<tr>
<td>SMI</td>
<td>4.88</td>
<td>-143</td>
<td>ND (NA)</td>
</tr>
<tr>
<td>IOH</td>
<td>7.51</td>
<td>98</td>
<td>ND (NA)</td>
</tr>
</tbody>
</table>

<sup>a</sup> Initial concentration of Cd = 50 ppm, Cu = 50 ppm, and Pb = 50 ppm.

<sup>b</sup> Based on three batch test replicates. ND = not detected. NA = not applicable.

<sup>c</sup> ORP is oxidation/reduction potential.

<sup>d</sup> NFM is the notation for “no filter material”.
<table>
<thead>
<tr>
<th>Column Test</th>
<th>Filter Material</th>
<th>Effluent pH Average and (Standard Deviation for Low Flow or Range for High Flow)</th>
<th>Effluent Contaminant Concentrations&lt;sup&gt;a&lt;/sup&gt;</th>
<th>Low Flow Rate</th>
<th>High Flow Rate</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td>Average&lt;sup&gt;b&lt;/sup&gt;, - Start to Finish Values&lt;sup&gt;b&lt;/sup&gt;, and (Standard Deviation for Low Flow or Range for High Flow)&lt;sup&gt;b&lt;/sup&gt;</td>
<td>ppm</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>As</td>
<td>Cr</td>
<td>Se</td>
</tr>
<tr>
<td>1</td>
<td>Empty Column (NFM&lt;sup&gt;c&lt;/sup&gt;)</td>
<td>6.15 (0.14)</td>
<td>NA</td>
<td>21.93 (22.1 to 21.7)</td>
<td>24.31 (24.4 to 24.1)</td>
</tr>
<tr>
<td>2</td>
<td>ZVI</td>
<td>10.08 (0.20)</td>
<td>13.37 (9.66 to 16.6)</td>
<td>ND (NA)</td>
<td>17.57 (16.0 to 19.3)</td>
</tr>
<tr>
<td>3</td>
<td>PIC</td>
<td>10.33 (0.11)</td>
<td>11.73 (10.8 to 12.9)</td>
<td>ND (NA)</td>
<td>15.78 (17.0 to 15.2)</td>
</tr>
<tr>
<td>4</td>
<td>SMI</td>
<td>3.80 (0.24)</td>
<td>ND (NA)</td>
<td>ND (NA)</td>
<td>ND (NA)</td>
</tr>
<tr>
<td>5</td>
<td>IOH</td>
<td>7.98 (0.16)</td>
<td>0.05 (0.08 to 0.06)</td>
<td>ND (NA)</td>
<td>18.23 (ND to 27.9)</td>
</tr>
</tbody>
</table>

<sup>a</sup> Initial concentration of As = 25 ppm, Cr = 25 ppm, and Se = 25 ppm.

<sup>b</sup> ND = not detected. NA = not applicable.

<sup>c</sup> NFM is the notation for “no filter material”.
Table 8
Column test results for Cd-Cu-Pb solution.

<table>
<thead>
<tr>
<th>Column Test</th>
<th>Filter Material</th>
<th>Effluent pH Average and (Standard Deviation for Low Flow or Range for High Flow)</th>
<th>Effluent Contaminant Concentrations&lt;sup&gt;a&lt;/sup&gt;</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>Low Flow Rate</td>
<td>High Flow Rate</td>
<td>Cd</td>
</tr>
<tr>
<td>6</td>
<td>Empty Column (NFM&lt;sup&gt;c&lt;/sup&gt;)</td>
<td>4.84</td>
<td>NA</td>
<td>25.84 - 26.3 to 25.1 - (0.20)</td>
</tr>
<tr>
<td>7</td>
<td>ZVI</td>
<td>6.46</td>
<td>5.00</td>
<td>ND</td>
</tr>
<tr>
<td>8</td>
<td>PIC</td>
<td>8.47</td>
<td>6.37</td>
<td>ND</td>
</tr>
<tr>
<td>9</td>
<td>SMI</td>
<td>4.16</td>
<td>5.30</td>
<td>ND</td>
</tr>
<tr>
<td>10</td>
<td>IOH</td>
<td>7.91</td>
<td>7.41</td>
<td>ND</td>
</tr>
</tbody>
</table>

<sup>a</sup> Initial concentration of Cd = 25 ppm, Cu = 25 ppm, and Pb = 25 ppm.

<sup>b</sup> ND = not detected. NA = not applicable.

<sup>c</sup> NFM is the notation for “no filter material”.
Fig. 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, while 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, while open square symbols denote contaminant measurement samples, and (d) measured contaminant concentrations for Cd-Cu-Pb ZVI column test 7.