

Remediation of Hg in groundwater using Zero-Valent Iron: Field Column Tests

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Abstract

Metal release from mine tailing impoundments or industrial effluents can pose significant problems to surface water and groundwater systems. Passive *in situ* technologies (i.e. permeable reactive barriers, PRBs) are becoming an attractive and less expensive alternative compared to conventional pump and treat systems and other *ex situ* treatments for water remediation. A field column treatability test using zero-valent iron to evaluate the removal of dissolved mercury from groundwater using permeable reactive materials was conducted at site in the eastern United States. The column test was conducted over a six-week trial period. The test involved the use of two columns, one that was operated at a flow approximately 2 L (9.5 pore volumes) per day, and the other at a flow rate of approximately 0.465 L (2.2 pore volumes) per day. These flow rates corresponded to ten and two years of simulated flow of groundwater through a potential full-scale treatment system during the six-week test period. Samples of the influent and effluent groundwater from each column were collected 2-3 times per week during the test period. Profiles of water quality with distance through each column were determined after three and six weeks of flow. The groundwater was characterized by elevated pH (7.8 to 9.5) and moderately reducing conditions (Eh of 0 to 120 mV). The total mercury concentration of the groundwater was approximately 40 µg/L. Within the columns, the pH increased by as much as 0.5 pH units and the Eh decreased slightly. Mercury was removed from the groundwater as it flowed through the columns. Effluent in the high-flow column contained approximately 0.5 µg/L of mercury during the first three weeks of testing. The concentration increased to as much as 4 µg/L by the end of the testing period. The concentration of mercury in the effluent from the low-flow column was generally less than 0.1 µg/L, and was less than 0.035 µg/L for most of the final three weeks of the testing period. Profile sampling in the low-flow column prior to the end of testing suggested that most of the mercury removal had occurred in the initial 50 % of the 20 cm column.

Introduction

Mercury is a well-known environmental pollutant. The toxicological concern to both fish and wildlife remains undisputed and often human health concerns arise when humans consume fish and wildlife near contaminated sites (King et al., 2002). The complexation and mobility of Hg in aquifers can undergo a variety of complex cycling pathways; one of the more important is its conversion to methylmercury (CH₃Hg⁺). Bacteria play an early role in this formation. Bacteria which process sulfate in the environment will take up mercury in its inorganic form (Hg) and will subsequently metabolize the mercury converting it to methylmercury (Domagalski, 2001; King et al., 2002; Mason et al., 1996). The conversion to methylmercury is important for two reasons: (1) in this form it remains highly toxic compared to inorganic mercury and (2) biota require considerably longer times to effectively remove methylmercury from their system (Mason et

al., 1995). Ultimately this form of mercury can end up in the sediment horizon via surface and/or ground water. The effects of dissolved organic carbon (DOC) and pH can also have a strong effect on the ultimate fate of mercury in contaminated ecosystems. Laboratory and field column trials suggest that permeable reactive barriers (PRB's) show promise for the passive *in situ* interception and treatment of groundwater contaminated with mercury. The focus of this paper highlights the performance and efficiency of mercury removal from two field column tests using zero-valent iron.

Materials and Methods

Column Design and Field conditions

Field-testing using two columns for removal of mercury was performed at an industrial site in the eastern United States. A schematic diagram illustrating the configuration of a single treatment

column is shown in Figure 1. The field columns were constructed at the University of Waterloo from acrylic material with dimensions consisting of an overall length of 21.7cm and 5 cm diameter. The internal volume of each column was approximately 426 mL. The sampling ports consisted of small threaded nylon connectors. In the columns, zero-valent iron was the only reactive material used. The reactive material was placed within a zone approximately 18.4 cm in length in each column, and was bounded by sand layers approximately 1.8 and 1.6 cm in thickness at the base and the top of each column, respectively. The zero-valent iron is available commercially (iron aggregate ETI-CC-1004; Connelly-GPM, Inc, Chicago). The iron ranged in grain size from less than U. S. Standard Mesh 8 (2.38 mm grain diameter) to in excess of Standard Mesh 50 (0.3 mm grain diameter), and was similar in character to a medium-coarse sand.

In column A (low-flow column), 95.74 g of sand were incorporated in the sand filter layers. The column contained 1084.96 g of zero-valent iron. Column B (high-flow column) contained 93.29 g of silica sand and 1066.85 g of zero-valent iron. Column A had a dry weight of 2,319.06 g and a wet weight of 2,554.4 g. column B had a dry weight of 2,272.93 g and a wet weight of 2,506.8 g. The pore volume for column A was 210.34 mL and the pore volume for column B was 208.87 mL. The porosity of the contents of both columns was 0.49. These porosity values are similar to those typically measured for zero-valent iron columns and field scale PRBs. Prior to transporting the columns to the field site, the columns were flushed with CO₂ gas for several hours to remove most atmospheric air. The influent and effluent tubes were then sealed for transport.

The column-test apparatus was housed in a mobile trailer positioned over a monitoring well. Each column had a dedicated pump and length of narrow-diameter (0.125 in (3.15 mm)) teflon® tube extending into well. An extension PVC pipe and socket-fitting couple was attached to the upper end of the monitoring well to minimize the potential for the introduction of surface runoff to the groundwater while the test was in progress

Groundwater sampled from the well was pumped directly into the influent base plates of each column using low-flow peristaltic pumps. Initially, the columns were filled with groundwater over a period of approximately an hour to displace all gas from the column and tubing. The columns were then temporarily disconnected from the pumps so that the water-saturated mass of each column could be measured.

The pumping rates for the test were established to simulate approximately ten years of groundwater flow through a permeable barrier system in the high-flow column (column B) and approximately one year of flow through the low-flow column (column A) during a period of three weeks. The target flow rates for the two columns were approximately 2 and 0.4 L/day, respectively.

The collection of groundwater samples was done from the sampling ports. A syringe was attached to each port so that it filled at the same rate as the introduced water to the column (approximately 10 and 100 mL per hour for the low-flow and high-flow columns, respectively). The collected water was transferred to 40 mL VOA vials for mercury analysis, and into plastic vials for the analysis of major anions, cations and metals. The samples for cation and metal analyses were preserved to pH < 2 with nitric acid. Mercury preservation was maintained using ultrapure HCL acid to pH < 2. The samples for total and methyl mercury were shipped in ice-packed coolers to Frontier Geosciences, Seattle WA.

Alkalinity, Eh and pH measurements were made immediately following the collection of the samples. Alkalinity was measured in a laboratory building adjacent to the test site using a Hach digital titrator (Titration Method 2320 B; American Public Health Association (APHA), 1992). Eh (Oxidation-Reduction Potential Method 2580 B; APHA, 1992) and pH (Electrometric Method 4500-H⁺ B; APHA, 1992) measurements were made in the field trailer using Orion and Orion Ross electrodes, respectively, immediately after the sample had been collected in the syringe at the field site.

Total mercury was determined using cold vapor- atomic fluorescence spectrometry (CV-

AFS) by Frontier Geosciences. Methyl mercury analysis was also performed by Frontier Geosciences using aqueous-phase ethylation, purging onto carbon trap, isothermal Gas Chromatographic separation, and cold vapor atomic fluorescence spectrometry. Sulfate and other anions were analyzed using Ion Chromatography (IC; EPA Method 300.0).

Following completion of the filed tests the columns were transported to the University of Waterloo and stored in a cold room (4°C) under sealed static conditions. After several months, samples of the zero-valent iron from columns A and B were extracted from three representative sampling points (bottom, port 3 and top) within an argon-purged glove box to minimize oxidation. The samples were sealed in argon purged glass vials until the surfaces could be characterized using a field emission scanning electron microscope (FE-SEM) and a Time of Flight Secondary Ion Mass Spectrometer (TOFSIMS). The advantage of using the latter technique is that it has ultra-high sensitivity to surface layers (one atomic layer), detection of atomic concentrations can be as low as 10 ppm for some elements, and offers excellent mass resolution for isotopic characterization. Another advantage to using this surface technique is that it provides information on the spatial distribution of adsorbed surface species in the form of secondary ion maps (i.e. spatial resolution <1µm).

Surface characterization of the reacted column materials was performed using a LEO 1530 FE-SEM (operating at 15kV with a resolution of 1.5nm). The ion maps and mass spectra were collected using an ION-TOF, TOF SIMS IV using a pulsed, isotopically enriched 25 keV (⁶⁹Ga) primary ion beam, with a beam current of 2.5 pA. The beam was rastered over a 350x350 µm area. This mode has a mass resolution of greater than 10000, above 200 daltons. The beam diameter (and lateral resolution) is approximately 1 micron in this mode.

Results and Discussion

Aqueous Flow Characteristics

Flow to the columns was uniformly maintained over a 42-day period. The total volumes of flow over the 42 day period through column A and B was 19.54 L and 83.14 L respectively. This flow corresponded to 92.9 pore volumes of flow for column A and 398.0 pore volumes for column B. On average 0.465 L/day, or 2.2 pore volumes per day, of groundwater was introduced to column A. The residence time of groundwater in column A was 10.8 hours. On average the daily volume of groundwater flow through column B was 1.98 L/day or 9.5 pore volumes per day. The residence time of water in column B was approximately 2.5 hours.

Water Chemistry and Mercury Removal Characteristics of Column A and B

The pH of the groundwater was consistently high, and ranged from 7.8 to 9.5. The Eh of the groundwater was moderately reducing and was typically between 0 and 120 mV. The influent groundwater contained between 30 and 40 mg/L Cl, typically less than 1 mg/L NO₃, and 150 to 600 mg/L SO₄. Alkalinity ranged from 270 to 500 mg/L (expressed as CaCO₃). The groundwater contained approximately 300 mg/L Na, between 5 and 70 mg/L Ca and between 2 - 25 mg/L Mg. Iron was not detected (<0.05 mg/L) in any samples. The total mercury concentration ranged from 18 to 42.5 µg/L. Methyl mercury concentrations in the influent were below <0.0335 µg/L.

The pH of the effluent from column A ranged from 8.95 to 10, and was typically slightly higher than the pH of the influent groundwater measured on the same day. The Eh values of the effluent from column A were low ranging from -45 to 75 mV. The Eh and alkalinity of the effluent was slightly lower than that of the influent groundwater. The alkalinity values were typically in the range from 100 to 435 mg/L calcium (as CaCO₃). Chloride (25 to 40 mg/L) and sulfate (150 to 580 mg/L) concentrations were similar to those of the influent groundwater, but the concentration of nitrate in the effluent was less

than 0.2 mg/L (NO₃) and less than 0.07 mg/L for the final four weeks of testing. The concentration of Na in the effluent was similar to that in the influent (approximately 300 mg/L), but the concentrations of both Ca and Mg were typically less than 5 mg/L and lower than those in the influent groundwater. Similar to the groundwater, iron was not detected in any samples of the effluent from column A. The iron concentration in the effluent from Column A was below the detection limit of 0.05 mg/L in all samples.

The total mercury concentration in the effluent was as low as 0.021 µg/L. The data for the port profiling suggest that the changes in chemical characteristics between the influent and effluent in column A evolved with distance through the zero-valent iron. Figure 2a shows a comparison of the total mercury concentrations as a function of time in the effluent and the influent ground water from column A and Figure 2b shows the distribution profile of total mercury as a function of distance traveled up the column through the zero-valent iron. These points are representative from samples collected at the middle and end of the testing period.

The quality of the effluent from column B was generally similar to that of column A with a few exceptions. The values of Eh, pH, Cl and SO₄ concentrations for the column B effluent were comparable to those of column A. However, slight differences were observed in the performance of column B when compared to column A. Changes in alkalinity between the influent and effluent was not apparent in column B. The effluent from column B also showed evidence of dissolved iron, although the concentration was low (< 0.5mg/L), it was still present on several sampling occasions and staining was observed at the top of the end plate and effluent tubing. The concentration of total mercury in column B increased from < 0.5 µg/L within the first week of testing to 4 µg/L on day 37. Figure 3 shows the total mercury concentrations with time in the effluent from column B, and illustrates the distribution of total mercury with distance through the zero-valent iron. The reactive capacity of the zero-valent iron to remove mercury from the groundwater to levels of less than 1 µg/L was exceeded by the middle of

the testing period at a high flow rate of approximately 2 L per day.

Discussion of Column Performance

The removal of mercury and other electroactive metals by zero-valent iron occurs as a consequence of reductive precipitation or coprecipitation reactions on the grain surfaces of the iron. The reactions have kinetic limitations, but generally occur at sufficiently rapid rates to have potential application in the subsurface. The flux of contaminants through zero-valent iron in the subsurface is influenced by the concentration of the contaminant and the groundwater velocity. The groundwater velocity in many hydrogeologic settings is of the order of 0.5 (15 cm) feet per day or less, so the contaminant flux in the subsurface can be modest and amenable to treatment using PRB's.

The column tests at this site were operated at higher flow rates. The high-flow column (column B) was designed to simulate ten years of groundwater flow that could be expected to occur through a PRB at the site over the six-week testing period. The low-flow column (column A) was designed to simulate two years of groundwater through a PRB over the same period. The residence time of groundwater in the high-flow column was approximately 2.5 hours. Thus, groundwater moved the length of the column (21.7 cm) every 2.5 hours, which corresponds to a groundwater velocity of 2.06 m per day (approximately 6.7 ft/day). The estimated groundwater velocity in the low-flow column was 0.48 m per day (approximately 1.5 ft/day).

The results of the field column test suggest that removal of mercury by zero-valent iron was more successful under the low-flow in comparison to the high-flow conditions. Total mercury in the effluent of the high-flow column was decreased to less than 0.5 µg/L at early time when the influent contained 40 µg/L. In contrast, the low-flow column reduced the total mercury concentration to less than 0.035 µg/L for a sustained period during the final three weeks of the testing period. The mercury-removal performance was inversely related to the flow rate through the columns. It may also be reasonable to suggest that improved

mercury removal could be achieved with longer residence time of groundwater anticipated within the proposed zero-valent iron treatment zone in the field. Profile sampling in the low-flow column prior to the end of testing suggested that most of the mercury removal had occurred in the initial 50 % of the zero-valent iron.

Another possible influence on the performance of zero-valent iron was the lack of contrast between the Eh and pH characteristics of the influent groundwater and the pore water in the column. The monitoring data indicate a slight decrease in Eh conditions as groundwater enters and passes through the zero-valent iron, and an increase of less than 0.5 pH units. Strongly reducing conditions within the zero-valent iron as a consequence of its corrosion reaction with water were evident in the removal of much of the influent nitrate, probably by its abiotic reduction to ammonia. Nitrate concentrations in the influent groundwater were in general less than a few milligrams per liter.

The Eh conditions observed in the field columns, however, were more oxidizing than are typically observed in zero-valent iron barriers in the field. The lowest Eh observed in Column A was approximately 30 mV. Eh values observed in field installations of PRB systems are typically less than -500 mV (i.e. Elizabeth City (Blowes et al., 1999b)). These much reduced conditions occur as a result of the reduction of water to H₂ gas. However, this reaction is kinetically limited. The residence time of groundwater in the columns during the field test was too short to permit extensive reduction of water. It is anticipated that more reduced conditions would be observed in a field scale installation for mercury removal.

Precipitation of carbonate and other mineral phases is common in zero-valent iron PRB systems. The removal of several milligrams per liter of both calcium and magnesium as groundwater moved through the columns indicates that some secondary precipitates were forming i.e. carbonates. SEM micrographs of material collected from the base of the column A show a cluster of calcite crystals formed on the surface of the zero-valent iron particle Figure 4. The mass of precipitates, however, is very small

relative to the flow through the columns. The overall mass of mercury introduced to each column in relation to the total mass of iron (zero-valent) was very small. Thus it was very difficult to detect physical evidence of precipitated mercuric phases. TOFSIMS analysis suggests that the distribution of Hg on the surfaces of the zero-valent iron appears to be proportional to distance traveled up the column (i.e. an increase in the relative amounts of adsorbed mercuric species are observed on both columns at the base as compared to port 3; Figure 5). As the Hg contaminated influent enters the columns adsorption of Hg on to the zero-valent iron occurs reducing the solution concentrations. This observation is consistent with the data presented in Figures 2b and 3b which showed gradual decrease in effluent concentration as the flow moves up the columns. It remains inconclusive whether the mercuric products detected are indeed adsorbed species or co precipitated compounds related to the oxidation of the zero-valent iron caused by its interaction with the groundwater. These data are insufficient to identify the nature of the mercury on the zero-valent iron surface.

Conclusions

Profile sampling in the low-flow column prior to the end of testing suggests that most of the mercury removal had occurred in the initial 50 % of the zero-valent iron. The concentration of mercury in the effluent from the low-flow column was generally less than 0.1 µg/L over the 42 day test period. In contrast the high-flow column contained approximately 0.500 µg/L of mercury during the first three weeks of testing with the concentration increasing to as much as 4 µg/L by the end of the testing period. Mercury speciation on the zero-valent iron surfaces tends to decrease with increased flow distance and resident times.

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SCHEMATIC DIAGRAM OF COLUMN APPARATUS

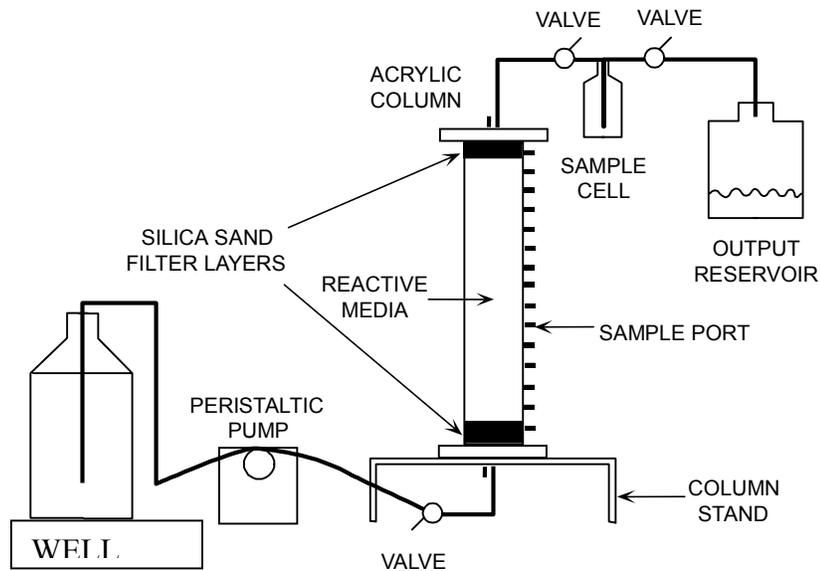
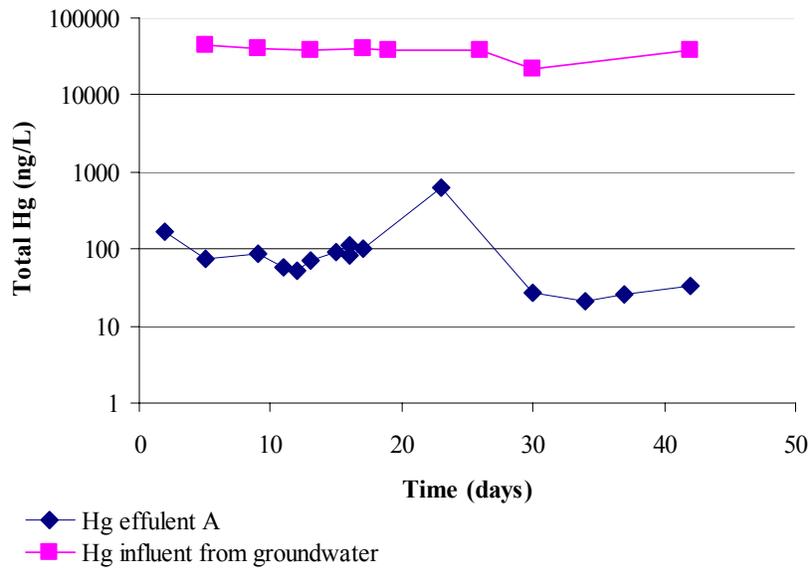


Figure 1 A schematic diagram of the column-testing apparatus. Groundwater from the well was pumped directly into the influent base plate of each column using low-flow peristaltic pump. The effluent was discharged through the top plate of the column. The input samples were collected from the control valve in the influent line, and the effluent samples collected from the sampling cell. Each column was 21.7 cm (0.72 ft) in length and 5 cm (2 in) in diameter. Six lateral sampling ports were located along the length of the columns.

A



B

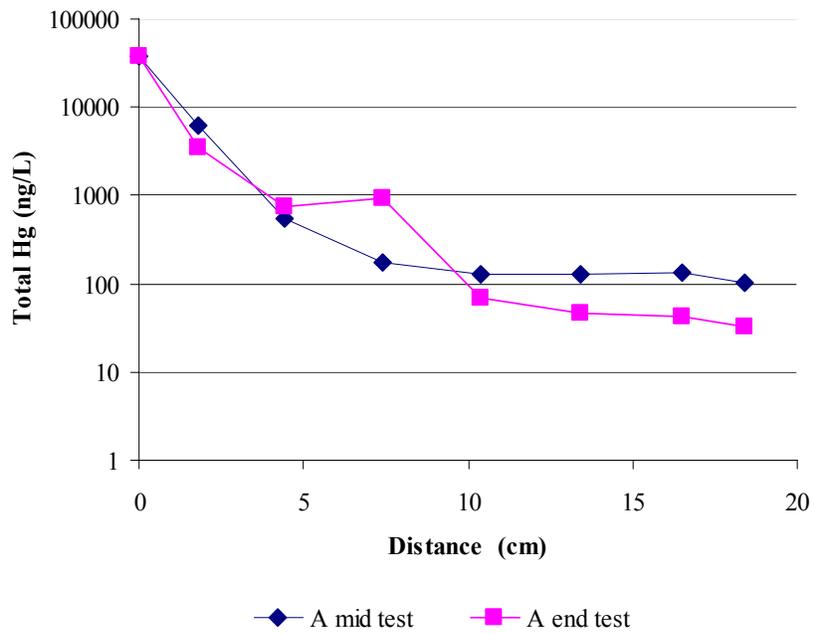
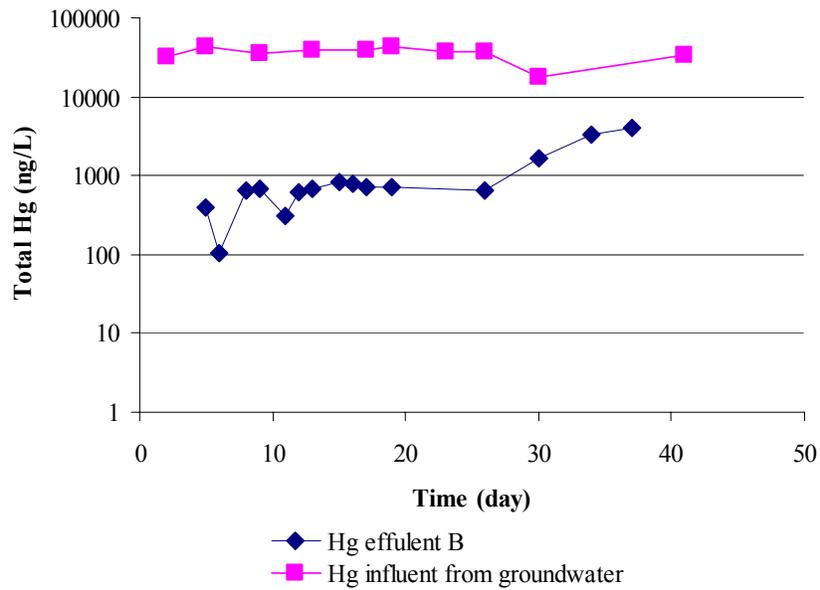


Figure 2 (A) a comparison of the total mercury concentrations as a function of time in the effluent and the influent ground water in column A over the 42 day period (B) the distribution profile of total mercury as a function of distance traveled up through the reactive media in column A.

A



B

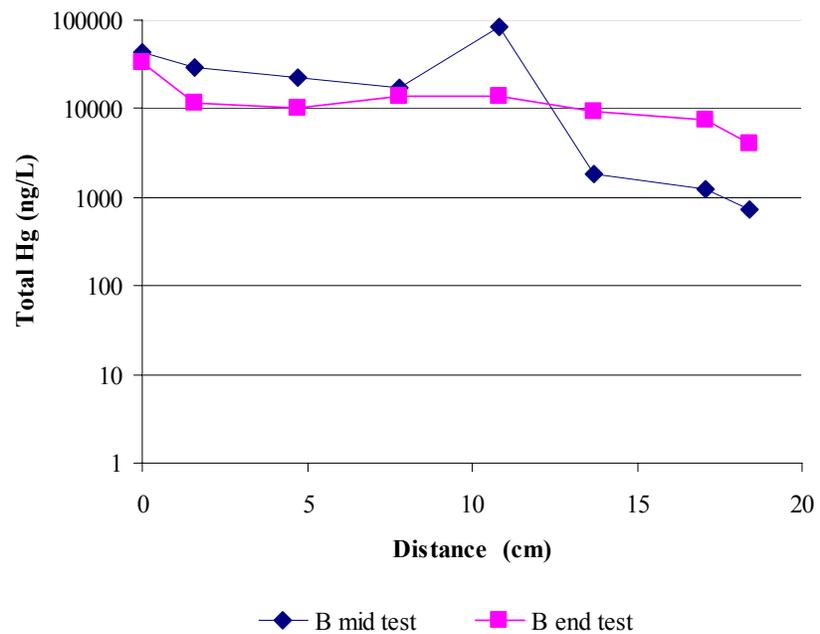


Figure 3 (A) Shows a comparison of the total mercury concentrations as a function of time in the effluent and the influent ground water in column B over the 42 day period (B) shows the distribution profile of total mercury as a function of distance traveled up through the reactive media in column B.

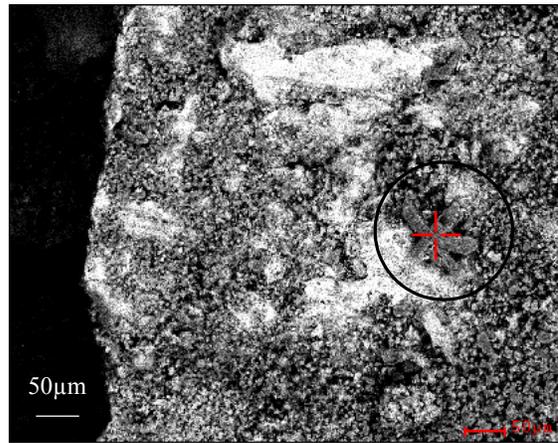


Figure 4 A cluster of calcium carbonate crystals confirmed by EDX form as a precipitate on the surface of oxidized iron filing sampled from the base of column A.

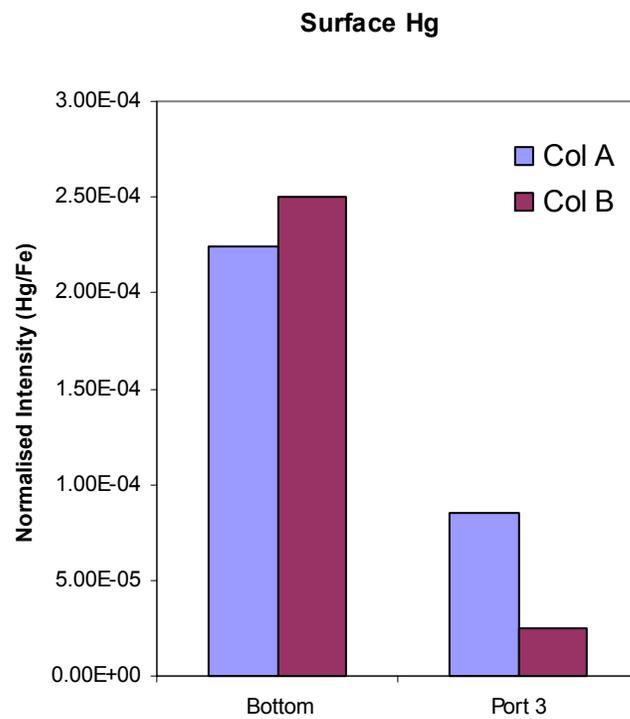


Figure 5 A comparison of surface mercury on zero-valent iron particles sampled from the base and port 3 for columns A and B. The relative proportions of mercury on the surface of the zero-valent iron particles decreases from the base towards port 3 in both columns.