



Mercury removal from contaminated groundwater: Performance and limitations of amalgamation through brass shavings



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ARTICLE INFO

Article history:

Received 6 February 2016

Received in revised form

25 April 2016

Accepted 2 May 2016

Available online 3 May 2016

Keywords:

Mercury

Groundwater

Brass

Remediation

Permeable reactive barrier (PRB)

Pilot plant

ABSTRACT

Brass shavings have been proposed as a cost-effective filter material to remove Hg from contaminated groundwater. This method, which is based on the reduction of reactive Hg(II) and subsequent formation of amalgams, has been shown to be fast and effective in the short term. However, the effectiveness of brass filters and their stability over the long term, especially if used in passive filter systems such as permeable reactive barriers (PRB) under high flow conditions, is unknown. To evaluate the performance and limitations of brass shavings for Hg removal from contaminated groundwater, we performed long-term pilot scale filtration tests (6 and 28 months) at two former wood impregnation sites with severe groundwater contamination (up to $870 \mu\text{g L}^{-1}$ Hg). The results showed that even under high flow conditions ($>60 \text{ m d}^{-1}$), 60–80% of the Hg was removed in the first 8 mm of the brass shavings filter bed. The kinetics of filtration, Hg total removal performance ($>99.95\%$), and loading capacity (164 g L^{-1}) surpassed those of a Hg-specific synthetic resin (LEWATIT® MonoPlus TP-214). However, under natural pH conditions (pH 6.4 and 6.7), Zn was leached from the brass and exceeded the threshold value (0.5 mg L^{-1}) in the filter outflow by up to a factor of 40. Increasing pH (>8.5) decreased the Zn concentration ($<0.05 \text{ mg L}^{-1}$) but affected Hg removal due to the formation of Zn-hydroxide/carbonate coatings on the brass (up to 15% performance reduction). Thus, the use of brass shavings as an exclusive filter material in PRBs is restricted to aquifers with high pH. However, brass is ideal as a low-cost, thin-bed prefilter in onsite systems to remove the main Hg load from groundwater when Zn release is managed.

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1. Introduction

Mercury (Hg) is one of the most toxic trace metals (Drasch et al., 2004); it has been released to the environment by numerous industrial processes (Hylander and Meili, 2005) and is still emitted in large quantities due to the burning of fossil fuels (UNEP, 2013). Global Hg emissions from contaminated sites (e.g. polluted industrial/urban sites) are estimated to be 198 Mg yr^{-1} (~60% hydrologically controlled) (Kocman et al., 2013). Inorganic Hg(II) species (e.g., HgCl_2) are distinctly more soluble than elemental Hg(0) and are found at many Hg-contaminated sites, such as chlor-alkali plants (Biester et al., 2002) and former wood treatment facilities (Bollen et al., 2008; Richard et al., 2016). When groundwater is

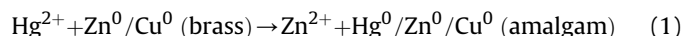
affected, reactive Hg(II) species tend to adsorb on Mn/Fe-oxyhydroxides or organic matter (Barringer et al., 2013). Hg adsorption to soil or aquifer material and the related long-term release of Hg into groundwater often requires long and cost-intensive remediation. At such sites, in situ treatment with permeable reactive barriers (PRBs) is an appropriate remediation strategy because the extensive energy costs for the long-term pumping necessary for onsite treatment can be avoided (Obiri-Nyarko et al., 2014). Several filter materials exist to remove Hg from contaminated water. Sulfurized activated carbon (AC) (Asasian and Kaghazchi, 2015), Hg-specific resins with thiol or thiourea functional groups (Monier et al., 2015), zero valent-iron (ZVI) (Vernon and Bonzongo, 2014), and mineral adsorbents, such as zeolites (Azizi et al., 2013), are among the most frequently used Hg sorbents. Two PRBs for Hg remediation have been reported, both using AC as the reactive material. One PRB can treat $\sim 25 \text{ m}^3 \text{ h}^{-1}$ at Hg concentrations of $\sim 10 \mu\text{g L}^{-1}$ (Merly and Hube, 2014). The other PRB can treat higher Hg concentrations (max.

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360 $\mu\text{g L}^{-1}$; Nobre et al., 2012), but the reported aquifer permeability ($<5 \times 10^{-6} \text{ m s}^{-1}$) suggests that the groundwater flow must be low. Therefore, AC is a satisfactory filter material for PRBs when either the Hg concentration or the groundwater flow velocity is low. However, use of conventional filter materials in PRBs at sites where both the Hg concentration and flow are high is limited due to low sorption capacity, (bio)fouling, filter clogging, or high costs (Newcombe et al., 1997; Weisener et al., 2005; Gönder et al., 2006; Bilardi et al., 2015; Mudasir et al., 2016). Hg amalgamation with metals such as tin (Sn) (Biester et al., 2000) or copper (Cu) (Huttenloch et al., 2003) has been proposed as a cost-effective alternative (Table S1). Here, Hg(II) is reduced to elemental Hg(0) by less “noble” metals and forms insoluble amalgams (solid solutions). The method offers fast kinetics and high Hg loading capacities but also has the disadvantages of filter instability and elevated Cu release at the filter outflow. The latest approach in this field to overcome these drawbacks is the use of brass shavings for Hg filtration (Wenke et al., 2016). Here, Hg(II) is reduced by metallic zinc (Zn(0)) to Hg(0) and subsequently forms a Cu–Zn–amalgam, according to Eq. (1).



Based on the results of successful lab experiments (Wenke et al., 2016), we conducted long-term tests with brass shavings filters at two mercuric chloride (HgCl_2)-contaminated sites under high-flow conditions (up to 70 m d^{-1}). At site A, the appropriate brass type and minimum filter bed length were identified for further experiments in a pilot plant at site B, where a PRB is planned.

2. Materials and methods

2.1. Tested filter materials

Two types of brass shavings were tested at site A to identify the appropriate brass type to use in the pilot plant at site B. Both brass types were high-purity copper and zinc (Zn) alloys with low lead (Pb) contents (elemental composition shown in Table S2 and Fig. S1). Brass type 1 is a commercially available process media used for the removal of chlorine and heavy metals from drinking water (KDF 55[®], KDF Fluid Treatment, Inc., USA) that has already been tested as a Hg filter material (Sites and Oberholtzer, 1992; Wenke et al., 2016). Brass type 2 is a recycled material made from cable scrap (M2000[®] Cabo GmbH, Germany) containing a black, fine, hydrophobic powder (most likely residuals of cable sheaths) that must be removed by rinsing with tap water before use. At site B, pure brass shavings (type 1) and brass–gravel mixtures (grain size distribution: Fig. S2) were tested, as well as two commercial mercury filter materials (Hg-specific adsorber resin based on sulfur ligands (LEWATIT[®] MonoPlus TP 214, Lanxess AG, Germany) and a mineral adsorber (absorption agent 3, sulfurized, Dr. Ecker GmbH, Germany)).

2.2. Lab tests: synthetic groundwater test rig

The probability of brass dezincification at the field sites was estimated by plotting the chloride (Cl^-) concentration of groundwater against alkalinity in a Turner's diagram (Turner, 1961; in Sarver, 2010; see Fig. S3). When elevated Zn concentrations were encountered in the outflow of the filters at site B (Section 2.4), a synthetic groundwater test rig was installed in the laboratory (Fig. S4). The influence of pH on Zn solubility was studied, and pH-increasing approaches for the development of a modular filter system to prevent Zn leaching were pretested before installation in the pilot plant at site B.

Tap water was deionized in an ion exchange unit and stored in a 220 L polyethylene (PE) reservoir tank. Adjustment to groundwater conditions at site B was performed by bubbling with CO_2 and the addition of precalculated amounts of Ca, Mg, K, and Na salts (CaCO_3 , NaCl, $\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$, $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$, $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$, $\text{Mg}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, and KHCO_3 , all p.a., Carl Roth GmbH, Germany). Then, the process water was pumped through polyvinylchloride (PVC) tubing to an overhead tank with a constant water table to maintain a steady pressure level. From the overhead tank water was guided to the test columns (polymethyl methacrylate PMMA, 10 cm diameter, EMC GmbH, Germany) filled with brass shavings, following the hydraulic gradient. The water flow was regulated with PP needle valves to 5.3 L h^{-1} ($\hat{=}$ 58 m d^{-1}) and was measured with PP rotameters (871, GEMÜ GmbH & Co. KG, Germany). To predict the Zn concentrations in the outflow of the filters at site B at different pH values, the pH of the process water in the lab test rig was set to values between 5.2 (minimal achievable pH with CO_2) and 12 and was continuously adjusted to the target value by bubbling with compressed air or CO_2 . To achieve pH values greater than 8.2, NaOH solution (p.a., Carl Roth GmbH, Germany) was added. The water at the outflow of the test columns was sampled, and the Zn concentrations were measured.

2.3. Geochemical modeling

To predict the Zn solubility and precipitate composition during the increasing pH experiments, geochemical modeling was conducted based on the cation–anion balances from site B, including the field parameters temperature, pH, dissolved O_2 , alkalinity, and Eh. PhreePlot version 1 ($\times 64$) (Kinniburgh and Cooper, 2014) was used to calculate pH sweeps by repetitive execution of embedded PHREEQC (Parkhurst and Apello, 2013) code using the minteq.v4.dat database supplied with the program. The water was equilibrated with metallic Zn at a ratio of 100 mg Zn per liter of water.

2.4. Field tests: site description and experimental setup

2.4.1. Pre-tests at site A

At site A, two types of brass shavings (Section 2.1) were tested with three different filter bed lengths under field conditions to determine the appropriate brass material for a pilot plant at site B. Site A was a former wood treatment facility in the Black Forrest (Southern Germany), where HgCl_2 was applied as a protective agent, resulting in severe contamination of the soil and groundwater. Detailed information can be found in Richard et al. (2016). Nine PMMA filter columns (10 cm diameter, EMC GmbH, Germany) filled with brass type 1 or 2 in three different filter bed thicknesses (2, 7, and 15 cm) were run in bypass to an existing groundwater remediation plant (Fig. 1).

The brass shavings were installed between layers of quartz sand and gravel to ensure homogeneous water distribution. To simulate the conditions in a PRB, the flow was set to 2 L h^{-1} , corresponding to an effective groundwater velocity of 21 m d^{-1} . The flow velocities were regulated with diaphragm valves and were measured with polypropylene (PP) rotameters (617 and 871, respectively, GEMÜ GmbH & Co. KG, Germany). The duration of the experiment was 192 days.

2.4.2. Pilot plant at site B

At site B, the installation of a PRB is currently under consideration. Therefore, a pilot plant (EH Wassertechnik GmbH, Germany) was installed to perform detailed tests on the filtration performance and the physico-chemical behavior of brass shavings under realistic conditions, compared to other filter materials. The total

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