Corrosion product and precipitate distribution in two-component Fe(0) permeable reactive barriers

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HIGHLIGHTS

- Secondary minerals preferentially accumulate on corroding surfaces.
- Pore space of porous filter materials only partly filled with precipitates.
- Complete conversion of ferric minerals to magnetite.

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ABSTRACT

In situ Fe(0) permeable reactive barriers are suitable for the passive treatment of various hazardous substances in groundwater. Unavoidable secondary minerals on cast iron granules (Fe(0)) in permeable reactive barriers cause passivation and reduction of pore volume. Precipitate agglomeration on mixing components might reduce the passivating layers on Fe(0). Mixtures of Fe(0) with different conventional, porous or reactive granular materials (sand, gravel, pumice, anthracite, wood, granular ferric hydroxide, calcite) were analyzed with different methods after 200 days exposure to contaminated groundwater in column studies. Gravimetric analyses indicate that the weight increase of the Fe(0) granules was greater than that of all mixing materials except calcite indicating preferential formation of secondary minerals on Fe(0) granules. A greater weight increase compared to Fe(0) was only observed for calcite, which was transformed during the experiment into large and compact aragonite crystals on the granule surfaces. Microscopic analyses of cross-sections showed a corrosion build-up on Fe(0) but only minor precipitate layers on mixing materials. Akaganeite, a non-magnetic ferric hydroxide as major component of the granular ferric hydroxide, was transformed into magnetite during ground water treatment as revealed by X-ray diffraction. Hence iron hydroxides are intermediate phases that further transform to the final product magnetite.

1. Introduction

Passive in situ treatment of contaminated aquifers with Fe(0) permeable reactive barriers (PRB) shows economic and environmental advantages over conventional pump-and-treat measures [1,2]. A large number of organic and inorganic hazards can be successfully removed in the corrosion reactors [3,4] but reactivity losses are the main risk for the long-term efficiency of Fe(0) PRB, depending on water constituents. Corrosion products and precipitates reduce both the Fe(0) reactivity and the available pore volume [5–11]. If it is possible to redistribute passivating minerals away from the Fe(0) surface towards mixing materials the long term efficiency could be enhanced. Mackenzie et al. [9] advised

to mix Fe(0) with sand to prevent mineral clogging. Inner pores of porous mixing materials have been discussed as internal "storage room" for secondary minerals [12]. The distribution of secondary minerals on different surfaces within a Fe(0) permeable reactive barrier has not been sufficiently investigated yet.

While sand has been used as mixing material in very early investigations [13], only limited investigation focused on the combination of porous or reactive materials with Fe(0) yet. Mixtures of pumice and Fe(0) for the removal of chromate achieved promising results [14]. Fe(0) was mixed with compost for the reductive precipitation of heavy metals [15]. However, detailed solid phase characterizations of hybrid PRB material have not yet been reported to our knowledge.

We had previously reported about Fe(0)-gravel mixtures that the major corrosion products chukanovite or magnetite developed in simple model solutions; they were only found on the reactive

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iron but not on inert gravel surfaces [16]. The present investigation aimed at analyzing precipitates and their distribution in mixtures of granular cast iron and different supplemental granular materials after treatment of a complex groundwater contaminated with trichloroethylene. Seven different inert, porous or reactive filter materials were compared in column experiments of 200 days duration as two-component PRB [17,18]. The filter materials have been intensively characterized gravimetrically and with scanning electron microscopy, energy dispersive X-ray spectroscopy and X-ray diffraction before and after the column investigations.

2. Experimental

2.1. Materials

Different inert compact (sand and gravel) and porous (pumice and anthracite) granules [17] and reactive materials (granular ferric hydroxide (GFH), wood, and calcite) [18] have been mixed with 100 g granular cast iron to achieve a bed volume of 90 mL with additional supporting gravel layers. The filter volume of 100 g cast iron granules alone is only 30.3 mL. A comparative overview of granules of cast iron and the mixing materials is given in Fig. 1.

Granular cast iron (grain size 0.3–2.0 mm, Gotthart Maier Metallpulver) has already been investigated in multiple investigations [8,19–21]. The grain size ranges of sand and gravel were 0.8–1.2 mm and 2.0–4.0 mm. Pumice (Hydro-Filt-PS, Rheinkalk Akdolit) and anthracite (Hydroanthrasit-P, Rheinkalk Akdolit) are typical granular materials used in rapid filters. Granular ferric hydroxide (GFH, GEH Wasserchemie) is an adsorbent developed for the removal of arsenic with a large surface area of 250–300 m^2/g, a porosity of 75–80% and a bulk density of approximately 1.32 g/mL [22]. It consists of a poorly crystallized β-FeOOH and akaganeite [22]. The wood granules were originally intended for animal bedding, and calcite (Hydro-Calcite CG, Rheinkalk Akdolit) is a material typically used for neutralization filters.

The different mixtures were used to treat contaminated groundwater from the Bernau site close to Berlin (TCE contaminated groundwater) over 200 days as reported previously [17,18]. Briefly, influent concentrations of TCE and cis-DCE ranged from 60 to 110 µmol/L and from 4 to 5 µmol/L, respectively. TCE was largely dechlorinated to ethene and ethane within the first 100 days but effluent concentrations of cis-DCE increased to levels comparable to the TCE influent concentrations in all columns except the GFH containing column. At the same time a microbial sulfate reduction was observed that probably contributed to the incomplete dechlorination. Under abiotic conditions sulfate is not reduced [23]. The influent concentrations of inorganic carbon and calcium were between 40 and 44 mg/L and between 100 and 120 mg/L, respectively. Only slight indications for passivation have been observed besides the increase of cis-DCE in the effluent. The GFH containing mixture revealed an elevated reactivity while all other columns behaved similarly. After the long-term experiments with a volume flow of 4.5 mL/h and a total permeate volume of 20 L (0.2 mL per gram Fe(0)), the columns including the filter materials have been dried by flushing with a continuous flow of nitrogen (approximately 50 mbar) until no more weight decrease could be detected between two subsequent days.

2.2. Analytics

The filter materials were removed from the columns by tapping and by using a spatula, when necessary. After withdrawal of determined masses of specimens for further analyses, the magnetic fractions were separated form the bulk with a magnet. Both the magnetic and the non-magnetic fractions were quantified before and after the experiments on a digital balance (Sartorius, 0.1 mg accuracy).

Scanning electron microscopic images of the granular materials were recorded before and after exposure. Samples were additionally fused in epoxy resin and stepwise ground to 1 µm to obtain cross-sectional images. A high-resolution scanning electron microscope (Hitachi S-4000) with cold field emission electron source and secondary and back-scattered electron detectors was used. Elemental analysis was carried out with an energy dispersive X-ray
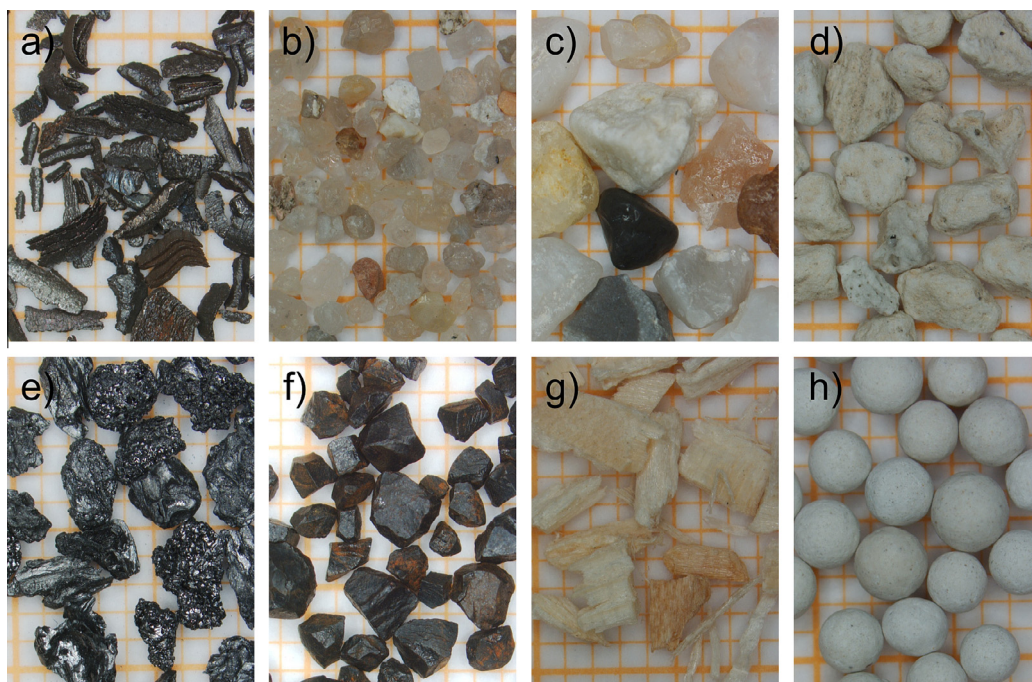

Fig. 1. Comparative overview of (a) granular cast iron, (b) sand, (c) gravel, (d) pumice, (e) anthracite, (f) granular ferric hydroxide (GFH), (g) wood granules and (h) calcite; photographs taken with identical magnification on graph paper (1 mm distance between the lines).