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# Integrated evaluation of the performance of a more than seven year old permeable reactive barrier at a site contaminated with chlorinated aliphatic hydrocarbons (CAHs)

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ABSTRACT

An important issue of concern for permeable reactive iron barriers is the long-term efficiency of the barriers due to the long operational periods required. Mineral precipitation resulting from the anaerobic corrosion of the iron filings and bacteria present in the barrier may play an important role in the long-term performance. An integrated study was performed on the Vapokon permeable reactive barrier (PRB) in Denmark by groundwater and iron core sample characterization. The detailed field groundwater sampling carried out from more than 75 well screens up and downstream the barrier showed a very efficient removal (>99%) for the most important CAHs (PCE, TCE and 1,1,1-TCA). However, significant formation of cis-DCE within the PRB resulted in an overall insufficient efficiency for cis-DCE removal. The detailed analysis of the upstream groundwater revealed a very heterogeneous spatial distribution of contaminant loading into the PRB, which resulted in that only about a quarter of the barrier system is treating significant loads of CAHs. Laboratory batch experiments using contaminated groundwater from the site and iron material from the core samples revealed that the aged iron material performed equally well as virgin granular iron of the same type based on determined degradation rates despite that parts of the cored iron material were covered by mineral precipitates (especially iron sulfides, carbonate green rust and aragonite). The PCR analysis performed on the iron core samples indicated the presence of a microbial consortium in the barrier. A wide range of species were identified including sulfate and iron reducing bacteria, together with *Dehalococcoides* and *Desulfuromonas* species indicating microbial reductive dehalogenation potential. The microbes had a profound effect on the performance of the barrier, as indicated by significant degradation of dichloromethane (which is typically unaffected by zero valent iron) within the barrier.



## 1. Introduction

More than 120 permeable reactive barriers (PRBs) containing granular zero valent iron ($Fe^0$) have been installed worldwide to remediate sites contaminated with chlorinated aliphatic hydrocarbons (CAHs) such as tetrachloroethylene (PCE), trichloroethylene (TCE) and 1,1,1-trichloroethane (1,1,1-TCA) ((ITRC), 2005). An important issue of concern is the long-term efficiency of the barriers due to the long operational periods required, usually being decades. Mineral precipitation resulting from the anaerobic corrosion of $Fe^0$ can lead to significant decreases in reactivity (Farrel et al., 2000; Klausen et al., 2001) and barrier permeability (Kamolpornwijit et al., 2003; Vikesland et al., 2003). Research has also proven that bacteria may play an important role in the long-term performance of PRBs (Lampron et al., 2001; Rosenthal et al., 2004; Van Nooten et al., 2007; 2008). These issues have been

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intensively studied primarily through laboratory column studies and modeling. In a few cases, iron core samples have been collected from field-scale PRBs for mineralogical (Phillips et al., 2000) and microbial (Gu et al., 2002; Wilkin et al., 2003) characterization (Table 1). Most PRBs, however, have been cored only a few years after the establishment of the PRB (1–4 years). Microbial activities have in most cases been evaluated by indirect methods looking at the formation of several precipitates. Only in a few cases advanced DNA-based microbial techniques such as polymerase chain reaction (PCR) analysis were used (Gu et al., 2002; Phillips et al., 2010). Investigations of the hydraulic conditions in $Fe^0$ PRBs often revealed rather heterogeneous flow patterns (Liang et al., 2005; Phillips et al., 2010). This can make precise evaluation of the efficiency of full-scale PRBs difficult if the evaluation is based on concentration changes in a few wells upstream and downstream of the PRB.

The objective of this study is to evaluate the performance of the Vapokon PRB 7–8 years after establishment and to link it to mineralogical and microbial processes observed in the PRB. Therefore, an integrated study was performed consisting of 1) a detailed field investigation of contaminant removal in the PRB with sampling and laboratory analysis of groundwater and core samples, 2) mineralogical and microbial characterization of core samples, and 3) batch experiments to compare the reactivity of the 8 year old iron material with the reactivity of virgin granular iron.

## 2. Site description

The Vapokon site is located on Funen Island in Denmark. From 1976 to 1997 a solvent recycling factory (Vapokon Petrochemicals Industry A/S) was located at the site, treating used solvents and paint containing CAHs and BTEX (Fig. 1A). Leakage in an underground concrete tank lead to a soil and groundwater contamination, resulting in a 80 × 200 m contaminant plume containing CAHs and BTEX (Lai et al., 2006b). The groundwater table at the Vapokon site is about 1.5 m below ground surface (bgs), which is located about 22.2 m above sea level (masl). The upper soil layer consists of about 1.5–2.0 m of moraine clay underlain by a sandy aquifer with a thickness of about 9 m. Beneath the sandy aquifer a thick clay layer is situated (Lai et al., 2006b).

To remediate the contaminated groundwater at the Vapokon site, a funnel-and-gate $Fe^0$ PRB was installed in 1999. The funnels consist of two 110–130 m long sheet pilings. The reactive gate consists of 100% granular $Fe^0$ (ETI-CC-1004, Connelly-GPM Inc.) and has the dimensions 14.5 × 9 × 0.8 m (W × D × L). The upper border of the PRB is located at 20.85 m above sea level (or 1.35 m below average ground surface). Both up- and downgradient, a 1 m thick gravel pack layer was installed (Fig. 1B). More details of the Vapokon PRB are given in Lai et al. (2006a).

The major CAHs found in the contaminant plume are PCE, TCE, 1,1,1-TCA, and *cis*-dichloroethylene (*cis*-DCE). In addition, minor concentrations of vinyl chloride (VC), 1,1-dichloroethlyene (1,1-DCE), *trans*-dichloroethylene (*trans*-DCE), 1,1-dichloroethane (1,1-DCA), 1,2-dichloroethane (1,2-DCA), dichloromethane (DCM) and chloroform are found in the plume. Typical concentrations of contaminants and inorganic constituents observed in the core of the contaminant plume in the period 2000–2001 (Birkelund and Harrekilde, 2003) are shown in Table 2. The table shows the range observed in 12 well screens (upstream wells M8, M9, M10 and M11; Fig. 1B)

**Table 1**
Overview of full-scale PRBs where coring of iron material has been performed with subsequent mineralogical and/or microbial characterization.

| PRB name | Location | Age at coring | Contaminants | Bacteria identified | Minerals identified | Remarks | Reference |
|---|---|---|---|---|---|---|---|
| Y-12 plant | Oak Ridge, TN, USA | 15 months | Uranium | n.a. | Aragonite<br>Siderite<br>FeS | High nitrate present<br>Most precipitates in the front end | Phillips et al.(2000) |
| Y-12 plant | Oak Ridge, TN, USA | 15 months | Uranium | SRB<br>IRB<br>DNB | n.a | High nitrate present | Gu et al.(2002) |
| Y-12 plant | Oak Ridge, TN, USA | 3.8 years | Uranium | n.a | n.a. | Porosity loss of up to 42% was observed | |
| US Coast Guard Support Center | Elizabeth City, NC, USA | 4 years | Cr(VI), TCE | n.a. | Ferrihydrite<br>Magnetite<br>Green rust<br>Calcite (and others) | Most precipitates in the front end<br>Highest biomass (as measured by PFLA method) in the front end | Furukawa et al. (2002)<br>Wilkin et al. (2003) |
| Denver Federal Center | Lakewood, CO, USA | 4 years | TCE, TCA, DCE | n.a. | Ferrihydrite<br>Magnetite<br>Green rust<br>Calcite (and others) | Most precipitates in the front end<br>Highest biomass (as measured by PFLA method) in the front end | Furukawa et al. (2002)<br>Wilkin et al. (2003) |
| Cornhusker Army Ammunition Plant | Grand Island, Nebraska, USA | ? (PRB installed in Nov. 2003 | Explosives | n.a. | Iron sulfides | Permeability reductions were observed | Johnson et al. (2008) |
| Avigliana waste site | Avigliana, Italy | 2 and 3 years | TCE, DCEs | n.a. | Calcite<br>FeS<br>Ferrihydroxides | High CH4 concentrations observed | Zolla et al.(2009) |

SRB: sulfate-reducing bacteria.
IRB: iron(III)-reducing bacteria.
DNB: denitrifying bacteria.