

The use of column experiments to predict performance and long term stability of iron treatment walls

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Abstract: Column tests with groundwater from a contaminated site are carried out to estimate reduction rates of chlorinated hydrocarbons and to predict the long-term performance of a reactive barrier. The results of the preliminary investigation are used to determine an appropriate flowthrough thickness for a Fe⁰ reactive wall. However, validation of the prognoses derived from the experiments is still outstanding and so the validity of column tests remains questionable. The possibilities which are given for the examination of the prognoses by standard field investigation can be illustrated by the example of a field application (Rheine, Germany). The comparison of field and laboratory results shows that the general change in groundwater composition within the barrier as well as downgradient can be derived from column experiments. The influence of microbes is only predictable by using geochemical models (i.e. PHRREQC), because of the lag time of microbial activity. Comparison of data is difficult due to an ambiguous hydraulic situation and a time-variable water composition at the site. Therefore it can only be shown that the remediation efficiency at the site is in the same order of magnitude as expected from column experiments, but a direct comparison of the reduction rates is impossible. For the same reasons, it can not be distinguished whether the loss of reactivity observed in the laboratory experiments becomes not (or not yet) effective in the field.

Recently, Fe⁰ permeable reactive barrier (PRB) technology (Gillham and O'Hannesin 1994) is used as an alternative to pump and treat systems at several sites for in situ groundwater remediation mainly in North America but also in Europe (RTFD). Most of these PRBs are used to mediate volatile organic compounds (VOCs) by reductive dehalogenation (Gillham and O'Hannesin 1992). Reaction rates for most chlorinated relevant compounds have been determined in both batch or column reactors under laboratory conditions. Actually, interest is directed more toward the impact of other groundwater constituents on the degradation rates, as well as on the long-term stability of PRBs, because a lifespan of more than 5 to 10 years is usually requested. The effects of solution chemistry on reaction rates have been investigated in several studies, with sometimes conflicting results. In some investigations VOC degradation rates have been found highly pH dependent, while other studies outline minimal pH effects. Conflicting results have also been reported on the effects of chloride, nitrate or hydrocarbons on dechlorination rates. In most cases VOC degradation has been described by a pseudo first-order rate law with respect to dissolved VOC concentration normalized to the BET iron surface. Other kinetics are used to consider reactive site saturation and increased iron surface passivation (i.e. Wüst et al. 1999, Farrel et al. 2000) or more complex reaction pathways (Arnold and Roberts 2000)

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Geochemical conditions within in situ Fe^0 PRBs are responsible for the corrosion of iron fillings and the formation of precipitates. The extent and type of precipitates may vary broadly due to the variety in groundwater geochemistry. For example, green rust was reported as well as iron and calcium carbonate, magnetite or iron sulfides, in case of sulfate reduction. The accumulation of some precipitates, either individually or as a mixture, may decrease reactivity due to iron surface passivation or may restrict flow and eventually clog the system. These possible reactions and processes which may effect the reactivity are described, for example, by Gavaskar et al. 1998.

Generally, the long-term performance of an in situ Fe^0 remediation system depends on the continued effectiveness of the iron to serve as an electron donor and a couple of reactions may increase or decrease its life time. So far, there is no theoretical approach for successful prediction of the reactivity of PRBs for long times. Therefore, column studies are performed preliminary to the reactive barrier installation in a contaminated aquifer. The results of the column experiments are used to predict the in situ degradation rates, as well as the long term performance. However, validation of the prognoses derived from the experiments is still outstanding and so the force of expression of column tests remains questionable.

A permeable reactive barrier (PRB) was installed at a former drycleaning site in an urban area (Rheine, Germany) in June 1998 (Ebert et al. 1999). Tetrachloroethene (PCE) and 1,2-Dichloroethene (1,2-DCE) are the primary contaminants of concern at the site. Initial maximum concentrations in the plume vary between 10 mg/l and 30 mg/l PCE and about 0.5 mg/L for 1,2-DCE. The 500m long, 250m wide plume is present in a loamy sand aquifer that extends 5-10m below ground. The water table is about 3m below surface and the overall pore velocity is about 0.06 m/d. The distance from the center of contamination to the treatment wall is about 400m. The PRB is a continuous reactive wall that varies between 0.6m and 0.9m thickness and is 22.5m long. The pilot scale PRB uses two reactive media: 69 tons of granular iron (Fe^0) mixed with gravel at a 1:2 volume ratio (34.5 tons each of Fe^0 and gravel) in 10m of the wall and 85 tons of sponge iron in 12.5m of the wall. A concrete-filled borehole separates the two segments. For monitoring, observation wells were installed 1m upstream and downstream as well as within the reactive media for each section of the PRB. Groundwater sampling was done monthly during the first half year and two times a year afterwards.

The results of two column experiments were used to design an appropriate flowthrough thickness of the PRB and to estimate the production of hydrogen gas by anaerobic corrosion, respectively. The experiments were performed with contaminated water derived from the site and only with sponge iron. The results of the experiment (accelerated flow) show non-steady state conditions during the runtime of about four month (60 exchanged pore volumes). Furthermore, the degradation behavior was pseudo zero order with respect to PCE at the influent end of the column at higher concentrations and pseudo first order at concentration below 500-1000 $\mu\text{g/l}$. With increasing elapsed times a migration of PCE concentration fronts was observed and the zero order degradation rates decreased from about 500 $\mu\text{g l}^{-1} \text{h}^{-1}$ to 150 $\mu\text{g l}^{-1} \text{h}^{-1}$. The half life times describing the degradation at lower concentrations increased from about 12 h to maximal 40 h. Consistent with the PCE front migration, a shift in pH, Mg, Ca and TIC concentration profiles could be observed indicating an iron surface passivation. Derived from the experimental results, a residence time of 240 h to 300 h was calculated to be appropriate for the degradation of 10 mg/l PCE to a level below 0.1 mg/l for a lifespan of five years at in situ conditions. The second

column experiment showed a mean hydrogen gas release rate of $2.7 \text{ cm}^3 \text{ h}^{-1} \text{ kg(Fe)}^{-1}$, which is about $130 \text{ l m}^{-3} \text{ d}^{-1}$. This result was responsible for the installation of a gas drainage at the top of the PRB because it is constructed directly below a footway.

The comparison of laboratory and 2.5-year monitoring results shows that the general change in groundwater composition within the barrier, as well as downgradient can be well derived from the column experiments. Except for the sulfate and ammonium concentrations the development of inorganic ground water constituents is predictable from column experiments keeping the buffer capacity of the aquifer in mind. The sulfate concentration decrease within the PRB from 80 mg/l to 20 mg/l during the first six month and to below the detection limit in a span of a year. The removal of sulfate by sulfate reducing bacteria has been observed at all implemented Fe^0 -PRBs but it was not significantly noticeable in short-time column experiments. In contrast to sulfate, nitrate is abiotically reduced by zero valent iron stoichiometrically producing ammonium (Schlicker et al. 2000). The monitoring results show a decreasing release of ammonium within the PRB simultaneously to the increasing removal of sulfate. At the same time the release of hydrogen gas decreased from a level comparable to the laboratory results. The impact of microbes on the groundwater composition was not observed in the laboratory experiments and therefore can only be estimated by using geochemical models like PHREEQC (Parkhurst 1995) with an adjusted data set. Further difficulties in data comparison are caused by an ambiguous hydraulic situation and a time variable water composition at the site. Therefore it can only be shown that the remediation efficiency at the site is in the same order of magnitude as measured in the column experiment. For the same reasons, it can not be distinguished whether the loss of reactivity observed in the laboratory experiments becomes not (or not yet) effective in the field. So far, an inhibition of PCE reduction was not observed and the downgradient concentrations stay between $10 \text{ }\mu\text{g/l}$ and $100 \text{ }\mu\text{g/l}$. In the future, an investigation series will be started including new observation wells, multilevel sampling, tracer tests (conservative and reactive), and pumping tests, as well as sampling the aged iron fillings from within the barrier for laboratory studies. These studies shall expose the processes within the barrier to evaluate the quality of the predictive column experiments.

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