Laboratory and field results of Fe(0) reaction walls - a first resumé

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ABSTRACT: Fe(0) reaction walls (FERW) are reported as a cost effective alternative to classical pump & treat technologies for the remediation of chromate and chlorinated hydrocarbon plumes. But critical and up to now more or less unknown factors controlling the long term performance (in most cases more than 10 years) are the evolution of permeability and reaction rates over time. These uncertainties make a prognosis with respect to the economical benefit of FERW quite difficult. In this study we present experimental results for long term performance predictions, which are based on numerous column studies with Fe(0) and TCE in the presence of common groundwater anions as Cl^-, HPO_4^{2-}, $H_2SiO_4^{2-}$, HCO_3^-, NO_3^-, CrO_4^{2-}, SO_4^{2-} and well defined humic acid.

1 OBJECTIVES

As described in several publications, the application of granular zero-valent iron provides a cost effective alternative to classical pump & treat technologies for in situ remediation of groundwater contaminated with chlorinated hydrocarbons, nitrate, chromate or uranium. Field demonstrations at sites contaminated with chorinated aliphatics (O´Hannesin & Gillham, 1998) or chromate (Puls et al., 1997) have shown a long term performance over five years. In contrast to these positive results an increasing number of studies are indicating that under special hydrochemical conditions a passivation of the Fe(0)-surfaces and/or clogging of the pore volume due to mineral precipitation have to be expected.

The reduction process at zero-valent iron is known to be a heterogeneous surface reaction and thus degradation can only take place after the contaminants have been sorbed at the iron surface (Matheson & Tratnyek, 1994). Hence, groundwater constituents, which are able to alter the Fe^0-surface, may have also a significant effect on the degradation rate. Oxidants act as competitors to TCE at the Fe(0) surface. High bicarbonate and sulfate concentrations lead to the precipitation of minerals, reducing the reactivity and permeability of the FERW (Gu et al., 1999). As mentioned these results contradict most of the field observations and at the moment it is not known, if these lab results are directly transferable to field applications (Gavaskar et al., 1998).

2 MATERIALS AND METHODS

Column experiments were performed to investigate the effect of common groundwater anions such as Cl^-, HPO_4^{2-}, $H_2SiO_4^{2-}$, HCO_3^-, NO_3^-, CrO_4^{2-}, SO_4^{2-} and humic acid on the reduction kinetics of TCE in a Fe(0) (DIAMANT® GH-R, round, diameter 1-1.6) -water system. Cl^- has been chosen as a candidate for the enhancement of TCE degradation rates in analogy to corrosion research. HPO_4^{2-} and $H_2SiO_4^{4-}$ are known inhibitors of iron corrosion processes because of the formation of coherent precipitates on the Fe^0-surface. The oxidants NO_3^- and CrO_4^{2-} should act like O_2 as possible competitors to TCE at the iron surface. Humic acid was chosen as a representative of natural dissolved organic matter, which is normally known as an inhibitor for iron corrosion. A more detailed description of the experimental and analytical set up is given elsewhere (Wüst et al., 1999; Schlicker et al., in press).

3 RESULTS

High Cl^--concentrations up to 5000 mg/l have no or only little increasing effect on the TCE degradation rate. High concentrations of HPO_4^{2-}, $H_2SiO_4^{2-}$ and SO_4^{2-} lead to a dramatic decrease of the TCE degradation rate. A considerable decrease in the degradation of TCE and a shift from pseudo-first order kinetic to zero-order kinetic was found at a concentration of 500 mg/l SO_4^{2-}. Higher sulfate concentrations (> 500 mg/l) did not enhance the inhibition effect significantly. Sulfate fixation is reversible and TCE degradation rate is fully recovered after SO_4^{2-} desorption or dissolution of an unknown $Fe-SO_4^{2-}$-precipitate. Microbial SO_4^{2-} reduction was only observed in a column containing Fe^0-particles from a pilot reactor, causing an increased degradation rate of TCE by a factor of 3-4. Whether surface-properties of the iron-sulfides such as the higher electrical conductivity or microbial mediated reactions are responsible for these observations is still in discussion.

High HCO_3^--concentrations are leading to a significant increase of the TCE-degradation rate, corresponding to publications from corrosion research. The transformation of HCO_3^- to CO_3^{2-} due to pH increase results in a release of H^+ with a following reduction to H_2. REM-examinations of the Fe-particle-surfaces give hints that this process reduces the thickness and coherency of the Fe(II/III)-coatings and does not build up passivating Fe-carbonate layers. But clogging of the pore volume may be an important process for long times and can be predicted by a kinetic reaction-transport model using the oversaturation state of different carbonates in solution.

Abiotic nitrate and chromate reduction on zero-valent iron were found to be faster than the degradation of TCE. Nitrite as an intermediate product was detected only in traces, depending on pH NH_3 or NH_4^+ are the terminal products of nitrate reduction. Long-term column experiments with nitrate and chromate indicate a passivation of the iron, resulting in a delayed onset of TCE degradation along the column axis. The passivated and non-reactive flow path increases with time, resulting in a migration of the contaminants into the iron metal treatment zone. The migration velocity of TCE seems to be linear correlated to the initial concentration of nitrate and chromate (Schlicker et al., in press).

According to (Gavaskar et al., 1997) high concentrations of dissolved organic matter (DOC) are exclusion criteria for the use of FERW´s. Our lab-results confirm that humic acid concentrations of only 1 mg/l cause a modification of 1.-order kinetics to the less effective 0.-order kinetic for TCE degradation. At higher humic acid concentrations this effect becomes more and more important.

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