

Removal of TCE and Chromate in a Permeable Reactive Barrier using Zero-Valent Iron

Peter Kjeldsen¹, Thomas Locht² and Andrew P. Karvonen³

Abstract: Permeable reactive barriers containing zero-valent iron as iron filings are able to remove the chromate by a combined reduction/precipitation reaction, and to degrade TCE. However, due to the passivation of the reduction capability of the iron surfaces by the precipitation of chromate and other groundwater constituents, the barrier may have a limited capacity for chromate removal. By performing column experiment with iron filings it was shown that the capacity was slightly lower at high chromate concentration (500 ppm) in comparison to low concentration (20 ppm). Mixing in sand had no significant enhancing effect on the removal capacity, in contrast to a pH adjustment of the groundwater to pH 4, which significantly increased the removal capacity. Increasing the hardness of the groundwater led to lower chromate removal capacities. The degradation rate for TCE was more than a factor of 100 lower after breakthrough of chromate in comparison to before loading chromate to the columns.

Chlorinated solvents and hexavalent chromium (as chromate) are some of the most serious threats to groundwater resources. Chlorinated solvents have been used for degreasing of metal agents and dry cleaning of clothing, while chromate has been used for wood preservation, electroplating and tanning leather. At electroplating facilities both pollutants are often observed at the same time.

Chlorinated solvents are chemically degraded in contact with iron surfaces (Gillham and O'Hannesin 1994). Chromate can be reduced to a less mobile and toxic compound in contact with iron surfaces (Blowes et al. 1997). Zero-valent iron in reactive barriers is used in several places especially in the USA (US Environmental Protection Agency 1999).

The objectives of the laboratory experiments were to examine the capacities of chromate removal for different zero-valent iron sources and the simultaneous long-term removal of TCE. Other governing factors were looked at such as flow velocity, chromate concentration, groundwater composition (hardness and pH), and mixing the iron with sand. Having an extra non-reactive support surface for precipitation products formed in the column may in theory lead to higher capacities, since the reactive surfaces will be covered to a less extent than in a pure iron system. More details of the performed experiments are given in Kjeldsen et al.(2001).

¹ Associate Professor, Environment & Resources DTU, Technical University of Denmark, Building 115, DK-2800 Kgs. Lyngby, Denmark

² Research Assistant, Environment & Resources DTU, Technical University of Denmark, Building 115, DK-2800 Kgs. Lyngby, Denmark

³ Research Assistant, Environment & Resources DTU, Technical University of Denmark, Building 115, DK-2800 Kgs. Lyngby, Denmark

The study included 30 column experiments using 25 or 50cm long 54mm inner diameter Plexiglas columns fitted with 18 side-ports for sampling of water along the column. The columns were fed with solutions having constant concentrations through the full experimental time of each experiment. The concentration profiles along the column lengths were drawn for different times. Figure 1 shows an example of concentration profiles for chromate using high chromate concentrations (500ppm) and the Master Builder iron type. The figure shows that the iron has a certain capacity for chromate removal since the chromate is breaking through the column after a certain time. On the basis of the positions of the front the specific chromate reduction capacities (in mg Cr(VI)/g Fe(0)) are calculated. The specific capacities found in the experiment using 500ppm inlet chromate concentrations were in the range of 1-3 mg Cr(VI)/g Fe(0) depending on the iron source. Lowering the inlet concentration to 20 ppm only slightly increased the specific capacity by a factor of 1.5-2.0. Mixing in sand in iron percentages of 5, 10, 25, and 50% did not lead to a significant increase in specific capacities. This means that the sand did not act as an extra non-reactive support surface for precipitation products formed in the columns. The specific surface of the sand may be too low in comparison to the high specific surfaces of the iron filings used.

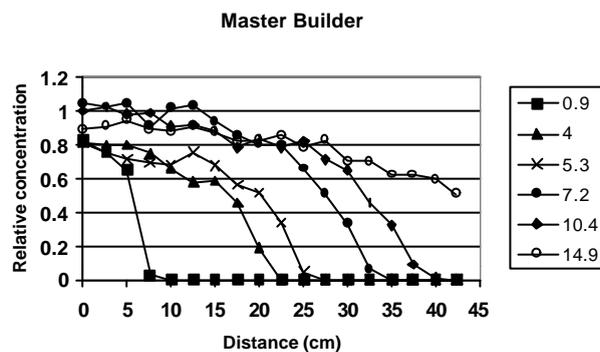


Figure 1 - Chromate profiles through a column containing Master Builder iron receiving an inlet concentration of 500 ppm Cr(VI). The relative chromate concentration as function of retention time (proportional to distance from inlet in column) and pore volumes passed through the column (given in the legends).

Figure 2 shows all sets of measured pH-values as a function of relative chromate concentration for the same column. The figure shows that there is a very good correlation between pH and the relative chromate concentration. A simple pH-measurement is a good indicator of the condition of a chromate removing PRB, since decreasing pH-values is a direct sign that the chromate reduction capacity of the PRB is about to be reached.

The composition of the groundwater had a significant effect on specific capacities with decreasing capacities by increasing the hardness of the water. Decreasing the pH of the groundwater to 4.0 had a very significant effect leading to much higher capacities. Including a pH-control (for instance by addition of acid) in in-situ technologies is, however, a difficult process to manage.

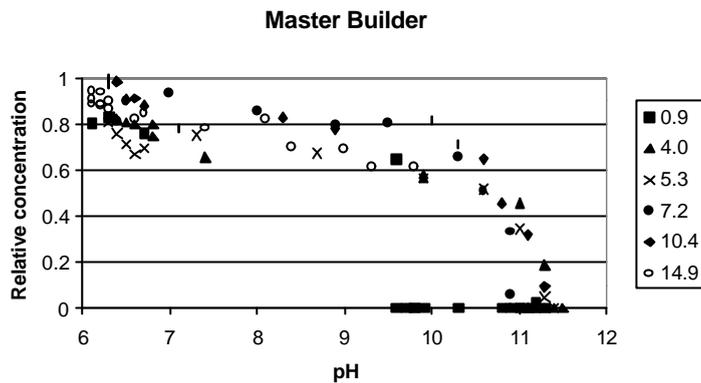


Figure 2 - Relationship between measured pH and relative chromate concentration for column with Master Builder iron type. The legends show the number of pore volumes test solutions passed through the column for each data point.

The TCE transformation rate in the columns before and after breakthrough of chromate was studied as well. A very significant decrease was observed with rates about 100 times lower after the chromate breakthrough (see Figure 3). This means that the chromate load to a reactive barrier needs to be estimated if an adequate simultaneous removal of TCE should be maintained through the whole lifetime of the barrier system.

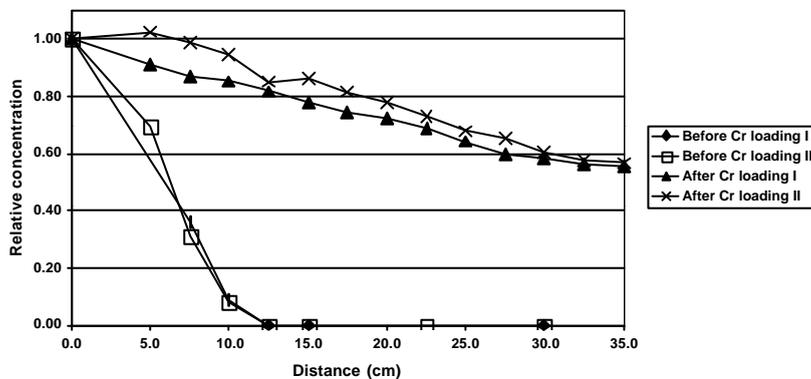


Figure 3 - Relative TCE concentration as a function of the column distance (x-axis) measured at two different times prior to chromate loading and two different times after chromate loading in column 1B – low flow velocity (20 mL/h).

References

- Gillham, RW and O'Hannesin SF (1994) "Enhanced degradation of halogenated aliphatics by zero-valent iron". *Ground Water*, 32, 958-967.
- Blowes DW, Ptacek CJ and Jambor JL (1997) "In-situ remediation of Cr(VI)-contaminated groundwater using permeable reactive walls: Laboratory studies". *Environ. Sci. Technol.* 31(12), 3348-3357.
- Kjeldsen P, Loch T and Karvonen AP (2001) "Chromate removal capacities of zero-valent iron for groundwater treatment in permeable reactive barriers", in preparation.
- U.S. Environmental Protection Agency (1999) "Field Applications of In Situ Remediation Technologies: Permeable Reactive Barriers". Solid Waste and Emergency Response, Washington DC 20460, EPA-542-R-99-002.