

PhD

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Remediation of chromate contaminated groundwater by a permeable reactive barrier: field investigations, laboratory experiments, and geochemical modeling

This study focus on the remediation of chromate contaminated groundwater. Geochemical, mineralogical and hydrological investigations have been carried out at two field sites, in laboratory experiments, and by geochemical modeling.

At the Willisau site (central Switzerland), a new design of a permeable reactive barrier (PRB) was emplaced to treat the chromate contaminated groundwater. The reactive material used is a mixture of zero-valent iron (ZVI) shavings and gravel. The barrier was installed in the setup of a single and a double array of piles (1.3 m in diameter with a gap of 1 m in between) where the contaminants are treated by a redox-reaction within the piles and in the Fe⁰-plume generated downstream of the barrier. Advantages of this new setup are that less reactive material is needed compared to a continuous barrier and that the application is feasible in geotechnical difficult subsoil or at greater depth. Main objectives of this study are to give an assessment of the effectiveness of the new PRB-design, to elucidate the relevant processes within the barrier and to determine limiting factors for the long-term performance and the longevity of the system.

Chromate accumulated in the unsaturated zone through former industrial activities is constantly washed out and subsequently mobilized by groundwater flowing through the contaminated subsoil. Thus, the amount of chromate in the groundwater strongly depends on the groundwater level and the rate of level variation. The 4-years of groundwater monitoring upstream, downstream and within the barrier shows that the remediation by the double array of piles is successful and highly effective. The setup is only limited by extraordinary high water level events that result in a substantial mobilization of chromate. These promising results support the new PRB design. In contrast, the remediation by the single array of piles is not effective enough to treat the chromate contamination. The reason for the failure is the too large gap between the piles and an insufficient lateral overlap of their Fe⁰-plumes. Two campaigns with optical tracers reveal that the lateral extension of the barrier is sufficient except for times of extraordinary high groundwater levels resulting in a broader expansion of the contamination plume. The depth of the piles is adequate as the contaminants are transported in the uppermost meters of the aquifer and do not migrate vertically.

The reactive material within the piles is in unconsolidated condition indicating that the flow through the piles is still assured. The ZVI-shavings feature corrosion rinds whereas their formation depends on different factors such as size and shape of the shavings, amount of graphite lamellae, position within the barrier, and life time. Generally, maximum corrosion rinds are found in the inflow and a minimum in the outflow of the piles. Mineralogical analyses of samples show that the corrosion rinds mainly consist of the Fe^{III}-hydroxides goethite and ferrihydrite. Fe⁰-oxides are only detected in small amounts due to the continuous supply of oxygen deriving from upstream groundwater and groundwater table variations.

Micro X-ray absorption fine structure spectroscopy measurements shed light on the corrosion processes and redox mechanisms taking place in the reactive zone. Ferrous iron is pro-

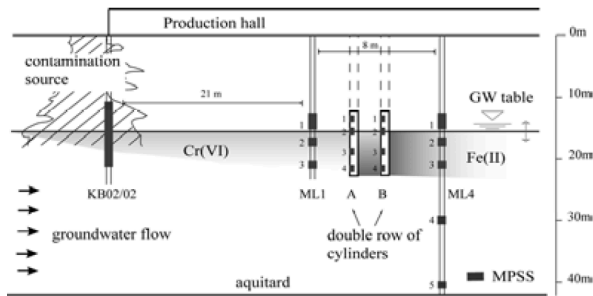
duced during the corrosion process and diffuses to the corrosion surface. It serves there either in dissolved or surface-bound form as reducing agent for the Cr^{VI}-reduction. X-ray absorption near edge structure analyses record two different spectra for Cr^{III}. Based on these data, two different redox mechanisms are suggested. The dominant process is the reduction of chromium in a homogeneous reaction by dissolved Fe⁰. This results in homogeneously distributed Cr^{III} in mixed chromium-iron-hydroxide phases with a Cr/Fe ratio of around 1/3. The other process implies the reduction of chromium by ferrous iron that occurs either bound to surfaces or bound in redox-reactive phases (e.g. green rust). This leads to the formation of Cr^{III}-rich clusters that feature a smaller proportion of Fe in the chemical coordination environment of Cr.

The results of the column experiments define the relevant geochemical processes in the Fe-system. The corrosion of ZVI generates reducing conditions in the reactive zone. With time and ongoing iron oxidation, reducing conditions change to oxidizing conditions and from the inflow, the oxidized zone gets larger. The oxidizing zone is characterized by a positive redox potential (Eh) and an increased amount of the redox-sensitive species as oxygen, chromate, nitrate, and sulfate. The reactive material is coated with reddish Fe-(hydr-)oxide precipitates. In contrast, the reduced zone implies negative Eh, and a lack of all oxidized species (except sulfate). Analyses from that part of the column indicate that oxygen, chromate, and nitrate are completely reduced at the reactive front but also partly in the oxidized zone. Sulfate is not reduced due to the lack of the specific bacteria needed. The pH slightly increases within the system due to the proton consuming iron oxidation reactions that exceed the effect of the proton producing Fe⁰-precipitation reaction. As the chemical composition of the used water is close to carbonate saturation, carbonate phases precipitate. These findings perfectly fit the results gained at the field site. Within the PRB, sulfate is additionally reduced and precipitates as amorphous iron sulfides in the back part of the barrier. Reduced nitrogen species (nitrite and ammonium) are detected downstream of the barrier but in very low concentrations.

Clogging of the barrier system presents a minor risk as the amount of precipitates in the pore space is low. In contrast, geochemical investigations indicate that the chemical composition of the groundwater has a crucial effect on the chemical reactions within barrier system. The redox-sensitive species of the groundwater strongly influence the long-term availability of iron. The reduction of nitrate and sulfate involves biotic reactions, where the specific bacteria promote the anaerobic iron corrosion by using the formed H₂ as reducing agent. Thus, a large amount of nitrate and sulfate beside the contaminant negatively contribute to the iron consumption. Moreover, the reactive material of the transition zone (saturated-unsaturated) is exposed to an additional amount of oxygen and is therefore more oxygenated. Estimations for the Fe-reservoir in Willisau result in ~10 years of total operation time. Nevertheless, precipitation of calcite on the shavings surface and the increasing dense layer of Fe-oxides will lead to a decrease of the iron corrosion rate. These processes provoke a significant surface passivation of the ZVI-shavings. Results from the geochemical

modeling indicate that this effect represents the most restrictive factor for the long-term effectiveness of the reactive material. Thus, a significant decrease in the iron reactivity is predicted before the entire Fe-reservoir is consumed.

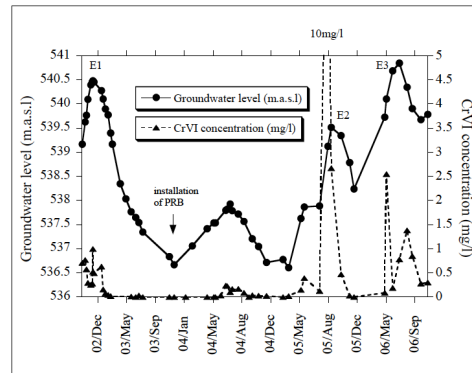
The Rivera site (southern Switzerland) presents a chromium contaminated site in a completely different hydro-geological and geochemical environment. The main interest is directed to organic and clay mineral rich layers which are embedded in the aquifer material. The investigations focus on the natural retention capacity of this intermediate layers in respect of the adsorption or even reduction capacity for the chromium contaminants. Further, the results provide a basis for the evaluation of the remediation and disposal strategy of this site. Chemical analyses show an enrichment of chromium in the fine-grained layers. Laboratory experiments (batch tests and flow-through experiments) suggest however that the contaminants are rather retained than permanently adsorbed or degraded. The natural retention potential of the organic and clay mineral rich layer is therefore not effective enough to prevent the migration of chromium compounds into lower groundwater levels.



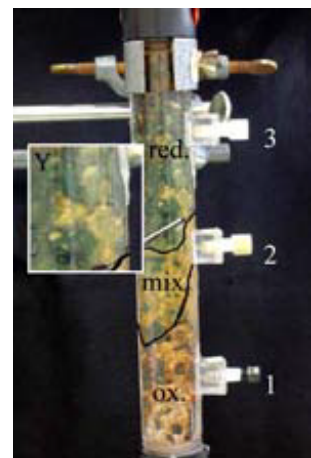
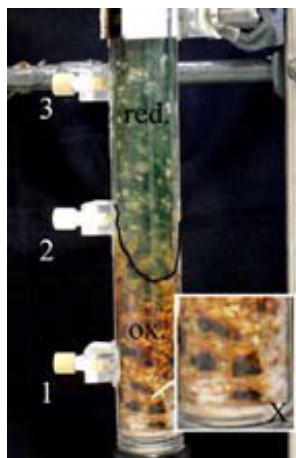
Profile across contamination source and double row of cylinders. The PRB is constructed as a "hanging" barrier. The Multi-Port Sampling System allows sampling of groundwater upgradient (ML1) and downgradient (ML4) of the barrier. Within the cylinders, groundwater and reactive material is sampled at four levels (numbers along cylinders and piezometers) of depths in four localities (A, B). To keep the illustration simple, the localities within the cylinders are only marked in the profile as one single element in the direct inflow of the cylinders.

Regarding a remediation by a PRB, the Rivera site features several advantages and disadvantages compared to the Wilisau site. The groundwater chemistry is less mineralized (e.g. less concentrated in Ca and HCO₃) which lowers the risk of surface passivation and pore space clogging. In contrast, the Rivera site features a young and very sensitive aquifer system with highly variable parameters (pH, EC, O₂, HCO₃, NO₃, SO₄,...). This implies a high vulnerability to geochemical changes thereby complicating predictions regarding geochemical processes. In addition, the complex hydro-geological subsoil makes an appropriate placement of a reactive barrier difficult.

The remediation of chromate contaminated groundwater is a contemporary issue and will also be up for debate in the future. The progress made by this study ensures an improved knowledge of the remediation mechanisms and the controlling processes in a PRB, and contributes to an advanced understanding of the behavior of chromium in the subsoil.



Cr^{VI}- concentrations measured in well KB02/02 (downgradient of the hotspot) plotted against the fluctuation of the groundwater table (m.b.s.l.: meters below surface level) over time. The diagram shows the direct connection between rising groundwater tables and increasing Cr^{VI}- concentrations. E1 to E3: Events of exceptionally high groundwater levels.



Column A (left side), B (centre) and C (right side) after 4 months of operation. Numbers 1- 3 indicate sampling ports. The geochemical different zones (oxidizing, mixing and reducing zone) were well distinguishable by colors. Column A presents the most oxidized column but showed within the oxidized zone still reduced areas (framed). Column B shows the sharpest reactive front, whereas column C features a mixing zone. Different Detail X shows the influence of the influent oxygen. Detail Y shows an area with gravel grains within the reduced zone where concentrations of Fe^{II} seem decreased. The size of the large images is about 20 cm.