IN-SITU REDUCTION OF Cr(VI) IN A CONTAMINATED AQUIFER ASSESSED BY LAB-SCALE COLUMN TESTS AND A FIELD TRIAL

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EXTENDED ABSTRACT

Chromate is among the ground water contaminants often encountered at former metal plating sites ore processing facilities etc. In-situ reduction Cr(VI) to far less toxic Cr(III) may be a cost-effective alternative to conventional pump & treat remediation. For contaminant plumes in low-productivity aquifers this may even be the only viable option since pumping may cause settlement cracks in buildings and damage the infrastructure. This study focuses on the in-situ reduction of a Cr(VI) plume by a blend of ferrous sulphate and sodium dithionite at a former metal plating site in Upper Bavaria, Germany. The hot spot (Cr(VI) concentrations of up to 10 mg/L) is localized approximately 70 m downstream the former plant. Efficiency of the reductive mixture was assessed in a lab-scale column study and a field trial. The column study was performed with aquifer material and ground water from the site under saturated conditions. Four columns (void volume 2 L) were equipped with redox sensors connected to a data logger. An infiltration port made of porous polypropylene was inserted in the middle of the columns and attached to a peristaltic pump for reductive delivery. One column served as the control (infiltration of deionized water). To the other three, the reductive blend was applied at molar ratios of FeSO₄:Na₂S₂O₄ of 1:1, 2:1, and 3:1. The infiltration was performed as a single pulse under cross-flow conditions while the Cr(VI) contaminated ground water was continuously upstream-fed through the columns. In the effluent heavy metals, Cr(VI) and redox indicators were analysed. In the field trial, 2m³ of the reductive were infiltrated into a 5 inch screened well. During the injection the piezometric level in the well was monitored with a light plummet. Stationary conditions were achieved within 15 minutes as indicated by a constant ground water elevation of 30 cm above at-rest water level. Upon completion of the injection a multiparameter probe was inserted in the well to monitor basic hydrochemical parameters. Well samples were collected every two weeks for chemical analysis. Both in the lab-scale study and in the test field trial Cr(VI) could be eliminated to below detection limits. As the reductive blend was infiltrated the pH and the redox potential dropped due to Fe(II) oxidation and the initial excess of reducing species. Acidification triggered a short-term mobilization of co-contaminants in the column study but not in the field trial. In the lab experiment reducing conditions were sustained until the end of the experiment (16 days after infiltration). In the field experiment Cr(VI) concentrations returned to pre-injection level after three months indicating that the reductive had migrated downstream and/or was consumed. On both scales the blend of Na₂S₂O₄ and FeSO₄ proved suitable for Cr(VI) reduction. As a prerequisite for the full-scale implementation the operation distance of infiltration needs to be established.

Keywords: chromate, in-situ reduction, column testing, field trial
1. INTRODUCTION

Leakage, poor storage, and improper disposal practices have released chromium to the environment causing contamination of ground and surface water (Palmer and Wittbrodt, 1991). Potentially affected sites include electroplating shops, wood and pulp processing plants, tanneries and pigment production facilities (Franco et al., 2009) as well as ore processing sites (Dermatas et al., 2006). Both the toxicity and the mobility of Cr in subsurface systems are determined by redox conditions. In aqueous systems, Cr occurs in two valence states; hexavalent chromium \{Cr(VI)\} and trivalent chromium \{Cr(III)\}. Under circumneutral pH conditions, Cr(VI) is soluble, highly mobile and toxic whereas Cr(III) is insoluble, strongly adsorbing and far less toxic (Comber and Gardner, 2003). Remediation of Cr(VI) contaminated aquifers is often performed by pump and treat methods (P&T). In a P&T remediation set-up the contaminated water is pumped out of the aquifer and treated at the surface and potentially returned to the aquifer (Voudrias, 2001). The main advantage of this remediation strategy rests with the fact, that treatment may be performed according to established water and waste water treatment techniques, e.g., adsorption onto (bio)sorbents, membrane filtration, anion exchange and electrochemical processing (Owlad et al., 2009). However, P&T concepts require the passage of a sufficient volume of ground water through the contaminated section of the aquifer, in order to remove not only the dissolved contaminants, but also to capture contaminants released from the aquifer material by desorption of diffusion (Voudrias, 2003). Particularly, pumping of excess groundwater may encompass land subsidence (Ayvaz and Karahan, 2008) and cause damage to the infrastructure in populated areas.

Asides the unforeseeable duration of P&T remediation this limitation has evoked research on in-situ remediation strategies for Cr(VI) contaminated aquifers. Proposed techniques involve among others the use of permeable reactive walls installed in the path of flowing ground water (Blowes et al., 1997), the injection of reductive agents such as sodium dithionite into the contaminant plumes (Khan and Puls, 2003) or the electrokinetic remediation by use of direct current electric fields (Wieczorek et al., 2005). Iron-based in-situ remediation schemes have received considerable attention since reduced Fe not only acts as a reductive for Cr (VI) but also provides the precipitation agent for the formation of mixed Fe(III)/Cr(III) hydroxides (e.g. Cundry et al., 2008). Infiltration of ferrous salts such as FeSO₄ requires that an appropriate volume of solution is prepared and stored at the site. However, immediate precipitation of Fe-(hydr)oxides may occur either in the storage tanks or in the infiltration wells (Eary and Rai, 1988). This may hamper in situ-reduction of Cr(VI) since the reductive is partially consumed and the clogging of aquifer pores or well screens may decrease the infiltration rates. To overcome this problem, the use of blends of Na₂S₂O₄ and FeSO₄ has been suggested (Su and Ludwig, 2005; Ludwig et al., 2008). In this study we focussed on the use of such a blend for the in-situ treatment of a Cr(VI) contaminated aquifer at a former metal plating site. In-situ reduction of Cr(VI) is the only viable option site since the low-productivity aquifer and the dense building development impedes a P&T remediation. Our research encompassed a lab-scale feasibility column study followed by a test field trial.

2. MATERIALS and METHODS

2.1. Study site

The study site is located in Upper Bavaria, Germany. The subsoil is build-up of backfilling materials and silty-clayey layers followed by Riss glacial sediments (silty-sandy gravel) underlain by more finely grained Tertiary material. The groundwater table of the unconfined aquifer rises from 6 m below ground in the west to 1.5 below ground surface in the east. In the 1970s a soil and ground water contamination by Cr(VI) took place due to improper management of metal plating baths and the solid wastes derived thereof. As
an immediate countermeasure the contaminated soil material was excavated. The electroplating activities were ceased and the site was developed as a housing area. In the early 2000s Cr(VI) concentrations in the mg/L-range were detected in ground water monitoring wells installed downstream the former impact area. Plume migration is oriented towards a tributary located 150 m downstream the actual hot spot. The position of monitoring wells at the site and the ground water elevation (as monitored on 02/11 of 2009) is shown in Figure 1. The original impact area is located in vicinity of the monitoring well P3 and the actual plume centre is suspected around well P5.

**Figure 1.** Monitoring wells and ground water elevation at the study site (scale 1:1000).

### 2.2. Lab scale feasibility study

The feasibility of an in-situ Cr(VI) reduction by blend of Na$_2$S$_2$O$_4$ and FeSO$_4$ was first tested in lab scale column experiments under water saturated conditions. Aquifer material collected during the construction of the new monitoring well P10 and ground water collected from well P2 (cf. Figure 1) were used. Experiments were conducted with a computer-controlled column device [ipm-isc 01, emc GmbH, Erfurt, Germany]. The packed beds had diameters of 9.0 cm and a lengths of 30 cm and were equipped with two Pt-electrodes, a common Ag/AgCl-reference electrode, and an infiltration port made of porous polypropylene [all ecoTech Umweltmesssysteme, Bonn, Germany]. Redox potential was recorded every 10 minutes with a Micromec Multisens data logger [Techmetics GmbH, Freiburg Germany] and normalized to the standard hydrogen electrode by addition of 207 mV. The column setup is shown in Figure 2.

The column experiments differed in the composition of the infiltrated reductive blends. At a constant concentration of FeSO$_4$ (130 mM on a water-free basis) the level of Na$_2$S$_2$O$_4$ was varied to yield molar concentration ratios FeSO$_4$: Na$_2$S$_2$O$_4$ of 1:1 (column A), 2:1 (column B) and 3:1 (column C). To column Ø (control) distilled water was supplied instead of the reductive blend. Throughout the experiment (42 days) the columns were continuously fed from bottom to top with Cr(VI)-contaminated ground water from well P2 using a peristaltic pump. The volumetric flow rate averaged 0.53 cm$^3$/min. The resulting Darcy velocity was equivalent to the conditions at the site. At day 26 a volume of 1.2 L of the reductive blends was delivered through the lateral infiltration ports at a volumetric flow rate of 5.5 cm$^3$/min. These values were derived by a downscaling a previous field slug test performed at well P2.
2.3. Field trial

To validate the results of the feasibility study a field trial was conceived consisting of a tracer test followed by the infiltration of the reductive blend. Criteria for the selection of infiltration and monitoring points was their orientation in direction of the ground water flow, their lay-out as 5-inch screened wells, and a good accessibility. This was to ensure correlation between downstream effects and upstream infiltration, sufficient space for sampling and instrumentation and safe storage of equipment during the tests. Following these criteria P2 was chosen as the infiltration well and P10 (located approximately 10 m downstream) as the potential monitoring well. The tracer test involved the infiltration of 2 m³ NaCl solution (Ph. Eur. grade) having a concentration of 25 g/L (430 mM). To follow the tracer pulse a multiparameter probe with integrated data logger [600 LLM-M, YSI Inc, Yellow Springs, OH, USA] was installed in well P 10 and set to record hydrostatic pressure, pH, redox potential, dissolved oxygen, electric conductivity, and temperature.

For the reductive infiltration the blend with the lowest level of Na₂S₂O₄ (molar ratio FeSO₄ / Na₂S₂O₄ = 3: 1) was chosen to minimize adverse side effects. The amount of FeSO₄ was based on the stoichiometry of Cr(VI) reduction, the Cr(VI) concentration in well P2 and an estimate of the aquifer volume affected by the reductive infiltration. The solution was prepared in two intermediate bulk containers (IBC) with a volume of 1 m³. To each IBC 2.3 kg Na₂S₂O₄ was added and dissolved in tap water using an electrically powered agitator. Upon complete dissolution 11.2 kg of FeSO₄ × 7 H₂O were added yielding molar concentrations (water-free basis) of 39.6 mM FeSO₄ and 13.2 mM Na₂S₂O₄. The infiltration test was approved by the corresponding water management authority.

2.4. Analytical

Effluent samples of the column tests and pump samples of the field trial were analysed by ICP-MS for Cr, Ni, Zn as typical contaminants at metal plating sites, Fe and Mn as redox indicators. Hexavalent chromium was determined photometrically. Ion chromatography was used to analyse major anions.
3. RESULTS and DISCUSSION

3.1. Feasibility study

Figure 3(a) documents the temporal evolution of the redox potential measured in the lower and upper sections of the packed bed of column B (upstream and downstream the infiltration port, respectively). Upon infiltration of the reductive at day 26 the downstream redox potential dropped sharply from around 300 mV to ~500 mV indicating strongly reducing conditions. With continued feed of the contaminated ground water values recovered slightly and stabilized around ~300 mV. For the remainder of the experiment the redox potential was 600 mV lower than prior to infiltration. Unlike the downstream redox data the upstream redox potential remained constant over time.

The development of the Cr(VI) concentration in the effluent of all soil columns is shown in Figure 3(b). Four days after start of the experiment effluent Cr(VI) approached the influent concentration (~3.5 mg/L) in all columns. This was not expected given the slow advance of the contaminant plume at the site. Most probably, fast breakthrough was due to the use of Cr(VI) contaminated aquifer material that had been pre-equilibrated with Cr(VI).

![Figure 3](image_url)

**Figure 3.** Redox potential in the packed bed of column C (a) and Cr(VI) in the column effluents during continuous feed with Cr-contaminated ground water (b).

Consistent with the downstream redox potential, the reductive infiltration lead to a drop of effluent Cr(VI) in all treated columns to concentrations close to or below the limit of quantification while the effluent of the control remained unchanged. Complementary analyses of total Cr by ICP-MS showed that the disappearance of Cr(VI) was not merely due to a reduction to Cr(III) but by retention of the contaminant in the packed beds.
As a side effect of the reductive infiltration Ni and Zn briefly peaked in the effluent of the treated samples (concentrations in the µg/L-range). This may have been due to the temporary pH drop from values around 8 to below 4 induced by the oxidation of ferrous iron (Gemeinhardt et al., 2006) or to a temporary dissolution of sorbents at very low redox potentials (Antić-Mladenović et al., 2011). Shortly after the reductive infiltration sulphide was detected in the column effluent. Maximum concentrations correlated with the amount of Na₂S₂O₄ in the reductive blend and were 309 mg/L and 4.1 mg/L in columns A and B, respectively. In column C the sulphide concentration was below the limit of quantification, however, all treated columns turned black in the upper section indicating the formation of FeS.

3.2. Field trial
After the NaCl infiltration in well P2 the ground water composition in the downstream well P 10 was monitored for 20 weeks using a multiparameter probe. During this period no systematic change of the electric conductivity occurred, indicating that P 2 and P 10 were not oriented in the direction of ground water flow. Therefore, the monitoring well was given up in favour of following the effects of the reductive application directly in the infiltration well using both the data logged by the multiparameter probe and chemical analyses of pump samples.

The response of ground water quality data to the reductive infiltration is given in Figure 4. The course of the water temperature (Figure 4 a) is characterized by a sharp peak immediately after the infiltration caused by the higher temperature of the reductive blend and a pronounced drop around day 80 after infiltration due to intrusion of thawing water (winter period). The water level above the pressure sensor of the probe decreased until day 80 and recovered as the aquifer was replenished by thawing water and rainfall eventy. The course of the electrical conductivity was dominated by a peak with a maximum of 6 mS/cm caused by infiltration of the reductive. Coincidence of secondary peaks with temperature drops and increasing water levels point to the intrusion seepage water containing de-icing salts. Unlike the laboratory findings, only a minor change of the ground water pH occurred in response to the reductive infiltration. This points to more effective buffering by the solid phase constituents under field conditions, possibly due to a larger ratio of aquifer solids and reductive volume. Similar to the findings of the lab scale column study, the field scale test lead to a sharp drop of the redox potential (Figure 4 b). Following a minimum of −600 mV the redox potential increased to values of around −150 mV within 30 h after the infiltration. Within a period of 70 to 80 days after infiltration readings returned to pre-infiltration level.

Consistent with the laboratory findings the chromate concentrations dropped upon the reductive infiltration (Figure 4 c). While pre-infiltration levels were in the mg/L-range, non-detect levels were observed after infiltration. Again, cross-checks against total Cr indicated that the contaminant was not only reduced but also removed from the solution phase. Anti-correlation of Cr(VI)- and Fe-concentrations suggests that Cr was precipitated as mixed Cr(III)/Fe(III) oxides. At day 85 after the reductive infiltration Cr(VI) concentrations in the infiltration well returned to levels above the limit of quantification and until day 120 a continuous recovery to pre-infiltration levels was observed. The time course was consistent with the recovery of the ground water redox potential and the depletion of dissolved iron. Overall, the findings support the existence of a chromate source located upstream the infiltration well P2.
Addition of the FeSO₄/Na₂S₂O₄ blend caused a reduction of the contaminant load to below legal limits for a period of 3 months, approximately. After this period upstream delivery of chromate and export/exhaustion of the reductive caused the Cr(VI) concentration to re-increase. Unlike the laboratory findings no adverse side effects associated with a temporary increase of further metal plating-specific contaminants was observed.

5. CONCLUSIONS
The lab scale and field trial investigation demonstrated that the Cr(VI)-contamination of ground water may be effectively addresses by in-situ reduction with FeSO₄/Na₂S₂O₄.
Before a full-scale implementation the impact area of infiltration wells needs to be established. Corresponding research is currently underway.

REFERENCES