Implementation of fluidized granulated iron reactors in a chromate remediation process

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HIGHLIGHTS

- Fe-granules show high Cr(VI)-reduction rates using fluidized bed conditions.
- No respective negligible passivation effects on the surface of the iron granulates.
- P&T-method by using ZVI in a FBR is very effective for Cr(VI) remediation.
- The process provides no increase in salinity of the treated effluent.

ARTICLE INFO

ABSTRACT

A new approach concerning in-situ remediation on source ('hot-spot') decontamination of a chromate damage in connection with an innovative pump-and-treat-technique has been developed. Iron granulates show significant higher reduction rates, using fluidized bed conditions, than a literature study with a fixed bed installation of small-sized iron granules. First results from an abandoned tannery site concerning injections of sodium dithionite as a chromate reductant for the vadose zone in combination with a pump-and-treat-method, allying the advantages of granulated zero valent iron (ZVI), are reported. Reduction amounts of chromate have been found up to 88% compared with initial values in the soil after a soil water exchange of 8 pore volumes within 2.5 months. Chromate concentrations in the pumped effluent have been reduced to under the detection limit of 0.005 mg/L by treatment with ZVI in the pilot plant.

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1. Introduction

In the EU, there are potentially millions of sites where land contamination could pose a risk to water resources, ecosystems, and/or human health. As a result, over € 2000 millions are believed to be spent annually on-site characterization, risk management and remediation (NICOLE, 2009). According to the Federal Ministry of Agriculture, Forestry, Environment and Water Management in Austria (BMLFUW, 2007) national remediation targets require the completion of clean-up measures at the most heavily contaminated sites until 2050. In Austria it was found, that the main pollutants of these abandoned areas are chlorinated hydrocarbons followed by mineral oil and heavy metals, which pose a significant health risk to humans (UBA, 2012). One of these heavy metals is chromium.

Especially in urban areas, remediation of abandoned hazardous sites is a challenging task both in financial terms and with regard to operational aspects. Due to restricted field conditions and sometimes continued activities on the site, in-situ techniques are often the method of choice.

Based on a R&D-project on chromium contaminated soil, a new approach on source ('hot-spot') decontamination in connection with pump-and-treat-technique has been developed. This process combines two advantages in one step: the reductive force of zero valent iron (ZVI) with the fast procedure of pump-and-treat (P&T).

1.1. Challenging on-site remediation

Many brownfields are built-up areas, where in-situ-remediation is an appropriate method. Basically, there are two main possibilities to apply on-site technology at a contaminated site: passive methods like permeable reactive barriers (PRBs) and active methods like P&T-procedures.

ZVI is already successfully proven in PRBs to treat several hazardous pollutants by providing additional electrons to the redox

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process. This treatment is already a state of the art, but problems arise from precipitation, surface passivation and clogging-effects at the wall. These problems make it difficult to predict the exact life time of the material and duration of treatment. Exchanging the ZVI material results in higher maintenance costs compared with no replacement, a reason why these systems are usually oversized (Bürger et al., 2003).

Active P&T-methods have no limitations in life time, but they have nearly constant operating costs, even though the contaminants decrease with duration of the clean-up process. Apart from energy consumption, when applying a hydraulic recirculation mode, increasing salinity of seepage water emerges with time due to the chemical application for waste water conditioning and treatment up to the threshold values of e.g. conductivity in pore- and groundwater.

1.2. Chromium characteristics

The potential toxicity and mobility of chromate ($Cr(VI)$) – a hexavalent chromium species – led authorities to strictly regulate its environmental concentrations. Besides being the most stable species in water, hexavalent and trivalent chromium ($Cr(III)$) show very different characteristics: whereas the cationic trivalent Cr^{3+} is considered to be an essential trace element (Schwarz and Mertz, 1959), the anionic chromate (CrO_4^{2-}), is a noxious compound for humans, known to be carcinogenic and very mobile, especially in water. Thus the goal of remediation is mainly focused on the aqueous reduction of chromium into its trivalent state, in order to precipitate it out of solution. For this reason, various techniques to remediate contaminated soils have been developed or are still in the experimental stage.

1.3. Redox reactions of chromium

Chemical species of chromium in aqueous solutions present in soils and aquifers are rather complex systems. Interactions of the solid and aqueous phase in different oxidation states may lead to various redox processes in the soil.

1.3.1. Effects on chromate reduction

Humid soils and sediments that are at partial equilibrium with atmospheric oxygen enable those conditions, in which oxidation and reduction processes can take place simultaneously. Under this environment, $Cr(III)$ could be oxidized to $Cr(VI)$ in soil by oxidizing compounds (e.g. MnO_2). If the oxidizing capacity of the soil is greater than the reduction capacity, the soil reductants could be exhausted and chromium could be oxidized and ultimately mobilized in the soil (Palmer and Puls, 1994). Concurrently, as part of the chromium cycle in soil, $Cr(VI)$ can be reduced to $Cr(III)$ in presence of MnO and organic acids originating from organic soil matter such as humic and fulvic acids. Additional reactions leading to chromate reduction can take place under the influence of dissolved ferrous iron and reduced sulphuric compounds (Bartlett, 1991).

Precipitation of chromium hydroxides and fixation via adsorption on soil surfaces depends strongly on the physicochemical conditions in the soil. The success of a geochemical fixation and, thus, an immobilization of chromium depend on the question, how much insoluble and stable chemical chromium compounds can be generated. $Cr(III)$ forms soluble complexes with NH_3, OH^-, Cl^-, F^-, CN^-, SO_4^{2-} and soluble organic ligands, but at pH < 5 its mobility decreases by adsorption to clayey soils or oxide minerals and at pH > 5 due to the formation of low soluble hydroxides (Chrostowski et al., 1991).
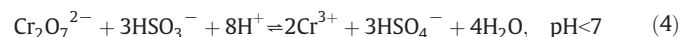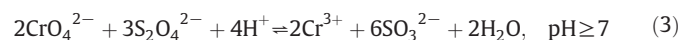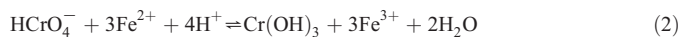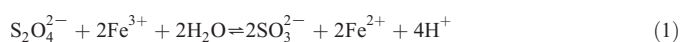
Modifying the soil environment by artificially injecting an appropriate reducing agent into the vadose zone will decrease the redox potential and therefore reduce existing chromate compounds. Under mildly acidic to alkaline conditions, $Cr(III)$ can be precipitated as an amorphous

chromium hydroxide ($Cr(OH)_3$) and crystallize as $Cr(OH)_3 \cdot 3H_2O$ or Cr_2O_3 (Swayambunathan et al., 1989). The aqueous solubility product of $Cr(OH)_3^0$ is 6.7×10^{-31} mol^4/L^4 (at 25 °C). If the pH within the contaminant plume is between 5 and 12, the aqueous concentration of $Cr(III)$ should be less than 1 μmol/L (<0.05 mg/L) (Palmer and Puls, 1994).

1.3.2. Unsaturated zone

Soils rich in iron enhance the reduction of chromate by sodium dithionite ($Na_2S_2O_4$). Reduction reactions with the dithionite or hydrosulfite ion ($S_2O_4^{2-}$) typically involve two steps (Amonette et al., 1994): firstly the dissociation of the ion to $SO_2 \cdot^-$ radicals and secondly the reaction with the oxidized species to yield a reduced species and sulfite (SO_3^{2-}) or hydrogen sulfite (HSO_3^-). Dithionite also disproportionates in aqueous solution into thiosulfate ($S_2O_3^{2-}$) and HSO_3^- ions.

In addition, structural iron is chemically reduced from ferric to ferrous iron, which itself reacts with aqueous chromate (USEPA, 2000):

$$S_2O_4^{2-} + 2Fe^{3+} + 2H_2O \rightleftharpoons 2SO_3^{2-} + 2Fe^{2+} + 4H^+ \tag{1}$$

$$HCrO_4^- + 3Fe^{2+} + 4H^+ \rightleftharpoons Cr(OH)_3 + 3Fe^{3+} + 2H_2O \tag{2}$$

$$2CrO_4^{2-} + 3S_2O_4^{2-} + 4H^+ \rightleftharpoons 2Cr^{3+} + 6SO_3^{2-} + 2H_2O, \quad pH \geq 7 \tag{3}$$

$$Cr_2O_7^{2-} + 3HSO_3^- + 8H^+ \rightleftharpoons 2Cr^{3+} + 3HSO_4^- + 4H_2O, \quad pH < 7 \tag{4}$$

SO_4^{2-} is produced as a byproduct and can act as an inhibitor to $Cr(VI)$ adsorption, thus allowing any residual $Cr(VI)$ to remain in the mobile phase to be reduced to $Cr(III)$ (USEPA, 2000).

1.3.3. Saturated zone

Removal of chromate via Fe^0 is caused by redox reactions in the first place. Sorption processes, especially at neutral conditions, play comparatively a minor role (Köhler, 2004). Electrons are needed for reduction, which are generated by oxidation of the elemental iron accordingly.

The conversion of Fe^0 to Fe^{3+} takes place via two steps, involving the oxidation state of Fe^{2+}:

$$Fe^{2+} + 2e^- \rightleftharpoons Fe^0, \quad E^0 = -0.44 \text{ V} \tag{5}$$

$$Fe^{3+} + e^- \rightleftharpoons Fe^{2+}, \quad E^0 = +0.77 \text{ V} \tag{6}$$

Generally, the simplified redox process with Fe^0 and chromate is favored in acidic conditions and can be written as follows:

$$Fe^0 + CrO_4^{2-} + 4H_2O \rightleftharpoons Fe(OH)_3 + Cr(OH)_3 + 2OH^- \tag{7}$$
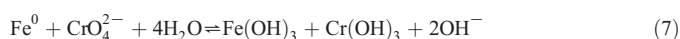
Solid chromium hydroxide in solutions may precipitate as coprecipitates with other metals, especially with iron in its oxidized state $Fe(III)$, rather than pure $Cr(OH)_3$. It will generate an amorphous hydroxide coprecipitate in the form of $Cr_xFe_{1-x}(OH)_3^0$ (Palmer and Wittbrodt, 1991).

$$xCr^{3+} + (1-x)Fe^{3+} + 3H_2O \rightleftharpoons CrxFe(1-x)(OH)_3 + 3H^+, \quad \text{with}: 0 < x < 1 \tag{8}$$
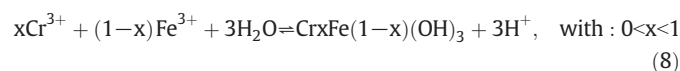
This compound has a lower solubility equilibrium than the pure chromium hydroxide which reduces further with increasing Fe-content (Rai and Sass, 1987).