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Bioremediation of Hexavalent Chromium: A Few Significant Site Histories in Italy

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ABSTRACT: In Lombardy (Italy), about 25% of the sites ranked in the Regional Plan of Contaminated Sites are affected by Cr(VI) in groundwater and/or soil. Therefore, innovative sustainable remediation techniques are under investigation, with pilot- or full-scale applications. In situ bioremediation has a significant role in the remediation techniques for its general sustainability in terms of environmental impact and costs. However, while organics can be mineralized, inorganics can only change their oxidation state, hopefully reducing their toxicity and mobility in the environment. Various patented products were used at five polluted sites in order to reduce Cr(VI) to Cr(III) via bio-induced reduction, bioreduction and bioimmobilization. The experience pointed out that Cr(VI) concentration in groundwater can be significantly reduced (up to three order of magnitudes), but the unsaturated zone should be treated as well in order to solve the problem definitely. Soil heterogeneity is a critical issue and mixtures usually have to be injected at different depths. Iron, manganese and sulphate side-contamination can result in groundwater after injections.

INTRODUCTION

Chromium is an important industrial metal having a wide range of applications in metal plating, leather tanning, metal corrosion inhibition, pigment production, refractory materials and wood-preserving industries (Nriagu, 1988; Apte et al., 2005).

In northern Italy such uses has affected large areas. At many industrial and waste disposal locations, chromium has been released to the environment via leakage and poor storage during manufacturing or improper disposal practices, resulting in contamination of soil and groundwater. In Lombardy, about 25% of the sites ranked in the Regional Plan of Contaminated Sites are affected by Cr(VI) in groundwater and/or soil, and in large areas of the region groundwater shows Cr(VI) concentrations above the Italian regulatory limit (5 µg/l) (Regione Lombardia, 2014). In Piedmont, Cr(VI) is the major inorganic species affecting groundwater, apart from Fe and Mn, which have natural origin. The impact assessment of hexavalent chromium over the 2009-2011 period for the deep aquifer system emphasizes that this parameter represents, along with the aliphatic chlorinated solvents, one of the main problems for groundwater quality (ARPA Piemonte, 2012).

Therefore, innovative sustainable remediation techniques are under investigation with pilot- or full-scale applications.

CHROMIUM IN SOIL-WATER SYSTEMS

The migration of chromium in soils, surface and groundwater and its toxicity is strictly related to its speciation. Chromium primarily exists in two valence states, trivalent Cr(III) and hexavalent Cr(VI). Cr(III), the most common form of naturally occurring chromium, is relatively stable and has low solubility in aqueous solution; thus it is largely immobile in the subsurface at typical environmental conditions (pH 6-9). (Dhal et al., 2013). The oxidized hexavalent form is highly soluble in water and therefore mobile;

moreover, it is a proven carcinogen, mutagen, and teratogen and exhibits acute toxicity to different biological systems.

Chemical species occurring in the environment are strongly affected by pH and redox potential (Eh), as shown in Figure 1. Cr(VI) is stable under oxidizing conditions, whereas Cr(OH)_3 is stable under reducing conditions (James et al., 1997; Massacheleyn et al., 1992). Under proper pH and Eh conditions or in presence of reducing/oxidizing agents, the prevailing chemical species can change (Dhal et al., 2013; Accornero et al., 2010).

The oxidation of Cr(III) to Cr(VI) can take place in the presence of Mn(IV) oxides (Richard and Bourg, 1991). However, the kinetics is slow, as the process is 10 times slower than reduction of Cr(VI) to Cr(III) (Bartlett et al., 1988). Cr(VI) can be reduced to the trivalent form by redox reactions involving organic substances in soil (carbohydrates, proteins and humic species), Fe(II), S^{2-} or as part of the metabolism of some microbial species (Figure 2).

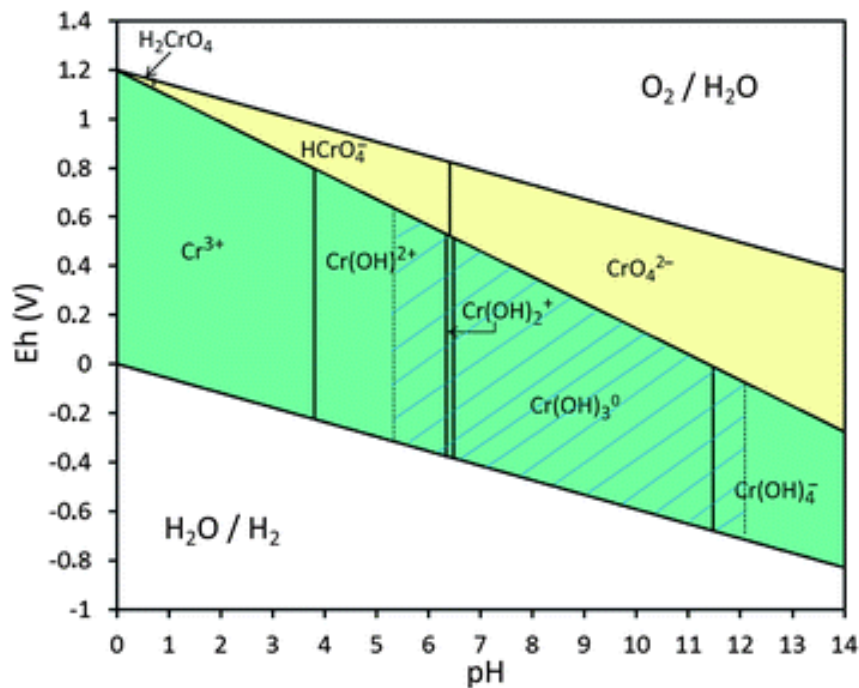


FIGURE 1. Simplified Eh-pH diagram showing dominating Cr species in diluted aqueous solutions without any complexing agents other than H_2O and OH^- (modified from Ščančar and Milači, 2014).

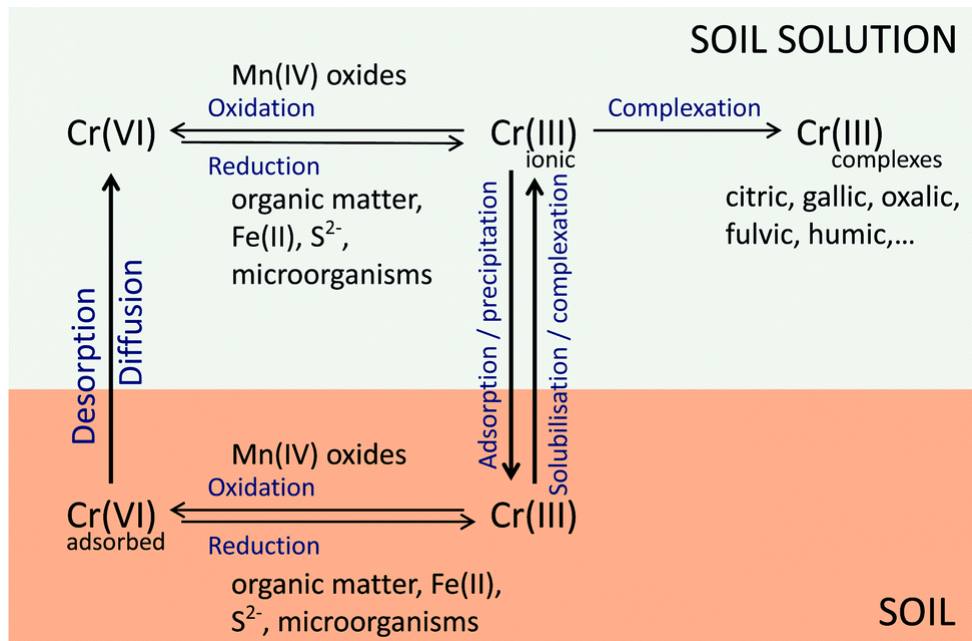


FIGURE 2. Simplified scheme of cycling and transformation of Cr species in soil/soil solution (Ščančar and Milači, 2014).

REMEDICATION TECHNOLOGIES

Traditionally groundwater pump & treat has been used to remediate chromium-contaminated plumes. Although this method allows interception and hydraulic containment of the plume, it requires long-term application to meet Cr(VI) remediation goals and may not be effective at remediating source-zones. Contamination in the vadose zone has typically been addressed via soil excavation and disposal.

In the last decade, innovative and promising in situ clean-up technologies for Cr(VI) have been tested, mostly at lab- and pilot-scale. Among these, bio-induced reduction, bioreduction and bioimmobilization, in which both chemical and biological mechanisms are used to reduce hexavalent chromium to the trivalent form, so as to stabilize the pollutant. Below a few experiences are described.

SITE HISTORIES

Site n. 1. Site n.1 is a chromium plating facility (5000 m²) in business since the 1950s. During site characterization, hexavalent chromium was found in soil down to 20 m below ground surface (bgs). (values up to 2000 mg/kg) and in the shallow groundwater (100 mg/l on average, concentration peaks up to 690 mg/l). Soil at the site is silty gravel and sand, with local lenses of sandy silt with gravel. The water table is at 12 m bgs (± 5 m) and the aquitard is at 28 m bgs.

In 2008, a hydraulic barrier was installed as the emergency action. After three years operation, a stable Cr(VI) concentration in groundwater was achieved, though it was very high (20 mg/l). In order to speed up site remediation, an in situ treatment was applied. In 2012 injections of a mixture of MRC[®] (Metal Remediation Compound) and 3D-Me[®] (3-D MicroEmulsion) were carried out. The injection system consisted of 10 HDPE injection clusters screened at different depths (14-19 m bgs and 20-25 m bgs). A total volume of 28,000 l of reagent was injected.

Post-treatment monitoring showed a very rapid decrease in redox potential (down to about -400 mV); total organic carbon increased from about zero to 1800 mg/l, suggesting the presence of organic substrates in groundwater. Oxygen and nitrates dropped down, while iron and manganese rose respectively to 260 mg/l and 113 mg/l. Cr(VI) concentrations in groundwater decreased by 59% to 99%, depending on the specific monitoring well, reaching residual concentrations of about 100 µg/l.

Site n. 2. Site n.2 is a metal processing factory in business since 1800. The environmental investigations at the site highlighted high concentrations of hexavalent chromium in groundwater (200-600 µg/l) and in soil (up to 5000 mg/kg). The lithology of the area is very heterogeneous, with presence of boulders.

Since 2007 a hydraulic barrier has been operating at the site to prevent Cr(VI) migration in groundwater. In 2012, 1300 kg of 3D-Me[®] and 1300 kg of MRC[®] were injected through 8 vertical wells in the saturated soil zone, over an area of about 1000 m²: Injections in the capillary fringe were also combined (800 kg of 3D-Me[®] and 800 kg of MRC[®] at 16 points over an area of about 250 m²), in order to protect the aquifer from vadose zone leaching.

During the post-injection monitoring, the products were found in the hydraulic barrier pumping wells. Therefore, the pumping rate was reduced to increase the contact time of the reactants in groundwater and an upstream barrier was also installed to reduce groundwater seepage velocity in the reactive zone. After that, Cr(VI) concentrations decreases in all monitoring wells, resulting in groundwater concentrations at the point of compliance of about 150 µg/l, above the target value.

Site 3. EHC-M[®] was used for full-scale remediation at a former chromium plating factory. In the semi-confined silty sand aquifer, a 30 m long Cr(VI) plume, with values up to 200 mg/l, was observed.

Initially, a pump and treat system was installed at the site but, as no appreciable reduction in chromium concentration was observed in more than three years operation, stabilization via injection of EHC-M[®] was carried out. In the pollution source area and immediately downgradient, direct push injections (90 kg EHC-M[®]) at 46 points were carried out in the unsaturated soil and groundwater. The distance between the points of injection was about 1 m. The injection pressure was up to 15 atm.

A rapid decrease in redox potential (down to values of -300 mV in a couple of weeks) and Cr(VI) (down to values <5 µg/l in few months) were observed. Later on, redox potential stabilized at values around zero. Dissolved iron, manganese and sulphates also increased in groundwater.

Site n. 4. At site n. 4, the phreatic aquifer (a mix of conglomerate, gravel and sand, with hydraulic gradient of 0.2-0.3%) was affected by Cr(VI) with values up to 20 mg/l, in a plume 260 m wide and 2.6 km long. Despite the installation of a pump and treat system, the dissolved plume remained quite stable.

In 2011 a Biosearch patented product, based on food-grade organic nutrients for bacteria biostimulation, was injected at 4 points located about 40 m downgradient of the pollution source area.

After 40 days, Cr(VI) in the monitoring wells, located 50 m and 300 m downgradient of the source area, decreased to values <5 µg/l. These results allowed turning off the pump-and-treat system, even if dissolved iron, manganese and arsenic were found in the injection area as side-effect.

Site n. 5. Site n. 5 is a former chromium plating factory, covering a very small area (150 m²). The industrial activities ceased in 2012. Cr(VI) was found in groundwater at concentrations up to 540 mg/l.

Before full-site characterization, the patented product used for site n. 4 was injected downgradient of the source area as an interim measure. Cr(VI) at two monitoring wells, located about 90 m and 200 m downgradient of the source area, decreased down to values of <5-100 µg/l.

After industrial plants removal, further injections in the unsaturated zone will be carried out.

CONCLUSIONS

The experience at these sites pointed out that Cr(VI) groundwater pollution cannot be solved unless the unsaturated zone is treated as well. Soil heterogeneity is a critical issue and mixtures usually have to be injected at different depths. Localized iron, manganese, arsenic and sulphate side-contamination can result in groundwater after injections.

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