

METALS STABILIZATION USING GEOCHEMICAL FIXATION

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INTRODUCTION TO CHEMICAL FIXATION

There are several approaches to treatment of chromium and other toxic metals such as lead, arsenic, and cadmium in soil and groundwater, including isolation, immobilization, toxicity reduction, physical separation, and extraction (U.S. EPA, 2002).

BRIEF OVERVIEW OF METALS REMEDIATION METHODS:

CONVENTIONAL METHODS

Conventional approaches to ex-situ remediation include excavation and disposal of the impacted soil. Case studies are not necessary in this type of remediation, since the problem has only been moved from the source property to another, the landfill. Ex-situ electrokinetics of metals contaminated soil is another, less common ex-situ method, where-in the metals are pulled to the cathode. The soil moisture content must be near saturation to allow for electromigration of the metals. Various acids, such as acetic or citric can be used for the electrolyte solution to enhance the migration of the metals to the cathodes.

For conventional groundwater remediation of toxic metals, pump and treat methods have been used for decades with varying degrees of success. Pump and treat is effective at controlling hydraulic movement, but mass removal tends to be difficult with this technology. A chemical enhancement of pump and treat system may add a reductant to the remedial program. The reductant is useful to overcome the tailing effect and reduce the overall time required for the in-situ pump and treat remedial program.

There are generally three main remediation zones: 1) the source zone, whereby the concentrated chromium compound is leaked into the ground and down through the vadose zone to the top of the groundwater table. This area has high levels. 2) The concentrated zone is the main and highest part of the dissolved chromium groundwater plume. This is the zone where pump and treat technology helps to maintain hydraulic control of the area. 3) The zone outside the concentrated zone, the dilute zone, which contains lower levels. This zone is less likely to be successful with a pump and treat system, as levels are fairly low and significant mass reduction is unlikely in a short period of time.

LESS CONVENTIONAL METHODS

In-situ remediation of chromium, for example, uses chemical reduction or fixation. The goal of chemical reduction or fixation of hexavalent chromium is to reduce it to the more thermodynamically stable trivalent chromium, which will precipitate or fix onto aquifer solids. There are primarily four main technologies or approaches:

- 1) Geochemical Fixation
- 2) Permeable Reactive Barriers (PRBs)
- 3) Reactive Zones
- 4) Natural Attenuation

In addition to the above mentioned methods, there are several other methods available for in-situ chromium remediation:

- 1) Soil Flushing and Enhanced Extraction
- 2) Electrokinetics
- 3) Biological Processes:
 - A) Bioreduction
 - B) Bioaccumulation
 - C) Biomineralization
 - D) Bioprecipitation
 - E) Phytoremediation

RECOMMENDED CHARACTERIZATION

Site characterization should include numerous soil borings with groundwater samples to fully characterize the vertical and lateral extent of the heavy metals contamination. Total organic carbon (TOC), dissolved organic carbon (DOC), particulate organic carbon (POC), cation exchange capacity (CEC), alkalinity, and other analytes should be evaluated before performing an in-situ pilot test.

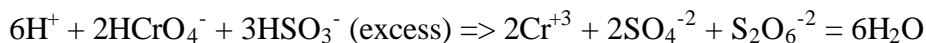
GEOCHEMICAL FIXATION: CHROMIUM EXAMPLE

Geochemical fixation of chromium reduces Cr(VI) in groundwater and impacted soil to the thermodynamically stable Cr(III). The reduced chromium is geochemically fixed onto aquifer solids (U.S. EPA, 2002). Some methods use pump and treat systems where the water is treated on the surface and reinjected with a reductant (Figure 2). Other delivery methods use trenches, filter galleries, wells and injection ports to introduce the reductant into the subsurface.

CHEMISTRY: Various reductants are available, and the more common ones include metabisulfite, ferrous sulfate, and calcium polysulfide. The reactions are described below:

REDUCTANT: Metabisulfite ($S_2O_6^{-2}$)

In the presence of excess sulfite, Cr(VI) is reduced (Palmer and Wittbrodt, 1991):

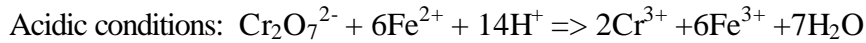


In the presence of excess Cr(VI), the reduction to Cr(III) by sulfite is performed by this reaction (Palmer and Wittbrodt, 1991):

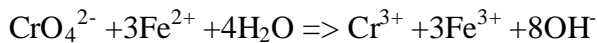


REDUCTANT: Ferrous Sulfate (FeO_4S)

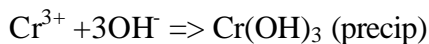
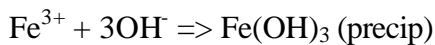
Dissolved Cr(VI) can be precipitated as $\text{Cr}(\text{OH})_3$ by injecting ferrous sulfate (Suthersan, 2002)



Neutral or alkaline conditions:



Both Cr(III) and Fe(III) ions are highly insoluble under natural groundwater conditions, and these ions precipitate out as hydroxides as follows (Suthersan, 2002):



REDUCTANT: Calcium Polysulfide (CaS_5)



A case study in Windsor, California shows the use of calcium polysulfide (INSERT E powerpoint)

GEOCHEMICAL FIXATION CONCERNS

As in the example for chromium, the reductants must be in contact with the Cr(VI), consequently aquifer heterogeneities and low permeability sediments require injection spacing closer together than high permeability sediments. Although unlikely, the reduced Cr(III) potentially could reoxidize to Cr(VI) under certain conditions, such as in the presence of manganese dioxide (MnO_2), field evidence of this reoxidation has not been observed (U.S. EPA, 2002). Reductants containing iron, such as ferrous sulfate, could result in precipitation of the iron and cause clogging near the injection locations. Excess reductants or reductant byproducts must be monitored so as not to create new groundwater contamination.

CONCLUSIONS

Toxic and soluble metals, such as chromium, lead, arsenic and cadmium, as well as other heavy metals can be a major health risk. Geochemical fixation using a chemical reductant such as calcium polysulfide, sodium metabisulfite or ferrous sulfate converts the toxic and soluble metal into an insoluble nontoxic compound, typically sulfides for most metals and hydroxide in the case of chromium. Since these reductants last a long time in the environment, injection events can be spaced far apart in time, sometimes on

the order of years. This makes the in-situ geochemical fixation of heavy metals to be quite attractive in terms of low on-site disruption and low cost.

REFERENCES AND ADDITIONAL READING

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