

REDUCTIVE TREATMENT OF METALS IN GROUNDWATER

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ABSTRACT

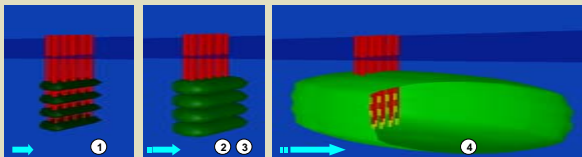
Metals are a natural part of the environment and are required for the normal functioning of many organisms; however, elevated levels of certain metals are linked to health problems in humans. Thus, remediation of soil and groundwater impacted with metals is often required. Unlike organic contaminants metals cannot be degraded or destroyed by microorganisms. The mobility of metals in groundwater is affected by various chemical reactions, including dissolution-precipitation, oxidation-reduction, adsorption-desorption and complexation.

A specially formulated remediation technology, EHC-M, consisting of controlled-release organic carbon, zero valent iron (ZVI) and a source of sulfide was designed for treatment of metals in soil and groundwater. The mechanism of subsurface metal immobilization via EHC-M is dependant on characteristics of the metal. Reducible metals (Cr, As, U, Se, Mo) are removed via reductive precipitation on ZVI surfaces and with iron oxy-hydroxides that form on the ZVI surfaces. Metal cations (Cu, Zn, Hg, Pb, Cd, Ni) precipitate as metal sulfides following microbial reduction of sulfate or are adsorbed onto surfaces of iron corrosion products, including iron oxides and iron oxy-hydroxides and thereby removed from groundwater.

A bench scale treatability study was conducted with soil impacted with antimony (Sb) from a site in the northeastern USA. Control and EHC-M (1% by weight) columns were set up with soil and groundwater samples collected from the Site. Dissolution of Sb from the soil was observed in the control while the EHC-M column demonstrated the ability to immobilize the Sb present in the impacted Site soil.

Groundwater at a manufacturing facility in Washington was impacted with ca. 6.1 ppb trichloroethene (TCE) and ca. 165 ppb hexavalent chromium (Cr(VI)). The targeted treatment area measured an estimated 60 ft wide x 100 ft long x 10 ft deep (from 75 to 85 ft bgs). Performance monitoring showed TCE and all related daughter products below the detection limit of 0.05 ppb. Cr(VI) was reduced by >90% to 11 ppb one month following the injections and has remained below the detection limit of 5 ppb.

EHC-M TREATMENT MECHANISMS



- 1 Direct ZVI corrosion effects
- 2 Indirect ZVI effects (H₂ gas and iron corrosion product generation)
- 3 Carbon substrate fermentation produces volatile fatty acids (VFAs), sulfide released from EHC-M
- 4 Biostimulation of the aquifer zone by the dissolved components

Contaminant	Treatment Mechanisms in the EHC-M zone
cVOCs	Chemical and microbiological dechlorination stimulated by a combined effect of the organic components and ZVI contained in EHC
As (III, V)	Reductive precipitation with oxidized iron minerals. Precipitation as As sulfide and mixed Fe-As sulfide
Cr(VI), Mo(VI), Se(IV,VI), U(VI)	Reductive precipitation with oxidized iron minerals and adsorption to iron oxides.
Me ²⁺ (Cu, Zn, Pb, Cd, Ni)	Metal cations precipitate as sulfides, following stimulated heterotrophic microbial sulfate reduction to sulfide. Adsorption to iron corrosion products (e.g., iron oxides and oxyhydroxides).

BENCH STUDY #1: Treatment of Arsenic

R&D Study	
Purpose	Evaluate the treatment of As with EHC-M under various pH and Eh conditions
Column Treatability Study	PVC columns (13 cm long x 5 cm ID) loaded with 1% EHC-M by mass Control system contained only sand Flow rate set at 50 ml/day Sampled influent and final effluent routinely for total arsenic (via Method 6010)
Results & Conclusions	Influent As concentrations of 500 to 1,700 µg/L were quickly reduced to below 10 µg/L in the 1% EHC-M column About 30 mg of As was immobilized in the EHC-M column during the initial 380 days Less than 3% of the immobilized As was released from the EHC-M column during the subsequent leaching test

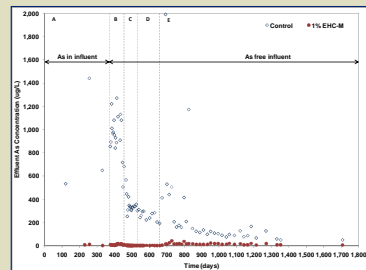


Figure 1. Total dissolved arsenic concentrations in the EHC-M and control column effluents. Various Eh and pH conditions were evaluated as summarized below:

- A – ambient Eh and pH
- B – Eh > 0; ambient pH
- C – ambient Eh; pH 4
- D – Eh > 0; pH 4
- E – Eh > 0; pH 9

BENCH STUDY #2: Treatment of Antimony

Treatability Study	
Purpose	Evaluate EHC-M for the treatment of Sb in groundwater
Column Treatability Study	Plexiglas columns (50 cm long x 5 cm ID) loaded with 1% EHC-M by mass One down gradient soil microcosm supplemented with 1% EHC-M by mass Control system contained only site soil Flow rate set at 75 ml/day Sampled influent and final effluent routinely for 56 days (Total and dissolved antimony via Method 6010)
Results & Conclusions	The site groundwater was impacted with low concentrations (<2 ppm) of Sb while the effluent of the control column had an average Sb concentration of 23 ppm. Dissolution of Sb from the soil was observed in the control while the EHC-M system demonstrated the ability to immobilize the Sb present in the impacted Site soil.

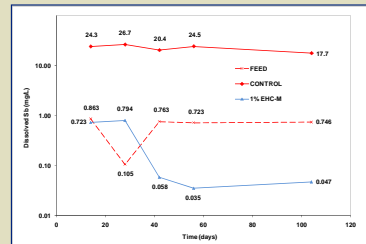


Figure 2. Total dissolved antimony concentrations in the feed, control and EHC-M column effluents.

FIELD PROJECT #1: Treatment of Copper, Cobalt and Nickel

Description	
Site	Groundwater was contaminated with metals from what was believed to be an off-site source, Ontario, Canada
Impacts	The heavy metals of concern included: copper (max. of 86 µg/L), Cobalt (max. of 210 µg/L) and nickel (max. of 350 µg/L).
Objective	The goal of this project was to reduce heavy metal concentrations to the Ministry of Environment Remedial Criteria
Remedial Approach	A total of 600 kg of EHC-M was injected with reactive gas over twelve locations, along the Site boundary line, using a borehole and packer injection system



- Sulfate reducing conditions (Eh < -250 mV) were established within 5 days
- Remedial objectives were met for all metals: Copper (within 10 days of injection); Cobalt (within 55 days of injection); Nickel (within 139 days of injection)
- Regulatory approval was obtained

(Field Data Courtesy of Vertex Environmental Solutions)

FIELD PROJECT #2: Co-Treatment of TCE and Chromium

Description	
Site	Manufacturing Facility, Washington
Impacts	Groundwater was impacted with trichloroethene (TCE) and hexavalent chromium (Cr(VI)).
Objective	The goal of this project was to clean up an isolated hot-spot which would allow for the shut down of an extraction system currently operating at the Site.
Remedial Approach	A total of 9,600 lbs of EHC were injected into the suspected hot-spot, resulting in an average application rate of 0.15% to soil mass. The EHC-M slurry was injected into 32 points with a spacing of 10 to 15 ft.

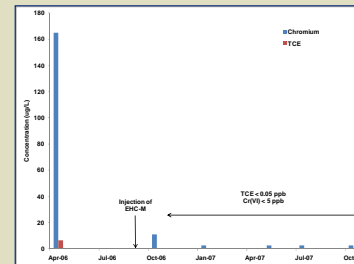


Figure 3. Influence of EHC-M on TCE and Cr(VI) concentrations at MW-41. Following the EHC-M injection, Cr(VI) concentrations were reduced to 11 ppb after one month and less than 5 ppb after four months. TCE has remained below the detection limit (0.05 ppb) and no daughter products have been detected.

(Field Data Courtesy of EA Engineering, Science and Technology, Inc.)