

In Situ Chemical Reduction (ISCR) Technology for Treatment of Heavy Metals and Persistent Organic Compounds in Groundwater

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Abstract:

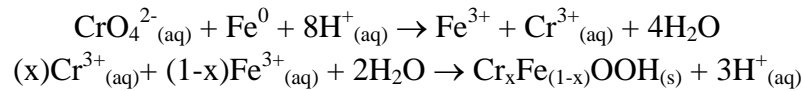
EHC-M[®] combines controlled-release carbon, zero-valent iron (ZVI) and sulphate as a slow-release source of sulfide ions. Following placement of EHC substrate into the subsurface zone, a number of physical, chemical and microbiological processes combine to create very strong reducing conditions. Under these conditions, many organic compounds are rapidly mineralized. Moreover, if dissolved metals are present, various reductive precipitation and adsorption reactions, unique to EHC-M, will rapidly reduce their dissolved concentrations.

This paper reviews the biogeochemistry associated with long-term immobilization of arsenic and other heavy metals under *in situ* chemical reduction (ISCR) conditions induced via the addition of EHC-M. Laboratory and field-scale data are discussed.

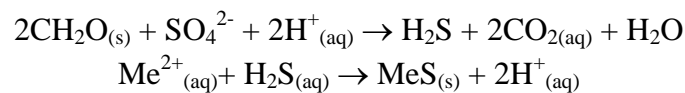
Key words: EHC-M; ISCR; dissolved metal treatment; reductive immobilization; anaerobic; biodegradation

INTRODUCTION

EHC-M is a specially formulated integrated treatment material containing controlled-release organic carbon, ZVI, a source of sulfate, and other additives designed for treatment of dissolved trace metals. The two main reactive components of EHC-M, ZVI and organic carbon substrate, are well-established reactive materials used for *in situ* reductive immobilization of different types of metals in groundwater. The treatment mechanisms using these materials are well understood (*e.g.*, Blowes *et al.*, 2000; Manning, *et al.*, 2002; Wilkin and McNeil, 2003; Puls, *et al.*, 1999). ZVI permeable reactive barriers (PRBs) have been applied for treatment of reducible metals (*i.e.*, Cr, As, U, Se, Mo) via reductive precipitation on ZVI surfaces and with iron oxyhydroxides that form on the ZVI surfaces. For example, the reaction sequence for Cr(VI) can be described as (Blowes *et al.*, 2000):



PRBs containing a wide range of solid-phase organic carbon (*e.g.*, compost, wood chips, saw dust, etc.) have been used for treatment of metal cations (*i.e.*, Cu, Zn, Hg, Pb, Cd, Ni). These cations precipitate as metal sulfides following microbially mediated reduction of sulfate present in the groundwater. The internal source of sulfate in EHC-M enables metal immobilization in groundwaters depleted in dissolved sulfate. The labile carbon stimulates sulfate-reducing bacteria. This process can be represented by the following reaction sequence (Blowes *et al.*, 2000):



where: CH₂O represents organic carbon and Me²⁺ represents a divalent metal cation.

Another important mechanism of metal cation removal in the presence of corroding ZVI is adsorption onto and co-precipitation with secondary iron corrosion products, like iron oxides and iron oxy-hydroxides (Dzombak and Morel, 1990).

LABORATORY EVALUATION

Arsenic Treatment Column Test. A 13 cm long and 5 cm diameter column was packed with a mix of 1% EHC-M and a sandy aquifer material. A similar column containing the unamended aquifer material was used as a control. The aquifer material used in the test was contaminated by arsenic. Both columns were exposed for 380 days to groundwater spiked with arsenic. Subsequently, a series of influent arsenic-free groundwater conditions were introduced into the columns: aerated influent; aerated and pH 4 influent; and finally aerated and pH 9 influent. Concentrations of total arsenic, along with pH and Eh were measured periodically in aqueous samples collected from the effluents of the two columns.

After about 1,000 days of total test period, three solid samples were collected from the EHC-M column and one sample was collected from the control column. These samples were analyzed in duplicate using a sequential extraction method (Hall *et al.*, 1996) to identify the solid forms of arsenic retained in the columns. The solid phases selected for extraction using this method are as follows: adsorbed/exchangable/carbonate (using CH₃COONa as extractant); amorphous Fe oxyhydroxide (0.25M NH₂OH·HCl); crystalline Fe oxide (1M NH₂OH·HCl); sulfides and organics (KClO₃/HCl); and residual, mainly silicates (HF-HClO₄-HNO₃-HCl). Total As and Fe were analyzed using ICP-MS/OES.

Results. Dissolved As in the influent groundwater was rapidly and consistently reduced from an influent concentration ranging from 500 to 1,000 ug/L to below 10 ug/L within the EHC-M amended aquifer material, while no significant change or an increase in arsenic concentration

was observed within the control column (**Figure 1**). Under continuous-flow conditions, removal efficiencies exceeding 98% were achieved in the EHC-M column. Based on a cumulative As mass flux, about 35 mg of As was immobilized in the column containing about 5 g of EHC-M during the 380 day period of loading the column with arsenic (**Figure 1**). Subsequent leaching tests using As-free, aerated groundwater at various pH showed that less than 3% of the mass of arsenic sequestered in the EHC-M column was released during the *ca.* 620 day period.

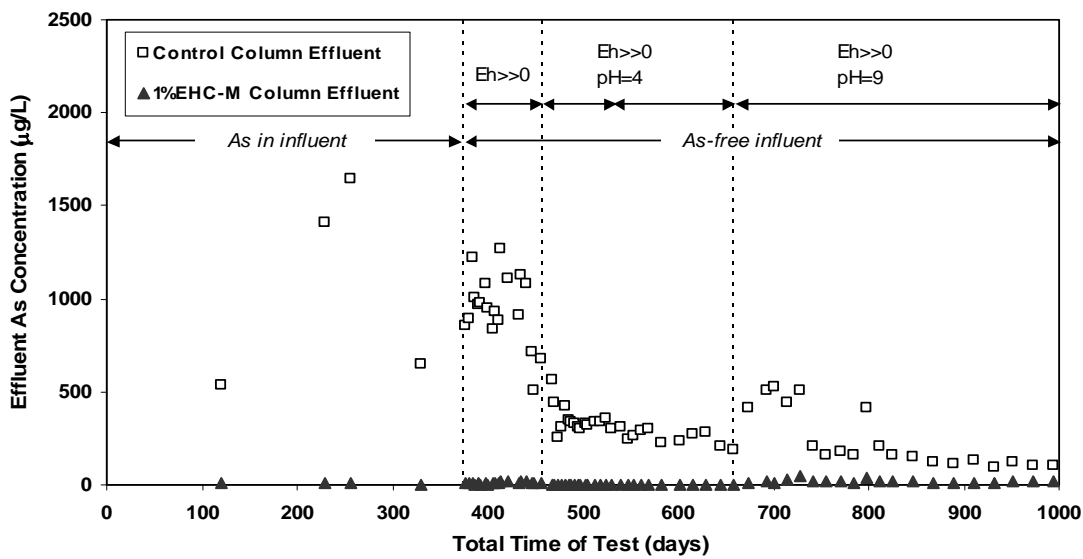
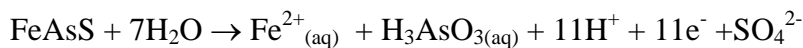


Figure 1. Total dissolved As concentrations in the EHC-M and control columns.

Trends in pH along the EHC-M column showed a consistent buffering of the influent pH 4 water to pH values ranging from 6.2 to 7.0, while the pH 9 influent water was buffered to a pH range of 7.5 to 7.8. Positive redox potential values, ranging from +150 mV to +320 mV, were maintained within the EHC-M column during the entire As leaching part of the study (620 days). Craw et al. (2003) used thermodynamic calculations and experimental methods to show that arsenopyrite is extremely insoluble under reducing conditions ($E_h < -100$ mV), but it is highly soluble in oxic conditions:



Therefore, As was retained in the EHC-M column despite conditions that should in theory reverse the As immobilization processes. Based on previous published results, the observed persistence of As-Fe reduced solid phases in the EHC-M column under oxic conditions could be due to development of protective submicron iron oxide and oxyhydroxide coatings on As-bearing grain surfaces (Craw *et al.*, 2003). EHC-M contains a source of microscale ZVI, corrosion of which is a continuous source of dissolved Fe.

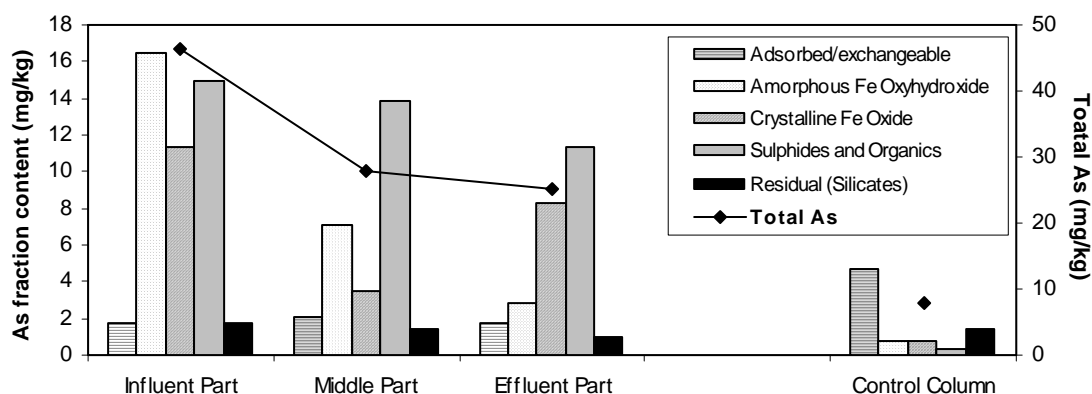


Figure 2: Total As concentration and As fraction distribution along the EHC-M and control columns. Based on sequential extraction analyses.

Figure 2 shows the results of sequential extraction analyses, which were performed at the end of the 1,000 day flow-through test. Total arsenic concentrations were 47 mg/kg in the influent section, 28 mg/kg in the middle section and 25 mg/kg in the effluent section of the EHC-M column (**Figure 2**). About 8 mg/kg of total arsenic was present in the control column (the middle section was sampled only), which contained As-contaminated site aquifer. The majority of As in the EHC-M column was bound in sulfide and iron oxide/oxyhydroxide phases, while most of As in the control column was present in an adsorbed/exchangeable form.

Based on the distribution of total As along the EHC-M column length, dissolved As was immobilized preferentially in the influent section of the column during the time of exposure to As-contaminated groundwater. The influent column section was then exposed to sharp geochemical gradients during the leaching part of the test under oxic conditions with varying pH. A visual inspection of the column material during collection of core material detected a color change indicative of ferric oxides in the influent part of the column, but not further downgradient.

Oxic groundwater used in the leaching part of the test likely influenced the variability in As species distribution along the column EHC-M length. In particular, sulfide and crystalline iron oxide As forms accounted for 57%, 62% and 78% of the total arsenic in the influent, middle and effluent sections of the column, respectively (**Figure 3**). The content of As associated with amorphous iron oxyhydroxides were 35%, 25% and 11% in the influent, middle and effluent sections of the column, respectively. This spatial distribution is undoubtedly the result of a prolonged exposure to oxic water.

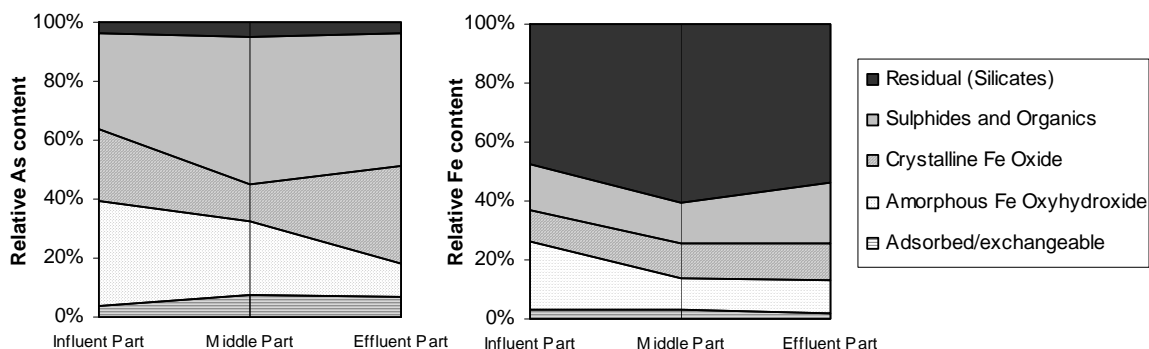


Figure 3: Relative content of As and Fe fractions along the EHC-M column. Based on sequential extraction analyses.

Trace amounts of dissolved As observed in the effluent of the EHC-M column in the leaching part of the test were likely influenced by the adsorbed/exchangeable fraction of As (**Figure 3**). Arsenic leaching, albeit limited, was observed only at the onset of exposure to pH 9 leaching water (**Figure 1**). Iron oxides and oxyhydroxides are known to alternate surface charge in response to ambient pH levels (Dzombak and Morel, 1990). Therefore, weakly adsorbed arsenate, and possibly arsenite, anions were desorbed in response to the change in residual surface charge from positive to negative as the pH increased through the zero-charge point of those mineral phases. However, the observed release of As was transient; likely limited by the occlusion of surface adsorption sites by freshly precipitated iron oxides and hydroxides.

Iron distribution along the EHC-M column indicated that between 48% of total iron in the influent part and 62% of total iron in the effluent part of the column was retained in the “residual” fraction (**Figure 3**). This fraction was obtained as the final, strong acid extraction. The “residual” iron content in the EHC-M was about 20 times higher than that in the control column, therefore this fraction represents the amount of un-oxidized ZVI remaining within the EHC-M amended material.

The total length of this study was 1,000 days, or 2.7 years. Consequently, a sufficient amount of ZVI remained within the EHC-M column for additional 2 to 3 years of ferrous iron generation. The relative content of iron obtained in the sulfide extraction step were similar to the As “sulfide” fraction (Figure 3). The absolute concentrations of iron associated with sulfides were more than an order of magnitude higher than those for As. Therefore, arsenopyrite was the most likely As sulfide phase that was formed in the EHC-M column.

The observed changes in solid arsenic and iron distribution along the EHC-M column appear to confirm the importance of a source of ferrous iron from ZVI present in EHC-M. That is, continuous formation of Fe oxide layers may not only protect the precipitated reduced As mineral phases but also aid in precipitation and/or adsorption of any As that is potentially mobilized under extreme changes in geochemical conditions.

Other Testing for Dissolved Metal Immobilization using EHC-M. Long-term column tests with metal contaminated groundwaters have shown that EHC-M is capable of providing a rapid, persistent and irreversible immobilization of both reducible metals (e.g.; As and Cr) and metal cations (e.g.; Zn, Hg, and Pb). Based on these data, EHC-M is applicable for treatment of those metals in a wide range of environmental applications. A summary of observed treatment efficiencies using EHC-M is provided in Table 1.

Table 1: Results of EHC-M in laboratory and field tests for selected metals.

Compound	Influent (ppb)	Effluent (ppb)	% Removal
Antimony	24,500	35	>99
Arsenic	500	9	98-100
Cadmium	11	<1	>99
Chromium VI	200	<5	>99
Cobalt	210	<5	>99
Copper	86	<5	>99
Lead	64,000	600	>99
Nickel	350	5	>99
Zinc	50,400	3,900	92 -100

FIELD CASE STUDY 1

The site soil and groundwater is impacted with TCE and elevated levels of Cr (VI). An extraction system is currently in operation at the site, which has cleaned up portions of the downgradient end of the plume to below the treatment goals of 5 ppb for TCE and 80 ppb for Cr(VI). However, an isolated area experienced rebound when the extraction system was not operated and it appeared that the extraction system was not effective for treatment of the source of this rebound. A concentration of 6.1 ppb TCE and 165 ppb Cr(VI) was measured at the former extraction well MW-41 in April 2006. The conditions were relatively oxidic with a DO of 5 mg/L and ORP of 200 mV.

The goal was to clean up this isolated hot-spot area to allow for the extraction system to be shut down completely at the downgradient end of the plume, which would result in significant cost and energy savings. In September 2006, EHC-M was injected into the suspected hot-spot area upgradient of extraction well MW-41. The targeted treatment area measured an estimated 20 m wide x 30 m ft long x 3 m deep (from 75 to 85 ft bgs). The EHC-M was injected as a slurry using 32 direct injection spaced 3 to 4.5 m apart. A total of 4,360 kg of EHC-M was injected into the area, resulting in an average application rate of 0.15% to soil mass. The

application rate applied was higher than the concentrations of TCE and Cr(VI) would suggest given the relatively toxic conditions at the site.

Subsequent performance monitoring conducted in October 2006 and January, May, July and October 2007 showed TCE below the detection limit at the former extraction well MW-41 (**Figure 4**). Cr(VI) was reduced by >90% to 11 ppb one month following the injections. Four months following the injections of EHC-M, Cr(IV) in groundwater had been reduced to below the detection limit of 5 ppb. Subsequent monitoring has shown that the chromium remained immobilized. An additional monitoring well, AMW-63, was installed in November 2006 at the center of the injection zone. TCE was non-detect and Cr was measured at 9.5 ppb at this new well in January 2007.

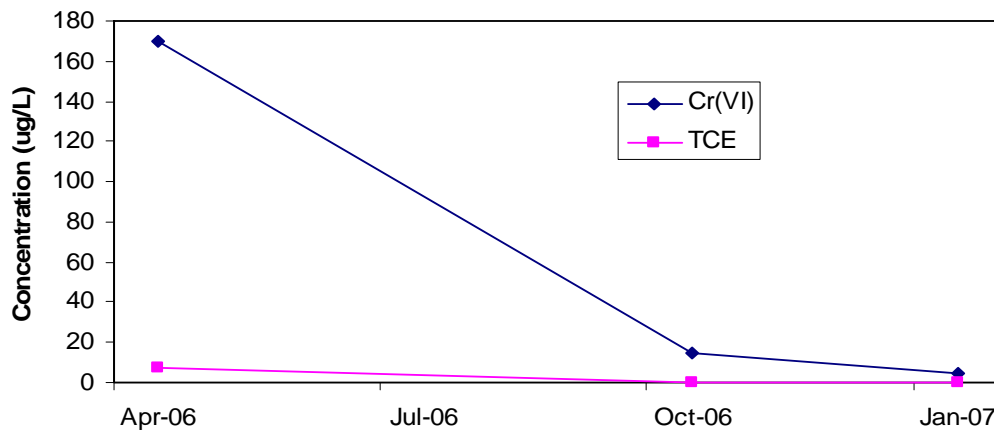


Figure 4. Influence of EHC-M Injections on concentrations of TCE and Cr(VI) at MW-41.

TCE has remained below the detection limit of 0.05 ppb since July 2007, whereas total Cr was measured at 6.3 ppb in the latest monitoring event conducted in October 2007. All related daughter products from TCE degradation (cis-DCE, VC) remained below their analytical detection limits (ca. <1 ppb) at both MW-41 and AMW-63.

FIELD CASE STUDY 2

The site groundwater is impacted by lead up to a maximum concentration of ca. 600 ppb. The impacts have migrated from the former battery recycling facility and the main groundwater plume measure an estimated 250 m long x 150 m wide x 15 m deep (from 15 to 30 m bgs). There is also a smaller plume to the north measuring 50 m long x 50 m wide x 15 m deep (from 15 to 30 m bgs). The goal is to immobilize the lead in situ to limit the migration of groundwater plume. This will be achieved via the injection of EHC-M, which will promote precipitation of soluble lead as stable sulfides. Baseline conditions are relatively oxidic with a DO of 2 to 6 ppm and ORP generally in the range of 80 to 400 mV. Shallow groundwater is very acidic with a pH as low as 2.5 and a key portion of the treatment include adjusting the pH to around 8. Geology is fine sand / sandy clay and the groundwater flow is estimated at 3 m/year.

Lead and all of its corrosion products are soluble in acidic environments. To complement the influence of EHC-M and facilitate the biological component of its mode of action, finely pulverized limestone was added to the subsurface in order to basify the aquifer, ideally to a pH above 7.

A pilot-scale field effort was undertaken to: i) validate EHC-M performance under field conditions, and ii) assess the effectiveness of the construction methodology (*i.e.*, direct injection of EHC-M/dolomite slurry). A mixture of EHC-M, dolomite and water was injected into 12 injection points spaced 3 m on centers using direct push technology. The pilot study area measure an estimated 12 m long x 9 m wide x 10 m deep.

A total of 1,000 kg of EHC-M was injected from ca. 17 to 27 m bgs, which resulted in an application rate of approximately 0.05% to soil mass. A total of approximately 5,000 kg dolomite was injected into the same area to increase the pH; the application of dolomite was limited to the upper 5 m of the treatment zone and dosed in accordance with the results from pH titration testing. This resulted in an application rate of approximately 0.5% to soil mass in the targeted depth interval.

Subsequent performance monitoring conducted in January, February, March and June 2008 showed Pb below the detection limit of 10 ppb at the pilot study well PB-01, which represents a >97% decrease in soluble Pb from the November data of 306 ppb (**Figure 5**). Subsequent monitoring has also confirmed that the injections have been successful in establishing reducing conditions and a significant increase in the aquifer pH. The redox potential has remained around -100 mV since January 2008, compared to a baseline value of 300 mV measured in November 2007. The pH in the upper aquifer increased from a baseline value of around 4 to a maximum of 13 measured in January 2008; the pH has since decreased to just below 10 measured in the latest sampling round conducted in June 2008. pH in the lower aquifer remained between 7 to 8. Continued monitoring is expected to show that *in situ*

chemical reduction using the EHC-M technology offers a safe, effective and cost-efficient remedial solution for similarly impacted environments.

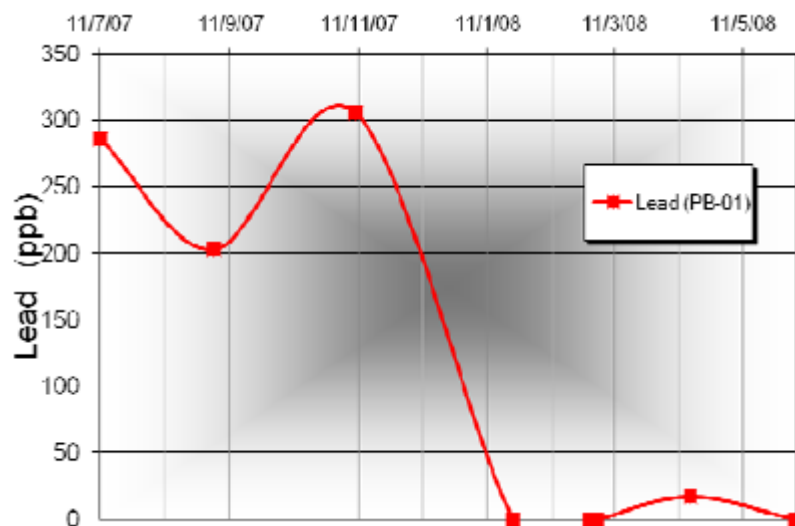


Figure 5. EHC-M/dolomite effect on dissolved lead.

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