

ZVI + Organic Carbon + Potassium Magnesium Sulfate (EHC® Metals) for Anaerobic Bioremediation:

1. Dr. Alan G. Seech, FMC Corporation
2. Micro-scale zero valent iron (ZVI) + organic carbon including wheat bran, wheat germ, and wheat flour + potassium magnesium sulfate.
3. MSDS & Technical Data Sheet - Attached
4. Number of Field-scale Applications to Date: 100+ sites.
5. Case Studies – Attached
6. Technical Summary: EHC® Metals ISCR Reagent is an *in situ* chemical reduction (ISCR) product for remediation of groundwater impacted with heavy metals and/or halogenated organic contaminants. It is composed of a mixture of food grade organic carbon (wheat bran, wheat germ, wheat flour) with micro-scale zero-valent iron and potassium sulfate + magnesium sulfate in a blended powder. Such conditions promote the adsorption and precipitation of heavy metals. Heavy metals can be adsorbed on iron oxide or iron sulfide mineral surfaces. They can also be precipitated as stable heavy metal iron sulfides, such as arsenopyrite.

EHC Metals contains only natural compounds that are non-toxic to humans and the environment. EHC Metals is not intended for treatment of potable water or for human or animal consumption.

The formulation of EHC Metals will also promote rapid and complete dehalogenation of halogenated organic compounds in soil and groundwater through the creation of strong reducing conditions and maintaining ambient pH in soil and groundwater. Such dehalogenation reactions are enhanced because the thermodynamics of dehalogenation become more favorable under highly reduced conditions. Reduced Eh/neutral pH conditions favor the growth and physiological activity of native bacteria that mediate dehalogenation reactions (e.g., *Dehalococcoides* sp.). Typically, a single injection of EHC Metals will support reductive dehalogenation reactions for a period of at least three to five years. The product has been employed for soil and groundwater remediation since 2007.

This product is food grade material and there are no health and safety issues involved with its use.

Material Safety Data Sheet

EHC® Metals Amendment

MSDS #: EHCM-C
Revision Date: 2013-09-17
Version 1.02



This MSDS has been prepared to meet U.S. OSHA Hazard Communication Standard 29 CFR 1910.1200
And Canadian Workplace Hazardous Materials Information System (WHMIS) requirements.

1. PRODUCT AND COMPANY IDENTIFICATION

Product name	EHC® Metals Amendment
Alternate Commercial Name	EHC®-M
Recommended use:	For the remediation of contaminated groundwater
Restrictions on use:	Not for use in potable drinking water
Manufacturer	Emergency telephone number
FMC CORPORATION Environmental Solutions 1735 Market Street Philadelphia, PA 19103 Phone: +1 215/ 299-6000 (General Information) E-Mail: msdsinfo@fmc.com	For leak, fire, spill or accident emergencies, call: +1 703-527-3887 (CHEMTREC) 1 303 / 595 9048 (Medical - U.S. - Call Collect)

2. HAZARDS IDENTIFICATION

Emergency Overview

CONTAINMENT HAZARD:

Any vessel that contains wet wet EHC must be vented due to potential pressure build up from fermentation gases

Potential health effects

Acute Toxicity

Eyes

No significant health effects anticipated
Product dust may cause mechanical eye irritation.

Skin

None known .

Inhalation

Inhalation of dust in high concentration may cause irritation of respiratory system.

Ingestion

Ingestion may cause gastrointestinal irritation, nausea, vomiting and diarrhea.

Chronic Toxicity

No known chronic effects of components present at greater than 1%.

3. COMPOSITION/INFORMATION ON INGREDIENTS**Ingredients**

Chemical Name	CAS-No	Weight %
Organic amendment	Proprietary	25-35
Iron	7439-89-6	25-35
Potassium Magnesium Sulfate	14977-37-8	25-35

4. FIRST AID MEASURES

Eye contact	In case of contact, immediately flush skin with plenty of water. Get medical attention if irritation develops and persists.
Skin contact	Wash off with soap and water.
Inhalation	Remove person to fresh air. If signs/symptoms continue, get medical attention.
Ingestion	Rinse mouth with water and afterwards drink plenty of water or milk. Call a poison control center or doctor immediately for treatment advice. Never give anything by mouth to an unconscious person.

5. FIRE-FIGHTING MEASURES

Flammable properties	Combustible material.
Suitable extinguishing media	Dry chemical, CO ₂ , sand, earth, water spray or regular foam.
Explosion Data	
Sensitivity to Mechanical Impact	Not applicable
Sensitivity to Static Discharge	Not applicable
Specific hazards arising from the chemical	Dry or powdered ingredients are combustible. Dispersal of finely divided dust from products into air may form mixtures that are ignitable and explosive. Minimize airborne dust generation and eliminate sources of ignition.

NFPA	Health Hazard 1	Flammability 1	Stability 0	Special Hazards -
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6. ACCIDENTAL RELEASE MEASURES

Personal precautions	Avoid dust formation. For personal protection see section 8.
Methods for containment	Cover powder spill with plastic sheet or tarp to minimize spreading and keep powder dry.
Methods for cleaning up	Sweep or vacuum up spillage and return to container.

7. HANDLING AND STORAGE

Handling	Minimize dust generation and accumulation. Keep away from open flames, hot surfaces and sources of ignition. Refer to Section 8.
Storage	Keep tightly closed in a dry and cool place. Keep away from open flames, hot surfaces and sources of ignition. Any vessel that contains wet EHC-M must be vented due to potential pressure build up from fermentation gases.

8. Exposure controls/personal protection

<u>Exposure guidelines</u>	Ingredients with workplace control parameters.
<u>Occupational exposure controls</u>	
Engineering measures	Ensure adequate ventilation, especially in confined areas.
Respiratory protection	Whenever dust in the worker's breathing zone cannot be controlled with ventilation or other engineering means, workers should wear respirators or dust masks approved by NIOSH/MSHA, EU CEN or comparable organization to protect against airborne dust.
Eye/face protection	Safety glasses with side-shields
Skin and body protection	No special precautions required.
Hand protection	Protective gloves Please observe the instructions regarding permeability and breakthrough time which are provided by the supplier of the gloves. Also take into consideration the specific local conditions under which the product is used, such as the danger of cuts, abrasion If used in solution, or mixed with other substances, and under conditions which differ from EN 374, contact the supplier of the EC approved gloves
Hygiene measures	Handle in accordance with good industrial hygiene and safety practice Wash hands before breaks and immediately after handling the product.

9. PHYSICAL AND CHEMICAL PROPERTIES

Information on basic physical and chemical properties

Appearance	Light-tan powder
Physical state	solid
Odor	odorless
pH	5.6 (as aqueous solution)
Melting Point/Range	No information available.
Freezing point	No information available.
Boiling Point/Range	Not applicable
Flash Point	Not applicable
Evaporation rate	Not applicable
Flammability Limits in Air	upper 46.0 lower 3.3
Flammable properties	Combustible material
Vapor pressure	No information available.
Vapor density	No information available.
Density	1.03 g/mL
Bulk density	No information available.
Water solubility	practically insoluble
Percent volatile	No information available.
Partition coefficient:	Not applicable
Viscosity	No information available.
Autoignition Temperature	248 - 266 °C

10. STABILITY AND REACTIVITY

Stability	Stable.
Conditions to avoid	Heat, flames and sparks
Materials to avoid	Oxidizing agents Strong acids
Hazardous decomposition products	None known .
Hazardous polymerization	Hazardous polymerization does not occur.

11. TOXICOLOGICAL INFORMATIONAcute effects

Remarks The product has not been tested. Data is based on component.

Eye irritation No data available for the formulation. Non-irritating (rabbit) (based on components)
Skin irritation No data available for the formulation. Non-irritating (rabbit) (based on components)

LD50 Oral Iron: 98.6 g/kg (Rat)
LD50 Dermal No information available.
LC50 Inhalation: Iron: > 100 mg/m³ 6 hr (Rat)

Chronic Toxicity

Chronic Toxicity No known chronic effects of components present at greater than 1%.

Carcinogenicity Contains no ingredient listed as a carcinogen

Target Organ Effects No known effects under normal use conditions.

12. ECOLOGICAL INFORMATIONEcotoxicity

Contains no substances known to be hazardous to the environment or that are not degradable in waste water treatment plants

Persistence and degradability No information available.

Bioaccumulation No information available.

Mobility Is not likely mobile in the environment due its low water solubility.

Other adverse effects None known

13. DISPOSAL CONSIDERATIONS

Waste disposal methods This material, as supplied, is not a hazardous waste according to Federal regulations (40 CFR 261). This material could become a hazardous waste if it is mixed with or otherwise comes in contact with a hazardous waste, if chemical additions are made to this material, or if the material is processed or otherwise altered. Consult 40 CFR 261 to determine whether the altered material is a hazardous waste. Consult the appropriate state, regional, or local regulations for additional requirements.

Contaminated packaging Dispose of in accordance with local regulations.

14. TRANSPORT INFORMATION

DOT not regulated

TDG not regulated

ICAO/IATA not regulated

IMDG/IMO not regulated

15. REGULATORY INFORMATION

International Inventories

TSCA Inventory (United States of America)	Complies
DSL (Canada)	Complies
NDSL (Canada)	Complies
EINECS/ELINCS (Europe)	Complies
ENCS (Japan)	-
IECSC (China)	Complies
KECL (Korea)	Complies
PICCS (Philippines)	Complies
AICS (Australia)	Complies
NZIoC (New Zealand)	Complies

U.S. Federal Regulations

SARA 313

Section 313 of Title III of the Superfund Amendments and Reauthorization Act of 1986 (SARA). This product does not contain any chemicals which are subject to the reporting requirements of the Act and Title 40 of the Code of Federal Regulations, Part 372.

SARA 311/312 Hazard Categories

Acute Health Hazard	no
Chronic Health Hazard	no
Fire Hazard	no
Sudden Release of Pressure Hazard	no
Reactive Hazard	no

CERCLA

This material, as supplied, does not contain any substances regulated as hazardous substances under the Comprehensive Environmental Response Compensation and Liability Act (CERCLA) (40 CFR 302) or the Superfund Amendments and Reauthorization Act (SARA) (40 CFR 355). There may be specific reporting requirements at the local, regional, or state level pertaining to releases of this material.

International Regulations

Mexico - Grade

Slight risk, Grade 1

Canada

This product has been classified in accordance with the hazard criteria of the Controlled Products Regulations (CPR) and the MSDS contains all the information required by the CPR.

WHMIS Hazard Class

not determined

16. OTHER INFORMATION

HMIS	Health Hazard 1	Flammability 1	Stability 0	Special precautions -
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NFPA/HMIS Ratings Legend

Severe = 4; Serious = 3; Moderate = 2; Slight = 1; Minimal = 0

Revision Date: 2013-09-17
Reason for revision: Name change.

Disclaimer

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Prepared By

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End of Material Safety Data Sheet

Specially Formulated Metals Remediation Compound for *In Situ* Immobilization of Soluble Metals *via* Enhanced Precipitation and Adsorption.

EHC[®]-M is a composite remediation product for immobilization of metals. It combines controlled-release carbon, micro-scale zero-valent iron (ZVI), and a slow-release source of sulfate. Following placement of EHC[®]-M substrate into the saturated zone, a number of chemical and microbiological processes combine to create strong reducing conditions under which a number of heavy metals can be sequestered *via* reductive precipitation as relatively insoluble iron-metal-sulfides and adsorption onto secondary ZVI corrosion products. A wide range of chlorinated volatile organic compounds (CVOCs) can also be degraded in these highly-reduced environments.



Benefits include:

Immobilization of metals

- Limits movement of metals in groundwater downstream of a treatment zone

Mixed plume treatment

- Combined treatment of chlorinated solvents and metals

Ease of use

- Non-hazardous and safe to handle

Potential Applications for use in the saturated zone:

Direct push injection

Hydraulic and pneumatic fracturing

Direct soil mixing

Contaminant Treatment Mechanisms

As (III, V)

Reactive 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

M²⁺ (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)

For more information and detailed case studies, please visit our website.

In-Situ Groundwater Remediation of Heavy Metals at an Active Manufacturing Facility

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ABSTRACT: A 1983 release of metal plating rinse water was initially remediated by soil excavation and operation of four groundwater extraction wells. In 2007, an evaluation of interim action and remediation options was completed to address the remaining hexavalent chromium, nickel and lead concentrations in groundwater. Because the affected groundwater is located beneath an active manufacturing facility where large stationary equipment is operated nearly 24-hours a day, a minimally invasive remedy was necessary. The selected remedy is chemical fixation using Adventus EHC-M™ (product). This product is mixed with water to create slurry and is delivered through direct push injection tooling to the target interval. To date, 71,000 pounds/32,205 kilograms(kg) of product have been injected at 166 locations. This technology has successfully reduced concentrations of heavy metals in groundwater to below cleanup standards. Concentrations of hexavalent chromium previously detected as high as 24,400 micrograms per liter (µg/L) are below laboratory reporting levels one to two months following injections and have remained reduced for more than one year.

INTRODUCTION

A release of plating rinse water in 1983, containing primarily hexavalent chromium and nickel was initially remediated by excavating 7,000 tons/6,000,000 kg of soil and operating four groundwater extraction wells. Due to the low permeability of the saturated soils, the operation of the extraction wells ceased in 1989. In 2007, a corrective measures study was completed to select a remedial technology to further reduce concentrations of metals in groundwater.

Working in an active manufacturing facility containing large stationary equipment and a network of underground utilities led to the selection of an in-situ chemical fixation remedial technology that was minimally invasive and could be implemented during non-production periods. The product selected for the in-situ fixation is a controlled-release mixture of integrated carbon and zero valent iron. The product enhances reduced geochemical conditions which promote the precipitation of metals with iron and other inorganic compounds. Because the removal mechanisms are coprecipitation and adsorption, the metals are transferred to the solid phase and are therefore, immobilized.

The objective of this paper is to demonstrate the effectiveness of in-situ chemical fixation to reduce concentrations of metals in groundwater. This paper provides descriptions of the site conceptual model, technical approach, results, conclusions and lessons learned.

SITE CONCEPTUAL MODEL

The lateral extent of affected groundwater prior to the implementation of chemical fixation was 1.25 acres/0.51 hectare and the vertical extent was from 13 to 20 feet/4 to

6 meters below the concrete floor of the facility (top of **Figure 1**). The affected groundwater is limited to perched water contained in silty sand with a hydraulic conductivity of approximately 0.3 feet/0.09 meter per day and a groundwater velocity of approximately 1.1 feet/0.34 meter per year. Depth to groundwater is 13 to 14 feet/4 to 4.2 meters. The constituents of concern are provided in **Table 1** with the highest concentration detected prior to implementation of chemical fixation and the cleanup standard for each metal.

TABLE 1. Constituents of concern and cleanup standards.

Constituent of Concern	Maximum Detected Concentration in µg/L	Cleanup Standard in µg/L
Hexavalent Chromium	24,400	100
Nickel	1,100	100
Lead	13	4

TECHNICAL APPROACH

The technical approach included a pilot test to evaluate the effectiveness of the product and the delivery method; collection of baseline groundwater data; injection of product; and implementation of performance groundwater monitoring.

Pilot Test. A pilot test was completed in July 2007 to evaluate the feasibility of immobilizing chromium and nickel in-situ using the selected product. Monitoring well IW-4 was installed approximately 5 feet/1.5 meters from the formerly operational extraction well CR-1. Groundwater samples were collected from both IW-4 and CR-1 prior to injection. Analysis included a heterotrophic plate count, alkalinity, nickel, hexavalent chromium and total dissolved chromium. Results indicated that nickel, hexavalent and total dissolved chromium were at concentrations above cleanup standards. A soil boring was advanced between IW-4 and CR-1 and used to inject a mixture of product and water. The mixture was injected into the borehole using a GeoProbe® grout pump from the bottom of the borehole (23 feet/7 meters) to the perched water table (an approximate depth of 13 feet/4 meters) for a total injected interval of 10 feet/3 meters.

Performance monitoring samples were collected for the same analysis described above from IW-4 and CR-1 monthly for three months. Results indicated that hexavalent chromium concentrations decreased in groundwater samples from 748 µg/L to 0.7 µg/L at CR-1, and from 196 µg/L to 1.6 µg/L at IW-4 two months after injection. Similarly, dissolved nickel decreased in groundwater samples from 190 µg/L to 63 µg/L at CR-1 and from 91 µg/L to and 35 µg/L in IW-4. Field parameters indicated a sharp and sustained decrease in oxidation reduction potential (ORP) after two months.

Groundwater samples were collected six months after injection for heterotrophic plate counts and the constituents of concern. The number of colonies per milliliter present was ten times greater than prior to injection, although the colony numbers were beginning to exhibit a decreasing trend. Hexavalent and total dissolved chromium and nickel concentrations did not increase. The successful reduction in the concentrations of the constituents of concern led to subsequent larger-scale injection events using the same delivery method as the pilot test.

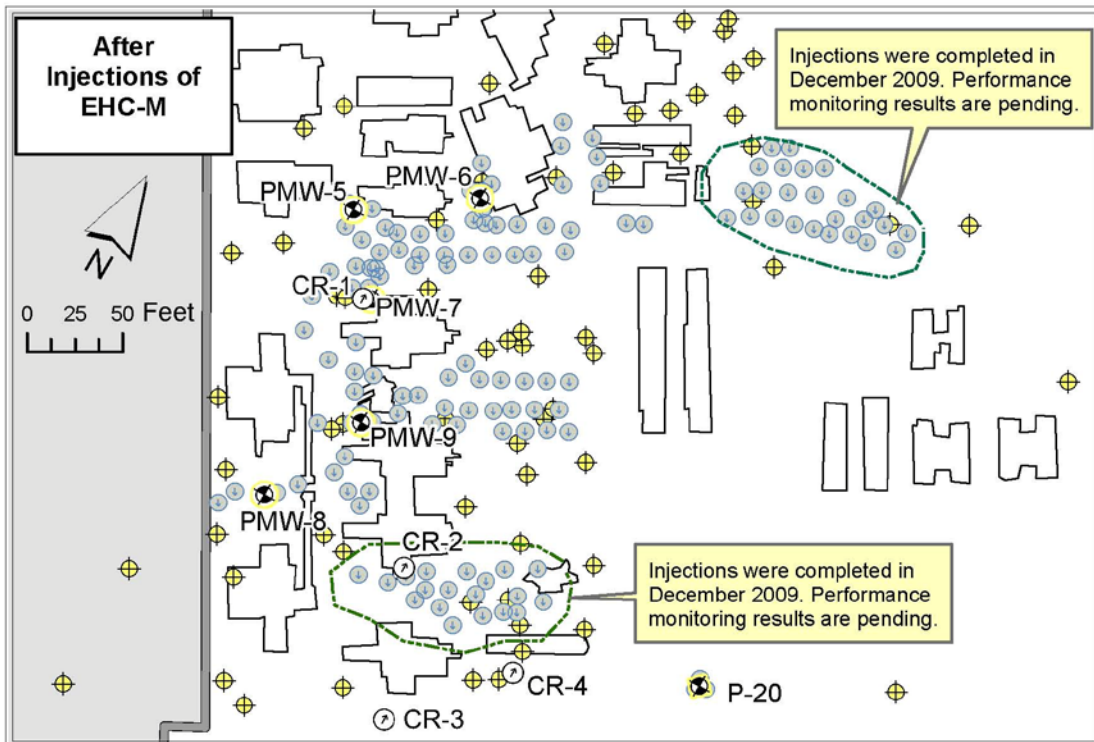
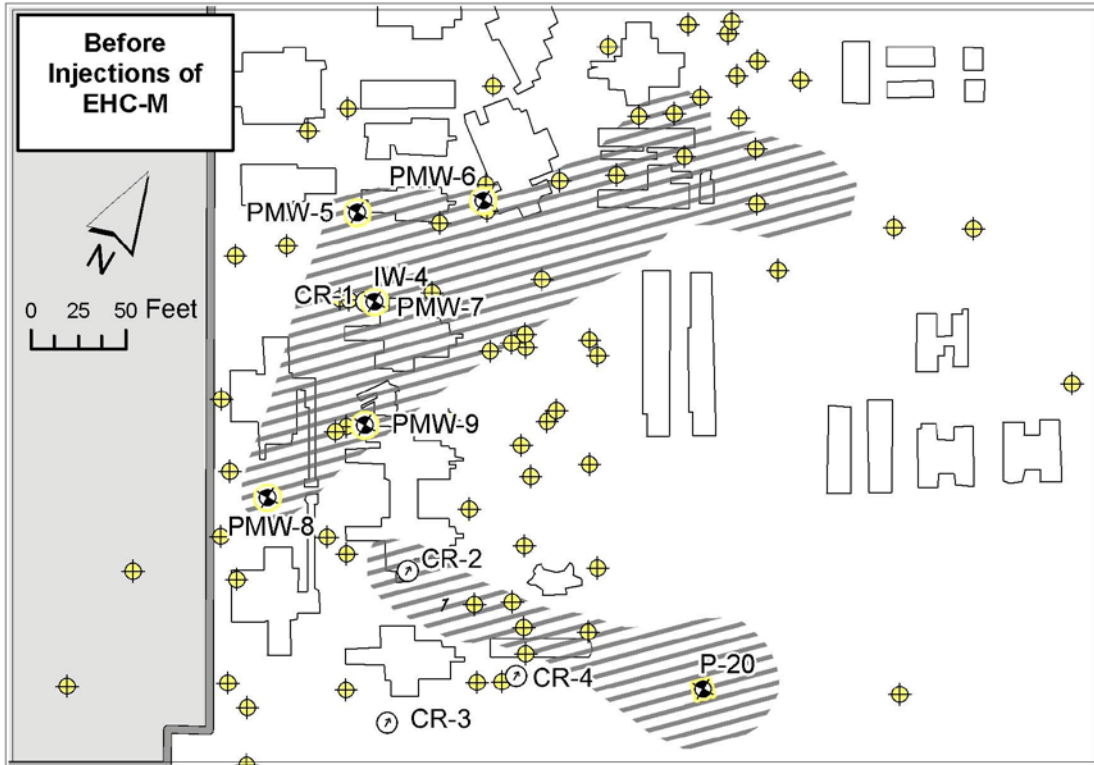


FIGURE 1 Before and after injections: approximate lateral extent of hexavalent chromium or nickel in groundwater above cleanup standards.

- Performance Monitoring Well
- Former Groundwater Extraction Well
- EHC-M Injection Point
- Soil Boring for Soil or Groundwater Sample
- Large Stationary Equipment
- Manufacturing Facility
- Extent of Hexavalent Chromium or Nickel in Groundwater

Baseline Groundwater Data. To establish baseline concentrations of metals in groundwater and to determine product dosing and spacing requirements, 12 soil borings were completed across the affected area. Temporary monitoring wells were installed in 11 of the soil borings, and groundwater samples were collected for analysis of the constituents of concern. Based on the results of the temporary monitoring well data, five performance monitoring wells (PMW-5 through PMW-9) were installed where the highest concentrations of metals in perched water was observed. The locations of the performance monitoring wells are depicted on **Figure 1**. Performance monitoring well PMW-8 served as a control well initially. The area near PMW-8 did not receive injections until December 2008.

Injections. Injection points were located 8 to 10 feet/2.5 to 3 meters apart in accessible areas. Large stationary equipment, overhead conveyor belts, buried utilities, electrical accessibility and variable production and maintenance schedules required flexibility in determining the location and schedule for each injection point. Prior to injecting, static water levels were obtained from all performance monitoring wells in the area to determine the target injection intervals (zone of saturation). After measuring static water levels, performance monitoring wells in the area were securely capped to prevent slurry from migrating to the surface through the wells.

The standard equipment used for the injections include the following: GeoPump® hopper to mix the product and water; and, GeoProbe® 6620DT equipment to install injection tooling. The injection tooling is comprised of a steel rod with drilled holes in the bottom 1 foot/0.3 meter, protected by a sliding steel sheath. Once the target depth is reached, the steel sheath is pulled up 1 foot/0.3 meter, exposing the drilled holes and leaving the tip of the injection tooling at the desired depth.

The injection process begins with mixing product and water at a ratio of 50 pounds/22.7 kg of product to 15 gallons/57 liters of water. This ratio results in a thicker mixture than initially used during the pilot test. The mixture is injected in 1-foot/0.3 meter intervals into the perched water beginning at the bottom of the zone of saturation (approximately 20 feet/6.1 meters). Each interval receives at least 17.5 gallons/66 liters of the mixture. Alternating depth intervals receive up to 35 gallons/132.5 liters of the mixture. After the contents of each hopper are injected, generous amounts of water are added to wash any remaining product into the borehole and to ensure that the injection tooling remains clear of soil while pulling the drilling rods up to the next interval. Injection rates range from 1.8 to 8.9 gallons per minute (gpm) or 6.8 to 33.7 liters per minute (lpm), with an average injection rate of approximately 5.2 gpm or 20 lpm at pressures between 100 and 200 pounds per square inch (psi) or 690 to 1380 kilopascals.

During a weeklong non-production period in July 2008, 11,000 pounds/5000 kg of product were injected in 29 locations. Refer to the bottom of **Figure 1** for the injection locations. Five months after the first injection event, soil borings were completed 5 feet/1.5 meters and 12 feet/3.7 meters from an injection location to determine the radius of influence of the product. A temporary monitoring well was installed in each boring. Groundwater samples were collected for laboratory analysis of dissolved metals and hexavalent chromium. Parameters including ORP, pH, dissolved oxygen, temperature, chromate and sulfate were measured in the field. The radius of influence was determined

to be at least 12 feet/3.7 meters. This information was used to plan the subsequent injection events.

Four additional injection events have occurred during subsequent weekly nonproduction periods: December 2008, and July, August and December 2009. During these subsequent injection events, 60,000 pounds/27,000 kg of product were injected in 136 locations. Prior to each injection event, temporary wells were completed to confirm remediation goals were met and to determine if additional areas required injections.

Performance Monitoring. Groundwater samples were collected from the performance monitoring wells monthly following injections for at least three months and less frequently thereafter depending on the results of the analysis. The samples were submitted for laboratory analyses of the same parameters analyzed during the baseline sampling event (prior to injection). These parameters include dissolved metals, hexavalent chromium, sulfate, sulfide, nitrate, nitrite, TOC and alkalinity. Since the initial investigation and injections in July 2008, two additional monitoring wells were installed and two previously existing wells (including P-20 located on **Figure 1**) were added to the performance monitoring program. The data collected during these events were compared to earlier events for trend analyses and to evaluate further evidence of remediation.

RESULTS

Performance monitoring results indicate that concentrations of constituents of concern in groundwater have decreased. For example, the hexavalent chromium concentration detected in PMW-9 decreased from 24,400 $\mu\text{g/L}$ prior to injection to 5 $\mu\text{g/L}$ after the first month. Since February 2009, concentrations of hexavalent chromium in groundwater samples collected from PMW-9 have been below laboratory reporting levels. Continued monitoring has demonstrated reduction of all nickel, chromium and hexavalent chromium concentrations to below cleanup standards (bottom of **Figure 1**) throughout the affected area. **Figure 2** and **Figure 3** provide a graphical depiction of decreasing hexavalent chromium concentrations over time for all of the performance monitoring locations, with

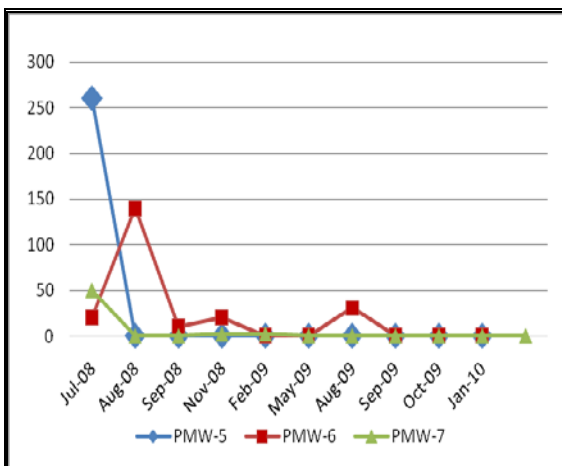


FIGURE 2. Hexavalent chromium concentrations ($\mu\text{g/L}$) over time.

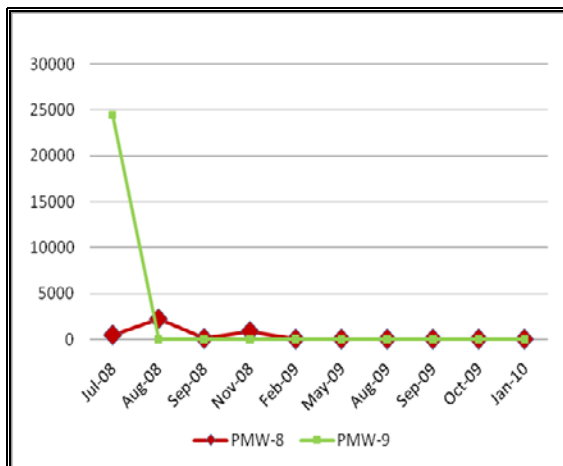


FIGURE 3. Hexavalent chromium concentrations ($\mu\text{g/L}$) over time.

different scales based on concentrations. **Table 2** illustrates ORP values measured in the performance monitoring wells at 3 months, 12 months and 18 months after the initial injections. **Figure 4** and **Figure 5** illustrate the influence of a decreasing ORP on iron concentrations. The increase in the concentration of iron is believed to result from oxidation (and dissolution) of the zero valent iron, which caused a shift to more reducing conditions, resulting in dissolution of the naturally occurring iron oxyhydroxides.

TABLE 2. ORP in millivolts over time.

Performance Monitoring Well	Baseline	Post-Injection		
	Jul 2008	3 months	12 months*	18 months
PMW-5	8	-285	-227	-185
PMW-6	-3	-161	170	-114
PMW-7	3	-252	-267	-115
PMW-8	-7	--	-249	-280
PMW-9	7	-366	-237	-83
Average:	1.6	-266	-245	-155

*The calculated average does not include the positive ORP reading (170 mV) measured at 12 months in a groundwater sample from PMW-6. Dashed lines indicate sampling was not completed that month.

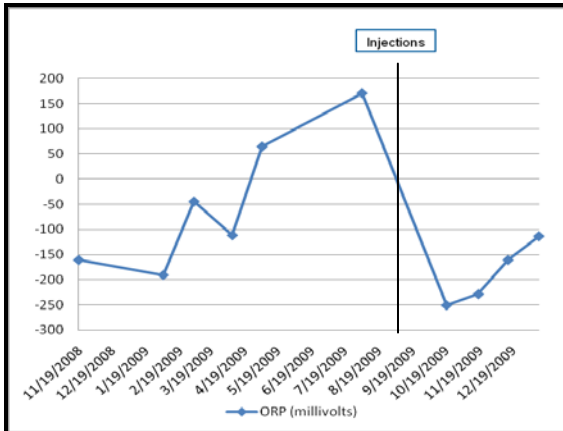


FIGURE 4. PMW-6 ORP over time.

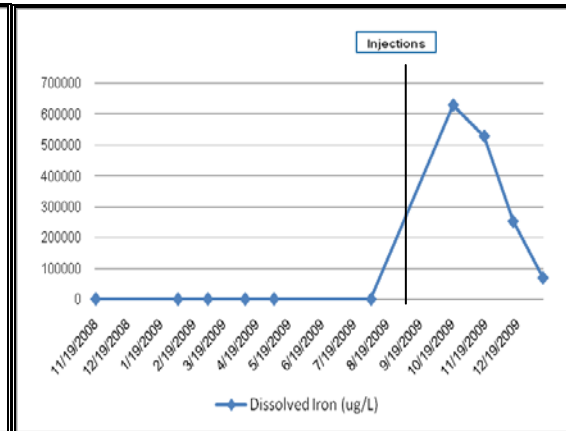


FIGURE 5. PMW-6 dissolved iron over time.

The injection of the product enhanced reducing conditions in the perched water. Although the perched water is becoming less reduced, concentrations of nickel, hexavalent chromium and chromium remain stable.

Underground infrastructure had an impact on the implementation of this remedy in some locations. For example, a building footer near PMW-6 limited the lateral distribution of product in the subsurface. This area was re-injected after 12 months.

In several locations, arsenic concentrations temporarily increased. This is believed to be an intermediate phase for arsenic before precipitating in a stable form. As illustrated in **Table 3**, arsenic concentrations increased following an injection. This is likely the result

TABLE 3. Arsenic concentrations ($\mu\text{g/L}$) in performance monitoring wells over time.

Performance Monitoring Well	Jul 2008	Aug 2008	Sep 2008	Nov 2008	Feb 2009	May 2009	Aug 2009	Sep 2009	Oct 2009	Jan 2010	Feb 2010
PMW-5	ND	4.8	ND	4.4	8.8	13.8	ND	25.9	ND	15.2	--
PMW-6	ND	ND	ND	ND	1.3	ND	ND	--	15.8	19.7	--
PMW-7	ND	8.2	ND	12	15.4	5.3	ND	--	--	--	17.9
PMW-8	ND	ND	ND	ND	6.7	7.6	6.2	6.0	--	8.9	--
PMW-9	2.4	5	10.5	12.6	8.6	12.3	22.2	19.4	13.0	15.5	--

Dashed lines indicate sampling was not completed that month.

of reductive dissolution of iron and manganese oxides and oxyhydroxides in soil that contained adsorbed arsenic. It is expected that the arsenic concentration will decrease in groundwater with time as the dissolved ferrous iron oxidizes and reprecipitates, sorbing or co-precipitating the dissolved arsenic. Dissolved arsenic concentrations will continue to be measured during performance monitoring events.

CONCLUSIONS AND LESSONS LEARNED

This technology quickly reduced groundwater conditions that led to the immobilization of heavy metals. Concentrations of heavy metals in groundwater have decreased to below cleanup standards within a short timeframe at a site where further excavation is not possible and groundwater extraction is complicated by low permeability soils. Under these reduced groundwater conditions, naturally occurring arsenic and iron oxyhydroxide have the potential to be temporarily mobilized. As the conditions become less reducing (as evidenced by the rise in ORP values shown in **Table 2**), the concentrations of iron and arsenic in groundwater are expected to precipitate out of solution. These geochemical reactions occur over a longer period of time; therefore, performance monitoring will continue until arsenic, iron, sulfate, sulfide, pH and ORP measurements become stable.

Lessons Learned. Our field experiences from the first round of large-scale injections were applied to subsequent injection events. High pressure exerted on the soil caused the injected mixture to migrate to the surface when the injection tooling was removed. The mixture would also migrate to the surface through adjacent injection points. To keep the mixture in the ground, two important changes were implemented. First, locations adjacent to each other were not completed on the same day. Second, the drilling rods were left in the ground overnight to allow the pressure to dissipate. This required the purchase of more injection tooling in order to meet the scope of work within the timeframe allowed. Eight injection rods were available each day so that all areas injected could have rods in the ground overnight. The next morning, all the rods were pulled and cleaned before resuming injections.

Injecting generous amounts of water between injection intervals and during the time the drilling rods are pulled up to the next interval ensures that the injection tooling remains free of soil and pushes the mixture further into the perched water.

Determining a radius of influence early on allowed us to increase the distance between our injection points, reducing our overall costs.

After the initial injection event, we determined what equipment worked optimally in the soils at this site. Replacement parts for injection tooling and the pumps were always on hand. O-rings in the pumps are especially susceptible to disintegration from the product and were frequently replaced.

Performance monitoring must be completed over an extended period of time (at least a year) to demonstrate incidental metals, such as arsenic, are continuing to precipitate. Verifying that heavy metals remain removed from solution over a range of changing pH, ORP and TOC conditions is important for demonstrating effectiveness with the regulatory agency.

Working with the plant personnel daily and modifying our scope of work was important for the successful completion of this effort. Production and maintenance schedules for the process equipment are constantly in flux and require a robust and flexible plan for how to meet the needs of the project without interfering with production schedules. The injections and much of the investigation work were completed over holidays when production was reduced or stopped. Planning began months before with weekly updates from the plant engineer on changes that were occurring to their schedule. This information was used to modify our plans and include alternative options during the project implementation.

REFERENCES

- Adventus Group. 2006. "Immobilization Processes for Dissolved Trace Metal Treatment using EHC-M." < http://www.adventusgroup.com/library/tech_bullet.shtml > *EHC-M[®] Mechanisms*, June.
- Ford, R.G., D.B. Kent, R.T. Wilkin. 2007. "Arsenic." In R.G. Ford, R.T. Wilkin, and R.W. Puls (eds.), *Monitored Natural Attenuation of inorganic Contaminants in Ground Water*. Vol. 2, pp. 57-70. EPA/600/R-07/140. October.
- Langmuir, D. 1997. "Iron and Sulfur Geochemistry." *Aqueous Environmental Geochemistry*, pp. 431-485. Prentice-Hall, Inc., Upper Saddle River, NJ.
- Manning, B.A., M.L. Hunt, C. Amrhein, and J.A. Yarmoff. 2002. "Arsenic(III) and Arsenic(V) Reactions with Zerovalent Iron Corrosion Products." *Environmental Science and Technology*. 36(24): 5455-5461.
- Puls, R.W., D.W. Blowes, R.W. Gillham. 1999. "Long-term performance monitoring for a permeable reactive barrier at the U.S. Coast Guard Support Center, Elizabeth City, North Carolina." *Journal of Hazardous Materials*. 68: 109-124.
- Wilkin, R.T., D. Wallschläger, and R.G. Ford. 2003. "Speciation of arsenic in sulfidic waters." *The Royal Society of Chemistry and the Division of Geochemistry of the American Chemical Society 2003*. *Geochemical Transactions*, 4(1): 1-7.

Project – Pilot Study Injection of EHC-M® for Lead

Former Battery Recycling Facility - Brazil
Lead Consultant – SGW Services, Sao Paulo, Brazil

Summary

EHC-M® has been shown to effectively immobilize lead (Pb) from groundwater at a former battery recycling facility in Brazil. Following the injection of EHC-M performed in November 2007, subsequent performance monitoring conducted in January, February, March and June 2008 showed Pb below the detection limit of 10 ppb, which represents a >97% decrease in soluble Pb. The treatment also involved adjusting the pH to around 8 at the upper portion of the aquifer.

The Challenge

The site groundwater is impacted with 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 groundwater plumes extend under ranch areas with residential areas adjacent.

The goal is to immobilize the lead in situ to limit the migration of the groundwater plumes. 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 linear groundwater flow is estimated at 3 m/year.

EHC-M for In Situ Immobilization of Lead

Metallic Pb is stable at very low redox potentials and from slightly acidic to extremely basic pH conditions (Figure 2, EPA 2007). In general, the aqueous solubility of Pb is low at near neutral to alkaline pH, whereas Pb is expected to be mobile at low pH, oxidizing conditions in the absence of sulfate. In pure water, Pb is mainly present as Pb²⁺ at a pH below 7. However, in groundwater high in sulfate, Pb precipitates as anglesite (PbSO₄). The concentration of Pb²⁺ in equilibrium with anglesite varies inversely with the concentration of sulfate. At near neutral to slightly alkaline pH, carbonate complexation is most important (e.g., cerussite [PbCO₃]) and hydrocerussite [Pb₃(CO₃)₂(OH)₂], whereas hydroxyl complexation dominate at high pH. In sulfidic environments, galena (PbS) is stable over a wide pH range.

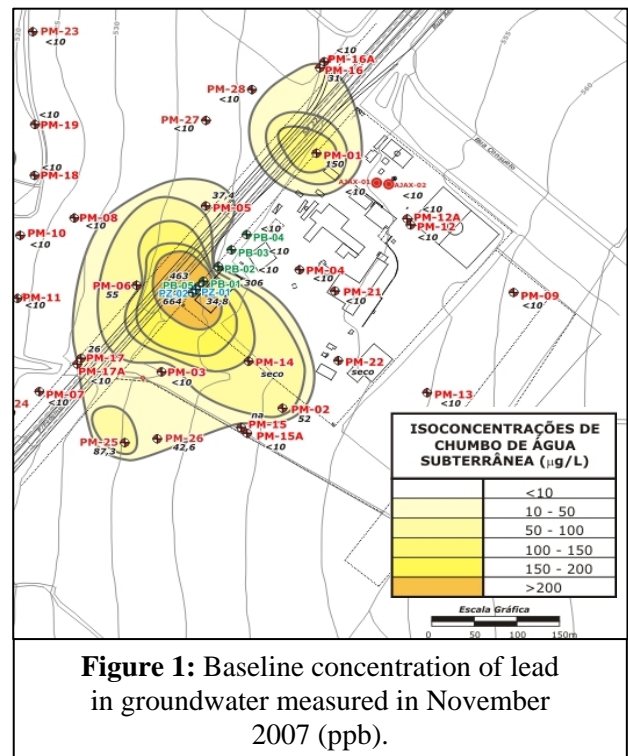


Figure 3 shows the pH-dependent solubilities of cerussite, anglesite and galena (EPA, 2007). Cerussite is highly insoluble at a pH above 8, but can be highly soluble at a pH below 6. Anglesite solubility is pH independent at a pH above 2. The solubility of galena decreases inversely with pH, but galena is highly insoluble even at low pH and below the MCL for Pb of 0.015 mg/L (or an activity of ca 7.2×10^{-8} assuming ideal behavior) in groundwaters with total sulfide equal to or above 0.001 molal.

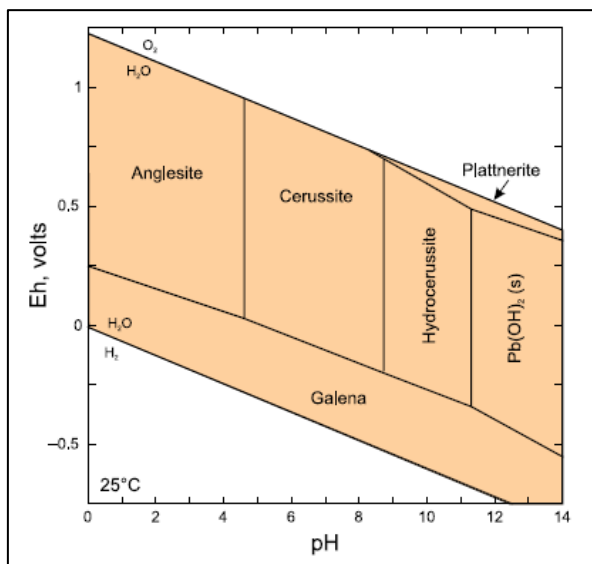


Figure 2: Eh-pH diagram for Pb in groundwaters with sulfate present (total Pb = 10^{-5} molal, total C = 10^{-3} molal, total S = 10^{-3} molal; all organic Pb complexes are suppressed; activity coeff. for all species are set equal to 1).

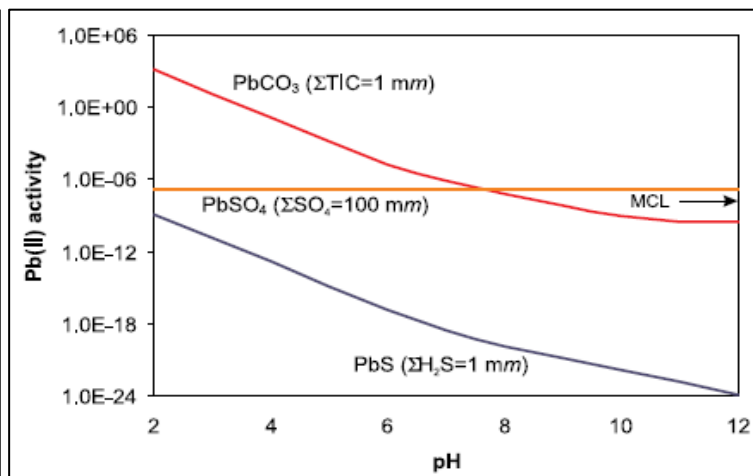


Figure 3: Pb^{2+} activity in equilibrium with cerussite (at total inorganic carbon equal to 0.001 molal), anglesite (at total sulfate equal to 0.1 molal) and galena (at total sulfide equal to 0.001 molal).

EHC-M combines controlled release carbon, ZVI and a slow-release source of sulfide ion (sulfate). Following placement of EHC-M into the subsurface, a combination of biological and chemical reactions will serve to establish very low Eh conditions and elevated levels of reduced iron and sulfide, under which conditions reduced Pb(s) will precipitate as galena and strongly adsorb onto Fe-oxides (EPA, 2007). To complement the influence of EHC-M and facilitate the biological component of its mode of action, finely pulverized dolomite/limestone can also be added to the subsurface in order to basify the aquifer, ideally to a pH above 7. This increase in pH will reduce the solubility of galena and other possible precipitates including hydrocerussite and cerussite, which have minimum solubility's near pH 9. A raise in aquifer pH will also improve conditions for microbiological activity. The addition of dolomite/limestone will also increase the total carbonate concentration resulting in increased capacity to limit Pb mobility.

Field-Scale Pilot Study

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 center using direct push technology (**Figure 4**). The pilot study area measure an estimated 12 m long x 9 m wide x 10 m deep and is located directly upgradient of monitoring well PB-01 (**Figure 5**).

The following dosing of EHC-M and pulverized dolomite was injected into the pilot treatment area:

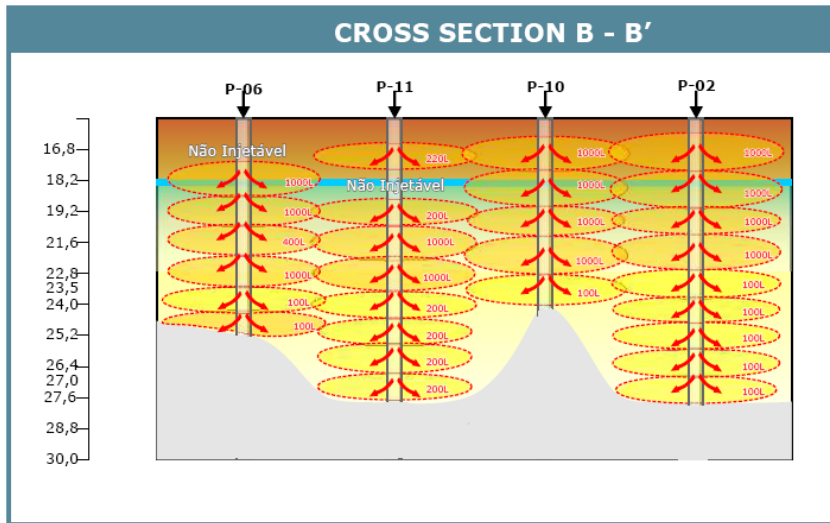


Figure 4: Cross Section of injection points. EHC-M/ dolomite slurry injected in discrete intervals from the groundwater table (accounting for seasonal variation) down to DPT refusal (from approximately 17 to 27 m bgs).

- 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 on average (1000 kg / (1,080 m³ x 1800 kg/m³)).
- A total of approximately 5,000 kg dolomite was injected into the same area to increase the pH, dosed in accordance with the results from pH titration testing. The application of dolomite was mainly limited to the upper 5 ft of the treatment zone based on soil acceptance. It was not possible to effectively inject the dolomite slurry at the less permeable lower interval.

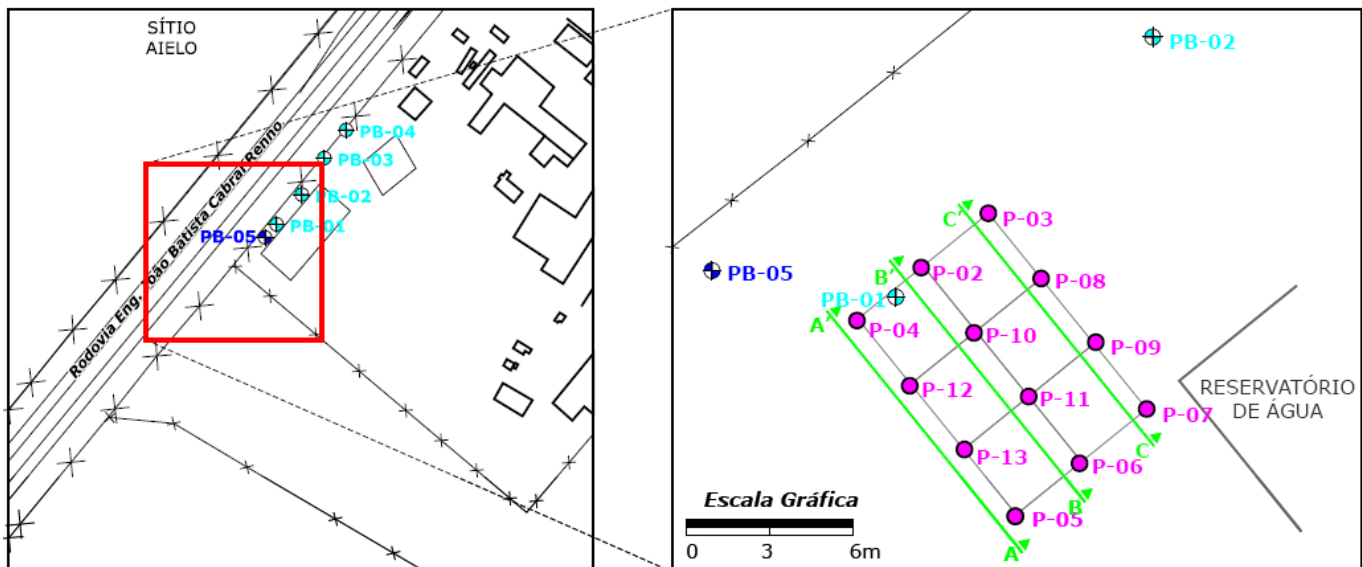


Figure 5: Layout of direct push injection points (3 m grid).

The Result

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 6). Subsequent monitoring has also confirmed that the injections have been successful in establishing reducing conditions and a significant increase in the aquifer pH (Figure 7). 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 has 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. 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.

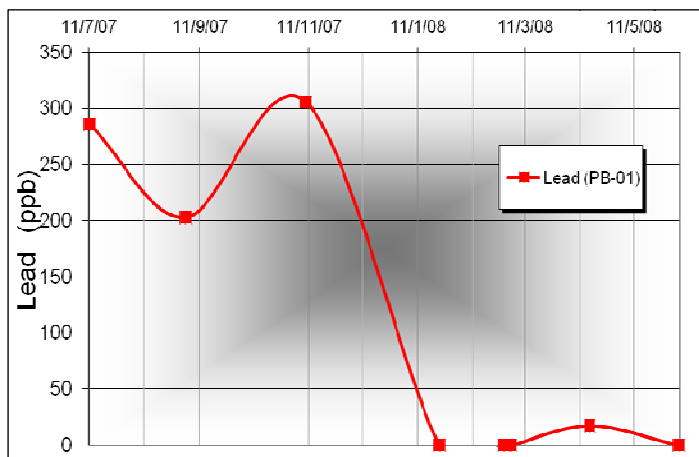


Figure 6: EHC-M/dolomite effect on dissolved lead.

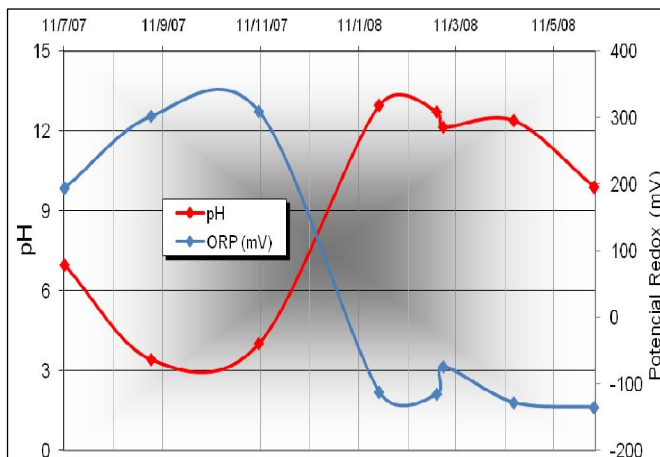


Figure 7: EHC-M/dolomite effect on geochemistry.

The Cost

The material cost of using EHC-M was \$4.50/m³.

Reference

EPA, 2007. Monitored Natural Attenuation of Inorganic Contaminants in Ground Water Volume 2 Assessment for Non-Radionuclides Including Arsenic, Cadmium, Chromium, Copper, Lead, Nickel, Nitrate, Perchlorate, and Selenium. EPA/600/R-07/140.



Project

EHC[®]-M ISCR[™] Technology for Treatment of Dissolved Arsenic
Confidential Golf Course Related Site - Florida, USA

Summary

EHC-M *in situ* chemical reduction (ISCR) reagent was used to create an *in situ* treatment zone to control the migration of a dissolved arsenic (As) plume in a shallow sandy aquifer at a Site in southern Florida proximal to a golf course. Data were collected over a 14 month period from multiple performance monitoring wells located downgradient and within the EHC-M treatment zone. These data indicated significant reduction in the concentration of dissolved As over time. In the last round of monitoring reported here, the As levels were below the drinking water standard of 10 $\mu\text{g/L}$ in the majority of monitoring wells. At the same time, reducing conditions and ISCR activity were established as demonstrated by negative ORP values and decreased sulfate concentration attributed to sulfate reduction.

The Challenge

Initial remedial action at a residential development site proximal to a golf course involved removal and disposal of approximately 7,000 tons of As-impacted soil. However, disperse and relatively low level impacts of arsenic (e.g.; less than 550 $\mu\text{g/L}$) were detected in the shallow aquifer (**Figure 1**).

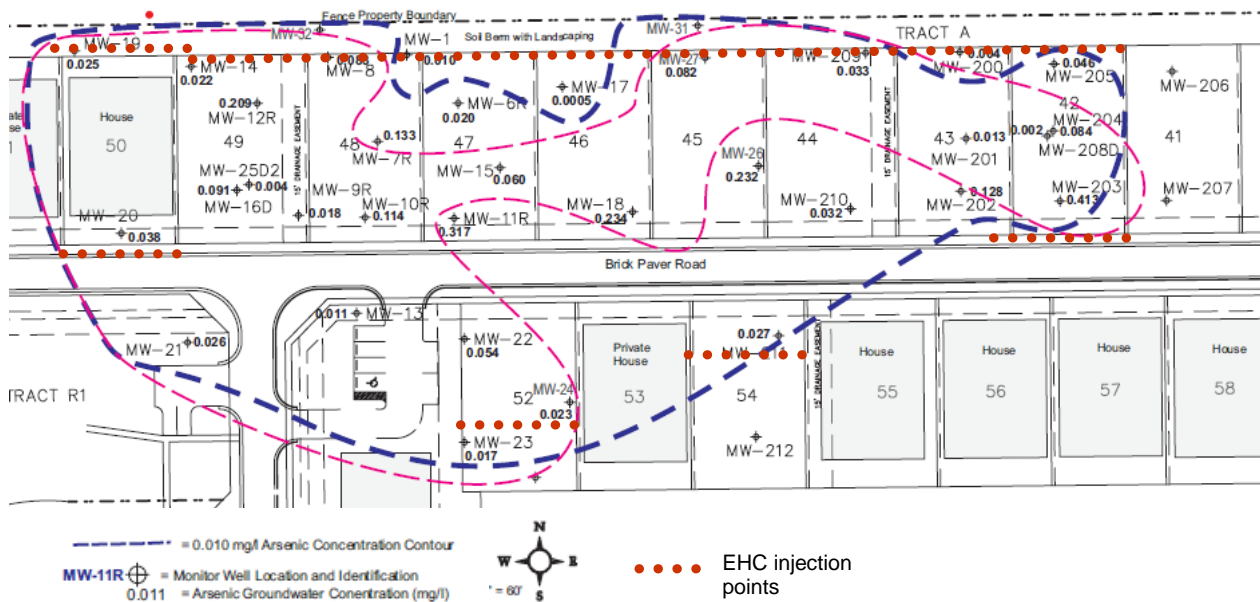


Figure 1: Arsenic impacts in shallow groundwater prior to EHC-M implementation and EHC-M injection layout.

The impacted groundwater zone extended vertically from the water table at a depth of ca. 5 ft bgs to ca. 20 ft bgs in an aquifer composed of medium to fine sand. Groundwater flow direction was predominantly to the north, with significant seasonal variations influenced by water level fluctuations in a water retention pond (not shown on Figure 1) located directly south of the As impacted area. The objective of groundwater remediation was to control the As plume migration to the north and reduce the on-site As impacts.

The Solution

EHC-M ISCR technology was identified as the preferred *in situ*, passive remedial option for this application. EHC is a patented combination of controlled-release carbon and zero valent iron (ZVI) particles used for reductive treatment of persistent organic compounds and metals in groundwater. Depending on site-specific conditions such as the presence of background levels of sulfate EHC-M materials are uniquely formulated for optimal performance.

In November and December 2010, several rows of EHC-M injection points were installed using direct push technology (DPT) to directly target the As plume (**Figure 1 – red lines**). The EHC-M application rate was 0.2%wt to soil mass within an assumed injection radius of influence of 5 ft. For each injection point, 100 USG city water was mixed with 325 lbs EHC-M (30% EHC-M solids) resulting in 120 USG injected per location into the targeted depth from 5 to 20 ft bgs.



Results

Performance monitoring over a period of 14 months following EHC-M placement showed a significant overall reduction in dissolved As concentrations, which were initially present at levels ranging from ca. 20 $\mu\text{g/L}$ to 550 $\mu\text{g/L}$ (**Figure 2**). In the northern treatment area (Figure 2a), the temporal trends in dissolved As concentrations suggested an initial increase in dissolved As levels, subsequently followed by stabilization and a rapid decrease. With groundwater flow to the north, this phenomenon was less pronounced in the southern treatment area (Figure 2b), In general, dissolved As concentrations $< 10 \mu\text{g/L}$ were detected in 10 out of 13 performance wells at the end of the 14 month monitoring period. Arsenic levels in the other three wells decreased significantly, to most recent values of $< 27 \mu\text{g/L}$.

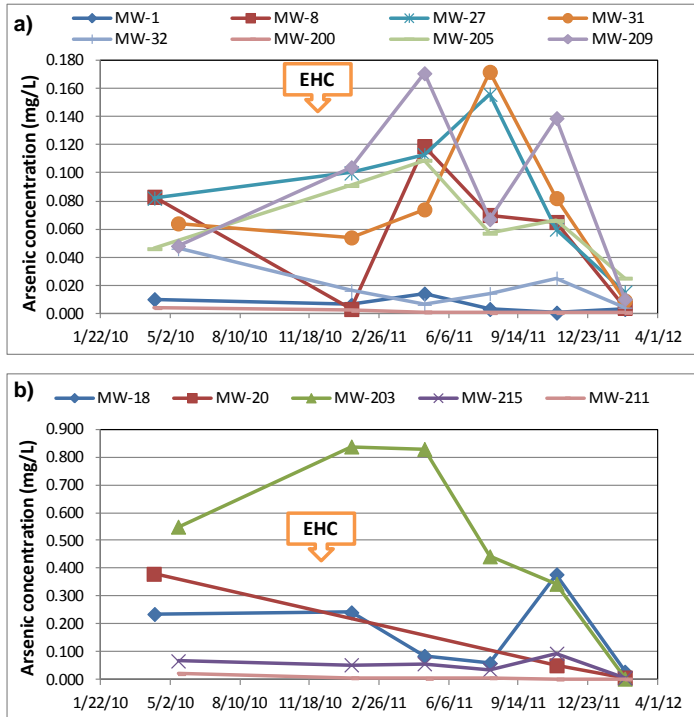


Figure 2: As concentrations in performance monitoring wells: a) the northern EHC-M injection row; b) middle and southern EHC-M injection rows.

As illustrated in **Figure 3**, the onset of dissolved arsenic removal coincided with the development of sulfate reducing conditions (ISCR) which resulted in subsequent precipitation of mixed iron and arsenic sulfide.

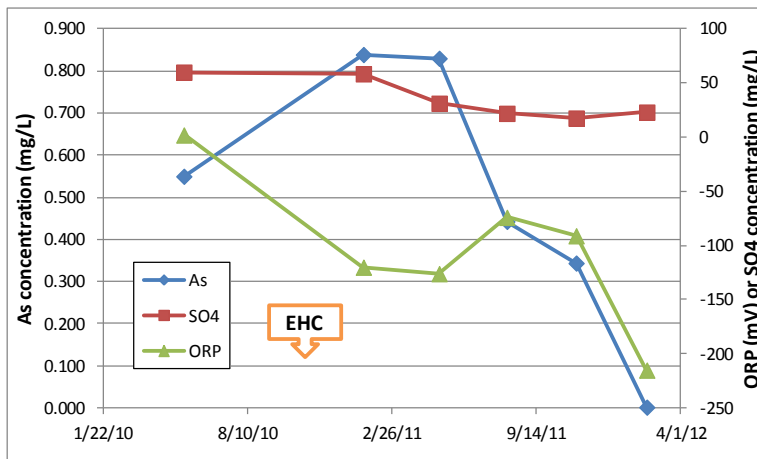


Figure 3: Temporal trends in ORP, and As and sulfate concentrations in well MW-203 (located downgradient of the easternmost EHC-M treatment area). Similar trends were observed in other monitoring wells.

The observed initial increase in the As levels may be attributed to a physical mobilization of arsenic carrying solid phases such as iron/manganese oxyhydroxides and aluminosilicates during high-pressure injection, as well as a potential intermittent release of As during reductive dissolution of the iron mineral phases prior to the development of ISCR conditions. Hence, these temporary increases were observed mainly in the direction of groundwater flow (north). Selected analyses of total (unfiltered) and dissolved As (filtered using a 0.45 μm filter) showed no significant difference between the values, indicating that colloid-associated As did not likely influence the obtained results. The impacted aquifer had a circum-neutral pH initially and the pH values were not affected significantly after EHC-M application. Therefore, it is likely that the latter mechanism (*i.e.*; reductive dissolution of iron/manganese oxides) may have been responsible for the initial As behaviour. The expected lag period between EHC-M placement and the onset of ISCR conditions is expected to be site-specific with longer lag periods likely for applications in shallow and aerobic aquifers, as observed at this site.

Summary

The EHC-M ISCR technology successfully reduced the concentration of dissolved As from ca. 550 $\mu\text{g/L}$ to < the drinking water standard of 10 $\mu\text{g/L}$ within a period of about 14 months. The relatively long time required for complete As treatment was related to the lag prior to establishment of ISCR conditions in the shallow, initially aerobic aquifer at this site.

Cost

The material cost of using EHC-M was \$0.74/ft³ in the EHC-M injection rows.

Reference

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CONFIDENTIAL CLIENT/CONSULTANT SITE IN SOUTHERN ARIZONA

SUMMARY

Type: Other

Definition: Study/Analysis

DESCRIPTION

Confidential Client/Consultant Site in Southern Arizona

Purpose: Stabilization of Chromium in Groundwater

Summary

As a result of historical site operations by prior owners groundwater at this site was impacted by hexavalent chromium (Cr(VI)). Historical total chromium concentrations were as high as 0.68 mg/L, which exceeded the Arizona Aquifer Water Quality Standard (AWQS) of 0.1 mg/L. Following a review of available technologies, the Consultant selected a combination of Adventus' in situ chemical reduction (ISCR™) technologies for use in a pilot test at the site. The pilot utilized a relatively unique method of Adventus product installation to meet the challenges of site-specific geological constraints. Subsequent field monitoring has shown reduction in and stabilization of both total chromium and Cr(VI).

The Challenge

In addition to the presence of both total chromium and Cr(VI) in excess of AWQS, site geology confounded more traditional injection techniques that may otherwise have been used at this site. In particular, the presence of alluvium over conglomerate eliminated the traditional direct push injection techniques that may otherwise have been readily applicable to the site.

To effect treatment under these conditions, a suitable dosage of Adventus products was selected to enable creation of In-Situ Chemical Reduction (ISCR) conditions favorable to chromium treatment. For the pilot, this amounted to a 0.15 wt % to soil mass dosage over a 25' x 30' by 13' thick saturated interval, or an equivalent EHC® dosage of 1,650 pounds. This was installed in a 'chimney' configuration using 12" diameter well bores using a mixture of DARAMEND® and EHC-A®.

Field-Scale Pilot

By configuring three such 'chimney' borings just upgradient of the pilot test target well, a minimum of drilling to achieve product placement was accomplished. To provide adequate treatment permeability within the sand backfill, 20 wt % DARAMEND® was amended to the sand during 'chimney' construction. EHC-A® (a cold-water soluble formulation of EHC®) was subsequently flushed through the 'chimney' well pipe. Overall, 450 pounds of DARAMEND® and 1,200 pounds of EHC-A® were utilized to effect treatment.

The Results

Following installation of the 'chimneys' in February of 2008, concentrations of both total Cr and Cr(VI) quickly fell below AWQS. In addition, these concentrations have remained low in all subsequent monitoring events. Results in the Figure below after April 2008 are posted at laboratory detection limit values.

The Conclusion

The DARAMEND® 'chimney' approach was highly effective in the treatment of chromium in groundwater at this site. Overall product cost was less than \$3,000, and was coupled with a relatively unique product delivery and drilling approach. This approach enabled rapid, cost effective, and lasting treatment in a challenging geological environment.

COMPANIES ON THIS PROJECT

ADVENTUS GROUP

