

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

*Patti J. McCall* ([pmccall@geotransinc.com](mailto:pmccall@geotransinc.com)), Lesa A. Bagby ([lbagby@geotransinc.com](mailto:lbagby@geotransinc.com))  
and Jason E. Blocker (GeoTrans, Inc., Ann Arbor, Michigan, USA)

**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.**

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

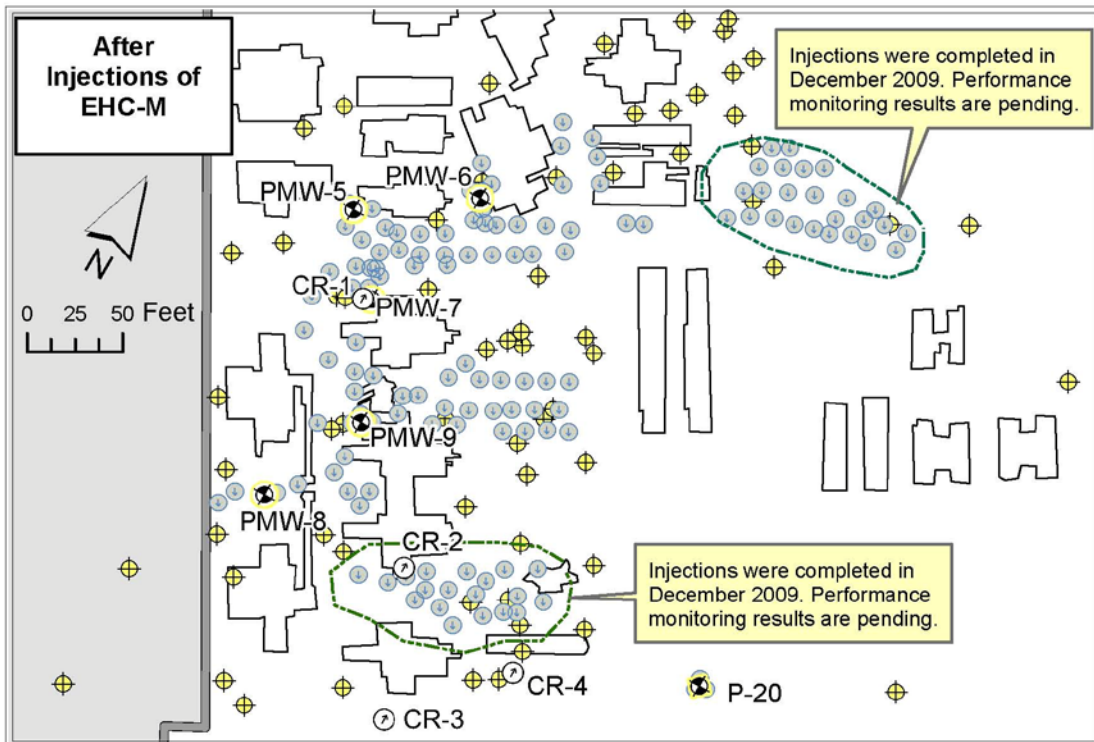
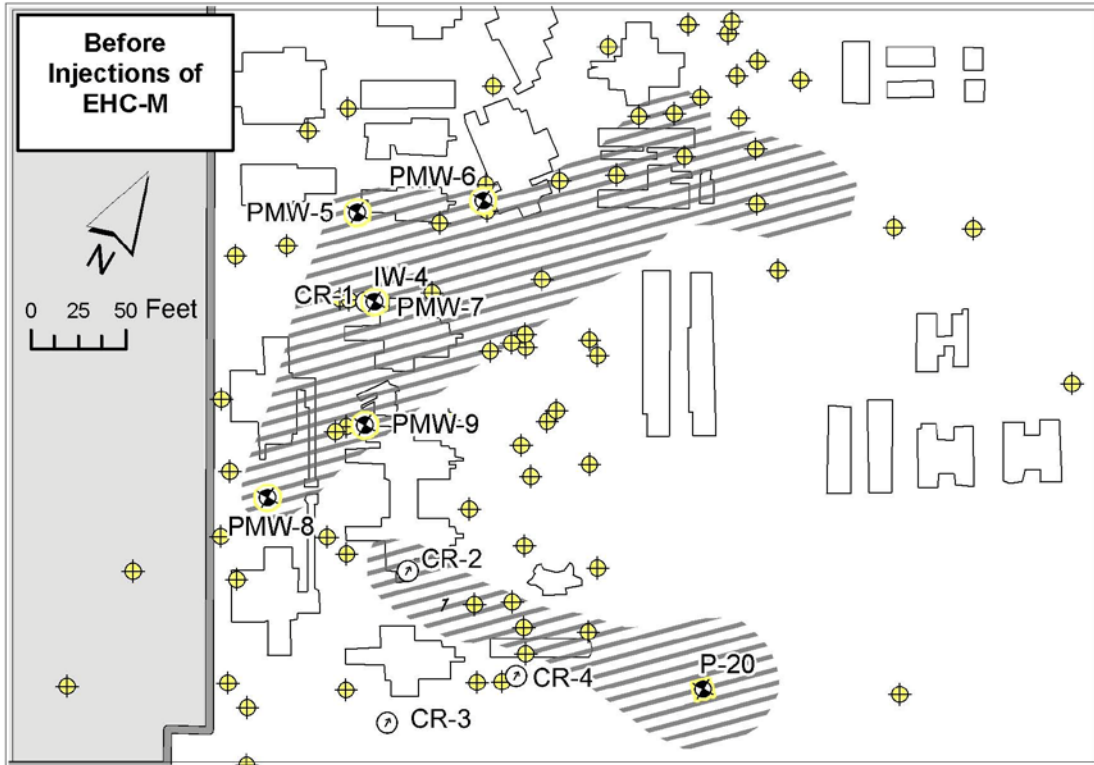
### **TECHNICAL APPROACH**

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

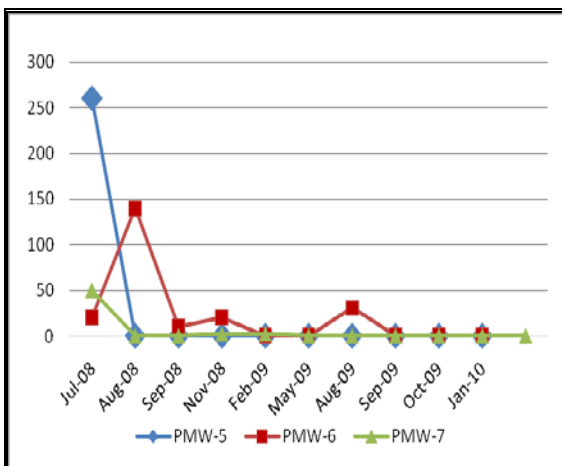
to be at least 12 feet/3.7 meters. This information was used to plan the subsequent injection events.

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.

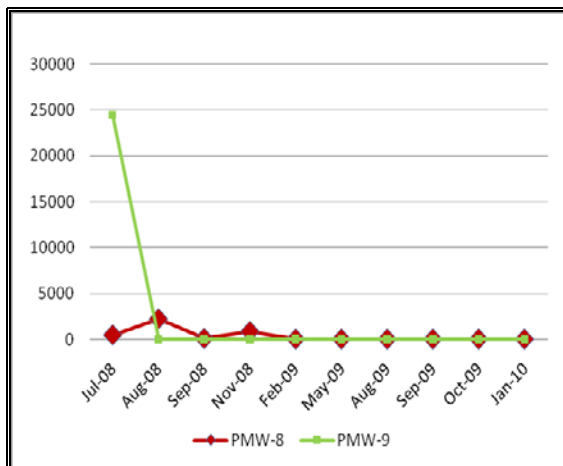
**Performance Monitoring.** Groundwater samples were collected from the performance monitoring wells monthly following injections for at least three months and less frequently thereafter depending on the results of the analysis. The samples were submitted for laboratory analyses of the same parameters 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 µg/L prior to injection to 5 µg/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 (µg/L) over time.**



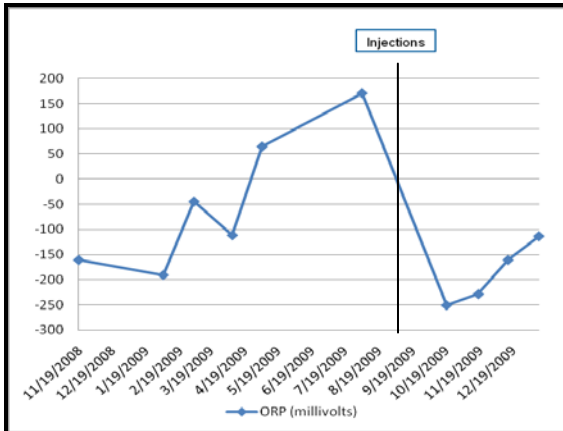
**FIGURE 3. Hexavalent chromium concentrations (µg/L) over time.**

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.

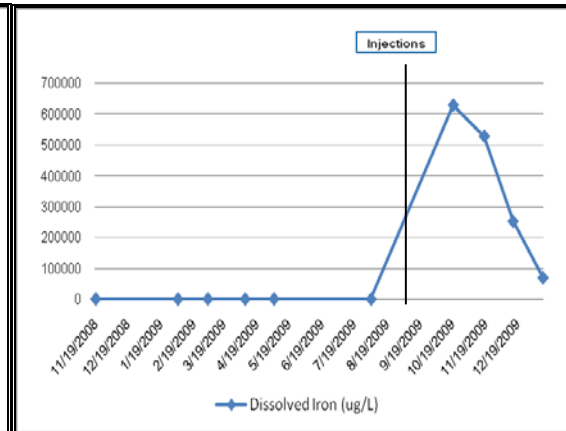
**TABLE 2. ORP in millivolts over time.**

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
<b>Average:</b>	<b>1.6</b>	<b>-266</b>	<b>-245</b>	<b>-155</b>

\*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 ( µg/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.

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