



EHC[®] Metals Pilot Study Injection for Lead Treatment

Summary

EHC[®] Metals Reagent has been shown to effectively immobilize lead (Pb) from groundwater at a former battery recycling facility in Brazil. Following the injection of EHC Metals 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 below ground surface (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 Metals, which will promote precipitation of soluble lead as stable sulfides. Baseline conditions were relatively oxic with a DO of 2 to 6 ppm and ORP generally in the range of 80 to 400 mV. Shallow groundwater was 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 was estimated at 3 m/year.

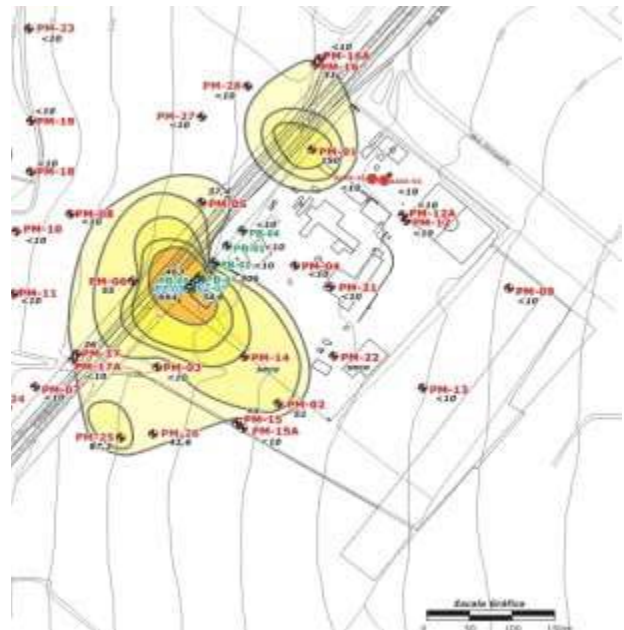


Figure 1. Baseline concentration of lead in groundwater measured in November 2007 (ppb)

EHC Metals 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 Pb^{2+} at a pH below 7. However, in groundwater high in sulfate, Pb precipitates as anglesite ($PbSO_4$). The concentration of Pb^{2+} 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 [$PbCO_3$]) and hydrocerussite [$Pb_3(CO_3)_2(OH)_2$], 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.

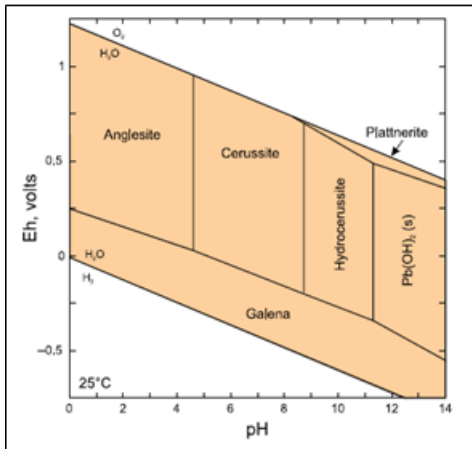


Figure 2. Eh-pH diagram for Pb in groundwaters with sulfate present (total Pb = 10^{-5} molal, total C = 10^{-3} molal, total S = 10^{-3} molal; all organic Pb complexes are suppressed; activity coeff. for all species are set equal to 1).

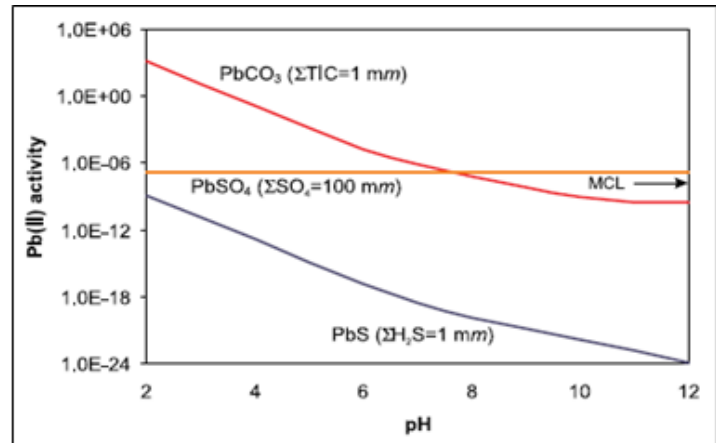


Figure 3. Pb²⁺ activity in equilibrium with cerussite (at total inorganic carbon equal to 0.001 molal), anglesite (at total sulfate equal to 0.1 molal) and galena (at total sulfide equal to 0.001 molal).

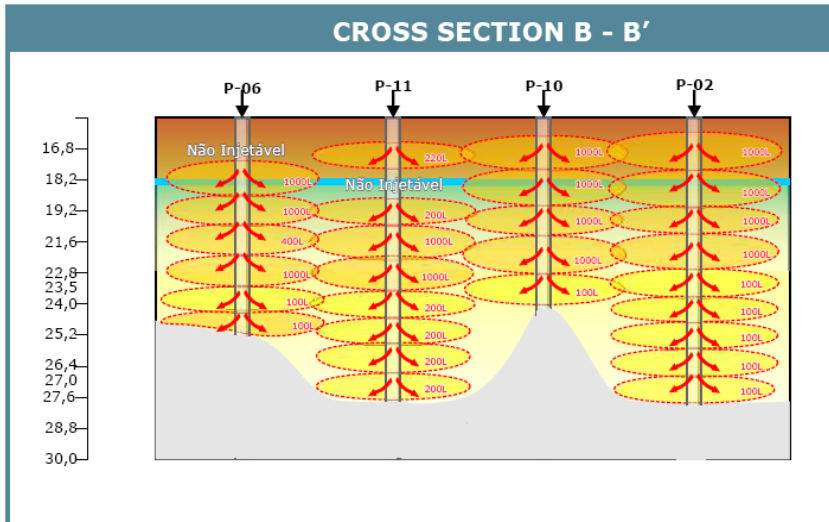
EHC Metals combines controlled release carbon, ZVI and a slow-release source of sulfide ion (sulfate). Following placement of EHC Metals into the subsurface, a combination of biological and chemical reactions will serve to establish very low Eh conditions and elevated levels of reduced iron and sulfide, under which conditions reduced Pb(s) will precipitate as galena and strongly adsorb onto Fe-oxides (EPA, 2007). To complement the influence of EHC Metals 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 solubilities 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 Metals performance under field conditions, and ii) assess the effectiveness of the construction methodology (i.e., direct injection of EHC Metals/dolomite slurry). A mixture of EHC Metals, dolomite and water was injected into 12 injection points spaced 3 m on center using direct push technology (Figure 4). The pilot study area measures 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 Metals and pulverized dolomite was injected into the pilot treatment area:



- A total of 1,000 kg of EHC Metals 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 4. Layout of direct push injection points (3 m grid).

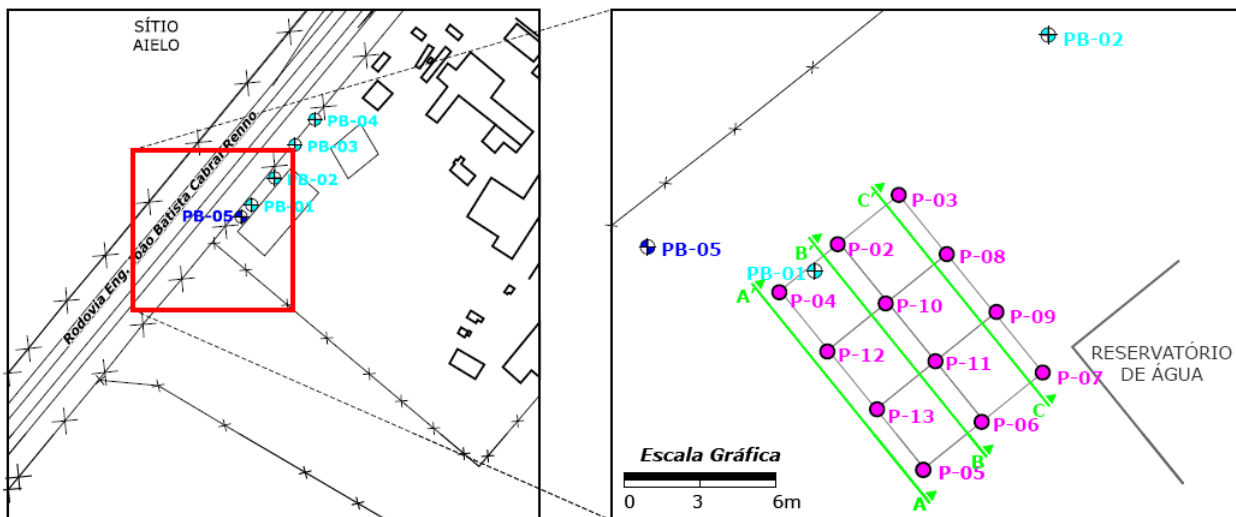


Figure 5. Layout of direct push injection points (3 m grid).

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 Metals technology offers a safe, effective and cost-efficient remedial solution for similarly impacted environments.

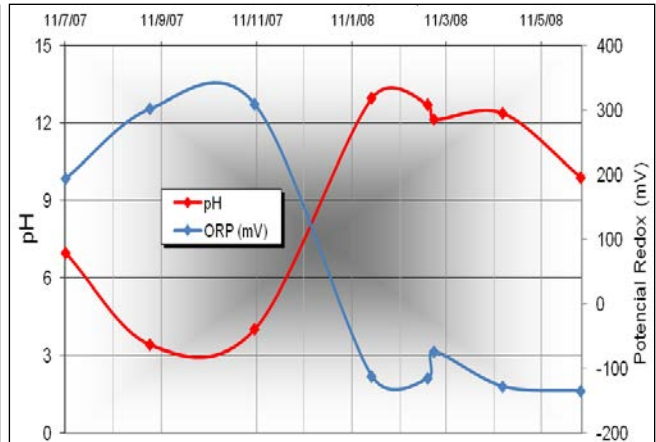
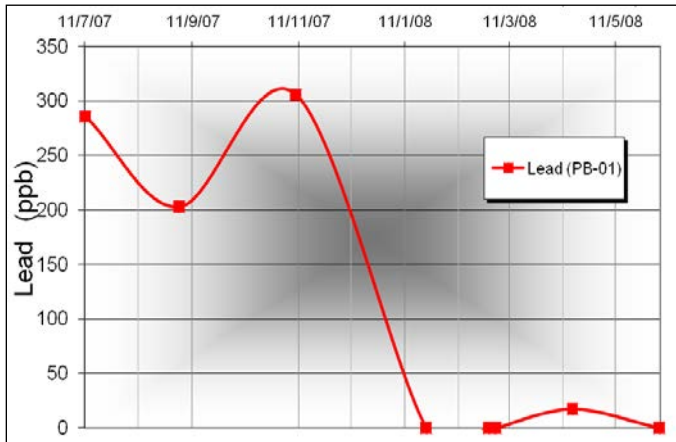


Figure 6. EHC Metals /dolomite effect on dissolved lead. Figure 7. EHC Metals /dolomite effect on geochemistry



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.

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