

# **IN SITU STABILIZATION OF LEAD IN GROUNDWATER AT A MANUFACTURING FACILITY IN RIO DE JANEIRO**

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## **Resumo**

As águas subterrâneas em uma fábrica localizada no Rio de Janeiro, Brasil, é impactada por chumbo (Pb) com concentração máxima de 497 mg/L. O objetivo desse estudo é imobilizar *in situ* o Pb para limitar a migração da pluma. Para este objetivo, foi injetado o EHC-M<sup>®</sup> para promover a precipitação de Pb solúvel em sulfetos estáveis. O EHC-M combina a liberação controlada de carbono, o ferro zero-valente (ZVI) e uma fonte de enxofre. As águas subterrâneas são ácidas em partes da pluma com um pH próximos a 4,3. A solubilidade aquosa de Pb depende do valor do pH e, em geral, a solubilidade do Pb é baixa, quando o pH é neutro ou alcalino. Dessa forma, o hidróxido de magnésio (Mg(OH)<sub>2</sub>) foi injetado junto com a solução de EHC-M para ajustar o pH próximo a neutro. Este artigo resume os resultados da injeção em escala piloto de EHC-M e da aplicação de campo subsequente em grande escala.

## **Abstract**

Groundwater at a manufacturing facility located in Rio de Janeiro, Brazil, is impacted by lead (Pb) up to a maximum concentration of 497 µg/L. The remedial objective is to immobilize Pb *in situ* to limit plume migration. Toward this end, injection of EHC-M<sup>®</sup> was conducted to promote precipitation of soluble Pb as stable sulfides. EHC-M combines controlled-release carbon, micro-scale zero-valent iron (ZVI) and a slow-release source of sulfur. Groundwater is acidic in parts of the plume with a pH as low as 4.3 measured historically. The aqueous solubility of Pb is highly pH-dependent and, in general, Pb solubility is lower at near neutral to alkaline pH. Therefore, magnesium hydroxide (Mg(OH)<sub>2</sub>) was injected together with the EHC-M slurry to adjust the pH to around neutral. This paper summarizes the results from the pilot-scale evaluation of EHC-M and the subsequent full-scale field implementation.

## **Key words**

lead, *in situ* stabilization, heavy metals

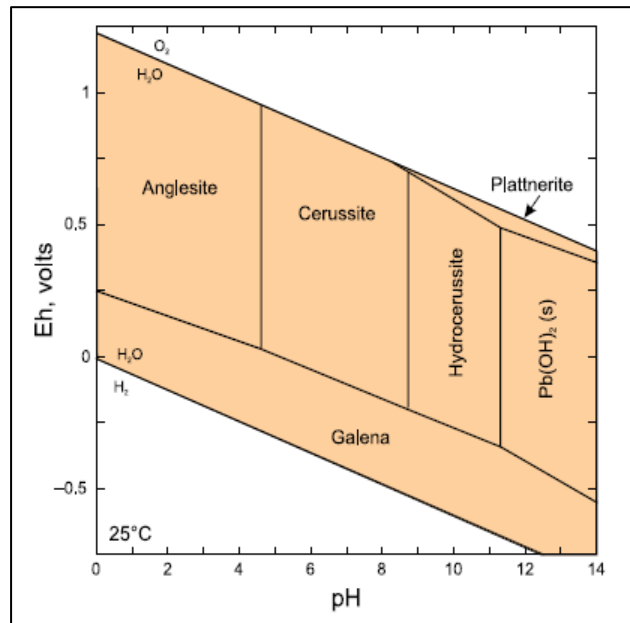
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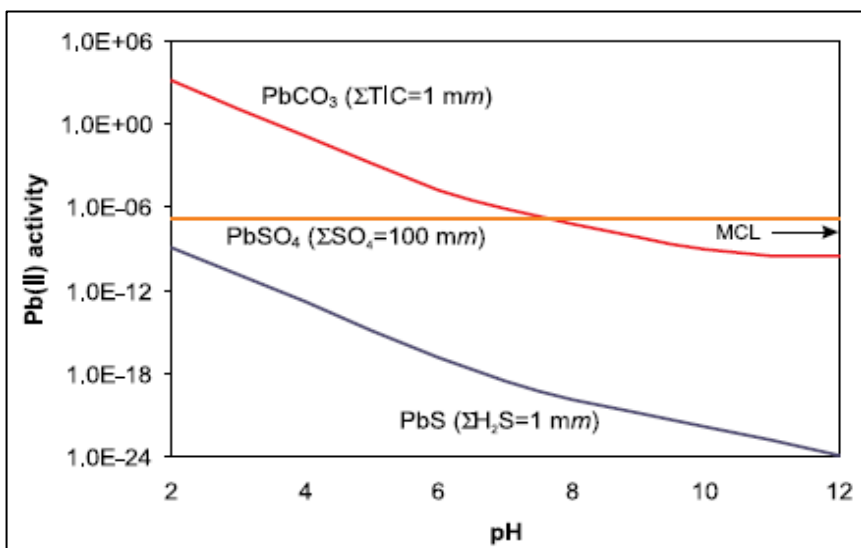
# 1 - INTRODUCTION

Metallic Pb is stable at very low redox potentials and from slightly acidic to extremely basic pH conditions (Figure 1, 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<sup>2+</sup> at a pH below 7. However, in groundwater high in sulfate, Pb precipitates as anglesite (PbSO<sub>4</sub>). The concentration of Pb<sup>2+</sup> 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<sub>3</sub>] and hydrocerussite [Pb<sub>3</sub>(CO<sub>3</sub>)<sub>2</sub>(OH)<sub>2</sub>], whereas hydroxyl complexation dominate at high pH. In sulfidic environments, galena (PbS) is stable over a wide pH range.



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

Figure 2 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



**Figure 2. Pb<sup>2+</sup> 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).**

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 x 10<sup>-8</sup> assuming ideal behavior) in groundwaters with total sulfide equal to or above 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, a buffer 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.

## **2 – SITE BACKGROUND**

Groundwater at the Site was impacted by dissolved metals, including lead, boron and cobalt. The primary constituent of interest was Pb, which has been measured at concentrations up to 497 µg/L in groundwater; the treatment goal was to reduce dissolved concentrations to below 10 µg/L. Depth to groundwater ranged from 1.1 to 1.9 m bgs in the targeted treatment area. The impacted wells were screened in the upper 2 m of the saturated zone (down to a maximum of 4.4 m bgs). The aquifer lithology was clayey down to an estimated 6 m bgs, where a more permeable layer was expected. Site groundwater flowed to the north and was estimated to be slow .

## **3 - FIELD-SCALE PILOT STUDY**

A pilot-scale injection of EHC-M was conducted in November 2010, with the goals to: i) validate EHC-M performance under the site-specific field conditions, and ii) assess the effectiveness of the construction methodology employed (*i.e.*, direct injection of EHC-M slurry). A total of 925 kg EHC-M was injected into eight injection points spaced 3 m apart and centered around a performance evaluation well (PM-10). The EHC-M powder was mixed with water on site into slurry and injected via direct push technology. With the construction method employed, it was not possible to inject into the targeted clay layer, and most injection points were completed at around 6 m bgs, in the underlying sand unit.

Although injection was not possible into the screened interval of the performance evaluation well, post injection data showed a decrease in the oxidation-reduction potential (ORP) and dissolved oxygen (DO), confirming the establishment of reducing conditions within the targeted zone (Table 1). Furthermore, dissolved phase Pb was reduced from 113 ppb to below the detection limit of 1 ppb in 30 days.

**Table 1. Pilot study performance data measured at PM-10.**

<b>Date</b>	<b>Time post injection</b>	<b>Dissolved Pb (ug/L)</b>	<b>pH</b>	<b>DO (mg/L)</b>	<b>ORP (mV)</b>
3/11/2010	Baseline	113	4,45	0,79	369,02
8/12/2010	1 month	<1	4,30	0,80	-152,24
23/3/2011	4 months	<1	6.49	0,25	-326.3

#### **4 - FULL-SCALE TECHNOLOGY APPLICATION**

Based on the confirmatory results at the pilot-scale, full-scale application was implemented in March, 2011. The injections were performed top-down using conventional direct push technology (Figure 3). A total of 11,200 kg of EHC-M was injected into a total of 73 injection points spaced 3 to 4 m apart, to target an overall plume area measuring approximately 1,400 m<sup>2</sup> x 3 m thick. This resulted in an average application rate of ca. 0.2% EHC-M by soil mass. Mg(OH)<sub>2</sub> was injected in conjunction with the EHC-M slurry to raise the pH to around neutral and to be in line with background conditions measured upgradient of the plume. Post-injection performance monitoring will be conducted on a quarterly bases. Full-scale results will be presented at the seminar, including more detailed geochemical data.



**Figure 3. Preparation and direct injection of EHC-M slurry.**

#### **REFERENCES**

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