Reductive Precipitation of Heavy Metals in Soil and Groundwater using Abiotic and Biologically Mediated Processes

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Resumo: EHC® Metals é um produto para remediação que promove a imobilização de metais composto de carbono orgânico, ferro zero valente (ZVI) e sulfato. Com a injeção do EHC Metals na zona saturada, uma série de processos químicos e microbiológicos atuam criando condições redutoras nas quais um número de metais pesados são sequestrados por precipitação redutora como metal-sulfetos pouco solúveis e através de adsorção em produtos secundários da corrosão do ZVI. Estas reações ocorrem microbiologicamente dependendo da fermentação microbiana do carbono orgânico para gerar condições de redutoras e na redução do sulfato para sulfeto por bactérias sulfato-redutoras. Em concentrações muito elevadas, os metais pesados podem ser altamente tóxicos para os microrganismos. Abordagens que dependem somente de processos microbianos podem não funcionar bem em tais ambientes se a atividade microbiana for reduzida ou inibida. Reagentes METAFIX ™ são uma família completamente nova de reagentes para o tratamento de metais pesados, composta de misturas de agentes de redução (ZVI, sulfetos de ferro), minérios reativos (óxidos de ferro, oxi-hidróxidos de ferro), modificadores de pH, silicatos e catalisadores. Esta nova abordagem é abiótica e alheia à toxicidade. Dados serão apresentados, incluindo a avaliação de ambos os EHC Metals e Metafix em um site no Brasil.

Abstract: EHC® Metals is a remediation product for immobilization of metals composed of organic carbon, micro-scale zero-valent iron (ZVI) and sulfate. Following placement of EHC Metals substrate into the saturated zone, a number of chemical and microbiological processes combine to create strongly reducing conditions under which a number of heavy metals are sequestered via reductive precipitation as scarcely soluble metal-sulfides and via adsorption onto secondary ZVI corrosion products. These reactions are microbially mediated, in part relying on microbial organic carbon fermentation and on the reduction of sulfate by sulfate-reducing bacteria. At very high concentrations, heavy metals can be acutely toxic to microorganisms and approaches that rely on microbial processes may not function well if microbial activity is significantly slowed or inhibited. MetaFix™ reagents represent an entirely new family of reagents for treatment of heavy metals, composed of mixtures of reducing agents (ZVI, iron sulfides), processed reactive minerals (iron oxides,

iron oxyhydroxides), pH modifiers, silicates, and catalysts. This new approach is abiotic and therefore insensitive to toxicity. Performance data will be presented, including an evaluation of both EHC Metals and Metafix for a site in Brazil.

Keywords: Heavy metals, immobilization, in situ remediation

1 – INTRODUCTION

High concentrations of heavy metals are found in many soil and sediment environments, with the source being either anthropogenic or naturally occurring. The solubility of heavy metals in groundwater is impacted by several geochemical factors including the redox potential of the system, pH and the presence of iron sulfides, phosphates and other minerals. Based on the chemical properties of dissolved species, trace metals can be divided into two distinct groups: reducible metals and metalloids, which are present in natural waters as anions and oxyanions (e.g. Cr, As, Se, Mo, U), and metal cations, which occur in aqueous environment as divalent cations (e.g. Cu, Zn, Cd, Pb, Hg, Ni). Depending on their aqueous form, the mobility of trace metals in groundwater is affected by various chemical reactions, including dissolution-precipitation, oxidation-reduction, adsorption-desorption and complexation. Several different remediation technologies based on those reactions have been implemented for subsurface metal immobilization (e.g. reactive zones containing zero valent iron (ZVI), organic carbon substrates, zeolite, limestone).

2 – BIOLOGICALLY MEDIATED VS ABIOTIC REDUCTION OF HEAVY METALS

EHC® Metals is a remediation product for immobilization of metals combining controlled-release organic carbon, micro-scale zero-valent iron & a slow-release of sulfate. Following placement of EHC Metals substrate into the saturated zone, a number of chemical and microbiological processes combine to create strongly reducing conditions under which a number of heavy metals are sequestered via reductive precipitation as scarcely soluble metal-sulfides and via adsorption onto secondary ZVI corrosion products. Broadly, reducible metals are immobilized via reductive precipitation with iron oxides and iron oxyhydroxides and metal cations precipitate as metal sulfides under sulfate reducing conditions. These reactions are microbially mediated, in part relying on microbial organic carbon fermentation to generate reducing conditions and on the reduction of sulfate to sulfide by sulfate-reducing bacteria.

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At very high concentrations, heavy metals can be acutely toxic to microorganisms. Approaches that rely on microbial processes may not function well in such acutely toxic environments because processes important to their treatment mechanisms, including carbon fermentation, oxygen consumption, and sulfate reduction, can be significantly slowed or even completely inhibited. Hence, in such toxic environments, metals treatment reagents that do not rely on microbial activity but rather combine chemical reduction with adsorption and precipitation of heavy metals may be advantageous. MetaFix™ reagents represent an entirely new family of reagents for treatment of soil, sediment, industrial wastes, and groundwater contaminated with heavy metals. Their treatment mechanisms are based on iron, iron sulfides, and other iron-bearing minerals and therefore result in heavy metal precipitates that include iron. These iron-bearing heavy metal precipitates generally have lower solubility and greater stability than precipitates that do not incorporate iron (i.e., heavy metal sulfides or heavy metal hydroxides). The new reagents are composed of mixtures of reducing agents (ZVI, iron sulfides), processed reactive minerals (iron oxides, iron oxyhydroxides), pH modifiers, silicates, and catalysts. This new approach is insensitive to toxicity and will perform well even in environments that have high metals concentrations, high concentrations of organic contaminants such as chlorinated solvents, high salt content, or pH levels (high or low) that would inhibit carbon fermentation and sulfate reduction. *In situ* reactive zones can be constructed with the reagents to prevent migration of heavy metals into sediments or surface water.

3 – REACTION CHEMISTRY

EHC Metals provide “raw materials” that are transformed by microbial and chemical processes in situ:

- Organic carbon is consumed to produce volatile fatty acids (VFAs) that serve as reducing agents;
- ZVI itself is a strong reducing agent that corrodes to release hydrogen, alkalinity, and ferrous iron;
- Iron corrosion results in deposition of new reactive minerals such as magnetite and green rust;
- Sulfate is reduced by sulfate reducing bacteria to yield sulfides that can combine with ferrous iron to generate iron sulfides (very strong reducing agents);
- Performs best in soil/groundwater where conditions are not extreme with respect to acute toxicity (i.e., pH, contaminant concentrations, salinity) because carbon fermentation and sulfate reduction to sulfide are microbially mediated.

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Metafix includes reducing agents and reactive minerals that more directly binds with the metals:

- Metafix reagents DO NOT depend upon in situ transformation of iron and sulfate into sulfides and iron-bearing minerals;
- Instead we are enriching the aquifer with a mixture of reducing agents (ZVI, iron sulfides) and processed reactive minerals (iron oxides, iron oxyhydroxides);
- The key differentiator to EHC Metals is that the MetaFix approach is insensitive to toxicity and will perform well even in environments that have high metals concentrations, high concentrations of organic contaminants such as solvents, high salt content, or baseline pH levels (high or low) that would inhibit carbon fermentation and sulfate reduction.

4 – TREATABILITY TESTING

Considering the complexity of these reactions in terms of the multitude of possible precipitation products for different metals under varying geochemical conditions, bench testing is commonly recommended as a first screening step to verify treatment and to identify the best suited product formulations. Many sites impacted with heavy metals also require pH modification for optimal results and bench testing can help determine the amount of pH buffer required and screen the requirements for different types of pH buffers. A bench study was completed for a site in Brazil impacted by a range of heavy metals and with a starting pH of 2.5. The evaluation included three different pH buffers and three different reagents (two MetaFix formulations and EHC Metals). The study showed the importance of pH modification in combination with these reagents, with close to a complete reduction in all dissolved metals observed in the systems combining pH modification with CaO together with MetaFix or EHC Metals. Performance data from this and other studies will be presented showing reductions in leaching of key metals under different geochemical conditions.

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