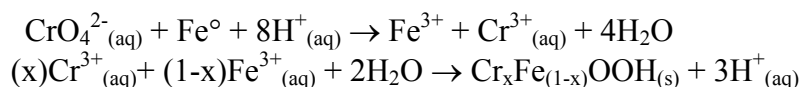




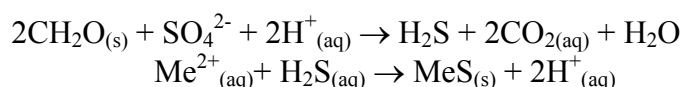
Immobilization Processes for Dissolved Trace Metal Treatment Using EHC-M

Trace metals constitute a significant class of groundwater contaminants originating from mining effluents, industrial wastewater, landfill leachate, agricultural wastes and fertilizers, and fossil fuels (1). Based on the chemical properties of dissolved species, trace metals can be divided into two distinctive 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 (Figure 1), the mobility of trace metals in groundwater is affected by various chemical reactions, including dissolution-precipitation, oxidation-reduction, adsorption-desorption and complexation (2). 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) (3).

EHC-M™ is a specially formulated integrated treatment material containing controlled-release organic carbon, ZVI, a source of sulfate, and other additives designed for treatment of dissolved trace metals. The two main reactive components of EHC-M, ZVI and organic carbon substrate, are well-established reactive materials used for in-situ reductive immobilization of different types of metals in groundwater. The treatment mechanisms using these materials are well understood (4,5,6,8,10). ZVI permeable reactive barriers (PRBs) have been applied for treatment of reducible metals (i.e.; Cr, As, U, Se, Mo) via reductive precipitation on ZVI surfaces and with iron oxyhydroxides that form on the ZVI surfaces. For example, the reaction sequence for Cr(VI) can be described as (4):



PRBs containing a wide range of solid-phase organic carbon (e.g.; compost, wood chips, saw dust, etc.) have been used for treatment of metal cations (i.e.; Cu, Zn, Hg, Pb, Cd, Ni). These cations precipitate as metal sulfides following microbial mediated reduction of sulfate present in the groundwater. The internal source of sulfate in EHC-M enables metal immobilization in groundwaters depleted in dissolved sulfate. The liable carbon stimulates sulfate-reducing bacteria. This process can be represented by the following reaction sequence (4):



where: CH₂O represents organic carbon and Me²⁺ represents a divalent metal cation.

Another important mechanisms of metal cation removal in the presence of corroding ZVI is adsorption onto iron corrosion products, like iron oxides and iron oxy-hydroxides (Figure 2).

Our long-term column tests with metal contaminated groundwaters have shown that an EHC-M in-situ zone will provide a rapid, persistent and irreversible immobilization of both reducible metals (As and Cr) and metal cations (Zn, Hg, and Pb). Based on these data, the cumulative effect of ZVI and carbon substrate in EHC-M is applicable for a wider range of environmental applications, and tests are ongoing to document EHC-M's ability to remove other trace metal contaminants. Table 1 provides a summary of metal-specific immobilization mechanisms, which may occur in an EHC-M zone, based on the known chemical and microbial processes in the presence of ZVI and organic substrates. Upon request, we would be pleased to provide summaries of laboratory studies noted above, and the references quoted in this note.

Table 1. Metal-specific immobilization mechanisms in groundwater for an EHC-M treatment zone. (Underlined symbols indicate metals immobilized in EHC-M column tests conducted by the Adventus Group).

Metal	Dissolved species	Immobilization Mechanism	Reference
<u>As</u>	As (III, V)	Reductive precipitation with oxidized iron minerals. Precipitation as As sulfide and mixed Fe-As sulfide.	4,6,7
<u>Cr</u>	Cr(VI)	Reduction to Cr(III) and precipitation with oxidized iron minerals and adsorption to iron oxides.	4,8
Mo, Se, U	Mo(VI), Se(IV,VI), U(VI)	Reductive precipitation with oxidized iron minerals.	4
Cu, <u>Zn</u> , <u>Pb</u> , Cd, Ni	Me ²⁺	Organic carbon source stimulates heterotrophic microbial sulfate reduction to sulfide. Subsequently, metal cations precipitate as sulfides. Strong adsorption to iron corrosion products (e.g.; iron oxides and oxyhydroxides).	2,4,5,9,10
<u>Hg</u> *	Hg ²⁺	If not complexed, indirect reductive precipitation as mercury sulfide. Strong adsorption to iron corrosion products (e.g.; iron oxides and oxyhydroxides).	2,4,9

* Mercury is commonly transferred by microorganisms to monomethyl mercury (CH₃Hg) and dimethyl mercury [(CH₃)₂Hg]

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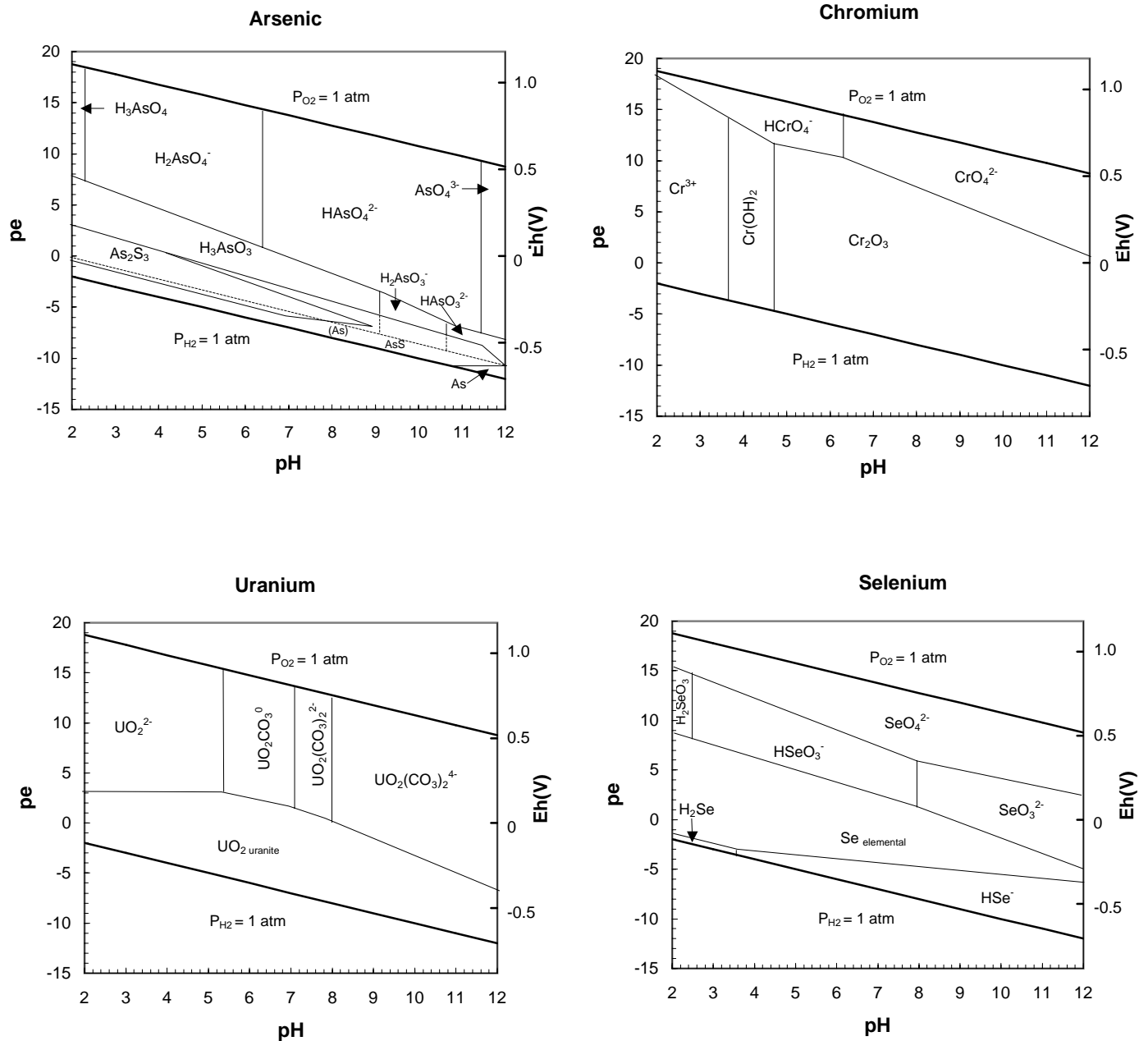


Figure 1a. Simplified pe-pH diagrams for common metals which occur in subsurface as anions and oxyanions. (Data from Ref. 2). Me-O-H₂O systems with a metal (Me) activity of 10⁻⁶, at 25°C and one atmosphere. For arsenic, total activity of sulfur species = 10⁻², light lines are boundaries for dissolved species only, dashed line is field of elemental arsenic in the absence of sulfur. For uranium, P_{CO₂} = 10⁻² atm.

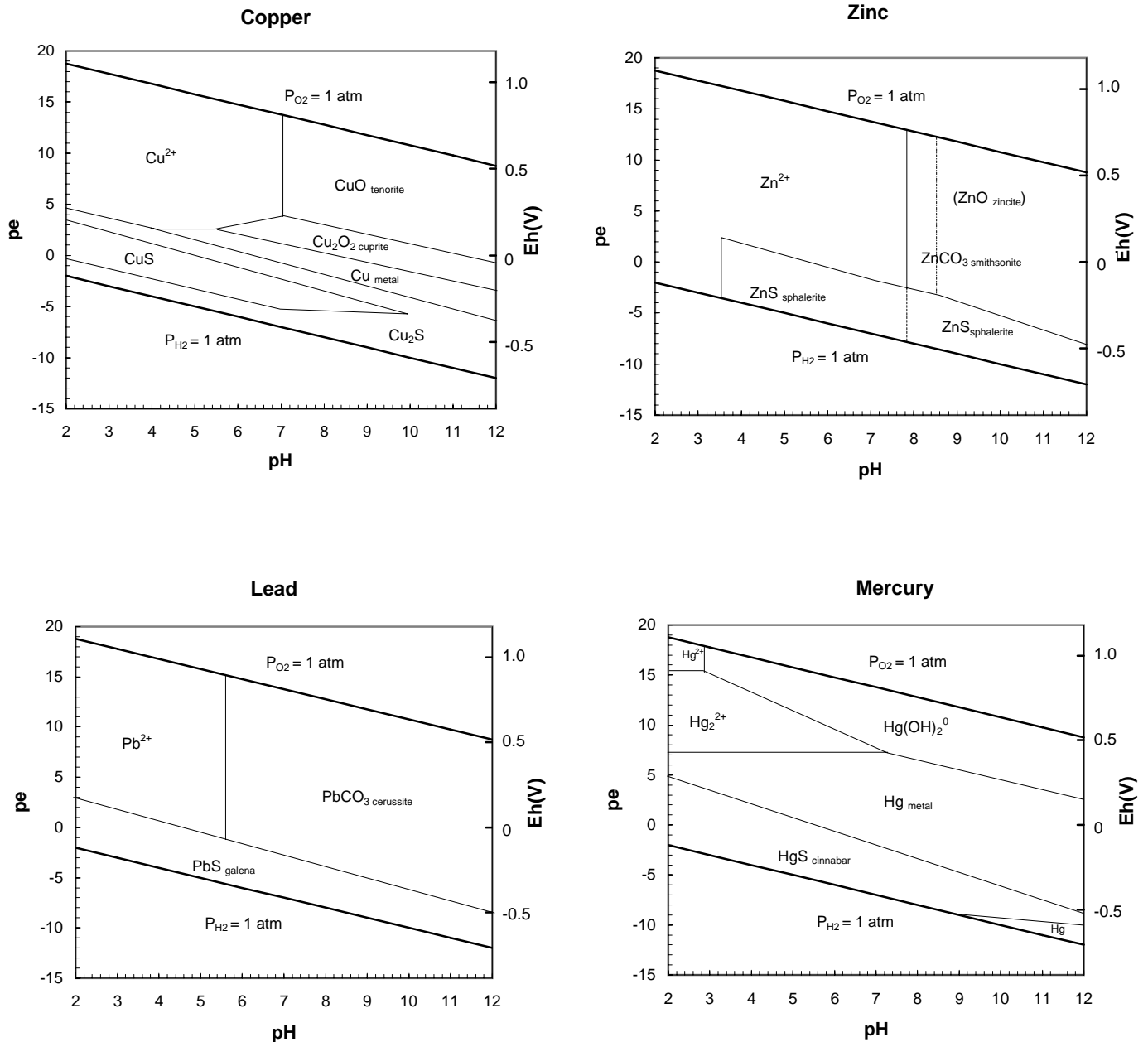


Figure 1b. Simplified pe-pH diagrams for common metals which occur in subsurface as divalent cations. (Data from Ref. 2). Me-S-O-H₂O systems with a metal (Me) activity of 10⁻⁶, at 25°C and one atmosphere. Total activity of sulfur species = 10⁻². For zinc and lead, P_{CO2} = 10⁻² atm. Solid lines are solubilities in the presence of S species, and dashed lines are solubilities of carbonates in the absence of sulfur.

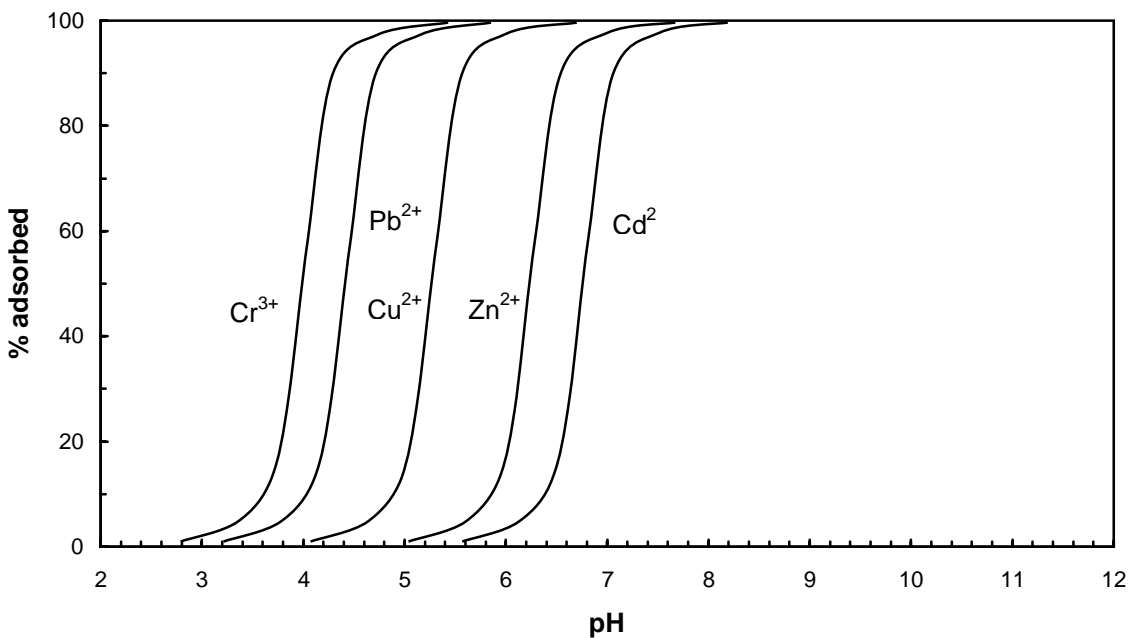


Figure 2. Adsorption of Cr³⁺, Cu²⁺, Cd²⁺, Zn²⁺, and Pb²⁺ on hydrous ferric oxide as a function of pH. Each metal shows adsorption "edge"; at pH values below the edge, the ion is not adsorbed. At pH values above the edge, the ion is strongly adsorbed. High ratios of hydrous ferric oxide to adsorbing ion and an ionic strength of 0.1 M were assumed. (Data from Ref. 9).