IN-SITU REMEDIATION OF HEAVY METALS USING SULFUR-BASED TREATMENT TECHNOLOGIES

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THE METALS PROBLEM: Highly toxic and highly soluble metals are contained in numerous waste streams including those from power, chemical, electronics facilities, general manufacturing plants, and mining facilities. Lead, chromium, arsenic, zinc, cadmium, copper, and mercury are the most common metal contaminants found on remediation project sites (US EPA, October, 2000). Cyanide is a common inorganic contaminant as well. Metal concentrations in excess of established health guidelines have been shown to create significant health risks to humans.

PAST REMEDIATION OPTIONS: In the past, conventional remediation of soil impacted by heavy metals has relied on excavation, which was expensive and disruptive. In addition, moving the soil only moved the problem, without treating the soil or reducing the long-term liability. For groundwater, pump and treat remediation relied on pumps to remove groundwater from the aquifer through a series of extraction wells or trenches. The extracted water was then treated above ground or disposed of off-site. Pump and treat methods fail to address the source of the contamination in the vadose zone. Although the construction of passive permeable treatment walls containing zero valent iron filings can reduce some metals to less toxic varieties, the passive barriers are expensive and do not treat source areas (Thomasser and Rouse, 2001).

High-pressure remediation injection lance system for metals stabilization treatment.

Metal	Arsenic	Lead	Copper	Zinc
Treatment notes:	Acid medium only forms various arsenic sulfides; pH>7; arsenic-sulfur compounds are soluble; pH<7 the compounds are insoluble.	Wide Range (pH: 4-9); forms lead sulfide	Close to neutral (Optimal pH; 5-7); forms copper sulfide	Wide range (pH: 4-9); forms zinc sulfide
Metal	Cadmium	Molybdenum	Uranium	Cyanide
Treatment notes:	Wide range (pH: 4-9); forms cadmium sulfide	Wide range (pH: 4-9); forms molybdenum sulfide	Wide range(pH: 4-9); forms uranium sulfide	Chemical conversion produces thiocyanate*

**Thiocyanate can be biotreated, or it can be treated with lime, producing calcium carbonate, gypsum and ammonia. Chromium (Cr VI) can be treated with calcium polysulfide, and the Cr (VI0 is reduced to Cr (III), which is then precipated as chromium hydroxide.*

SULFUR-BASED TREATMENT TECHNOLOGY: Recently, sulfur-based metals treatment technologies have been the focus of an increasing number of research studies and commercial applications for treating metals contamination in soil and groundwater. The solubility of these metals is highly pH dependent. A reagent, such as calcium polysulfide (CaS_4; brand name: Cascade®), precipitates the highly soluble metals (arsenic, lead, copper, zinc, cadmium, molybdenum, uranium) as less soluble, and non-toxic sulfides. As shown in Figure 1, metal sulfides are far less soluble than metal hydroxides. Metal hydroxides change solubility with changes in pH. Metal sulfides remain insoluble within a pH range of about 5 to 9.

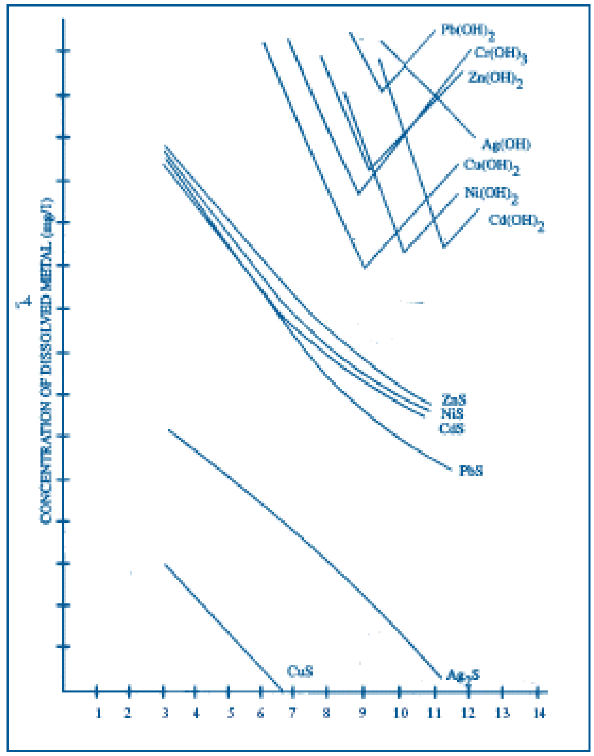

Figure 1– *Solubility of Metal Hydroxides and Sulfides as a Function of pH (EPA, 1981)*

Hexavalent chromium is reduced from Cr (VI) to trivalent chromium, Cr (III), and then precipitates as chromium hydroxide (US EPA, October, 2000). The cyanide ion, a common inorganic contaminant, reacts with calcium polysulfide to form thiocyanate, which is further degraded with excess calcium polysulfide or lime to ammonia, calcium carbonate and gypsum, eliminating the CN^- radical.

Cascade® has a pH of 11.3 to 11.5, a specific gravity of 1.273 and is deep orange-red solution. Calcium polysulfide is water soluble and comes as 29% active ingredient solution. Polysulfide has been used to conduct *in situ* remediation of uranium, selenium, arsenic, copper, and chromium contamination.

REMEDIATION PHASES: The authors recommend a review of the existing physical and chemical data, including pH, permeability, lithology, and water depth, concentrations of metals, alkalinity, and other data and a simple bench test which can take a few days. Pilot scale tests are recommended to verify treatability. The *in-situ* pilot-scale or full-scale remediation can be performed shortly after the bench test results are available.

DELIVERY SYSTEM: *In-situ* delivery is one of the key factors in successful remediation, since the treatment chemicals must fully contact and react withthe contaminant. High-pressure injection technology, also called jetting, uses a direct push method as well as a specialized lance system for the delivery of treatment chemicals has proved successful for metals remediation (Jacobs, 2001). Adjustments to pH of the treatment liquids can enhance the metals precipitation process.

Installation of treatments liquids using the high-pressure Remediation Injection Process (RIP®)

CASE STUDY:
UKIAH, CALIFORNIA WOOD TREATING PLANT: A high pressure injection delivery system was developed for a Cr (VI) project in Ukiah, California. The site had been subjected to more than a decade of conventional pump and treat remediation, with little impact on the contamination. Up to 300 gallons (up to 20 gallons per minute) of calcium polysulfide was injected into the groundwater in 114 injection ports to a maximum depth of 20 feet in 1997. The result was an almost instant decline in chromium concentration in the groundwater (Thomasser and Rouse, 2001). A second injection program was used to address local areas of remaining contamination. The site is now conducting a program of monitoring of existing wells.

SUMMARY:

Sulfur based metals treatment technologies show promise in being able to precipitate toxic and highly soluble metals into less soluble, less toxic metal sulfides for arsenic, lead, copper, zinc, cadmium, molybdenum, and uranium. Mobile hexavalent chromium is reduced to the insoluble chromium hydroxide, while cyanide forms less toxic thiocyanate. In all cases, treatment is pH dependent and can be an attractive remedial action compared to more conventional metals remediation methods such as excavation and pump and treat.

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