Environmental Solutions

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Treatment of Heavy Metals in Soil & Groundwater with Iron/Iron-sulfide-based MetaFix® Reagents

A New Approach to Treatment of Heavy Metals

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Presentation Outline

- Background: Definitions, MetaFix® composition, features, dosage, and application methods
- Chemistry: Solubility and Stability of Heavy Metal Hydroxides, Heavy Metal Sulfides, and Heavy Metal Iron Sulfides
- Treatment Mechanisms: Focus on major heavy metals
- Bench-scale Tests: Some results from comparisons of MetaFix and other reagents, mixed metals, and metals with cVOCs
- Case Studies: USA and China
- Questions & Answers

Some Definitions

- **Adsorption**: Binding of a soluble species on the surface of a solid, driven by surface forces.
- **Coprecipitation**: A form of adsorption in which soluble species are bound onto the surfaces of a precipitating solid phase. The operative adsorption force can be chemi-, physico-, Van der Waal's, or by dipole-dipole interactions.
- **Precipitation**: Conversion of a soluble metal into an insoluble form by addition of a chemical to create a supersaturated environment. An example is conversion of aqueous lead (Pb^{+2}) into lead sulfide (Galena) by enriching the contaminated environment with sulfide (S^{-2}).
- **Solidification/Stabilization**: Incorporation of a metal into a cement-like matrix to make it less subject to leaching. An example is treating metal contaminated sludge with Portland cement and fly ash.

MetaFix® Reagents

MetaFix® is a new family of injectable reagents designed to treat heavy metals in soil and groundwater using chemical reduction, precipitation, and adsorption.

- Reagents do not rely on *in situ* biological sulfate reduction or carbon metabolism so their performance is not inhibited by high toxicity (e.g., alkalinity, acidity, salts, high COI concentrations)
- Composed of ZVI, iron sulfides, iron oxides, alkaline earth carbonates, and activated carbon
- Treatment results in conversion of aqueous heavy metals to low solubility mineral precipitates with broad pH stability
- Unique made-to-order formulations for all commonly found metallic contaminants and site conditions

MetaFix® Reagents

- Low Dosage Rates
  - 1.0% - 4.0% (w/w) for soil
  - 0.1% - 1.0% (w/w) for groundwater

- Application by soil mixing, trenching, or injection (40 – 50% solids)

- Low cost treatability testing to determine dosage and enable custom formulation ($2,000)




Composition of MetaFix® Reagents

- **ZVI**: reductant, source of Fe^{+2}
- **Iron Sulfides**: source of sulfide and Fe^{+2}, catalyst, provide both cationic and anionic adsorption surfaces, can make aqueous iron more reactive
- **Iron Oxides**: provide both cationic and anionic surfaces, adatoms of ferrous iron are very reactive
- **$CaCO_3$**: pH balance and source of carbonate
- **Activated Carbon**: strong adsorbent for organically-bound metals including arsenic, mercury, and nickel.
- **Supplementary reagents**: ion exchange, pH modification when needed, inclusion based on results of bench-scale work optimization

MetaFix® Reagents

Metal	Precipitation as Metal Hydroxides or Iron Metal Hydroxides	Precipitation as Metal Sulfides/Iron Metal Sulfides	Adsorption and Co-precipitation with Iron Corrosion Products	Precipitation as Metal Carbonates	Adsorption of organo-metal species
As (III, V)		●	●		●
Cr(VI)	●		●		
Pb, Cd, Ni	●	●	●	●	●
Cu, Zn	●	●	●		
Se	●	●	●		
Hg		●	●		●

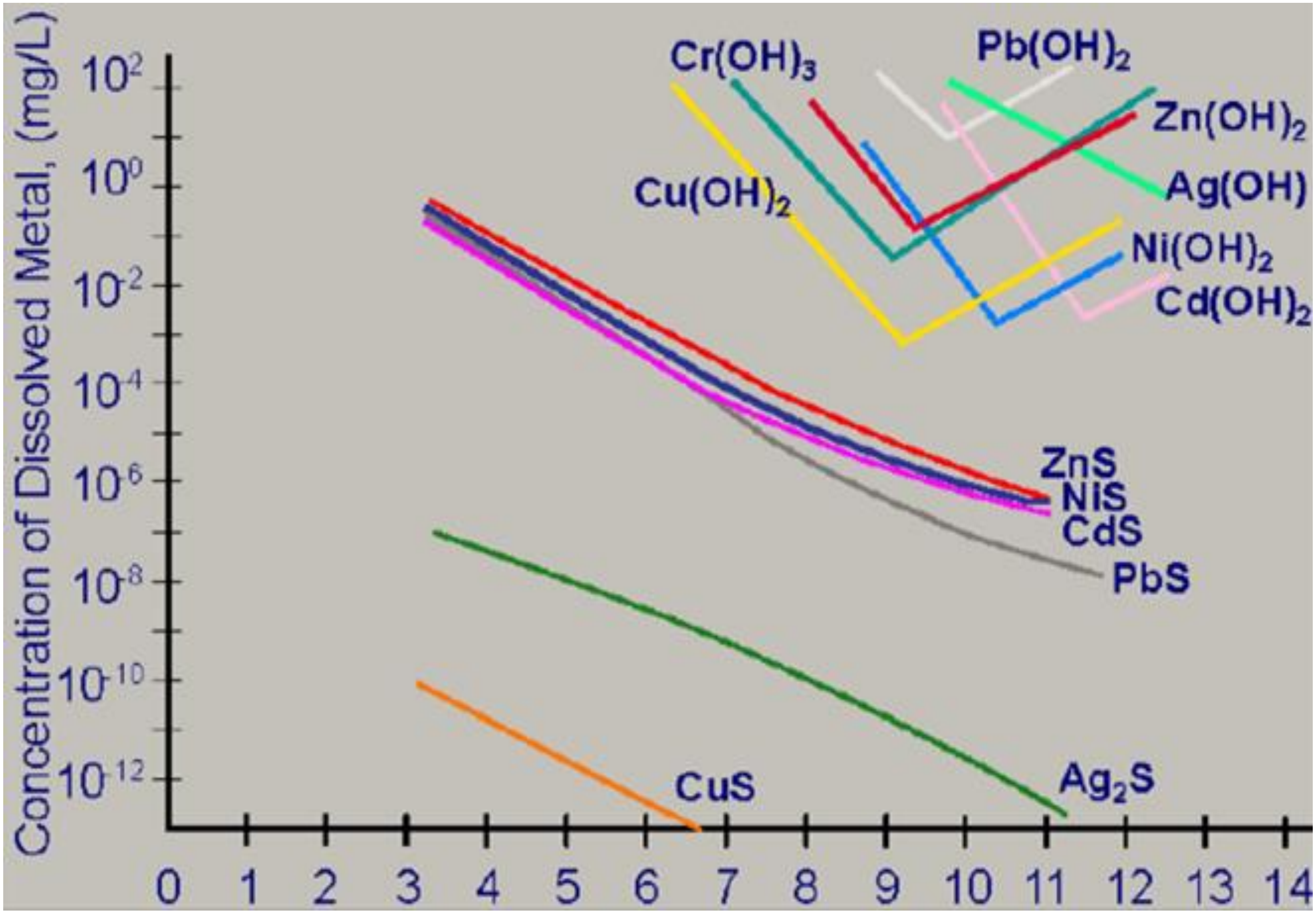
Metal Sulfides *vs* Metal Hydroxides

Table 2-1
Theoretical Solubilities of Hydroxides, Sulfides, and Carbonates of Selected Metals in Pure Water at 25°C (All Units are mg/L)

Metal	*As Hydroxide*	*As Sulfide*	*As Carbonate*
Cadmium (Cd^{2+})	2.3×10^{-5}	6.7×10^{-10}	1.0×10^{-4}
Chromium (Cr^{+3})	8.4×10^{-4}	No precipitate	—
Cobalt (Co^{2+})	2.2×10^{-1}	1.0×10^{-8}	—
Copper (Cu^{2+})	2.2×10^{-2}	5.8×10^{-18}	—
Iron (Fe^{2+})	8.9×10^{-1}	3.4×10^{-5}	—
Lead (Pb^{2+})	2.1	3.8×10^{-9}	7.0×10^{-3}
Manganese (Mn^{2+})	1.2	2.1×10^{-3}	—
Mercury (Hg^{2+})	3.9×10^{-4}	9.0×10^{-20}	3.9×10^{-2}
Nickel (Ni^{2+})	6.9×10^{-3}	6.9×10^{-8}	1.9×10^{-1}
Silver (Ag^{+})	13.3	7.4×10^{-12}	2.1×10^{-1}
Tin (Sn^{2+})	$1.1. \times 10^{-4}$	3.8×10^{-8}	—
Zinc (Zn^{2+})	1.1	2.3×10^{-7}	7.0×10^{-4}

EPA 625/8-80-003, 1980

Aqueous Solubilities of Heavy Metal Hydroxides, Iron Hydroxides, and Sulfides



EPA 625/8-80-003, 1980; Banerjee et al., 2013. Veolia Water Inc.

Solubility of Mixed Fe-Cr Oxyhydroxides

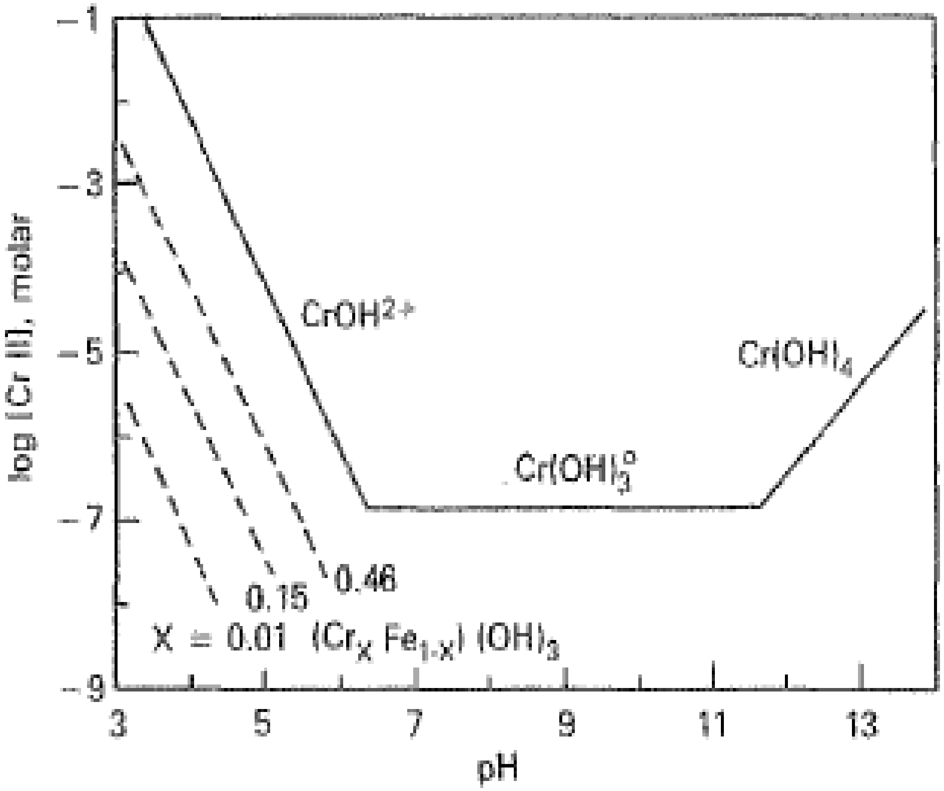


Fig. 3. Solubility-controlling solids of Cr(III). Solid line represents $Cr(OH)_3$. Dashed lines represent $(Cr,Fe)(OH)_3$ at different values of $Cr(OH)_3$ mole fractions (x).

Reduction of Cr(VI) to Cr(III) by Fe^{+2} is rapid (minutes) and the main product is a mixed Fe-Cr oxyhydroxide. Precipitates with more Fe/less Cr have lower solubility but all are much less soluble than $Cr(OH)_3$ and have solubility well below most remedial standards for groundwater. The free energy of formation for Fe-Cr oxyhydroxide is lower than that for $Cr(OH)_3$, so it will be preferentially formed when free Fe^{+2} is available.

Rai et al., 1989. Sci. Tot. Env. 86:15-23.

Oxidation of Cr(III) to Cr(VI)

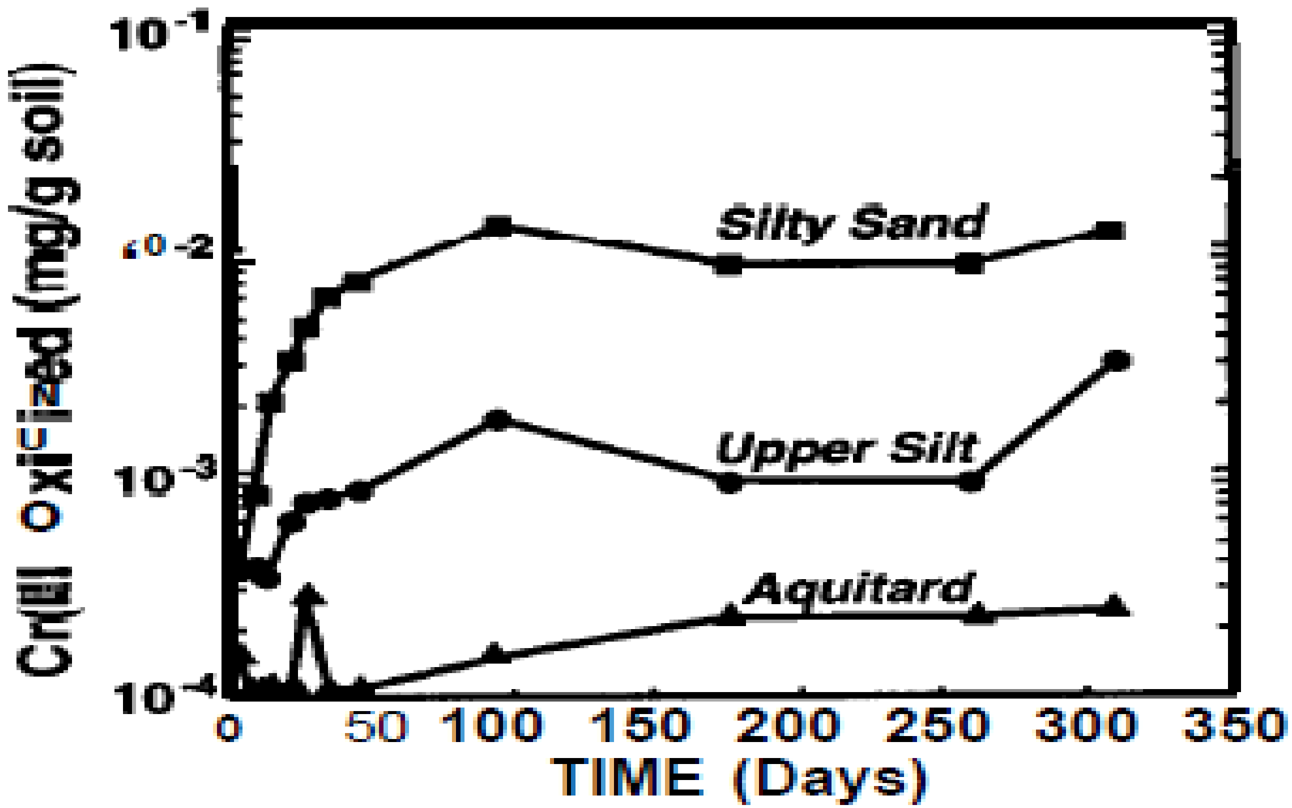


Figure 5. Cr(III) oxidized to Cr(VI) in a suspension of Willamette silt loam.

Relatively slow process that takes place over several months, but resulted in aqueous Cr(VI) concentrations as high as 7 mg/L (Palmer and Wittbrodt, 1990; Palmer and Puls, 1994).

EPA/540/5-94/505

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Chromium Treatment with ZVI

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- Reduction of Cr^{+6} to Cr^{+3} by ZVI is followed by its precipitation as mainly mixed Fe-Cr oxyhydroxides with a mineral structure similar to that of goethite (α-FeOOH) with some Cr^{+3} also deposited into a hematite-like structure (Fe_2O_3).[1,2]
- Solubility of Fe-Cr oxyhydroxides is less than 0.05 µg/L over a broad pH range of 5.0 to 12.0[3]

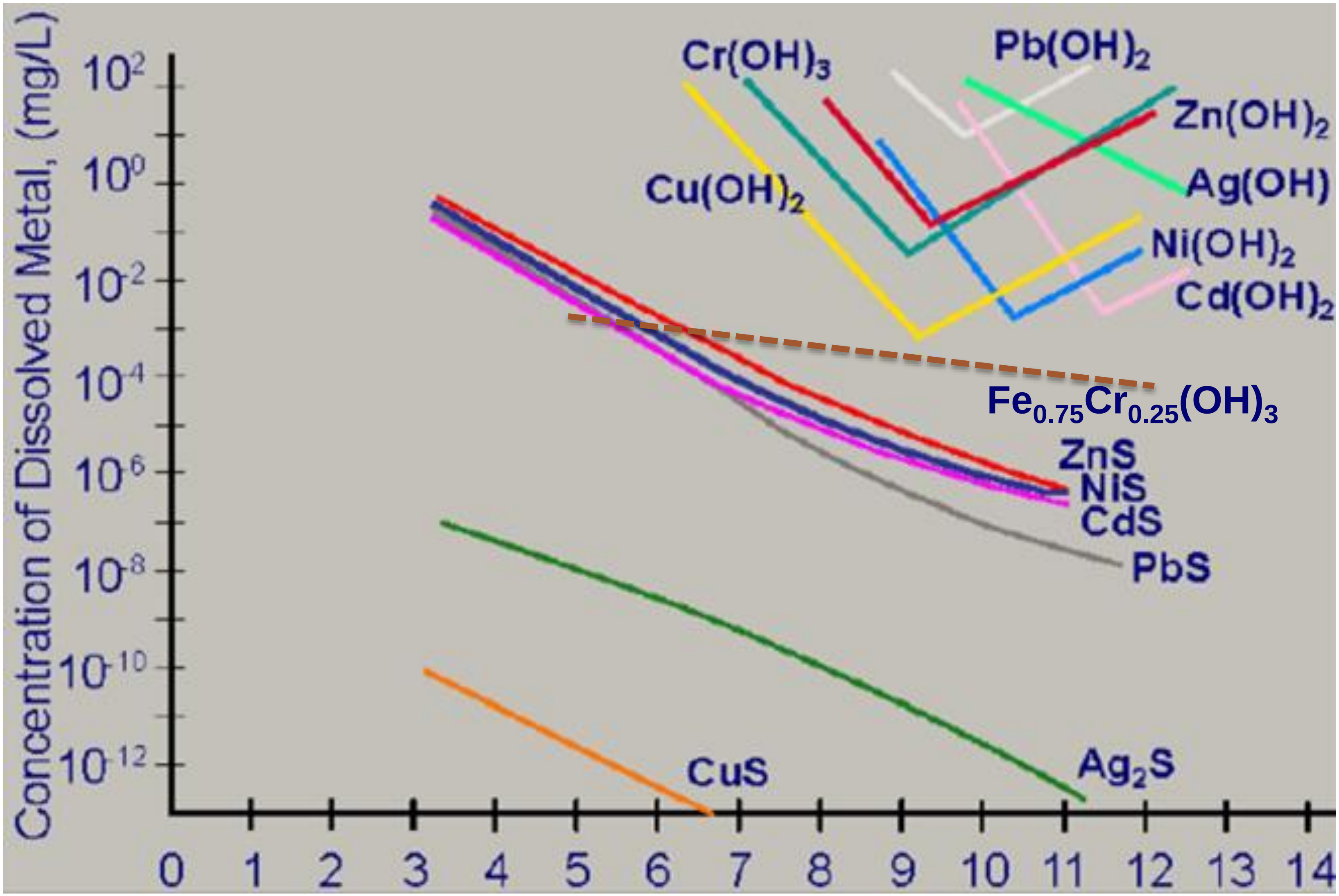
$$Fe^0_{[solid]} + CrO_4^{2-} + 8\,H^+ \longrightarrow Cr^{+3} + Fe^{3+} + 4\,H_2O \quad (1)$$

$$(1-x)\,Fe^{3+} + (x)\,Cr^{3+} + 4\,H_2O \longrightarrow Fe_{(1-x)}Cr_{(x)}OOH_{[solid]} + 3\,H^+ \quad (2)$$

- The Fe-Cr oxide which has the form of hematite (Fe_2O_3) is primarily deposited on the surface of precipitates[2]

1. Blowes et al., 2000. J. Contam. Hydrol. 45: 123-137
2. Tratnyek et al., 2003. In: Tarr, M. Chemical Degradation Methods for Wastes and Pollutants
3. Eary and Rai. 1988. Env. Sci. Technol. 22:972-977.

Aqueous Solubilities of Heavy Metal Hydroxides, Iron Hydroxides, and Sulfides



EPA 625/8-80-003, 1980; Banerjee et al., 2013. Veolia Water Inc. Environ. Sci. Technol. 1988, 22, 972-977

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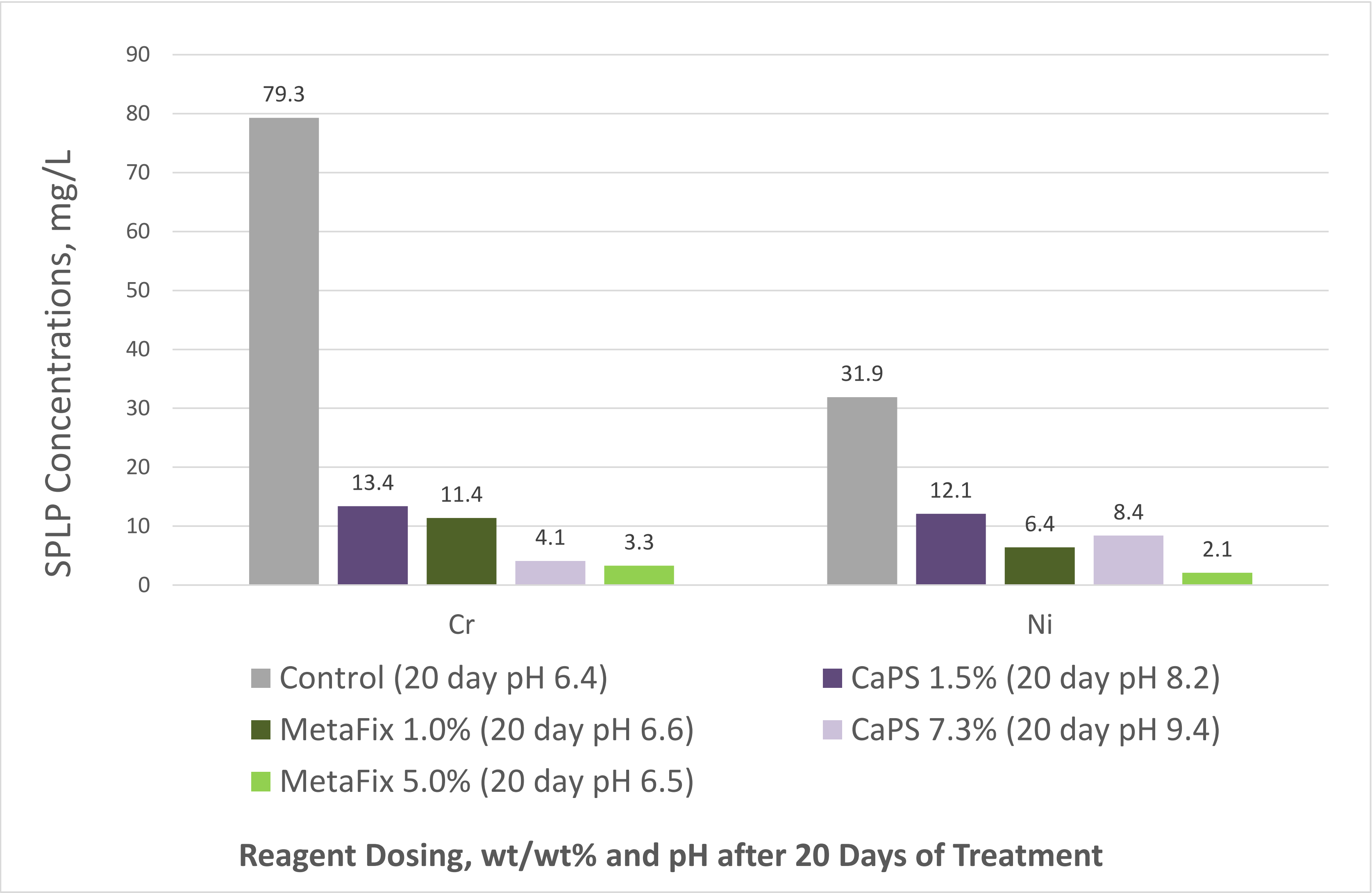
Independent Evaluation of MetaFix® Reagent for Treatment of Chromium and Nickel

- Bench-scale treatability studies on soil and groundwater impacted with chromium VI (Cr^{+6}, commonly referred to as "hexavalent Cr") and nickel (Ni) associated with historical plating operations at a site located in Michigan. The treatability study was completed in two phases.

- The first phase of the study consisted of a series of batch reactors with the reagents to test their effectiveness in reducing groundwater concentrations of the metals and reducing future leaching of the metals. The purpose of the batch studies was to determine amendments and amendment doses that might be suitable for treatment of the source area. The "leachability" of Cr^{+6} and Ni in soil samples was measured using the Synthetic Precipitation Leaching Procedure (SPLP).

- The second phase of the study tested a subset of the amendments using flow-through column reactors, selected based on their performance in the batch tests. The purpose of the column reactors was to evaluate selected amendments for their potential to be used in a permeable reactive barrier (PRB) near the Site boundary, designed to reduce dissolved phase Cr^{+6} and Ni groundwater impacts at the Site.

Influence of MetaFix and calcium polysulfide on SPLP chromium and nickel in soil/groundwater slurry

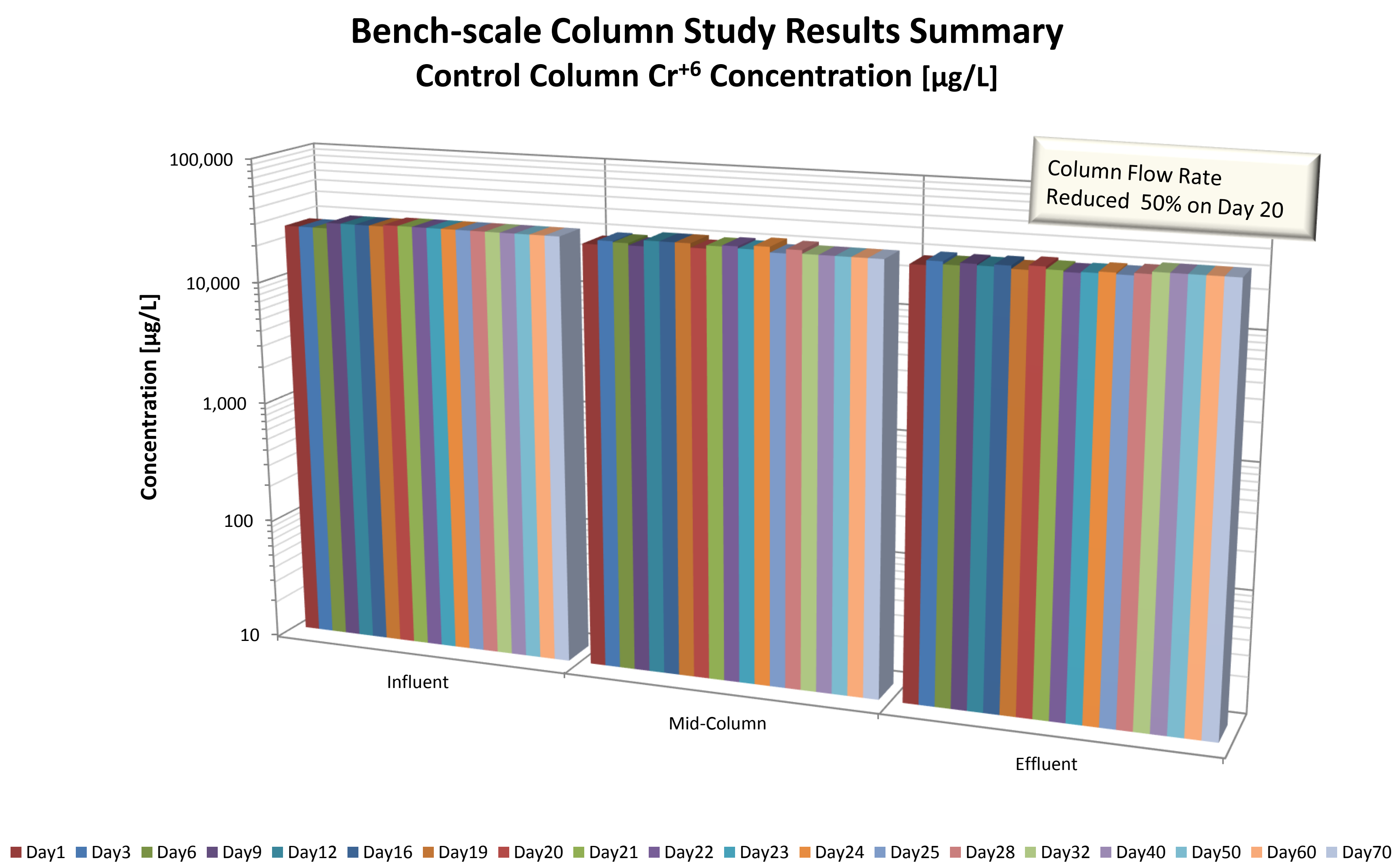


D. Cassidy, WMU. , D. Gray AECOM. 2014

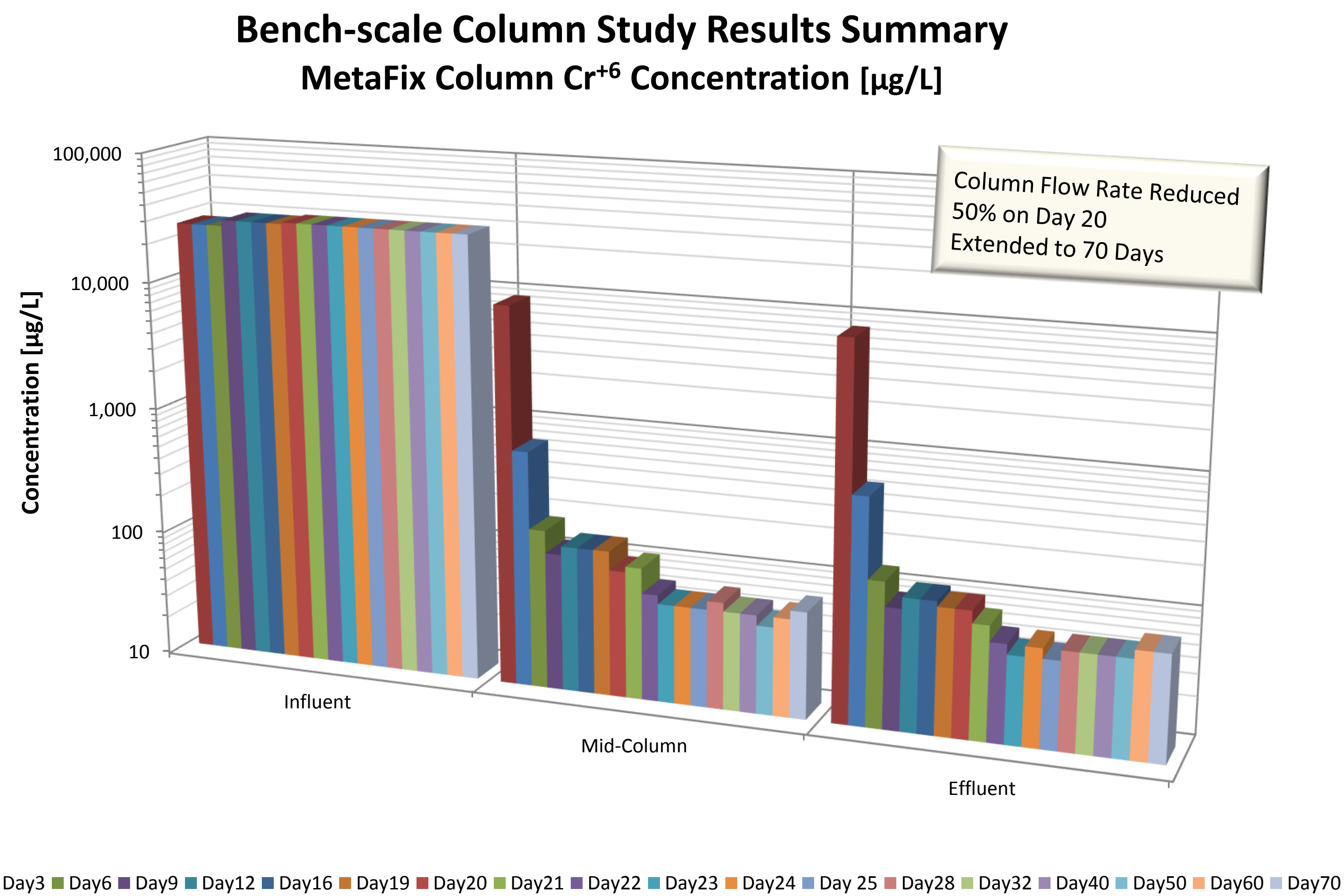
Phase II Flow-through Columns

Site groundwater flow set to 1.2 ft/day for the first 20 days then reduced to 0.6 ft/day for the final 50 days: total of 54 pore volumes in 70 days.

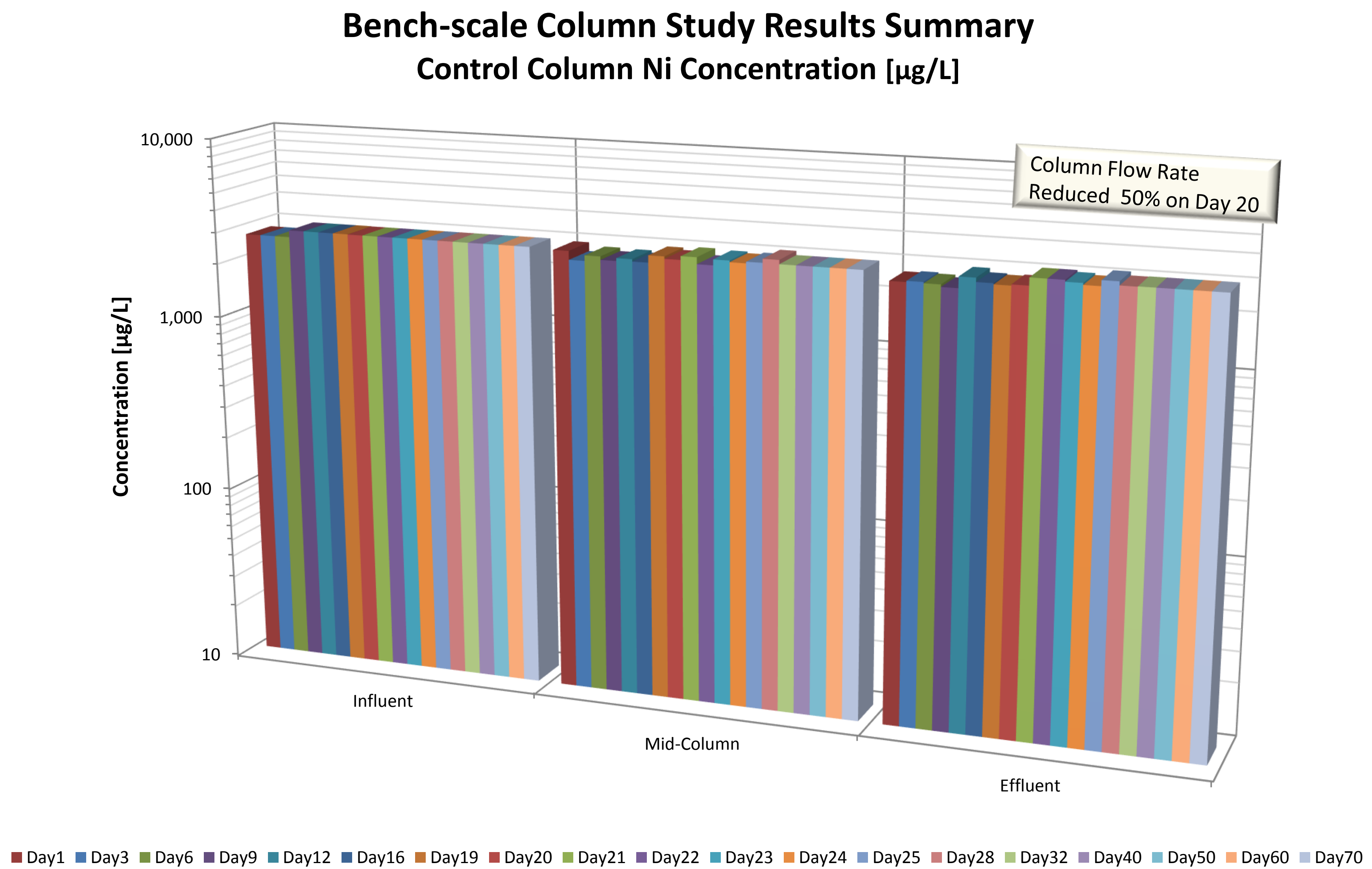
Independent Evaluation of MetaFix™ Phase II Chromium Results: Control



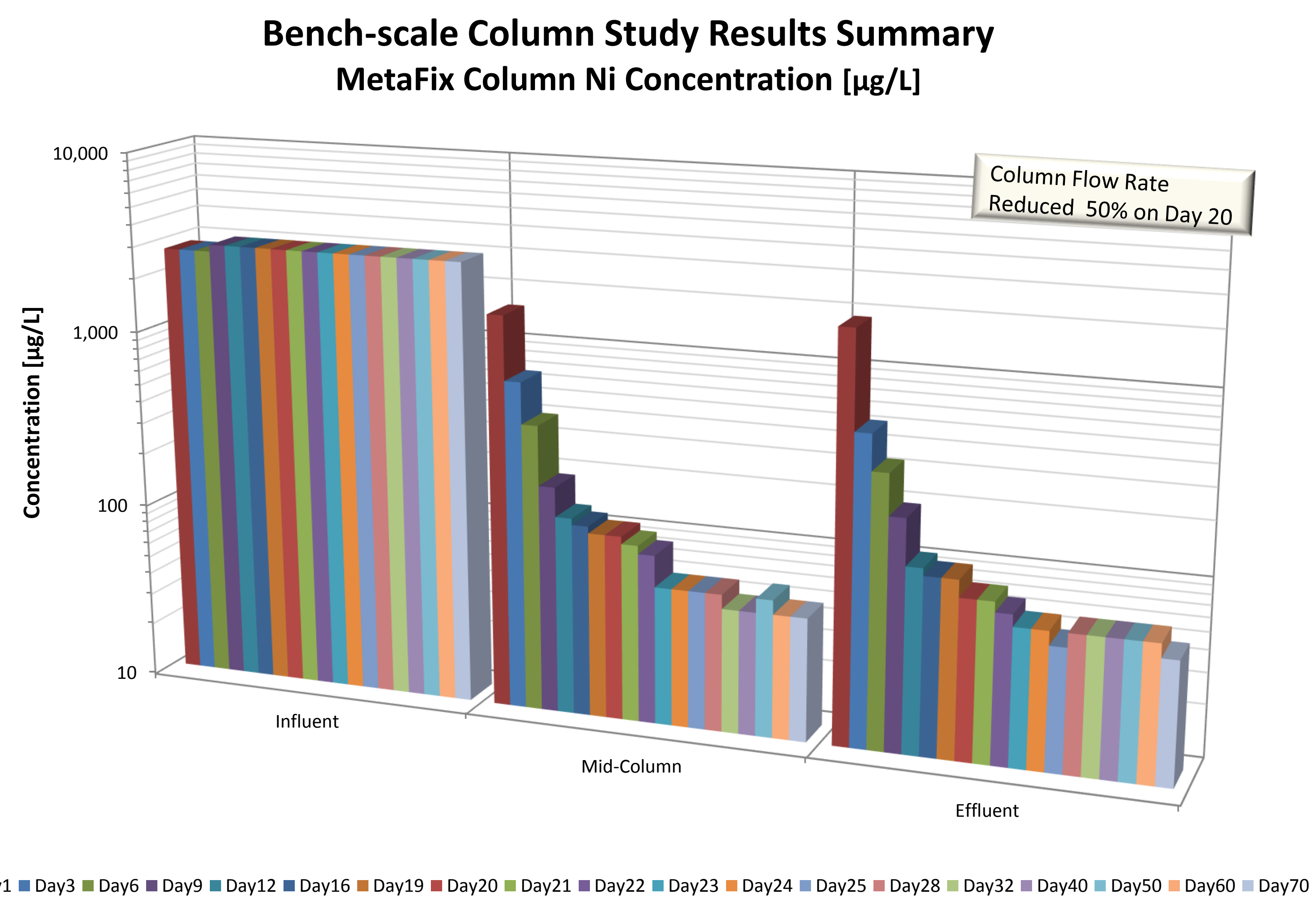
Independent Evaluation of MetaFix Phase II Chromium Results: MetaFix



Independent Evaluation of MetaFix
Phase II Chromium Results: Control



Independent Evaluation of MetaFix
Phase II Chromium Results: MetaFix



Influence of EHC Metals and MetaFix on TCLP lead and arsenic (WA Site)

Sample ID	Total Metals (mg/kg)		TCLP-Metals (mg/L)	
	Arsenic	Lead	Arsenic	Lead
IAS-1	475	16	2.46	0.083
IAS-2	1570	5.6	4.80	<0.030

Sample ID	Reagent	Dose (wt%)	TCLP-Metals (mg/L)			Percent Reduction (%)	
			Final pH	Arsenic	Lead	Arsenic	Lead
IAS-1	Untreated	0	5.14	2.46	0.083	--	--
	EHC-M	2	4.98	0.042	0.014	98.3	83.1
	EHC-M	4	5.15	0.087	0.019	96.5	77.1
	MetaFix I-6A	2	5.14	0.019	<0.005	99.2	97.0
	MetaFix I-6A	4	5.48	0.009	<0.005	99.6	97.0
	MetaFix I-7	2	5.27	0.017	0.013	99.3	84.3
	MetaFix I-7	4	5.21	0.010	<0.005	99.6	97.0
IAS-2	Untreated	0	5.04	4.80	<0.030	--	--
	EHC-M	2	5.20	0.12	<0.005	97.5	--
	EHC-M	4	5.27	0.13	0.014	97.3	--
	MetaFix I-6A	2	5.33	0.061	0.011	98.7	--
	MetaFix I-6A	4	5.43	0.022	<0.005	99.5	--
	MetaFix I-7	2	5.19	0.033	<0.005	99.3	--
	MetaFix I-7	4	5.24	0.026	0.011	99.5	--

Batch study, 10.0 g soil + 200 mL groundwater, 7 days incubation,

Mixed Metal/cVOC Plumes

Table 1. Influence of control and treatment on heavy metal concentrations.

Biotic Control

Date	Day	Cr (diss) mg/L	Cu (diss) mg/L	Fe (diss) mg/L	K (diss) mg/L	Mg (diss) mg/L	Mn (diss) mg/L	Na (diss) mg/L	Ni (diss) mg/L	Sb (diss) mg/L	Sr (diss) mg/L	Zn (diss) mg/L
10-Apr-14	0	149	0.0317	0.139	1.91	90.9	1.75	296	1.77	< 0.002	0.438	0.014
		115	0.0331	0.039	1.93	90.8	1.8	294	1.88	< 0.002	0.441	0.01
9-Jul-14	90	106	0.0225	0.064	1.89	93.2	1.55	304	1.7	< 0.002	0.43	0.032
		108	0.0247	0.043	1.85	91.7	1.53	303	1.7	< 0.002	0.432	0.037

MetaFix® I-6

07-May-14	27	0.0027	0.0264	0.526	361	353	10.1	345	0.377	< 0.002	0.345	0.02
		7.94	0.0371	0.121	438	353	3.07	342	0.451	< 0.002	0.243	0.003
04-Jun-14	55	0.002	0.0048	6.17	378	351	10.9	352	0.235	< 0.002	0.262	0.008
		0.0021	0.0056	7.46	366	363	11.2	356	0.231	< 0.002	0.266	0.002
09-Jul-14	90	0.0036	0.0124	18.2	707	525	7.5	399	0.249	< 0.002	0.284	0.008
		0.0025	0.0114	17.4	561	459	7.14	380	0.24	< 0.002	0.316	< 0.002

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Mixed Metal/cVOC Plumes

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Table 1. Influence of control and treatment on VOC concentrations in microcosms.

Biotic Control

Date	Day	TCE mg/L	cDCE mg/L	VC mg/L	Ethene mg/L	Ethane mg/L	CF mg/L	DCM mg/L	CM mg/L	Methane mg/L
10-Apr-14	0	1.6	<0.010	<0.010	<0.010	0.013	0.25	<0.010	<0.010	0.27
		1.6	<0.010	<0.010	<0.010	0.014	0.25	<0.010	<0.010	0.29
04-Jun-14	55	1.5	<0.010	<0.010	<0.010	<0.010	0.25	<0.010	<0.010	0.076
		1.5	<0.010	<0.010	<0.010	<0.010	0.26	<0.010	<0.010	0.079
09-Jul-14	90	1.5	<0.010	<0.010	<0.010	<0.010	0.24	<0.010	<0.010	0.051
		1.5	<0.010	<0.010	<0.010	<0.010	0.27	<0.010	<0.010	0.08

MetaFix® I-6

10-Apr-14	0	1.6	<0.010	<0.010	<0.010	<0.010	0.16	<0.010	<0.010	0.15
		1.4	<0.010	<0.010	<0.010	<0.010	0.16	<0.010	<0.010	0.18
07-May-14	27	0.27	0.02	<0.010	0.029	0.017	0.063	<0.010	<0.010	0.081
		0.62	0.011	<0.010	0.024	0.014	0.12	<0.010	<0.010	0.11
04-Jun-14	55	0.051	<0.010	<0.010	0.052	0.021	0.022	0.017	<0.010	0.099
		0.022	<0.010	<0.010	0.047	0.023	0.011	<0.010	<0.010	0.13
09-Jul-14	90	0.017	<0.010	<0.010	0.046	0.022	<0.010	0.023	<0.010	0.094
		0.013	<0.010	<0.010	0.04	0.023	<0.010	0.021	<0.010	0.12

Confidential Client, Independent Laboratory

MetaFix® Case Study

Ex-situ treatment of Lead-impacted industrial process waste in United States. TCLP lead reduced from 11.7 mg/L to 0.22 mg/L (RG is 0.75 mg/L).

- Direct soil mixing with excavator
- MetaFix dosage at 6.0 % w/w
- Soil water content set to 80% of WHC (wet, not saturated)
- 7 day treatment time
- Earlier attempts at treatment with lime + $FeSO_4$ + fly ash at 40% w/w could not reach the RG

MetaFix® Case Study

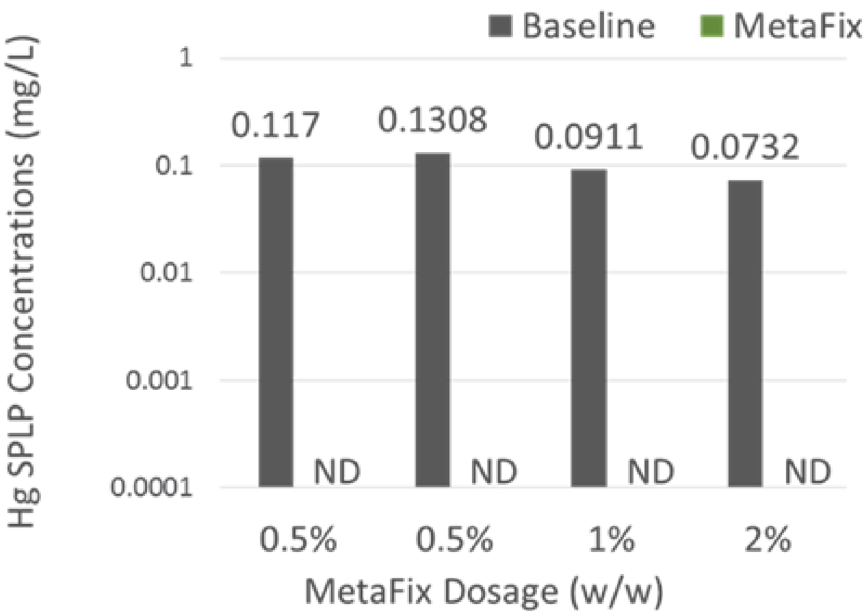
Mercury Treatment to Non-Detect Levels at Former Industrial Site

- Mercuric chloride was used as a catalyst the production of VC at this former chemical plant
- Soil Hg concentrations in the contaminated area ranged from 300 - 420 mg/kg.
- The remedial goal was to stabilize the soil and to then dispose of the treated soil at an offsite landfill and the land will be developed for residential use.

MetaFix® Case Study

Mercury Treatment to Non-Detect Levels at a Former Industrial Site

- A pilot study was conducted on four treatment cells
  - MetaFix applied at 0.5,% 1.0,% and 2.0% (w/w)
  - ~ 50 - 100 m^3 batches
  - MetaFix was spread on soil and mixed with an excavator
  - Further mixing with a screening bucket
  - Water added to adjust the moisture content close to the saturation level while the soil was mixed with an excavator bucket
  - Final mixing was completed with the screening bucket to assure homogeneity
  - Soil was covered to react anaerobically for 7 days



Hg was treated to non-detect level of < 0.0001 mg/L

MetaFix® Case Study

Mercury Treatment to Non-Detect Levels at a Former Industrial Site

- The MetaFix dosage of 0.5% w/w selected for the full scale treatment.
- Full scale implementation utilizes an integrated soil mixing system where soil crushing/screening and reagent dosing/mixing are completed in a single process.
- Treatment time is 7 days and soil is treated in 500 y^3 batches.

MetaFix® Summary

- Heavy metals converted into low solubility mineral precipitates, primarily sulfides and iron sulfides
- Heavy metal sulfides and iron sulfides are stable over a broader pH range than their hydroxide counterparts
- Low susceptibility to rebound
- Simultaneous treatment of heavy metals and chlorinated solvents
- Much lower dosage rates than some alkaline treatment reagents
- Custom-formulations enable successful treatment of even complicated sites
- Low cost treatability study to verify efficacy & develop custom formulations

Questions?

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