Environmental Solutions

PeroxyChem

Reduction, Adsorption, and Precipitation of Heavy Metals by Elemental Iron, Iron Sulfides, and Related Reactive Minerals

A New Approach to Treatment of Heavy Metals

Mike Mueller, Dr. Alan Seech
PeroxyChem Environmental Solutions, Austria
mike.mueller@peroxychem.com

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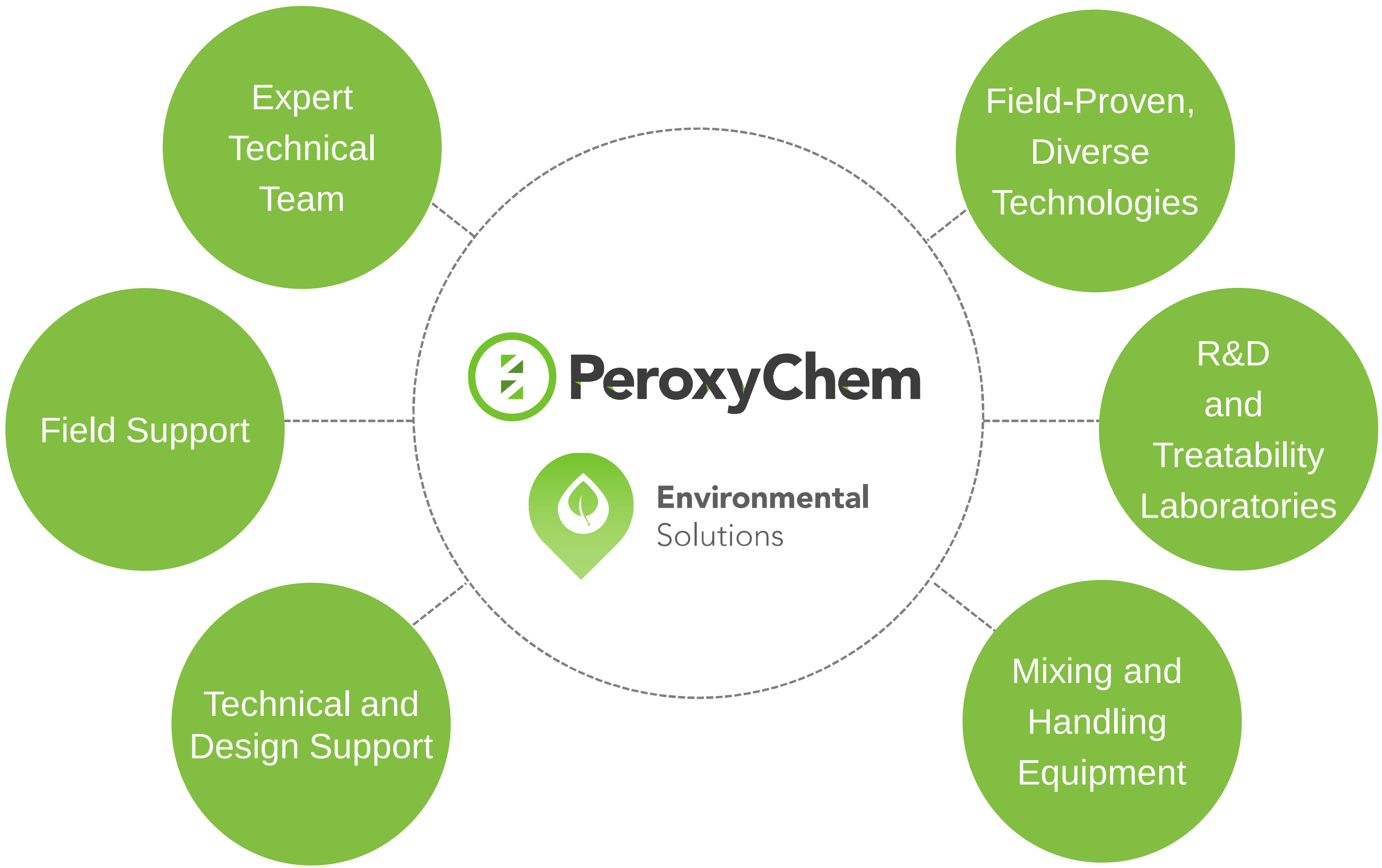
Presentation Outline

- 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: Mercury and Lead

Our business model…



Field-Proven Portfolio of Remediation Technologies for Impacted Soil and Groundwater

***In Situ* Chemical Oxidation**

1. Klozur (persulfates)
2. Klozur CR (persulfate + calcium peroxide)

In Situ Chemical Reduction

3. EHC (ZVI + plant carbon)
4. EHC Liquid (organo-iron + lecithin)
5. Daramend (ZVI + plant carbon)

Aerobic Bioremediation

6. Terramend (nutrients)
7. PermeOx Ultra (calcium peroxide)

Reduction, Adsorption, Precipitation

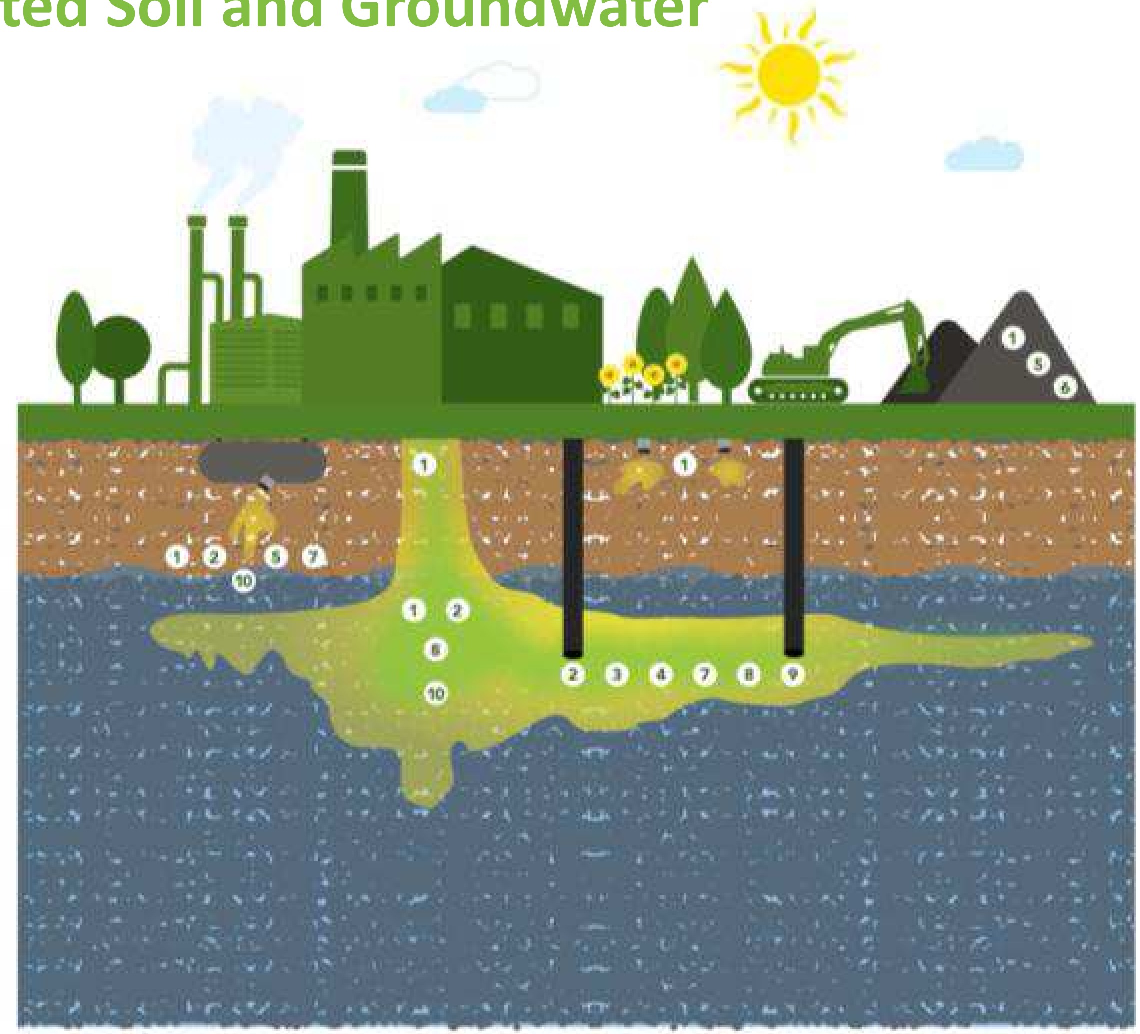
8. EHC Metals and MetaFix

Enhanced Reductive Dechlorination

9. ELS (lecithin)

NAPL Stabilization/Mass Flux Reduction

10. ISGS (modified permanganate)



Some Definitions

- **Adsorption**: Binding of a soluble species on the surface of a solid, driven by surface forces.
- **Co-precipitation**: 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 Waals, or by dipole-dipole interactions. An example is capture of heavy metals during precipitation of iron corrosion products such as iron oxides.
- **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 by reducing permeability. The techniques are aimed at physico-chemical fixation and immobilization of metals in-situ. E.g. treating metal contaminated soil or sludge with lime, Portland cement or fly ash.

MetaFix® Reagents

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

1. Reagents do not rely on *in situ* biological sulfate reduction or carbon metabolism so their performance is not inhibited by high acute toxicity (e.g., alkalinity, acidity, salts, high COI concentrations)

2. Composed of ZVI, iron sulfides, iron oxides, iron oxyhydroxides, alkaline earth carbonates, aluminosilicates, and activated carbon

3. Treatment results in conversion of aqueous heavy metals to low solubility mineral precipitates with broad pH stability

4. Customized formulations provided for special site conditions such as high acidity or alkalinity

Composition of MetaFix Reagents

- **ZVI**: A reductant; Long lasting source of Fe^{+2}
- **Iron Sulfides**: A source of soluble sulfide and Fe^{+2}, Acts as a catalyst; Provides both cationic and anionic adsorption surfaces; Can make aqueous iron more reactive
- **Iron Oxides & Oxyhydroxides**: Provide both cationic and anionic surfaces; Adatoms of ferrous iron are very reactive
- **Calcium Carbonate**: For pH balance and source of carbonate
- **Activated Carbon**: A strong adsorbent to address organically-bound metals including arsenic, mercury, and nickel
- **Supplementary reagents**: For ion exchange, pH modification when needed; Inclusion based on results of bench-scale work optimization

MetaFix Reagents

Low Dosage Rates

- 1.0% - 6.0% (wt/wt) for soil
- 0.1% - 1.0% (wt/wt) for groundwater

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

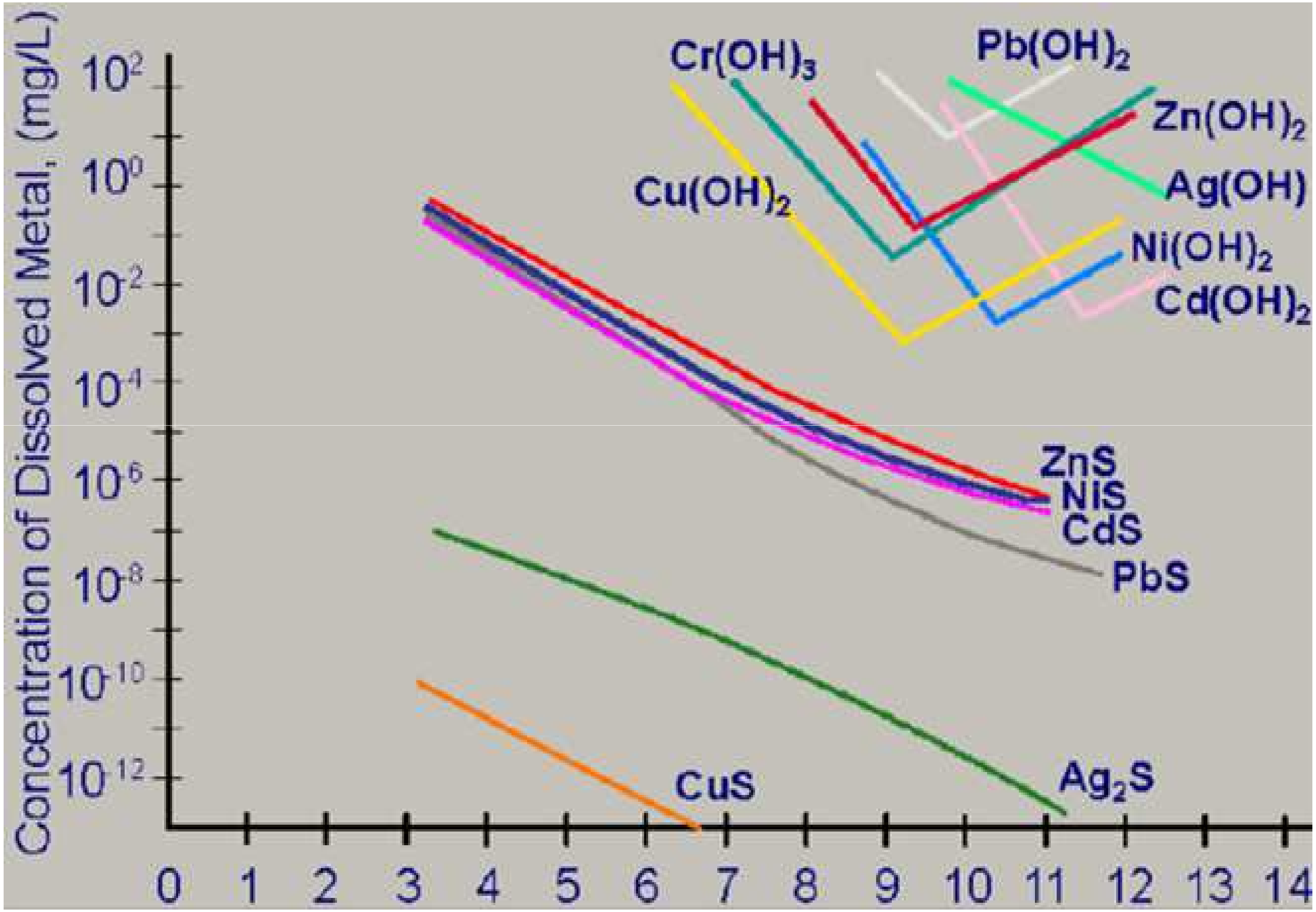
Low-cost Treatability Testing available

- Goals are to determine proper dosages, and
- to inform the bespoke formulation required (€ 1900 / 3 weeks)

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		●	●		●

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



EPA 625/8-80-003, 1980; Environ. Sci. Technol. 1988, 22, 972-977

Chromium Treatment with ZVI

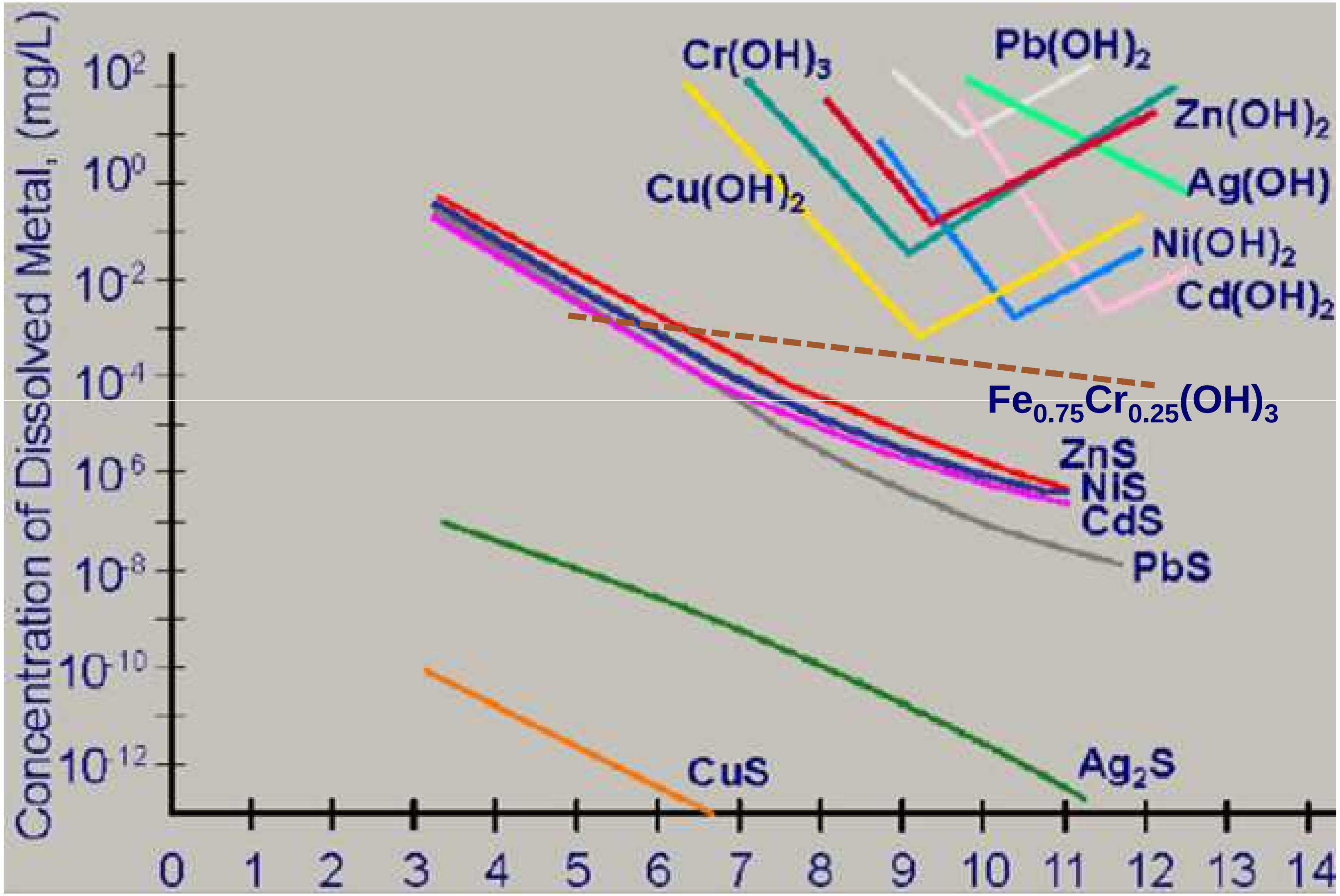
- Reduction of Cr^{+6} to Cr^{+3} by ZVI is followed by its precipitation as mainly mixed Fe-Cr oxyhydroxides with a mineral structure similar to that of goethite (α-FeOOH) with some Cr^{+3} also deposited into a hematite-like structure (Fe_2O_3).[1,2]
- Solubility of Fe-Cr oxyhydroxides is less than 5 ppb over a broad pH range of 5.0 to 12.0[3]

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

- 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

Daniel Cassidy, Ph.D.
Western Michigan University
Department of Geosciences
1187 Rood Hall
Kalamazoo, Michigan USA 49008-5241
Phone: 1-269-873-0016
E-mail: daniel.cassidy@wmich.edu

Doug Gray, CGWP
AECOM
Innovative Remedial Technologies Group Manager,
Midwest DCS
Phone: 1-216-622-2283
1375 Euclid Avenue, Suite 600
Cleveland, Ohio USA 44115
doug.gray@aecom.com

Influence of MetaFix and Calcium Polysulfide on SPLP Chromium and Nickel in soil/groundwater slurry

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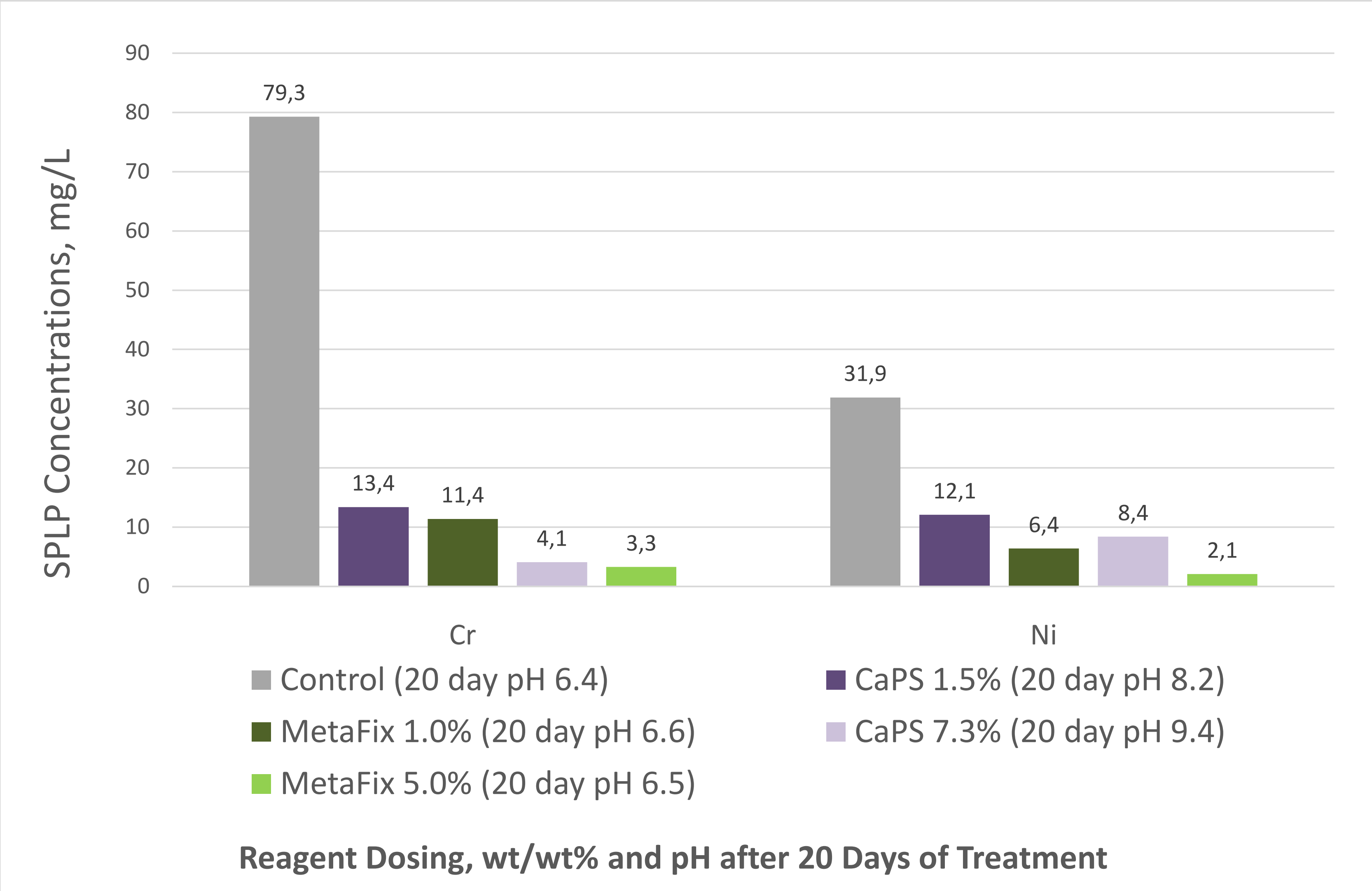

D. Cassidy, WMU. , D. Gray AECOM. 2014

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Influence of “EHC-Metals” and “MetaFix” reagents on TCLP Lead and Arsenic

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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

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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

Mixed Metal/cVOC Plumes

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

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	<0.010	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

MetaFix Case Study 1: Mercury

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

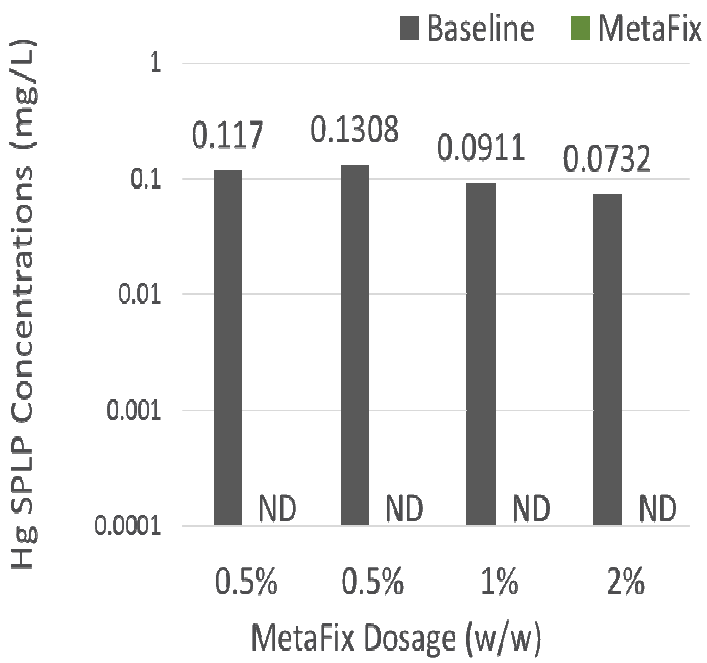
- Mercuric chloride was used as a catalyst at former chemical industry facility.
- Total soil Hg concentrations ranged from 300 - 420 mg/kg.
- Remedial Goal to stabilize the soil, and then dispose treated material at an offsite landfill.
- Site to be developed for residential use, mandating SPLP Mercury of < 1 ppb.

MetaFix Case Study: Mercury

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

Pilot-scale demonstration was conducted in four treatment cells

- MetaFix dosages of 0.5%, 1.0% and 2.0% (w/w) were compared in 100 ton batches
- MetaFix blended with soil using excavator bucket followed by additional mixing with a screening bucket
- Water added to adjust the moisture content close to the saturation level
- Soil was covered with a tarp during 7 day reaction period
- No difference observed between dosages, so the lowest dosage (0.5% w/w) selected for use at full-scale



Hg treated to non-detect levels of <1.0 µg/L in response to low, moderate, and highest dosages

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MetaFix Case Study: Mercury

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

Full-scale Treatment Process

- The MetaFix dosage of 0.5% (w/w) used 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
- 500 ton batches
- Treatment time of 7 days
- Repeated achievement of the site specific remedial goal for mercury (1.0 µg/L SPLP)

MetaFix Case Study 2: Lead

Ex Situ Treatment of Industrial Process Waste

- Sand blasting residue from remediation of buildings painted with lead based paint
- MetaFix dosage at 6.0 % (w/w)
- Direct soil mixing with excavator
- Soil water content set to 80% of WHC (wet, not saturated)
- 7 day treatment time
- Previous attempts at treatment with lime + iron salts + fly ash at 40% (w/w) were ineffective
- Remedial objective for lead was achieved (0.75 mg/L TCLP)

TCLP lead reduced from 11.7 mg/L to 0.22 mg/L

Key MetaFix product-family Advantages

1. Lower solubility of heavy metal precipitates based on iron and iron-sulfide chemistry provides high assurance of attaining remedial goals.

2. Not dependent on alkalinity for removal of metals. Broad pH range stability of metal precipitates based on iron and iron-sulfide chemistry reduces the danger of rebound.

3. Proven ability to address multiple heavy metals including:
   Al, As, Cd, Cr, Cu, Hg, Ni, Pb, Se, Tc(VII), V, and Zn. Superior Cr(VI) treatment with the formation of more stable mixed (Cr, Fe) hydroxides.

4. Ability to treat heavy metals successfully at sites where the soil/groundwater has high acute toxicity.

5. Capable of treating comingled plumes. Simultaneous removal of soluble heavy metals, and dehalogenation of chlorinated solvents.

6. Longevity of treatment (micro-scale ZVI and FeS estimated > 10 years).

7. Low overall treatment costs based on lower reagent dosing rates, as low as 0.1% - 4% (wt/wt), versus other metals treatment technologies.

Thank you for your attention.

E: mike.mueller@peroxychem.com
T: +43 664.180.3060

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