An Innovative Approach to Treat Heavy Metals in Soil and Groundwater Using Elemental Iron, Iron Sulfides, and Related Reactive Minerals

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Presentation Outline

- Background: History, Definitions, MetaFix® Reagent composition, features, dosage, and application methods
- Chemistry: Solubility and Stability of Heavy Metal Hydroxides *vs*. Heavy Metal Sulfides *vs*. Heavy Metal Iron Sulfides
- Removal Mechanisms for major heavy metals
- Bench-scale Tests: Some results from comparisons of MetaFix® and other reagents, mixed metals, and metals with cVOCs
- Case Study
- Questions & Answers

MetaFix® Reagents

MetaFix® is a *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 iron-bearing reducing agents, pH modifiers and related additives
- Treatment results in conversion of aqueous heavy metals to low solubility mineral precipitates with broad pH stability
- Adsorption on iron corrosion products and co-precipitation with iron oxides and iron oxyhydroxides is also an important aspect of the process
- Formulations are customized for site-specific conditions

MetaFix Chemistry

- Mechanisms involved will vary based on solution chemistry:
  - pH, Eh, supply of reactive iron, sulfides, carbonates
  - reactive surfaces (i.e., iron oxides and oxyhydroxides).

- Reductive precipitation is important in the immobilization of both arsenic and chromium in soil or groundwater treated with MetaFix. This involves:
  - reduction of arsenate [As(V)] anions to arsenite [As(III)], and
  - reduction of hexavalent chromium (Cr^{6+}) to trivalent chromium (Cr^{3+}).

- These reduction processes are facilitated by two components of MetaFix. Zero valent iron (ZVI) and iron sulfides, both of which are powerful reductants (electron donors), as indicated in the following redox half-reactions:

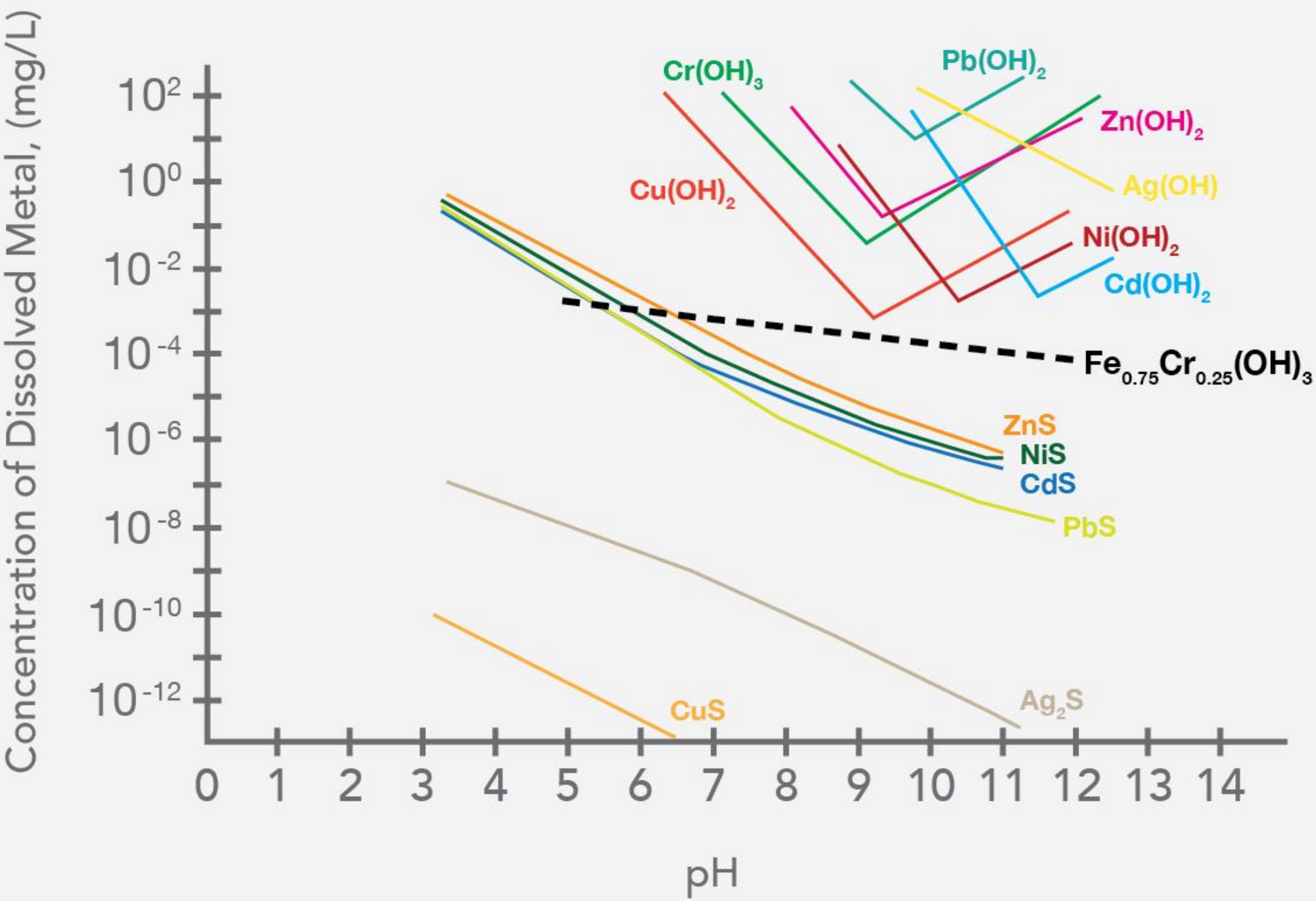
ZVI Corrosion (oxidation): $Fe^0 \rightarrow Fe^{2+} + 2e^-$

Iron Sulfide Oxidation: $FeS \rightarrow Fe^{2+} + HS^-$

MetaFix® Mechanisms

Metal	Precipitation as Metal Hydroxides or Iron Metal Oxyhydroxides	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; Banerjee et al., 2013. Veolia Water Inc.
Environ. Sci. Technol. 1988, 22, 972-977

Heavy Metal Precipitates: Sulfides, Carbonates, and 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

Iron-based Chromium Treatment

- **Reduction of Cr^{+6} to Cr^{+3} by ZVI mainly precipitates 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]**

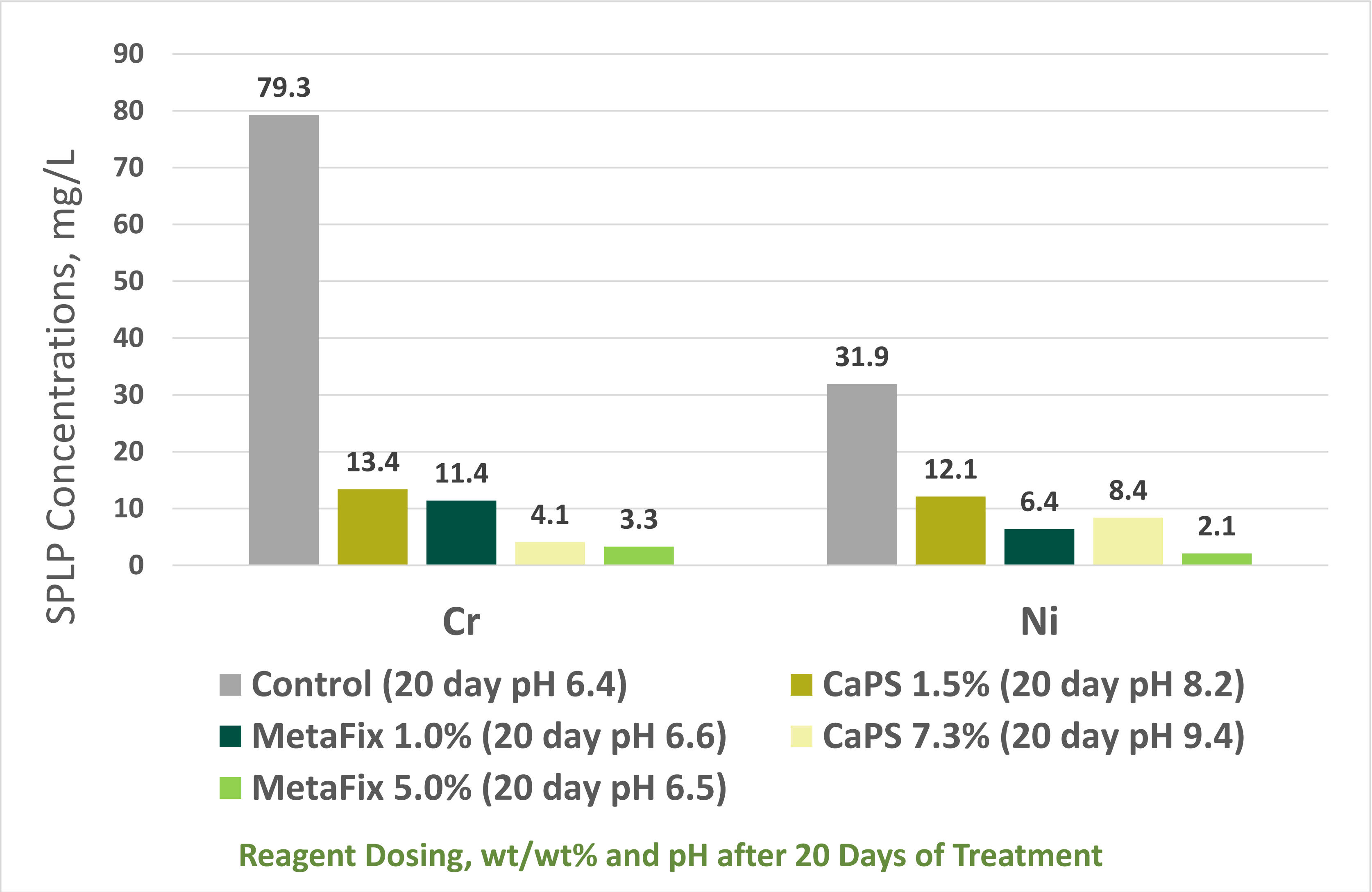
$$Fe^0_{[solid]} + CrO_4^{2-} + 8\,H^+ \longrightarrow Cr^{+3} + Fe^{3+} + 4\,H_2O \qquad (1)$$

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

- **The Fe-Cr oxide which has the form of hematite (Fe_2O_3) is primarily deposited on the surface of precipitates[2]**
- Precipitates with more Fe and less Cr have lower solubilities but all are much less soluble than $Cr(OH)_3$.
- 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[4].

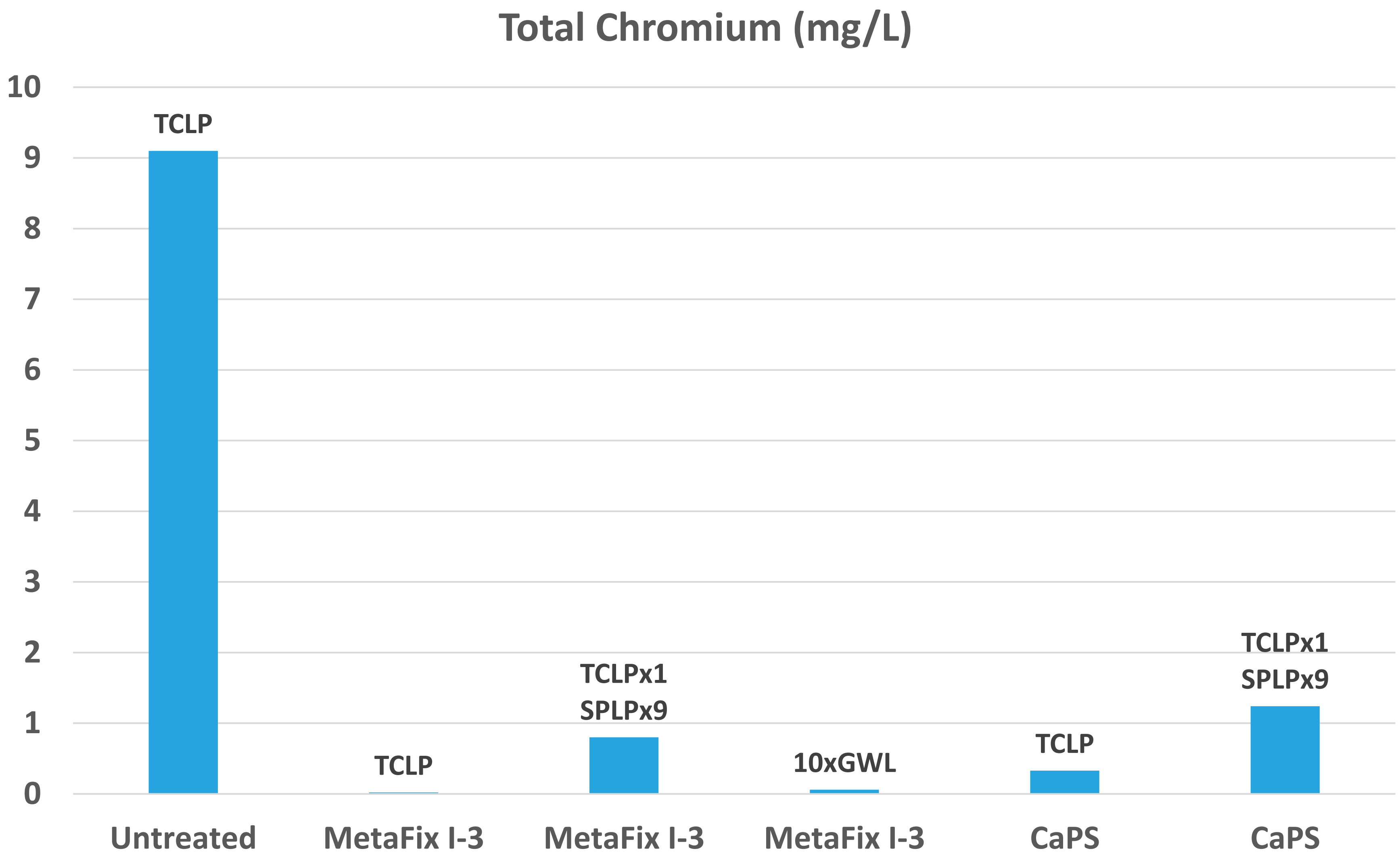
1. ***Blowes et al., 2000. J. Contam. Hydrol. 45: 123-137***
2. ***Tratnyek et al., 2003. In: Tarr, M. Chemical Degradation Methods for Wastes and Pollutants***
3. ***Eary and Rai. 1988. Env. Sci. Technol. 22:972-977.***
4. *Rai et al., 1989. Sci. Tot. Env. 86:15-23*

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



Independent Test Results from Professor D. Cassidy, WMU. , D. Gray AECOM. 2014

Stability of MetaFix® Mineral Precipitates



Independent Laboratory Multiple Extraction Testing; Values (mg/L) are 9.02, 0.02, 0.80, 0.06, 0.33, and 1.24

How long will reactive minerals last? Influence of pH on Fe^{+2} release from FeS

Environmental Solutions

PeroxyChem

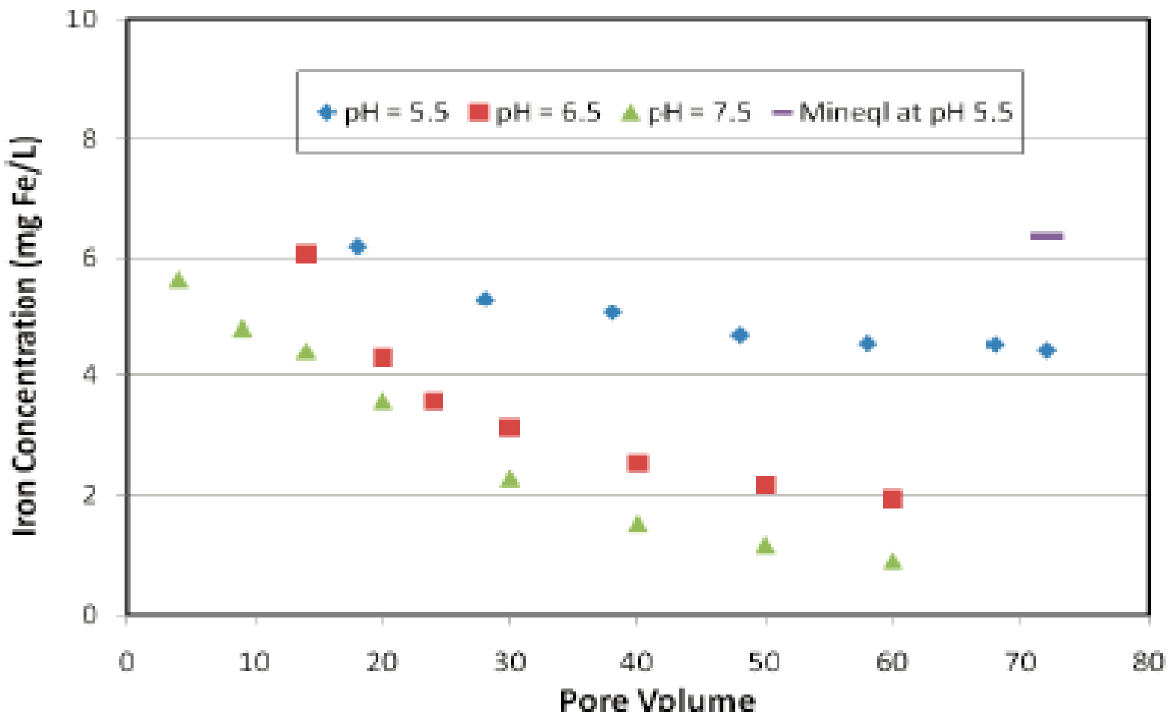


Figure 3.6. Eluted dissolved iron as a function of pH in FeS coated sand column I = 0.01M, Darcy Velocity-0.024 cm/s. Purple horizontal line indicated MINEQL+ prediction of saturation iron concentration with respect to FeS at pH 5.5 s.u.

Upflow columns packed with FeS coated sand. Effluent Fe^{+2} between 1 µg/L and 5 µg/L. Indicates that thin layers of FeS will last for 16 years under pH 5.5 conditions and 15 cm/day GW velocity. About 2% Fe released over 60 PV.

Hayes et al., 2009. SERDP ER-1375

MetaFix® Treatability Testing

Environmental Solutions

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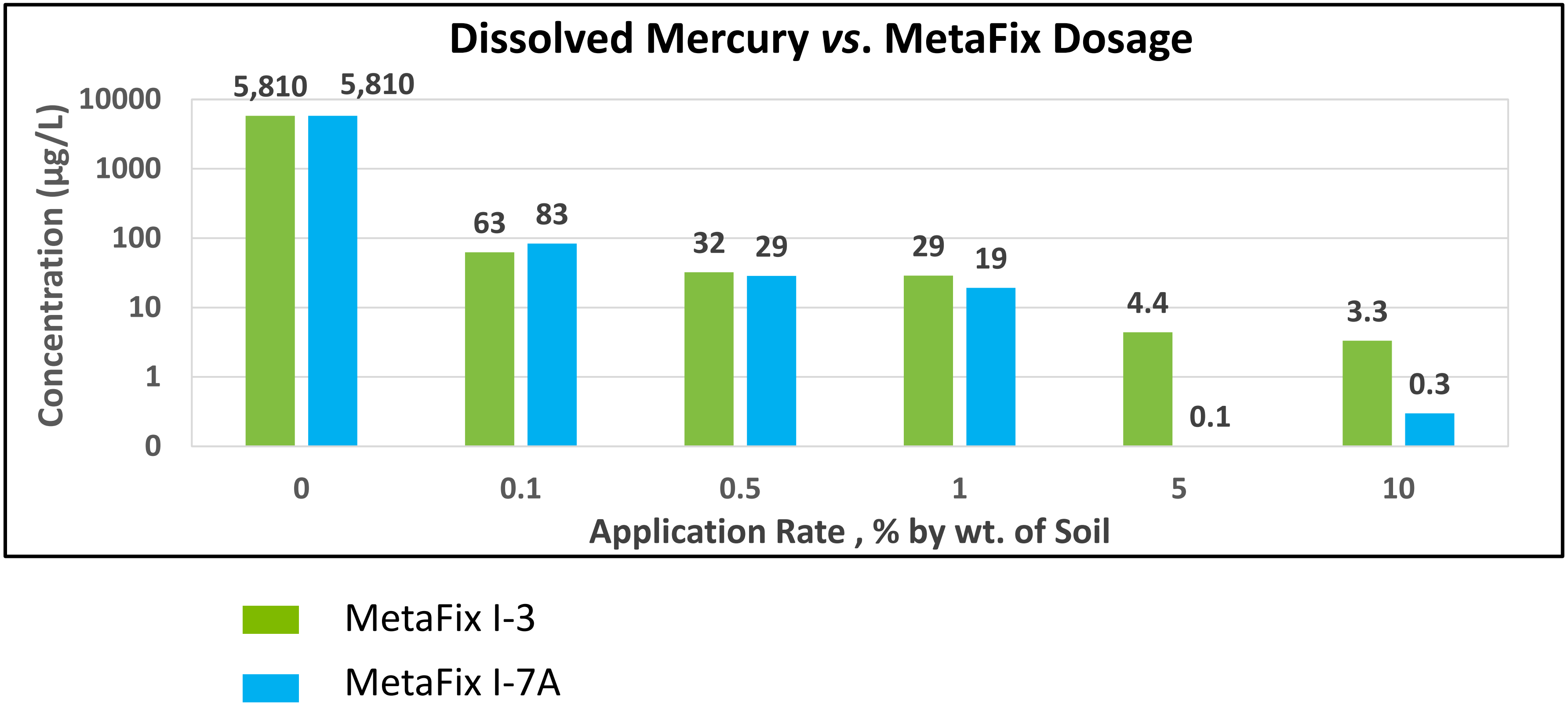

More than two orders of magnitude reduction in concentration of mercury can be achieved at low dosage of MetaFix.

Treatment of 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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Treatment of 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

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

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MetaFix® Case Study 1

Ex-situ treatment of lead-impacted industrial process waste in US.

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

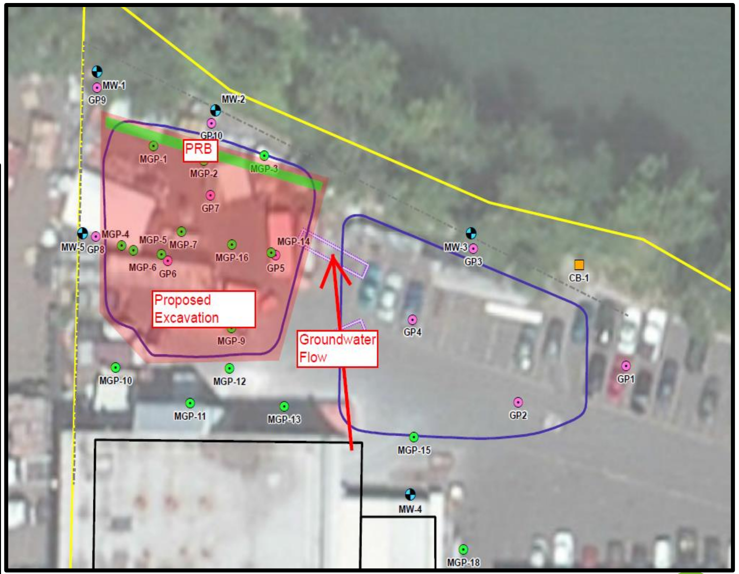
- Direct soil mixing with excavator
- MetaFix dosage at 6.0 % w/w
- Soil water content set to 80% of WHC (wet, not saturated)
- 7 day treatment time
- Earlier attempts at treatment with $FeSO_4$ and fly ash at 40% w/w were ineffective

MetaFix® Case Study 2
PRB Treatment of Mixed Heavy Metals

Environmental Solutions

PeroxyChem

- **Site:** Manufacturing facility in Pacific Northwest
- **Consultant:** Maul Foster & Alongi
- **COCs:** Mixed heavy metals (aluminum, arsenic, copper) and high alkalinity
- **Treatment:** Excavation of source area soil combined with MetaFix® PRB designed to prevent migration of residual metals into adjacent river
- **Application:** MetaFix® mixed into to backfill to cover downgradient wall of excavation to form PRB (80 ft long x 3 ft wide x 15 ft thick)
- **Dosage in Soil:** 6% by soil mass
- **MetaFix Cost:** $ 50,000



Influence of pH on Aluminum Solubility

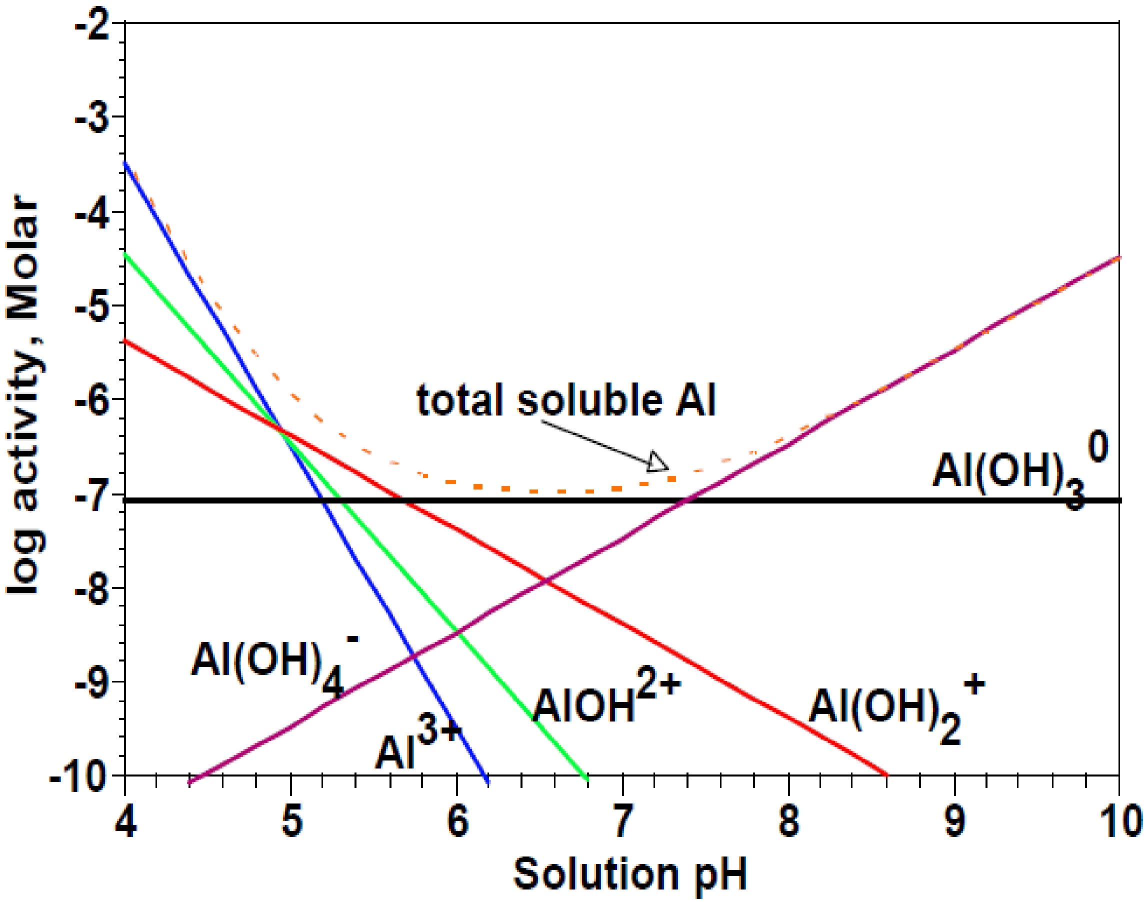
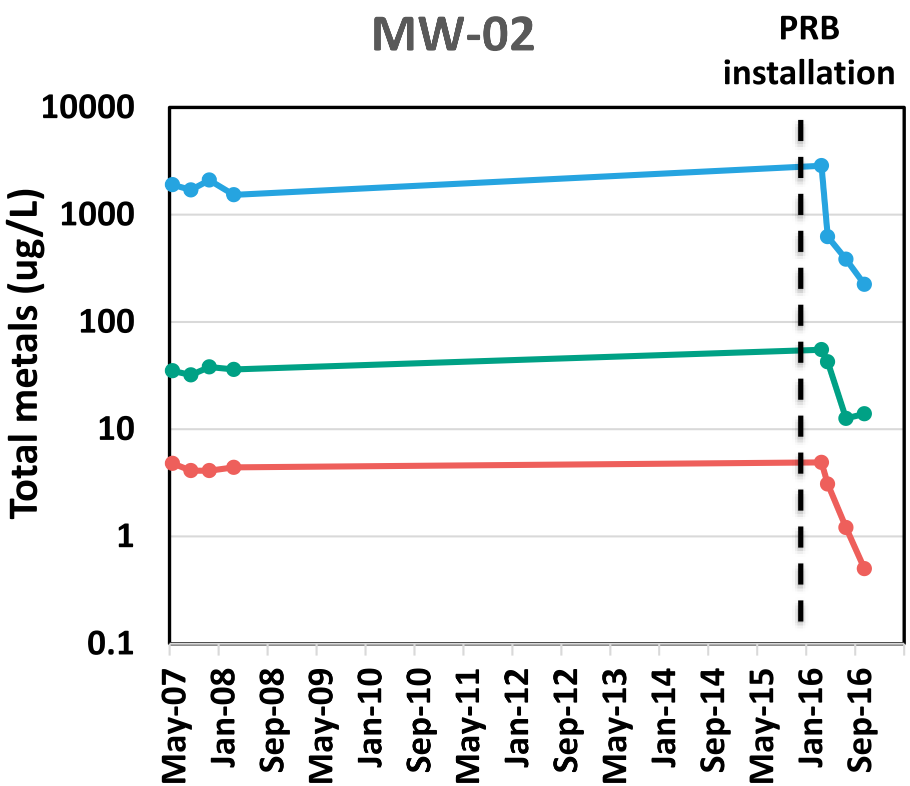


Figure 2.1. Solubility diagram of the most significant species of aluminum in an aqueous solution of $AlCl_3$. Gibbsite ($AlOH_3$) is present as the solid phase at all pH values. The broken line depicts total soluble aluminum (sum of all species concentrations). Polymetric aluminum- hydroxy cations are not significant species under the conditions of this system (from McBride, 1994).

Soluble species of Aluminum

- **Solubility sharply influenced by aqueous pH**
- **At low pH a trivalent cationic form exists but as pH moves toward neutral protons are lost and charge falls from +3 to +2 to +1 and on to neutral**
- **As pH moves alkaline solubility of the neutral form $Al(OH)_3$ increases**

MetaFix® Performance



Al 2,860 → 622 → 384 → 224

As 4.0→ 3.1 → 1.2 → n.d.

Cu 55.1 → 42.4 → 12.6 → 13.9

	pH	Eh (mV)	DO (mg/L)	Cond. (µS/cm)
Baseline	10.2	-62	0.88	1,800
3 months	9.8	-47	0.09	6,360
4 months	9.8	10	0.91	7,061
7 months	8.0	-702	0.06	14,679
10 months	7.7	-281	0.30	13,439

- Monitoring data at 3, 4, and 7 months post installation
- Transient post installation increase in concentration due to physical mobilization of metals
- RGs achieved for Al (750 µg/L), As (2.1 µg/L), and Cu (12 µg/L)

MetaFix® Case Study 3: Mercury Treatment at Former Industrial Site

- Mercuric chloride was used as a catalyst in chemical synthesis at this former chemical plant.
- Soil Hg concentrations in the contaminated area ranged from 300 to 420 mg/kg.
- The remedial goal was to stabilize Hg in soil followed by disposal at an offsite landfill.
- Property to be developed for residential use.

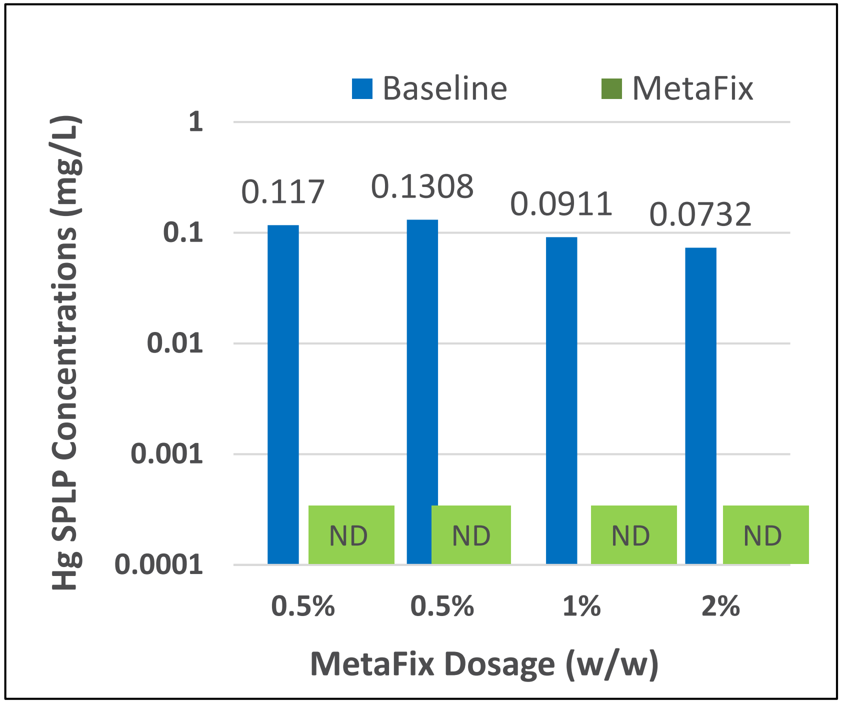
	Control	MetaFix 0.5% (wt/wt)	MetaFix 1.0% (wt/wt)
Moisture (%)	18.3	18.5	20.0
pH	8.6	8.0	7.9
Total Hg (mg/kg)	315	293	314
SPLP Hg (µg/L)	35.1	<1.0	<1.0

Results from the treatability study indicated that MetaFix dosage as low as 0.5% (w/w) could achieve the RG (<1.0 µg/L) of SPLP Hg.

MetaFix® Case Study 3

Pilot study conducted in four treatment cells

- **MetaFix applied at 0.5,% 1.0,% and 2.0% (w/w)**
- **~ 50 - 100 m³ 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 levels of <1.0 µg/L

MetaFix® Case Study 3

Full-Scale Treatment

- 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.
- Thousands of tons successfully treated.

Environmental Solutions

MetaFix® Applications

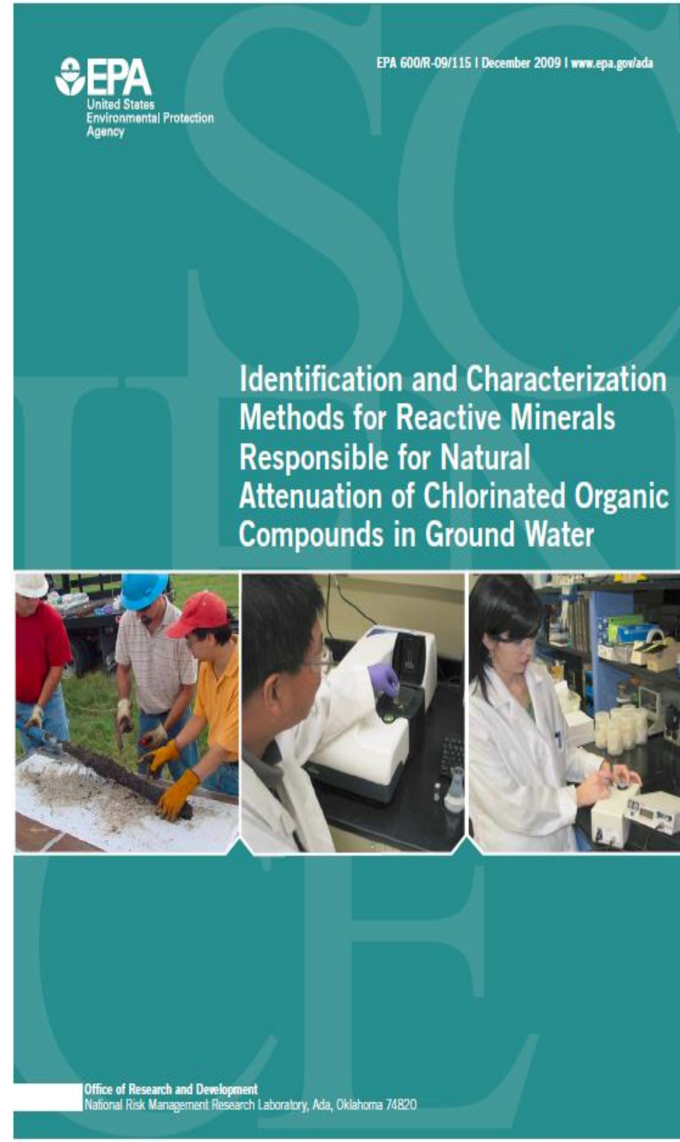
PeroxyChem

Low Dosage Rates:

- 0.5% - 4.0% (w/w) for soil
- 0.1% - 1.0% (w/w) for groundwater

- Application by soil mixing, trenching, or injection (40% – 50% solids) aqueous suspension
- Low cost treatability testing to determine dosage and enable custom formulation ($2,000)




EPA
United States Environmental Protection Agency

EPA 600/R-09/115 | December 2009 | www.epa.gov/ada

Identification and Characterization Methods for Reactive Minerals Responsible for Natural Attenuation of Chlorinated Organic Compounds in Ground Water

Office of Research and Development
National Risk Management Research Laboratory, Ada, Oklahoma 74820

MetaFix® Bench-Scale Treatability Results

Site Location	Soil or Groundwater	Metals Treated	Chlorinated Organics Treated	MetaFix Reagent	Dosage (% w/w)	Test Method	Results Initial (µg/L)	Results Final (µg/L)	Removal (%)
California	groundwater	Hg	-	I-7A	2.0	GWL	5,810	0.065	99.9
"	groundwater	Hg	-	I-3	1.0	"	40.3	0.01	99.9
Florida	both	As	yes	I-7Ad	4.5	GWL	55,300	930	98.3
"	both	-	α,β,δ,γ-BHC	I-7A	2.1	"	7.3	0.031	99.6
South Carolina	both	Cd	-	I-8A	2.0	GWL	99	1.5	98.5
Italy	both	Hg	-	I-3	1.0	GWL	1.5	0.1	93
Italy	both	Cr (VI)	-	I-3f	4.0	GWL	17,800	5	99.9
Washington	both	As	-	I-3a	4.0	GWL	190	13	93.2
Georgia	both	Hg	-	I-7A	1.0	GWL	39.9	0.07	99.8
China	soil	Hg	-	I-3	0.5	SPLP	35.1	0.5	98.4
Washington	groundwater		-	I-3a	1.0	GWL	76,000	40	99.9
Oregon	both	Al	-	I-6Af	2.0	GWL	1,500	36	97.6
"	"	Cu	-	I-7A	1.0	"	110	2.5	97.7
Washington	soil	As	-	I-7	1.0	TCLP	4,800	33	99.3
"	groundwater		-	I-6A	1.0	GWL	12,900	14	99.9
Kentucky	both	Cr (VI)	-	I-6A	4.0	GWL	149,000	31	99.9
"	"	-	TCE	I-6A	4.0	"	1,600	13	99.1
"	"	-	cis-DCE	I-6A	4.0	"	5	5	-
"	"	-	VC	I-6A	4.0	"	5	5	-

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MetaFix® Summary

- Heavy metals are converted into low solubility mineral precipitates, primarily metal sulfides, metal iron sulfides or metal iron oxides/oxyhydroxides.
- These precipitates are complex and are stable over a broader pH range than their hydroxide counterparts.
- Simultaneous treatment of heavy metals and chlorinated solvents is possible.
- It is a cost effective treatment which uses lower dosage rates than some alkaline treatment reagents.
- Custom-formulations enable successful treatment of even complicated sites.
- Low cost ($2K) treatability study to verify efficacy & develop custom formulations.

Questions

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