CrVI Remediation at Chrome Plating and Chromite Ore Processing Facilities

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C.E.R.E.S.
Remediation Products

C.E.R.E.S. Remediation Products

MTS® Metals Treatment Solution

BGCR Bio-Geo-Chemical Reduction

ZVI Zero Valent Iron

PTS™ Petroleum Treatment solution

PTS Advanced™ Surfactant Enhanced Remediation

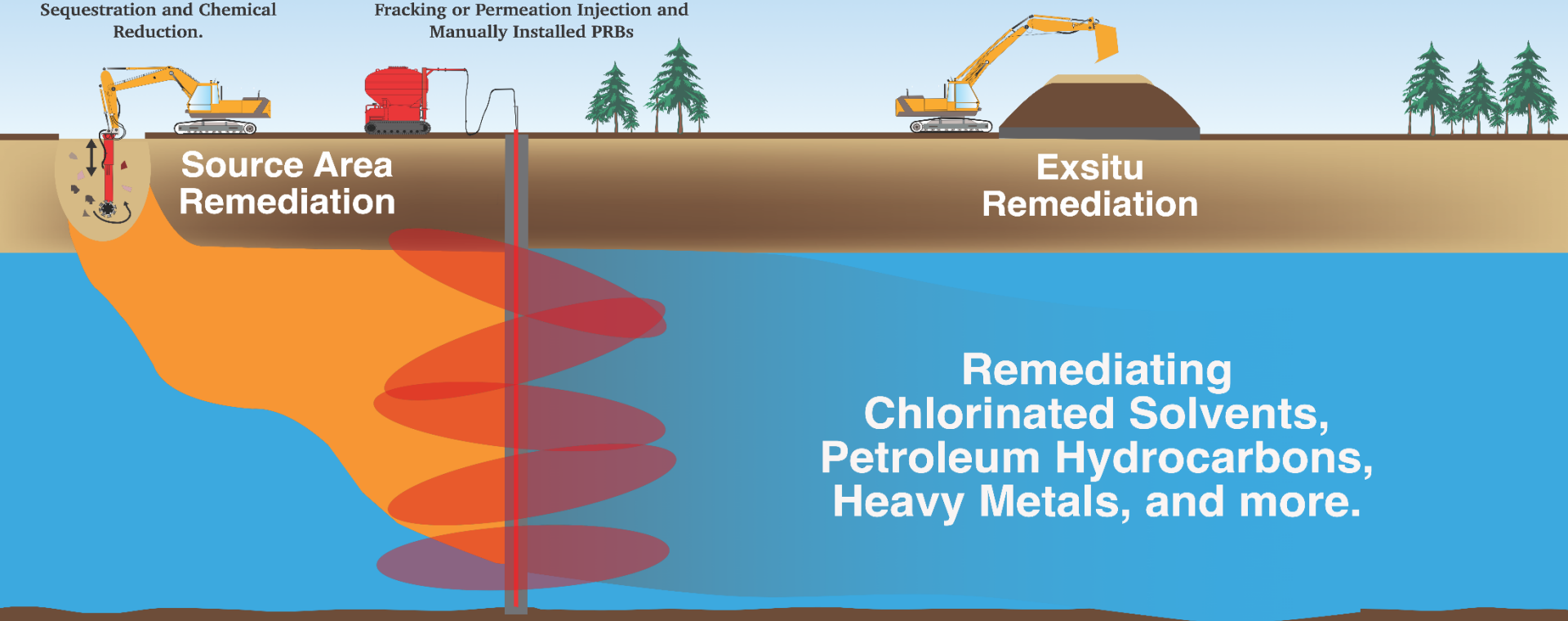
PTBAC Petroleum Treatment Bacteria

iPAC Injectable Powder Activated Carbon

Advanced Chemistries for Soil Remediation: In-Situ Mixing, Stabilization, Sequestration and Chemical Reduction.

Innovative Solutions for Groundwater Remediation: Permeable Reactive Zones, Adsorption Boundaries emplaced by Fracking or Permeation Injection and Manually Installed PRBs

Ex-Situ Soil Remediation and Pre-Treatment for Landfill Disposal



Remediating Chlorinated Solvents, Petroleum Hydrocarbons, Heavy Metals, and more.

Chemical Engineering for Remediation and Environmental Sustainability

Contact us today

Heavy Metal Remediation Approaches & Processes

1. Immobilization – In-situ or Ex-Situ – Organic or inorganic amendments
2. Sequestration/Chemical stabilization– In-situ or Ex-Situ – chemicals or biological

- Sorption
- Precipitation
- Reduction
- Complexation
- Cation exchange

3. Solidification –In-situ or Ex-Situ- binding agents

- Cementation
- Sorption

C.E.R.E.S. Customized Solutions

Chemical Reduction and Sequestration (Heavy Metals and Organics)

Metals Treatment Solution (MTS®)- *Customized* chemistry to reduce heavy metals (As, CrVI, Pb, Mo, Ba, Bo, Co, Cd, Ag, Zn, Hg, Ni, Cu, Li, + others).

- Apatite
- Ion-exchange / zeolite
- Iron sulfide - Mackinawite
- Iron-oxy-hydroxide
- Oxides/hydroxides
- Cation Exchange
- Silicates
- Activated Carbon
- Engineered biochar
- Proprietary reagents and activators

Quick Overview of Remediation Process

Typical process for the collection of data and defining the contamination conditions, establishing goals for remediation, verifying the performance of MTS® to successfully achieve goals, and document the testing verification process as part of the remediation design.

CERES can help with the entire process for customers!

1. Site Characterization
   - Collect samples from soil and groundwater to define the problem
2. Treatment Goals Identification / Establishment
   - Determine treatment requirements based on future land use
3. Dosage / Treatability Testing
   - Confirm MTS® performance in laboratory with site soil samples
4. Remediation Design and Implementation
   - Support Customer
5. Performance Testing / Verification
   - Develop a plan for verification of results

Heavy Metal Design Challenges

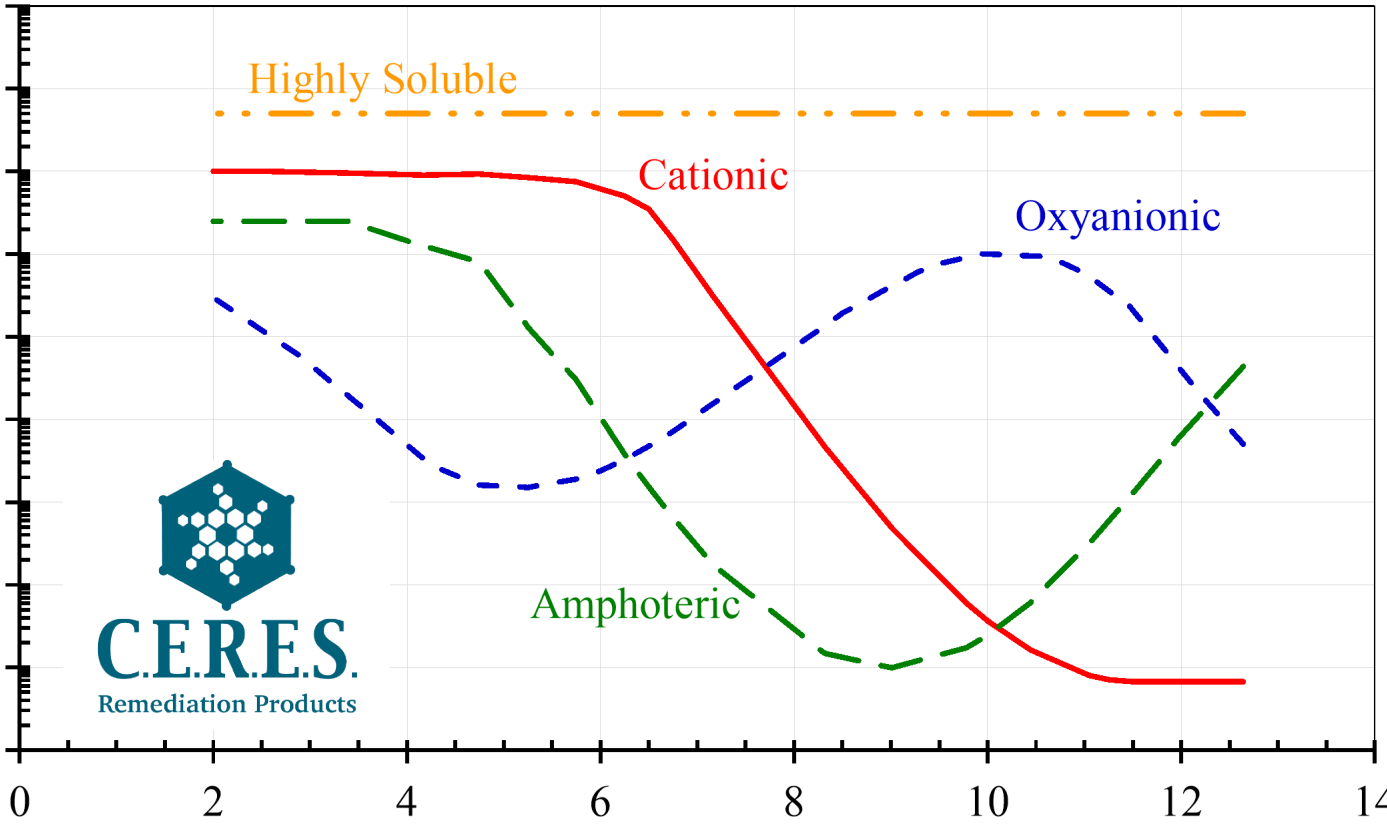
Some metals are sensitive to curtain changes post immobilization/ sequestration/stabilization methods

- pH (e.g., Al and Zn)
- Oxidation/Reduction potential (e.g., Thallium)
- Both pH and redox potential (e.g., As, Cr, Cu, Mn, Se, and Vn)
- Cation exchange (e.g., Ca, Mg, K, Na)
- Sensitive to many of the above (e.g. B, Li, Mo, Sb)

Scavengers or site replacement by anions

- PO_4
- CO_3
- SiO_4
- SO_4- Sulfate at high pH
- NO_3-
- Many others…

Generic behaviors of several inorganic contaminant types showing generalized minima/maxima as a function of pH



Cationic- Ag, As, B, Ba, Cr(III), Cd, Hg, Li, Ni, Pb, Se, Tl, Zn

Amphoteric- Co, Cr(III), Pb, Cu, Be, Zn

Oxi-anionic- [CrO4], As, B, Se, Mo,

High Solubility- Na , K , Cl, Br, I

Chromium Forms

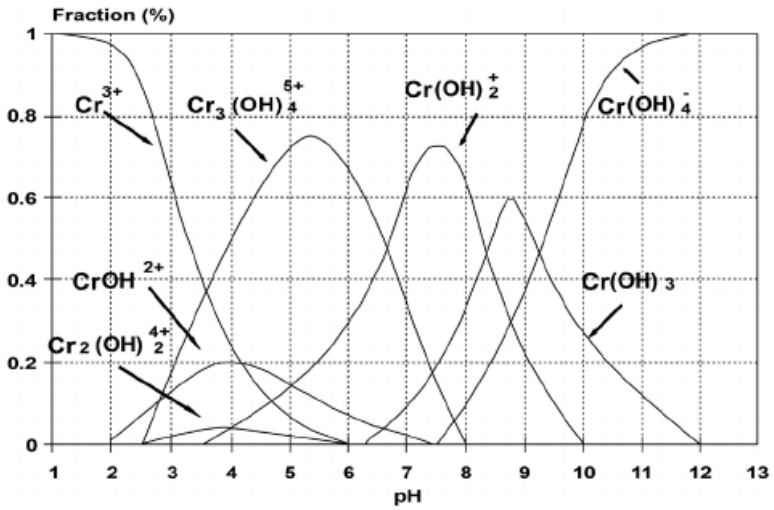
Oxidized chromium: (chromates with +6 charge)

- $H_2CrO_4^0$, $HCrO_4^-$, CrO_4^{2-}, $Cr_2O_7^{2-}$, Cr_2O_3

Reduced chromium: (with +3 charge)

- $CrOH_2^+$, $Cr(OH)_2^+$, $Cr(OH)_3$, $Cr(OH)_4^-$

Redox controls chromium valence and pH controls speciation



Chromium (III) speciation diagram
Santos Et al 2011,
DOI: 10.1590/S0100-40422012000800021

Chromium Reduction - Basic

Hexavalent chromium

- More mobile and toxic than trivalent form
- Strong oxidizer is readily and rapidly reducible to trivalent form
- Can be sorbed by Fe and Mn oxides

Trivalent chromium

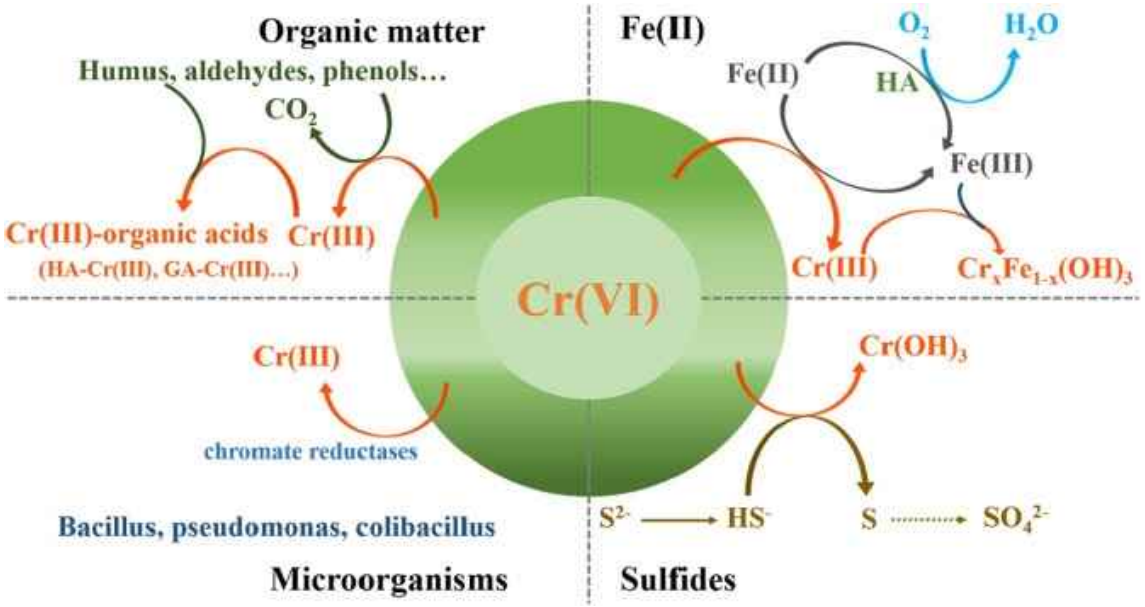
- Forms Fe-mineral at pH>4 or amorphous Cr-hydroxide solids near pH of 7
- Trace human nutrient and immobile

Mechanisms for Cr Reduction-Advanced

Reduction of chromate by organic matter
$2CrO_4^{2-} + 3C^0 + 4H^+ \rightarrow 2Cr^{3+} + 3CO_2 + 2H_2O$.

Reduction by zero valent iron (Fe^0)
$CrO_4^{2-} + Fe^0 + 4H_2O \rightarrow Cr_xFe_{1-x}(OH)_3 + 2OH^-$.

Susceptible to redox change



Stable over a wider range of pH and redox conditions

Susceptible to redox change

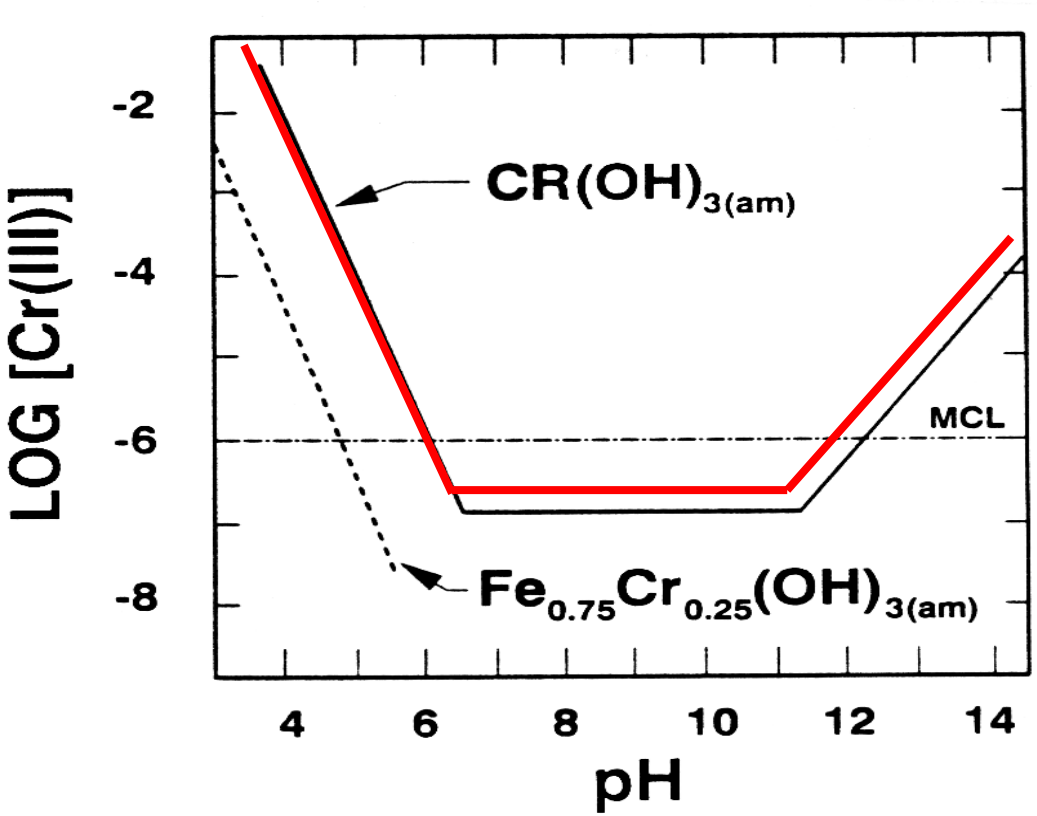
Susceptible to redox change

Enzymatic Reduction by microorganisms with sulfate transport channels
$CrO_4^{2-}+3S^{2-}+8H^+ \rightarrow Cr^{3+}+3S+4H_2O$

Reduction by sulfides
$CrO_4^{2-}+3S^{2-}+8H^+ \rightarrow Cr^{3+}+3S+4H_2O$

Modified from Liang et al, 2021
https://doi.org/10.1016/j.scitotenv.2021.145762

Chromium III Solubility



Cr(OH)3 as achieved through bio stabilization pH 7-11

From Palmer & Wittbrodt (1991), concentration in mg/L.

Solubility of Fe-Cr oxyhydroxides is less than 0.05 µg/L over a broad pH range of 5.0 to 12.
Reduction of Cr(VI) to Cr(III) with Fe occurs in minutes to form 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. Thus more Fe improves performance and long term stability.

Treatability Purpose and Goals

1. **Selection of reagents** for site-specific goals, end-uses and geochemical conditions
   - Evaluate performance of different reagents
2. Establish treatment **goals**
3. Determination of **application approach**
4. Establish a **performance monitoring plan**

Scenario Planning and Design

Evaluate performance under changing conditions

- Redox conditions (past, present, future)
- Upgradient geochemistry such as cations, anions, pH or biogeochemical influences

Climate Change Considerations

- Climate (precipitation, temperature, flooding, wind erosion, groundwater elevation)
- Sea level (flooding, saltwater intrusion, groundwater elevation near shore)

Common site remedies or land use changes that cause future challenges

- Capping
- Hydraulic loading changes
- Dewatering
- Removal actions
- In-situ Treatment

Case Studies

Former Chrome Plating Facility 1

Site in Los Angeles, California

- 390 tons of CrVI impacted soils
- Most transported offsite.

In-Situ treatment beneath the building performed with MTS®

- Max 860 mg/kg of CrVI in sidewalls and beneath footings
- No groundwater impacts

Competitive treatability study

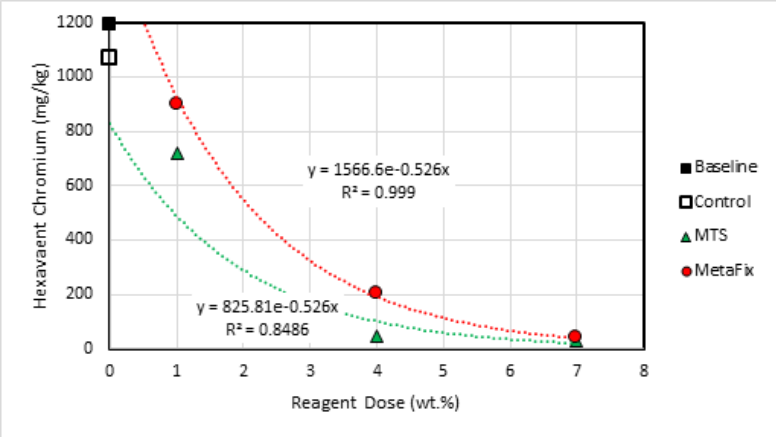


Table 1. Reduction in Hexavalent Chromium

Sample	Moisture Content (%)	Soil pH (units)	Hexavent Chromium (mg/kg)	Percent Reduction Relative to Control
Baseline	2.8	4.22	1190	--
Control	11	3.99	1070	--
MTS 1%	12.1	4.15	717	33%
MTS 4%	12.3	4.15	46.6	96%
MTS 7%	13.8	5.31	30.5	97%
MetaFix 1%	11.4	4.57	900	16%
MetaFix 4%	12	5.40	202	81%
MetaFix 7%	11.8	5.43	38.3	96%

Former Chrome Plating Facility

Results

Treatment goal =12.3 mg/kg

Cr(VI) reductions 82% to 100% exceeding treatment goals across the treatment area.

Project completed in 20 days

Acknowledgements
Jag Consulting
Gary Cronk

Active Chrome Plating Facility 3

Sandy gravely soils. Impacts to 30 ft bgs

No GW impacts. GW depth at 240 ft bgs.

- Chromium (Cr) up to 890 mg/kg,
- hexavalent chromium (Cr^{6+}) up to 18 mg/kg and
- nickel (Ni) up to 720 mg/kg.

Soil composites A to D (shallowest to deepest) not the same as site investigation results but are depth related.

Soil Composition				
Analyte	Composite A	Composite B	Composite C	Composite D
pH (SU)	7.95	8.87	6.74	4.92
Cr (mg/kg)	692	1,140	375	78.2
Cr^{6+} (mg/kg)	36.9	207	101	4.00
Ni (mg/kg)	593	241	204	240
Fe (mg/kg)	20,900	16,700	14,300	12,300
Moisture (%)	7.1	6.2	2.4	2.6

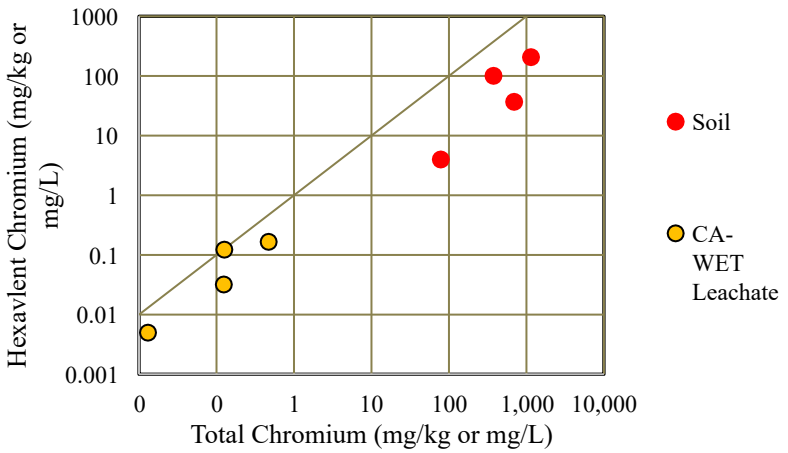
Active Chrome Plating Facility 3

The CA WET leachate dissolved Cr at 3x CrVI concentration.

Composites B &C had 5x greater CrIII than CrVI. Composites A and D had 20x greater CrIII than CrVI. B & C more proned to CrVI conversion.

Leachable Ni increases from A to D and with increasing depth.

Fraction of Leachable Metals x 1000			
Sample	Cr^{6+}	Cr	Ni
Composite A	0.87	0.18	0.16
Composite B	0.80	0.41	0.90
Composite C	1.2	0.34	1.5
Composite D	1.3	0.17	34

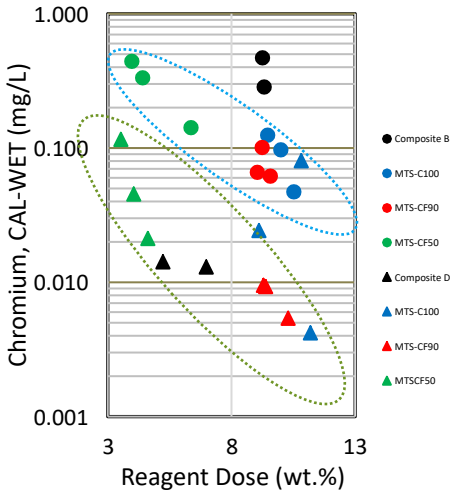


Active Chrome Plating Facility 3

Performance Results

Challenges from geochemical differences in soil, amount of Ni and Cr by depth, required site specific customized MTS formulation to achieve goals.

Treatment	Dose (wt.%)	CAL-WET (mg/L)			
		pH (SU)	Cr^{6+}	Cr	Ni
Control	0	9.50	0.18	0.428	0.0225
MTS®	2	9.09	<0.01	0.0183	0.0127
MTS®	5	9.54	<0.01	0.019	0.0077
MTS®	10	9.58	<0.01	0.0102	0.0071
Remediation Goals				0.05	0.01



Former Chromite Ore Processing Residue (COPR) Site

Worlds Largest COPR Facility located in Changsha China

- byproduct of high lime based roasting of chromate
- 350,000 cu yds of soil
- 85,000 cu yds of COPR after ball milling and soil washing

Total Chrome = 48,5 mg/kg

Water leachable CrVI = 825 mg/l

GW CrVI up to 3,140 mg/l

Remediation objective= 0.05 mg/l

Former Chromite Ore Processing Residue (COPR) Site

Previous Remediation Attempts

Ferrous Sulfate Monohydrate

Ferrous Sulfate Heptahydrate

Zero Valent Iron

Results

High doses achieved target initially but CrIII conversion to CrVI began to occur in less than 1 year.

No Long term stability.

Treatability Study Program

New Reagents to Test

Sulfides

NaS

CaSx

Organic Sulfur

Proprietary products

MTS®

Testing Media

- Soil
- COPR Slag

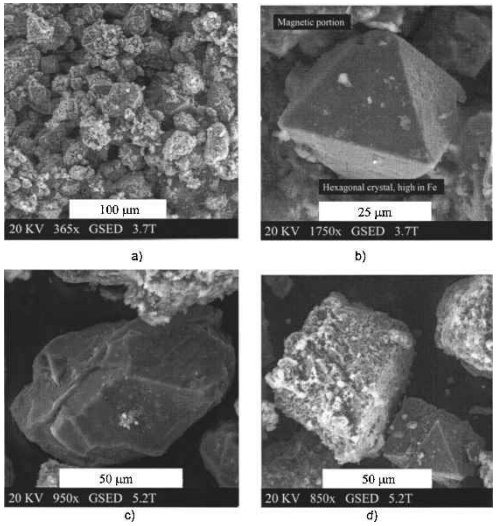
Dosages by wt%

- 5%
- 10%
- 15%
- 20%

Treatment Goal

- Leachable CrVI = 0.05 mg/l

Challenges-
Crystalline Chromite
>Ball Milling



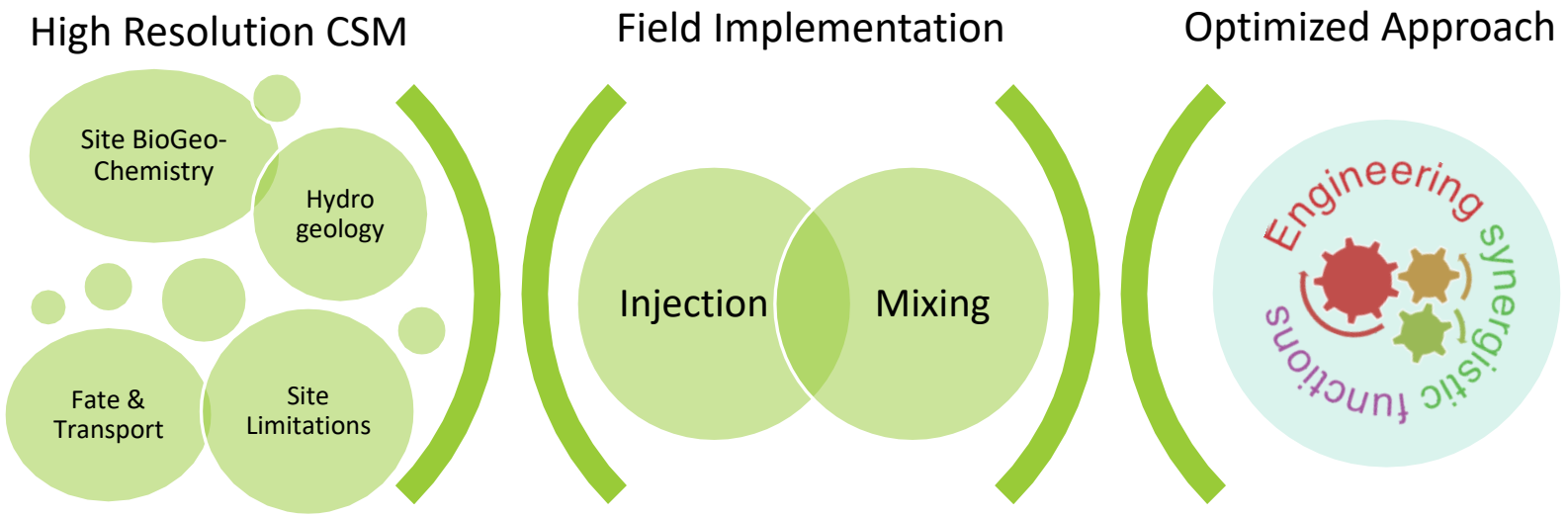
COPR Soil Treatment

Experiment number	Soil mass g	Reagent	Dosage	Dry Moisture Content %	Cr^{6+} acid leaching (mg/L)
gywdh-2-1	200	Industrial sodium sulfide	5%	4.52	1.46
gywdh-2-2	200		10%	7.93	0.44
gywdh-2-3	200		15%	11.18	0.56
gywdh-2-7	**200**	**Ceres MTS®**	**5%**	**3.79**	**0.137**
gywdh-2-8	**200**		**10%**	**4.47**	**0.081**
gywdh-2-9	**200**		**15%**	**4.98**	**0.004**
gywdh-2-10	200	Industrial calcium polysulfide	5%	1.97	2.73
gywdh-2-11	200		10%	2.46	0.04
gywdh-2-12	200		15%	2.79	0.01
gywdh-2-13	200	Modified organic sulfur stabilizer	5%	2.18	0.17
gywdh-2-14	200		10%	2.69	0.03
gywdh-2-15	200		15%	3.44	1.16
gywdh-2-16	500	blank	/	4.43	123.35

COPR Slag Treatment Trials

Serial number	Total chromium mg/kg	Chromium (water immersion) mg/L	Chromium (acid leaching) mg/L	Cr^{6+} (acid leaching) mg/L
gywdh-2-33	200	Industrial sodium sulfide	10%	10.29
gywdh-2-34	200		15%	10.33
gywdh-2-35	200		20%	0.35
gywdh-2-39	**200**	**Ceres MTS®**	**10%**	**0.178**
gywdh-2-40	**200**		**15%**	**0.006**
gywdh-2-41	**200**		**20%**	**0.001**
gywdh-2-42	200	Industrial calcium polysulfide	10%	0.78
gywdh-2-43	200		15%	0.43
gywdh-2-44	200		20%	0.36
gywdh-2-45	200	Modified organic sulfur stabilizer	10%	0.87
gywdh-2-46	200		15%	10.93
gywdh-2-47	200		20%	1.48
gywdh-2-48	500	blank	/	103.90

CERES Remediation Products Assessment & Design Method



Remediation Products Options Assessment

ISCO, ISCR, Bio, Sequestration, others, combos → Reduced options → Ideal Product/Approach

Thank you

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C.E.R.E.S.
Remediation Products

Utilizing SMART Science, motivated by Sustainable principles to deliver AWARD WINNING chemistries to valued clients.

SMART = Specific, measurable, achievable, relevant, and time-specific
C.E.R.E.S. = Chemical Engineering, Remediation, Environmental Sustainability

Some Processes

- **Adsorption**: Binding of a soluble species on the surface of a solid, driven by surface forces.
- **Complexation** is a process where molecules or ions form a complex by bonding together through coordinate covalent bonds. This involves: Formation of a Coordination Complex: Typically involves a central atom, usually a metal ion, surrounded by several other molecules or ions called ligands. These ligands donate electron pairs to the metal ion to form stable water-soluble complexes that are less toxic.
- **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 chemical, physical, 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).
- **Reduction:** Specifically alters the oxidation state by electron gain, which can fundamentally change the chemical and physical properties of the substance involved. This is unlike complexation, which mainly alters the chemical environment without changing oxidation states, and coprecipitation, which focuses on physical entrapment or inclusion within a solid matrix.
- **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.

Metals Remediation Process

Add chemical reagents to form minerals in soil and aquifers to:

- Reduce Leaching from soil
- Reduce Groundwater concentrations
- Reduce Toxicity to Humans
- Stable for 100's of years (testing required)

CERES Chemistries:

- Environmentally Safe- Pose little to no hazard to the environment
- Requires simple equipment that is low in cost

Remediation Design Challenges

SITE CHALLENGES

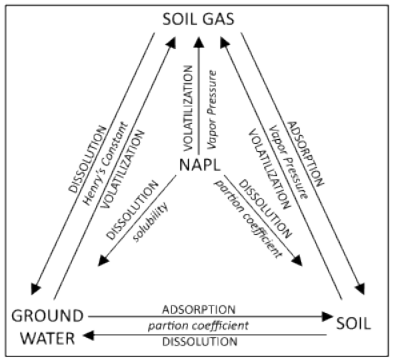
Mixed plumes – organics + metals

Indestructible – PFOS/PFOA, heavy metals

Low Permeability sites - Clay, glacial till, fractured rock, saprolite

Fate and Transport

DNAPL or LNAPL



PHYSICAL & ORGANIC CHEMISTRY

COC Destruction

- Bioremediation- PTS, EVO, BGCR/ZVI
- ISCO- PSOX

COC Sequestration or Sorption

- iPAC, MTS®

COC Chemical Reduction

- ZVI, MTS®, BGCR

Reagent Performance Depends on:
Quality-Purity-Size-Shape-Reactivity