

In Situ Metals Remediation of Tailings, Soil and Groundwater



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

Presented by: Lowell Kessel, MS, PG
Email: LOWELL@CERESRP.COM

WWW.CERESRP.COM



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



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

**Source Area
Remediation**

**Exsitu
Remediation**

**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
 - Sorption
 - Precipitation
 - Reduction
 - Complexation
 - Cation exchange
 2. Sequestration/Chemical stabilization– In-situ or Ex-Situ – chemicals or biological
-
3. Solidification –In-situ or Ex-Situ- binding agents
 - Cementation
 - Sorption

Heavy Metal Design Challenges

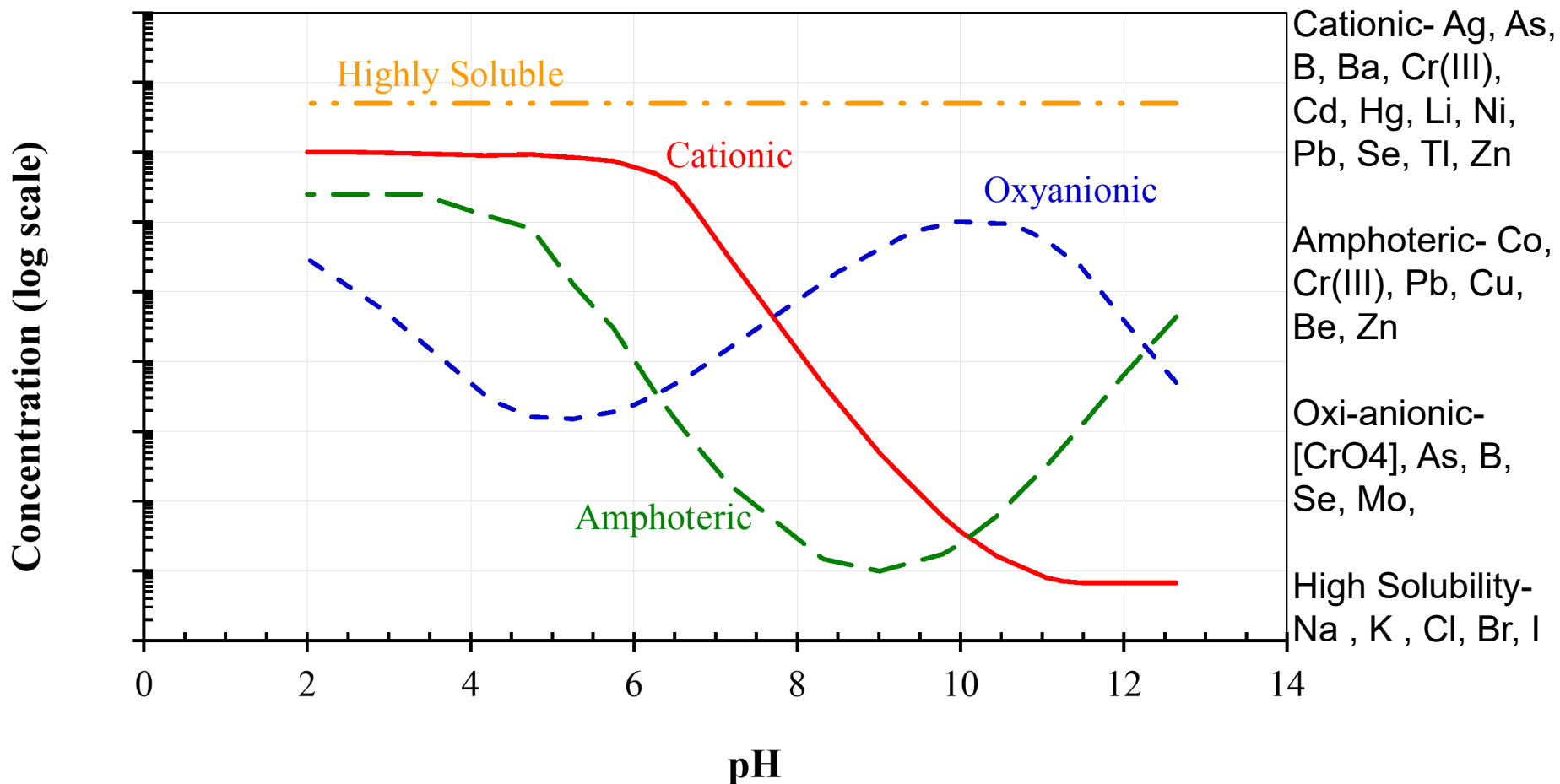
Some metals are sensitive to certain changes post immobilization/sequestration/stabilization methods

- pH (e.g., Pb, 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



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

Design must include evaluations of treatment performance under changing conditions. It's important for long term performance and it is good science.

Considerations include:

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

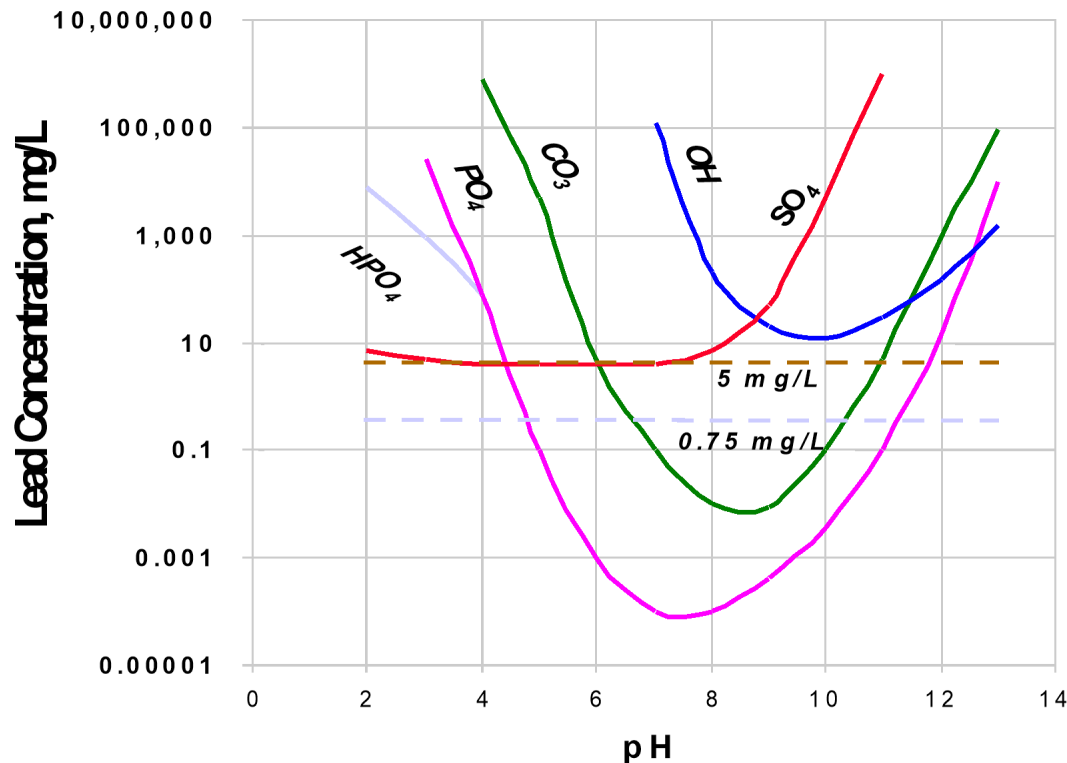
Climate Change Considerations

- 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

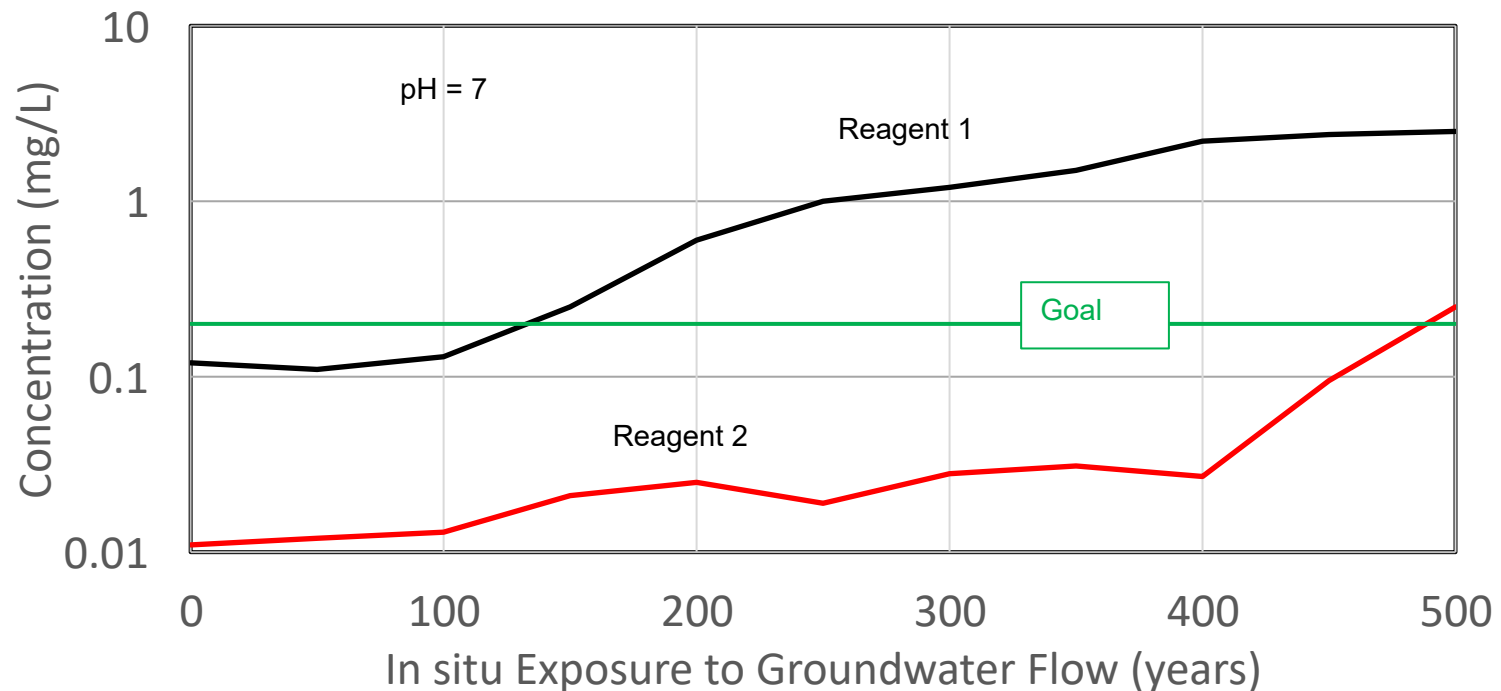
- Capping
- Hydraulic loading changes
- Dewatering
- Removal actions
- In-situ Treatment

Lead Solubility vs pH



Horizontal dotted lines correspond to the current threshold toxicity characteristic concentration for lead (5.0 mg/L), and the universal treatment standard (0.75 mg/L UTS) for lead. *Federal Register*. Volume 60, Number 162. August 22, 1995. pp. 43682-43683.

Can you predict future GW redox conditions?



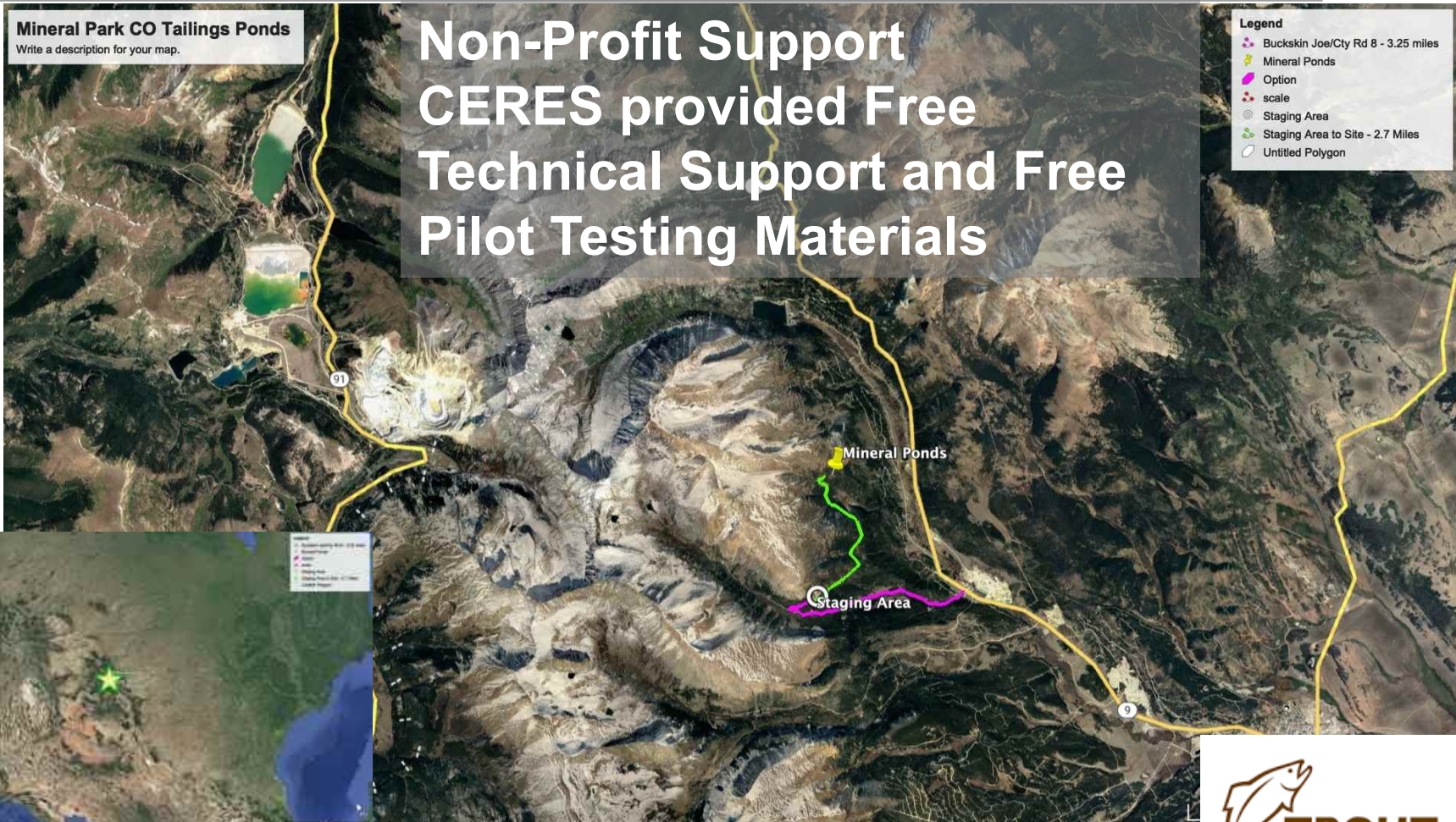
Multiple Batch Extraction Procedure or Column Studies
USEPA SW-846 Method 1320 or Method 1314
Reagent selection for long term stability and reactivity

C.E.R.E.S. Products = Customized Solutions

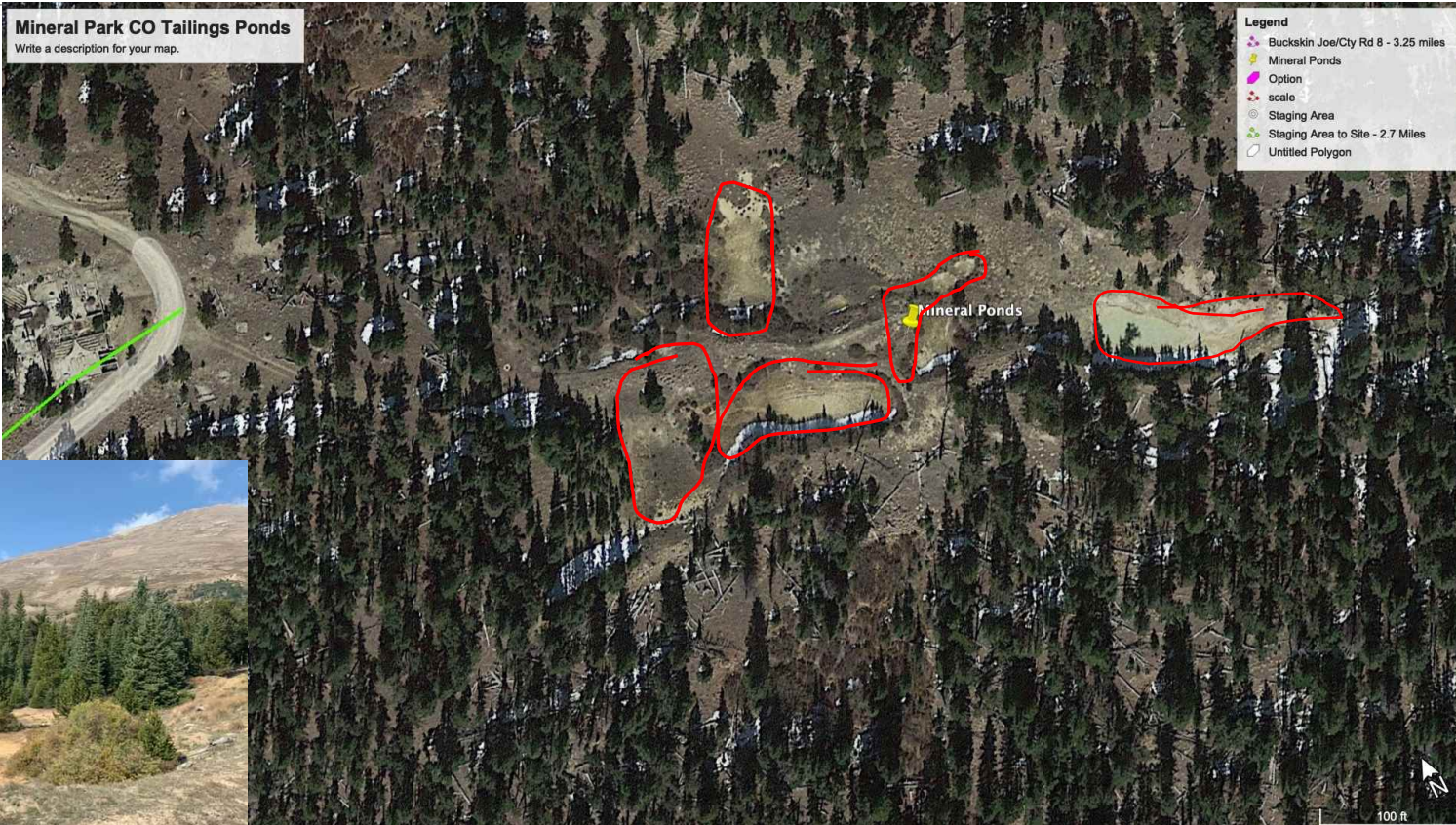
- Chemical Reduction and Sequestration (Heavy Metals and Organics)
- Metals Treatment Solution (MTS®)- Customized chemistry to reduce heavy metals (As, CrVI, Pb, Mo, Ba, Bo, Co, Cd, Ag, Zn, Hg, Ni, Cu, Li, + others).
 - Apatite/Phosphate
 - Ion-exchange/Zeolite
 - Iron sulfide - Mackinawite
 - Iron
 - Magnesium
 - Oxides/hydroxides
 - Silicates
 - Sulfates/sulfides
 - Carbon
 - Engineered biochar
 - Proprietary reagents and activators



Mineral Park Tailings Ponds CO at 11,000 ft Elevation



Mineral Park Tailings Ponds



Multiple Metals Present- Lead was the primary target



Project Goals

- Prevent the migration of hazardous substances, pollutants, or contaminants in Site surface soils (tailings/mine waste);
- Reduce potential human and ecological receptor exposure to metal-bearing soils and water in the area of the settling ponds;
- Reduce or eliminate potential physical hazards associated with settling ponds;
- Achieve compliance with Applicable, Relevant and Appropriate Requirements (**ARARs**) and To Be Considered (TBC) guidance, to the extent possible in accordance with Comprehensive Environmental Response, Compensation, and Liability Act (**CERCLA**) requirements.
- **Reduce lead and other heavy metals leachable concentrations** to below human and ecological health risk criteria. USEPA Tapwater RSL for lead is 0.015 mg/l and Colorado DPHE SL is 0.05 mg/l.

Approach

In-situ chemical stabilization and capping was determined to be the most cost effective and viable solution.

This method involves the introduction of chemical reagents directly into the contaminated medium (in-situ means "in place") to react with the toxic metals and convert them into stable mineral forms that are less mobile, less bioavailable, and less toxic.

This prevents the spread of contamination through water flow and reduces the uptake of metals by plants and microorganisms.

Treatability- Pilot Test

Non-Profit Support
CERES provide Free Technical
Support and Free Testing Materials

- Eight Test Plots- 24 sqft ea
- CERES provided technical support throughout the remedial design and implementation process at no additional cost.
- 200 lbs of MTS® donated by CERES Remediation Products.
- MTS® was applied at a dosage ranging from 1.0% to 4.5% by weight of soil.
- Toxicity characteristic leaching procedure (TCLP) testing was used to evaluate performance of the Pb stabilization.



Stabilization pilot trials found that MTS® addition to soil reduced leachable lead concentrations to below 5 µg/L (CDPHE SL) resulting in a greater than 98% reduction of lead at a dosage of 2.0 wt. %.

Full Scale

Treatment Area= 74,000 sq ft

Treatment Depth= ~2 ft

Volume 2,700 cubic yards

MTS[®] Dosage= 2%wt

Equipment: Bulldozer and long reach excavator



Performance Results and Site Reclamation

100% reduction of leachable lead



Soil Confirmation Sample Results

Method		6020 - SPLP		6020 - SPLP	
Analyte		Lead		pH	
Units		mg/L		Mg/L	
Target Remedial Goal		<10.0		>9.5	
Sample ID	Date Collected	Result	Q	Result	Q
Samples Collected From Blending Area (0 and 2' BGS)					
Pond 1 Pretreatment	7/8/22	10.7		0.0957	
Pond 2 Pretreatment	7/8/22	21.2		ND <0.050	
Pond 3 Pretreatment	7/8/22	33.8		0.190	
Pond 4 Pretreatment	7/8/22	4.95		ND <0.050	
Pond 3 Post Treatment	7/8/22	ND <0.050		ND <0.050	
Pond 4 Post Treatment	7/8/22	ND <0.050		ND <0.050	
Pond 1 Post Treatment	7/10/22	ND <0.050		ND <0.050	
Pond 2 Post Treatment	7/10/22	ND <0.050		ND <0.050	
Pond 3 Post Treatment	7/10/22	ND <0.050		ND <0.050	
Pond 4 Post Treatment	7/10/22	ND <0.050		ND <0.050	
Performance Assessment	% Reduction	100%		100%	

Acknowledgements

Tanner Banks | AML Project Manager

tanner.banks@tu.org | (970) 390-9492



Thank you

Lowell Kessel, MS, P.G.
General Manager,
Remediation Specialist
Hydrogeologist
CERES Remediation Products

lowell@CERESRP.com

www.CERESRP.com

Phone: (714) 709-3683



*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*

Site Background: The Antler Mine project involved removal of mill tailings and impacted soil from BLM land, and consolidation of the mill tailings and impacted soil in an onsite waste repository on previously impacted BLM land. Due to the acid generating potential and low pH of the mill tailings, neutralization and stabilization of waste is required during placement of waste in the repository.

The mine tailings have a low pH (2 to 3 pH units) that must be neutralized (6 to 8 pH units) as part of this study. Maximum concentration of total lead and arsenic found at the site is 3,400 milligram/kilogram (mg/kg) and 850 mg/kg, respectively. The two samples which exhibited the highest lead levels (DU-3 1445 and DU-3 1500) were analyzed for leaching potential using TCLP (Toxic Characteristic Leaching Potential) and SPLP (Synthetic Precipitation Leaching Potential). In addition, analysis of cadmium levels was added to the study based on prior testing which showed occasional high levels of cadmium in the DU-3 1500 tailings. A summary of the Baseline testing results is provided here.

Tailings Name	Metal of Concern	Total Level mg/kg	TCLP Limit mg/kg	Sample Result SPLP mg/kg	SPLP Limit mg/kg	Sample Result TCLP mg/kg	TCLP Limit mg/kg
DU-3 1445	Arsenic	590	50	ND	5.0	0.19	5.0
DU-3 1445	Cadmium	4.6	100	0.3	1.0	0.29	1.0
DU-3 1445	Lead	1,000	1,000	1.2	5.0	2.4	5.0
DU-3 1500	Arsenic	23	50	0.1	5.0	0.14	5.0
DU-3 1500	Cadmium	15	100	1.0	1.0	0.68	1.0
DU-3 1500	Lead	4,700	1,000	ND	5.0	0.15	5.0

CERES Remediation Products was asked to recommend reagent(s) that would reduce lead and arsenic and bring the pH back to neutral conditions after soil mixing and treatment at the site while considering long term resilience and performance of the treated tailings. CERES provided MTS® remediation chemistries to achieve the site goals during the treatment trials.

Solution: An inhouse laboratory for the contracting parties performed the treatability studies comparing MTS® performance to that of Enviroblend® and Portland Cement mixing reagents at dosages between 1 and 6% by wt.

Performance Testing Results:

pH: The MTS® was shown to be the best performing reagent to provide neutral pH (pH levels of 7.25 and 7.09) at the 1.5% dose. Note that Ordinary Portland Cement was not capable of maintaining the pH within the neutral range (exhibited low pH levels of 4.72 to 4.81 pH units) at the lower dose (1.5% dose).

Arsenic and Lead Reduction: MTS® reduced leachable Arsenic and Lead to acceptable criteria in the tailings as shown in the summary table below.

Sample Name	Treatment Reagent and Dose	Replicate	Metal	SPLP Leachable Arsenic mg/L	TCLP Leachable Arsenic mg/L	Metal	SPLP Leachable Lead mg/L	TCLP Leachable Lead mg/L	Metal	SPLP Leachable Cadmium mg/L	TCLP Leachable Cadmium mg/L
DU-3 1445	MTS 1.5-2	Replicate #2	Arsenic	ND	0.096	Lead	0.0064	0.220	Cadmium	0.0420	0.061
DU-3 1445	MTS 1.5-3	Replicate #3	Arsenic	ND	0.110	Lead	0.0086	0.210	Cadmium	0.0660	0.032
DU-3 1500	MTS 2-2	Replicate #2	Arsenic	ND	ND	Lead	0.0073	0.420	Cadmium	0.0440	0.053
DU-3 1500	MTS 2-3	Replicate #3	Arsenic	ND	ND	Lead	0.2100	0.500	Cadmium	0.0710	0.085

Comparison to Enviroblend®

A second treatability study was completed using a chemical reagent from EnviroBlend® for the stabilization of the mine tailings. Results from the treatability study show that:

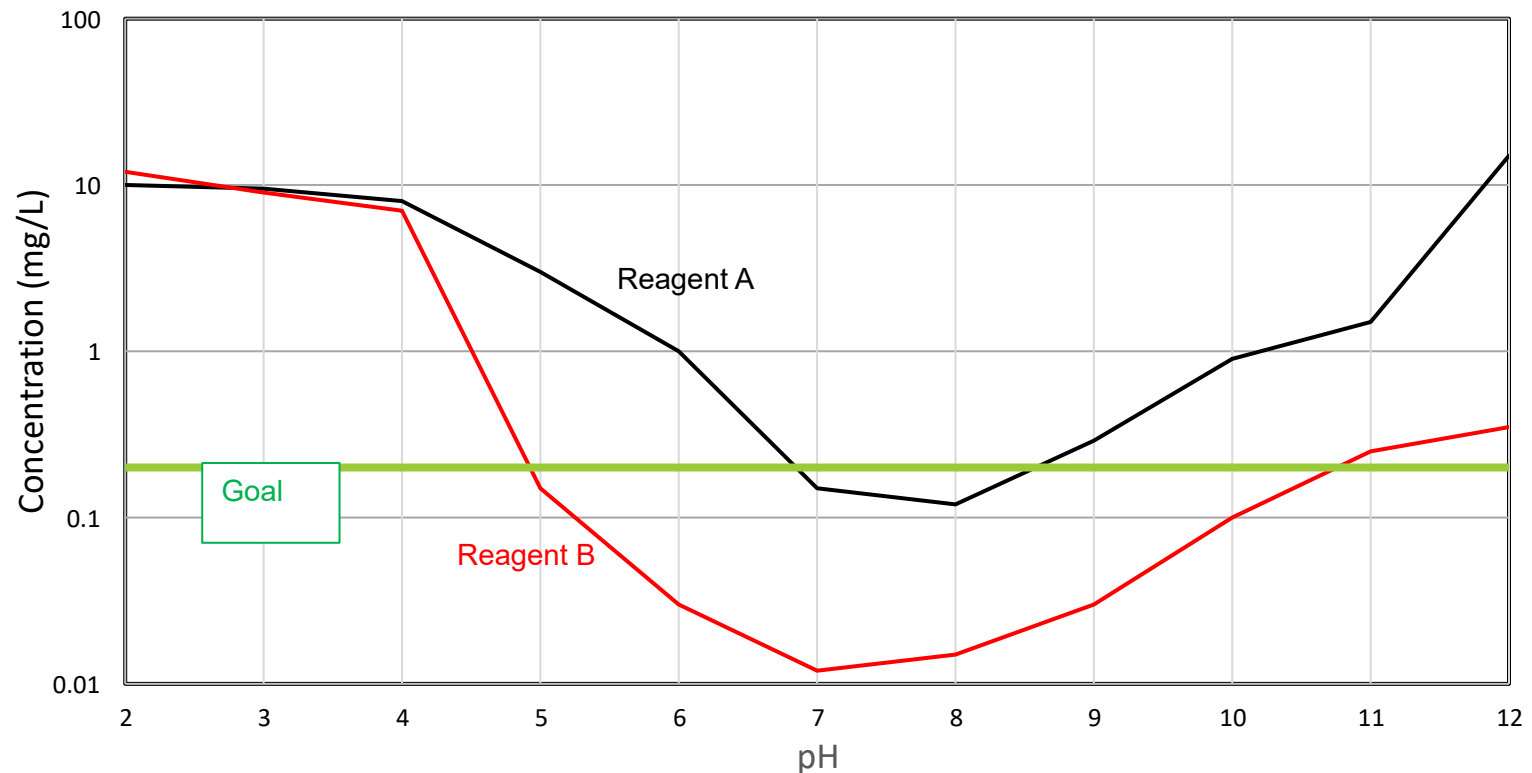
- pH of the tailings was not easily neutralized by EnviroBlend®.
- Higher dosage rates of 5% to 7%wt was required. **These rates are much higher when compared to the dosage rates needed for MTS (1.5%).**
- Dosage rates (5% to 7%) required to stabilize the **cadmium** to be within the metals leaching limit (SPLP) using EnviroBlend®.
- EnviroBlend® will not be practical as the costs are expected to be 4-5X higher \$\$\$.

***All test methods are not
applicable to all end uses and
remediation goals.***

Test Methods and Treatment Goals

Toxicity Characteristic Leaching Procedure (TCLP)	Land Disposal
Synthetic Precipitation Leaching Procedure (SPLP)	All 3 used when stabilized soil is placed above the water table
Site-specific leaching procedures (SSLP)	SSLP and PBEP may be used for PRBs / GW or waste water
Parallel Batch Extraction Procedures (PBEP)	
Multiple Extraction Procedure (MEP)- 1,000yrs	Long-term stabilization (1,000 years or longer)
Physiologically Based Extraction Test (PBET)	Risk to human gastro-intestinal tract

Can you predict future pH?



Parallel Batch Extraction with pH
USEPA SW-846 Method 1313

In-Situ Design- Planning for the Future

Long term sustainable design includes evaluation of possible scenarios.

- ❖ How likely are conditions to change?
- ❖ For groundwater applications, will upgradient redox conditions be different from the treatment area or downgradient plume?
- ❖ What about unforeseen catastrophic events?
E.g. 100 year storms, rising groundwater table, flooding from sea level rise or river bank collapse

Site Background: Arsenic in shallow stiff sandy silt and clay soils exceeds risk-based regulatory screening criteria and background level and thus required reduction to meet State and Federal cleanup standards. Potential sources of arsenic at the site are from the historical application of arsenate-containing herbicides used in the 1940s for fire control. Maximum concentration of total arsenic found at the site is 240 milligrams/kilograms (mg/kg) with the range of reported concentration of 3.04 to 240 mg/kg. Background arsenic concentrations are estimated to be approximately 10 mg/kg.



Approach:

In Situ-Stabilization (ISS) was evaluated as one of several remediation approaches to agency cleanup criteria. CERES Remediation Products was retained by WSP USA Environment and Infrastructure to provide non-hazardous and non-ecotoxic reagent(s) for ISS that would reduce arsenics bioavailability at the site and not result in more hazardous byproducts. CERES provided MTS® remediation chemistries to achieve the site remedial goals.

Bench-Scale Study:

A bench-scale treatability study was initially performed to assess optimal amendment and dosage rate applications for ISS treatment to occur as part of the field portion of the pilot study.

The results indicated that MTS® addition to soil reduced bioaccessible Arsenic concentrations to 5.1 mg As/kg soil resulting in a greater than 83% reduction at a 10% wt dosage after simple mixing of soil and reagent and addition of water for increased moisture. Soil conditions post treatment included a change in pH from 6 to 5 and short-term increased temperature by 3 degrees °F. Relative bioavailability was reduced from a background of 19.6% in the untreated soil to 7.0% in the treated soil, **resulting in a reduction of relative bioavailability of 64%.**

In-Field Portion of Pilot Study:

The pilot study plot was divided into four treatment areas approximately 20-feet wide by 10-feet long several remedial alternatives. Treatment depths were limited to the upper 12 inches of soil which is where the accumulated As remained.



The treatment was performed with rotary tilling equipment to mix in the MTS® reagent mixture and water.

Performance Criteria:

Performance criteria included 3- and 12-month post treatment soil testing to verify longer term performance and resilience of MTS® sequestration and reduction of relative bioavailable Arsenic.

The results are as follows:

3-month results:

As bioaccessibility reduced 86%

30.5 mg As/kg >> 4.4 mg As/kg

As relative bioavailability reduced 66%

19.6% >> 6.6%

This is 4% greater reduction than lab results!

12-month results:

As bioaccessibility reduced 92%

30.5 mg As/kg >> 2.4 mg As/kg

As relative bioavailability reduced 78%

19.6% >> 4.4%

This is 12% greater reduction than 3Month results!

MTS® continues to perform better than lab scale results 1 year after application on-site. MTS® ensures the highest level of sequestration resilience and long-term reduction of Arsenic bioaccessibility.

MTS® Outperformed leading competitor in competitive trial and at lower cost \$\$\$