Heavy Metals Remediation Design: Temporary or Long Term Solutions?

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What is metals stabilization?

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

- Leaching from soil
- Groundwater concentrations
- Toxicity

Reagents are typically:

- Common agricultural and industrial chemistries combined in proprietary blends
- Pose little to no hazard to the environment
- Requires simple (low tech) equipment that is low in cost
### Stabilization is a Green Remediation Alternative

<table>
<thead>
<tr>
<th>TRADITIONAL APPROACH</th>
<th>GREEN ALTERNATIVE</th>
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<tbody>
<tr>
<td>Excavation of metals-contaminated soil from site</td>
<td>Chemically stabilize metals to render non-hazardous</td>
</tr>
<tr>
<td>Backfill site with clean fill</td>
<td>Potentially reuse stabilized soil</td>
</tr>
<tr>
<td>Dispose as hazardous waste</td>
<td>Dispose as non-haz material</td>
</tr>
<tr>
<td>Haul hazardous materials to limited landfill locations (increased carbon footprint)</td>
<td>More disposal options locally for solid waste management (non-hazardous)</td>
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</table>
Stabilization Chemistry

In-House Chemical Engineering + Leachability Laboratory:

- Demonstrate short- and long-term stability
- Support reuse of remediated soil on-site
- Resolve source and groundwater plume impacts
- Guide field implementation and design
Quick Overview of Process

1. Site Characterization
2. Treatment Goals Identification / Establishment
3. Treatability studies
4. Remedy Design
5. Performance Testing / Verification

Implement!
Testing for Remedy Design

Stabilization design
- Site characterization
- Treatability studies
- End use evaluation

Remediation goals

Exposure risks

Cost implications
Stabilization Objectives Development

- Off-Site Disposal
  - Hazardous
  - $$$
  - Non-hazardous
  - Reagent Selection*

- On-Site Reuse
  - Direct exposure
  - Covered /Leaching
  - Reagent Selection*

* Reagent selection based on appropriate leaching lab test procedure, and the best performing, most cost-effective chemistry.
Treatability Study Program

1. Prepare a work plan
2. Collect test samples
3. Characterize the Initial Sample
   1. Homogenize raw materials o Perform physical testing
   2. Perform chemical testing
4. Perform treatability testing
   1. Identify appropriate reagents
   2. Conduct testing by mixing reagents with contaminated material and prepare formulations for further testing
   3. Optimize mix design
   4. Selection of mix design verification phase o Prepare final mix design and test
5. Analyze, Assess and Validate Data
6. Prepare treatability study report
Application Approaches

Methods

◦ Injection
◦ Mechanical mixing
◦ Permeable reactive barriers

Reagents can be applied *in situ* or *ex situ* in

◦ Dry, granular form
◦ As a solution, or slurry
Test Methods

- Toxicity Characteristic Leaching Procedure (TCLP). USEPA, SW-846 Method 1311
- State-specific procedures (i.e., CA WET)
- Synthetic Precipitation Leaching Procedure (SPLP). USEPA, SW-846 Method 1312
- Multiple Extraction Procedure (MEP). USEPA, SW-846 Method 1320
- Site-specific leaching procedures (e.g. SSLP with groundwater, waste water)
- In vitro Bioaccessibility (IVBA, EPA 9200.2-86, April 2012)
- Parallel Batch Extraction Procedures (PBEP). USEPA, SW-846 Pre-Methods 1313, 1314, and 1315 (L:S partitioning as a function of pH)
- ASTM Methods. e.g. D3987-85 (neutral leaching), D4842-89 (monolith leaching), D6234-98 (mining wastes)
## Test Methods and Treatment Goals

<table>
<thead>
<tr>
<th>Procedure</th>
<th>Land Disposal</th>
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<tbody>
<tr>
<td>Toxicity Characteristic Leaching Procedure (TCLP)</td>
<td>Used when stabilized soil is placed above the water table</td>
</tr>
<tr>
<td>Synthetic Precipitation Leaching Procedure (SPLP)</td>
<td>SSLP and PBEP may be used for PRBs / GW or waste water</td>
</tr>
<tr>
<td>Site-specific leaching procedures (SSLP)</td>
<td>PBEB used in resilience design</td>
</tr>
<tr>
<td>Parallel Batch Extraction Procedures (PBEP)</td>
<td></td>
</tr>
<tr>
<td>Multiple Extraction Procedure (MEP)- 1,000yrs</td>
<td>Long-term stabilization (1,000 years or longer)</td>
</tr>
<tr>
<td>Physiologically Based Extraction Test (PBET)</td>
<td>Risk to human gastro-intestinal tract</td>
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</tbody>
</table>
Design Planning for the Future

Long term sustainable design includes evaluation of possible scenarios.

- How well have you characterized the site?
- How likely are conditions to change?
- What about unforeseen catastrophic events?
- Are you considering resilience in your design?
Generic behaviors of several inorganic contaminant types showing generalized minima/maxima as a function of pH.

Figure B-3. Generic behaviors of several inorganic contaminant types showing generalized minima/maxima as a function of pH.

For organic contaminants, measured LSP concentrations are associated with partitioning between organic and aqueous phases, as well as complexation with dissolved carbon in the aqueous phase. The organic-aqueous partitioning of a contaminant is described in the literature using the octanol-water partitioning coefficient, $K_{ow}$. This partitioning is relatively tolerant of changes in pH; however, the dissolution of organic carbon, and hence the complexation with organic contaminants, are strongly dependent on pH, especially in the alkaline range. In Figure B-4, the relative concentrations of DOC and total PAHs in a leachate are shown before and after removal of the organic carbon through flocculation.

Figure B-4. pH-dependent leaching of DOC and associated PAH concentrations from contaminated sediment. Source: After Roskam and Comans 2003.

B.4.2 Preamethod

This percolation column method (EPA 2010b) is designed to provide the LSP of constituents as a function of L/S under conditions where water percolates through the solid material.
Parallel Batch Extraction Procedure
(Arsenic in pre-treated (a) and post-treated (b) coal fly ash)

by the Missouri University of Science & Technology (CTIS News, vol. 7, no. 2).
Lessons Learned

POOR CSM DEVELOPMENT

◦ Low resolution sampling
  ◦ Spatial and vertical delineation
◦ Wrong laboratory testing procedures
◦ Sample integrity
◦ Improper goal setting
◦ Baseline vs confirmation sampling design
◦ Material properties not considered

POOR IMPLEMENTATION

◦ No treatability study or poorly performed
  ◦ Sample collection method
  ◦ Sample integrity
◦ Wrong chemistry or product
  ◦ One size fits all solutions have higher failure rates
◦ Poor Mixing Design / Equipment
◦ Performance Sampling and sampling procedure
Case Study Review

Sustainable long term heavy metals design.

Goal: Many hundreds of years

Heavy Metal: Zinc

Result: Success! Immediate treatment goals achieved
Case Study: Brownfields Redevelopment - Zinc

Former large industrial site redeveloped into residential use

Petroleum hydrocarbon, chlorinated solvent, and zinc contamination in soil and groundwater

No further action for soil, continued groundwater and surface water monitoring

Post-development, surface water exceeded discharge standards for zinc

In situ remedy developed for saturated soil and groundwater
Case Study: Brownfields Redevelopment - Zinc

Bench-scale tests were performed to decrease zinc from 30 mg/L to:

- <0.020 mg/L in the bench study

Demonstrated stability equivalent to over 400 years with modified multiple extraction procedure (MEP)
Multiple Extraction Procedure
Permeable Reactive Barrier. Goal of 2 mg/L from 20 mg/L.
Represents 480 years of groundwater flow
Case Study: Brownfields Redevelopment - Zinc

Pilot Testing (6 injections, 5 borings, 3 monitoring wells)

- Visual observations of reagent distribution in soil cores
- Soil pH and SPLP measurements in cores
- Monitoring wells groundwater samples to assess “integrated” effect of heterogeneous reagent distribution

Only 2-days allowed for reagent effects to permeate the injection zone

RESULTS - 0.61 mg/L in the pilot study
Case Study: Brownfields Redevelopment – Zinc Pilot study determination of reagent distribution

**pH in soil**

Visual reagent observation
Case Study: Brownfields Redevelopment - Zinc
Case Study: Brownfields Redevelopment - Zinc

Full-scale implementation of 45,000 gallons of diluted reagent injected in 63 locations over a 4-week period

Within 1 year surface water zinc concentrations decreased by 50 to 70 percent and within 3 years surface water goal achieved
Lessons Learned: Brownfields Redevelopment - Zinc

Soil samples:
- pH “halos” around the heterogeneous reagent distribution
- 83 percent of post-injection soil samples SPLP <0.020 mg/L of zinc

Groundwater samples
2 of 3 noted > 97 percent reduction in zinc concentration
1 of 3 noted no concentration reduction
Conclusions

Significant cost savings can be achieved through metals stabilization.

Options are available for recycling and reuse of soil.

Design can consider long term sustainability.

Site-specific chemistries and appropriate test methods may be required to create greater project design flexibility.
Obrigado

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