Disposal of Arsenic Residuals

Innovations in Arsenic Management for Water Providers

The University of Arizona

February 17, 2006
Background and Motivation

• 2001 revised standard for As in drinking water
  • 10 $\mu$g/L MCL (from 50 $\mu$g/L)

• Predicted impacts
  • 4000 new utilities impacted ( >95% small)
  • ~ 400 Arizona utilities impacted
  • 6 – 24 Mlb solid residuals annually
  • ~ 30,000 lb As /yr
Arsenic-bearing Solid Residuals (ABSR)

Solid Residuals from Adsorption Processes

- Alumina-based Media (Alcan AA)
- Iron-based Media (GFH*, Sorb 33*, greensand)
- Zeolites (Z33*)
- Other Sorbents (SAMMS*, Mn Oxides*, As:Xnp*, TiO₂)

Metal (Fe, Al, Mn, Ca) Sludges

- Anion exchange (incl. enhanced media & recovery*)
- Reverse osmosis
- Precipitation/Softening
- Conventional coagulation / flocculation
- Coagulation assisted microfiltration
Commercial As Sorbents: Examples

Granular Ferric Hydroxide
55% Fe(OH)$_3$ and β-FeOOH, with a wet density of 1.26 g/cm$^3$ and particle sizes of 0.32-2 mm

Bayoxide Sorb-33
A synthetic iron oxide hydroxide containing about 90% α-FeOOH, with a dry density of 0.45 g/cm$^3$ and particle sizes of 0.5-2 mm
How to determine if a solid waste will be potentially classified as a hazardous waste under the toxicity characteristic criterion?

(1) Identify toxic components in the waste (e.g., EPA hazardous waste list)
(2) Subject the waste to the TCLP (Toxicity Characteristic Leaching Procedure) test.
(3) Analyze toxic component concentration in TCLP extract and compare with EPA MCL (Toxicity Characteristic – 5 mg/L for As)

In California: use Wet Extraction Test (WET)
## Residuals Assessment

<table>
<thead>
<tr>
<th></th>
<th>TCLP</th>
<th>WET</th>
<th>Mature Landfill</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>pH</strong></td>
<td>4.95</td>
<td>5.05</td>
<td>7-9</td>
</tr>
<tr>
<td><strong>Bioactivity</strong></td>
<td>abiotic</td>
<td>abiotic</td>
<td>biotic</td>
</tr>
<tr>
<td><strong>Duration</strong></td>
<td>18 hr</td>
<td>48hr</td>
<td>weeks/months</td>
</tr>
<tr>
<td><strong>Active Reagent</strong></td>
<td>acetate</td>
<td>citrate</td>
<td>Mix of organics &amp; inorganics</td>
</tr>
<tr>
<td><strong>Redox Condition</strong></td>
<td>oxidizing</td>
<td>neutral</td>
<td>reducing</td>
</tr>
</tbody>
</table>
Residuals Assessment: As leaching

Leachate Arsenic (µg/L)

- GFH
- AA

Leach Test

Init Ldg  TCLP  TCLP-48  CA-WET  Lndfl Lcht

0  200  400  600  800  1000  1200
Landfill Simulation Columns

SYRINGE PUMP (FLOW RATE 0.31 mL/min)

INFLUENT

GAS COLLECTION

MARIOTTE FLASK
10% NaOH SOLUTION WITH pH INDICATOR

DEAERATED, DEIONIZED WATER

SATURATED ZONE

GRAVEL

UNSATURATED ZONE

GRAVEL

COLLECTION FLASK

23% SHREDDED PAPER
46% YARD WASTE
31% SOLID RESIDUAL
4L ANAEROBIC DIGESTOR SLUDGE

WATER LEVEL

SAMPLING PORTS

EFFLUENT
GFH Landfill Column Leachate

- Time (days)
- Iron (mg/L)
- As (mg/L)

- Fe (total)
- As (total)
GFH Column Leachate: Arsenic Speciation

- As(III)
- As(V)
- As(dissolved)
- As(digested)
Management of ABSR

solid waste
- ad-hoc disposal
- hazardous waste landfill

stabilize
- crystallization

encapsulation
- vitrification
- cement
- polymer composite

leaching tests

MSW landfill
ABSR Stabilization: Approach

(1) Contain/isolate residuals, or

(2) Allow leaching of As at levels below MCL

But EPA has set MCLG (Goal) for As at 0 µg/L, hence we must seek to contain
Stabilization Strategies

(1) Encapsulate residuals in solid matrix to inhibit As leaching

(2) Dissolve and recrystallize As into more stable solid phases
Encapsulation Technologies

(1) Vitrification
(2) Grout/cement
(3) Polymer composites

Desired characteristics of encapsulation process and waste form:

- Durable (retains toxics under landfill conditions)
- Efficient (maximum toxics loading possible)
- Environmentally friendly (no use of flammable/toxic solvents or high temperatures in its manufacture)
- Cost effective
Vitrification

Encapsulate waste in molten glass and cool to solidify

It is the preferred encapsulation technology to stabilize low-level radioactive solid waste

Disadvantages:
- Energy intensive (high cost)
- Involves high temperatures (volatilization)
Cement

Encapsulate waste in cement matrix

Advantages:

(1) Cheap
(2) Readily available
(3) Easy to process
(4) Widely used (available durability data)
Cement Encapsulation


Mix until uniform (minutes)

Cure at 20°C for 40 days

Sand/Cement ratio = 3.0
Water/(Sand+Cement) ratio = 0.42
Cement Encapsulation of E-33

Legend shows wt% of sorbent in sample
Problems of cement encapsulation:

(1) Low maximum loadings
   (up to 15% E-33, 20% GFH)

(2) In contact with water, soluble cement components increase pH and enhance As solubility
Cement Encapsulated Leaching

As Concentration (ppm)

- GFH - 18% Loading
- E33 - 18% Loading
- AAFS - 15% Loading
Polymeric Waste Form

Waste form composed of a 1:1 weight ratio blend of polystyrene butadiene (PSB) rubber and epoxy resin.

Both polymers are inexpensive and widely used.

PSB is available as an aqueous emulsion, i.e. PSB latex.

Curing can take place at low temperatures.
Polymeric Waste Form Synthesis

Aqueous processing route

PSB latex
Epoxy resin
Surfactant (Span 80)

Mixing
Cross linking agent (DETA)
Solid waste
Mixing

Final Waste Form

Drying and curing at 80°C

Solid waste or salt solution
Polymer precursors as an emulsion

Phase inversion: polymers go from being the discontinuous phase to being the continuous phase, encapsulating solid waste

Encapsulated solid waste or salt
Continuous polymeric matrix
SEM/EDS Elemental Mapping

Sample composition: 10% Fe(OH)_3, 4.6% NaCl, 0.3% NaNO_3
Polymer Encapsulation of GFH

Maximum loading (GFH, E-33): >60%
Microstructure-SEM

60% w/w GFH Loaded Wasteform

Cut Interior of Wasteform

Skin and Fracture Surface of Wasteform
Polymer Encapsulated Leaching

As Concentration (ppm)

- Unencapsulated
- Large Monolith - 60% Loading
- Thin Rods - 60% Loading
- Dipped Rods - 60% Loading

GFH
- Unencapsulated: 9.3
- Large Monolith: 1.2
- Thin Rods: 1.9
- Dipped Rods: 0.05

E33
- Unencapsulated: 6.1
- Large Monolith: 5.0
- Thin Rods: 5.2
- Dipped Rods: 0.14

AAFS
- Unencapsulated: 5.0
- Large Monolith: 0.7
- Thin Rods: 0.8
- Dipped Rods: 0.01
Can a polymeric matrix be durable?

Amber: colloidal suspension in a resin polymer
Stabilization by Crystallization

After adsorption, As is on the exposed surface of sorbents and available for leaching.

What if As were incorporated into the crystal structure of the sorbent?
Amorphous Ferric Hydroxide Crystallization
## Stability of Natural As Minerals

<table>
<thead>
<tr>
<th>Time (d)</th>
<th>pH</th>
<th>Fe (mg/L)</th>
<th>As (mg/L)</th>
<th>pH</th>
<th>Fe (mg/L)</th>
<th>As (mg/L)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>3.5</td>
<td>--</td>
<td>3.0</td>
<td>8.1</td>
<td>--</td>
<td>--</td>
</tr>
<tr>
<td>9</td>
<td>--</td>
<td>0.2</td>
<td>3.0</td>
<td>--</td>
<td>&lt;0.2</td>
<td>28</td>
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<tr>
<td>27</td>
<td>4.8</td>
<td>&lt;0.2</td>
<td>3.6</td>
<td>8.15</td>
<td>&lt;0.2</td>
<td>27</td>
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<tr>
<td>48</td>
<td>4.5</td>
<td>&lt;0.2</td>
<td>1.6</td>
<td>7.85</td>
<td>&lt;0.2</td>
<td>16</td>
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<tr>
<td>241</td>
<td>5.3</td>
<td>&lt;0.2</td>
<td>1.4</td>
<td>6.85</td>
<td>&lt;0.2</td>
<td>6.7</td>
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<tr>
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<th>pH</th>
<th>Fe (mg/L)</th>
<th>As (mg/L)</th>
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</thead>
<tbody>
<tr>
<td>14</td>
<td>7.1</td>
<td>--</td>
<td>&lt;0.005</td>
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<tr>
<td>60</td>
<td>6.7</td>
<td>--</td>
<td>0.210</td>
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<tr>
<td>179</td>
<td>6.6</td>
<td>--</td>
<td>0.223</td>
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Recommendations

(1) “On the basis of available evidence, it is prudent not to use unlined MSW landfills for disposal of ABSR” (Conclusions of Rio Rico As Residuals Workshop, Feb. 06).

(2) If ABSR are disposed of in MSW landfills, collected leachate should be monitored for As. “Worst case scenario” calculations could be performed to assess leaching before disposal.

(3) Long term: more research on residuals leaching and stabilization.