Current Overview of Groundwater Remediation Options for CCR Units

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Christopher A. Robb, P.E.
March 21, 2018
Overview

• Introduction and Problem Statement
• Applicable Groundwater Remedial Alternatives
  – Monitored natural attenuation (MNA)
  – Hydraulic control (in-situ and ex-situ)
  – In-situ redox approaches
  – Biogeochemical injections
  – Slurry walls
  – Permeable reactive barriers (PRBs)
  – In-situ stabilization/solidification (ISS)
• Remedial Alternative Selection Process and Costs
Environmental Challenges

• Mostly unlined ponds
• Hydraulic head created by wet disposal
• Type of constituents and concentrations dependent on:
  – Source of coal
  – Boiler operating conditions/air pollution control devices
  – Age of materials
  – Wet (active) versus dry (inactive)
  – Chemical makeup of CCR materials (bottom ash, fly ash, FGD, etc.)
  – Geochemical conditions in CCR unit and subsurface (ash below water table?)
Environmental Challenges

- Potential groundwater impacts limited to inorganics
  - Boron (B), arsenic (As), selenium (Se), iron (Fe), manganese (Mn)
  - Sulfate (SO₄²⁻), chloride (Cl), total dissolved solids (TDS), pH
  - Site-specific issues (e.g., mercury [Hg], vanadium [V], thallium [Tl], ammonia [NH₃-N])

- Natural background versus leaching versus geochemical changes
  - Fe, Mn, pH
  - V (e.g., NC)

Leaching Results for 34 Fly Ashes EPA-600/R-09/151, December 2009

<table>
<thead>
<tr>
<th></th>
<th>Hg</th>
<th>Sb</th>
<th>As</th>
<th>Ba</th>
<th>B</th>
<th>Cd</th>
<th>Cr</th>
<th>Co</th>
<th>Pb</th>
<th>Mo</th>
<th>Se</th>
<th>TI</th>
</tr>
</thead>
<tbody>
<tr>
<td>Total in Material (ng/kg)</td>
<td>0.01 – 1.5</td>
<td>3 – 14</td>
<td>17 – 510</td>
<td>590 – 7,000</td>
<td>NA</td>
<td>0.3 – 1.8</td>
<td>66 – 210</td>
<td>16 – 66</td>
<td>24 – 120</td>
<td>6.9 – 77</td>
<td>1.1 – 210</td>
<td>0.72 – 13</td>
</tr>
<tr>
<td>Leach results (μg/L)</td>
<td>&lt;0.01 – 0.50</td>
<td>&lt;0.3 – 11,000</td>
<td>0.32 – 18,000</td>
<td>50 – 670,000</td>
<td>210 – 270,000</td>
<td>&lt;0.1 – 320</td>
<td>&lt;0.3 – 7,300</td>
<td>&lt;0.3 – 500</td>
<td>&lt;0.2 – 35</td>
<td>&lt;0.5 – 130,000</td>
<td>5.7 – 29,000</td>
<td>&lt;0.3 – 790</td>
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<tr>
<td>TC (μg/L)</td>
<td>200</td>
<td>-</td>
<td>5,000</td>
<td>100,000</td>
<td>-</td>
<td>1,000</td>
<td>5,000</td>
<td>-</td>
<td>5,000</td>
<td>-</td>
<td>1,000</td>
<td>-</td>
</tr>
<tr>
<td>MCL (μg/L)</td>
<td>2</td>
<td>6</td>
<td>10</td>
<td>2,000</td>
<td>7,000</td>
<td>5</td>
<td>100</td>
<td>-</td>
<td>15</td>
<td>200</td>
<td>50</td>
<td>2</td>
</tr>
</tbody>
</table>

Vanadium in Groundwater

- Infection Point
- V (ppb)
- 100
- 50
- 10
- 0.2
- 0.1

Grid Cell Interpolated Thematic Grid Cell = 0.0005
Groundwater Monitoring

- Appendix III
  - Detection monitoring
  - “Indicator” parameters
  - First annual reports are published
    - Statistically significant increases (SSIs) are wide-spread throughout the industry
  - Alternate source demonstrations (ASDs) currently being implemented
    - Many unlined units do appear to have “fingerprint” of CCR management
    - If ASD is unsuccessful, assessment monitoring is required

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Appendix III to Part 257—Constituents for Detection Monitoring

<table>
<thead>
<tr>
<th>Common name 1</th>
</tr>
</thead>
<tbody>
<tr>
<td>Boron</td>
</tr>
<tr>
<td>Calcium</td>
</tr>
<tr>
<td>Chloride</td>
</tr>
<tr>
<td>Fluoride</td>
</tr>
<tr>
<td>pH</td>
</tr>
<tr>
<td>Sulfate</td>
</tr>
<tr>
<td>Total Dissolved Solids (TDS)</td>
</tr>
</tbody>
</table>
Groundwater Monitoring

- Appendix IV
  - Assessment monitoring
  - Statistical significant levels (SSLs) above groundwater protection standards
    - MCL or background for constituents without MCL
  - Uncertainty related to timelines in the (revised) Rule, inclusion of B in App. IV, use of risk-based approaches
  - If App. IV ASDs are unsuccessful, assessment of corrective measures needed

Appendix IV to Part 257—Constituents for Assessment Monitoring

<table>
<thead>
<tr>
<th>Common name 1</th>
</tr>
</thead>
<tbody>
<tr>
<td>Antimony</td>
</tr>
<tr>
<td>Arsenic</td>
</tr>
<tr>
<td>Barium</td>
</tr>
<tr>
<td>Beryllium</td>
</tr>
<tr>
<td>Cadmium</td>
</tr>
<tr>
<td>Chromium</td>
</tr>
<tr>
<td>Cobalt</td>
</tr>
<tr>
<td>Fluoride</td>
</tr>
<tr>
<td>Lead</td>
</tr>
<tr>
<td>Lithium</td>
</tr>
<tr>
<td>Mercury</td>
</tr>
<tr>
<td>Molybdenum</td>
</tr>
<tr>
<td>Selenium</td>
</tr>
<tr>
<td>Thallium</td>
</tr>
<tr>
<td>Radium 226 and 228 combined</td>
</tr>
</tbody>
</table>
Groundwater Remedial Alternatives

- If groundwater impacts with Appendix IV constituents are attributable to a release from a CCR unit, active remediation beyond pond closure may need to be considered.

- Inorganics cannot be destroyed or degraded, but only captured/contained or rendered immobile.
  - Affects/limits potentially available remedial technologies:
    - Monitored natural attenuation (MNA)
    - Hydraulic control (in-situ and ex-situ)
    - In-situ redox approaches
    - Biogeochemical injections
    - Permeable reactive barriers (PRBs)
    - Slurry walls
    - In-situ stabilization/solidification (ISS)
Monitored Natural Attenuation
Monitored Natural Attenuation

- Established protocol to implement MNA for inorganics
  - Reliance on natural attenuation processes to achieve site-specific remediation objectives within a reasonable time frame
  - Tiered approach/"lines of evidence"
    1. Clear and meaningful trend of decreasing contaminant mass/concentrations over time
    2. Hydrogeologic and geochemical data to (indirectly) demonstrate type(s) of natural attenuation process active
    3. Use of data from field or microcosm studies to directly demonstrate occurrence of a particular attenuation process

MNA of CCR Leachate

Generalized Site Scenario

- Source Zone
- Seepage into Surface Water
- Threat to Water Supply Well
- Contaminant Plume
• Plume stability through immobilization on aquifer solids
• These constituents will remain present on aquifer solids
• Thus, the need for demonstration of attenuation mechanism, stability of attenuation
<table>
<thead>
<tr>
<th>Tier 1</th>
<th>Evaluation of plume stability</th>
</tr>
</thead>
<tbody>
<tr>
<td>Tier 2</td>
<td>Evaluation of rate and mechanism</td>
</tr>
<tr>
<td>Tier 3</td>
<td>Evaluation of capacity and stability</td>
</tr>
<tr>
<td>Tier 4</td>
<td>Development of LTM plan; contingencies</td>
</tr>
</tbody>
</table>
Hydraulic Control
Hydraulic Control (P&T)

- **Objectives**
  - Intercept migrating Contaminants of Concern (COCs)
  - Collect COCs from within a zone of influence
    - Extract with wells or collection trenches
  - Inject treated water to facilitate aquifer remediation

- **Fundamental Concepts**
  - Hydraulic containment of plume
    - Boundary control
  - Contaminant mass removal
  - Source control measures
  - Protect public drinking water wells
Hydraulic Control (P&T)

- Often considered “presumptive remedy” at many sites
- May require above-ground treatment to meet effluent discharge criteria
  - Surface water discharge (NPDES)
  - Groundwater injection (UIC)
- Reuse potential
  - Dust suppression
  - CCR conditioning
  - Irrigation/land application
  - Process make-up water/cooling towers
- May effectively address the mix of constituents expected at CCR sites
- Many facilities have existing wastewater treatment capabilities (retention ponds, treatment plants, etc.)
Hydraulic Control (In-Situ Treatment)

- Hydraulic control without the need for above-ground water management/treatment
- TreeWell® system
  - Engineered phytoremediation system
  - LDA installation approach
  - Tree acts as solar-driven pump
  - Design based on GW flow velocity and cross-sectional area to be “intercepted”
  - Achieves design hydraulic control parameters after about 3 growing seasons

Image: Applied Natural Sciences, Inc.
Engineered Phytoremediation: The *TreeWell* System

- Patented by Geosyntec’s partner firm Applied Natural Sciences, Inc. (ANS)
- Targets specific groundwater by directing root growth downward to capillary fringe
- Groundwater is drawn upward through the soil column, then absorbed by plant roots
- Highly adaptable – can be tailored to specific site conditions
- Effectively target deep or confined aquifers
- Optimizes growing conditions for trees
- Bioreactor effect – both oxidizing and reducing zones in each unit
- Increases soil temps – enhances biodegradation rates in vadose zone
- Pre-treatment option (reactive treatment media)
- Active treatment – in a passive manner
Case Study: Central FL
1,4-Dioxane in Groundwater

Site Background
- Fractured bedrock aquifer 5'-15' bgs; contaminant mass and flow in a thin fractured zone in the 10'-15' horizon
- Initial Remedy: Long-term pump & treat system with UV/Peroxide
  - >$300K/Year O&M costs
  - >10 Years to meet Remedial Goals

Phytoremediation Implemented
- Dense forest of low-quality non-native wetland species cleared for phytoremediation system
- Expedite permitting process by promoting wetland restoration

Remedial Goals
- Hydraulic Control
- Contaminant Treatment
Case Study: System Installation

System Installation Details

- 154 Units Installed
- 48” Borehole Drilled to 15’ bgs
- Set liner system to top of impacted zone
- Plantings set 20 feet on center
- Native trees:
  - Slash Pine (Pinus elliottii)
  - Sycamore (Platanus occidentalis)
  - Willow (Salix caroliniana)
  - Pond Cypress (Taxodium ascendens)

2013 Installation

Summer 2015
Case Study: Impact on Groundwater Flow

• **Yellow** indicates initial GW flow at time of Phyto System installation (away from source area towards site boundary)
• **Blue** indicates GW flow 18 months after Phyto System installed (gradient reversal/hydraulic control; flow towards the Phyto System)

Results have been very consistently positive:
• Groundwater flow had been historically to the west-northwest
• Some changes in flow were seen in the first season
• By the end of the second season, groundwater flow had reversed

*Demonstration of hydraulic capture enabled shutdown of the existing pump and treat system. The system has since been dismantled and removed.*
Case Study: Modeled vs Actual Groundwater Flow

Case Study: Modeled vs Actual Groundwater Flow

Modification of Groundwater Flow Regime – Comparison of Model to Actual Nov. 2014
In-Situ Redox-Altering Approaches
In-Situ Redox-Altering Approaches

- Chemical oxidants or reductants
  - ISCO and ISCR
    - Depending on mobility of compound

- Mechanical processes
  - Air sparging
    - Promote Fe precipitation and sorption/co-precipitation of As

- Biogeochemical processes

- Direct Reduction (As, Se, Cr)
- Indirect Reduction (As, Cr, Cd, Co, Mo, Hg, Pb, Sb, Tl)
- Chemical Reactions (Ba, Ra)
- Sorption in Biomass (Be)
Biogeochemistry

Oxidizer

Reduction

Sulfur Cycle

\[
\begin{align*}
SO_2^- & \rightarrow SO_3^- \\
S & \rightarrow S_2O_3^{2-} \\
S_2 & \rightarrow S_2O_3^{2-} \\
S_2O_3^{2-} & \rightarrow SO_3^- \\
SO_3^- & \rightarrow SO_2^-
\end{align*}
\]
Biogeochemical Stabilization of CCR

- Current approaches for stabilizing CCR focus predominately on physical technologies to manage ash.
- Could we stabilize metals in CCR with biogeochemical reactions that target assessment metals?

Diagram:
- Stimulate appropriate bacteria
- Alter biogeochemical conditions
- Precipitate metals
- Make metals insoluble
Little is known about the diversity of CCR microbial communities, but there is increasing effort to characterize these communities.

<table>
<thead>
<tr>
<th>Known Microbial Groups in Coal Ash</th>
</tr>
</thead>
<tbody>
<tr>
<td>Denitrifying Bacteria</td>
</tr>
<tr>
<td>Nitrifying Bacteria*</td>
</tr>
<tr>
<td>Selenate Reducing Bacteria*</td>
</tr>
<tr>
<td>Sulfur Reducing Bacteria*</td>
</tr>
<tr>
<td>Sulfur Oxidizing Bacteria</td>
</tr>
</tbody>
</table>

* Relevant biogeochemical processes for immobilization of metals present in CCR Waste
Power and Process of Biogeochemistry

- Direct and indirect biogeochemical reactions affect CCR metals
- Naturally occurring microorganisms can be harnessed to drive helpful reactions
- Conditions can be engineered to favor specific microbial activities that produce desirable end products or environmentally stable forms of potential pollutants
Behavior of Metals in Storage Cells without Biogeochemical Controls
Options for Biogeochemical Control of Metals Migration

Engineered control points where metals migration can be biogeochemically arrested.
Slurry Walls

- Slurry Wall (a.k.a. “Barrier Wall”) - a physical, low permeability barrier to groundwater flow
- Design and Installation:
  - Contain source area and prevent future migration of CCR constituents outside the “contained” area
  - Divert groundwater flow
- Implemented for several decades and accepted by regulators
- Most effective when there is a lower “cut off” layer
Soil-Bentonite Slurry Wall Concept

SB slurry wall concept

Track hoe excavation in slurry-filled trench
Types of Barrier Walls

• Installed in a slurry trench and backfilled
  – Soil-bentonite (SB)
  – Cement-bentonite (CB)
  – Soil-cement-bentonite (SCB)

• Reagents mixed with soil *in-situ*
  – One pass trenching (OPT)
  – Deep soil mixing (DSM)
  – Cutter Soil Mixing (CSM)

• Special Applications
  – Vinyl sheet pile
  – Vibrating beam
One Pass Excavator

(Courtesy DeWind)
Slurry Walls

- **Advantages**
  - Can be implemented around an active facility
  - Lower cost source control
  - Effective for all CCR constituents

- **Limitations**
  - Gradient control systems
  - Source control combined with cap
  - Key for toe of slurry wall (e.g., lower cutoff layer)

- **Design Considerations**
  - Bench scale testing is typically performed to develop a mix design (e.g., hydraulic conductivity, geostructural)
Permeable Reactive Barrier

Source: Provided by Geo-Solutions, Inc.
PRB Application to CCR

• Permeable Reactive Barrier (PRB) is especially useful for controlling off-site migration
• Passive treatment: no energy or equipment required after installation
  • No operating costs during PRB lifetime (e.g., 10-20 years)
• Various reactive materials for CCR-constituents
• Long-term treatment
• Conserves water
• Allows productive use of site
PRB Design Considerations for CCR

- Width of PRB depends on:
  - Type and concentrations of COCs
  - Groundwater flow velocity
  - Type of reactive material/COC removal process (adsorption/reduction/precipitation for CCR impacts)
- Rates of removal/required residence time
- Construction limitations
- Long-term performance considerations:
  - Reactivity loss with time
  - Permeability loss with time
  - Frequency of rejuvenation or reactive material change-out

<table>
<thead>
<tr>
<th>CCR COCs</th>
<th>ZVI</th>
<th>ZVI-carbon</th>
<th>Bio-barriers (solid carbon)</th>
<th>Apatite</th>
<th>Zeolite</th>
<th>Limestone/Alkali mat.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fluoride</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>P</td>
</tr>
<tr>
<td>pH (acidity)</td>
<td></td>
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<td></td>
<td>√</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Sulfate</td>
<td>√</td>
<td>√</td>
<td></td>
<td></td>
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<td></td>
</tr>
<tr>
<td>Arsenic</td>
<td>√</td>
<td>√</td>
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<td></td>
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<tr>
<td>Lead</td>
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<td>√</td>
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<td>P</td>
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<td>Molybdenum</td>
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<td>√</td>
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<td></td>
</tr>
<tr>
<td>Radium</td>
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<td>√</td>
<td></td>
<td>P</td>
<td>P</td>
<td>P</td>
</tr>
</tbody>
</table>
Backhoe trenching (20 ft, 6 m)

Biopolymer trenching (70 ft, 21 m)

Continuous trenching (40 ft, 12 m)

Reagent Placement

Cofferdam/trench box (30 ft, 9 m)
PRB Construction Methods - Injection (Solids)

- **Direct injection** (30 ft, 9 m)
- **Pneumatic fracturing** (90 ft, 27 m)
- **Jetting techniques** (60 ft, 18 m)
- **Hydraulic fracturing/Injection** (300 ft, 91 m)
Sulfate Reducing/Acid Neutralizing PRB

Benner et al., 1997
Sulfate Reducing/Acid Neutralizing PRB - Year 1

**Sulfate (mg/L)**
- >2000
- 1500-2000
- 1000-1499
- 500-999
- <500

**Iron (mg/L)**
- >350
- 250-350
- 150-249
- 50-149
- <50

**Acid Generating Potential (meq/L)**
- >20
- 10 - 20
- 0.0 - 10
- -10 - 0.0
- <-10

Benner et al., 1997
Sulfate Reducing/Acid Neutralizing PRB - Year 6

Blowes et al., 2000
In situ Stabilization/Solidification (ISS)
What is ISS?

- **Solidification**: contaminated materials are encapsulated “physically trapped” to form a solid material that restricts contaminant leaching by:
  - *Reduction of permeability*
  - *Increasing compressive strength and media durability*

- **Stabilization**: Chemical reaction between reagents and contaminated materials - designed to reduce the leachability of targeted contaminants by:
  - *Binding free liquids*
  - *Immobilizing targeted contaminants*
  - *Reducing solubility of the contaminated material*
Fly ash or other CCRs below water table may provide a source for groundwater impacts.
Excavation Approach

- Excavate Saturated Ash
- Excavate Dry Overburden Fly ash to Access Saturated Ash
- Remove source of groundwater impacts
Excavation Approach
Why ISS? “Surgical” Alternative

- ISS source of groundwater impacts
- Goal: “Surgical” approach – cost savings vs. excavation

Advance ISS Auger through Overburden Materials (e.g., fly ash) w/o Treatment

Treat Saturated Ash with Series of Overlapping ISS Columns
Key Considerations for CCR Units

• **Cost**
  – Potential for cost savings vs. excavation
  – Range: $50 to $100 per cubic yard (application dependent)
  – May be cost prohibitive for large impoundments

• **Geosyntec approach - niche applications:**
  – **Small source areas**
  – When cost/benefit outweighs standard remedies (e.g., pump and treat; excavation)

• **Geochemistry of COCs**
  – Boron, sulfate, As, Se, Mo, etc.
  – Design application to address site specific COCs and geochemical conditions influenced by cement chemistry
  – Select reagents compatible high SO$_{4}^{2-}$ conditions (e.g., GGBFS, PC V)

• **Access!!!**
Targeted Discrete Depth ISS

Borrow area from dike re-grading

ISS column advancement through overburden materials without treatment

Material Expansion (25%) + Material Balance from Dikes

Ground Surface

Seasonally High Water Table

Groundwater Flow Direction

NOT TO SCALE
Vertical Barrier Source Control

After ISS

Before ISS

Flow of Perched Water Around ISS Columns

Material Expansion (25%)

Cap

Ground Surface

Perched Water Table

Lateral Infiltration of Perched Water

Seasonally High Water Table

Lateral Flux of CCR Constituents

NOT TO SCALE
Discrete Depth ISS Containment

ISS column advancement through overburden materials without treatment

Borrow area from dike re-grading

Overlapping ISS columns

Material Expansion (25%) + Material Balance from Dikes

Saturated CCR

Groundwater Flow Direction

US Patent 9,909,277 B2 Mar. 6, 2018, In situ Waste Remediation Methods and Systems

NOT TO SCALE
Remedial Alternatives Selection Process

1. Exceedance attributable to CCR unit?
2. Alternate source demonstration (ASD)
3. Prioritize remedy implementation
   - Proximity to receptor, magnitude of release, toxicity/mobility of constituents, etc.
4. Evaluate MNA and IC after pond closure
5. Evaluate technologies likely to achieve stakeholder acceptance
   - Reliable, sustainable, and practicable
6. Take advantage of existing infrastructure
   - Retention ponds, treatment plants, connection to sewer, open (vegetated) spaces (irrigation)
7. Consider water reuse
   - Cooling towers, dust suppression, irrigation, ash conditioning, etc.

Note: CCR above groundwater table
Relative Cost

• Collaboration with EPRI *Groundwater Remediation Planning* – desktop reference

Modified from EPRI 3002012313 (2018, in press)
Solutions are Site-Specific

- Final selection of an active remedy, if necessary, should be:
  - Site-specific
  - Balance risks and the effectiveness in reducing these risks using a certain remedial approach
  - Implementability of a technology, and
  - Capital and long-term O&M costs.
Thank you for your time!

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