Bolstering Monitored Natural Attenuation to Overcome Obstacles for Meeting GWPS

USWAG CCR Workshop

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SUPPORTING
[DOING]
LEADING

Overview

The Challenge

It's Complicated!

- CCR closure activities disrupt geochemical conditions and complicate achieving GWPS.
- The geochemical environment during CCR unit operation is likely different than the long-term equilibrium condition after closure.

The Solution

Sorting Through the Complexities

- Navigate the vast amount of site data to determine if site conditions favor aerobic or anaerobic conditions.
- Identify corrective action alternatives and geochemistry to evaluate long term endpoints.
- Collect data now to demonstrate that monitored natural attenuation (MNA) is a potential corrective action strategy.

The Strategy

Can MNA and EA Work?

- Evaluate if MNA is viable and if the timeframe to achieve cleanup levels are reasonable.
- Use a step-wise strategy to assessing enhanced attenuation (EA) effects on groundwater conditions.
- Perform bench tests and pilot tests to evaluate corrective action strategies.
- Find a remedy that is not reversible.

The Challenge

Significant Changes Occur During and After CCR Removal

Active Operation

- Active hydraulic loading
- pH reflects process water
- Redox influenced by active loading
- Ongoing infiltration and leaching
- Decades of operation allow steady state conditions

Closure / Process Changes

- Cessation of hydraulic loading
- Dewatering
- Change in process water quality
- CCR removal
- Soil and CCR disturbance
- Capping to prevent infiltration

Geochemical and Hydrogeological Changes

- pH
- Redox
- Temperature
- Groundwater flow dynamics
- Soil properties/ backfill material
- Infiltration

Effects on Groundwater

- Change in concentrations
- Changes in flow direction/rate
- Mobilization of previously sequestered metals
- Pore water release
- Upgradient groundwater source
- Alternate source

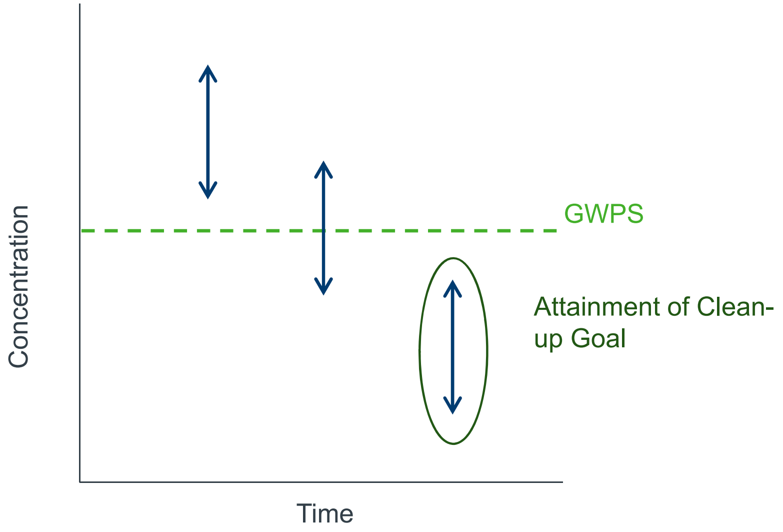
Achieving a GWPS Post-Closure Can Be Challenging

Its Complicated!

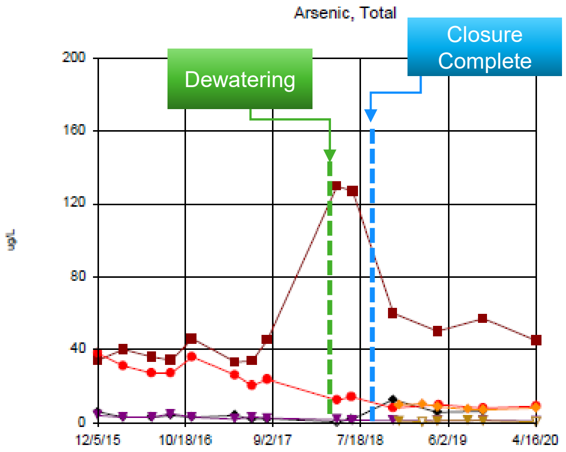
- Involves numerous inter-related considerations.
- Dealing with metals.
  - Which are anthropogenic or naturally occurring?
- Geochemical conditions influence groundwater quality.
  - Decades of active CCR operations
  - Significant hydrogeological and geochemical changes occur during and after closure
- Concentrations of metals in groundwater often tell only part of the story.
- Closure standards do not reflect risk based options…although at many sites exposure risks are well managed.

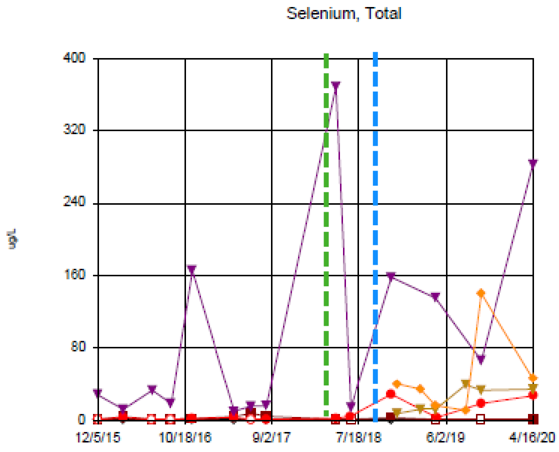
Corrective Action Monitoring

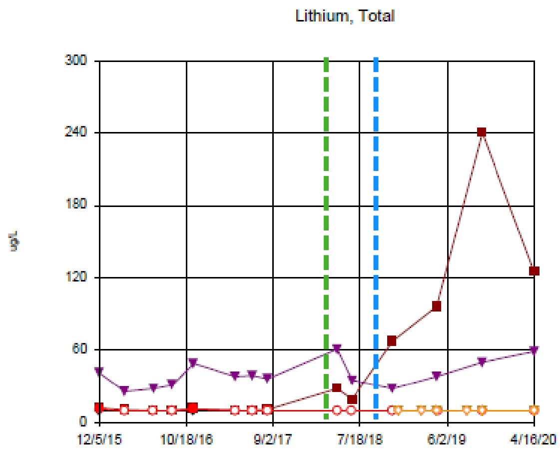
- **Goal:** compare post-closure data to clean-up goal or GWPS

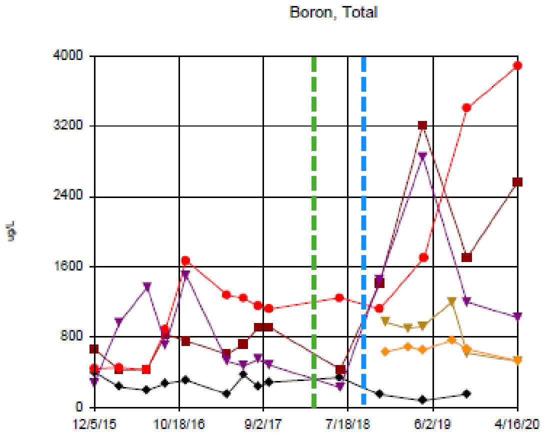


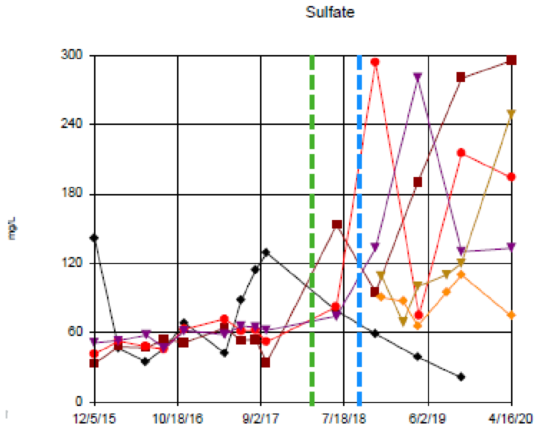
Geochemical Changes Post-CCR Removal





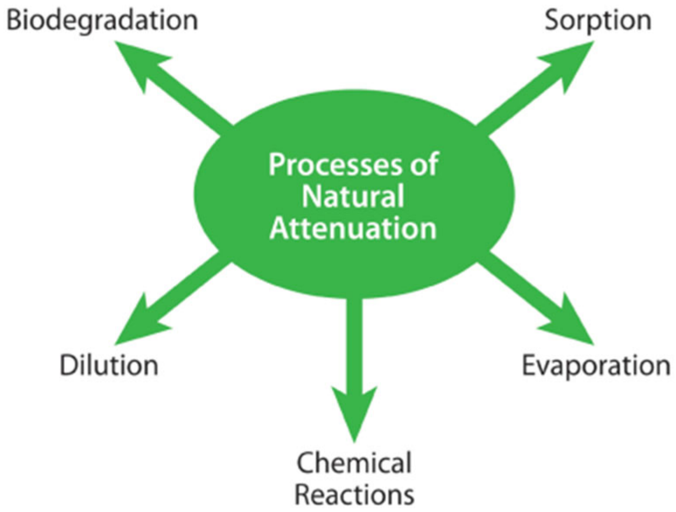






Considerations for Groundwater Remedy Selection

- A majority of Corrective Measures have selected MNA as a component of the remedy for achievement of GWPS.
- Recent EPA feedback related to Remedy Selection and MNA:
  - **Remedy Selection**: Select a remedy as soon as feasible based on Assessment of Corrective Measures evaluations.
  - **Monitored Natural Attenuation**: MNA for metals should not rely on dispersion and dilution as the primary mechanism.
  - **Corrective Action:** Evaluate lines of evidence supporting the selection of MNA, and whether it relies primarily on dispersion and dilution to mitigate groundwater impacts.



EPA Citizens Guide 2012

For more information see: EPA Issues Coal Ash Rule Interpretations, Setting New Compliance Expectations | TRC (trccompanies.com)

The Solution

Monitored and Enhanced Natural Attenuation

- **MNA -** Relies on natural processes to achieve site-specific remediation objectives within a timeframe that is reasonable compared to that offered by other more active methods.
- **Enhanced Attenuation** - EA is the use of low-energy, long-acting technologies in situations where MNA is not sufficiently effective, acceptable, or within a reasonable timeframe. EA can provide an effective and efficient “bridge” to MNA by reducing timeframes to remedial goals.

Often we are headed in the right direction, we just need some guidance and a gentle nudge!

Relevant MNA and EA Guidance Documents

- ITRC decision framework for applying MNA (ITRC, 2010).
- This is not a new decision framework….decades of metals sequestration and MNA evaluations.
- ITRC introduces the concept of EA as a bridge to allow facilities to rely on MNA as the endpoint remedy.
- Provides concepts/lines of evidence to support MNA approaches.

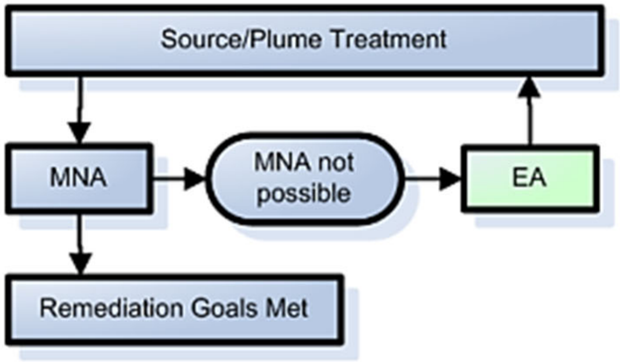
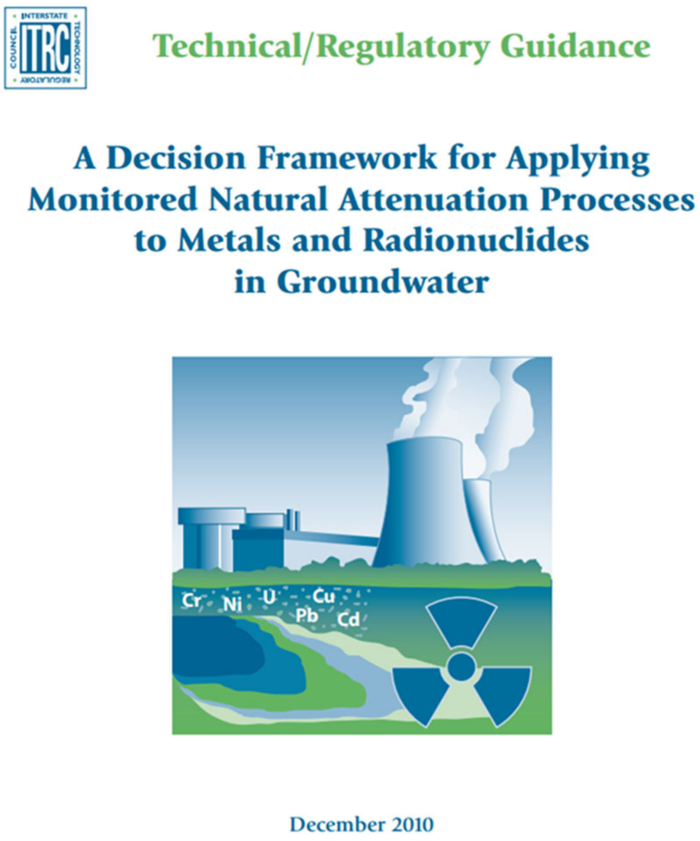


Figure 1-3. Simplified MNA decision framework for metals and radionuclides.

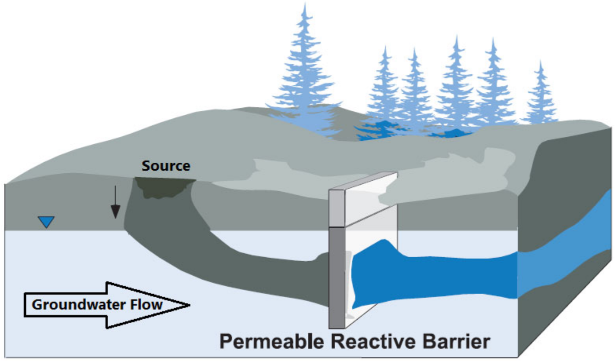


Technical/Regulatory Guidance

A Decision Framework for Applying Monitored Natural Attenuation Processes to Metals and Radionuclides in Groundwater

December 2010

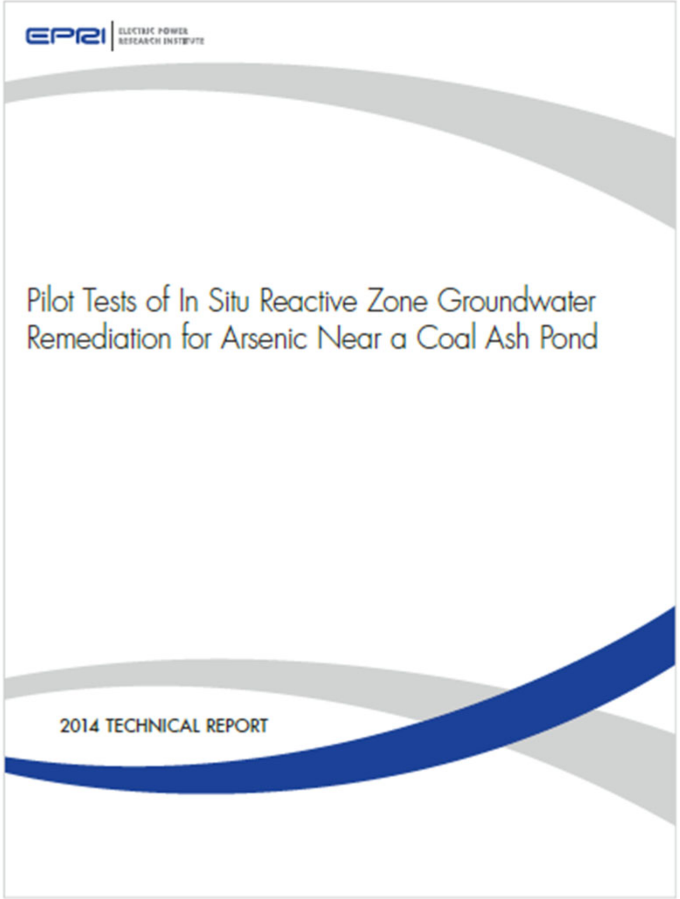
Reductant Technologies Are Not New!



Reductant technologies have been investigated and implemented for decades with the initial application of zero valent iron (ZVI) in a permeable reactive barrier (PRB) in 1991.

- Initial testing and implementation focused on chlorinated solvents…eventually became prevalent for metals etc.
- Commonly used chemical reductants include reduced metal species (e.g. ZVI, ferrous iron, iron oxide), reduced sulfur species, iron sulfides and others.
- Reducing agents have continued to advance, allowing practitioners to select products with varying reactivity, longevity, sorption capacity, etc..
- Hybrid amendments are also available that combine both chemical reduction and *in situ* bioremediation.

EPRI 2021 Technical Report – In Situ Arsenic Treatment



EPRI | ELECTRIC POWER RESEARCH INSTITUTE

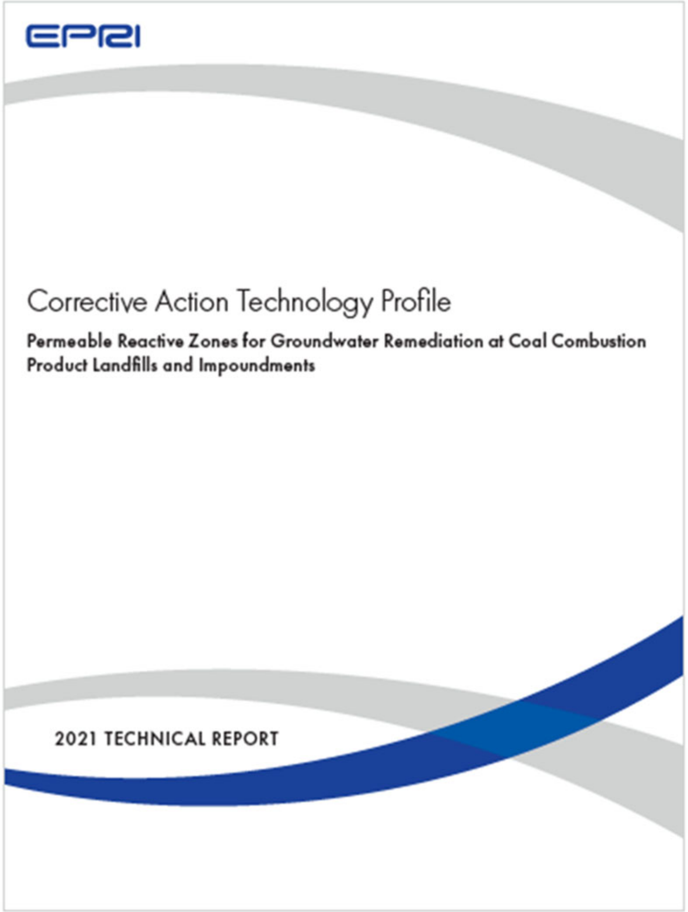
Pilot Tests of In Situ Reactive Zone Groundwater Remediation for Arsenic Near a Coal Ash Pond

2014 TECHNICAL REPORT

Key takeaways:

- In situ treatment can be a practical method to control arsenic in groundwater.
- In Situ Reactive Zone (IRZs) enhance natural processes for treatment.
- IRZs may achieve treatment targets more rapidly.
- Oxidative approach for groundwater systems that are naturally aerobic – e.g., ferrous iron reagent.
- Reductive approach for groundwater systems that are naturally anaerobic – e.g., sodium lactate reagent.

EPRI 2021 Technical Report – PRZ Treatment at CCR Sites



Corrective Action Technology Profile

Permeable Reactive Zones for Groundwater Remediation at Coal Combustion Product Landfills and Impoundments

2021 TECHNICAL REPORT

Documents the current status of Permeable Reactive Zones (PRZ) technologies, applicability, and effectiveness for CCR facilities.

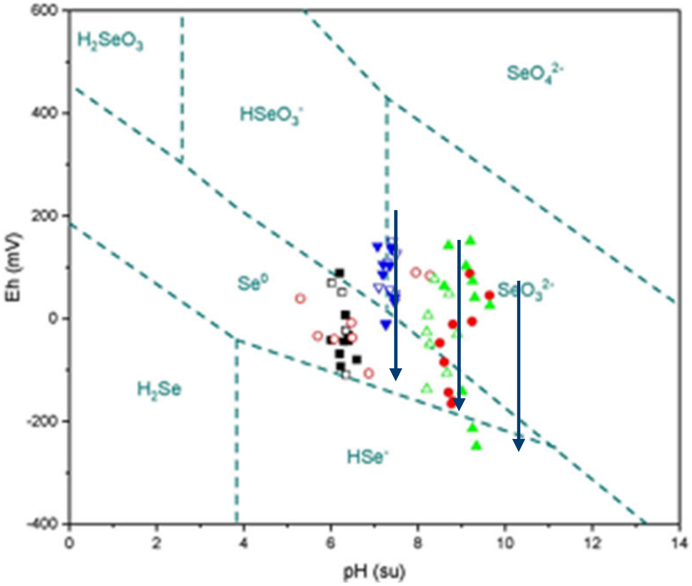
Key takeaways:

- Use of PRZs at non-CCR sites is well documented and viable.
- Primary Mechanisms:
  - Precipitation/Coprecipitation
  - Adsorption/Desorption
  - Ionic Exchange
  - Biotransformation
- Includes a summary of various media test results for the CCR relevant metals.

Enhanced Attenuation Methods

What is Zero Valent Iron (ZVI)?

- Most common reductive amendment used.
- ZVI is the elemental form of iron and refers to the zero-charge carried by each atom.
- This characteristic allows ZVI to convert oxidized elements into immobile solid forms.
- Available in various sizes for environmental applications ranging from granules, powders and nano-scale.
- For metal sequestration/stabilization, ZVI typically stabilizes metals through a mechanism involving adsorption, co-precipitation, and surface complexation.



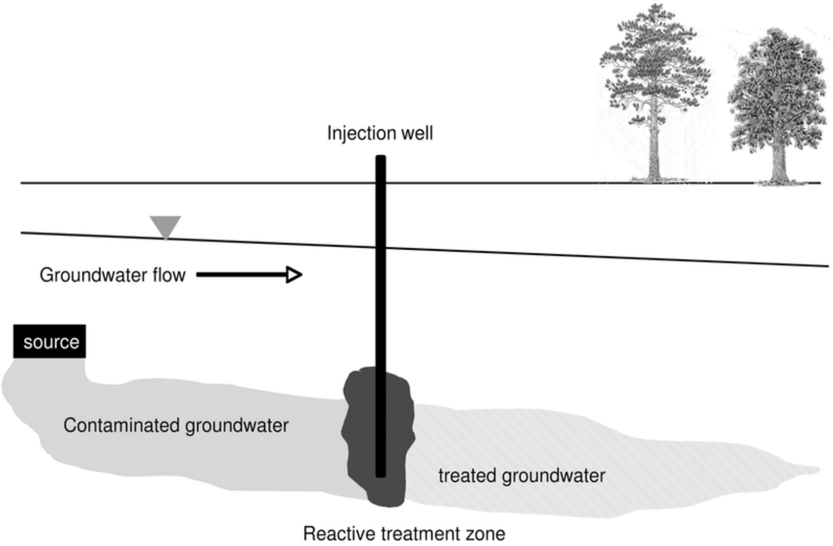
Granular Zero Valent Iron (ZVI)

Advantage of ZVI to Reduce Timeframes to Achieve Cleanup Goals

- ZVI quickly removes oxygen from groundwater to create a reducing environment (i.e. anaerobic).
- As iron oxides are generated through the corrosion of ZVI, adsorption and co-precipitation with metal contaminants occurs quickly.
- Even under alkaline conditions, pH and soil treated with ZVI have shown to converge to neutral conditions over time.
- ZVI has been shown to provide an effective and long-term solution for metal stabilization, producing hydrogen which is a food source for anaerobic bacteria that continue to drive long-term reducing geochemical conditions.

ZVI at CCR Sites

- Can be placed via injection (across the CCR unit), injected or trenched downgradient to form permeable reactive zones/barriers, or mechanically mixed/blended throughout soil media (within the CCR unit or downgradient).
- Can quickly create reducing conditions and promote sorption and co-precipitation of metals.



Source: ITRC 2011

The Strategy

Step-Wise Strategy to Evaluate EA → MNA

Review Data. Have The Data Changed Since Closure/Removal?

- Compare data before and after closure
- Is there a change?
- Trends…aerobic or anerobic?
- Is it significant?

Look at Geochemistry

Evaluate:

- Equilibrium constants
- Aqueous Speciation
- Oxidation-Reduction Reactions
- Microbial Reactions
- Site use history
- Geochemical gradients

Model Data and Update CSM

- Predict the future geochemical equilibrium
- Will the aquifer be aerobic or anerobic?
- Identify data gaps

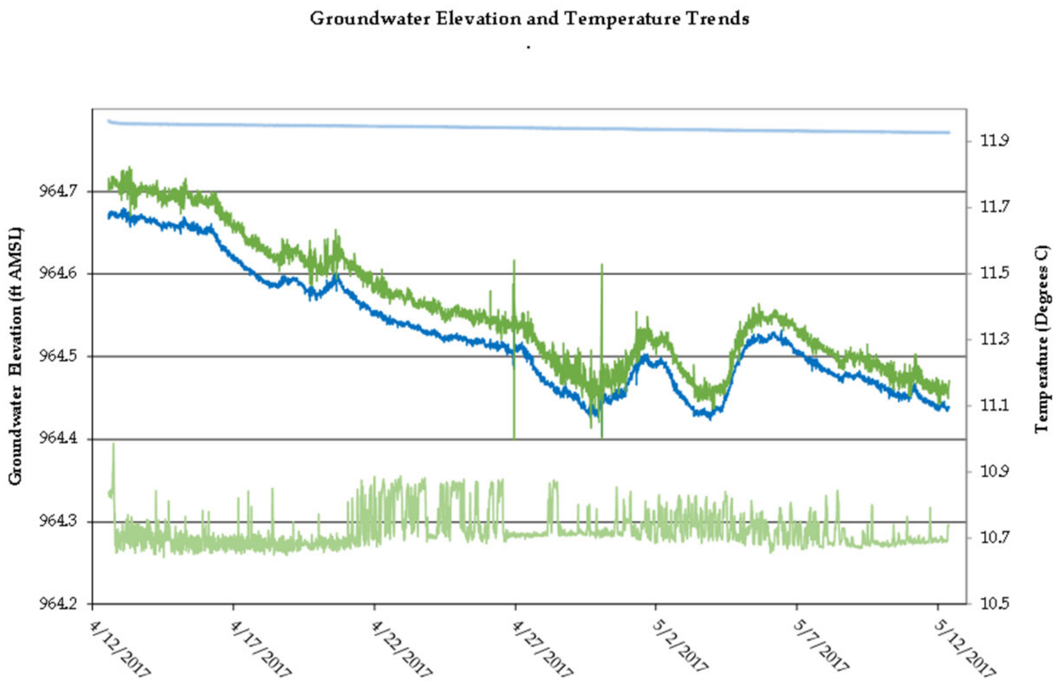
Perform Bench and Pilot Tests

- Evaluate pore water and aquifer matrix
- Does the aquifer matrix support the ability to rely on MNA?
- Can EA expedite to the endpoint?
- Is sequestration of metals sustainable?

Hydrogeologic Conceptual Site Model

Multiple variables influence groundwater conditions

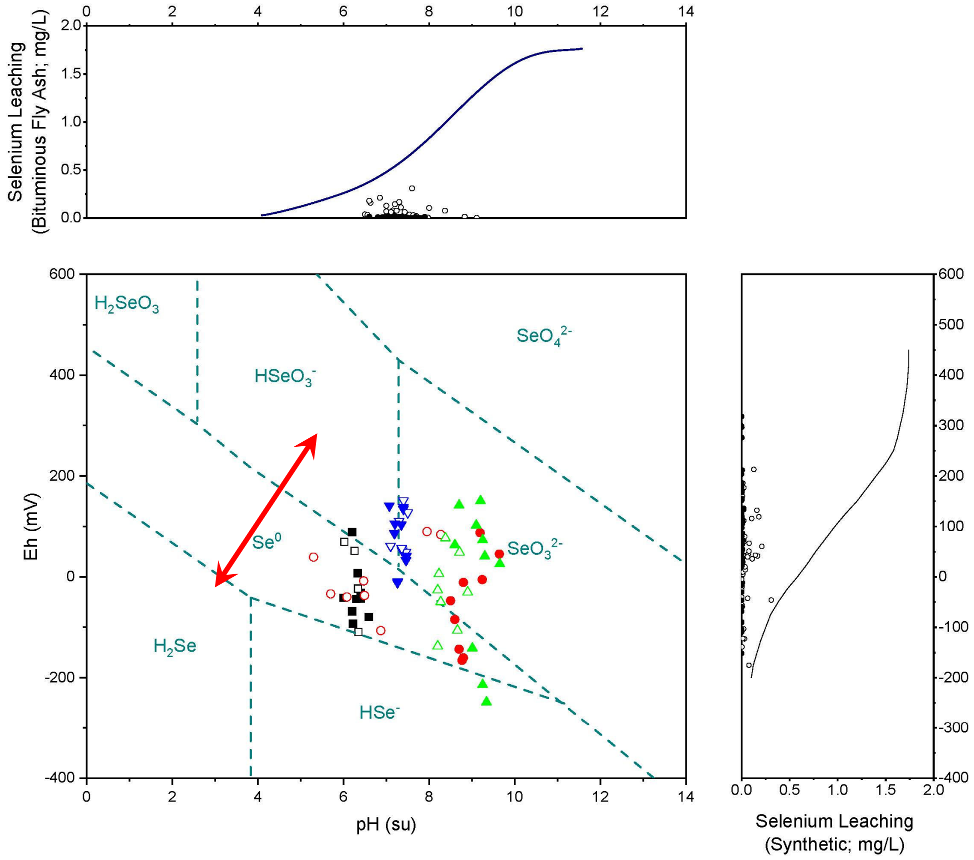
- Upgradient trends
  - Chemistry and groundwater use/extraction
  - Anthropogenic sources
  - Other CCR units
- Geology/soil characteristics
- Changes in redox and/or pH
- Groundwater flow direction and rate
- Changes in water levels
  - Influence of surface water levels (Great Lakes, rivers, inland lakes, and streams)
  - Precipitation
  - Seasonality
- Closure in place vs. closure by removal
- Timelines for CCR loading, dewatering, removal, capping, etc.



Understanding the Conceptual Site Model

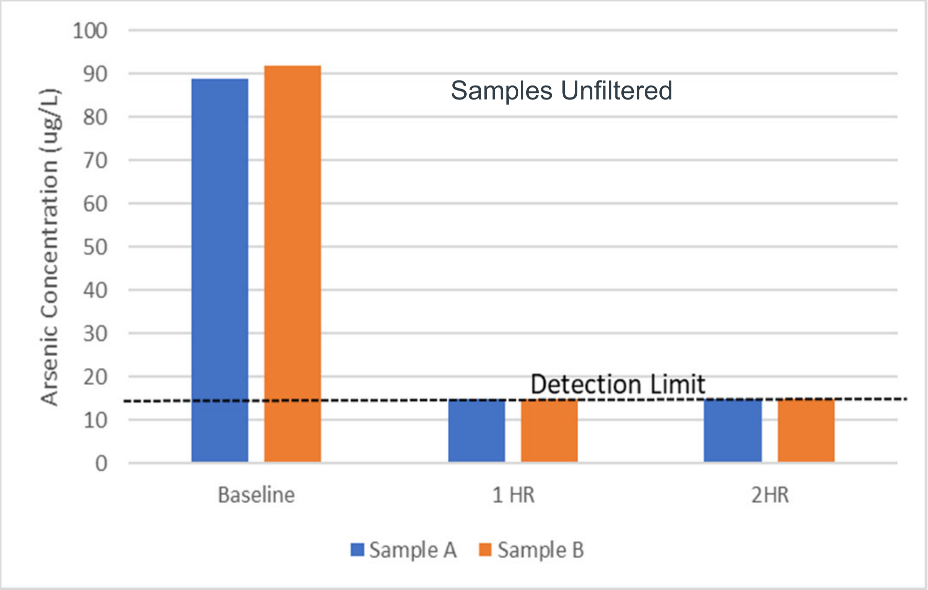
Develop a Geochemical Conceptual Site Model

- Plot available data into a geochemical framework including:
  - Background data
  - Pre CCR removal
  - Post CCR removal
- Distinguish between the data sets
- Evaluate geochemical framework and determine likely causes for the changes
- Do aquifer conditions favor attenuation through metals sequestration?
- Determine if site geochemical conditions support MNA and EA.
- Evaluate if aquifer matrix supports long term sequestration of metals after EA.
- If EA is performed, is the reaction sustainable or reversible?



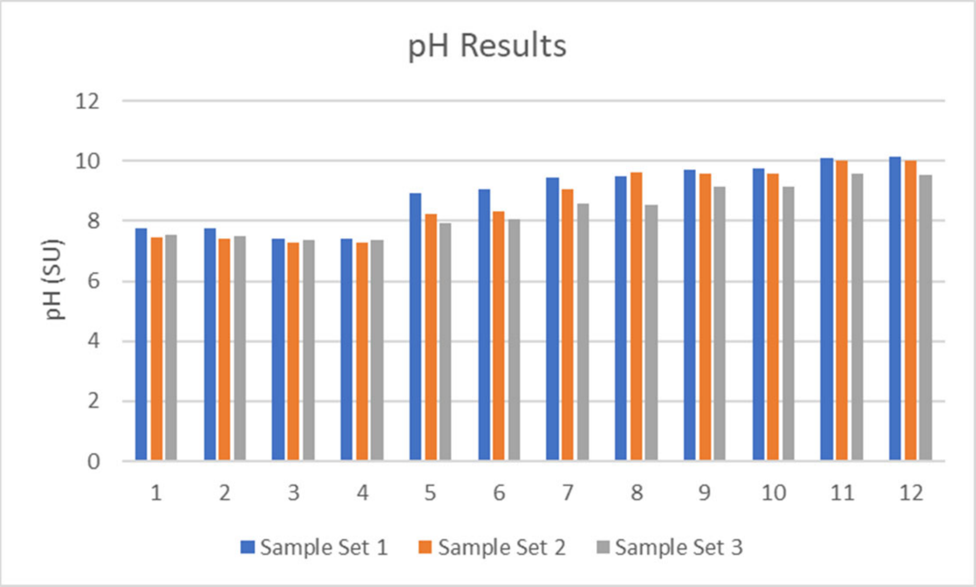
Bench Testing

- Treatability study was conducted to evaluate the use of ZVI for removing arsenic from groundwater.
- Testing included both an analysis of ZVI reaction kinetics and ZVI dose-response testing using site specific soil and groundwater.
- ZVI reaction kinetic testing was conducted to determine the appropriate timeframe for subsequential testing. Samples included 10 grams ZVI in a 40 mL vial filled with site groundwater.
- Initial test strategy was to analyze samples at 1-hr, 6-hr and 24-hr intervals.
- Arsenic was completely removed in the one-hour timeframe.



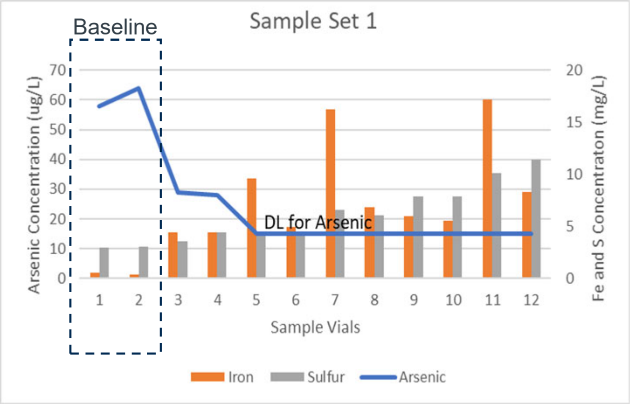
Bench Testing Results

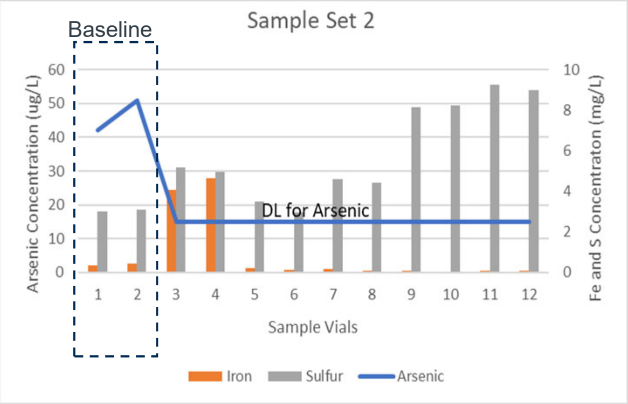
- Arsenic concentrations in untreated site groundwater ranged from 100 to 140 ug/L with pH around 7.50 SU.
- Site specific soil samples were collected and combined to form a single composite sample that was used in the treatability testing.
- Samples prepared combining varying amounts of ZVI in 50mL centrifuge tubes, filled with site groundwater and shaken overnight.
- Supernatant was poured off and replaced with fresh site groundwater to assess/estimate what may happen when fresh groundwater flows through a ZVI rich zone.
- Even with high amounts of ZVI, pH remained between 7 and 10 SU.

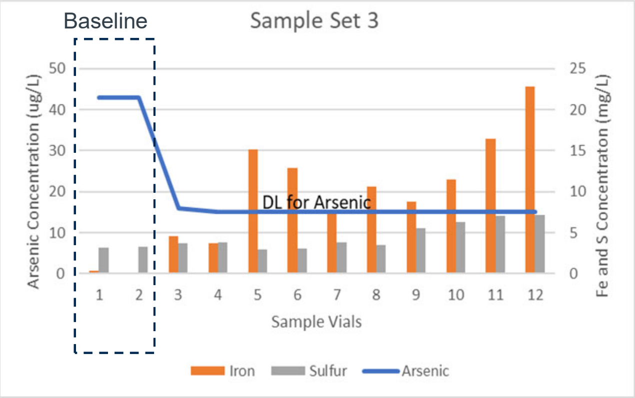


Samples 1&2 0 g ZVI	**Samples 3&4 1 g ZVI**	**Samples 5&6 2.5 g ZVI**	**Samples 7&8 5 g ZVI**	**Samples 9&10 10 g ZVI**

Bench Testing Results





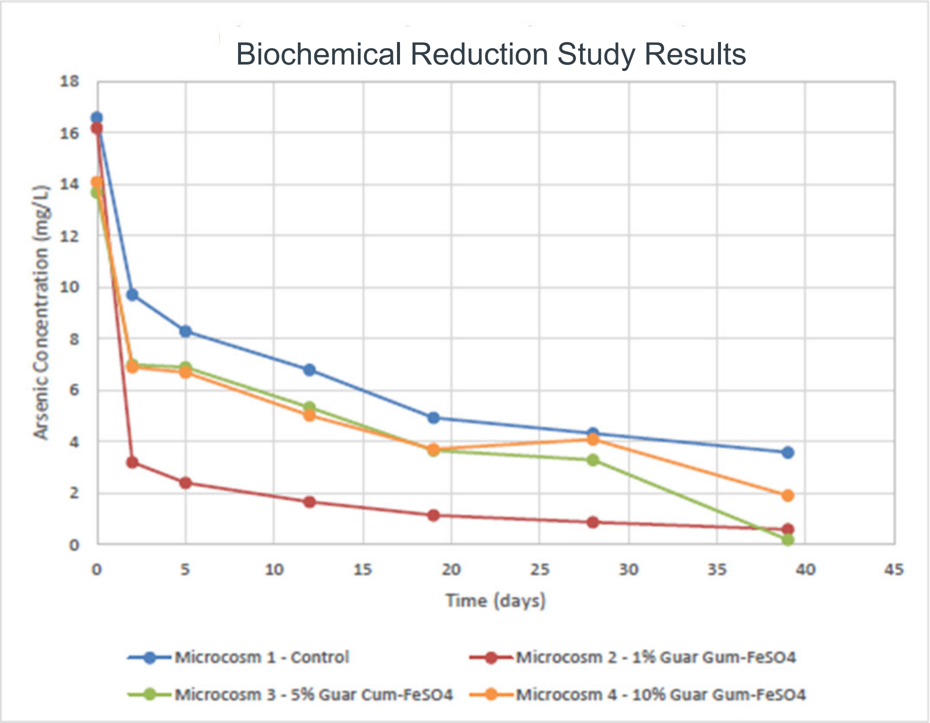


Samples 1&2 **0 g ZVI**	**Samples 3&4** **1 g ZVI**	**Samples 5&6** **2.5 g ZVI**	**Samples 7&8** **5 g ZVI**	**Samples 9&10** **10 g ZVI**

- ZVI is highly effective at treating As(V) and As(III) from groundwater in 2 days
- The site soil adsorbs both As (V) and As (III) from the site groundwater.
- ZVI contributes relatively low concentrations of iron to solution in the two-day period. Over time these concentrations would likely increase.
- Samples without ZVI showed a decrease in As concentrations, suggesting the soil itself removed As from solution.

Bench Testing – Biochemical Reduction Study

- A follow up study was performed to evaluate the bio-reduction of arsenic using a ferrous iron (ferrous sulfate)/guar gum solution.
- The conversion of ferrous sulfate to ferrous sulfide, through sulfate reducing bacteria under anaerobic conditions provides an effective process for immobilizing arsenic.
- Samples were prepared with varying amounts of guar gum and ferrous sulfate and site groundwater, then spiked with As(III) and As(V).
- At the end of 38 days, Microcosm 3 was spiked with 10 g/L ZVI and allowed to incubate overnight, resulting in a significant drop in As to 0.19 mg/L.



Data show that biochemical reactions will likely occur.

Bench Scale Testing Results

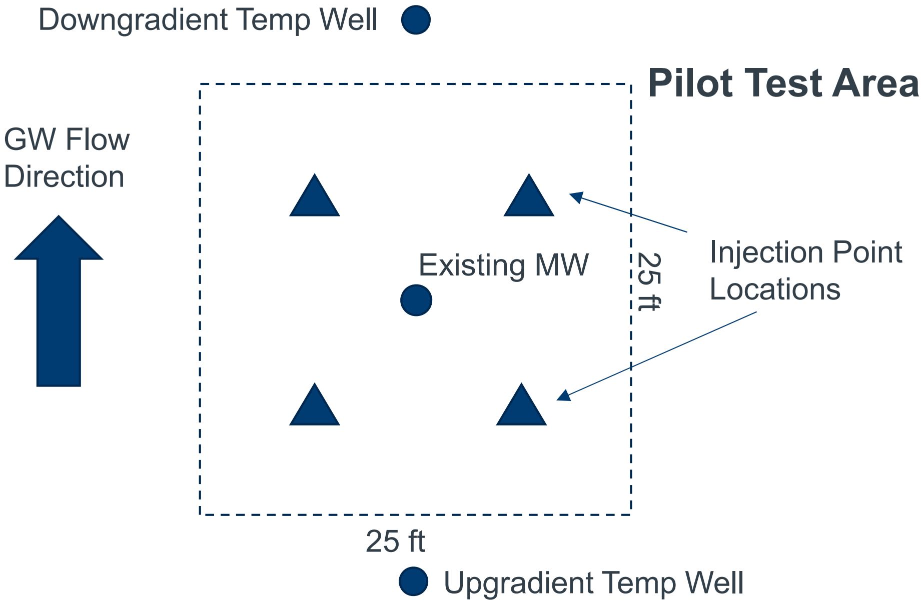
- ZVI can effectively remove both arsenate and arsenite from site groundwater.
- A ZVI dose of 1 g ZVI/L of solution was sufficient to remove 100 ug/L of arsenic from the water.
- ZVI treatment did not increase any of the other Appendix III or IV parameters (not presented).
- Microbial reduction of sulfate to sulfide is an effective technique to immobilize arsenic, however, reaching the target objective of 5 ug/L was not achieved in the time span tested.
- The key to achieving a successful arsenic removal approach via an injection strategy requires distributing the ZVI and ferrous sulfate uniformly throughout the treatment zone.
- Pilot Scale testing recommended to ensure effectiveness

Pilot Scale

- Many ZVI pilot tests have been conducted to affirm bench testing results
- There are several advantages to conducting pilot scale testing:
  - Ensures that the findings from bench scale testing can be effectively reproduced in the field.
  - Bench scale testing cannot typically recreate in situ geochemical conditions, especially long term, as groundwater flux through the treatment zone occurs
  - Allows implementation parameters to be adjusted prior to full scale implementation to optimize performance and maximize installation efficiencies.
  - Allows for more accurate full-scale cost and schedule estimates.
- Typically conducted in a small area within the highest contamination to represent "worse case conditions“.
- A successful pilot test provides a level of confidence that full scale implementation will also be successful.
- For small sites, the pilot test may be the remedy!

Pilot Scale

- Pilot scale test would involve injecting at four locations, equidistant around an existing monitoring well.
- Injections would be conducted at 1-ft increments across a 10-ft thick target zone to ensure vertical and lateral distribution of the amendment, consisting of a mixture of ZVI/ferrous sulfate and guar gum.
- The guar gum is used to help keep the ZVI suspended during injections.
- Post injection soil cores and temp wells within the test area can be installed to help assess distribution and effectiveness.



Downgradient Temp Well ●

Pilot Test Area

GW Flow Direction

Existing MW

Injection Point Locations

25 ft

25 ft

● Upgradient Temp Well

ZVI and amendments prepared as a slurry using a Grout Plant and injected directly through DPT drill rods

Source: ITRC 2011

From Concept to Implementation: EA → MNA Strategies

Geochemical Conceptual Model

Evaluate:

- Equilibrium constants.
- Aqueous Speciation.
- Oxidation-Reduction Reactions.
- Microbial Reactions.
- Geochemical gradients.

Bench Testing

- Collect evidence to determine if the aquifer supports EA and MNA.
- Understand biochemical reaction.
- Evaluate EA treatment chemistries.

Pilot Test

- Confirm bench testing results.
- Evaluate application approaches for EA reductants.

Implementation and Performance Monitoring

- Perform full scale implementation.
- Perform monitoring to affirm EA success.
- Verify stability and show reactions are not reversable.

Summary

Closure Complications

- Closure by removal doesn’t always result in quick attainment of GWPS due to operational and geochemical changes resulting from CCR removal.

MNA Considerations

- MNA is viable alternative at many CCR sites, but data are necessary to support that it will eventually achieve the desired outcome.
- If MNA cannot achieve the desired outcome in a reasonable timeframe, consider enhancement options.

EA Effectiveness

- EA is not a new approach, there are many reagents that can be used to bolster MNA.
- Select an EA reagent that nudges geochemical conditions towards the long-term endpoint (aerobic or anaerobic).
- ZVI has a proven track record with practical application technologies, but site-specific applicability still needs to be assessed.
- Alternate sources may influence MNA/EA effectiveness.

Implementation Strategies

- Well-developed hydrogeological and geochemical conceptual site model is key.
- Bench testing is recommended to evaluate MNA/EA potential and treatment chemistries.
- Pilot testing is critical to ensure effectiveness.
- If pilot is successful, move to full-scale implementation and verification of stability.

Questions?

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Abstract

Bolstering Monitored Natural Attenuation to Overcome Obstacles for Meeting GWPS

Regulated stakeholders are in various stages of compliance with the CCR Rule, especially with their unit closure and groundwater programs. Throughout the compliance process, the regulated community has been navigating many challenges brought forth by the initial CCR Rule, associated regulatory changes, and more recent interpretations by USEPA. Since 2015, a significant volume of groundwater data has been collected during the life cycle of CCR compliance monitoring, detection monitoring, assessment monitoring, and evaluation of corrective measures. These data have been used to make decisions related to potential CCR effects on water quality, remedy selection, and in many instances, the selection of a preferred closure option (closure in place or closure by removal).

Achieving a Groundwater Protection Standard (GWPS) can be complicated as metals are present naturally in the subsurface, in both soil and groundwater, and other anthropogenic activities at power generating facilities add to the complexities. Understanding the fate and transport of CCR-affected groundwater is further complicated by the significant changes that result from impoundment decommissioning. Capping, cessation of hydraulic loading, change in quantity and characteristics of process water, dewatering, CCR removal and other process changes can alter the equilibrium of metal chemistry in groundwater and can result in the mobilization of naturally occurring or previously sequestered metals and increase concentrations. Based on review of publicly available data, owner/operators of CCR units have selected Monitored Natural Attenuation (MNA) as the preferred option for a majority of corrective action remedies. Although closure by removal coupled with MNA is thought to be a more expedient way to improve groundwater quality and achieve compliance with GWPS, the expectation that compliance within the timeframe of the CCR Rule is, in most cases, unrealistic. Furthermore, recent USEPA interpretations of CCR compliance suggest that the selection of MNA as a remedy has not been sufficiently demonstrated as effective or viable. To that end, owner/operators are seeking ways to use in-situ technologies to expedite GWPS compliance, including bench and pilot tests to evaluate the efficacy of expediting compliance without periodically amending groundwater geochemistry to stabilize metals chemistry.

This presentation will summarize groundwater compliance challenges and geochemical processes experienced post-CCR removal. We will also present strategies to sort through the geochemical complexities of metals in the environment, to decide if in-situ treatment alternatives may be used to bolster MNA and expedite achievement of GWPS compliance.