Iron-Based Strategies for In Situ Treatment of Arsenic and Metals Impacts at Coal Ash Facilities

Michael B. Hay¹, Shannon Ulrich¹, Stephanie Offenberger², and Dave Liles²

¹Arcadis U.S., Inc., 11001 West 120th Avenue, Broomfield, CO 80021; ²Arcadis U.S., Inc., 4915 Prospectus Drive, Suite F, Durham, NC 27713

KEYWORDS: Arsenic, coal ash, in situ remediation, groundwater treatment, CCR rule

INTRODUCTION

With the recent Coal Combustion Residual (CCR) rule (40 CFR 257)¹,², power utilities are facing increased pressure in the monitoring and potential need for remediation of groundwater downgradient of coal ash impoundments. Of particular concern are the “Appendix IV” constituents which drive remedial action; these include metals (e.g., cadmium, cobalt, lead, and mercury) and constituents that exist as oxyanions under oxic conditions (e.g., arsenic, selenium, and molybdenum). These pressures drive the need for cost-effective and efficient means of groundwater remediation where impacts are observed. In situ groundwater treatment can be a preferred alternative to groundwater extraction and aboveground treatment; however, these strategies are subject to unique challenges – achieving reagent distribution, effective contact and reaction with constituents, chemical compatibility with aquifer geochemical conditions (e.g., pH and redox), potential for secondary effects, and achieving long-term stability to ensure limited constituent rebound. Removal of metals and oxyanions from water via coprecipitation with ferric iron is highly effective and is the go-to strategy in ex-situ water treatment, particularly for arsenic. Although this strategy can also be effective in situ, successful widespread distribution and targeted precipitation of iron within the aquifer presents the greatest hurdle, requiring site- and situation-specific strategies to overcome. This paper presents the results of treatability testing and pilot-scale field implementations conducted in collaboration with the Electric Power Research Institute (EPRI) evaluating ferrous iron and chemical oxidant-based approaches for coprecipitation of arsenic and other co-constituents in impacted groundwater, highlighting the successes, lessons-learned, and recommendations for in situ remediation in different geochemical environments.

ARSENIC GEOCHEMISTRY

Arsenic is ubiquitous, but spatially variable in the environment. The average crustal abundance of arsenic is between 2 and 5 mg/kg but can be particularly concentrated in coal and shale deposits, where arsenic is found associated with sulfide minerals³,⁴. In weathered environments such as soil and sediments, arsenic is frequently retained by iron, manganese, and aluminum oxyhydroxide minerals. Typical concentrations in soils
and sediments range between 3 to 10 mg/kg, but can be higher downstream of mineralized areas\(^4\).

Due to the presence of arsenic in coal, the presence and leachability of arsenic in CCR materials is of major concern. Concentrations of arsenic in CCR are highly variable, with a majority of arsenic retained in fly ash. Typical ranges for arsenic in flue gas desulfurization (FGD) gypsum and bottom ash are between 2 and 20 mg/kg (10\(^{th}\) to 90\(^{th}\) percentiles\(^5\)), while concentrations in fly ash can be an order of magnitude higher (ranging between 20 and 200 mg/kg\(^5\)). More important than the total abundance of arsenic in CCR, however, is its leachability from CCR materials, as this controls the ultimate risk to groundwater and surface water due to the release of CCR pore water to the environment. Typical leachabilities for coal ash as assessed using the Toxicity Characteristic Leaching Procedure (TCLP; United States Environmental Protection Agency [USEPA] Method 1311) are between 0.002 and 1 mg/L (10\(^{th}\) to 90\(^{th}\) percentile\(^5\)) which, although below hazardous waste regulatory limits, can exceed the USEPA Maximum Contaminant Level (MCL) of 10 \(\mu\)g/L, the compliance limit for groundwater under the CCR Rule.

![Arsenic pe-pH diagram](image-url)

**Figure 1.** Arsenic pe-pH diagram. Constructed using PHREEQC with the Wateq database\(^12\) for a total arsenic concentration of 0.1 mg/L.
Arsenic in groundwater is most commonly present as an oxyanion in either the +III oxidation state (as arsenite) or in the +V oxidation state (as arsenate). These oxyanion forms exhibit pH-dependent speciation based on protonation state (Figure 1), and the mobility of dissolved arsenic in the environment is strongly controlled by the interaction of these ions with mineral surfaces. Adsorption to metal oxyhydroxides is one of the most dominant mechanisms controlling arsenic transport; however, these mechanisms are even more extreme in redox-active environments where iron or manganese are actively dissolving or precipitating, pointing to the important role of arsenic coprecipitation within metal oxyhydroxides as a control on aqueous concentration. In natural environments, reductive dissolution of iron and manganese oxyhydroxides in reducing environments is frequently responsible for naturally-elevated arsenic in groundwater. Likewise, the precipitation of ferric oxyhydroxides under oxic conditions is both a widely-used strategy for arsenic removal in water treatment contexts as well as a natural attenuation mechanism for arsenic in natural systems.

REMEDIATION APPROACH

Coprecipitation of arsenic within oxyhydroxide or sulfide minerals can be an effective strategy for achieving in situ remediation and/or enhanced natural attenuation of arsenic. In situ-based strategies involving the emplacement of an “in situ reactive zone” or IRZ via reagent injection directly into the impacted aquifer have numerous advantages over traditional ex-situ pump-and-treat-based strategies, including reduced infrastructure, reduced sludge disposal and associated costs, and reduced treatment timeframes, particularly if residual treatment capacity results in long-term arsenic removal effectiveness. Particular care must be exercised when choosing between an oxic-based strategy (coprecipitation within metal oxyhydroxides) versus a reducing strategy (coprecipitation within sulfide minerals), taking into account the long-term redox condition of the aquifer. In shallow groundwater systems where dissolved oxygen is present, oxic-based approaches are far safer, given the potential for reoxidation of sulfide minerals in the presence of dissolved oxygen. In contrast, iron oxyhydroxides can be stable even under low-oxygen conditions, so long as electron donors (e.g., natural organic matter) are in sufficiently low abundance to limit microbial reduction.

The iron oxyhydroxide coprecipitation strategy relies on the effective distribution and controlled precipitation of iron within the target footprint of the IRZ; this represents the greatest challenge in implementation of this strategy. Ferrous iron (Fe[II]) is more soluble in groundwater at neutral pH than ferric iron (Fe[III]) and can be relatively easy to inject. Effective injection and distribution at neutral pH requires overcoming residual oxidation potential (including dissolved oxygen); however, precipitation within the IRZ requires eventual oxidation to Fe(III) for precipitation of oxyhydroxides. In this study, a strategy involving sequential injection of ferrous iron with a chemical oxidant was tested, illustrated conceptually in Figure 2. In addition to achieving in situ oxidation of iron, use of a chemical oxidant can be beneficial in the oxidation of As(III) to As(V), which can enhance arsenic uptake by oxyhydroxides under certain conditions. The arsenic coprecipitation strategy was tested at the bench and field-pilot scale at a confidential location.
coal-fired power plant site exhibiting minor arsenic impacts in groundwater downgradient of a CCR impoundment.

**Arsenic Oxidation**

![Diagram of Arsenic Oxidation](image)

**Iron Oxidation**

![Diagram of Iron Oxidation](image)

**Figure 2. Oxidation of arsenic(III) and ferrous iron by calcium peroxide, resulting in iron oxyhydroxide precipitation and arsenic uptake.**

**BENCH TEST APPROACH AND RESULTS**

The arsenic coprecipitation strategy was first tested at the bench scale in a series of batch-scale reactor tests. The batch tests involved suspension of site soil in arsenic-impacted site groundwater, with varying concentrations of added soluble iron (as ferrous sulfate) and chemical oxidants. Oxidants tested included calcium peroxide and sodium permanganate. Calcium peroxide was chosen specifically in these tests as means of simultaneously providing an oxidant and an alkaline reagent for balancing acidification from iron oxidation. Key objectives of the batch tests were to:

- Evaluate solubility of ferrous iron in the presence of site soil
- Confirm complete oxidation and precipitation of dissolved iron in the presence of an oxidant
- Understand oxidant demand of the soil and confirm complete oxidant consumption
- Evaluate and mitigate potential secondary effects, including metals release from soil and large pH swings due to acid generation/consumption reactions with added reagents

Batch tests were run at a solid to solution ratio of 100 g soil to 200 mL groundwater. Arsenic speciation measurements demonstrated that arsenic was predominantly present as arsenite. Site groundwater was spiked with additional arsenic as sodium arsenite to yield a starting concentration near 0.16 mg/L, consistent with historically-observed maximum groundwater arsenic concentrations. Representative results from the arsenic treatability tests are shown on Figure 3 for the following test conditions:
1) Control test (no iron or oxidant)
2) 600 mg/L iron (added as ferrous sulfate), 800 mg/L calcium peroxide
3) 600 mg/L iron, 800 mg/L calcium peroxide, 1,000 mg/L sodium permanganate
   (approximately 380 mg/L manganese)
4) 1,000 mg/L iron and 1,350 mg/L calcium peroxide.

![Figure 3. Results of arsenic treatment tests following the addition of ferrous sulfate and chemical oxidants. Open bars indicate non-detect values and are shown at one-half the detection limit.](image)

The results in Figure 3 demonstrate high arsenic removal in all tests, with arsenic reduced to below detection in the calcium peroxide + permanganate and high-dosed iron and calcium peroxide tests. The use of calcium peroxide as an alkaline oxidant (in addition to pH buffering by the added soil) was effective in countering the acid generation by iron oxidation and precipitation.

The results were also evaluated to understand both the removal of co-consituents present in the CCR-impacted groundwater (including boron, molybdenum, and selenium) as well as potential secondary byproducts of the oxidation reaction (Figure 4). The results demonstrate that both dissolved molybdenum (present in groundwater at 16
μg/L) and dissolved selenium (present at 8 μg/L) were removed in the process with use of calcium peroxide. However, selenium concentrations were observed to increase in the presence of permanganate, possibly due to desorption or oxidative release from soil and/or selenium contamination in the reagent. Chromium concentrations also increased with the addition of permanganate, also possibly due to desorption or the oxidative dissolution of chromium hydroxides naturally present in the soil. Due to these risks, permanganate was not advanced to field testing.

Figure 4. Boron, molybdenum, selenium, and chromium concentrations in batch reactors following addition of ferrous sulfate and chemical oxidants. Open bars indicate non-detect values and are plotted at one-half the detection limit.

**IN SITU PILOT TEST**

A small-scale in situ pilot test was conducted to evaluate the field-scale implementability of a sequential soluble iron/chemical oxidant injection-based approach for establishment of an arsenic immobilization IRZ. The pilot test included a single injection well (IW-1) located immediately downgradient of a site monitoring well (GW-41). Eight observation wells (OW-1 through OW-8) were installed at varying distance downgradient and side-
gradient of the injection, based on a variable groundwater flow direction predominantly to the west/southwest (Figure 5).

![Figure 5](image_url)

**Figure 5. Pilot test reagent injection and monitoring well network.**

The field pilot test involved injection of approximately 4700 gallons of reagent, comprising alternating solutions of ferrous sulfate (between 750 and 1500 mg/L as iron) and calcium peroxide (between 750 and 1500 mg/L as CaO). The target regent quantity was estimated to achieve a 10-ft radius of influence, corresponding to the first row of monitoring wells.

Arsenic concentrations during and following injections within the monitoring well network are provided on Figure 6. These results demonstrate that the pilot test was effective in reducing arsenic concentrations, despite challenges presented with achieving *in situ* distribution and mixing of the chosen reagents. Arsenic concentrations in the injection well were reduced from 60 µg/L to below the MCL of 10 µg/L, remaining below 5 µg/L for the duration of the post-injection monitoring phase (255 days). Effectiveness in arsenic removal was also demonstrated in downgradient monitoring well OW-3, showing a maximum arsenic concentration decrease of approximately 65%. Arsenic concentrations remained low in the injection well, while rebound in arsenic was observed at monitoring well OW-3. This subsequent rebound was likely the result of the well’s location on the periphery of the injection radius of influence, with fluctuating groundwater flow direction and slow groundwater velocity subsequent to the injection.
Figure 6. Arsenic concentrations in upgradient, injection, and downgradient monitoring wells following pilot test ferrous iron and oxidant injections.

Figure 7. Injection specific capacity during reagent injections with sequential ferrous sulfate and calcium peroxide reagent injection.
The results also demonstrate effectiveness of the sequential reagent injection method for achieving \textit{in situ} distribution and mixing, while highlighting the challenges inherent in this approach. In particular, injection of the calcium peroxide was complicated by the limited solubility of the reagent. The calcium peroxide was injected successfully as a dilute slurry; although decreases in injectability occurred with ongoing injection of the calcium peroxide, injectability was restored during the ferrous sulfate injection phases as a result of reacidification and dissolution of the emplaced calcium peroxide (Figure 7).

**SUMMARY AND CONCLUSIONS**

As a CCR Rule Appendix IV constituent, dissolved arsenic in groundwater downgradient of CCR impoundments poses a potential concern and may require remedial action. \textit{In situ}-based approaches for achieving enhanced arsenic attenuation provide many advantages over traditional \textit{ex situ} groundwater treatment approaches but may present technical challenges in implementation. In this study, a sequential ferrous iron/chemical oxidant injection approach was tested as a remedy for treating dissolved arsenic in shallow groundwater downgradient of a coal ash impoundment. Pilot testing demonstrated successful removal of arsenic from groundwater, while highlighting the challenges involved. Specifically, care must be taken to balance pH fluctuations that may occur with iron and oxidant reagents, while also weighing reagent injectability considerations to achieve the desired radius of influence.

**ACKNOWLEDGEMENTS**

Arcadis U.S., Inc. gratefully acknowledges partnership and funding provided by the Electric Power Research Institute (EPRI), as well as the collaboration and support of the confidential utility site where the pilot test was conducted. Drs. Jeff Gillow and Mary deFlaun (Geosyntec Consultants) also contributed to this work.

**REFERENCES**


