Conceptual Groundwater Remedial Alternatives at Coal Combustion Residuals (CCR) Sites

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ABSTRACT

Groundwater below many basins that have been used to store coal combustion residuals (CCR) may have concentrations of certain inorganic constituents in excess of applicable regulatory standards. Given that many inorganic CCR constituents are also naturally-occurring in the aquifer matrix, their detection may not always be indicative of a release from the CCR unit. Inorganics may be present at elevated levels in groundwater due to natural or background conditions, or due to changes to the aquifer geochemistry resulting from the presence of the CCR basin, which then mobilizes these naturally occurring constituents beneath the CCR unit. Care must be taken to identify the source(s) and the release mechanism(s) of potential CCR-related impacts. If a link between a CCR unit and an inorganic groundwater exceedance has been established, stakeholders may be faced with the need to evaluate groundwater remedial alternatives to address these impacts. This presentation conceptually discusses potentially applicable remedial approaches, including (i) monitored natural attenuation (MNA), (ii) hydraulic control using ex-situ and in-situ methods, (iii) permeable reactive barriers, (iv) slurry walls, and (v) oxidation-reduction (redox) altering approaches. Additionally, this presentation explores potential water re-use options available at many power generating stations.

INTRODUCTION

Some coal combustion residual (CCR) disposal units regulated by the Federal CCR Rule[1] may require groundwater remedies based on statistically significant levels of constituents regulated in Appendix IV of the Rule. Groundwater below basins that have been used to store CCR materials may have concentrations of certain groundwater constituents in excess of applicable regulatory standards and/or background conditions. These include mostly inorganic constituents such as metal(loid)s (e.g., As, Se, Fe, Mn, B) and anions (e.g., Cl, SO_4). While some of these constituents may not require remediation under the Federal Rule, they may be regulated by individual states and require some form of remedial action. Given that many inorganic CCR constituents are also naturally-occurring in the aquifer matrix, their detection may not be indicative of a release from the CCR unit. Inorganics may be present at elevated levels in groundwater due to background conditions, or due to changes to the aquifer redox geochemistry resulting from the presence of the CCR basin, which inhibits oxygenated precipitation infiltration and thereby mobilizes these constituents from aquifer solids beneath the CCR unit. Care must be taken to identify the source(s) and the release mechanism(s) of potential CCR-related impacts, and segregate these impacts from background conditions and redox-induced mobilization of naturally-occurring constituents. If a link between a CCR unit and a groundwater exceedance has been established, stakeholders may be faced with the need to evaluate groundwater remedial alternatives to address these impacts.

The driving force for releases of inorganic constituents to groundwater at CCR basins is created by the hydraulic head as a consequence of wet disposal. The type of constituents and their respective concentrations are dependent on:

- The source of the coal;
- Boiler operating conditions and air pollution control devices used;
- Age of materials;
- Active (wet) versus inactive (dry) conditions;
- Chemical make-up of the CCR materials (bottom ash, fly ash, FGD, or other materials); and
- Geochemical conditions in the CCR unit and in the subsurface (i.e., is the ash below the water table?).

Figures 1 and 2 depict conditions indicative of some active and inactive CCR basins, respectively. Inactive vegetated basins, where the groundwater table is below the CCR materials, are sometimes considered environmentally stable, with little potential for additional adverse impacts to groundwater beyond leaching which may have occurred while the basins were active.

Figure 1: Active CCR Basin

Figure 2: Inactive, Vegetated CCR Basin

Once released or mobilized, inorganics cannot be destroyed or degraded, but only captured/contained or rendered immobile, which affects (and also limits) the selection of potentially applicable remedial alternatives.

REMEDIAL ALTERNATIVES

Following the closure of CCR units through removal or capping (i.e., source control), a variety of groundwater remedial approaches may be evaluated for applicability, including (i) monitored natural attenuation (MNA), (ii) hydraulic control (ex-situ and in-situ), (iii) permeable reactive barriers (PRBs), (iv) slurry walls, and (v) oxidation-reduction (redox) altering approaches.

Monitored Natural Attenuation

As a first step, it is generally appropriate to include MNA in an evaluation of remedial alternatives for groundwater following closure of a CCR unit. While inorganic constituents typically associated with CCR units do not degrade, there are protocols to implement MNA for inorganic constituents. Amongst other entities, the United States Environmental Protection Agency (EPA) developed a series of guidance manuals starting with a more general guidance on the use of MNA published in 1999,[2] and subsequent publications focused more on MNA of on inorganic constituents, with manuals published in October 2007[3,4] and August 2015[5]. The EPA uses a tiered approach, also known as "lines of evidence," that include:

1. The demonstration of a clear and meaningful trend of decreasing contaminant mass and/or concentration over time at appropriate monitoring or sampling points using historical groundwater and/or soil chemistry data.
2. The use of hydrogeologic and geochemical data to demonstrate indirectly the type(s) of natural attenuation process active at the site, and the rate at which such processes will reduce contaminant concentrations to required levels.
3. The use of data from field or microcosm studies, which directly demonstrate the occurrence of a particular attenuation process at the site and its ability to degrade the contaminants of concern (typically only used to demonstrate biological degradation processes associated with organic constituents).

As related to groundwater, EPA defines MNA as "…[t]he reliance on natural attenuation processes (within the context of a carefully controlled and monitored site cleanup approach) to achieve site-specific remediation objectives within a time frame that is reasonable compared to that offered by other more active methods. The 'natural attenuation processes' that are at work in such a remediation approach include a variety of physical, chemical, or biological processes that, under favorable conditions, act without human intervention to reduce the mass, toxicity, mobility, volume, or concentration of contaminants in soil or groundwater. These *in-situ* processes include biodegradation; dispersion; dilution; sorption; volatilization; radioactive decay; and chemical or biological stabilization, transformation, or destruction of contaminants[5]."

Further, “MNA may, under certain conditions (*e.g.,* through sorption or oxidation-reduction reactions), effectively reduce the dissolved concentrations and/or toxic forms of inorganic contaminants in groundwater and soil. Both metals and non-metals (including radionuclides) may be attenuated by sorption reactions such as precipitation, adsorption on the surfaces of soil minerals, absorption into the matrix of soil minerals, or partitioning into organic matter. Oxidation-reduction (redox) reactions can transform the valence states of some inorganic contaminants to less soluble and thus less mobile forms (*e.g.*, hexavalent uranium to tetravalent uranium) and/or to less toxic forms (*e.g.*, hexavalent chromium to trivalent chromium)[5].”

Given that closure of CCR units by removal or capping is considered source control, the evaluation of MNA is an appropriate remedial approach that deserves serious consideration to address residual dissolved and/or mobile inorganic constituent groundwater impacts following closure. It is generally readily implementable and requires no extra space beside the groundwater monitoring network.

Hydraulic Control

Generally, hydraulic control refers to the use of groundwater pumping and extraction to artificially induce a hydraulic gradient. One example, groundwater pump and treat (P&T), is often considered to be a presumptive remedial technology at many sites[6]. This approach uses extraction wells or trenches to capture groundwater, which may subsequently require above-ground treatment and discharge to a receiving stream, reinjection into the groundwater, or reuse at the generating station. Groundwater P&T is often slow and costly as a means to restore groundwater quality, but can be effective in providing hydraulic control to limit contaminant migration. Given that some CCR sites located at power generating facilities will have existing above-ground treatment infrastructure available, which may include retention basins and/or wastewater treatment plants, the costs to handle extracted groundwater above-ground can be fairly manageable at some sites.

Extracted groundwater also has the potential to be beneficially reused as process makeup water or in cooling tower operations. In some cases, this extracted groundwater may be cleaner (i.e., free of sediment and total suspended solids) and/or easier to treat than some of the surface water used for these purposes. Furthermore, the water could be used for irrigation or dust suppression purposes as well as moisture conditioning of dry ash that is being landfilled at power plants that continue to use coal as a fuel, but have switched to dry-handling operations. In some instances, this extracted water may meet surface water standards with little or no treatment, alleviating potential compliance issues associated with a site’s National Pollution Discharge Elimination System (NPDES) permit when used in situations that could lead to a surface water discharge (i.e., irrigation water runoff).

Groundwater extraction for hydraulic control can often effectively address the variety of inorganic constituents encountered at these sites. Extraction technologies also have the ability to overcome the limitations of in situ injection-based technologies to access impacted groundwater in lower permeability geologic formations such as fractured bedrock. Space constraints are mainly limited to the above-ground treatment component of a P&T system since extraction wells can generally be fit into relatively tight spaces at the edge of waste or other points of compliance (e.g., state-specific compliance boundaries and/or property boundaries).

Figure 3 depicts the above-ground treatment components of a groundwater P&T system.

Figure 3: Pump and Treat Water Treatment System

On the other hand, not every CCR site will have existing above-ground water treatment capabilities, and hydraulic control can also be achieved without the need for above-ground extraction of water, through the use of an engineered phytoremediation system such as the TreeWell® system, which has been developed and marketed by Applied Natural Sciences, Inc. This type of system installs a tree within a well, which allows for groundwater to be extracted from a targeted zone to enter the root system of the trees. This method forces the tree to use groundwater rather than rainwater/surface water to meet its water needs and encourages downward root growth to the saturated zone. By installing a cased “well” for tree planting using large diameter auger (LDA) technology, extraction of deeper groundwater zones can be achieved. This type of system mirrors a traditional mechanical extraction system with the trees acting as solar-driven pumps. The advantage of the system includes no above-ground water management needs and minimal long-term operations and maintenance (O&M) requirements following the establishment of the tree system. Such systems have been observed to meet design hydraulic control parameters typically by the end of the third growing season, when properly designed and spaced.

Figure 4 illustrates the concept of the TreeWell® system.

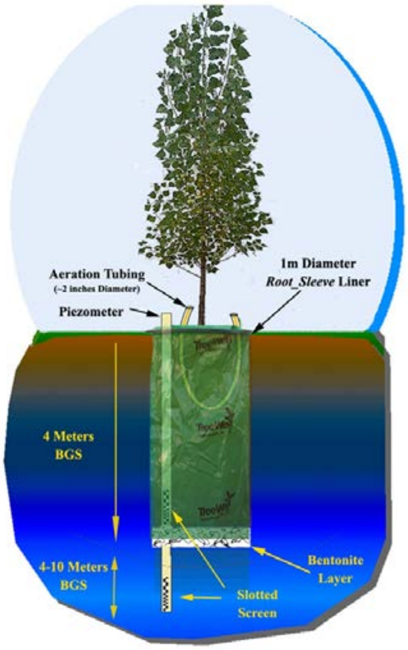

Figure 4: TreeWell® System (Image courtesy of Applied Natural Sciences, Inc.)

Permeable Reactive Barriers

Permeable reactive barriers (PRBs) can present a feasible alternative for in-situ treatment of various inorganic constituents that may be present in groundwater at CCR sites. The technology typically involves the installation of a subsurface wall constructed with reactive media such as zero-valent iron (ZVI), biologically active media (to induce aerobic or reducing conditions), clays and zeolites and peat moss (to promote ionic exchange and/or sorption). PRBs have proven to be effective in passively treating organic compounds, as well as inorganic constituents such as arsenic, selenium, and chromium, which may be present in groundwater below CCR units. Barrier walls can be installed in downgradient locations using conventional excavation methods or one-pass trenching technology. Excavated trenches get back-filled with reactive media to create a barrier that treats dissolved constituents as they passively flow through the PRB with the groundwater. These systems can either be constructed as continuous “walls” or as “funnel and gate” systems where (impermeable) slurry walls create a “funnel” that directs groundwater to permeable “treatment gates” filled with reactive materials. Since the costs for reactive materials (e.g., ZVI or similar) are generally higher than bentonite-based slurry wall construction, these configurations help to lower construction and maintenance costs. Similar to slurry walls (see discussion below), PRBs are typically keyed into an underlying low-permeability unit such as a clay layer or bedrock. The depth of such a unit can be a limiting factor for this technology and depth of construction has a direct impact on the cost of PRB construction.

While PRBs are effective at treating certain compounds, their applicability to CCR settings is somewhat limited given the expected mix of constituents that may be present at concentrations above regulatory standards. For example, while arsenic may be treated effectively, other constituents such as chloride, sulfate, boron, or total dissolved solids may not be treated concurrently.

However, there are certain innovative materials that are being tested and have shown promise in removing constituents that present big treatment challenges, such as boron. Laboratory-scale research has demonstrated the efficacy of certain low-cost adsorptive media (such as saw dust or natural clays) to remove boron from groundwater; however, this also requires pH adjustment as part of the removal process to alter the ionic state (i.e., charge) of the boron molecule. These media can be used in above-ground applications (such as P&T) or in-situ within a PRB. The installation of a PRB will generally require more space than extraction wells, but the system does not require above-ground treatment components and therefore, the overall treatment footprint is likely to be smaller compared to a P&T system.

Figure 5 depicts a conceptual treatment approach using a PRB approach for passive removal of boron from groundwater.

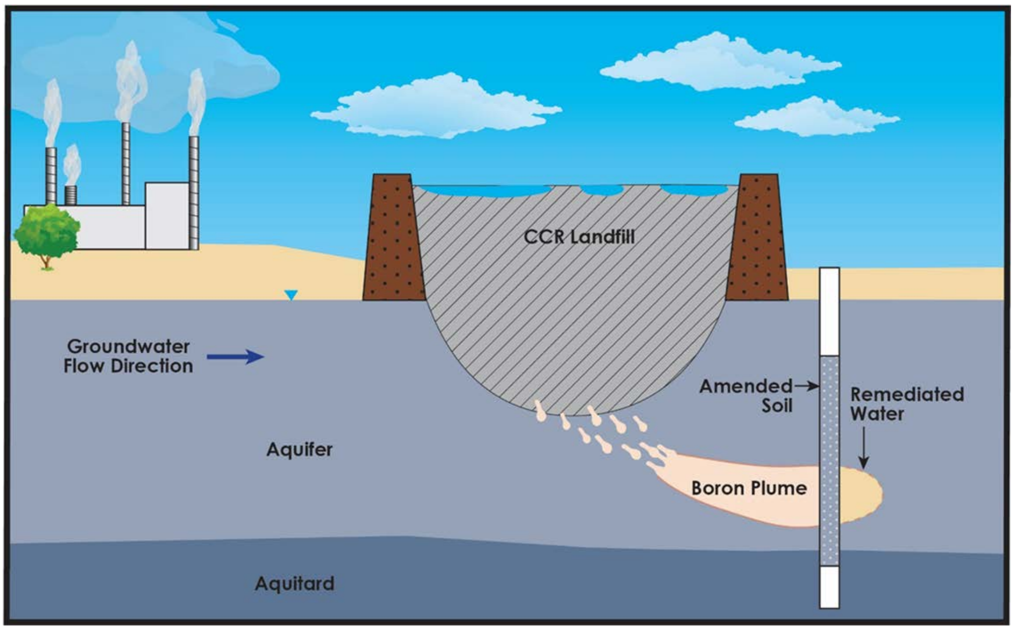

Figure 5: Conceptual In-Situ Boron Treatment Design

Slurry or Barrier Walls

Slurry or barrier walls are increasingly employed as a component of closure in conjunction with capping of CCR units to limit migration of constituents in groundwater away from a (capped) CCR unit. The installation of these (near impermeable) walls is similar to the methods described for PRBs above. In general, the applicability of slurry walls is limited by the depth of installation, which is approximately 100 feet below ground surface. However, site-specific and technology-specific considerations may limit this depth to shallower installations, but in certain cases the depth can even be increased beyond 100 feet.

As opposed to PRBs, slurry or barrier walls do not provide treatment, but only containment. Since groundwater cannot flow through zones of low permeability created by slurry or HDPE barrier walls, some groundwater pumping needs to be employed upgradient of the slurry or barrier wall to maintain an inward hydraulic gradient. Groundwater extraction can be limited by the capping of a CCR unit (which basically eliminates recharge via infiltration), but can generally not be totally eliminated.

Figure 6 depicts a slurry wall installation and Figure 7 conceptually illustrates the installation of an HDPE barrier wall.

Figure 6: Slurry Wall Installation

Figure 7: Containment Wall

(Source of Images: http://www.dewindonepasstrenching.com/)

In-Situ Redox Altering Approaches

While inorganic constituents cannot be degraded, these constituents can be precipitated and/or immobilized under different combinations of pH and redox conditions. A variety of pH and/or redox altering technologies are available in the remedial toolbox, which can incorporate biological processes, chemical oxidants and reductants, and mechanical processes such as air sparging, which can be used to render some of these constituents immobile and/or less toxic.

For example, insoluble (or sparingly soluble) arsenic-containing minerals such as arsenopyrite (FeAsS), realgar (AsS) or orpiment (As_2S_3) can be formed under sulfate-reducing conditions by the indigenous microbial population[7]. These conditions can be induced by injecting electron donors such as emulsified vegetable oil (EVO), lactate, or ethanol into the arsenic-impacted groundwater together with a sufficient supply of iron and sulfate. However, the groundwater geochemistry must be well understood and careful laboratory and field pilot studies need to be conducted to arrive at an effective “recipe” to create the appropriate conditions for the precipitation of these minerals. Once precipitated, these minerals are stable even if conditions revert back to a more oxygenated environment. Similarly, groundwater redox conditions can be manipulated to allow microbial reductions of other constituents such as selenium or chromium to render them less mobile and/or toxic. However, if not properly designed and implemented, manipulating redox conditions without forming the desired compounds can actually increase the mobility of released or naturally occurring constituents such as iron, manganese, and arsenic.

In addition, air sparging can be used to provide oxygen to the subsurface in an attempt to precipitate out (or make more “sorptive”) compounds that are generally more soluble and mobile under reducing conditions, such as iron, manganese, or arsenic. Again, care must be taken not to unintentionally increase the mobility of certain compounds that have the opposite redox behavior (e.g., chromium) than the compounds intended to be immobilized.

Furthermore, in-situ chemical oxidation (ISCO) or in-situ chemical reduction (ISCR) can be used to chemically alter the redox environment in the subsurface to affect the mobility and/or toxicity of certain inorganic compounds. As is the case with other in-situ remedial approaches, the delivery of the compounds within the area of interest is the main limiting process of these approaches. In addition, immobilizing one constituent may mobilize a different constituent as already described above.

Figure 8 conceptually illustrates potential processes occurring during in-situ bioremediation of arsenic.

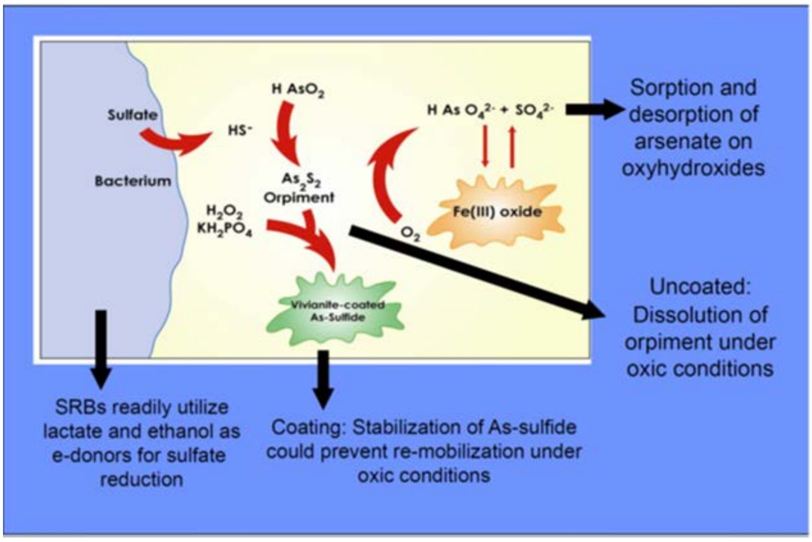

Figure 8: Various Processes Occurring During In-Situ Bioremediation of Arsenic

REMEDIAL ALTERNATIVE SELECTION PROCESS

The following general steps should be considered when selecting an appropriate remedial approach for groundwater at CCR sites:

1. Evaluate whether groundwater exceedances are likely attributable to leakage from a CCR unit, mobilization from aquifer solids beneath the unit, or are background-related;
2. Implement an “alternate source demonstration” (ASD), if applicable;
3. CCR sites are generally quite large (i.e., hundreds of hectares) and may require prioritization of remedy implementation (e.g., proximity to receptors, magnitude of release, toxicity/mobility of detected constituents, etc.);
4. MNA and institutional controls should always be part of the evaluation following closure of CCR units via removal or capping;
5. Evaluate technologies that are likely to achieve stakeholder acceptance and that are reliable, sustainable, and practicable;
6. Take advantage of existing infrastructure such as retention ponds, wastewater treatment systems, connections to sewer lines, open (vegetated) spaces (e.g., for effluent management such as irrigation, etc.); and
7. Consider water-reuse options of extracted groundwater (e.g., cooling towers, irrigation and/or land application, etc.).

The selection criteria for a remedial approach may include, but may not be limited to:

- Horizontal and vertical extent of plume;
- Types of contaminants and magnitude of exceedances;
- Proximity to potential sensitive receptors (e.g., private water supply wells, surface water bodies, etc.);
- Applicability of technology (e.g., injection technologies may be infeasible in some fractured bedrock environments);
- Space constraints vis-à-vis a point of compliance and/or for remedy construction; and
- Existing infrastructure and effluent management strategy (e.g., surface water discharge, groundwater infiltration, irrigation, water reuse, sewer discharge).

The final selection of an active remedy, if necessary, should be site-specific, and should balance risks, the effectiveness in reducing these risks using a certain remedial approach, implementability of a technology, and capital and long-term operation and maintenance (O&M) costs.

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