Conceptual Groundwater Remedial Alternatives at Coal Combustion Residuals Sites[†]

Herwig Goldemund^{1,*}, Jeffrey M. Ahrens²

¹ Geosyntec Consultants, Inc., 1255 Roberts Boulevard NW, Suite 200, Kennesaw, GA 30144, USA

² Geosyntec Consultants of NC, PC, 1300 S Mint Street, Suite 300, Charlotte, NC 28203, USA

ABSTRACT

Groundwater below many basins that have been used to store coal combustion residuals (CCRs) 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 paper conceptually discusses potentially applicable remedial approaches, including (i) monitored natural attenuation, (ii) hydraulic control using ex situ and in situ methods, (iii) permeable reactive barriers, (iv) slurry walls, and (v) oxidation-reduction-altering approaches. Additionally, this article explores potential water reuse options available at many power generating stations.

© 2019 The University of Kentucky Center for Applied Energy Research and the American Coal Ash Association
All rights reserved.

ARTICLE INFO

Article history: Received 31 January 2018; Received in revised form 16 November 2018; Accepted 19 November 2018

Keywords: CCR units; groundwater; remedial alternatives

1. Introduction

Some coal combustion residual (CCR) disposal units regulated by the Federal CCR Rule (U.S. Environmental Protection Agency [US EPA], 2015a) 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, background conditions, or both. These include mostly inorganic constituents, such as metal(loid)s (e.g., As, Se, Fe, Mn, B) and anions (e.g., Cl, SO₄). Although 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 because of background conditions or 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 effects and segregate these effects 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 effects.

The driving force for releases of inorganic constituents to groundwater at CCR basins is created by the hydraulic head as a

* Corresponding author. Tel.: 678-202-9530. E-mail: hgoldemund@geosyntec.com

[†] Adapted from the proceedings of the World of Coal Ash (WOCA 2017) Conference, Lexington, KY, 8–11 May 2017, sponsored by the American Coal Ash Association and the University of Kentucky Center for Applied Energy Research.

Fig. 1. Active coal combustion residuals basin.

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) vs. inactive (dry) conditions,
- chemical makeup of the CCR materials (bottom ash, fly ash, flue gas desulfurization (FGD) waste, 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 effects on groundwater beyond leaching that may have occurred while the basins were active.

Once released or mobilized, inorganic materials cannot be destroyed or degraded, but only captured/contained, rendered immobile, or allowed to migrate into the environment at concentrations deemed acceptable. This, in turn, affects (and also limits) the selection of potentially applicable remedial alternatives.

Fig. 2. Inactive, vegetated coal combustion residuals basin.

2. Remedial Alternatives

After 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 (1) monitored natural attenuation (MNA), (2) hydraulic control (ex situ and in situ), (3) permeable reactive barriers (PRBs), (4) slurry walls, and (5) oxidation-reduction (redox)-altering approaches.

2.1. Monitored natural attenuation

As a first step, it is generally appropriate to include MNA in an evaluation of remedial alternatives for groundwater after closure of a CCR unit. Although inorganic constituents typically associated with CCR units do not degrade, there are protocols to implement MNA for inorganic constituents. Among other entities, the U.S. Environmental Protection Agency developed a series of guidance manuals starting with a more general guidance on the use of MNA published in 1999 (US EPA, 1999), and subsequent publications focused more on MNA of inorganic constituents, with manuals published in October 2007 (US EPA 2007a,b) and August 2015 (US EPA, 2015b). The US EPA uses a tiered approach, also known as “lines of evidence,” that include the following:

1. the demonstration of a clear and meaningful trend of decreasing contaminant mass, concentration over time, or both at appropriate monitoring or sampling points using historical groundwater data, soil chemistry data, or a combination thereof;
2. the use of hydrogeologic and geochemical data to demonstrate indirectly the type(s) of natural attenuation processes active at the site, and the rate at which such processes will reduce contaminant concentrations to required levels; and
3. the use of data from field or microcosm studies that 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, US 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 (US EPA, 2015b, p. 7).

Furthermore,

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) (US EPA, 2015b, pp. 8–9).

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 or mobile inorganic constituent groundwater effects, or both, after closure. It is generally readily implementable and requires no extra space beside the groundwater monitoring network.

2.2. Hydraulic control

Generally, hydraulic control refers to the use of groundwater pumping and extraction to induce a hydraulic gradient artificially. One example, groundwater pump and treat (P&T), is often considered to be a presumptive remedial technology at many sites (US EPA, 1996). 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, wastewater treatment plants, or both, 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) 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 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 affected groundwater in lower permeability geologic formations such as fractured bedrock. Space constraints are mainly lim-

Fig. 3. Groundwater pump and treat water treatment system.

ited to the above-ground treatment component of a P&T system because 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, property boundaries). Figure 3 depicts the above-ground treatment components of a typical groundwater P&T 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 technology, extraction of deeper groundwater zones (i.e., in excess of 20 m below the ground surface) can be achieved because the surface of the “well” is sealed and only groundwater from a targeted zone is allowed into the cased-off borehole (e.g., Gatliff et al., 2016). 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 requirements after 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. The layout for a TreeWell plantation is generally based on groundwater flow modeling assuming a design uptake rate of approximately 40 gallons (150 L) per day per unit. Because of the relatively low concentrations of constituents in groundwater surrounding CCR units, contaminant uptake and accumulation within the above-ground biomass is generally not of concern but can be monitored if warranted under certain circumstances. Figure 4 illustrates the concept of the TreeWell system.

2.3. 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

Fig. 4. TreeWell® System (image courtesy of Applied Natural Sciences, Inc.).

of a subsurface wall constructed with reactive media such as zerovalent iron (ZVI), biologically active media (to induce aerobic or reducing conditions), clays and zeolites, and peat moss (to promote ionic exchange, sorption, or both). 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 backfilled with reactive media to create a barrier that treats dissolved constituents as they passively flow through the PRB with the groundwater (e.g., Interstate Technology & Regulatory Council, 2011). 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. Because 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 section 2.4), 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 effect on the cost of PRB construction.

Although 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, although 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 (e.g., Polat et al., 2004; Sasaki et al., 2011; Wei et al., 2011). Laboratory-scale research has demonstrated the efficacy of certain low-cost adsorptive media (e.g., 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 (e.g., 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; therefore, the overall treatment footprint is likely to be smaller compared with a P&T system. Figure 5 depicts a conceptual treatment using a PRB approach for passive removal of boron from groundwater.

2.4. Slurry or barrier walls

Slurry or barrier walls are increasingly used 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 30.5 m 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 30.5 m; a depth of up to 56 m has been documented for a soil-cement-bentonite cutoff wall (Ruffing and Evans, 2014).

As opposed to PRBs, slurry or barrier walls are designed to provide containment; localized treatment achieved through the sorption or chemical precipitation reactions from construction of the walls are incidental to the design objective. Because groundwater cannot flow through zones of low permeability created by slurry or high-density polyethylene 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.

2.5. In situ redox-altering approaches

Although inorganic constituents cannot be degraded, these constituents can be precipitated, immobilized, or both, under different combinations of pH and redox conditions. A variety of pH and redox-altering technologies is available in the remedial toolbox, which can incorporate biological processes, chemical oxidants and reductants, and mechanical processes, such as air sparging, which

Fig. 5. Conceptual in situ boron treatment design.

can be used to render some of these constituents immobile 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 (Onstott et al., 2011). These conditions can be induced by injecting electron donors such as emulsified vegetable oil, lactate, or ethanol into the arsenic-affected 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 sele-

mium or chromium to render them less mobile 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.

Additionally, air sparging can 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 or in situ chemical reduction can chemically alter the redox environment in the subsurface to affect the mobility 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. Additionally, immobilizing one constituent may mobilize a different constituent as already described above. Figure 7 conceptually illustrates potential processes occurring during in situ bioremediation of arsenic.

3. 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 background-related.
2. Implement an alternate source demonstration, if applicable.
3. CCR sites are generally quite large (i.e., hundreds of hectares) and may require prioritization of remedy implementation (e.g.,

Fig. 6. Slurry wall installation.

Fig. 7. Various processes occurring during in situ bioremediation of arsenic.

proximity to receptors, magnitude of release, toxicity/mobility of detected constituents).

4. MNA and institutional controls should always be part of the evaluation after closure of CCR units by 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, and open (vegetated) spaces (e.g., for effluent management such as irrigation).
7. Consider water reuse options of extracted groundwater (e.g., cooling towers, irrigation or land application, CCR conditioning for landfilling).

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

- horizontal and vertical extent of a plume,
- types of contaminants and magnitude of exceedances,
- proximity to potential sensitive receptors (e.g., private water supply wells, surface water bodies),
- applicability of technology (e.g., injection technologies may be infeasible in some fractured bedrock environments),
- space constraints vis-à-vis a point of compliance 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, ability to implement a technology, and capital and long-term operation and maintenance costs.

References

- Gatliff, E., Linton, P.J., Riddle, D.J., Thomas, P.R., 2016. Phytoremediation of soil and groundwater: economic benefits over traditional methodologies. In: Bioremediation and Bioeconomy (Prasad, M.N.V., ed.). Elsevier, Amsterdam, Netherlands, pp. 589–608.
- Interstate Technology & Regulatory Council (ITRC), 2011. Permeable Reactive Barrier: Technology Update. PRB-5. Interstate Technology & Regulatory Council, PRB: Technology Update Team, Washington, DC. <https://www.itrcweb.org/GuidanceDocuments/PRB-5-1.pdf>
- Onstott, T.C., Chan, E., Polizzotto, M.L., Lanzon, J., DeFlaun, M.F., 2011. Precipitation of arsenic under sulfate reducing conditions and subsequent leaching under aerobic conditions. *Applied Geochemistry* 26, 269–285.
- Polat, H., Vengosh, A., Pankratov, I., Polat, M., 2004. A new methodology for removal of boron from water by coal and fly ash. *Desalination* 164, 173–188.
- Ruffing, D., Evans, J., 2014. Case study: construction and in situ hydraulic conductivity evaluation of a deep soil-cement-bentonite cutoff wall. In: Geo-Congress 2014 Technical Papers: Geo-Characterization and Modeling for Sustainability (GSP 234), Atlanta, GA, 23–26 February 2014 (Abu-Farsakh, M., Yu, X., Hoyos, L.R., eds.). American Society of Civil Engineers, Reston, VA, pp. 1836–1848. doi:10.1061/9780784413272.180
- Sasaki, K., Takamori, H., Moriyama, S., Yoshizaka, H., Hirajima, T., 2011. Effect of saw dust on borate removal from groundwater in bench-scale simulation of permeable reactive barriers including magnesium oxide. *Journal of Hazardous Materials* 185, 1440–1447.
- U.S. Environmental Protection Agency (US EPA), 1996. Final Guidance: Presumptive Response Strategy and Ex-Situ Treatment Technologies for Contaminated Ground Water at CERCLA Sites. EPA 540/R-96/023. Office of Solid Waste and Emergency Response Directive 9283.1-12, October 1996.
- U.S. Environmental Protection Agency (US EPA), 1999. Use of Monitored Natural Attenuation at Superfund, RCRA Corrective Action, and Underground Storage Tank Sites. OSWER Directive 9200.4-17P. Office of Solid Waste and Emergency Response, April 1999.
- U.S. Environmental Protection Agency (US EPA), 2007a. Monitored Natural Attenuation of Inorganic Contaminants in Groundwater, Volume 1, Technical Basis for Assessment. EPA/600/R-07/139. Office of Research and Development, October 2007.
- U.S. Environmental Protection Agency (US EPA), 2007b. Monitored Natural Attenuation of Inorganic Contaminants in Groundwater, Volume 2, As-

- essment for Non-Radionuclides Including Arsenic, Cadmium, Chromium, Copper, Lead, Nickel, Nitrate, Perchlorate, and Selenium. EPA/600/R-07/140. Office of Research and Development, October 2007.
- U.S. Environmental Protection Agency (US EPA), 17 April 2015a. Hazardous and Solid Waste Management Systems; Disposal of Coal Combustion Residuals from Electric Utilities; Final Rule. 40 CFR Parts 257 and 261. Federal Register, Vol. 80, No. 74, pp. 21302–21501.
- U.S. Environmental Protection Agency (US EPA), 2015b. Use of Monitored Natural Attenuation for Inorganic Contaminants in Groundwater at Superfund Sites. Office of Solid Waste and Emergency Response Directive 9283.1–36, August 2015.
- Wei, Y.-T., Zheng, Y.-M., Chen, J.P., 2011. Design and fabrication of an innovative and environmental friendly adsorbent for boron removal. *Water Research* 45, 2297–2305.