Coal Combustion Residuals and Groundwater: It's Complicated

Bob Kleinmann, Ph.D., HDR

11 Stanwix Street, Suite 800, Pittsburgh, PA 15222-1357

CONFERENCE: 2017 World of Coal Ash – (www.worldofcoalash.org)

KEYWORDS: groundwater, CCR, remediation, water treatment, surface water, economics, potential at-source control measures, potential in situ control measures

INTRODUCTION

A number of potential remedial options can and should be considered if it appears that surface water or groundwater quality has been adversely affected or if there are concerns about future groundwater quality degradation due to the presence of coal combustion residuals (CCR). However, each site is different and these differences must be considered to develop a cost-effective remedial approach. Sites differ in the nature and extent of water quality degradation as well as important factors such as depth to water table, distance to water bodies and site boundaries, and the natural attenuation capacities of the soil and rock strata. Other site-specific aspects to consider include geographic location, whether the relevant state or federal regulations are more stringent, whether CCR disposal is continuing or has ceased, the characteristics (e.g., physical, geochemical, and hydrological) of the CCR material and disposal area, the local and regional geology, the nature (i.e., physical and geochemical) and hydrologic significance of the underlying strata, the nature of the CCR leachate (i.e., the documented contaminants of concern and their concentrations), groundwater flow rates, if groundwater is being extracted by wells in the area (and, if so, where those wells are relative to the CCR), and whether groundwater contamination has reached or could potentially approach site boundaries or surface water bodies.

It is important that operators, consultants, and regulators all remain open to innovation, while remaining aware that site-specific aspects typically determine which remedial option(s) will be the most cost effective. Although CCR leachates are typically much less toxic than leachates from other waste sites, the tendency has been to use only the most conservative approaches to deal with it. In general, this is because the sites that have already taken or are already taking remedial actions are responding to state regulations, such as the Coal Ash Management Act of 2014 in North Carolina, which required action before the Federal regulations. However, operators in other states need not simply repeat what has been done at such sites.

Recognizing that the groundwater will remain contaminated for a very long time unless action is taken to reduce contaminant release from the CCR, this paper will first discuss some alternative options that exist to control groundwater contamination at the CCR source. Then, we will review other potential innovative technologies (other than the very expensive option of pumping and treating the contaminated groundwater) to be considered when dealing with contaminated groundwater. We recognize some experimental work will be necessary to modify approaches used only at other types of waste sites or to scale up approaches proven to be effective in only small-scale laboratory tests, but now is the time to proactively proceed with such research.

AT-SOURCE CONTROL OPTIONS

With respect to at-source control, some regulatory authorities may push for excavation and removal of all CCR at all sites, but this conventional approach is neither cost effective nor wise at many sites, given the relatively low toxicity of most CCR. Excavation, hauling, and re-disposal of fly ash into a lined landfill can be very expensive, will not immediately improve groundwater quality, and can adversely impact neighboring communities because of the higher volume of truck traffic (e.g., CCR particles settling from the trucks). There is also the thorny question of how much underlying contaminated material has to be removed. If the existing CCR disposal site is located near a sensitive water body or an aquifer, then excavation and removal may be necessary. If not, other potential options often exist.

Short- and long-term benefits, anticipated cost effectiveness, and potential disadvantages of other potentially applicable remedial options should always be considered. For example, the most commonly used closure alternative to excavation and removal involves construction of impermeable caps or covers. As a closure method, this approach is fine. However, these covers are only effective in preventing groundwater contamination when all or nearly all of the CCR is stored above the water table. At sites where only a fraction of the CCR is currently exposed to groundwater, models can be used to predict whether restricting infiltration in this way will lower the water table enough to prevent further leaching of contaminants by the groundwater. However, if groundwater will continue to flow through much of the CCR after the impermeable cover is emplaced, other at-source control measures may be necessary.

If one starts with the assumption that capping will still be required even though much of the CCR lies under the water table, there are various ways to divert the groundwater around the ash.[8] Site-specific aspects, such as how much the water table has to be lowered, the anticipated groundwater pressure, and the nature of the subsurface, have to be considered to determine which approach will be most appropriate. For example, cutoff walls can be constructed with soil-bentonite slurry, cement grout, or geosynthetic materials. Slurry wall construction requires the excavation of trenches; the added slurry prevents the trench from collapsing. Reinforcement is then lowered in and the trench is filled, typically with a soil-bentonite or cement-bentonite mixture or with concrete, any of which will displace the slurry.[11, 15]

Grout curtains are similar to slurry walls, but typically do not require extensive trenching. They are thin, vertical grout walls constructed by injecting grout directly into the soil or rock at closely spaced intervals. The spacing is selected so the grout forms a continuous wall or curtain. Polymer grouts are usually used for barrier applications because they are impermeable to gases and liquids, and resist acidic and alkaline environments. Another possibility is to use geosynthetic materials similar to a sheet pile that can be vibrated into the ground, provided the overburden does not have too many obstructions that would complicate construction.[11]

However, diverting groundwater around the CCR is going to be expensive, so if the water table is going to be an issue, other options should be investigated. For example, one closure approach, that is often less expensive than installing groundwater barriers and an impermeable cover, is to mix the CCR and contaminated soils with pozzolanic materials, generally at proportions of 8 - 12 percent. Common pozzolans include portland cement and blast furnace slag. This approach is generally referred to as in situ solidification or stabilization (ISS) and is commonly used to prevent leaching of contaminants from more toxic waste materials, but may be appropriate for some CCR sites. The use of ISS will improve the strength of the CCR and greatly reduce its porosity, permeability, and hydraulic conductivity.[11, 14] The net effect of ISS is the potential leaching of contaminants from the source zones is virtually eliminated. At some sites, the basin can simply be covered with topsoil and revegetated instead of using an impermeable cap.

A relatively inexpensive approach would be to increase the adsorption capacity of the CCR and the basin itself. This could easily be done at some sites using iron oxide or hydroxide. The effectiveness of these iron compounds in binding many of the contaminants that commonly leach from CCR, especially arsenic, is well documented, though its effectiveness depends on the pH and Eh of the water as well as the concentrations of other ions in solution.[2, 9, 19] In laboratory tests, iron hydroxide even reduced boron mobility, as long as the pH was alkaline enough.[5]

Moreover, an inexpensive source of iron hydroxide, such as the treatment sludge created when acidic coal mine drainage is neutralized, is readily available in some areas. The approach has been tested in the laboratory and at mine sites,[12] and used at non-CCR waste sites where arsenic levels were the major problem, but as far as we know, this technology has never been tested at a CCR site. However, it would appear to be tailor-made for CCR sites located near coal mines. Mine drainage treatment sludge normally has a pH between 8 and 9 but is mostly water, which makes it easy to handle, but expensive to transport for long distances.

Treating one waste material with another is typically cost effective, as long as the transportation costs are not too high, and the concept is certainly intellectually pleasing. The possibility of adding potential contaminants of concern would have to be evaluated, but coal mine drainage water treatment sludge is generally quite innocuous, as long as it is not re-exposed to extremely acidic water and is benign enough that it has even been applied to farm land.

Although the concept has yet to be tested for CCR, its effectiveness in immobilizing arsenic and other contaminants suggests that bench-scale tests designed to mimic actual site conditions and using the actual mine drainage treatment sludge, not a laboratory simulation, should be initiated to confirm or deny its potential for this application. Moreover, follow-up pilot-scale tests would be easy to implement by looking at how effective the addition of coal mine drainage treatment sludge is in reducing the in situ concentrations of potential contaminants in the porewater of a small section of an actual CCR basin. Another advantage to this approach is that coal mine drainage sludge could be easily injected into already deposited CCR materials or added to CCR as it is conveyed to or placed into an operating disposal site.

Another possible additive that could be added to the CCR is guar gum, a carbohydrate polymer commercially produced from guar beans for use in foods and for medicinal purposes. It binds very tightly to boron and the boron actually increases the capacity of the guar gum to adsorb other contaminants. The combination of guar gum and boron has been used primarily to make fracking fluids more viscous, but because it also complexes metals, guar gum and some of its chemical cousins have been proposed as a potential means of polymer-enhanced ultrafiltration of boron.[3] The possible use of it for in situ immobilization of potential leachates from CCR materials is intriguing, although the cost for such an application would have to be evaluated. Additional research is clearly warranted.

IN SITU REMOVAL OF CONTAMINANTS

There is no reason to control contaminant migration if natural conditions will adequately remove, dilute, or disperse them to acceptable levels. This is referred to as natural attenuation and is well accepted by state and federal regulators as an appropriate mitigative factor that should be considered when evaluating the need for remedial options.[4, 16, 17, 18] Natural attenuation mechanisms can be both physical and chemical in nature. Physical attenuation includes dispersion and dilution. Chemical attenuation includes adsorption of contaminants, ion exchange, and the precipitation of contaminant-containing minerals. In addition to adsorption to soil, clay particles, and organic matter, iron and manganese oxides that commonly precipitate downgradient of CCR disposal sites will, in turn, remove other contaminants by adsorption. While model predictions can simulate long-term attenuation using a soil-water partitioning coefficient to estimate adsorption, natural conditions will dictate how contaminants migrate through the strata and how much of it is removed en route.

Empirical data are the best indicator of natural attenuation mechanisms, but groundwater monitoring is required to establish their projected long-term effectiveness and the variability of the site with respect to physical and chemical attenuation.

Monitoring results will verify the degree to which natural attenuation is occurring and plume stability (that the footprint of site-related impacts is not increasing).[4, 16, 17, 18]

At present, monitored natural attenuation (MNA) is the primary approach being used to deal with contaminated groundwater downgradient of most CCR deposits, although that will likely change in the future. However, before considering other more dramatic options, it is important to remember that natural attenuation is not limited to in situ contaminant removal.

Dispersion and dilution of contaminants should be fully considered and modeled using appropriate assumptions and, if possible, validated using naturally present ions like chloride and sulfate that are generally not affected by interactions with soil, clay particles, and mineral precipitates. Although dilution that occurs in the aquifers is typically incorporated into MNA calculations, other modes of dilution and dispersion may not be getting the attention they deserve. The Electric Power Research Institute (EPRI) points out that natural attenuation in the vadose zone, before the contaminated water even reaches the aquifer, can be significant and the dilution that occurs in hyporheic zones, where the groundwater approaches and mixes with the surface water beneath and approaching a stream or river, can dramatically attenuate contaminant concentrations. This type of mixing and dilution also occurs as groundwater approaches a large pond or lake.[4] Full consideration of these factors may require more monitoring wells, but could mean that potentially expensive groundwater remediation measures can be avoided.

In addition, at some sites, it may make sense to enhance natural attenuation. For example, an oxidant or a source of alkalinity can be added to accelerate precipitation of the aluminum, iron, and manganese already present in the groundwater, since these oxide and hydroxide precipitates will adsorb other contaminants. Iron and manganese oxidation and precipitation can be induced in low Eh water by the injection of a chemical oxidant, such as potassium permanganate, or in some cases, by air sparging, which simply involves pumping air into the targeted saturated zone. Although it would appear that air sparging would be less expensive since there are no chemical costs, lifetime costs may be comparable to the costs of using a chemical oxidant, since air sparging has operation and maintenance costs that may or may not outweigh the cost of chemicals and possible reinjection events. Consequently, if this technology were part of a selected alternative, both approaches should be tested with materials obtained from the site (bench-scale) or in onsite (pilot-scale) tests to see which works better, since there are other variables that may affect their comparative performance.

Adding alkalinity to enhance the formation of these precipitates, if there is sufficient dissolved oxygen already present, will also enhance adsorption of other contaminants, though the optimal pH for their adsorption is different for the various contaminants. These approaches are not radically new. In fact, they are commonly used to improve groundwater quality at other impacted sites.

If these approaches are not applicable, for example at sites where iron concentrations in the groundwater are low, it may make sense to add an adsorbent, like iron hydroxide sludge, or a carbohydrate polymer such as the guar gum mentioned earlier, into the strata through which the contaminated water is flowing, to enhance adsorption and in situ removal of the contaminants.

It is also possible to enhance natural attenuation by increasing infiltration of uncontaminated water into downgradient portions of a CCR site, thereby diluting and attenuating contaminant concentrations. There are various possible ways to do this, ranging from temporary methods (e.g., surface irrigation using mechanical sprayers) to the creation of groundwater infiltration galleries, ponds, or wetlands with a somewhat permeable bottom, which could be temporary or permanent. Such measures could be designed to significantly decrease groundwater contaminant concentrations before the groundwater even approaches a site boundary, while increasing the attractiveness and ecological diversity of the reclaimed site. Potential adverse effects would be that the groundwater plume, though less concentrated, would reach the site boundary somewhat earlier, and that such measures might increase the flow at existing seeps, cause new seeps to appear, or induce slope failures. Thus, once again, the use of this approach is highly dependent on site-specific characteristics.

PASSIVE WATER TREATMENT

At many non-CCR waste impacted sites, contaminated groundwater is pumped to the surface (pump-and-treat) or collected from surface seeps to provide hydraulic containment and prevent contaminant migration to sensitive receptors. Following treatment, the water may be discharged directly to a surface water body or reinjected underground, depending on the site conditions and permitting requirements. However, pump-and-treat is an expensive, long-term option that should not be needed at most CCR sites.

If water treatment is required because contaminated groundwater is already emerging at the land surface, threatening to enter a surface water body, or likely to adversely affect a water supply well, passive treatment options may be considered as they require much less attention and cost than a conventional water treatment system. However, it should be recognized that passive water treatment is low-maintenance and will become less effective over time.[12] Thus, passive water treatment will most likely be applicable where other measures have been implemented to significantly decrease contamination levels over time.

The most conventional form of passive treatment involves the construction of wetlands engineered to remove contaminants using natural processes.[13] However, this approach will likely not be useful, given the contaminants typically present in CCR leachates.

A more appropriate passive water treatment technique involves the placement of permeable reactive barriers (PRBs), which are placed in the path of the contaminated groundwater and engineered to remove the specific contaminants present. The simplest PRBs are typically constructed by excavating a trench that penetrates the saturated zone and typically extends through it to a confining layer (to prevent the contaminated water from going beneath the PRB). The trench is then backfilled with an appropriate reactive material. The reactive material may be media that absorbs and adsorbs the contaminants or forms precipitates that reduce dissolved contaminant concentrations.[1, 6]

Many successful PRBs have been constructed at impacted sites with a wide range of constituents, but only limited testing with water containing the constituents in CCR leachates.[6] Nonetheless, examples exist where virtually all of the individual constituents have been addressed successfully. The sole exception is boron, which has been successfully removed in the laboratory, but as of yet, not in the field. Pilot-scale tests based on the materials shown to be effective in the laboratory can and should be implemented.

Specialized equipment is available to simultaneously excavate the trench and backfill it with the appropriate reactive media to construct the PRB in locations that would not be feasible using conventional trenching. In addition, there are many potential ways to create a PRB, depending on the width of the contaminant plume and the contaminants of concern. For example, instead of creating a PRB that spans the entire width of the contaminant plume, a funnel-and-gate system can be used to channel the groundwater into a gate that contains the reactive material. The simplest design consists of a single gate with walls extending from both sides, but of course there can be many gates.[10] The main advantage of the funnel-and-gate system is that a smaller reactive region can be used to treat the plume, thereby reducing costs. In addition, the reactive media is much easier to replace. Another potential advantage of this approach is that the gates can be placed in such a way that the discharged groundwater is redirected away from a potentially sensitive area or a downgradient water supply well.

The design of a PRB can involve the use of multiple types of reactive material based on the anticipated concentrations of the contaminants of concern, their compatibility with certain PRB media, and whether pretreatment is required to enhance the effectiveness of the intended removal mechanisms. Depending on the contaminants, multiple types of reactive material may be mixed together to create a single reactive zone or emplaced sequentially, so that the groundwater passes through several different reactive zones. The appropriate composition of a PRB at a CCR site would depend on the contaminants of concern, but might include a combination of limestone aggregate (to provide PRB stability, transmissivity, and pH buffering), organic materials (e.g., mulch and wood chips) to promote the reduction of sulfate to sulfide and precipitation of contaminants as sulfide minerals, zero-valent iron to help promote and sustain reducing conditions, and/or other materials, such as rice husks,[7] iron, or guar gum, to adsorb the boron.

The PRB lifespan is a function of the concentrations of the contaminants and the media removal characteristics, which may be influenced by site-specific geochemical conditions and other competing ions. PRB lifespan is generally proportional to its cost, as effectiveness generally increases with the amount of emplaced reactive media. Based on practice, if it is anticipated that the contaminants will continue to persist at problematic concentrations in the groundwater for more than a decade, periodic replacement of the PRB's reactive media may be required.

CONCLUSION

Given the state and federal regulations enacted, operators of coal burning power plants have to assess whether their past and on-going CCR disposal practices have adversely affected or threaten to adversely affect off-site water quality. CCR disposal sites differ in the nature and extent of water quality degradation as well as important factors such as depth to water table, distance to water bodies and site boundaries, and the natural attenuation capacities of the soil and rock strata. If downgradient groundwater quality in a usable aquifer or surface water quality have been or are likely to become contaminated, remedial measures may be required. So far, operators have basically relied on excavation and removal of the CCR material, capping, and MNA to deal with the problem, but other cost-effective options have been successful at other waste sites and should be considered. Granted, CCR leachate has some unusual characteristics (especially the typical levels of boron), but that simply means that these techniques may have to be adapted.

Operators should carefully consider their relevant site-specific conditions and evaluate the potential use of appropriate alternative remedial measures. One or more of them may be much more cost effective than more conventional techniques at their specific site, although some modifications will likely be necessary. Research is especially needed to identify the most cost-effective ways to immobilize or otherwise remove boron from groundwater, while recognizing that the most cost-effective measure at one site may not be at another. Proactive bench-scale and pilot-scale tests of potential approaches should be initiated soon so that they are available when needed.

REFERENCES

[1] Blowes, D.W., Ptacek, C.J., and Jambor, J.L. In-Situ Remediation of Cr(VI)-Contaminated Groundwater Using Permeable Reactive Walls: Laboratory Studies. *Environmental Science and Technology*, 1997, 31(12), pp. 3348 - 3357.

[2] Cundy, A.B., Hopkinson, L., and Whitby, R.L.D. Use of Iron-based Technologies in Contaminated Land and Groundwater Remediation: A Review. *Science of the Total Environment*, 2008, 400, pp. 42 - 51.

[3] Easton, J.H. *From Power Plant Effluents to Flowback and Produced Water Treatment - An Innovative Approach to Boron Removal*. Proceedings of the International Water Conference, Paper 16 - 20 (CD), 2016.

[4] Electric Power Research Institute (EPRI). *Monitored Natural Attenuation for Inorganic Constituents in Coal Combustion Residuals*, Technical Report 3002006285, 2015.

[5] Goldberg, S. and Glaubig, R.A. Boron adsorption on aluminum and iron oxide minerals. *Soil Science Society of America Journal*, 1985, 49, pp. 1374 - 1379.

[6] Interstate Technology and Regulatory Council (ITRC). *Permeable Reactive Barriers: Lessons Learned/New Directions*; ITRC, Permeable Reactive Barriers Team, PRB-4, Washington, D.C., 2005, http://www.itrcweb.org.

[7] Man, H.C., Chin, W.H., Zadeh, M.R., and Yusof, M.R.M. Adsorption Potential of Unmodified Rice Husk for Boron Removal. *BioResources*, 2012, 7(3), pp. 3810 - 3822.

[8] Mann, M.J., Gupta, K.K., and Bower, B.C. *Interim Remedial Measure of a Radiological and Hazardous Waste Landfill Utilizing a Groundwater Diversion Barrier Wall and Exposed Geomembrane Cover System.* Proceedings of the Federation of New York Solid Waste Association Conference, 2009, *http://www.mmce.net/files/sof_Groundwater%20Barrier%20Wall%20and%20Geomembrane%20Cover,%20West%20Valley%20Facility%20NDA.pdf*

[9] Nicomel, N.R., Leus, K., Folens, K., Van Der Voort, P., and Du Laing, G. Technologies for Arsenic Removal from Water: Current Status and Future Perspectives. *International Journal of Environmental Research and Public Health*, 2016, 13: 62, 24; DOI:10.3390/ijerph13010062.

[10] Obiri-Nyarko, F., Grajales-Mesa, S.J., and Malina G. An Overview of Permeable Reactive Barriers for In Situ Sustainable Groundwater Remediation. DOI: 10.1016/j.chemosphere.2014.03.112. Published Online: May 8, 2014, http://www.sciencedirect.com/science/article/pii/S0045653514004731

[11] Pichtel, J. *Fundamentals of Site Remediation: for Metal- and Hydrocarbon-Contaminated Soils*, 2nd ed.; Government Institutions, Lanham, MD, 2007.

[12] Rait, R., Trumm, D., Pope, J., D Craw D., Newman, N., and MacKenzie, H. Adsorption of Arsenic by Iron Rich Precipitates from Two Coal Mine Drainage Sites on the West Coast of New Zealand. *New Zealand Journal of Geology and Geophysics*, 2010, 53(2-3), pp. 177-193.

[13] Skousen, J., Zipper, C.E., Rose, A., Ziemkiewicz, P.F., Nairn, R., McDonald, L.M., and Kleinmann, R.L. Review of Passive Systems for Acid Mine Drainage Treatment.

Mine Water and the Environment, 2016, 36(1), pp. 133-153, DOI: 10.1007/s10230-016-0417-1

[14] Spence, R.D. and Shi, C. (Eds.) *Stabilization and Solidification of Hazardous, Radioactive, and Mixed Wastes*, CVC Press, Boca Raton, FL, 2005.

[15] U.S. Environmental Protection Agency (USEPA). *Slurry Walls;* Engineering Bulletin 540 S-92/008; Office of Research and Development: Cincinnati, OH, 1992.

[16] USEPA. *Use of Monitored Natural Attenuation at Superfund*. RCRA Corrective Action, and Underground Storage Tank Sites. EPA/OSWER No. 9200.4-17P; Office of Solid Waste and Emergency Response: Washington D.C., 1999.

[17] USEPA. *Monitored Natural Attenuation of Inorganic Contaminants in Ground Water*. Volume 1, Technical Basis for Assessment. EPA/600/R-07/139, 2007.

[18] USEPA. *Monitored Natural Attenuation of Inorganic Contaminants in Ground Water*. Volume 2. Assessment for Non-Radionuclides Including Arsenic, Cadmium, Chromium, Copper, Lead, Nickel, Nitrate, Perchlorate, and Selenium. EPA/600/R-07/140, 2007.

[19] Yu, H., In Situ Groundwater Arsenic Removal Using Iron Oxide-Coated Sand. M.S. Thesis, Texas A&M University, College Station, TX, 2010.