Evaluation of Remedial Actions at Coal Combustion Residuals (CCR) Sites through Coupled Hydrogeological-Reactive Transport Modeling

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Abstract

Power companies across the US and abroad are currently being challenged to implement corrective measures to mitigate the effects of seepage from Coal Combustion Residuals (CCR) management facilities. The tools to fully evaluate the potential success of various remediation strategies typically rely on two approaches: groundwater modeling with solute transport and 1-D geochemical modeling. Historically, these have been conducted independently. While a solute transport approach may be reasonable for a (pseudo-)conservative constituent like boron, CCR seepage and other waste streams typically contain a diverse set of constituents that can be highly reactive in the environment, requiring use of more complex geochemical models. In this paper, we demonstrate multiple approaches currently being used at CCR sites to integrate results of groundwater modeling into geochemical software such as the USGS codes PHREEQC or PHAST. Examples include: 1-D reactive transport; MODFLOW incorporation into PHREEQC natural attenuation models; capacity evaluations; reversible attenuation due to variable Eh and pH; and full 3-D reactive transport closure models. The results of these models are then used to demonstrate the potential for long-term success of corrective measures and identify any potential side effects of remedies on groundwater quality. As demonstrated in this paper, geochemical modeling and groundwater modeling conducted in isolation can generate results with considerable certainty. However, the use of more robust site-specific models presented here represents an integrated approach that combines both groundwater and geochemical modeling into a single solution, providing greater certainty during remedy selection, including for monitored natural attenuation.

Introduction

Power companies across the US and abroad are currently being required to implement corrective measures to mitigate the effects of seepage from Coal Combustion Residuals (CCR) management facilities. Groundwater remedy selection at these facilities and other industrial sites presents a challenge to stakeholders in determining defensible and

scientifically appropriate corrective measures. To aid in remedy selection, many operators have turned to the use of groundwater and geochemical models as tools to help predict the long-term outcome and success of potential remedies. Historically, these modeling efforts have been conducted independently.

While a flow and transport (solute only) approach may be reasonable for a (pseudo-) conservative constituent of interest (COI) like boron, CCR seepage and other waste streams typically contain a diverse set of COIs that can be highly reactive in the environment, requiring use of more complex geochemical models. Multiple approaches are currently being used at CCR sites to incorporate results of groundwater modeling into geochemical software such as the USGS codes PHREEQC (Parkhurst and Appelo, 2013) or PHAST (Parkhurst et al., 2010).

Approaches to model incorporation can include: 1-dimensional reactive transport using flow parameters determined externally; MODFLOW incorporation into 1- dimensional PHREEQC; static evaluations of adsorption capacity and reversibility in response to changes to redox and pH; and full incorporation of MODFLOW and PHREEQC-RM in a 3-dimensional reactive transport model. In this paper, our focus is on the practical approaches of incorporating geochemical and groundwater modeling for remedy selection, with additional emphasis on the geochemical modeling. The details of groundwater flow and transport modeling are not discussed here.

Site Characterization

The quality of groundwater, porewater, and adjacent relevant surface water bodies (e.g., streams, lakes, ponds, etc.) at a CCR site should be adequately characterized and evaluated prior to any attempts of reactive transport modeling or integrating geochemical and groundwater models. Geochemical characterization of groundwater and porewater/ CCR leachate samples should include the determination of:

- Field parameters
- Parameters included in the CCR Rule Appendices
- Sulfide
- Redox sensitive metals (e.g., iron, manganese)
- Major groundwater cations and anions
- Dissolved gases and isotopic analysis *(as needed on a site-specific basis)*

Filtered and total samples should be included where leachates have high ionic strengths. These data can then be evaluated using static geochemical models or geochemical tools that can be extremely useful in this process. Some of these include:

- **Visual Plots:** Plots such as Piper, Ternary, Durov, Stiff, or Schoeller diagrams are useful tools to visualize data and identify water types, potential sources, or the presence of water mixtures.

- **Speciation evaluations:** The speciation of a COI (e.g., valence state, complexation) is important to understanding how it will behave geochemically.

- **Saturation index evaluation:** Mineral saturation should be evaluated to fully understand the site geochemistry and what minerals are likely to precipitate from groundwater or dissolve from the aquifer solids, thereby potentially controlling COI concentrations.

- **Ion relative abundance and balance:** An understanding of the relative abundance of COIs and conservative tracers can be useful for identifying and understanding potential sources. The charge balance of solutions represents an important quality assurance/quality control check.

- **Multivariate Analysis:** Multivariate analysis (e.g., Principal Component Analysis, Factor Analysis, Cluster Analysis) may be useful in identifying water types, potential source materials, aquifer conditions, etc.

Evaluation of Aquifer Solids

Multiple geochemical analytical methods are typically required to assess the mineralogical and chemical composition of the aquifer solids. The geochemical test methods may include:

- **Whole rock chemistry:** The total elemental composition of the aquifer materials needs to be determined using a standard digestion such as the aqua regia extraction. In combination with the sequential extractions of metals from soils, this determination helps identify if the aquifer material can act as a source or a sink of COIs.

- **Sequential Extraction Procedure (SEP):** This test consists of a multiple-step extraction from solids per Tessier et al. (1979) to identify the provenance of metals (i.e., the operationally defined fraction that contains the metal) and determine their potential environmental mobility. For instance, metals bound in the carbonate fraction, or that are exchangeable, are much more likely to become mobile due to changes in groundwater conditions than metals bound within a sulfide or silicate fraction. This test is of importance for assisting with the fate and transport evaluation of COIs.

- **Mineralogical Evaluation:** The purpose of the mineralogical analysis is to identify and quantify the mineral phases in each sample. The principal and most common method of mineralogical evaluation is Rietveld x-ray diffraction (XRD). This information can be useful in identifying potential current or historical sources of acidity and buffering capacity, for geochemical modeling of COI attenuation through sorption, and for geochemical modeling of mineral formation/dissolution (Hem, 1985).

- **Cation Exchange Capacity:** The CEC represents the total number of negative charge sites in a given amount of solid at which reversible cation adsorption and desorption can occur (Hem, 1985). Cation exchange also commonly refers to the replacement of one cation by another in a selective series or preferred adsorption. In this case, the sorption selectivity increases with the ionic radius of the ion, for

instance in the following series: $K^+ > Na^+ > Li^+ > Ba^{2+} > Sr^{2+} > Ca^{2+} > Mg^{2+}$ (Smith, 1999).

- **Total Organic Carbon:** Organic carbon represents a substrate for sorption of certain COIs and can also cause reducing conditions in groundwater that can promote, for instance, sulfide mineral stability, thereby potentially sequestering COIs as well.

Approaches to Geochemical Modeling

In any aqueous subsurface environment there are a large number of interrelated geochemical processes (e.g., solution speciation, gas exchange, mineral dissolution/precipitation, oxidation/reduction, and adsorption/desorption) that influence dissolved COI concentration and mobility. In addition, all of these processes are affected by key variables (temperature, pH, and redox) along the flow path away from the COI source. Incorporating all these processes and potential environmental conditions in a series of calculations by hand, while possible, can quickly become overwhelming. Thus, use of a quantitative model using a computer code that can simulate each process and include all the interrelations between the processes under a wide range of conditions is frequently required. The PHREEQC geochemical modeling code developed by the U.S. Geological Survey is one example of a general purpose geochemical modeling code that is freely available and used in the static and 1-dimensional reactive transport examples presented in this paper (Parkhurst and Appelo, 2013).

The U.S. Geological Survey also developed PHAST, a computer code that simulates multicomponent reactive solute transport in a three-dimensional saturated groundwater flow system (Parkhurst et al., 2010). PHAST is a versatile groundwater flow and solute-transport simulator with capabilities to model a wide range of equilibrium and kinetic geochemical reactions. The flow and transport calculations are based on a modified version of HST3D, a flow solver, that is restricted to constant fluid density and constant temperature. The geochemical reactions are simulated with the geochemical code PHREEQC-RM, a reactive transport module of PHREEQC 3.7, which is embedded in PHAST. The PHAST code is used for the 3-dimensional reactive transport examples in this paper.

Attenuation Modeling

The K_d approach to modeling adsorption typically assumes a constant partitioning between the solid and liquid fraction of a COI over a wide range of conditions. Thus, the ratio between the solid phase and liquid phase does not change in response to variation in pH, redox, soil metal hydroxide concentration, total organic carbon content, or clay content. As such, for almost all CCR COIs, such as arsenic, cadmium, cobalt, selenium, etc., use of the K_d approach is not appropriate because it is well known their partitioning behavior is affected by these types of changes in the aquifer and groundwater environment. Any model that uses a Kd value to calculate a retardation

coefficient is not a true reactive transport model because the model is not letting the constituent partition differently in response to changing geochemical conditions.

Surface complexation modeling (SCM) is a widely used mechanistic approach to modeling adsorption that allows for competitive sorption, reversible sorption, and the evaluation of varying pH, redox, and ionic strength on reactive surfaces such as Hydrous Ferric Oxides (Hfo), Hydrous Aluminum Oxides (Hao), or Hydrous Manganese Oxides (Hmo). Site-specific aquifer material characteristics for adsorption modeling (i.e., surface area, site density, types of sites) can easily be determined by laboratory testing, yielding highly accurate modeling results that will account for base surface loadings. Adsorption constants for the various metal (hydr)oxide surfaces are based on published thermodynamic values (Dzombak and Morel,1990; Karamalidis and Dzombak, 2010; Tonkin et al., 2004).

Practical Example: Monitored Natural Attenuation

A CCR site that had an existing groundwater flow model was subjected to an evaluation of the likely effectiveness of monitored natural attenuation (MNA), guided by the U.S. Environmental Protection Agency (USEPA 2007a; 2007b; 2015) approach, following best practices described by the Interstate Technology & Regulatory Council (ITRC, 2010). The site groundwater and aquifer solids were comprehensively evaluated using the methods previously described in this paper. The site-specific geochemistry data were incorporated with the groundwater flow model in a 3-dimensional reactive transport PHAST model to evaluate the effectiveness of long-term MNA, specifically looking at aquifer capacity to ensure no off-site exceedances occurred.

The model also was designed to evaluate the potential for long-term remobilization of constituents per the MNA tiers (USEPA 2007a; 2007b; 2015). Remobilization can result from the new equilibrium that will occur after the prescribed closure plan (in this case cap and closure) has been implemented, potentially resulting in geochemical changes in the aquifer. MNA tiers I through III can easily be simulated in this type of model, which can then be used to inform tier IV of MNA and set up triggers that would lead to enhanced MNA should MNA not perform as expected. A conceptual site model is shown in Figure 1.
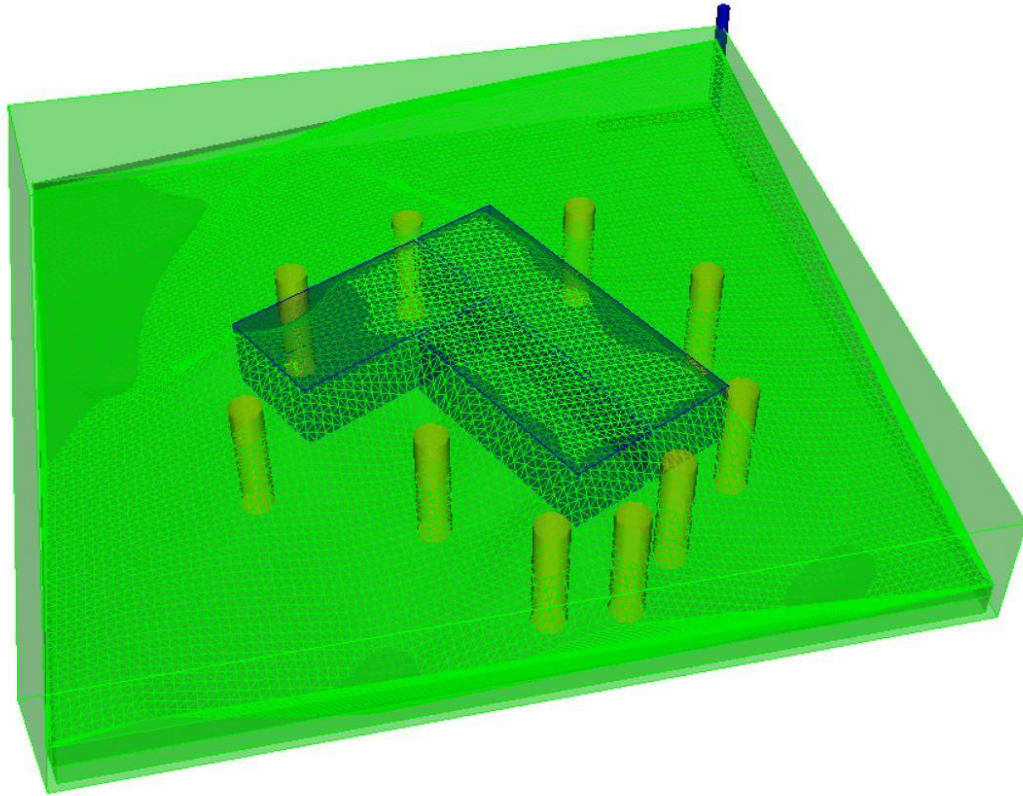
Figure 1. Conceptual site model of zone modeled for MNA

The reactive transport model was designed based on the results from hydrogeological modeling of the site. Model domain geometry, fluxes, boundary conditions, constant head values, and layer properties were directly imported into the reactive transport model using raster, ASCII, ARCMap (ESRI, 2015), and shapefiles and were not needed to be modified in any way for groundwater model convergence. The phases of the MNA reactive transport modeling followed the logical process:

- Current condition plume development (calibration)
- Aquifer capacity testing/loading (porewater titrating)
- Constituent concentration forecasting (capped and closed condition)
- Long-term stability evaluations (remobilization modeling)

The modeling produces concentrations in cells that can be used to determine a time to "achieve compliance" at the selected well locations. Concentrations for any groundwater COI can be extracted from any cell from the model, leading to great flexibility in output evaluations. The modeling results can also be evaluated by depth, depending on the model layering. Results of MNA modeling following capping and closure of the ash pond at a single depth (or model layer) are shown in Figures 2 through 5.
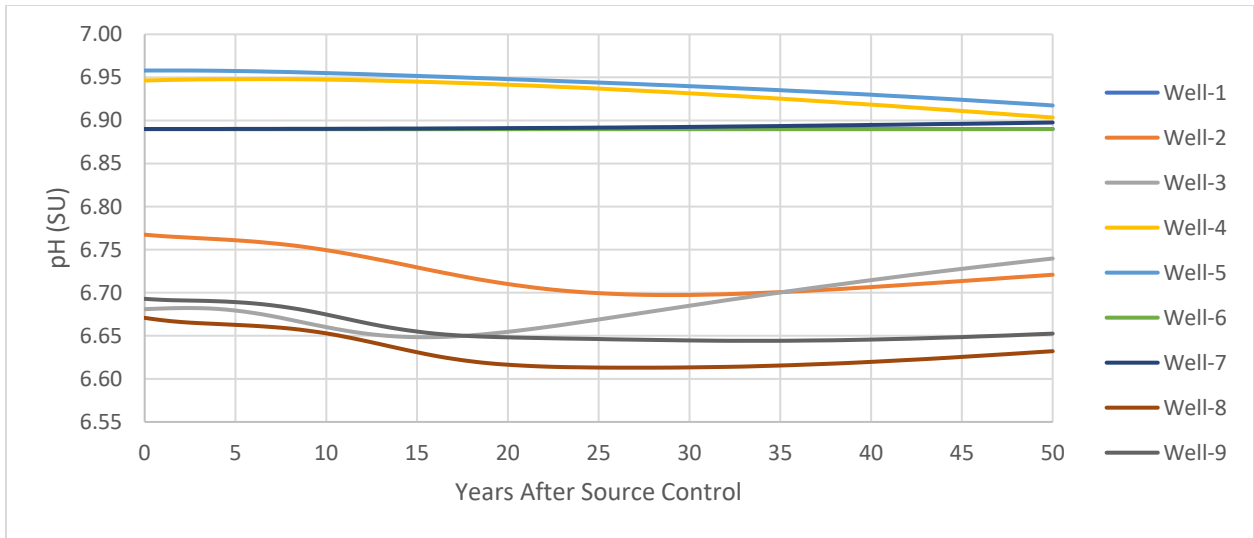
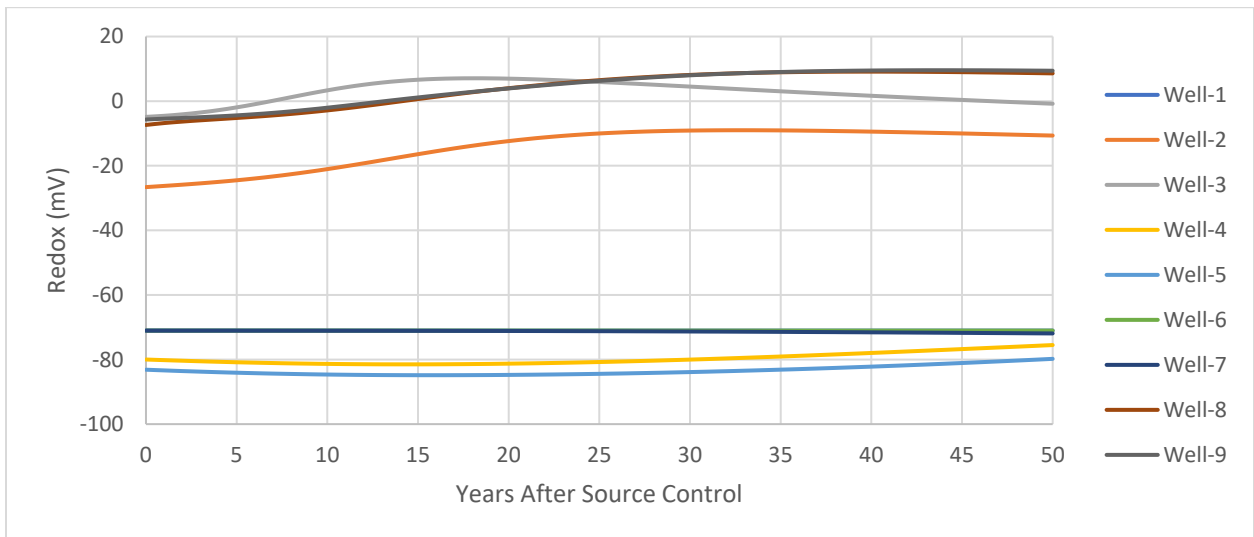**Figure 2.** Predicted pH at select compliance wells 50 years after capping and closure

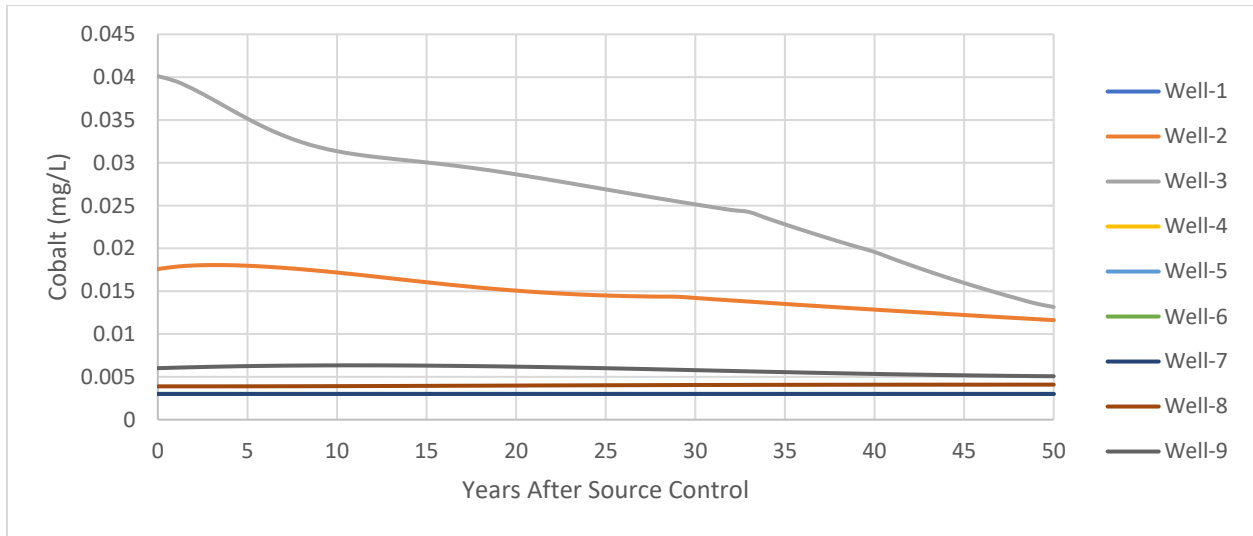**Figure 3**. Predicted redox values at select compliance wells 50 years after capping and closure

Figure 4. Predicted cobalt concentrations at select compliance wells 50 years after capping and closure
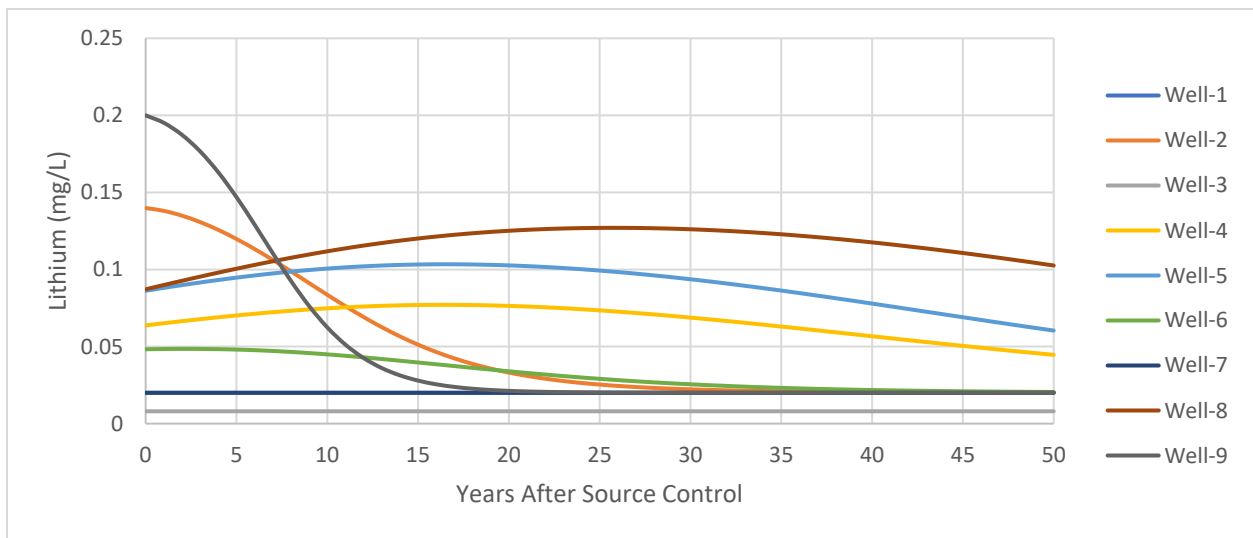

Figure 5. Predicted lithium concentrations at select compliance wells 50 years after capping and closure

The predicted pH and redox at compliance wells behaved as expected, gradually converging towards background values. Cobalt concentrations were predicted to decrease rapidly at an impacted well nearest the ash pond (Well-3) as the flux from the ash pond declined due to capping, but much slower at a side gradient well where groundwater velocities are slower and "pooling" is predicted due to the deflection of clean discharge water (Well-2). Lithium concentrations were predicted to decrease as well, as would be expected of a semi-conservative CCR tracer, however, at certain wells, some remobilization was also predicted to occur (Wells 4, 5, and 8). Initially this

was thought to be due to model instability, but upon further investigation it was realized that the remobilization of lithium occurred due to cation exchange reactions built into the simulation. This was confirmed through re-running the model with adsorption only, without cation exchange reactions, in which case lithium did not remobilize.

Conclusions

Based on the results of the discussion and example provided in this paper, the following overall conclusions or learnings are important to consider when integrating groundwater flow and geochemical modeling:

- Geochemical modeling and groundwater modeling should not be looked at as independent of one another. An integrated approach is generally required for a defensible and robust remedy selection.
- Comprehensive characterization of groundwater and aquifer solids is required.
- The use of integrated modeling supports evaluation of mitigation plans, allows for direct comparison between alternatives, identifies both positive and negative unforeseen outcomes, and helps manage risk!
- Constituents may be predicted to act in unexpected ways, but that does not mean the model is wrong. Consider the geochemical principles that may cause a COI concentration to increase over time.
- Integrated (reactive) transport modeling has become a regulatory expectation and its use will only increase.

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