Developing Enhanced Monitored Natural Attenuation Strategies Using Reactive Transport Models

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Keywords: Monitored Natural Attenuation; Geochemistry; Modeling; CCR

Abstract

Monitored Natural Attenuation (MNA) presents an economically-favorable strategy for long-term management of potential groundwater impacts from coal combustion residuals (CCR) impoundments. However, when inadequate native sorption potential is identified during an assessment of corrective measures, MNA is typically abandoned in favor of other approaches.

Rather than abandoning MNA entirely, an engineered approach to MNA (referred to as enhanced MNA) may present a viable, yet still mostly passive, management strategy. The mobility of constituents of interest from CCR impoundments or underlying groundwater depends on site-specific geochemical conditions, which sometimes can be leveraged to increase attenuation. Strategies such as lengthening flow paths, creating plume diversions, or constructing barrier walls present viable engineered approaches to meet MNA performance requirements.

Enhanced MNA strategies should be considered early during MNA feasibility studies. Using advanced 3-dimensional reactive transport models, potential engineering enhancements to MNA can be tested and tailored to site-specific conditions. For example, the construction of a low-permeability bentonite barrier wall, diverting leachate towards more oxic conditions, decreasing flow velocities, and increasing the pH of leachates through contact with the bentonite, can be tested with a geochemical model to evaluate the potential for MNA to successfully manage groundwater.

Examples are presented of an assessment of a series of proposed engineering approaches to enhanced MNA using 3-dimensional reactive transport modeling. Multiple scenarios are shown and the factors that influence their potential for long-term success are discussed. The results of such an evaluation allow stakeholders to be better informed during the selection of appropriate corrective measures.

Introduction

Coal combustion residuals (CCR) present a significant management challenge in the US and globally due to their vast production since the industrial revolution and the
potential for leaching into groundwater. The metals, metalloids, and other constituents of interest (COIs) present in CCR leachate vary depending on the coal source, the combustion process, and storage facility conditions. The mobility of COIs in a CCR impoundment or underlying groundwater aquifer will depend on site-specific geologic and geochemical conditions. Once COIs are mobile, sorption represents arguably the most determinate factor when considering the potential for success of a Monitored Natural Attenuation (MNA) strategy for groundwater protection. However, when inadequate sorption potential is identified in the receiving environment during an initial assessment of corrective actions, an engineered approach to MNA (referred to as “enhanced MNA”) should be considered (Figure 1).

**Figure 1.** Enhanced MNA conceptual process

**Evaluation of Enhanced MNA**

Enhanced MNA may present a viable, yet still mostly passive, management strategy. Geochemical reactive transport modeling under proposed MNA strategies presents an opportunity to evaluate different MNA concepts and their effectiveness as well as any potential unforeseen consequences. Reactive transport models are models that fully account for relevant geochemical conditions (e.g., pH, redox potential, mineral precipitation and dissolution, adsorption and desorption) that are fully integrated into a groundwater flow model. These models excel over simple solute transport engines (e.g., MT3DMS) as they consider real-world geochemical processes at each time step of the flow solution (Merkel et al. 2008).

Some common engineering enhancements to MNA and the benefits of using reactive transport models include:
- **Constructed subsurface barrier walls:** Constructed barriers can help divert transport of COIs to a more preferable location or can be used to lengthen the travel distance to regulatory boundaries, thereby increasing the potential for attenuation. Geochemical modeling can simulate the benefits of variable attenuation along different flow paths, as well as diversion to zones that may have a more beneficial pH or redox regime, both of which can positively impact COI sorption.

- **Grouting or in situ stabilization:** Stabilizing CCR materials or grouting materials in place can minimize migration of COIs. Geochemical modeling and bench scale studies can help evaluate long-term leaching potential post stabilization and evaluate the effect of increases in groundwater pH due to grouting on the COIs.

- **Hydraulic containment (injection/withdrawal):** Pumping wells (and sometimes injection wells) can be used to remove COI-bearing groundwater, decrease groundwater recharge to an ash zone or, in the case of injection, cause dilution or diversion of plumes to a preferred location. Geochemical models can simulate the effects of injecting dissolved oxygen into aquifers, and plume migration as withdrawal wells change groundwater flow.

- **Permeable Reactive Barriers (PRBs):** The use of PRBs provides a mechanism to intercept or transform COIs by removing them from the system (e.g., due to precipitation or adsorption) or forming less toxic compounds. Geochemical modeling can demonstrate the effectiveness of these PRBs and be used to evaluate their overall benefits as well as any potential unforeseen effects or unexpected challenges.

- **Geochemical manipulations:** Emerging and novel approaches to attenuation that enhance the effectiveness of MNA can be tested using geochemical modeling prior to bench-scale or in situ testing. Injection of materials that would change pH or promote reducing conditions, for example, may increase attenuation, but may also have consequences regarding the behavior and mobility of other COIs. Modeling can also help evaluate the quantity of reactive material or size and number of wells/drains for use in cost estimating. Secondary effects can be thoroughly evaluated using geochemical modeling.

Through a case study, this paper describes the development of a reactive transport model at a simulated site with a CCR impoundment and the COIs cobalt and molybdenum present in ash porewater as well as in groundwater downgradient from the impoundment at concentrations exceeding background levels. Using that model, we then evaluate the effectiveness of various enhanced MNA strategies to attenuate cobalt and molybdenum to meet groundwater protection standards.

**Case Study**

In this case study, cobalt and molybdenum are leaching from a CCR impoundment into native groundwater. Based on preliminary modeling, adequate attenuation does not
currently exist at the site to achieve regulatory downgradient groundwater levels of 0.006 mg/L and 0.1 mg/L for cobalt and molybdenum, respectively. Three scenarios were modeled, consisting of:

- Current condition plume development (calibration)
- Constituent concentration forecasting (capped and closed condition)
- Barrier wall emplacement with hydraulic control adjustment (pumping wells) to meet regulatory target levels.

The reactive transport model presented was designed based on the results from hydrogeological modeling of a simulated site. Model domain geometry, fluxes, boundary conditions, constant head values, and layer properties were directly imported into the reactive transport model using Raster, ASCII and ARCMap (ESRI 2011) Shapefiles (Figures 2 and 3). The reactive transport modeling was undertaken using the US Geological Survey software PHAST.

PHAST is a computer program developed by the US Geological Survey 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 were simulated with the geochemical model PHREEQC, which is embedded in PHAST (Parkhurst and Appelo, 2013).

Surface complexation in PHAST was used to model attenuation of cobalt and molybdenum. This mechanistic model for adsorption 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) and Hydrous Aluminum Oxides (Hao). Understanding the current sorptive load of the aquifer solids on the site is important. Borehole chemical and mineralogical data were used to account for background concentrations of COIs on the native sediment/soil and determine adsorption properties (i.e., surface area, site density, types of sites) using Hfo and Hao adsorption isotherms based on published thermodynamic values (Dzombak and Morel 1990; Karamalidis and Dzombak 2010).

The modeling was conducted using the thermodynamic database Minteq V.4, which is a widely-accepted database of thermodynamic data accumulated from numerous sources by the U.S. Environmental Protection Agency (EPA). Since this database was released, however, newer thermodynamic data have been published in the scientific literature the Minteq V.4 database was updated with information from recent literature for cobalt and molybdenum.

In reactive transport modeling, a balance exists between efficiency of a model and the detail required to obtain a result that is sufficiently accurate for decision making. As part of this balance, numerical dispersion must be managed, and an understanding the
Peclet and Courant numbers is essential. These values are calculated based on the cell size, time step, dispersivity, and average velocity of groundwater in the model. Formula 1.1 is used to control numerical dispersion based on documentation included with PHAST. For our modeling effort, we utilized an upstream-in-space and backwards-in-time differencing solution using the following derivation of both the Peclet and Courant numbers (Parkhurst et al. 2010):

\[
\Delta X/2 + (V_x \cdot \Delta t)/2 \ll \alpha
\]

Where:

\[
\Delta X = \text{Cell size (ft)} \quad V_x = \text{Average Velocity (ft/yr.)}
\]

\[
\Delta t = \text{Timestep (yr)} \quad \alpha = \text{Longitudinal dispersivity}
\]

**Figure 2a (top) and 2b (bottom).** Model design from the -y +45° angle looking south to north (a), and the +x angle looking west to east (b), showing the vertical barrier wall emplacement (orange), domain geometry with tops of layers (green), ash impoundment (orange/brown), and pumping wells (blue).
Results

The use of a reactive transport model in this case study to evaluate enhanced MNA strategies resulted in the following observations:

- **Achievement of target limits**: Both cobalt and molybdenum downgradient of the impoundment achieved their target levels within five years of the vertical barrier wall and hydraulic groundwater control additions. Well pumping rates were then adjusted to the lowest rate possible to achieve target levels.

- **Depth of the vertical barrier wall**: Based on preliminary model results, it became evident that groundwater mounding behind the vertical barrier wall may be a challenge in this approach. Hydraulic control can help aid and control this mounding during times of high flow and during initial drawdown phases of the impoundment head. However, one unexpected outcome was that by directing the remaining groundwater flows around and beneath the barrier wall to a planned location, groundwater that passed through the CCR impoundment could be diverted to a transect that offered a longer flow path and higher potential for natural attenuation of cobalt and molybdenum. Using the barrier wall as a partial diversion wall was not initially planned and would not have been realized without reactive transport modeling.

- **Barrier wall geometry**: Through trial and error, once the barrier was included in the model, the wall design was scaled back, and it was determined a fully enclosing wall would likely not be needed even with a conservative approach. With a fully enclosed barrier, groundwater would still mound in the ash impoundment due to groundwater and bedrock recharge, providing little to no additional benefit over the proposed barrier design (Figure 2a).

- **Effluent cobalt and molybdenum loads**: Total metal loads from the hydraulic control wells were estimated using the reactive transport model. It was determined that the metal loads in the discharge from those wells would likely meet regulatory limits and not need additional treatment. This was due to the hydraulic control largely preventing contact between native groundwater and the ash impoundment, rather than directly removing impoundment groundwater. Groundwater with cobalt and molybdenum escaping below the barrier wall also had lower velocities, and greater contact time with aquifer soils, allowing for greater attenuation.

- **Fill material**: During installation of a barrier wall or other perimeter controls, soil/sediment immediately around the impoundment can often be partially removed or influenced by construction. Based on soil borings, this perimeter material in the case study had the highest levels of attenuated cobalt and molybdenum. By studying the impact of removing this material, the modelling showed established of a new equilibrium with cleaner backfill material used to support the barrier wall, and lower resulting post construction cobalt and molybdenum concentrations in groundwater. The possibility also exists to amend
the backfill to further enhance its attenuation potential using a material high in metal hydroxides, but this was beyond the scope of this case study.

Some difficulties encountered during reactive transport model development were as follows:

- **Model computational times:** An initial grid size of 1 meter based on the original groundwater model was determined to be too small given model complexity and the geochemical processes that needed to be calculated for each timestep. Modeling grid spacing was enlarged to meet desired run times and also manage numerical dispersion. It became apparent that groundwater passing through more than one cell in a timestep, or groundwater reacting in a cell multiple times before reaching the next cell, had to be managed given variable groundwater velocities. Even when running PHAST in parallel with multiple processors and cores, processing time (given the complexity of computations in PHAST) was a concern.

- **Vertical barrier wall thickness:** The thickness of the vertical barrier wall had to be estimated and adjusted based on grid cell size. A barrier wall too narrow, would be ignored by the model as it did not represent enough space in a grid cell. Therefore, a sub grid established at the barrier wall location, or a thicker vertical barrier wall, would account for enough grid cell space to be recognized in the reactive transport model.

- **PHAST-specific challenges:** Numerous errors in PHAST were encountered during the design of the reactive transport model. For instance, in loading domain geometry, shapefile Z fields had to be removed, and shapefiles had to be pre-processed to not have overlapping polygons. In more complex model designs, an empty domain was required to be activated, and then set to inactive to avoid computing errors and inevitable model crashes. Faster computational times and greater stability in model runs occurred when PHAST was run from the MS-DOS command prompt from text input files, rather than using PHAST for Windows (Parkhurst et al. 2010).

**Conclusion**

The utilization of reactive transport modeling in conjunction with groundwater flow modeling for the evaluation and development of site specific enhanced MNA solutions can be very beneficial for strategy development and decision making. In this case study, basic MNA could not achieve the target cobalt and molybdenum concentrations that were required. However, by adding engineered enhancements in conjunction with MNA, target levels were simulated to occur within a reasonable time frame (5 years post controls installation). Based on our case study, we identified several benefits of using reactive transport modeling during the initial stages of an MNA assessment. In doing so, we were able to identify potential enhancements and engineered controls design optimizations that could positively influence MNA as well as identify any unforeseen consequences (e.g., mobilization of a native non-CCR constituent). This approach
presents a “try before you buy it” process, that, in combination with bench-scale testing and/or further site investigations, can focus corrective action designs early in the assessment process, leading to better, more economical outcomes.

References:


