WHITE PAPER

CCR Removal and Its Effects on Soil and Groundwater Geochemistry

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Introduction

Many of the estimated 120 owner/operators complying with Federal or State coal combustion residual (CCR) Regulations in the United States are faced with implementing corrective measures. While closure by removal and closure in place can be used to achieve groundwater corrective action goals associated with CCR-impacted groundwater (primarily metals), CCR removal is a common selected remedy. Closure by removal is generally thought to be the most expeditious way to improve groundwater quality and achieve compliance with groundwater protection standards (GWPS). However, it is not that simple.

Achieving a GWPS can be complicated because metals are often present naturally in the subsurface, in both soil and groundwater. Understanding the fate and transport of CCR-affected groundwater is further complicated by the significant changes that can result from impoundment decommissioning. Capping, cessation of hydraulic loading, change in process water, dewatering, CCR removal and a variety of other process changes can alter the status quo of metals chemistry in groundwater and can result in the mobilization of naturally occurring or previously sequestered metals and increase concentrations. For these reasons, a robust conceptual site model (CSM) along with a thoughtful understanding of the geochemical environment is key to understanding the cause of increasing concentrations and assessing the success of the remedy.

Closure Considerations

There are a significant number of closure considerations that can complicate fate and transport of metals in the environment. Significant changes in conditions may occur during and after unlined impoundment closure that may help explain how a corrective action like CCR removal may have unforseen effects on groundwater quality.

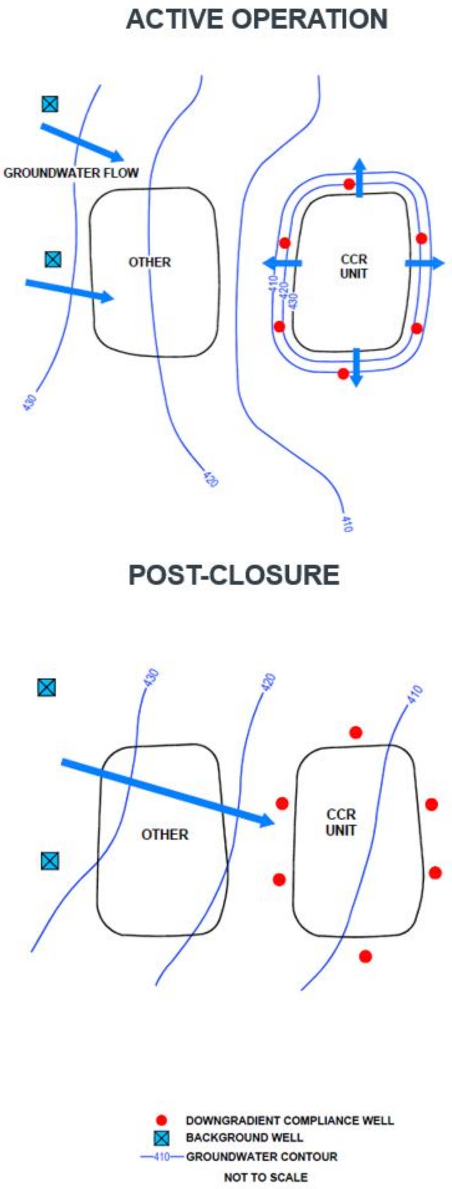

Figure 1: Significant hydrogeological changes occur before and after closure that can influence groundwater quality.

These include, but are not limited to:

- **Active loading conditions** established under decades of operation where pH and redox conditions reflect process water and ongoing infiltration and leaching are occurring.

- **Closure and/or process changes** that cause a change in the active steady state condition through cessation of hydraulic loading, dewatering, CCR removal, disturbance of soil and CCR material, or a change in process water, or capping to prevent infiltration.
- **Geochemical and hydrogeological changes** occur as a result of the closure activities where pH, redox, temperature, groundwater flow dynamics, soil properties/backfill materials, and infiltration rates change.
- **Effects on groundwater** can be seen as a result through changing groundwater concentrations that may result from mobilization of previously sequestered metals, release of pore water, change in upgradient groundwater source(s), and influence/visibility of alternate sources not previously seen under the active condition.

Sorting Through the Complexities

Several key considerations to navigating the vast amount of site data and understanding the data include a stepwise additive review of site conditions and a thoughtful CSM.

A well-developed CSM is key to sorting through changes in groundwater post-closure, however an accurate CSM must be built using an appropriate methodology. This methodology, described below, evolves from the simple to complex in such a way that each steps is informed by the previous step.

What's the Story?

The following stepwise strategy to developing a geochemical conceptual data model can be used to assess the effects that the geochemical environment has on groundwater concentrations and let the data tell the story.

Have the data changed?

Statistically compare data before and after closure. Start with the simple question, is there a statistically-significant change in metal(s) concentration, pH, oxidation reduction potential (ORP), total dissolved solids (TDS), etc.? A T-test at a 95% confidence interval is a useful place to start.

Look at Geochemistry

Review field parameters and major ion concentrations. Have they changed? If so, how? Define each relationship as direct, inverse, or other. Be sure to take lag and nonequilibrium into account. Compare total and leachable soil mass of metals with groundwater concentrations, using multi-stage sequential extraction of separate fractions including:

1. Exchangeable fraction;
2. Bound to carbonates;
3. Bound to iron and manganese oxides;
4. Bound to organic matter; and
5. Residual fraction,

as described in Tessier et al., 1979, is often more useful than Toxicity Characteristic Leaching Procedure (TCLP) or Synthetic Precipitation Leaching Procedure (SPLP) analyses.

Review the Mass

Determine the mass flux of conservative ions, such as boron, and pH and redox sensitive ions, such as arsenic or selenium, using seepage rates and retardation factors. How do the total mass flux of conservative ions compare to the mass of the dependent ions before and after the geochemical change? Evaluate these changes stepwise based on the previous two subsections.

One example might be:

1. Field-measured pH changed at a statistically-significant level;
2. The sequential reaction determined that leachable mass of a pH-dependent metal are found in the soil;
3. The flux of a pH-dependent ion changed at a statistically-significant rate concomitantly with the field-measured pH change;
4. The flux of the conservative species did not change; and
5. The mass of the soil-bound metal within the groundwater bearing unit is large enough to account for the additional flux.

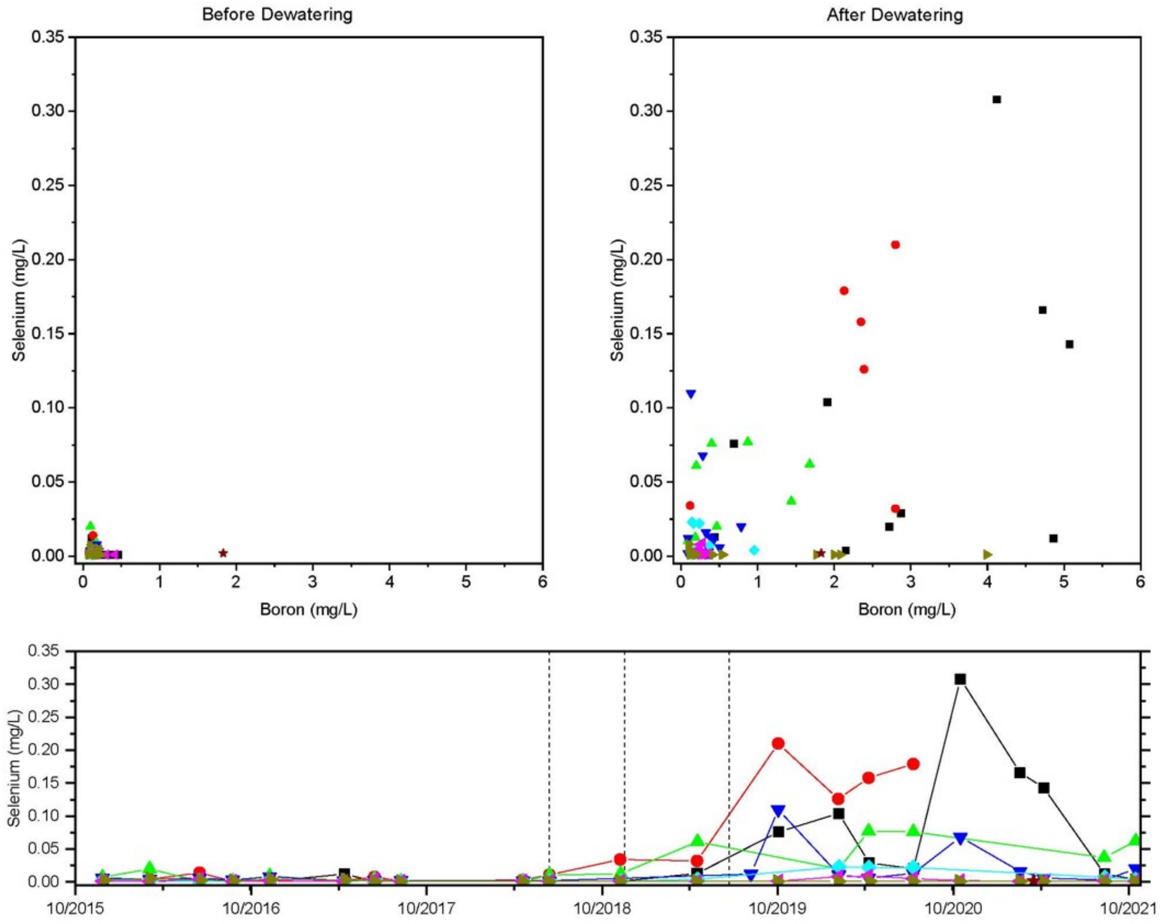

Figure 2: Review the mass by comparing conservative parameters with nonconservative ones, before and after dewatering, to assess changes in concentration relative to changes in active vs nonactive conditions.

It's important to connect the hydrogeology and the geochemistry to the extent possible to make sure all the pieces make sense when you put them all together within the CSM. Understanding site operations and history, site geology/soil types, surface run-off and infiltration, groundwater flow rates and direction, and water table elevation are crucial to assessing hydraulic conections, understanding the geochemical environment, and identifying alternate sources.

Model the Data

Following initial development of the CSM using steps similar to those above, it is necessary to test assumptions by putting all of the data into a geochemical framework. Plot data on Eh-pH diagrams, look at ion ratios, compare site-specific leaching curves to published CCR curves.

Additionally, a data management strategy that allows ready-access to all site data and visualization tools such as time-series plots will expedite the review of data and ensure data do not get overlooked.

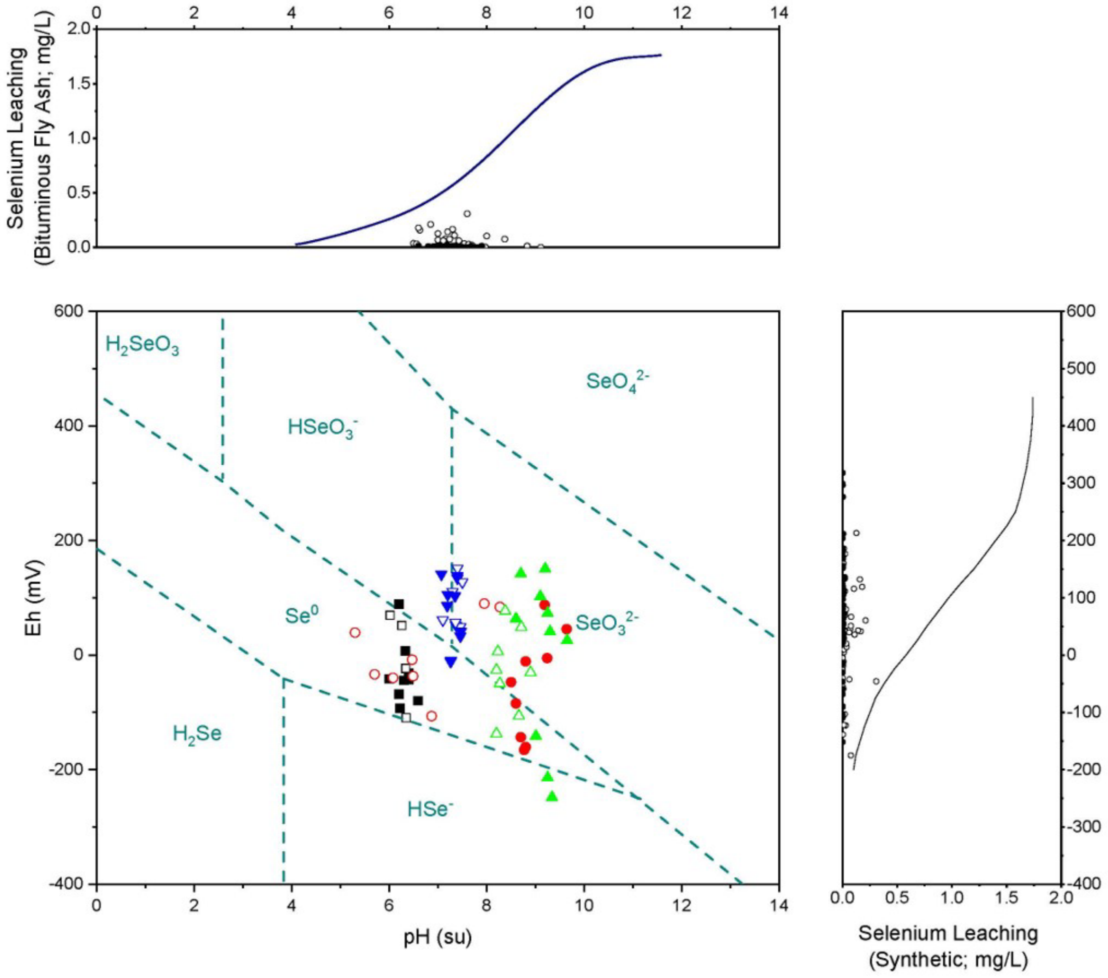

Figure 3: Pull all of the data into a geochemical framework and determine likely causes for the statistically significant chagnes.

Document operational milestones in a timeline to make comparisons between operational or remedial activities and changes in groundwater data. Look closely at compliance data AND field parameters along with available major cation and anion data (e.g. chloride, bicarbonate, potassium, manganese, iron, etc.) to identify what is and what is not changing and when the changes take place.

Summary

An increase in concentration post-closure does not necessarily mean the remedy was unsuccessful, rather, it's an indication that a more in-depth analysis is warranted to sort through the geochemical complexities associated with metals in the environment and look closer at alternate sources that could be influencing groundwater quality.

Additive not disparate methods, in combination with a thoughtful CSM, can be used to let the data tell the story. Start simple by determining what changed and what didn't. Characterize the system before and after the change by looking at the geochemistry and the mass flux. Then model the system, making sure that the hydrogeology agrees with the geochemistry. If they are out of alignment, then additional analysis is likely needed to explain the changes that are occurring.

Authors

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