Selenium Attenuation via Reductive Precipitation in Diverse Saturated and Unsaturated Environments

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INTRODUCTION

The Coal Combustion Residual (CCR) rule¹,² sets out new requirements for the monitoring and mitigation of groundwater impacts resulting from CCR impoundments. Under the CCR Rule, groundwater monitoring is to be conducted in two stages, with the first stage involving “detection monitoring” of constituents listed under Part 257 Appendix III (boron, calcium, chloride, fluoride, pH, sulfate, and total dissolved solids), to be measured and compared with site-specific background concentrations. If concentrations of any of these constituents are observed statistically above background, “assessment monitoring” for constituents listed under Part 257 Appendix IV must be initiated; these constituents include antimony, arsenic, barium, beryllium, cadmium, chromium, cobalt, fluorine, lead, lithium, mercury, molybdenum, selenium, thallium, radium-226, and radium-228. If any of these constituents are detected, the need for corrective action will be based on constituent concentrations relative to an established groundwater protection standard, which would be the greater of the site-specific background concentration or the U.S, Environmental Protection Agency maximum contaminant level (MCL).

Selenium impacts to groundwater and surface water are frequently a concern at coal mine sites and coal ash impoundments. Leaching from coal combustion residuals may impose even greater challenges moving forward as a result of CCR rule compliance; selenium is of particular concern as an Appendix IV constituent given its relative mobility in the environment at neutral/alkaline pH. Addressing selenium impacts – via well-formulated regulatory strategies as well as cost-effective approaches to remediation where necessary – requires a thorough understanding of the hydrogeological/geochemical system affecting fate and transport. Geochemical processes exert an important control on the fate and transport of selenium in groundwater. In particular, selenium concentrations may be attenuated in sub-oxic conditions through reductive precipitation.
In this paper, we summarize a previously-presented geochemical conceptual model for selenium release and attenuation in overburden in the southeast Idaho Phosphate Patch and present case studies demonstrating selenium release and attenuation at four former phosphate mine sites. Studies at these sites have documented selenium attenuation in reducing conditions in stream sediments, wetland environments, unsaturated sub-oxic conditions, and saturated sub-oxic conditions, among others. This study focuses on better understanding the diversity of subsurface conditions in which selenium reductive precipitation has been observed. This process represents an important natural attenuation mechanism for selenium, with implications for site planning/permitting and design of reclamation approaches. These examples also help to inform potential enhanced monitored attenuation-type strategies.

REGIONAL OVERVIEW AND SITE DESCRIPTIONS

Phosphate ore, present as phosphorite, is mined in the southeast Idaho Phosphate Patch from the Meade Peak Member of the Permian-age Phosphoria Formation. The Meade Peak Member comprises two phosphate-ore-rich zones (upper and lower ore units), sandwiched in three shale units referred to as footwall mud (lower waste shale), center waste shale, and hanging wall mud (upper waste shale). These shale units exhibit relatively high concentrations of selenium relative to underlying and overlying units.

The Phosphate Patch has been recognized as an important phosphate ore resource for approximately 100 years. The U.S. Geological Survey initiated geologic investigations of the region in 1912, with follow-up investigations conducted in 1948. Mining for phosphate in the region began as early as 1903 and continues to the present day to supply phosphate for fertilizer production and chemical manufacturing. At present, there are more than two dozen historical and currently operating mines within the region.

The current study focuses on field groundwater quality observations at four inactive phosphate mine sites including the Champ Mine, South and Central Rasmussen Ridge Area (SCARRA), North Maybe Mine, and Mountain Fuel Mine (Figure 1). Mining at these sites was conducted as early as 1950 and as late as 2004. During operations, Meade Peak Member phosphate ore was mined from open pits coinciding with portions of the phosphate-bearing Phosphoria Formation. To access the phosphate ore, alluvium/colluvium, bedrock overburden and non-economic shale (waste shale) was stripped and generally deposited in aboveground overburden piles. Reclamation at these sites have included backfilling or partially backfilling pits with overburden material, contouring overburden piles to promote drainage and prevent erosion, and seeding overburden piles with mixes of native grasses and alfalfa.
Figure 1. Southeast Idaho phosphate district mine sites.
Hay et al. previously presented a geochemical conceptual model describing the release and attenuation of selenium from overburden piles in the southeast Idaho Phosphate Patch. This geochemical conceptual model is summarized below and on Figure 2; case studies presented in this paper are an extension of this work and add to the understanding of selenium release and natural attenuation of selenium in the environment. The geochemical conceptual model is summarized as follows:

1) As precipitation infiltrates and percolates through overburden containing waste shale, selenium is released primarily via oxidation of sulfides and organic matter.

2) As oxidation proceeds, oxygen is consumed. Depending on the thickness, saturation state, and oxygen availability (i.e., extent of air exchange) in the overburden pile, leachate discharging from overburden can exhibit either oxic or sub-oxic character.

Figure 2. Geochemical conceptual model of the controls on selenium attenuation in saturated and unsaturated environments.
3) Leachate exiting overburden piles either as surficial runoff or as percolation through thin, shallow portions of dump material may remain oxic, thereby exhibiting limited or no selenium attenuation. In this scenario, alluvium and/or exposed bedrock located adjacent to overburden piles exhibit selenium impacts with no attenuation, with impacts well-represented by unsaturated laboratory column tests.

4) Leachate that percolates to depth in thicker portions of overburden exhibits more complete oxygen consumption. Under these conditions, release of constituents via oxidative dissolution of sulfides and organic matter will be limited. In addition, reducing conditions can develop that are sufficient for the reduction of selenate to selenite, and further to Se(0) or selenide, resulting in selenium attenuation. The following key points are suggested regarding the nature of the attenuation:

- Selenium reduction and precipitation is primarily microbially driven, with organic matter released from waste shale serving as an electron donor.
- It is assumed that the majority of the selenium attenuation occurs in the overburden. However, attenuation may also occur in the underlying aquifers if reducing conditions (i.e., low dissolved oxygen) are maintained and sufficient quantities of electron donors are present (e.g., organic matter, dissolved or adsorbed ferrous iron), or if selenium is partially reduced to selenite in the overburden, resulting in adsorption of selenite to mineral surfaces in bedrock.
- Selenium attenuation relative to sulfate can be observed as a decrease in the selenium to sulfate ratio of leachate emanating from overburden, provided that conditions are sufficiently reducing to result in substantial selenium reduction but minimal sulfate reduction. In this way, it is expected that saturated laboratory column results may be more representative of impacts than unsaturated laboratory column results.

5) Where overburden is present below the water table, additional selenium attenuation under saturated sub-oxic conditions occurs.

Field results from four former phosphate mine sites (described as case studies below) demonstrate the key points of this geochemical conceptual model and provide an update based on data collected since publication. Field results from Champ Mine and SCRRRA demonstrate that attenuation of selenium released from overburden can occur in saturated conditions, likely as a result of the consumption of oxygen due to sulfide and organic matter oxidation, followed by the microbial reduction of oxidized forms of selenium to more reduced forms, coupled to the oxidation of organic matter naturally present in marshy environments and waste shale backfill. The results presented for Mountain Fuel Mine provide evidence that selenium attenuation via reductive immobilization is also likely occurring in unsaturated zones with sufficiently low oxygen. Since publication, data collected from the North Maybe Mine also demonstrate selenium reductive precipitation in Meade Peak Member bedrock groundwater below and open pit likely as a result of the consumption of oxygen due to sulfide and organic matter oxidation, followed by the microbial reduction of oxidized forms of selenium to more reduced forms coupled to the oxidation of organic matter naturally present in Meade Peak Member bedrock.
CASE STUDIES

Four case studies are presented in which observations indicate selenium release and attenuation. While in each case attenuation was via reductive precipitation, the subsurface environment in each case study is different.

In the following case studies, selenium, sulfate, iron, and manganese concentrations in groundwater are compared across various monitoring wells installed to monitor groundwater in different formations at the sites. Importantly, in this study, sulfate is used as a relatively conservative indicator of mine-related impacts given the low concentrations of sulfate naturally present in groundwater compared to the high concentrations released from waste rock. Selenium and sulfate are correlated in waste rock leachate at these sites, therefore the selenium to sulfate (Se:SO$_4$) ratio is used as a metric for selenium attenuation, with relatively low Se:SO$_4$ ratios being indicative of attenuation. This method assumes that sulfate is relatively nonreactive; that is, selenium reduction may be occurring with minimal sulfate reduction, which is generally consistent with the site observations described below.

Additionally, the results of several laboratory column studies with waste shale$^{6,7,8}$ were used to put field results in context. Results from these studies indicated that because selenium is generally released from waste shale via sulfide oxidation, selenium and sulfate in waste shale leachate are correlated. As such, unsaturated laboratory column test leachate is representative of oxic mine impacts. Bounds on Se:SO$_4$ results from unsaturated laboratory column tests$^{6,7,8}$ are presented on Figures 3 through 6 (red lines). In leachate from saturated laboratory column tests, selenium concentrations and Se:SO$_4$ ratios are much lower than unsaturated tests; this is due to less sulfide oxidation within the column (saturated conditions) and selenium reductive precipitation. Average Se:SO$_4$ results from saturated laboratory column tests$^{6,7,8}$ are shown on Figure 3 through 6 (grey line).

**Champ Mine – Selenium Reduction in a Shallow Alluvium beneath Marshy Area**

Active mining occurred from 1982 to 1985 at the Champ Mine$^9$. During operations, Meade Peak Member phosphate ore was mined from two open pits coinciding with outcropped portions of the phosphate-bearing Phosphoria Formation. Following closure of the Champ Mine, reclamation efforts were initiated, including backfilling pits with overburden material, contouring overburden piles to promote drainage and prevent erosion, and seeding overburden piles with mixes of native grasses and alfalfa. As such, the current site condition includes two partially backfilled former mine pits, three reclaimed overburden piles, and a variety of surface water features$^9$.

Selenium concentrations in groundwater at Champ Mine range from non-detect to 0.7 mg/L, with the highest selenium impacts in shallow alluvial groundwater adjacent to overburden piles$^{10}$. Alluvial groundwater at the site is typically oxic and circumneutral$^{10}$. Se:SO$_4$ ratios in alluvial groundwater are typically similar to overburden contact water
(seeps) and fall within the bounds of unsaturated laboratory column leachate (Figure 2), indicating oxic mine-related impacts. However, Se:SO₄ ratios in two alluvial groundwater monitoring wells that receive runoff from overburden piles, CHMWA-04 and CHMWA-05, are similar to those observed in saturated laboratory column effluent and are significantly lower than observed for other alluvial wells and seeps (Figure 3). Lower Se:SO₄ ratios in CHMWA-04 and CHMWA-05 relative to overburden pile contact water (seeps) indicate selenium attenuation. The strong selenium attenuation inferred from the low Se:SO₄ ratios is consistent with redox indicators suggestive of reducing conditions, including dissolved oxygen, dissolved iron, and dissolved manganese (Figure 3). These monitoring wells reside along a surface water channel that is highly vegetated, and it is hypothesized that the marshy conditions in this area result in a

**Figure 3.** Selenium sulfate, iron, and manganese results at select Champ Mine monitoring locations.
reducing environment conducive to selenium reduction in surface water, which then recharges the alluvium. Therefore, despite receiving infiltration from mine-impacted seeps with selenium concentrations up to 1.46 mg/L, selenium is attenuated in the reducing conditions, resulting in low to non-detect selenium concentrations in underlying monitoring wells CHMWA-04 and CHMWA-05.

**Mountain Fuel Mine: Selenium Reduction in Unsaturated Waste Dump**

Active mining occurred from 1963 to 1993 at the Mountain Fuel Mine\textsuperscript{11}. During operations, Meade Peak Member phosphate ore was mined from two open pits coinciding with outcropped portions of the phosphate-bearing Phosphoria Formation. As mining progressed from north to south and after mining was completed, reclamation efforts were completed, including backfilling pits with overburden material, contouring overburden piles to promote drainage and prevent erosion, and seeding overburden piles with mixes of native grasses and alfalfa. As such, the current site condition

**Figure 4.** Se:SO\textsubscript{4} Ratios in Select Mountain Fuel Mine Surface water and Groundwater Samples
includes open and partially backfilled former mine, five reclaimed overburden piles, a variety of surface water, a former Facilities Area, and a former ore storage area. Selenium concentrations in groundwater at Mountain Fuel Mine range from non-detect to several hundred µg/L, with the highest selenium impacts in shallow alluvial groundwater adjacent to overburden piles\textsuperscript{11}. While slightly elevated selenium concentrations were observed in bedrock groundwater downgradient of the site, selenium concentrations in the same bedrock formations (Dinwoody Formation and Rex Chert Member of the Phosphoria Formation) located beneath site overburden piles show signs of selenium attenuation. Specifically, downgradient of the site in monitoring wells MFMWD-12 and MFMWR-20, Se:SO$_4$ ratios fall within the bounds of unsaturated laboratory column leachate and are consistent with dilution of site-related impacts, represented by impacted alluvium and overburden contact water (“MFSEP-03”) presented on Figure 4. In these monitoring wells, selenium reductive precipitation is not observed and slightly elevated selenium concentrations (greater than background but less than the MCL) are consistent with dilution of site-related impacts as groundwater flows downgradient of the site.

In contrast, Se:SO$_4$ ratios in bedrock monitoring wells MFMWD-14 and MFMWR-22, which are located beneath an unsaturated overburden pile at the site, are consistent with saturated laboratory column leachate and much lower than observed in oxic site-related impacts. The variation in Se:SO$_4$ ratios in these bedrock wells is believed to be due to the variable level of selenium attenuation that occurs in unsaturated overburden before leachate migrates into bedrock. Leachate that remains oxic during contact with overburden (including leachate dominated by surficial runoff and percolation through thinner edges of overburden piles) exhibits effectively no attenuation of selenium once it is released from overburden. Because this water remains oxic, selenium and sulfate impacts are consistent with unsaturated column tests performed in the laboratory. In contrast, water that percolates to depth in the thicker central portions of overburden piles exhibits a greater degree of selenium attenuation, likely resulting from sub-oxic or anoxic conditions developing at depth in the waste rock as oxygen is consumed through the oxidation of organic matter and sulfide. Bedrock monitoring points occurring directly beneath and downgradient of thick waste rock pile zones such as MFMWD-14 and MFMWR-22 exhibit signatures of this selenium attenuation.

**SCRRRA – Selenium Reduction in Mine Pit Backfill**

Mining activities at the SCRRRA Mine progressed from south to north, with development of the South Pit beginning in 1991 and progression to the Central Pit in 1997\textsuperscript{12}. The Central Pit was backfilled and reclaimed with relatively modern mine practices; the southern portion of the Central Pit was backfilled and overlaid with run-of-mine waste via plug dumping, and the Luxor Dump overlying the former Central Pit was completed and reclaimed in 2004 with a cap comprising 6 to 8 feet of limestone and 2 to 3 feet of low-selenium-content growth medium\textsuperscript{12}. Potential impact sources at the SCRRRA Mine include backfilled mine pits and external waste rock piles.
Groundwater impacts at SCRRA mine include selenium concentrations up to 1 mg/L and sulfate concentrations up to 2,000 mg/L in alluvium. Based on comparison with sulfate, selenium impacts across the mine exhibit variable levels of selenium attenuation depending on location. Of particular note are the monitoring wells screened in overburden, including BH-6, BH-1, and MWBR-9. BH-6 is screened in a shallow, unsaturated portion of overburden (7 to 18 feet below the surface) in an aboveground portion of an overburden pile. This well exhibits among the highest selenium and sulfate concentrations at the site, with no evidence for selenium attenuation (Figure 5). In contrast, BH-1 and MWBR-9 are screened at the bottom of the saturated and backfilled

**Figure 5.** Selenium, Iron, and Manganese Concentration at Select SCCRA Monitoring Wells.
South Pit and Central Pit, respectively, and exhibit similar sulfate concentrations to BH-6 but with selenium concentrations up to three orders of magnitude lower (Figure 5). Low Se:SO$_4$ ratios at BH-1 and MWBR-9 are accompanied by elevated concentrations of dissolved manganese, which suggests that the geochemical conditions in this saturated backfill are reducing and that observed selenium attenuation is the result of selenium reductive precipitation. BH-1 and MWBR-9 demonstrate that the level of selenium attenuation achievable in saturated backfill is greater than what is typically observed in saturated columns. This occurs even under high selenium loading conditions resulting from oxic release and percolation from above, as indicated by the Se:SO$_4$ ratios for these wells plotting below the saturated column dilution line (Figure 5). Therefore, whereas the lower selenium concentrations in saturated columns relative to unsaturated columns may have been due to a combination of a decrease in release and in attenuation subsequent to release under saturated conditions, the field results clearly demonstrate attenuation of initially-high aqueous selenium concentrations.

North Maybe Mine: Selenium Reduction in Shale Bedrock below an Open Pit

Active mining occurred at the North Maybe Mine 1950 and 1993 with several periods of inactivity$^{13}$. During operations, Meade Peak Member phosphate ore was mined from open pits coinciding with outcropped portions of the phosphate-bearing Phosphoria Formation. Currently, the site consists of a series of open pits (up to approximately 400 feet deep) advanced along the strike of the Meade Peak Member. The narrow pit floors consist of rocky, un-backfilled areas as well as areas that were partially backfilled with overburden$^{13}$. As a result of spring snowmelt and summer precipitation intermittent and ephemeral pit ponds form within the open pits; water from the pit ponds infiltrates into bedrock groundwater within the Grandeur Tongue Member (dolomite bedrock) and Meade Peak Member of the Phosphoria Formation (phosphatic shale)$^{13}$.

Due to contact with adjacent overburden piles and exposed shale within the open pits, water that accumulates within the pit ponds contains selenium up to 0.74 mg/L, sulfate up 100 mg/L$^{13}$, and Se:SO$_4$ ratios that are consistent with those of unsaturated laboratory column leachate (Figure 6), indicating oxic mine-related impacts. While this pit pond water infiltrates into both the Grandeur Tongue Member and the Meade Peak Member, the resulting water quality observed in these two formations is very different. Namely, selenium concentrations and (Se:SO$_4$ ratios) within Grandeur Tongue Member groundwater similar to impacted pit pond water (Figure 6), indicating no selenium attenuation as water infiltrates from the pit pond into groundwater. In contrast, selenium concentrations (and Se:SO$_4$ ratios) within Meade Peak Member groundwater are significantly less than those observed for pit pond water (Figure 6), indicating selenium attenuation as pit pond water infiltrates into the Meade Peak Member. Dissolved oxygen, dissolved iron, and dissolved manganese concentrations indicate that geochemical conditions within Meade Peak Member groundwater are reducing, suggesting that selenium attenuation within Meade Peak Member groundwater is the result of reductive precipitation. These reducing conditions are present likely because as oxic pit pond water infiltrates into the Meade Peak Member, dissolved oxygen is
consumed by oxidation of sulfides and organic matter (both of which are abundant in the phosphatic shale).

**Figure 6.** Selenium, sulfate, iron, and manganese concentrations in select North Maybe Mine surface water and groundwater locations
SUMMARY AND CONCLUSIONS

More stringent groundwater monitoring and compliance requirements as part of the new CCR rule will create significant challenges for the operators of CCR impoundments. This challenge is particularly acute as it relates to Appendix IV constituents like selenium, which is mobile in neutral to alkaline oxic surface water and groundwater. This study presents observations of selenium attenuation via reductive precipitation in several different subsurface conditions at four former phosphate mines. Reductive precipitation of selenium was observed to occur in both saturated and unsaturated low-oxygen environments. These observations are relevant to both groundwater monitoring and corrective actions as part of the CCR rule. Specifically, an understanding of selenium natural attenuation can support the determination of representative site-specific background selenium concentrations, which are used to determine if corrective action is required. Site-specific background selenium characterization should occur in unimpacted groundwater with similar geochemical and redox characteristics to the area of suspected impacts. If selenium concentrations indicate that corrective action is needed, the observations presented in this study demonstrate that selenium may be naturally attenuated if the geochemical conditions are conducive and active remediation may not be necessary. If the natural groundwater geochemical conditions are not conducive to selenium attenuation, enhanced natural attenuation via *in situ* selenium reductive precipitation should be achievable through injection of organic substrates and stimulation of reducing geochemical conditions.

REFERENCES


