Control of Tailing Seepage through Reactive Chemical Amendments

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Abstract Seepage from legacy tailings impoundments presents significant potential for leachate transport into adjacent groundwater and surface waters. Seepage typically retains the chemical composition of the milling chemistry and may exhibit undesirable chemical attributes, such as alkaline pH, lixiviant, sulfate, or elevated concentrations of trace elements or radionuclides. Seepage management is a major environmental effort in modern mining operations and legacy properties. Reactive phosphate amendment was evaluated at a legacy uranium mill tailings impoundment. The results of this work indicate that reactive chemical amendments may be an alternative or supplemental option to traditional physical methods of seepage control for some applications.

Keywords tailings, uranium, source control, seepage, amendments

Introduction

Tailings are typically transported in a slurry form to a tailings impoundment. In subaerial disposal, tailings are then discharged into the impoundment through a single point (which must be relocated occasionally) or through spigots, both of which create a succession of overlapping deltas (Vick 1990). Similar to natural depositional settings, coarser tailings (sands) settle from suspension close to the point of discharge, creating beaches. Finer tailings (slimes) are carried into the interior of the impoundment and tend to settle in the standing water of the decant pond. Both particle size and pulp density affect this segregation (Vick 1990). In some operations, tailings are cycloned prior to deposition to mechanically separate the sands and slimes, increasing the relative proportion of slimes tailings deposited in the impoundment. The separated sand tailings are often used to construct the embankment of the impoundment (EPA 1994).

The deposition of tailings slurry creates significant vertical and horizontal heterogeneity in geotechnical and hydraulic properties throughout the impoundment. Sands and slimes tailings exhibit considerable variability in permeability, density, plasticity, compressibility, consolidation, shear strength, and stress parameters, which impact the design, stability, and drainage of the impoundment (Vick 1990). Vertical and horizontal variability in hydraulic permeability is the primary consideration for the evaluation and management of seepage; layers of relatively high permeability sands are interbedded with relatively low permeability slimes, creating a complex hydrogeological regime (EPA 1994).

Review of Tailing Seepage Control

Understanding both the hydraulics and geochemistry of tailings seepage is important for effective mitigation as well as management. The direction and quantity of seepage flow is controlled by the vertical and horizontal heterogeneity of hydraulic permeability created by interbedded sands and slimes tailings. The movement of seepage is dominant in the relatively high permeability sands, which create preferential flow paths that may or may not be laterally as well as vertically continuous. Seepage flow can also be affected by hydraulic properties of the impoundment foundation and underlying aquifer, which determine the level of saturation and hydraulic connection between the impoundment and the aquifer (Vick 1990).

The chemical composition of tailings seepage can have a significant effect on adjacent water quality. The chemistry of tailings leachate typically retains the chemical composition of the milling process, which may exhibit undesirable characteristics, such as extreme pH, salinity, lixiviant (bicarbonate, cyanide, or acid), sulfate, or elevated concentrations of trace elements or radionuclides. Additionally, the oxidation of sulfides in legacy (partially unsaturated) tailings impoundments may create acid rock drainage and metal leaching (ARD/ML) concerns. Because of these possible characteristics, seepage may represent a risk to environmental or human health (Vick 1990).

Seepage mitigation and management methods can take either physical (hydraulic) or chemical approaches. Traditional seepage control methods are physical, and include seepage barriers, seepage return systems, liners, and hydraulic containment. While these methods reduce seepage transport through water management, in many cases, physical controls create an additional waste stream that requires management as well as treatment. Alternatively, chemical seepage control methods reduce leachate transport through geochemical alterations and ultimately reduce the mobility of chemical constituents in the leachate. Chemical seepage controls, which can be implemented *in situ* in impoundments, may be a preferable alternative or supplemental option to traditional physical methods for some applications.

Phosphate Mineral Precipitation Applied to Control Seepage Water Quality

An effective chemical mitigation approach for the treatment of dissolved metals includes removal from the aqueous phase via precipitation. This approach can be a challenge for the oxidized form of uranium (U[VI]), which tends to be highly soluble under typical tailing seepage geochemical conditions. A strategy currently under investigation involves the *in situ* precipitation of U(VI) within uranyl phosphate phases. The strategy involves injecting a soluble form of phosphate, which can react with uranium and other groundwater constituents (including calcium) to form a host of low-solubility uranium-containing phosphate phases. These include uranium phosphate pure phases such as chernikovite ($H[UO_2PO_4]\times4H_2O$), autunite ($Ca[UO_2PO_4]_2\times xH_2O$), and saleeite ($Mg[UO_2PO_4]_2\times10H_2O$) as well as uranium-substituted calcium phosphate phases such as apatite ($Ca_5[PO_4]_3[F,Cl,OH]$) (Fuller *et al.* 2002; Fuller *et al.* 2003; Fanizza *et al.* 2013). Generation of these phosphate phases also provides a long-term barrier for uranium treatment via sorption (Fuller *et al.* 2002; Fuller *et al.* 2003).

A challenge with the implementation of this injection-based approach is the distribution of phosphate in the subsurface before precipitation occurs. For example, phytic acid and tribasic sodium phosphate have the potential to precipitate rapidly in the vicinity of the injection well, limiting distribution and reducing aquifer permeability (Wellman *et al.* 2007; references therein). An approach currently under evaluation involves the injection of phosphate as tripolyphosphate. This phosphate polymer is relatively soluble compared to orthophosphate, allowing for enhanced distribution, while providing a long-term source of orthophosphate in the aquifer as the polymer hydrolyzes (Wellman *et al.* 2007; Vermuel *et al.* 2009).

Methods

Laboratory tests were performed on tailings samples and porewater collected from a tailings impoundment at a former uranium mill site in order to optimize the implementation strategy in the field. The tailings impoundment at the site has been actively flushed with water to accelerate movement of seepage to the underlying aquifer, where it is collected and treated *ex situ* to remove uranium. The laboratory tests were performed to understand the concentrations and chemical forms of uranium in tailing sands and slimes zones before implementing pilot testing activities described below. The relative abundance of different chemical forms of uranium present in the tailing sands and slimes was determined using a selective extraction approach. Sands- and slimes-dominated zones exhibited similar fractional abundance of uranium entrapped in mineral phases (65 to 80 % of total uranium), suggesting that a small fraction (20 to 35 %) of the uranium present in the tailings impoundment is potentially mobile. The majority of the sorbed uranium was weakly sorbed (*i.e.* desorbable by NaCl solution), while a slightly more than half of the mineral-bound uranium was in a form extractable by nitric acid (*i.e.* present in amorphous and crystalline metal oxide phases).

Field Tests of In Situ Uranium Phosphate Precipitation

A pilot-scale field testing program (Pilot Test) was implemented in the tailings impoundment, targeting the dissolved uranium phases in the tailings porewater. The primary objective of the Pilot Test was to evaluate the effectiveness of tripolyphosphate at immobilizing uranium *in situ*. In addition to demonstrating immobilization, specific objectives of the Pilot Test included 1) characterizing the *in situ* kinetics of the tripolyphosphate hydrolysis and precipitation reactions, 2) determining the injectability of the tripolyphosphate solution and subsequent distribution and transport in the tailings, and 3) evaluating any secondary geochemical as well as hydrogeological effects of tripolyphosphate (*e.g.* mobilization of other contaminants and reductions in hydraulic conductivity). To this end, the Pilot Test was conducted in three phases: hydraulic characterization, tripolyphosphate injection, and performance monitoring.

Hydraulic Characterization

Tracer testing was conducted to characterize the injection and hydraulic parameters of the impoundment in the Pilot Test area. Conservative (*i.e.* non-reactive, non-sorbing) tracers were injected into the proposed injection well. Two tracers were used concurrently: bromide (as potassium bromide) and a dye tracer fluorescein (as sodium fluorescein). The pilot test network is shown in Fig. 1. Wells were screened from 12 to 27 m below the surface of the tailings (total depth of the tailing was 30 m). Samples were taken from mid-point within the screened interval (approximately 20 m below the surface of the tailings). Tailing material was comprised of slimes (fine grained material) and sands.

Pilot Test Injections

Uranium immobilization through phosphate precipitation is inhibited in the alkaline envi-

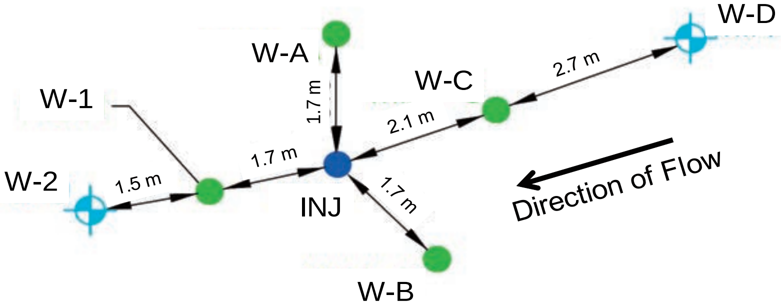

Fig. 1 *Pilot Test well network ("INJ" is the injection well; wells labeled "W" are monitoring wells).*

ronment of the tailings impoundment (due to the presence of highly soluble uranium carbonate complexes), so tripolyphosphate injections required a pH adjustment to lower pH and an addition of calcium. Prior to injecting tripolyphosphate, the tailings within the Pilot Test well network were "conditioned" with sulfuric acid metered into the injection supply water until a pH response was observed at the dose response monitoring wells (closest to the injection well). The Pilot Test proceeded when the field team determined that the pH adjustment caused no adverse effects (*e.g.* significant off-gassing or heat generation) that required additional engineering controls. In total, 12,900 L of pH-adjusted supply water were injected prior to injecting the tripolyphosphate solution.

The amendment solution used for the Pilot Test injections comprised tripolyphosphate, calcium chloride, and sulfuric acid mixed with the supply water. The target pH for the amendment solution was 5. The amendment solution also included conservative tracers: Rhodamine WT and deuterium. In total, 63,000 L of pH-adjusted amendment solution were injected over 8 days, delivering more than 105 kg of tripolyphosphate. The injection rate averaged approximately 23 L/min over the course of the injections. Seven monitoring events were conducted before or during active injections, and 12 post-injection monitoring events were conducted over 125 days to evaluate the performance of the tripolyphosphate amendment.

Pilot Test Results

Based on the results of post-injection performance monitoring, phosphate breakthrough curves were developed for the monitoring wells in the Pilot Test well network (Fig. 2). Peak phosphate concentrations were observed at the dose response wells during the injection because these wells were within the injection radius of influence (ROI); however, phosphate concentrations quickly declined in the upgradient and side-gradient wells after injections ended. Phosphate concentrations remained elevated in the downgradient dose response well (W-1) and peaked at downgradient monitoring well (W-2) after injections. In these two wells, phosphate concentrations were sustained long enough for uranium to be effectively immobilized and thus were the focus of continued monitoring.

The concentration of dissolved uranium and the pH (as measured in the laboratory) at these two downgradient wells are compared in Fig. 3. The pH-adjusted amendment solution decreased the ambient pH, which exceeded 8,

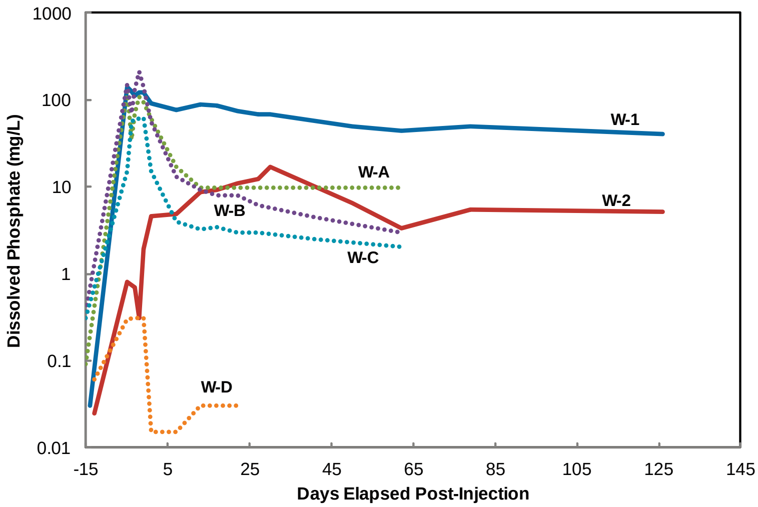

Fig. 2 *Concentration of dissolve phosphate measured at each monitoring well after injection.*

to a minimum of 6.7 and 7.7 for W-1 and W-2, respectively. This pH decrease was maintained more than 30 days post-injection at these two downgradient wells, whereas the pH quickly rebounded to ambient levels at the other monitoring wells.

Because of the sustained phosphate concentrations and pH decrease at W-1 and W-2, concentrations of dissolved uranium decreased significantly. Uranium concentrations were reduced to minimums of 0.464 and 0.300 mg/L at W-1 and W-2, respectively (Fig. 3) Using the baseline uranium concentrations measured before the Pilot Test injections, these concentrations represent 62 % uranium removal in W-1 and 67 % removal in W-2. It is important to note that, when pH increased post-injection, uranium concentrations in W-1 and W-2 did not return to baseline concentrations, indicating the stability and insolubility of the uranium-calcium-phosphate precipitate that was formed.

However, when evaluating performance, uranium concentrations of the injected amendment solution must be considered. The pore water from the nearby well used to supply water for the Pilot Test injections had higher concentrations of uranium (ranging from 2.6 to 3.5 mg/L) than the baseline concentrations in the monitoring wells in the Pilot Test well network. To correct for the additional uranium in the amendment solution, the deuterium analytical results were used; the normalized deuterium concentrations represent the fraction of the sampled water that is injected water from the amendment solution. Using this approach to correct the uranium immobilization calculations, 80 – 90 % of the uranium was immobilized within the treatment area. In addition, it was noted that tripolyphosphate was significantly retarded in the injection zone of the Pilot Test. This retardation is most likely due to adsorption of the polyphosphate onto tailings solids.

Conclusions

Conventional physical (hydraulic-based) approaches to seepage management at tailings impoundments often cannot prevent impacts to adjacent water quality. Reactive chemical approaches hold promise for fundamentally changing the tailings pore water chemistry, resulting in source control via reduced mobility of major and trace elements. Challenges related to amendment delivery and distribution within an impoundment, and overcoming extremely alkaline conditions that were unfavorable for uranium precipitation, were evaluated in the Pilot Test discussed here.

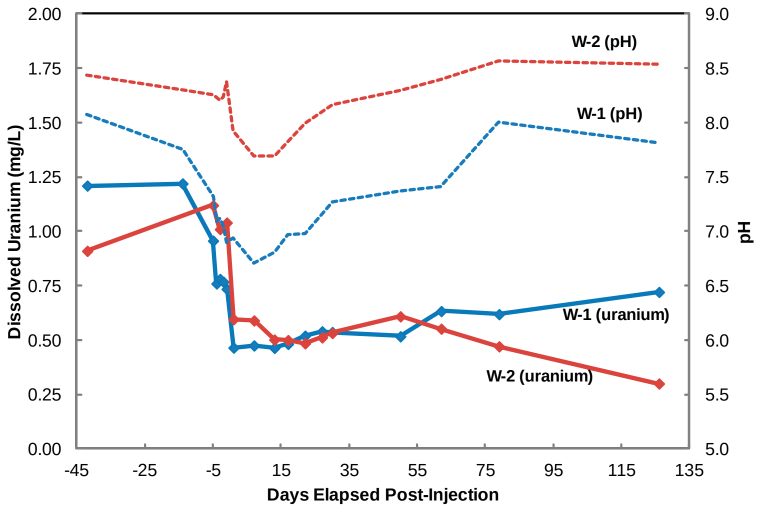

Fig. 3 *Uranium concentration and pH at downgradient monitoring wells.*

The Pilot Test successfully demonstrated that tripolyphosphate can be used to immobilize uranium *in situ* in tailings impoundments, even in the extreme hydrogeological and geochemical conditions of a legacy uranium tailings impoundment. Up to 81 % of uranium was immobilized where pH adjustments and phosphate concentrations were sustained long enough for precipitation to occur. More importantly, the phosphate minerals that were formed were stable and did not re-dissolve when the pore water geochemistry returned to pre-injection conditions.

Secondary geochemical and hydraulic effects of this approach can be successfully managed. During the Pilot Test, there was no indication of precipitate fouling of the injection system as well as the tailings matrix. Further, off-gassing and heat generation from the pH adjustment were minimal and successfully mitigated. These factors were effectively controlled throughout the Pilot Test and did not affect performance. The results demonstrate that, through a detailed understanding of tailings chemistry and hydraulics, reactive chemical amendments can be employed to control and improve seepage water quality.

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