

Chemistry and Engineering Aspects of the Application of Soluble Phosphates for Uranium Treatment in Groundwater – 17255

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ABSTRACT

Treatment of uranium in groundwater is challenging because of the equilibrium partitioning of uranium between sorbed and aqueous phase complexes in mobile and immobile pore space. *In situ* groundwater treatment strategies for uranium hold promise because of their reliance on fundamentally altering uranium chemical speciation as well as aquifer geochemical conditions. For the last 30 years uranium *in situ* reductive precipitation has been the leading technology; however, there have been only a handful of large-scale applications. Recently, within the last 10 years, the application of soluble phosphates has been identified as a viable means of treating soluble uranium, while at the same time changing the balance in terms of the availability of sorbed/immobile uranium to remobilize. Uranium reacts with soluble phosphate to form a range of low-solubility uranium minerals; surface passivation can also result, limiting the availability of uranium for dissolution. Here we discuss the application of dissolved phosphate in a small-scale pilot test in a tailings pile.

INTRODUCTION

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. A strategy being evaluated involves the *in situ* precipitation of U(VI) within uranyl phosphate phases. This relies upon the injection of a soluble form of phosphate into an aquifer system, 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 autunite ($\text{Ca}[\text{UO}_2\text{PO}_4]_2 \cdot x\text{H}_2\text{O}$), as well as uranium-substituted calcium phosphate phases such as apatite ($\text{Ca}_5[\text{PO}_4]_3[\text{F},\text{Cl},\text{OH}]$) [1], [2], [3]. 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 [4], [5].

METHODS

A pilot-scale field testing program (Pilot Test) was implemented in a mine tailings impoundment, targeting the dissolved uranium phases in the tailings porewater (Figure 1). The primary objective of the Pilot Test was to evaluate the effectiveness of tripolyphosphate at immobilizing uranium *in situ*. In addition, specific objectives of the Pilot Test included characterizing the *in situ* kinetics of the tripolyphosphate hydrolysis and precipitation reactions, and determining the injectability of the tripolyphosphate solution and subsequent distribution and transport in the tailings. To this end, the Pilot Test was conducted in three phases: hydraulic characterization, tripolyphosphate injection, and performance monitoring.

Uranium immobilization through phosphate precipitation is inhibited in the alkaline environment of the selected 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, when calcium concentrations are low (<100 mg/L) in order to promote formation of calcium-uranium-phosphate minerals. 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). In total, 12,900 liters 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 standard units (s.u.). The amendment solution also included conservative tracers: Rhodamine WT and deuterium. In total, 63,000 liters of pH-adjusted amendment solution were injected over 8 days, delivering more than 105 kilograms of tripolyphosphate. The injection rate averaged approximately 23 liters per minute 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.

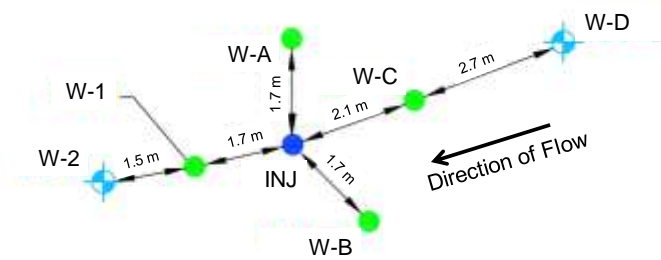


Figure 1 Pilot Test well network (“INJ” is the injection well; wells labeled “W” are monitoring wells).

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 (Figure 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.

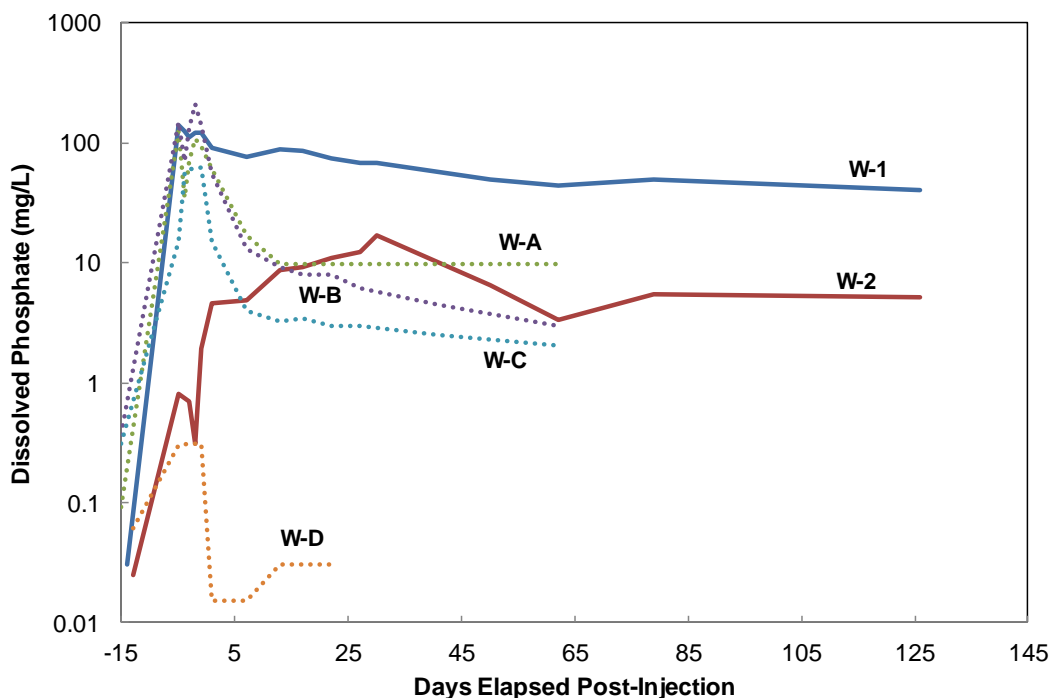


Figure 2 Concentration of dissolve phosphate measured at each monitoring well after injection.

The concentration of dissolved uranium and the pH (as measured in the laboratory) at these two downgradient wells are compared in Figure 3. The pH-adjusted amendment solution decreased the ambient pH, which exceeded 8, 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 milligrams per liter (mg/L) at W-1 and W-2, respectively (Figure 3). Using the baseline uranium concentrations measured before the Pilot Test injections, these concentrations represent 62 percent uranium removal in W-1 and 67 percent 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.

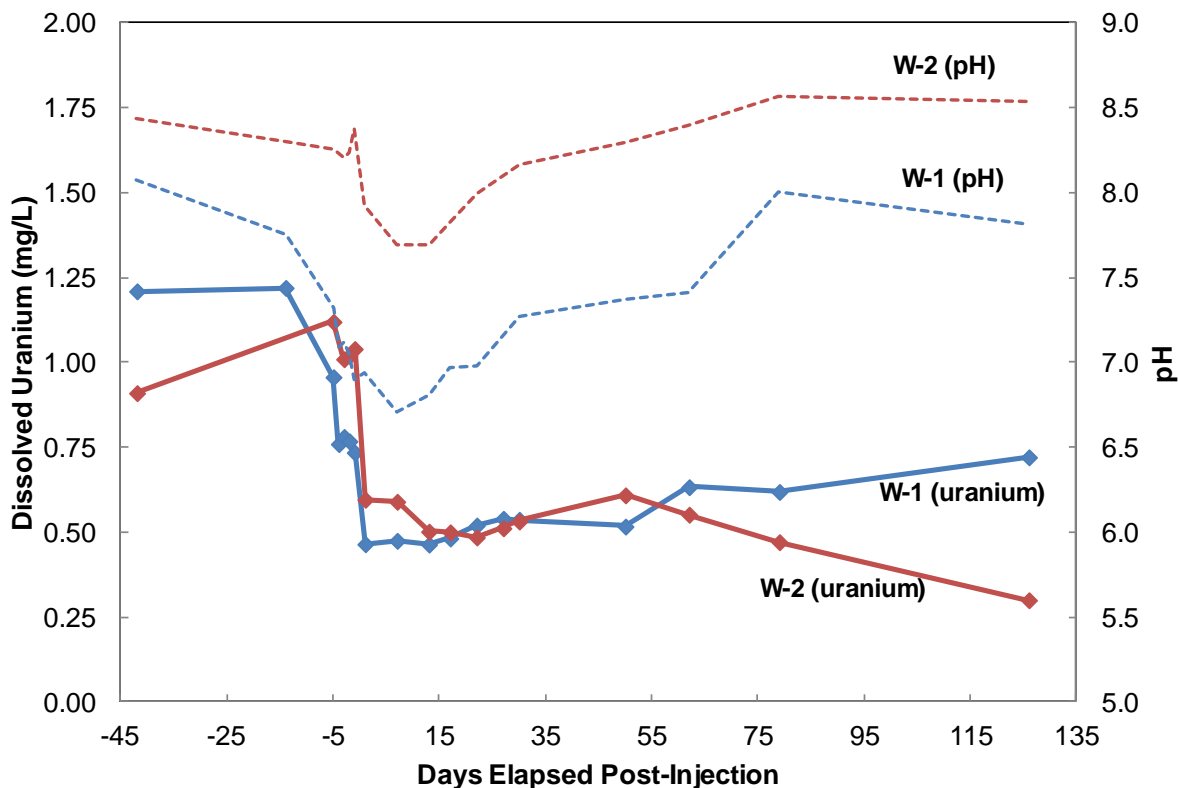


Figure 3 Uranium concentration and pH at downgradient monitoring wells.

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 percent 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

The Pilot Test successfully demonstrated that tripolyphosphate can be used to immobilize uranium *in situ*, even in the extreme hydrogeological and geochemical conditions of a tailing impoundment. Up to 81 percent 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 and/or 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 reactive chemical amendments, based upon promoting the precipitation of uranium as phosphate minerals, can be successfully deployed.

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