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Geochemical evaluation of uranium sequestration from field-scale infiltration and injection of polyphosphate solutions in contaminated Hanford sediments

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ABSTRACT

To remediate persistent groundwater uranium contamination in the 300 Area of the Hanford Site, located in southeast Washington State, U.S.A., approximately 7 million liters of polyphosphate solutions (mixture of 90% orthophosphate and 10% pyrophosphate) were delivered in high concentrations to the vadose zone and top of the aquifer over a 13-day period via infiltration and injection. The persistence of uranium in the aquifer is attributed to leaching of residual uranium contamination from the vadose zone by periodic rewetting due to fluctuating water table controlled by daily and seasonal variations of nearby Columbia river stage.

The remedy relies on in-situ availability of Ca^{2+}, primarily from cation-exchange and dissolution of carbonate mineral phases, to form calcium phosphate (Ca-P) bearing precipitates that incorporate and adsorb available uranium and form a relatively insoluble coating on sediments thereby reducing the dissolution of residual uranium bearing mineral phases. During injection and infiltration some dissolution of mineral phases is expected to occur along with rapid nucleation of Ca-P and the resulting precipitates are likely to incorporate components from the dissolving phases.

The phosphate loading following treatment is calculated to be about 1000–2500 μg/g of sediment surface exposed. Of this amount, approximately 50–650 μg/g is associated with the solid phase that is extractable with acetic acid indicating association with carbonate phase. The observations at the monitoring wells during remedy implementation indicate an initial decrease in pH and an increase in dissolved uranium concentration with delayed breakthrough of phosphate due to reactions with mineral surfaces. Following the initial breakthrough, as the phosphate concentrations increase the uranium concentrations show a sharp decline and then remain low afterwards. Comparison of total uranium concentration profiles from collocated pre- and post-treatment borehole sediment samples indicate limited uranium leaching to the aquifer. The total uranium concentrations remained within the range of variability expected in the field.

Sequential extraction tests conducted on sediment samples indicate that prior to treatment uranium is associated primarily with crystalline oxides of iron and clay minerals and to a lesser extent with carbonate minerals. In the post-treatment samples, appreciable reduction in uranium fraction associated with crystalline oxides of iron and clay minerals is observed indicating that uranium has been remobilized due to mineral dissolution, which later complexed with Ca-P-carbonate phases. The formation of surface complex of calcium-carbonate-phosphate likely structurally incorporated or surface adsorbed any available uranium in solution. Surface complexation with oxyhydroxides of iron (and other trace metals) also occurred.

To evaluate the significant reactions resulting from introduction of phosphate bearing solutions a reactive transport model is developed to simulate the infiltration event. The results indicate that the extent of HPO_4^{2-} reaction front is a net result of several reactions. As HPO_4^{2-} is added to the sediments, the resulting deprotonation reactions lead to excess H^+ and pH reduction that are buffered via surface complexation reactions and mineral phase dissolution. The cycle of deprotonation followed by consumption of H^+ will continue as long as supply of both phosphate and reacting iron oxyhydroxide surfaces and minerals, primarily uranium bearing carbonates, uranium silicates, and calcite, are maintained. Due to excess supply, the phosphate will react with the available calcium (primarily from ion-

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exchange reactions) and start forming Ca-P bearing precipitates. In this process, any uranium in the solution will adsorb or get bound to forming precipitate and be sequestered.

1. Introduction

Uranium contamination in the groundwater has persisted over past two decades in the 300 Area of the U.S. Department of Energy's Hanford Site located in southeastern part of the Washington State, U.S.A. The uranium contamination in the 300 Area has resulted from historic discharge of nuclear fuel fabrication wastes to several liquid waste sites over the period from 1943 to 1971. Although excavation of highly contaminated surface sediments occurred in 1990s, residual contamination exists in deeper unexcavated vadose zone sediments below the historic disposal facilities. Fig. 1 shows the extent of the typically mapped uranium plume (for 2011) that continues to discharge to the nearby Columbia River. The extent of the plume varies seasonally based on the low-river stage and high-river stage conditions. A persistent high dissolved concentration zone, significantly above primary drinking water standards of 30 μg/L has historically been observed near the process trench (316-5) and the north process pond (316-2) used for infiltrating the liquid waste. A lower concentration zone is observed near the south process pond (316-1).

Completion of 300 Area clean-up on the Hanford Site is being accomplished under the 2013 U.S. Environmental Protection Agency (EPA) and U.S. Department of Energy (DOE) record of decision (ROD) and amendment (U.S. EPA and U.S. DOE, 2013), which identifies uranium as a contaminant of concern. Part of the selected remedy for uranium contamination in groundwater is enhanced attenuation of uranium over a 12,140 m^2 (3 acre) area using phosphate solutions to reduce the uranium concentrations in the aquifer. The desired goal of injection and infiltration is to deliver phosphate in high concentrations to the vadose zone and top of the aquifer to precipitate calcium-phosphate (Ca-P) bearing phases that can bind with residual uranium in the pore water and sediment surfaces and sequester it. To avoid forming Ca-P precipitates prior to injection/infiltration, the polyphosphate solutions were prepared without any calcium with the understanding that there is sufficient available calcium in the sediments to react in-situ with the phosphate.

The enhanced attenuation remedy is being implemented in two stages, namely, Stage A that covers an area of 3035 m^2 (0.75 acre) and Stage B that covers the remaining portion of 9105 m^2 (2.25 acre). Stage A remedy was implemented in November 2015 to test the approach with Stage B remedy planned later on. Stage A treatment area was chosen to be at the southern end of the process trenches (316-5) as shown in Fig. 2, which covers part of the north process pond to the east. The selection of Stage A treatment area was based on estimate of residual uranium soil concentration distribution from various sampling events conducted over past two decades along with the mapping of dissolved uranium plume based on sampling of groundwater in the monitoring wells. The total volume of injected and infiltrated polyphosphate solutions in Stage A was about 6.8×10^6 L (1.8 million gallons) that occurred over a 13-day period. Approximately, half of this volume (3.3×10^6 L) was infiltrated.

Selection of the polyphosphate based remedy is based on detailed laboratory investigations conducted over multi-year period that demonstrated the efficacy of the technology in sequestering uranium (Wellman et al., 2008; Szecsody et al., 2012). It was found that although phosphate treatment did not completely eliminate uranium leaching from sediments a significant decline in long-term leaching rate and leached mass was observed compared

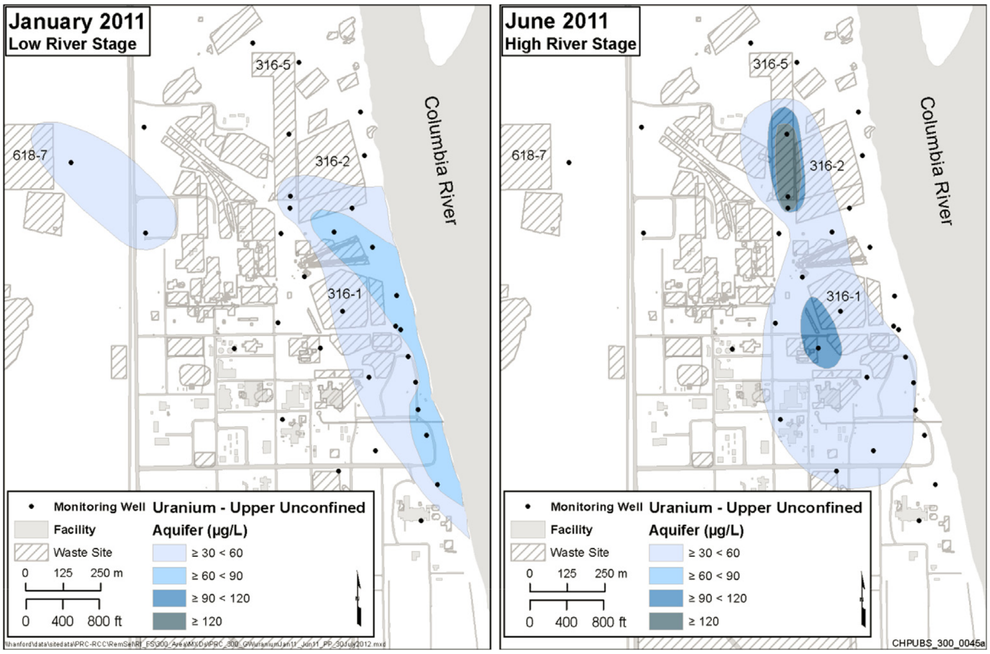

Fig. 1. Uranium plume in groundwater in winter and summer of 2011.