

**Uranium Sequestration – Field Test to Remedial Action –
17151**

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ABSTRACT

The Hanford Site historical nuclear weapons production has resulted in legacy soil and groundwater contamination and is now one of the nation's largest superfund sites. The 300 Area of the Hanford Site is adjacent to the Columbia River close to the city of Richland, Washington. It contained facilities and waste disposal sites that supported uranium fuel production and research and development activities. Contaminated liquid waste discharged to the waste disposal sites caused persistent uranium contamination within the underlying groundwater, which flows into the Columbia River.

The DOE performed field scale treatability studies in the 300 Area to assess the use of phosphate to sequester uranium as a potential remediation strategy. The Record of Decision was issued in November 2013 and requires DOE to use phosphate to sequester uranium over a 1.2 hectare area by applying phosphate to the highest uranium concentration areas of the vadose zone and the periodically rewetted zone using a combination of surface infiltration, periodically rewetted zone injection, and shallow aquifer injection.

Due to the inherent difficulties in scale-up from a limited field test to a full-scale remedial action, it was determined that uranium sequestration would occur in two sequential stages: Stage A and Stage B. Stage A would treat a 0.3 hectare area, while Stage B would treat the remaining 0.9 hectare area. The purpose of Stage A was to test the remediation approach on a smaller area, refine the process based on the results, and then implement it in a larger area. Stage A of the phosphate application to sequester uranium was implemented in November 2015.

This paper includes a description of the Stage A uranium sequestration process (objectives, observations, and conclusions), the sampling and monitoring approach, the physical sequestration system, and recommended changes for Stage B.

INTRODUCTION

The 300 Area is adjacent to the Columbia River in the southern portion of the Hanford Site. During Hanford's historical nuclear weapons production, the 300 Area contained facilities and waste sites that supported uranium fuel production and R&D activities. Releases from these waste sites have contaminated the underlying subsurface, specifically the lower vadose zone (LVZ) and the periodically rewetted zone (PRZ). The PRZ serves as the primary contributor of uranium to groundwater. When groundwater rises into the PRZ, it mobilizes residual uranium contamination. This

mobilized uranium moves with the groundwater, which flows out to the Columbia River. This periodic input of mobile uranium to the groundwater results in a persistent uranium plume and continued discharge of relatively low uranium concentrations to the Columbia River until the source of uranium is depleted.

Enhanced attenuation (EA) of uranium is being implemented within the 300-FF-5 Operable Unit (OU) by infiltrating and injecting phosphate solutions at high concentrations into the vadose zone and PRZ in order to form calcium-phosphate minerals that can bind labile uranium and sequester it in-situ. Uranium sequestration is being implemented at a 1.2 hectare area of high residual uranium contamination in the 300 Area Industrial Complex in accordance with the 300 Area Record of Decision (ROD) and ROD Amendment [1]. Uranium sequestration is occurring in two sequential stages (Stage A and Stage B).

This paper describes the evolution from treatability studies to remedial action of EA of uranium using phosphate solutions. It includes what has been learned during Stage A and the recommended changes for implementation of Stage B.

TREATABILITY TEST

A treatability test was conducted at the 300 Area Industrial Complex to evaluate the use of phosphate as a remedial technology to sequester uranium [2]. The treatability test included both laboratory and field studies.

The laboratory studies evaluated the application of phosphate to the vadose zone and PRZ sediments in order to immobilize uranium and prevent it from leaching to the aquifer. Laboratory tests demonstrated that when a soluble form of polyphosphate is injected into uranium-bearing saturated porous media, immobilization of uranium can occur due to formation of relatively insoluble uranyl-phosphate minerals, such as autunite ($\text{Ca}(\text{UO}_2)_2(\text{PO}_4)_2 \cdot n\text{H}_2\text{O}$). The field study evaluated direct sequestration of dissolved uranium in groundwater by injecting phosphate into the aquifer. Results of the field study demonstrated that upon direct injection the polyphosphate amendment could be effectively distributed over a relatively large lateral extent.

Monitoring wells located at a radial distance of 23 m showed phosphate concentrations as high as 40 to 60 percent of the injection concentrations, which indicated that uranium sequestration could be effectively implemented at full field scale. Based on the results of the treatability study, uranium sequestration using polyphosphate solutions was adapted for use as a groundwater remedy for the 300-FF-5 OU.

While the small-scale treatability test was successful, it did not provide field scale-up recommendations specific to the 300-FF-5 OU, such as the amount of phosphate solution to be applied (number of pore volumes), the actual chemical formulation (e.g., pyrophosphate, orthophosphate, and their relative concentrations), and the rate of application. In addition, a more thorough analysis of the chemical interactions within the soil would have been beneficial to determine the longevity of the treatment.

OVERVIEW OF THE STAGE A TREATMENT SYSTEM

The purpose of Stage A was to perform the remedy, uranium sequestration using polyphosphate, on an area of approximately 0.3 hectare, evaluate effectiveness in meeting the goals of the ROD[1], and establish a baseline from which to refine operations for Stage B. The PRZ is the principal target zone of the remedy because it is deemed to be the primary contributor of uranium to the aquifer. To a lesser extent the LVZ (1.5 m above the PRZ) is also a target zone of the remedy to account for years when the water level is higher than normal.

The Stage A Uranium Sequestration System was designed and installed between October 2014 and October 2015, and it was operated from November 6 through 18, 2015, at a total cost of approximately \$6M. The Stage A EA operational concept included near-surface phosphate infiltration into the vadose zone; phosphate injection into the aquifer before, during, and immediately after infiltration; and injection into the PRZ after the final injection into the aquifer. The design for Stage A included the number and spacing of injection and monitoring wells and infiltration lines, phosphate solution formulations, and injection and infiltration volumes and rates. This design was based on chemical arrival responses observed during previous treatability tests in the 300 Area. The Stage A Treatment System included injection wells, monitoring wells, an infiltration system, chemical mixing skids, and an electrical resistivity tomography (ERT) network. Figure 1 is an aerial view of the Stage A uranium sequestration system showing the location of the river pumps, chemical mixing skids, chemical storage tanks, and general location of the Stage A treatment area.

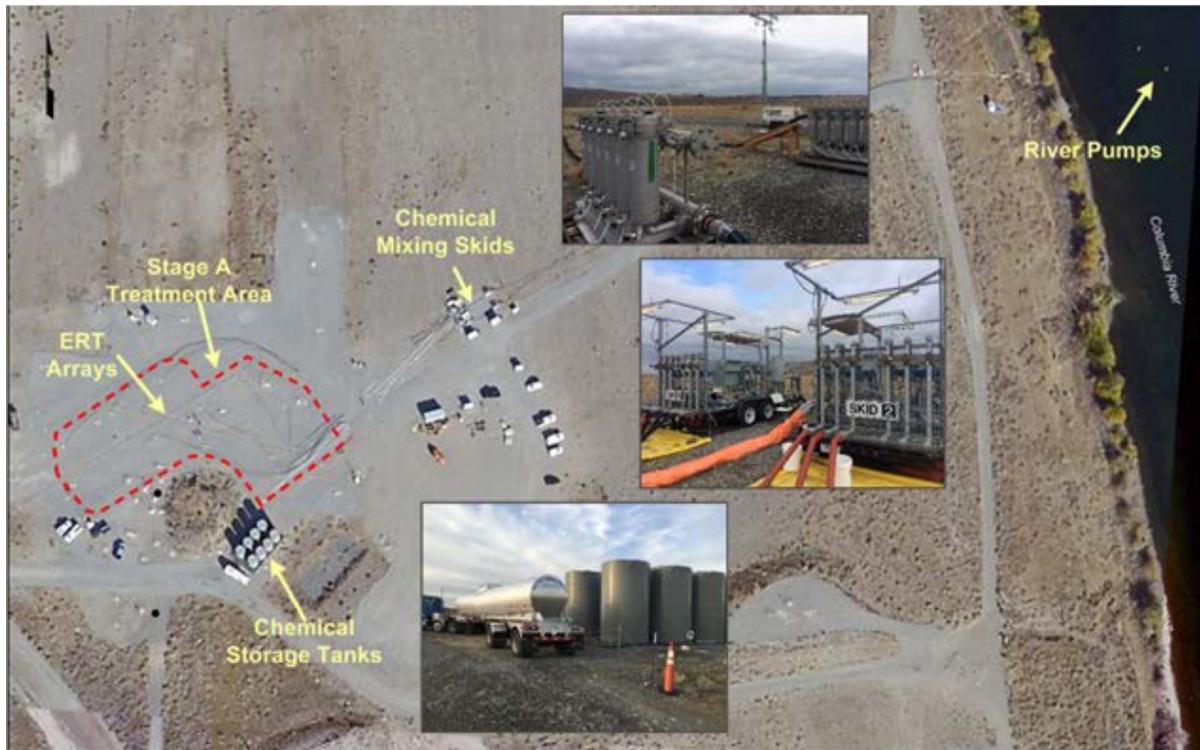


Fig. 1. Aerial View of the Stage A Uranium Sequestration System

During Stage A, two different phosphate solutions were blended and then infiltrated and injected into the vadose zone, PRZ, and top of the unconfined aquifer. The blend of orthophosphate^a and pyrophosphate solutions was used to take advantage of the reaction kinetics of each compound. Orthophosphate combines with naturally occurring calcium in the vadose zone pore water for rapid formation of a monocalcium phosphate rind around sediment surfaces, some of which contain mobile uranium. Pyrophosphate hydrolyzes, or breaks down, slowly to orthophosphate over time, which would allow for enhanced transport of phosphate to the LVZ and PRZ and formation of the calcium phosphate rind. The primary sequestration mechanism to be achieved is the formation of an amorphous (unstructured) monocalcium phosphate rind that coats the sediments containing uranium and thereby reduces the dissolution of uranium bearing mineral phase. Over months to years, this rind is expected to crystallize to form a stable calcium phosphate mineral, hydroxyapatite ($\text{Ca}_{10}(\text{PO}_4)_6(\text{OH}_2)$), which has very low solubility. During crystallization some incorporation of uranium into the hydroxyapatite structure is also expected.

^a Orthophosphate refers to phosphate associated with monosodium (primarily) along with disodium species.

DESCRIPTION OF THE STAGE A SYSTEM DESIGN

Injections

The Stage A injection system included nine combination PRZ and aquifer injection wells (Figure 2). Each injection well was constructed with two screened intervals, with one screen in the PRZ and one screen in the upper part of the aquifer. The screens were separated by a grout seal at the interface of the bottom of the PRZ and top of aquifer to allow isolated injection (using inflatable packers) into either the PRZ or top of the aquifer.

Infiltration

A phosphate solution infiltration system was installed within the Stage A area (Figure 2). The specification of liquid distribution lines was selected to achieve a liquid application rate of at least 511 L/min over the 0.3 hectare Stage A treatment area. The infiltration network consisted of high-density polyethylene liquid distribution lines installed approximately 1.8 m below ground surface (bgs) to prevent accumulation and wicking of sodium and phosphate up into the surficial soil, which might inhibit the establishment and growth of vegetation. The drip lines were spaced approximately 2 m apart, resulting in a total of 44 lines aligned southeast to northwest. Each drip line was designed to infiltrate phosphate solutions at a rate of 8 L/hr from each of the emitters spaced 0.36 m apart along drip lines. Each drip line was installed with a pressure regulator set at 103.4 kPa and was connected to a flexible header hose through which the phosphate solution was delivered.

Electrical Resistivity Tomography

Infiltration of phosphate solutions into the vadose zone and PRZ increased the electrical conductivity of the soil by increasing both liquid saturation and pore fluid specific conductance. These changes enabled use of time-lapse ERT for remotely monitoring the advancement of the wetting front of the phosphate solution through the vadose zone and PRZ. An ERT network was installed in the Stage A area (Figure 2). The longer ERT array (Line A), bisecting the length of the Stage A area, was monitored using 64 electrodes at 1.5 m spacing. The shorter array (Line B), bisecting the width of the Stage A area, was monitored using 48 electrodes at 1.5 m spacing.

Groundwater Monitoring

The monitoring well system included three monitoring well pairs upgradient of the Stage A treatment area, six monitoring well pairs within the Stage A treatment area, and four monitoring well pairs downgradient of the Stage A treatment area (Figure 2). For each well pair, one well was screened in the PRZ, and one well was screened in the aquifer to enable monitoring of these two zones.

phosphate solution to the infiltration network; the target design rate was 511 L/min. The chemical feed pumps were set to mix the phosphate chemicals and feed water automatically at the specified ratios. Flow meters and sample ports were provided on each skid to monitor and collect samples of the phosphate solution. Feed water for the phosphate solutions was obtained using two separate submersible pumps, each capable of supplying up to 1,136 L/min. Following mixing, a manifold routed the phosphate solutions to transfer hoses for distribution to the injection wells and infiltration lines.

STAGE A TREATMENT PERFORMANCE

The Stage A treatment performance was evaluated in accordance with the sampling and analysis plan [3], based on:

- Laboratory analysis of uranium leaching characteristics and uranium mineral phase association following treatment
- Post-treatment assessment of phosphate distribution within the subsurface
- Monitoring of dissolved uranium concentrations in nearby wells screened within the aquifer
- Conducting fate and transport modeling to predict the uranium concentrations

Soil samples were collected before and after treatment from three pairs of collocated boreholes to compare uranium concentrations and uranium leaching characteristics before and after the application of phosphate solutions and evaluate post-treatment phosphate distribution and concentration. Groundwater samples and water levels were collected before, during, and after application of phosphate solutions to evaluate the distribution of phosphate solutions in the PRZ and aquifer. ERT was used in near real-time to monitor the migration through the vadose zone and PRZ of phosphate solutions applied using infiltration.

Daily sampling of all 26 monitoring wells during the treatment application was not feasible with available resources so only seven wells within the treatment area were sampled daily. Some wells could not be configured with instrumentation due to lack of available equipment, and manual monitoring of this number of wells at 4-hour intervals was not feasible with available resources so water level and field parameters (conductivity, temperature, pH, and oxidation-reduction potential) were monitored every 30 minutes using downhole instruments in only 6 monitoring wells rather than in all 26 monitoring wells. This limited number of sampling locations presented challenges in thoroughly evaluating Stage A performance.

STAGE A RESULTS AND DISCUSSION

The Stage A objectives were to determine if the phosphate was delivered to the targeted areas (e.g., PRZ and LVZ); if the addition of phosphate flushed a significant amount of uranium into the groundwater; if the phosphate effectively “sequestered”

the uranium; and if the phosphate delivery mechanism(s) could be improved. The Stage A uranium sequestration process included phosphate injection into the aquifer before, during, and immediately after infiltration; infiltration into the vadose zone; and injection into the PRZ after the final injection into the aquifer.

Injections

The data collected during and following the Stage A phosphate treatment indicate that delivery of high phosphate concentrations to the PRZ and to the top of aquifer was successful. Both the PRZ and aquifer injections were able to deliver high phosphate concentrations to the target depths containing residual uranium. Direct injection into the PRZ was successful in delivering phosphate at high concentrations to both the PRZ and to the top of the aquifer. PRZ injections effectively delivered phosphate to surrounding sediments at levels conducive to precipitation of calcium-phosphate bearing mineral phases. Aquifer injections were not as effective at delivering sustained high phosphate concentrations in the aquifer due to high groundwater velocities and dilution effects.

Infiltration

Phosphate was infiltrated into the vadose zone starting at a nominal depth of 1.8 m bgs with the intent to deliver phosphate to the LVZ and PRZ. Stage A infiltration performance data indicate that the infiltration system was not effective in distributing phosphate uniformly through the vadose zone. The wetting front as shown by the ERT data, moved laterally and vertically to saturate the vadose zone through the PRZ to the aquifer as expected, but the sampling results indicate that a majority of phosphate precipitated in the upper vadose zone compared to the LVZ.

Electrical Resistivity Tomography

Analysis of Stage A ERT imaging determined that the vertical movement of the phosphate solution wetting front varied across the enhanced attenuation area (EAA), with downward velocities ranging from 0.75 to 3 m/d. Areas with lower wetting front velocities exhibited higher concentrations of phosphate at shallow depths followed by sharp decline in concentrations with increased depth. Areas with higher velocity showed more phosphate traveling deeper into the vadose zone.

Soil Sampling

Soil samples were collected and analyzed before and after Stage A phosphate application to determine changes in mineral formation and uranium mobility resulting from the phosphate treatment. The post-treatment soil samples showed variable vertical distribution of phosphate with a larger proportion delivered through surface infiltration precipitated on soils in the upper vadose zone. The delivery of phosphate using infiltration to the LVZ and PRZ was uneven because of the subsurface media heterogeneities that led to variable vertical flow velocities along the infiltrated depth. Due to varying travel times, the chemical reactions between infiltrated solutions and the soil column resulted in phosphate precipitating non-uniformly within the vadose

zone, with a majority of the phosphate precipitating within shallow portions of the vadose zone above the target depth.

A series of laboratory tests were performed on the soil samples including sequential acid extraction, flow-through soil column leaching, scanning electron microscopy, energy-dispersive X-ray, and electron microprobe analysis. The sequential acid extraction tests showed that most of the phosphate in the soil samples was extracted by the harshest acid, indicating that calcium-phosphate mineral formation (e.g., amorphous monocalcium phosphate) had occurred after phosphate treatment. The flow-through soil column leaching tests demonstrated that after phosphate treatment the uranium leaching rate will be reduced. Scanning electron microscopy, energy-dispersive X-ray, and electron microprobe analysis found uranium in the soil samples to be either coated to the surface of or sorbed to soil particles but not yet incorporated into a mineral formation. The chemical interactions have resulted in conditions favorable for formation of the amorphous calcium-phosphate phases that result in sequestration of uranium.

The column leach testing of soil samples collected from deeper depths, where high phosphate concentrations were delivered, indicates that residual uranium in the post-treatment samples is less leachable compared to uranium in the pre-treatment samples. Results of the sequential extraction tests indicate that the chemical interactions from addition of phosphate solutions to the vadose zone, PRZ, and aquifer led to some initial mobilization followed by re-precipitation of uranium.

Groundwater Sampling

Sampling and monitoring during treatment operations did not detect a significant amount of uranium mobilized into the groundwater with the exception of a temporary spike in uranium in one of the PRZ monitoring wells within the treatment area. Groundwater samples collected from the two closest wells downgradient of the Stage A area over 6 months following the treatment show a significant decline in dissolved uranium concentrations. Concentrations have remained below the drinking water standard (30 µg/L). Periodic monitoring of downgradient wells is underway through at least one re-wetting cycle (summer high water) to assess effectiveness of sequestration in the PRZ.

A conceptual model of the chemical interactions resulting from phosphate application was developed based on the laboratory analyses and field observations. A fate and transport model has also been developed to predict the future uranium concentrations in and around the Stage A area. However, detailed laboratory testing has not been conducted to confirm the conceptual model or to evaluate potential secondary effects of adding high concentration polyphosphate solutions to the 300 Area sediments.

DESCRIPTION OF STAGE B ENHANCED ATTENUATION

Based on the results of Stage A uranium sequestration, Stage B uranium sequestration operations will follow the same general design approach as used during

Stage A treatment, with refinements made on how the phosphate solutions are delivered to the treatment zone. The Stage B Uranium Sequestration System will take 1 year to design, install, and complete the injections and another year to complete the performance evaluation and issue the final report at an estimated cost of approximately \$8M. The Stage B EA shall deliver three pore volumes of phosphate solution uniformly to the LVZ and the PRZ to sequester uranium. The treatment area consists of two spatially distinct segments where injections are required. A layout of the proposed Stage B EA area and LVZ/PRZ injection wells is shown in Figure 3.

To maximize the delivery of phosphate to the LVZ and PRZ where the contamination is present, a combination of LVZ and PRZ injections will be employed for Stage B instead of near-surface infiltration. Stage A infiltration performance data indicate a large proportion of phosphate delivered through infiltration precipitated on soils in the vadose zone above 6 m bgs. Much of the Stage B EA area overlies the former North Process Pond and 300 Area Process Trenches excavation areas, where contaminated soil was removed to depths of approximately 4.5 to 6 m bgs. These areas were backfilled with clean fill. Therefore, use of infiltration is not recommended for Stage B.

One of the Stage A design objectives of combining near-surface infiltration with injection was to provide more uniform horizontal and vertical coverage of the EAA than could be achieved with injection alone. In order to provide uniform coverage with the revised injection only Stage B approach, the number of injection wells will be increased from 27 (based on the nine Stage A wells scaled up by a factor of 3) to 48 wells. Assuming a conservative injection radius of influence (ROI) of 8 m, 48 wells with overlapping ROI will provide lateral coverage of the Stage B treatment area.

Up to 24 monitoring wells, an ERT network, pre-treatment and post-treatment soil sampling, and downgradient groundwater sampling are planned for evaluation of the Stage B performance. As noted earlier, daily sampling at a limited number of monitoring wells presented challenges in evaluating the Stage A performance. Therefore, daily sampling at all monitoring locations will be performed during Stage B.

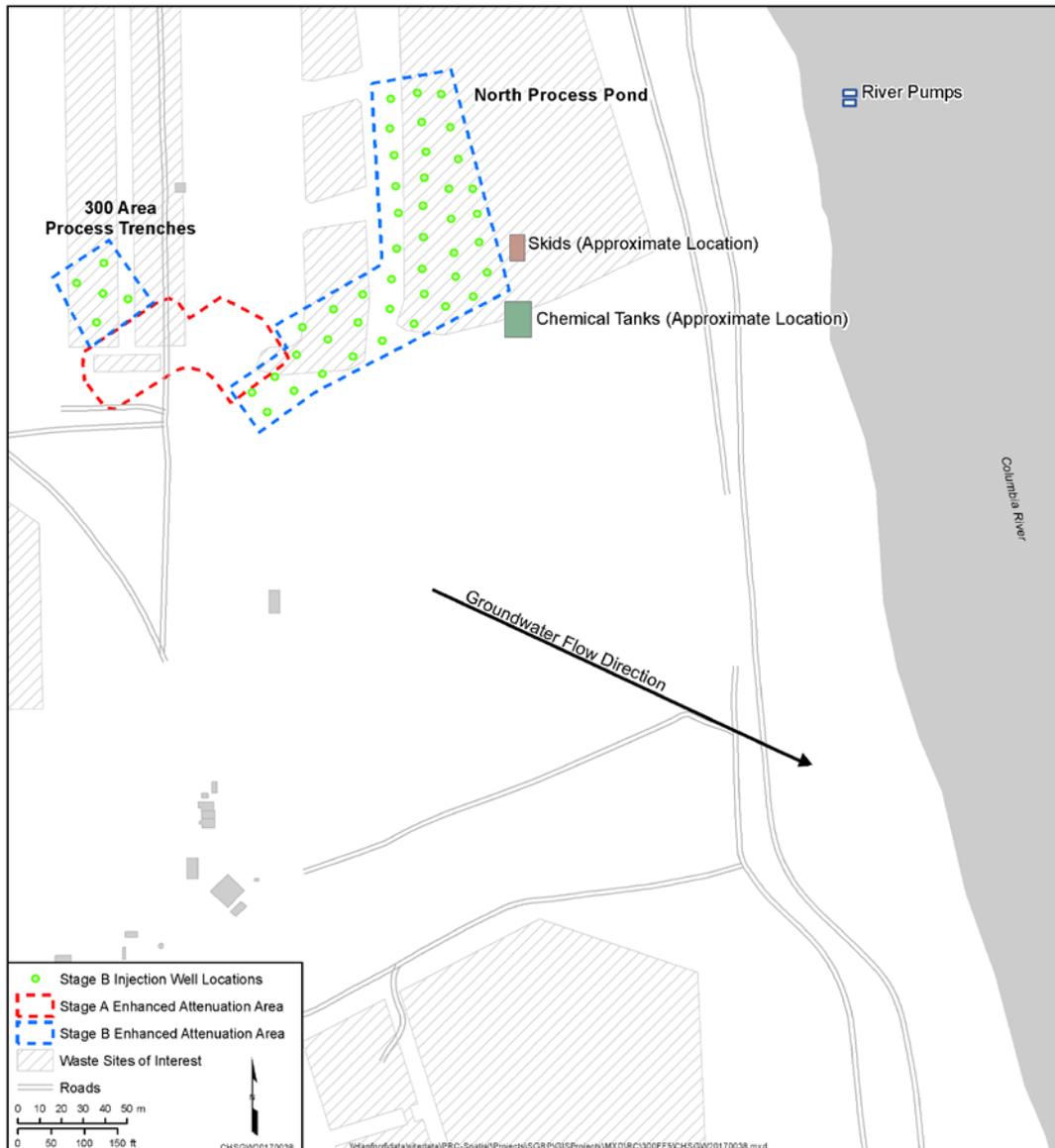


Fig. 3. Layout of the proposed Stage B Design

CONCLUSIONS

Stage A operations demonstrated that higher and more persistent spikes of phosphate concentrations in the top of the aquifer resulted from PRZ injections compared to direct injection into the aquifer. This led to the decision to not inject directly into the aquifer for Stage B and to deliver phosphate to the PRZ before injection into the LVZ allowing for a more sustained release to the aquifer and longer contact of phosphate with sediments in the PRZ.

Stage A operations also demonstrated that near surface infiltration of solution was not effective at uniformly delivering high phosphate concentrations in the LVZ or PRZ. This led to the decision to not use near surface infiltration and to achieve the

infiltration objective via direct injection to the LVZ. Additional injection wells will be used to ensure adequate lateral coverage within the treatment area.

In addition, a sample collection system will be installed for Stage B to facilitate daily sampling from all 24 monitoring wells, data loggers will be installed in all 24 monitoring wells, and the downgradient monitoring wells will be included in the set of 24 monitoring wells. This will address some of the issues of insufficient data from Stage A.

Treatability field tests were extremely valuable; however, the value could have been enhanced by providing more detailed recommendations for scale up. Stage A took 2 years to design, install, operate, and evaluate the performance at a cost of approximately \$6M, and Stage B will take an additional 2 years to design, install, operate, and evaluate performance at a cost of approximately \$8M. It is anticipated that Stage B will deliver phosphate to the target areas more effectively based on lessons learned from Stage A. Furthermore, Stage B will likely reduce the concentration of uranium in the groundwater. It is unknown at this time if the reduction in uranium concentration will be as significant as the one seen from Stage A. If the entire 1.2 hectare area had been treated at one time instead of the staged approach it would have been completed 2 years sooner for an approximate \$3.5M less total cost. The question remains if the benefits realized will be worth the extra time and cost.

REFERENCES

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