**Supplemental Groundwater Remediation Technologies to Protect the Columbia River at the Hanford Site, Washington - An Update - 8149**

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**ABSTRACT**

This paper provides an update on supplemental groundwater remediation technologies originally presented at the Waste Management 2007 Conference in Tucson, Arizona. In fiscal year (FY) 2006, the U.S. Congress authorized $10 million dollars to the Hanford Site for protecting the Columbia River from groundwater contamination. After a peer review and selection process, nine projects were selected to meet the objectives of the appropriation funds. Subsequent to the initial funding, an additional $2 million dollars was made available by the U.S. Department of Energy's Office of Environmental Management (EM-20) in FY 2007. An additional three projects were selected for funding using a similar peer review process.

Six of the selected projects are targeted at hexavalent chromium contamination in 100 Area groundwater at the Hanford Site. Progress on the five original chromium projects is reported in this paper. One of the new projects, started in fiscal year 2007, involves drilling additional groundwater monitoring wells to refine the source area.

One of the unknowns in predicting the movement of carbon tetrachloride from the Hanford Site's 200 West Area towards the Columbia River is the rate of abiotic hydrolysis of the carbon tetrachloride. One of the EM-22 projects will improve this situation by measuring the hydrolysis rates at various temperatures to extrapolate the hydrolysis constant to ambient temperatures (approximately 10°C).

Three of the projects involve treating Sr-90 contamination at the 100-N Area. Phytoremediation is a technology in which plants are used to extract or isolate soil contamination. The technology would not be used alone but employed with other methods of remediation (e.g., apatite barrier or monitored natural attenuation) as an additional step. One of the newly funded projects is investigating the issue of food-chain transfer of contaminated plant material via insect uptake.

Uranium in groundwater at the 300 Area is another environmental concern. One of the projects has performed laboratory tests using long-chain polyphosphate materials. Subsequently, a field test was conducted to determine if it is possible to treat groundwater in the unconfined aquifer at the 300 Area

using polyphosphate materials.  Another new project is to investigate the feasibility of infiltrating the polyphosphate into the ground to treat uranium contamination in the deep vadose and smear zones.

## BACKGROUND

For FY 2006, the U.S. Congress authorized $10 million dollars to the Hanford Site for "…analyzing contaminant migration to the Columbia River, and for the introduction of new technology approaches to solving contamination migration issues."  These funds are administered through the U.S. Department of Energy Office of Environmental Management (specifically, EM-22).  After a peer review and selection process, nine projects were selected to meet the objectives of the appropriation funds.  Subsequent to the initial funding, an additional $2 million was made available by EM-20 in FY 2007.  An additional three projects were selected for funding using a similar peer review process.

All of the selected projects are targeted at one of four major Hanford Site groundwater contaminants: hexavalent chromium, Sr-90, carbon tetrachloride, and uranium.  The original nine projects were initiated in late FY 2006, and the three supplemental projects began in late FY 2007.

## GROUNDWATER CONTAMINATION AT THE HANFORD SITE

The Hanford Site is a former nuclear-defense production facility that was acquired by the federal government in 1943 and operated into the 1980s.  A number of groundwater contaminant plumes exist at the site as the result of former operations.

The Hanford Site is located within the Pasco Basin of south-central Washington State.  Due to the rain shadow of the Cascade Range, the climate of the Pasco Basin is semiarid (approximately 15-cm rainfall per year).  In most areas, the depth to the water table ranges from 15 to 90 m.  The Columbia River flows through the northern part of the site and forms part of the site's eastern boundary.  The unconfined aquifer consists largely of fine sands, sands, gravels, and cobbles of glacial and fluvial origin.  Virtually all groundwater underlying the Hanford Site ultimately flows into the Columbia River.

The groundwater contaminant plumes originated from a combination of purposeful discharges of wastewater to cribs, trenches and ponds, along with some accidental leaks and spills.  Currently, the most widespread contaminants are tritium, nitrate and I-129.  However, some of the smaller plumes along the river shore, particularly hexavalent chromium, Sr-90, and uranium, are considered to pose a greater threat to the Columbia River (Fig. 1).  There are also groundwater plumes of carbon tetrachloride, Tc-99, uranium, and hexavalent chromium, which may eventually migrate to the river, but continue to remain at a significant distance.

Groundwater remediation at the Hanford Site is conducted under the *Comprehensive Environmental Response, Compensation, and Liability Act* (CERCLA [1]) regulations [2].  Currently, there are four pump-and-treat systems targeted at hexavalent chromium contamination.  Two of the pump-and-treat systems are in the 100-HR-3 Operable Unit and two are in the 100-KR-4 Operable Unit.  Additionally, a permeable reactive barrier for hexavalent chromium contamination, called the In Situ Redox Manipulation (ISRM) Barrier, is located in the 100-HR-3 Operable Unit.
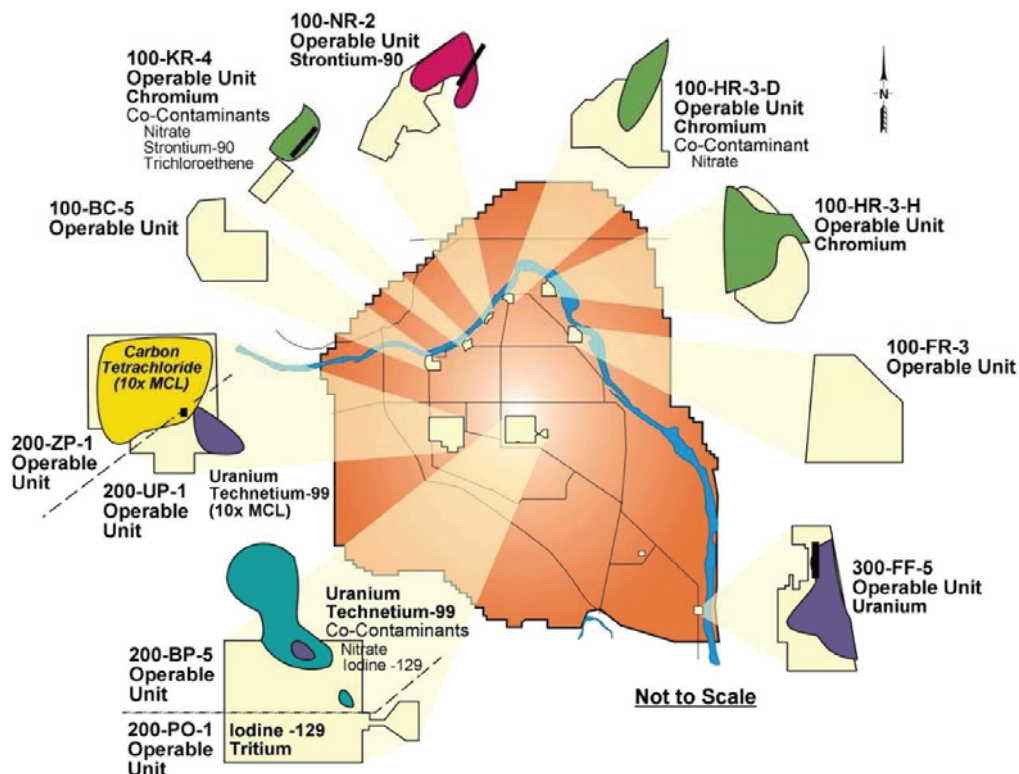
**Fig. 1. Map showing the location of groundwater contaminant plumes and *Comprehensive Environmental Response, Compensation, and Liability Act* operable units at the Hanford Site.**

There is also a pump-and-treat system in the 200-ZP-1 Operable Unit targeted at carbon tetrachloride contamination. Recently, there was a pump-and-treat system for Sr-90 at the 100-NR-2 Operable Unit and another at the 200-UP-1 Operable Unit targeted at uranium and Tc-99 contamination. However, both of these systems are currently on standby. The current remediation treatment for uranium at the 300-FF-5 Operable Unit is natural attenuation. Finally, there is an ongoing treatability test for a permeable reactive barrier at the 100-NR-2 Operable Unit targeted at sequestering Sr-90 contamination. All twelve of these selected projects supplement at least one of these current treatment efforts.

**PROJECTS TARGETED AT HEXAVALENT CHROMIUM CONTAMINATION**

An integrated strategy (shown in Fig. 2) has been developed for the treatment of hexavalent chromium contamination in Hanford Site groundwater.

This strategy includes the following objectives as shown in Fig. 2:

- Mend the ISRM barrier by injecting zero-valent iron into areas that show signs of breakdown. Coupled with upgradient bioremediation, longevity of the ISRM barrier will be substantially increased, leading to a final Record of Decision (ROD) (Fig. 2, #1).

- Identify the hexavalent chromium sources for groundwater plumes in the 100-D Area. This information will be used to remediate the source(s), which will also accelerate groundwater cleanup and lead to a finalized ROD (Fig. 2, #2).
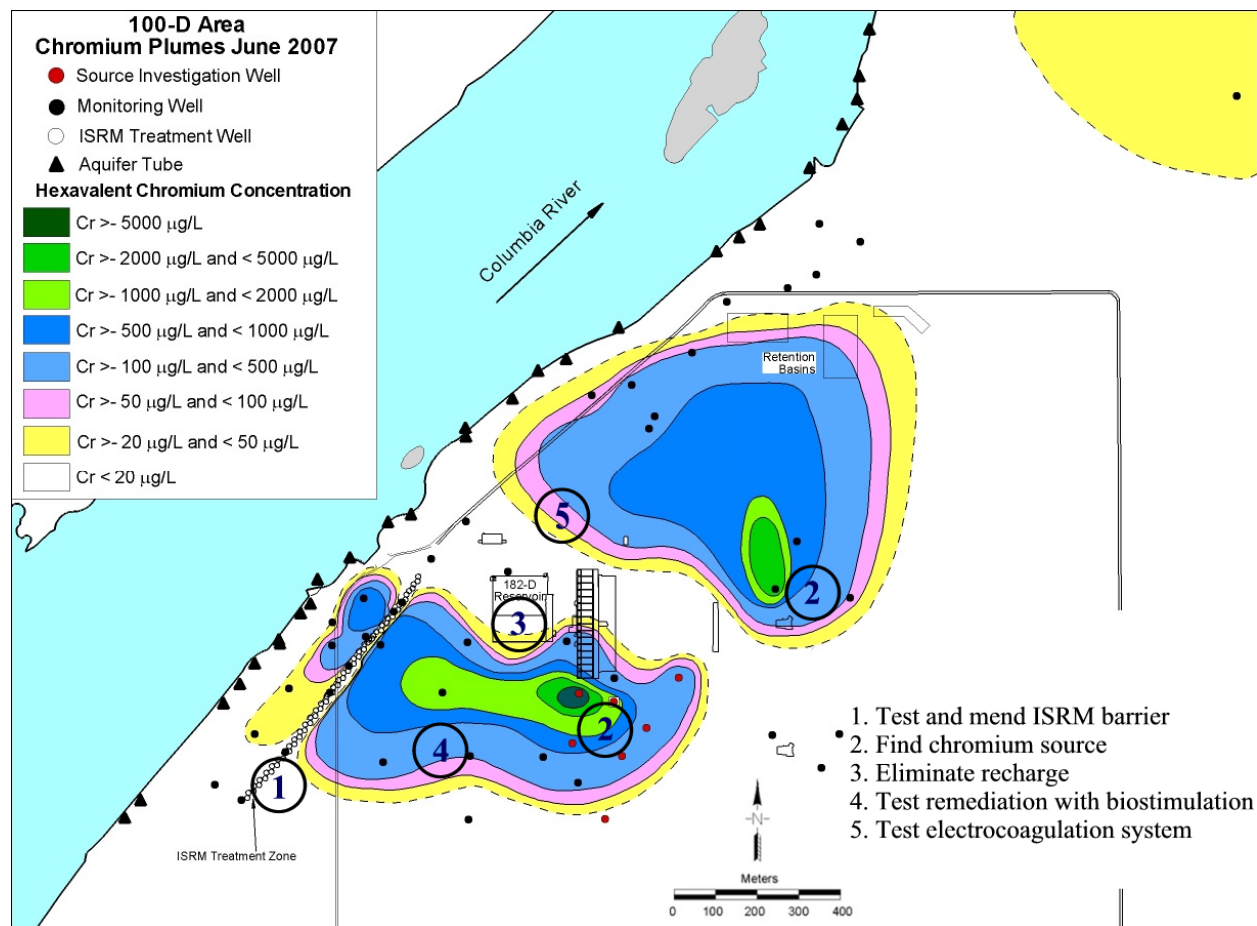
**Fig. 2. Map showing the integrated approach to the hexavalent chromium groundwater plume at the 100-D Area, Hanford Site.**

- Characterize the geochemistry of hexavalent chromium sources in the vadose zone (Fig. 2, #2).

- Continue to prevent future groundwater contamination by reducing artificial recharge; e.g., remove or repair leaking water lines (Fig. 2, #3).

- Increase the pace of groundwater remediation by extracting and treating significantly more groundwater. The existing ion-exchange technology may not be cost effective for treating higher volumes of more concentrated chromium; therefore, alternative technologies need to be tested.

- Remediate waste sites along the Columbia River by 2012 through the Hanford Site River Corridor contractor.

In this integrated approach to chromium cleanup, three innovative technologies will be deployed in the 100-HR-3 Operable Unit (Fig. 2, #1, 4a, and 4b). In addition, the location and characterization of the hexavalent chromium sources will be supported by EM-22. Waste site remediation, recharge reduction, and additional source characterization are supported by Hanford Site baseline funding (DOE, RL-30).

**Injecting Iron into the Aquifer**

Beginning in 1999, the In Situ Redox Manipulation (ISRM) barrier was installed to remediate a chromium groundwater plume in the 100-D Area at the Hanford Site. Using a network of 65 wells to access the groundwater, the ISRM technology was used to create a reducing zone in the aquifer by injecting sodium dithionite. This chemical reduced the native ferric iron [Fe(III)], which is naturally present in the aquifer sediments, to ferrous iron [Fe(II)]. When groundwater contaminated with hexavalent chromium flows through the ISRM barrier, it is converted to trivalent chromium [Cr(III)] by the reoxidation of Fe(II). Trivalent chromium is virtually immobile in water and much less toxic than Cr(VI). Localized signs of failure were discovered in the barrier after only 18 months. Although some of these wells were reinjected with sodium dithionite in 2002 to maintain the effectiveness of the barrier, several wells began to show signs of failure again in less than 2 years. Approximately 20 wells within the barrier have lost a significant amount of reductive capacity only a few years after installation.

This project will test a new method to mend the ISRM barrier by injecting zero-valent iron (ZVI) into the most permeable zones of the barrier through existing injection wells. Laboratory tests [3, 4] have demonstrated that a slurry of ZVI and polymer can be injected into sediments and remain in suspension for a distance of over 1 m. At this distance, ZVI concentrations are approximately 0.6 wt%. The goal of this test is to emplace ZVI into the formation at least 7 m from the injection well, which would result in overlapping treated zones between the ISRM wells, which are 12 m apart. Laboratory tests indicate that ZVI emplaced by injection will not cause a long-term reduction in the conductivity of the formation.

The iron injection technology is ideally suited to mending the ISRM barrier because the ZVI can be injected into the preferential pathways that exist in the 100-D Area aquifer. These pathways, the result of natural physical heterogeneity within the aquifer, are the most likely cause of premature barrier breakdown because groundwater flowing through the pathways may flush large quantities of oxic water rapidly through the treatment zone, thereby reducing its reductive capacity and longevity of the barrier [5]. Emplacing ZVI directly into these pathways will significantly augment the reductive capacity of the ISRM barrier and increase its longevity.

Laboratory testing is being performed to determine the most suitable ZVI material for this application. These include 1) batch tests to determine the ability of the candidate materials to remove chromium from a mixture of silica sand and water; 2) column injection tests to evaluate changes in the permeability, the amount of iron that can be injected into soils, and the physical stability of the iron subjected to simulated groundwater flow after injection; and 3) column geochemistry tests to assess reactivity of the different ZVI materials. The tests began with 8 iron compounds chosen from a matrix of 30 commercially available ZVI materials with diameters between 1 nm and 50 μm. At each stage of testing, some of these compounds were eliminated because they did not meet the test criteria (e.g., low reactivity, poor injectability).

After identification of the most suitable iron compound(s), preparations will be made to inject the ZVI into two ISRM wells that have shown signs of premature loss of reductive capacity. After injection, verification samples of aquifer materials will be collected to evaluate the effective radius of injection and the distribution and abundance of iron. Groundwater samples will also be periodically collected to verify that Cr(VI) is being reduced to Cr(III) in the test area and to evaluate longevity of reducing conditions.

**Refine Location of the Chromium Source**

Sodium dichromate was added to the cooling water for Hanford Site production reactors as a corrosion-prevention agent. Concentrated solutions of sodium dichromate were delivered to the Hanford Site in rail tank cars for this purpose. Some of these railcars likely leaked or dichromate solutions spilled

during handling.  Subsurface pipelines also transported concentrated sodium dichromate over hundreds of meters to water treatment systems, increasing the potential of chromate being introduced to the vadose zone and subsequent migration to the groundwater.  Although most dichromate use ended in the 1960s, residual concentrations in the vadose zone are apparently still serving as sources for the current hexavalent chromium groundwater contaminant plumes.  Given the myriad of opportunities to inadvertently introduce chromium solutions to the vadose zone, and the uncertainty surrounding the location of spills and leaks, finding the locations of chromium in the vadose zone has been difficult.

Under this project, seven wells were installed in February and March 2007, with the goal of localizing the source area of the southwestern chromium plume in the 100-D Area (see Fig. 2) by monitoring groundwater concentrations and flow directions.  Two of the seven wells tapped areas of the aquifer with groundwater concentrations in excess of 6,000 µg/L.  A groundwater sample from one of these wells had Cr(VI) concentrations over 14,000 µg/L.  None of the vadose zone soil exhumed in this or previous studies has contained significantly high concentrations of hexavalent chromium despite drilling directly through a transfer facility where chromate was pumped from tanker cars to the pipelines via flexible hoses.

Study results have been used to refine the location of the vadose zone source for the southwest plume in the 100-D Area to approximately 2 ha.  Four more wells are planned to be drilled in this vicinity to further refine the source, with the goal of refining the source area to 1 ha.

In FY 2007, EM-22 funded three additional projects to analyze contaminant migration.  One of these was to investigate vadose zone source(s) feeding the northern chromium groundwater plume at the 100-D Area (Fig. 2).  Two facilities near the proximal portion of this plume processed highly concentrated (6M) sodium dichromate, and yellow staining indicative of chromate at fairly high concentrations has been observed on the foundations of one of the facilities.  This investigation, to begin the winter of 2008, will utilize an innovative push-technology to collect samples in the shallow and intermediate vadose zone in an attempt to directly find the source(s).  Three groundwater wells will also be installed to assist in source location.

**Chromium Vadose Zone Characterization and Geochemistry**

The reduction of Cr(VI) to Cr(III) can occur in the presence of aqueous and sorbed Fe(II), reduced sulfur compounds, soil organic matter, and via microbial processes [6 and references therein; 7, 8].  However, the Hanford Site vadose zone is an oxic, very low organic-carbon content oligotrophic environment, and any substantive microbial reduction of Cr(VI) requires major additions of both $NO_3^-$ and organic carbon [9].  While there are minerals bearing ferrous iron Fe(II) on the Hanford Site and upper Ringold Formations, researchers [6] previously demonstrated no retardation of Cr(VI) occurred in these sediments except after pretreatment with a strong (0.5 M HCl) acid.  Similar studies with these sediments demonstrated no Cr(VI) retardation in the absence of a strong base (simulating the leaching of highly alkaline, saline underground storage tank leaks) [10, 11].  In both of the latter cases, Fe(II) solubilized by mineral dissolution (acid or base) subsequently reduced Cr(VI) to Cr(III).  Therefore, low pH stock dichromate solutions spilled/discharged to the ground could result in solubilization of ferrous iron from dissolution of Fe(II)-bearing mineral phases.

The primary objectives of this study are to 1) determine the leaching characteristics of Cr(VI) from contaminated sediments collected from 100 Area spill sites; 2) elucidate possible Cr(VI) mineral and/or chemical associations that may be responsible for Cr(VI) retention in the Hanford Site 100 Areas through the use of macroscopic solubility studies and microscale characterization of contaminated sediments; and 3) from these data, construct a conceptual model of Cr(VI) geochemistry in the 100 Area vadose zone.

During FY 2007, hexavalent chromium-contaminated sediments were collected from the 100 B/C Area and the 100-D Area at the Hanford Site.  Some sediments in the cores were freshly contaminated from pipeline leaks.  Other sediments were contaminated up to 40 years ago, and represented aged contamination.  Various column-leaching experiments were completed on the core sediments.  In all column-leaching studies, the majority of hexavalent chromium was released in the first pore volume, indicating that it remains highly soluble and mobile.  However, at least some tailing was observed in all of the columns.  The leaching behavior from sediments of common provenance sometimes exhibited different behavior, and the amount of tailing did not correlate well with the age of the spill.  Column experiments were also conducted in which fresh hexavalent chromium solution was introduced.  In all cases, the retardation coefficient was close to 1, showing that fresh hexavalent chromium acts as a conservative tracer.  This behavior was independent of the influent concentration of chromium on the solutions.  The next step in this project is to characterize the form of the hexavalent chromium in the various sediments using various techniques.

**Treatment of Chromate in Groundwater Using Electrocoagulation**

Groundwater at the 100-D Area, located at the Hanford Site, is contaminated with hexavalent chromium.  Remediation of chromate in the 100-D Area currently includes the operation of two pump-and-treat systems to extract groundwater for treatment.  Hexavalent chromium is removed from extracted groundwater using ion-exchange resin and the effluent is re-injected into the aquifer.  The current treatment capacity of the existing systems is approximately 600 L/minute.  As part of an effort to accelerate remediation of the chromium plume, pump-and-treat extraction rates may be increased up to 2,000 L/minute.  Using ion exchange at this treatment rate and likely higher concentrations than currently treated may not be the most cost-effective practice.

Electrocoagulation is an alternative treatment technology that may effectively and efficiently remove hexavalent chromium from the process stream at the desired flow rate.  This technology typically utilizes a sacrificial anode of iron, which corrodes and releases iron into solution;  in this case, groundwater pumped through the reaction chamber.  This reduces the water and initiates the coagulation process typically forming hydroxide complexes.  A treatability test was performed in 2007 at a rate of approximately 200 L/minute to verify the efficacy of electrocoagulation to remove hexavalent chromium from extracted groundwater.  This test demonstrated that electrocoagulation can treat groundwater to below a concentration of 20 µg/L hexavalent chromium.  Plugging of the injection wells was experienced during the test, owing to the addition of physical and/or chemical constituents from the electrocoagulation process.  A report on the results is being prepared that will include removal efficiency of electrocoagulation, causes of injection well plugging, documentation of treatment costs, and evaluation of the solid waste stream generated during treatment.

**PROJECTS TARGETED AT STRONTIUM-90 CONTAMINATION**

The remediation approach to Sr-90 at the 100-N Area includes a combination of an apatite sequestration barrier and phytoremediation in the riparian zone (Fig. 3).
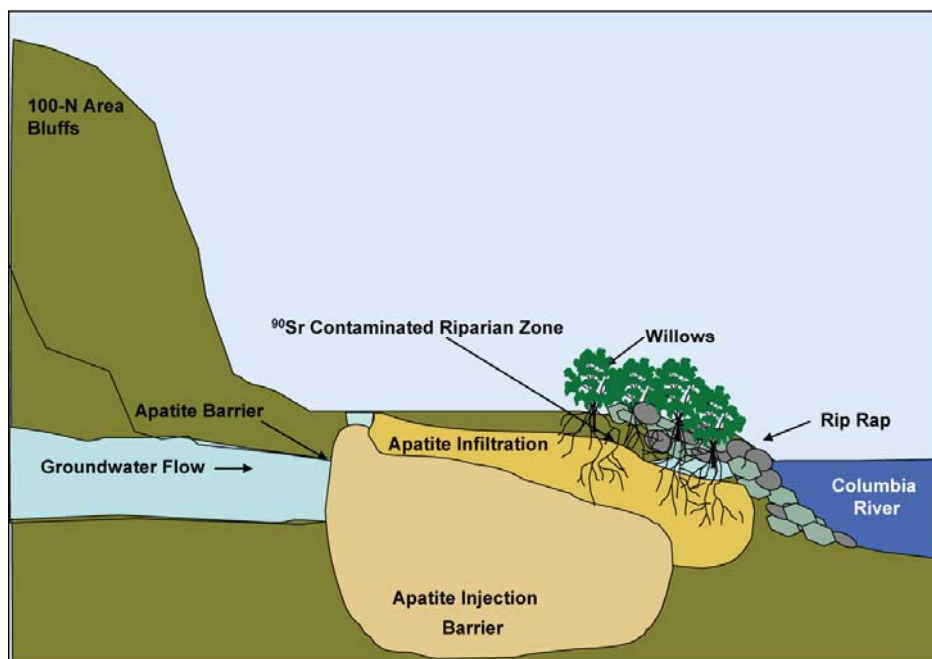
**Fig. 3.  Approach to Sr-90 remediation at the 100-N Area located at the Hanford Site.  Illustration shows sequestration of Sr-90 subsurface contamination by surface infiltration of an apatite solution.**

The Sr-90 discharge from past-practice liquid waste disposal sites at the 100-N Area resulted in Sr-90 release to the groundwater, Columbia River, and biota on the river bank.  Although liquid discharges were terminated in 1993, Sr-90 adsorbed on aquifer solids remains as a continuing source to the Columbia River.  As a result of Sr-90 radioactive decay and adsorption, only the Sr-90 within the near river environment is at risk to discharge to the river, so the inland pump-and-treat system that removes Sr-90 does not reduce potential discharge to the river.  A 90-m apatite permeable reactive barrier test wall near the shore was installed in FY 2006 and 2007.  Strontium-90 sequestration by this technology occurs by injection of Ca-PO$_4$-citrate solution, in situ biodegradation of citrate resulting in apatite [Ca$_6$(PO$_4$)$_{10}$(OH)$_2$] precipitation, adsorption of Sr-90 to the apatite, and then apatite recrystallization with Sr-90 substitution for Ca (permanent) with radioactive decay of Sr-90.  Laboratory-scale studies have quantified the sequential processes of this technology in 100-N Area sediment.  Because most (60 to 70%) of the Sr-90 contamination is in the shallow, variably saturated Hanford formation, the most efficient means of treating this zone may be surface infiltration of the apatite solution.

Primary objectives of this project are to develop an infiltration strategy that defines apatite solution precipitation rate and strontium sequestration processes under variably saturated (low water content) conditions, and with variable apatite concentrations.  Laboratory studies have demonstrated that 1) apatite precipitation occurs under variable water saturation; 2) the small mass of apatite precipitate formed can be measured by multiple methods; and 3) Sr-90 is slowly incorporated into the apatite structure.  The apatite precipitation rate is controlled primarily by the in-situ biodegradation of citrate, where the initial Ca-citrate complex prevents immediate precipitation of apatite.  Citrate degradation to CO$_2$ quantified over a range of initial citrate concentrations (5, 10, 25 and 125 mM) and water saturation of the sediment (35 to 100%) generally showed no consistent trends between water content and the mineralization rate or extent.  At low citrate concentration (5 to 10 mM), mineralization rates were slower at water saturations below 65%.  The 48- to 70-hour citrate degradation half-life (at aquifer temperature and sediment/water ratio) provides sufficient time for the infiltrating solution to reach the location where apatite precipitate is needed.  Although microbial biomass decreases by five orders of magnitude with depth, transport of

shallow in situ microbes and biomass associated with the river water used during infiltration results in citrate biodegradation rates that vary by less than one order of magnitude. Apatite precipitate in sediment was characterized by electron microbe analysis with elemental phosphorous and calcium detection, aqueous phosphate extraction of sediment, and fluorescence detection of substituted apatite. Sr-90 substitution in apatite was measured by sequential aqueous extractions to measure Sr-90 adsorbed on the sediment, Sr-90 adsorbed on the apatite, and finally (with acid dissolution of the apatite) Sr-90 incorporation in apatite. Long-term experiments showed that the half-life for Sr-90 incorporation into apatite was 5.5 to 16 months.

The 1-D and 2-D laboratory infiltration experiments quantified the spatial distribution of apatite that formed during solution infiltration. The 1-D infiltration studies demonstrated that zones of higher apatite formation resulted where there was sufficient residence time (and higher water saturation) of the Ca-citrate-PO4 solution. The 2-D infiltration studies in progress are evaluating the vertical and unconstrained lateral infiltration of the Ca-citrate-PO4 solution and resulting spatial distribution of apatite formation in heterogeneous systems. Factors that control the spatial distribution of apatite include adsorption/precipitate of injected phosphate, the rate of citrate biodegradation, and microbial transport processes. Preliminary 2-D experiments show the apatite precipitate concentrated in the upper third of the area of solution infiltration, indicating the infiltration rate was slower than the apatite precipitation rate. Because it is hypothesized that there are likely higher concentrations of Sr-90 in low-K zones of the vadose zone, 2-D experiments are focused on the spatial distribution of apatite that precipitates in these low-K zones. The 2-D experiments have demonstrated that changes in the infiltration rate can be used to manipulate the spatial distribution of the solution within low-K zones. Through the development of an understanding of the apatite-forming processes, evaluation of infiltration tests in laboratory 1-D and 2-D flow systems, and reactive transport modeling, study results will be used to design an efficient and effective infiltration strategy that will be tested at a field scale.

**Phytoremediation - Treatability Study along the 100-N Riparian Zone**

Sr-90 exceeds the U.S. Environmental Protection Agency's drinking water standards for groundwater (8pCi/L) by as much as a factor of 1000 at several locations along the 100-N Area. Sr-90 is present in the aquifer near the Columbia River and within the vadose zone of the river's shoreline at the 100-N Area. A radiological survey of shoreline vegetation along the Hanford Reach identified areas where the vegetation exhibited elevated levels of radionuclides. Of major concern was the 100-N Area where elevated Sr-90 was found in a number of vegetative species [12, 13, 14].

The bulk of the Sr-90 in the sediments between the bluffs and the river's edge (about 30 m) is bound to the sediments in a relatively thin layer that corresponds to the top of the elevated water table formed during the period of active disposal from 1963 to 1991 and the current water table. The layer of contaminated vadose zone is fairly shallow, between 1- and 3-m thick. The riparian zone, approximately 10 m in width, is shallow (0.2 to 1.5 m) and contains approximately 1 Ci of Sr-90. Sr-90 (both stable and fission product) is held by the soil/sediment primarily via an ion-exchange mechanism that retards Sr-90 transport [15]. Its sorption coefficient, or $K_d$, is between 15 mL/g to 40 mL/g, which means approximately 99% of the Sr-90 is sorbed to the sediment with 1% associated with the groundwater.

Phytoremediation is a managed, remediation technology in which plants or integrated plant/rhizosphere systems are employed to extract and/or sequester soil contaminants [16]. Recent greenhouse and growth chamber studies have demonstrated the viability of phytoextraction to remove Sr-90 from this area's soil and water; in conjunction with monitored natural attenuation and an apatite barrier, the process would make an effective treatment for remediation of the 100-N Area Sr-90 plume.

During FY 2007, a demonstration plot consisting of 66 coyote willow (*salix exigua*) starts was constructed in March 2007 along the banks of the Columbia River at the Hanford Site 100-K Area.  The experiment was a cold test; i.e., the area chosen for the test was not contaminated by Sr-90, nor any other radionuclide.  Fertilization was by tree fertilizer spikes driven into the ground.  The area was surrounded by a chain-link fence to discourage mammalian herbivores.  All of the willow starts sprouted.  At this particular site, the willows were at least partially submerged for at least 12 hours a day from planting in March through the month of June.  At times, they were totally submerged.  The plants were harvested (all leaves and branches removed) in three stages during July, September, and October.  Harvesting is a strategy that would be used during actual remediation of Sr-90 to prevent leaf drop from spreading contamination.  The willow shrubs recovered quickly after harvesting, with new shoots and leaves visible after a few weeks.  The recovered leaves and twigs were weighed after each harvest to determine biomass production.  The more frequent than planned submergence did appear to have a negative effect on growth rate.  Biomass production in the field varied between 40% to 75% of that achieved in previous greenhouse studies.  The field study will continue in FY 2008 to determine growth during the second year.

Predation by herbivores is a possible mechanism for spreading Sr-90 contamination absorbed by the coyote willows.  Although larger herbivores can be excluded from the shrubs through engineering and procedural controls, the close proximity of the Columbia River prohibits the use of pesticides to control insects that feed on plant tissue during their life cycles.  Further, insects are capable of transporting the contaminant for large distances before they may be subject to predation.  Therefore, a new project to study the effects of feeding by phytophagous insects was initiated during FY 2007.  The primary project objective is to evaluate the potential for offsite food-chain transfer of Sr-90 from plants that may be growing in contaminated soil on the shoreline of the 100-N Area at the Hanford Site.

Potential pathways of contaminant transfer can occur in specific stages of an insect's life cycle, including several stages post-hatching from their eggs.  In addition, different insect species may have unique methods of plant tissue consumption that could affect their ability to carry the material offsite.  Therefore, specific objectives include the potential for food-chain transfer in 1) sucking insects; 2) the larval stages of Lepidoptera, which may ingest large quantities; and 3) mobile adults that may spend long periods consuming the contaminated tissue.

The following four work elements will form the scientific basis for the study of proposed food-chain transfer potential of phytoremediation of Sr-90 along the Columbia River's riparian zone.  These work elements are 1) soil, plant, and insect colony preparation; 2) uptake by sucking insects (aphids); 3) uptake during the larval stage  (caterpillars) by Lepidoptera species; and 4) data analysis and report preparation.

**PROJECTS TARGETED AT URANIUM CONTAMINATION**

**300 Area Uranium Plume Treatability Demonstration Project:  Uranium Stabilization Through Polyphosphate Injection**

A groundwater plume containing uranium from past-practice discharges of liquid waste associated with nuclear fuel-fabrication activities has persisted beneath the 300 Area for many years.  The uranium plume is upstream of the City of Richland municipal water supply intake on the Columbia River.  In addition, elevated uranium concentrations enter the river along the shoreline and enter the riparian and river biota through seeps.  The 1996 Record of Decision (ROD) [17] for the 300-FF-5 Operable Unit stipulated an interim action program of natural attenuation process accompanied by increased groundwater monitoring.  The remedial action objective of the ROD is to lower the concentration of groundwater uranium to the U.S. Environmental Protection Agency's maximum contaminant level concentration of 30 µg/l.  Despite the cessation of uranium releases and the removal of shallow vadose zone source materials, the second 5-year review of the ROD stated that as of 2006, dissolved uranium concentration below the cleanup criteria

established by the ROD has not been achieved within the anticipated 10-year time period. A Phase III Feasibility Study was initiated in 2005 to identify and evaluate remedial alternatives that will accelerate monitored natural attenuation of the uranium plume. Polyphosphate application is judged to be the most promising among five other active remedial technologies for uranium at this site. Presently, a focused application of polyphosphate is proposed in source or "hot spot" areas to reduce the inventory of available uranium that contributes to the groundwater plume (Fig. 4) through direct precipitation of uranyl-phosphate solids and secondary containment via precipitation of apatite acting as a long-term sorbent for uranium [18, 19, 20, 21].
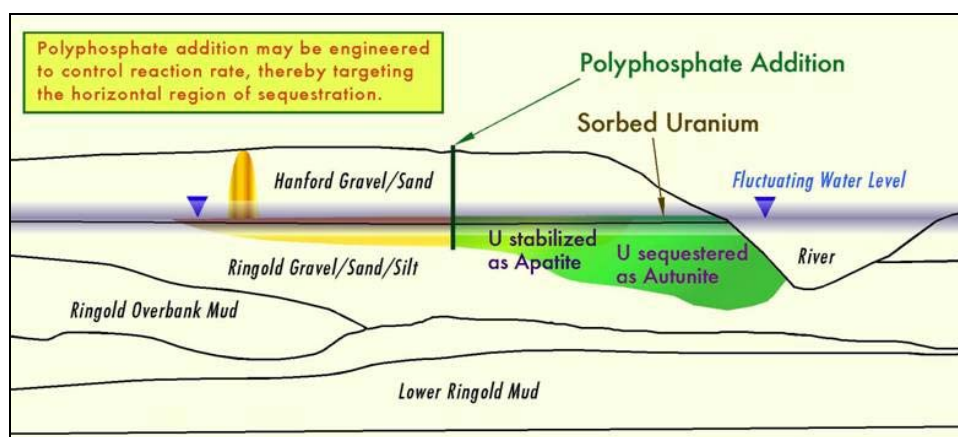


**Fig. 4. Schematic depicting the 300-FF-5 Operable Unit geology and the treatability test of polyphosphate to sequester uranium.**

The objective of the proposed treatability test is to evaluate the efficacy of using polyphosphate injections to treat uranium-contaminated groundwater in situ. A test site consisting of an injection well and 15 monitoring wells was installed in the 300 Area near the process trenches that had previously received uranium-bearing effluents. In December 2006, a tracer test was conducted using a bromide tracer. The tracer test showed that groundwater velocities in this area were very high at approximately 15 m per day. The laboratory tests were completed in May 2007 and test results were used to devise a test formulation. In June 2007, approximately 3.8 million L of test solution were injected. The initial results of this treatability test looked promising with respect to direct treatment of uranium by polyphosphate injection, with concentrations in most monitoring wells located within a radial distance of 23 m reduced to well below the drinking water limit. The results of the test injection continue to be monitored.

The remediation of uranium in the 300 Area aquifer does not address a potential continuing source in the deep vadose and smear zones above the aquifer. Therefore, a new project was initiated to examine whether the polyphosphate approach could be used to treat uranium contamination in the vadose zone as well. The objective of this investigation is to evaluate the efficacy of using polyphosphate infiltration either from ground surface or some depth of excavation to stabilize (in situ) uranium within the deep vadose and zone of the water-table fluctuation above, and over the upper portion of the 300 Area aquifer. Source treatment in the deep vadose zone will accelerate the natural attenuation of uranium to thermodynamically stabilize uranium-phosphate minerals, enhancing the performance of the proposed polyphosphate remediation in the 300 Area aquifer. The approach used in this investigation will consist of a combined laboratory and intermediate-scale experimental approach which includes the following elements summarized in the following subsections.

**Behavior of Polyphosphate Amendment Under Unsaturated Conditions.** Objective:  1) Quantify the effect of hydraulically unsaturated conditions on the degradation and mobility of polyphosphate.

**Interaction of Polyphosphate with Calcite-Bound Uranium.**  Objectives:  1) Identify the mechanism of interaction between polyphosphate and calcite-bound uranium; and 2) quantify the rate of autunite formation via the reaction of polyphosphate with calcite-bound uranium.

**Effect of Polyphosphate on Uranium Mineralogy.**  Objectives:  1) Identify the mechanism of interaction between polyphosphate and uranium minerals existing in the 300 Area; 2) quantify the rate of autunite formation via the reaction of polyphosphate with uranium minerals; 3) evaluate the effect of chemical microenvironments on the mechanism and rate of polyphosphate hydrolysis and autunite formation (e.g., adjacent to calcite versus quartz); and 4) quantify the effect of periodic wet-dry cycling on the transformation of existing uranium minerals to autunite.

**Autunite Solubility.**  Objective: Quantify the solubility of autunite as a function of water activity ranging from hydraulically saturated conditions to water activities representative of the vadose zone.  Results of this task will establish reliable equilibrium solubility values for autunite under hydraulically unsaturated conditions, allowing accurate prediction of the long-term stability of autunite, and thereby assess the performance of polyphosphate remediation within the vadose zone and capillary fringe.

**Effects of Sediment Type and Infiltration Characteristics on Vadose Zone Polyphosphate Transport.**  Objective:  Quantify the effects of sediment properties and infiltration type, volume, and concentrations on polyphosphate transport in meter-scale columns experiments.

## PROJECT TARGETED AT CARBON TETRACHLORIDE AND CHLOROFORM CONTAMINATION

Between 1955 and 1973, an estimated 750,000 kg of carbon tetrachloride were discharged to the soil in the 200 West Area of the Hanford Site as part of the plutonium production process.  Of this amount, some carbon tetrachloride reached the groundwater more than 70 m below the ground surface and formed a plume of 10 km$^2$.  Recent information has shown that the carbon tetrachloride plume extends to a depth of at least 60 m below the water table.  Some carbon tetrachloride has degraded either by the original process or subsequent transformations in the subsurface to form a coexisting chloroform plume.

Although current characterization efforts are improving the conceptual model of the source area, more information is needed to effectively assess the fate and transport of carbon tetrachloride and chloroform to support upcoming remediation decisions for the plume.  As noted in a simulation study [22], parameters describing porosity, sorption, and abiotic degradation have the largest influence on predicted plume behavior.  The new project will improve the ability to predict future plume movement by better quantifying abiotic degradation mechanisms and rate.  This effort will help define how much active remediation may be needed and estimate where the plume will eventually stabilize—key factors in determining the most appropriate remedy for the plume.

Previous determinations of the hydrolysis rate for carbon tetrachloride in water (i.e., homogeneous hydrolysis) have been made [23, 24], but they involved experiments at high temperatures (>70$^{\circ}$C).  Arrhenius parameters developed from these data were used to extrapolate the hydrolysis rate to ambient groundwater temperatures.  However, the uncertainty in these values is so large that the current information is not sufficient to determine whether the attenuation rate by hydrolysis will have a significant impact on the plume.

The primary objectives of this project are to 1) determine the neutral and base-catalyzed homogeneous hydrolysis rates for chloroform under near-ambient temperatures; 2) determine the impact and mechanisms of representative Hanford Site mineral surfaces on the hydrolysis of carbon tetrachloride at near-ambient temperatures; and 3) determine the impact and mechanisms of representative Hanford Site mineral surfaces on the neutral and base-catalyzed hydrolysis of chloroform at near-ambient temperatures. During fiscal year 2007, the minerals smectite, illite, anorthite and albite were selected for the mineral surface experiments. All of the mineral experiments were initiated. There is some evidence for a heterogeneous effect for carbon tetrachloride at 50°C. The homogeneous neutral and base-catalyzed experiments were also initiated for chloroform.

## CONCLUSION

Using a peer review process, 12 projects were selected for funding by the U.S. Department of Energy's EM-22 Columbia River Protection Supplemental Technologies Project during FY 2006 and 2007. These projects are targeted at developing new treatment technologies for four of the major groundwater contaminants at the Hanford Site: hexavalent chromium, Sr-90, uranium, and carbon tetrachloride. These new technologies will augment the existing groundwater cleanup technologies at the Hanford Site to accelerate the time table for achieving the remedial action objectives for the various CERCLA groundwater operable units.

## ACKNOWLEDGEMENT

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