

Supplemental Groundwater Remediation Technologies to Protect the Columbia River at  
Hanford, WA

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## **ABSTRACT**

Nine projects have been recently selected by the US Department of Energy (EM-22) to address groundwater contaminant migration at the Hanford Site. This paper summarizes the background and objectives of these projects.

Five of the selected projects are targeted at hexavalent chromium contamination in Hanford 100 Area groundwater. These projects represent an integrated approach towards identifying the source of hexavalent chromium contamination in the Hanford 100-D Area and treating the groundwater contamination.

Currently, there is no effective method to stop strontium-90 associated with the riparian zone sediments from leaching into the river. Phytoremediation may be a possible way to treat this contamination. Its use at the 100-N Area will be investigated. Another technology currently being tested for strontium-90 contamination at the 100-N Area involves injection (through wells) of a calcium-citrate-phosphate solution, which will precipitate apatite, a natural calcium-phosphate mineral. Apatite will adsorb the strontium-90, and then incorporate it as part of the apatite structure, isolating the strontium-90 contamination from entering the river. This EM-22 funded apatite project will develop a strategy for infiltrating the apatite solution from ground surface or a shallow trench to provide treatment over the upper portion of the contaminated zone, which is unsaturated during low river stage.

Uranium in groundwater at the Hanford 300 Area is another environmental concern. Preliminary laboratory tests indicate that it may be possible to inject water-soluble phosphate compounds into the uranium contamination to stabilize it. One of the projects will perform laboratory tests using long-chain polyphosphate materials. Then, a field test will be conducted to determine if it is possible to treat groundwater in the unconfined aquifer at the Hanford 300 Area using polyphosphate materials.

The rates of abiotic hydrolysis of are key parameters needed to predict the movement of carbon tetrachloride and one of its reductive degradation products, chloroform, from the Hanford 200 West Area towards the Columbia River. Current values for these rates have high uncertainty associated with them because they are extrapolated from determinations made at high-temperatures ( $>70^{\circ}\text{C}$ ) to ambient groundwater temperatures ( $\sim 19^{\circ}\text{C}$ ) and have ignored possible contributions from sorptive interactions with sediments. One of the EM-22 projects will improve this situation by measuring the hydrolysis rates at temperatures down to  $20^{\circ}\text{C}$  and in contact with various sediment solids.

## **BACKGROUND**

For fiscal year (FY) 2006, the United States Congress authorized \$10 million dollars to Hanford 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 US Department of Energy Office of Environmental Management (specifically, EM-22). After a peer review and selection process, nine projects have been selected to meet the objectives of the appropriation.

## **GROUNDWATER CONTAMINATION AT HANFORD**

The Hanford Site is a former nuclear defense production facility. The site 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 the former operations.

The Hanford Site is located within the Pasco Basin of south-central Washington. Due to the rain shadow of the Cascade Range, the climate of the Pasco Basin is semiarid ( $\sim 15$  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 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 iodine-129. However, some of the smaller plumes along the river shore, particularly hexavalent chromium, strontium-90, and uranium, are considered to pose a greater threat to the Columbia River (Fig. 1). There are also groundwater plumes of carbon tetrachloride, technetium-99, uranium, and hexavalent chromium, which may eventually migrate to the river but remain at a significant distance from the river. All of the selected projects are targeted at one of four major Hanford groundwater contamination issues, hexavalent chromium, strontium-90, carbon tetrachloride, or uranium. The nine projects were all initiated in late FY 2006.

Groundwater remediation at Hanford is conducted under the *Comprehensive Environmental Response, Compensation, and Liability Act* (CERCLA [1]) regulations [2]. Currently, there are

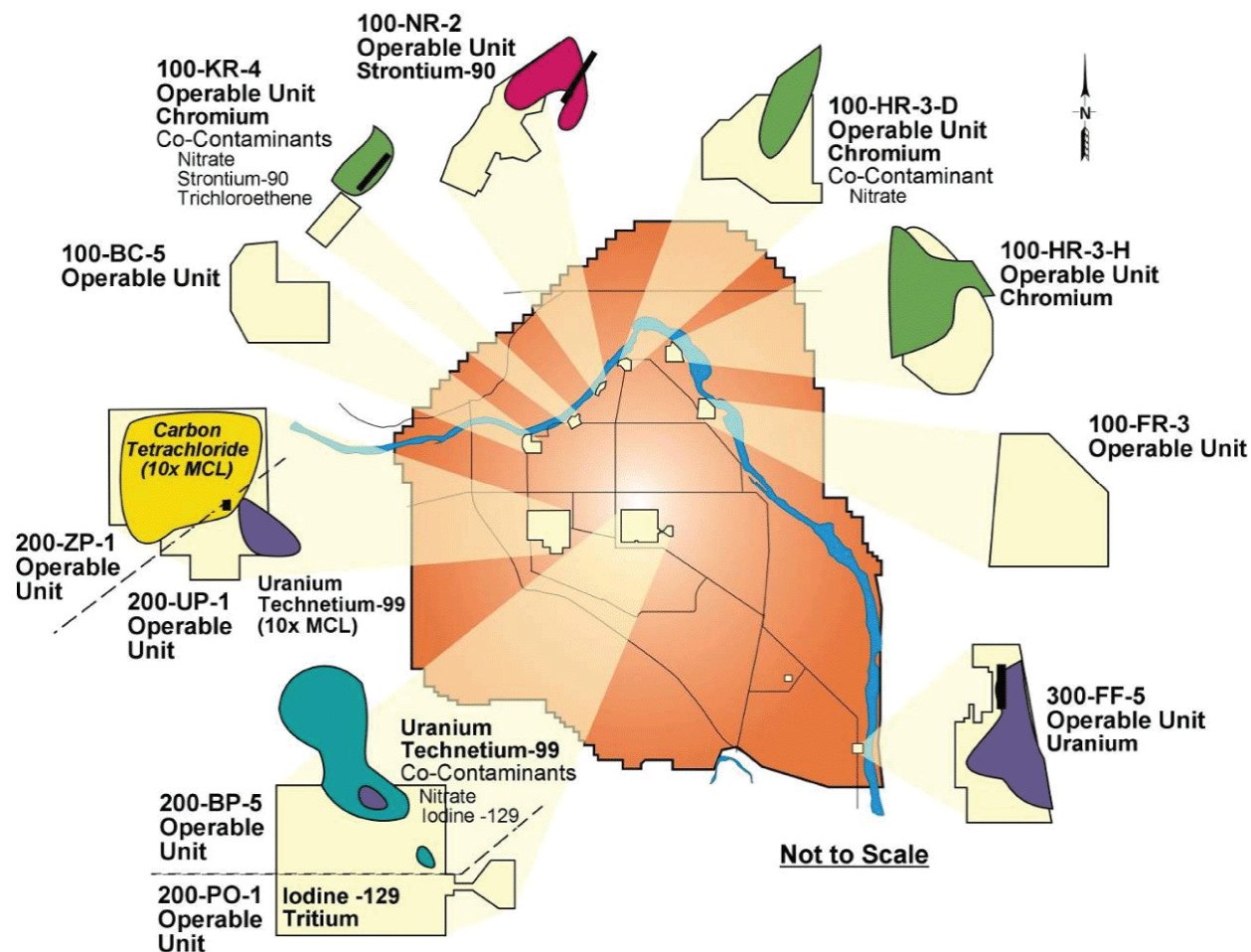


Fig. 1. Map showing the location of groundwater contaminant plumes and CERCLA Operable Units at the Hanford Site.

three 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 one is at the 100-KR-4 Operable Unit. Additionally, a permeable reactive barrier for hexavalent chromium contamination is located in the 100-HR-3 Operable Unit called the In Situ Redox Manipulation (ISRM) Barrier.

There is also a pump-and-treat system in the 200-ZP-1 Operable Unit targeted at carbon tetrachloride contamination. In the recent past, there was a pump-and-treat system for strontium-90 at the 100-NR-2 Operable Unit and another at the 200-UP-1 Operable Unit targeted at uranium and technetium-99 contamination. However, both of these systems are currently on standby. The currently selected remedy 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 strontium-90 contamination. All nine of the selected projects supplement at least one of these current treatment efforts.

## **PROJECTS TARGETED AT HEXAVALENT CHROMIUM CONTAMINATION**

An integrated strategy has been developed for the treatment of hexavalent chromium contamination in Hanford groundwater and includes the following objectives (Fig. 2):

- Mend the ISRM barrier by injecting micron-size 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).
- Find 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 cleanup and lead to a final ROD (Fig. 2, #2).
- 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).
- Immobilize chromium mass and reduce nitrate and dissolved oxygen concentrations in the southwestern plume upgradient of the ISRM barrier. Treatability testing will be conducted for applying in situ biostimulation as a potential low-cost, long-lasting means to provide treatment of chromate and nitrate over a large areal extent upgradient of the ISRM barrier. At least two electron donors will be tested (Fig. 2, #4a).
- Increase the pace of groundwater remediation by deploying an electrocoagulation treatment system that is capable of treating high flow rates and high concentrations of chromium in an expanded pump-and-treat system. The existing ion exchange technology cannot support the more aggressive treatment scheme required to accelerate remediation and will be decommissioned when the new system is in place. The initial system will be online in 2007. After expansion of this new technology, the ion exchange system will be shut down by 2010 (Fig. 2, #4b).
- Remediate waste sites along the Columbia River by 2012 through the 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 and recharge reduction are supported by Hanford baseline funding (DOE, RL-30)

### **Injecting Iron Into the Aquifer**

Beginning in 1999, the ISRM barrier was installed to remediate a chromium groundwater plume in Hanford's 100-D Area. 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

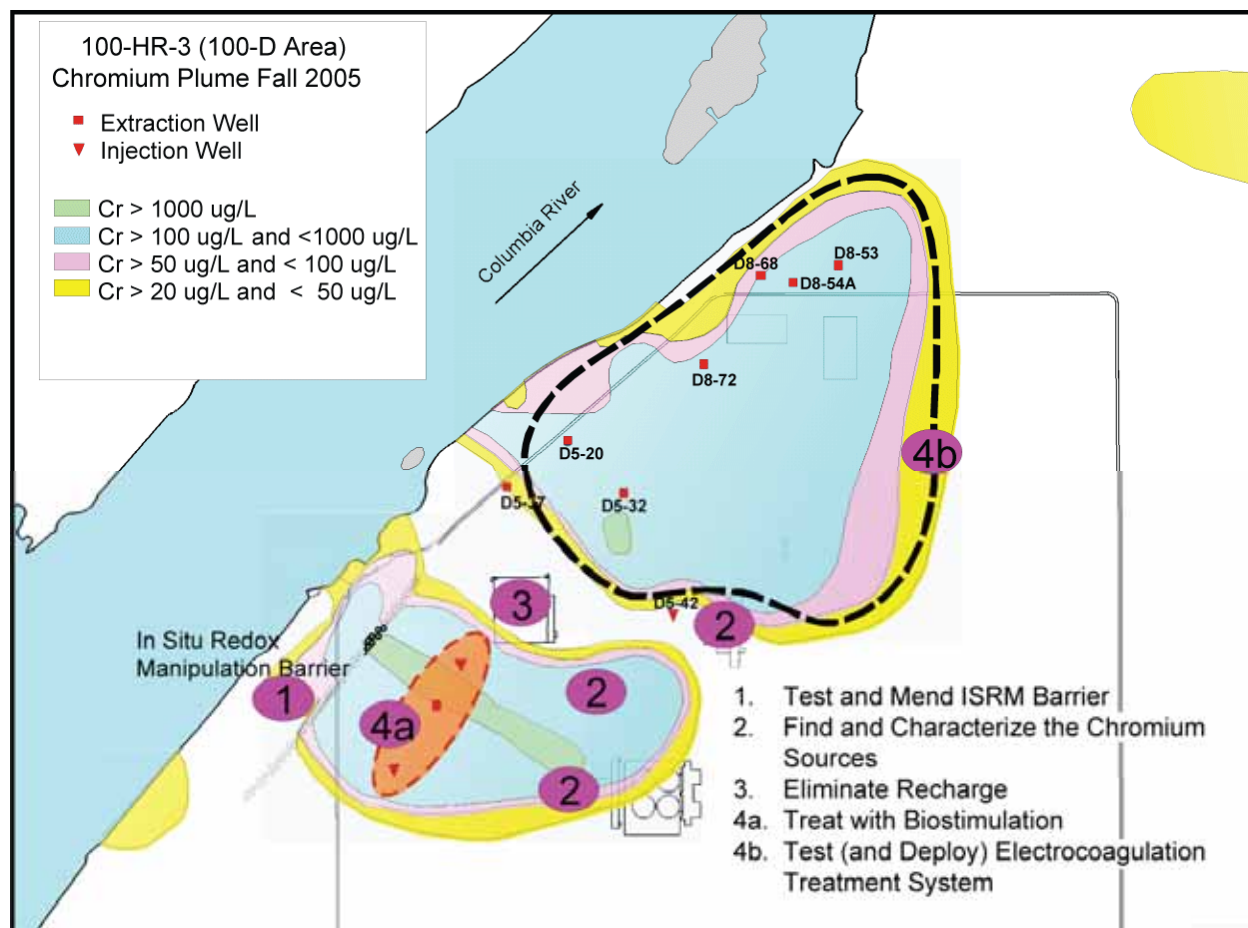


Fig. 2. Map showing the integrated approach to the hexavalent chromium groundwater plume at the Hanford 100-D Area.

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 re-injected with sodium dithionite in 2002 to maintain the effectiveness of the barrier, several of these began to show signs of failure again in less than two years. Approximately 20 wells within the barrier have lost a significant amount of reductive capacity only a few years after installation.

This work will test a new method to mend the ISRM barrier by injecting micron-size zero-valent iron (MZVI) into the most permeable zones of the barrier, together with a shear-thinning fluid containing a polymer. This polymer will aid in the suspension of MZVI and allow it to move further into the aquifer through existing injection wells. Laboratory tests have demonstrated that a slurry of MZVI and polymer can be injected into sediments and remain in suspension for a distance of over 1 m. At this distance MZVI concentrations are approximately 0.6 wt%. The goal of this test is to emplace MZVI 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. Correct formulation of MZVI and polymer should not cause a long-term reduction in the conductivity of the formation.

This technology has never been tested outside of the laboratory and is ideally suited to mending the ISRM barrier because the slurry 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, reducing its reductive capacity and longevity of barrier [9]. Emplacing MZVI directly into these pathways will significantly augment the reductive capacity of the ISRM barrier and increase its longevity.

### **Chromium Vadose Zone Characterization and Geochemistry**

Sodium dichromate was added to the cooling water for the Hanford production reactors as a corrosion prevention agent. Concentrated solutions of sodium dichromate were delivered to Hanford in rail tank cars for this purpose. Some of these railcars leaked or dichromate solutions spilled during handling. 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. Thus, it is important to understand the chemistry and mineralogy of Cr(VI) in the Hanford vadose zone.

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 [3 and references therein; 4, 5]. The Hanford vadose zone, however, is an oxic, very low organic carbon content oligotrophic environment, and any substantive microbial reduction of Cr(VI) requires major additions of both  $\text{NO}_3^-$  and organic carbon [6]. While there are minerals bearing ferrous iron Fe(II) present in the Hanford and Upper Ringold formations, Ginder-Vogel et al. [3] demonstrated no retardation of Cr(VI) occurred in these sediments except after pretreated 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) [7, 8]. In both of the latter cases Fe(II) solubilized by mineral dissolution (acid or base) subsequently reduced Cr(VI) to Cr(III). Hence, low pH stock dichromate solutions spilled/discharged to 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 (i) macroscopic solubility studies and (ii) microscale characterization of contaminated sediments, and (3) from these data construct a conceptual model of Cr(VI) geochemistry in the Hanford 100 Area vadose zone. These objectives are based on locating and obtaining contaminated sediment at different depths and at varying Cr(VI) concentrations. We hypothesize that mineral/chemical-Cr(VI) associations should be related to the total Cr concentration and other master geochemical variables (e.g., pH, counter-cation type and concentration, and water content). In addressing these objectives, additional benefits accrued will be (1) a more complete understanding of Cr(VI) entrained in the vadose zone that can be critical to modeling potential Cr(VI) source terms, and (2) accelerating the Columbia

River 100 Area corridor cleanup by developing remedial action based on a fundamental understanding of Cr(VI) vadose zone geochemistry.

In a companion project, researchers will collect vadose zone samples from the 100-D Area in regions that were likely contaminated by discharge of concentrated sodium dichromate solution to the surface. The boreholes used to obtain the samples will also be completed as groundwater wells and monitored in order to refine the location of the chromium source. Groundwater data will be used in a geostatistical study, coupled with analysis of groundwater flow in the area, to refine a conceptual model for chromium in the vadose zone and groundwater. The dynamic nature of groundwater flow will be considered, using hourly measurements of groundwater levels collected by an automated system. Once the general area of the chromium source is located, different remediation technologies could be applied to reduce it. The first is infiltration of a liquid reductant (e.g., calcium polysulfide) through a drainage field constructed above the source area. This technique has been successfully applied in other areas with chromate contamination. Another technology for reducing hexavalent chromium to trivalent chromium is infusion of a strongly reducing gas (e.g., hydrogen sulfide) into the vadose zone.

### **In Situ Biostimulation**

Although the primary purpose of the ISRM barrier was to immediately protect the Columbia River, additional remediation is required to address the high concentration portion of the chromium plume behind the ISRM barrier and to increase the longevity of the barrier, portions of which have been exhibiting signs of premature breakdown. The proposed method to accomplish this is to use in situ biostimulation to reduce hexavalent chromium and other oxidizing species (i.e., nitrate and dissolved oxygen) and establish a permeable reactive barrier that will continue to treat chromium, nitrate, and dissolved oxygen under natural groundwater flow conditions.

It is clear from monitoring data that the chromium plume is being fed by a continuing source of hexavalent chromium. Locating and remediating this source is a high priority task for the Groundwater Remediation Project. However, even after source remediation the 700-m-long plume will continue to be a threat to the Columbia River. Current modeling predicts it will take at least 40 years for the plume with concentrations > 20 ppb to move through the ISRM barrier, which is well in excess of the 20-year design life of the barrier.

In situ biostimulation has been extensively researched and applied to remediate various contaminants in aquifers over the last 20 years. In situ biostimulation, in the context of this project, is the process of amending an aquifer with a substrate that induces growth and/or activity of indigenous bacteria for the purpose of producing a desired reaction. For application at the 100-D Area, the purpose of biostimulation is to induce reduction of chromate, nitrate, and oxygen to remove these compounds from the groundwater. Chromate can be biologically reduced to insoluble Cr(III) [10] and in situ chromate reduction has been recently demonstrated using polylactate as a substrate at the 100-H Area of Hanford [11, 12, 13, 14]. Nitrate can be biologically reduced using a variety of organic substrates including vegetable oil [15], and in situ nitrate reduction has been demonstrated at the Hanford Site [16]. Biological nitrate reduction occurs as a step process where the initial intermediate degradation product is nitrite. Under some conditions, nitrite concentrations can accumulate during nitrate reduction, and nitrite needs to be

monitored as a potential unwanted product of nitrate reduction. The final desired product of biological nitrate reduction is nitrogen gas. Dissolved oxygen is readily reduced by a wide variety of bacteria in the presence of a wide variety of organic substrates.

Due to the potential for continuing chromate and nitrate sources, upgradient dissolved oxygen and a relatively long (700-m) chromate plume length, the upgradient treatment would also need to be effective over a long period of time (tens of years).

The overall objectives of the treatability test are to (1) demonstrate field-scale reduction of chromate, nitrate, and dissolved oxygen concentrations and the longevity of treatment to evaluate the effectiveness of the process at full scale, (2) demonstrate field scale application of biostimulation to evaluate implementability of the process at full scale, and (3) determine the number of wells, type of substrate, operational strategy, and longevity for biostimulation such that costs for full-scale application can be effectively estimated.

Key biostimulation design parameters associated with these objectives include the radius of influence for injection of the substrate; mass of substrate that can be injected; biomass yield for the substrate; bioreduction yield for chromate, nitrate, and oxygen for the substrate and biomass; and the rate of substrate and biomass depletion. It is also recognized that site-specific hydrogeological characteristics influence the biostimulation design parameters and need to be determined to conduct the treatability test and to determine how the process will be designed for full-scale application.

### **Treatment of Chromate in Groundwater Using Electrocoagulation**

Groundwater at Hanford's 100-D Area 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 567.8 L/minutes. As part of an effort to accelerate remediation of the chromium plume, pump-and-treat extraction rates will be increased up to 1,892.7 L/minute. Using ion exchange at this treatment rate is not feasible.

Electrocoagulation has been identified as an alternative treatment technology that may effectively and efficiently remove hexavalent chromium from the process stream at the desired flow rate. A 189 L/minute treatability test will be performed to verify the efficacy of electrocoagulation to remove hexavalent chromium from extracted groundwater, document treatment cost, collect scale-up data for building a 1,892.7 L/minute electrocoagulation system, and evaluate the solid waste stream generated during treatment.

### **PROJECTS TARGETED AT STRONTIUM-90 CONTAMINATION**

The approach to strontium-90 at the Hanford 100-N Area includes a combination of an apatite sequestration barrier and phytoremediation in the riparian zone (Fig. 3).



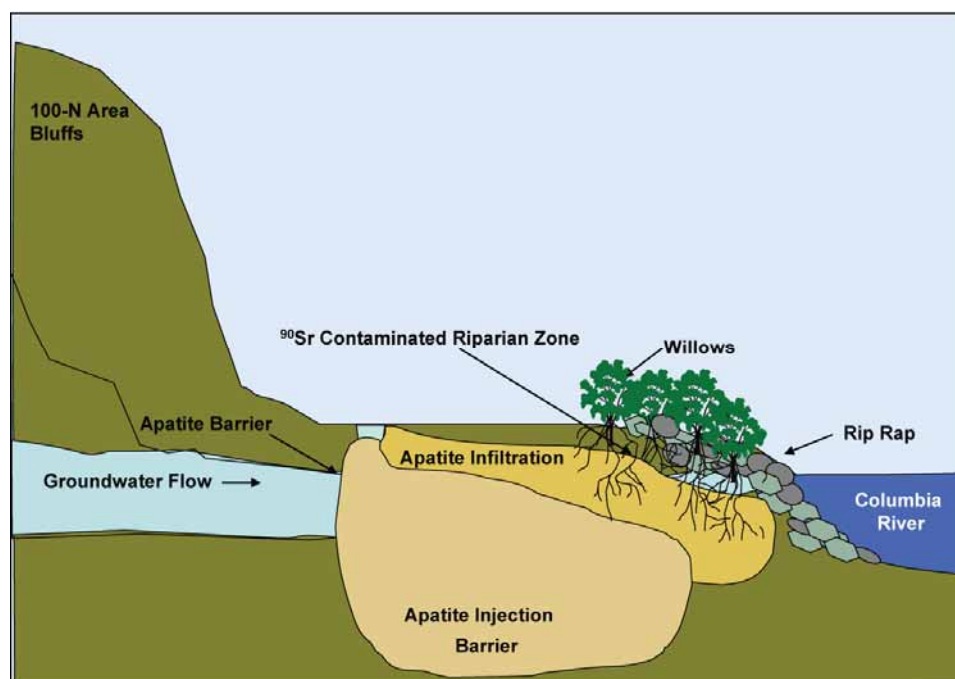


Fig. 3. Illustration of the approach to strontium-90 remediation at the Hanford 100-N Area.

### Sequestration of Strontium-90 Subsurface Contamination in the Hanford 100-N Area by Surface Infiltration of an Apatite Solution

Strontium-90 discharge from past-practice liquid waste disposal sites at the Hanford 100-N Area resulted in strontium-90 release to groundwater, Columbia River, and biota on the river bank. Although liquid discharges were terminated in 1993, strontium-90 adsorbed on aquifer solids remains as a continuing source to the Columbia River. Due to strontium-90 radioactive decay and adsorption, only the strontium-90 within the near river environment is at risk to discharge to the river, so the inland pump-and-treat system that removes strontium-90 does not reduce potential discharge to the river and, therefore, does not meet the remedial action objectives of the ROD [17]. Therefore, the pump-and-treat system has been placed on standby. A treatability test plan is in place to install a 90-m apatite permeable reactive barrier test wall near the shore in FY 2006/2007. Strontium-90 sequestration by this technology occurs by injection of  $\text{Ca-PO}_4$ -citrate solution, in situ biodegradation of citrate resulting in apatite  $[\text{Ca}_6(\text{PO}_4)_{10}(\text{OH})_2]$  precipitation, adsorption of strontium-90 to the apatite, then apatite recrystallization with strontium-90 substitution for Ca (permanent) with radioactive decay of strontium-90. Laboratory-scale studies have quantified the sequential processes of this technology in 100-N Area sediment. Because most (60 to 70%) of the strontium-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, but there has been no development of this technology for vadose zone application.

The primary objectives 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. This understanding will be

developed through small-scale column studies, intermediate-scale two-dimensional experiments, and numerical modeling, which will help to quantify individual and coupled processes associated with apatite formation and strontium-90 transport during and after infiltration of the Ca-PO<sub>4</sub>-citrate solution. Development of capabilities to simulate these coupled biogeochemical processes during both injection and infiltration will be used to determine the most cost effective means to emplace an in situ apatite barrier with longevity of 300 years to permanently sequester strontium-90 until it decays. Biogeochemical processes that will be investigated are citrate biodegradation and apatite precipitation rates at varying water contents. Coupled processes that will be investigated include the influence of the formation of apatite precipitation (which occupies pore space) on the hydraulic and transport properties of the porous media during infiltration.

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

Strontium-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. Strontium-90 is present in the aquifer near the Columbia River and within the vadose zone of the river's shoreline at 100-N Area. A radiological survey of shoreline vegetation along the Hanford Reach found areas where the vegetation exhibited elevated levels of radionuclides. Of major concern was the 100-N Area where elevated strontium-90 was found in a number of species [18, 19, 20].

The bulk of the strontium-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, is shallow (0.2 to 1.5 m) and contains approximately 1 Ci of strontium-90. Strontium-90 (both stable and fission product) is held by the soil/sediment primarily via an ion-exchange mechanism that retards strontium-90 transport [21]. Its sorption coefficient, or  $K_d$ , is between 15 mL/g to 40 mL/g, which means approximately 99% of the strontium-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 [22]. The 100-N Area Innovative Treatment and Remediation Demonstration (ITRD) identified phytoremediation as a potential technology both for the removal of strontium-90 from the soil of the riparian zone, and as a filter for groundwater along the Columbia River. Recent greenhouse and growth chamber studies have demonstrated the viability of phytoextraction to remove strontium-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 strontium-90 plume.

Once established along the riparian zone, the willows would be harvested twice a year, e.g., prior to high water (June) and prior to winter senescence (November). Harvested material would be disposed of in an appropriate manner. The growth and harvest cycle continues over the life of the remediation process, which may last between 5 and 30 years depending on the extraction rate

and the proximity of the upgradient apatite barrier. The primary determinant for the required remediation is biomass production, which is dependent on planting density, fertilization, and other management practices.

The primary objectives of this study are to (1) determine the most efficient fertilization method for Coyote willow that will generate the greatest biomass possible while protecting the Columbia River from excess nutrient runoff, and (2) demonstrate the efficacy of using Coyote willow as a strontium-90 phytoremediation tool along the riparian zone associated with the 100-N Area of the Hanford Site. In performing these two tasks the additional benefits accrued will be (1) accelerating the Columbia River 100-N Area corridor cleanup, and (2) developing alternatives to the existing pump-and-treat system as specified in the interim ROD [17] for strontium-90 in the 100-N Area.

## **PROJECT 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 Hanford Site 300 Area for many years. The uranium plume is just 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) [23] 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 maximum contaminant level concentration of 30  $\mu\text{g/l}$ . Despite the cessation of uranium releases and the removal of shallow vadose zone source materials, the second five-year review of the ROD will state that as of 2006, dissolved uranium concentration below the cleanup criteria established by the ROD have not been achieved within the anticipated 10-year time period. A Phase III Feasibility Study was begun 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 [24, 25, 26, 27].

The objective of the proposed treatability test is to evaluate the efficacy of using polyphosphate injections to treat uranium contaminated groundwater in situ. This study will be used to (1) develop implementation cost estimates, (2) identify implementation challenges, and (3) investigate the technology's ability to meet remedial objectives.

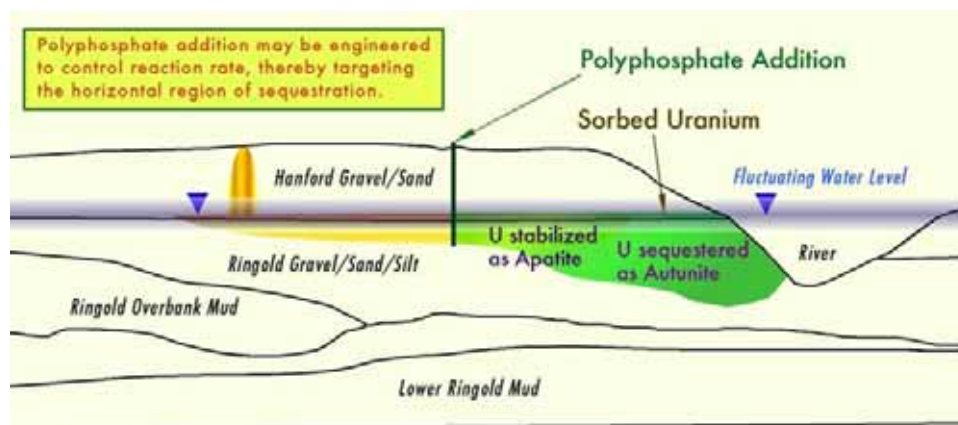


Fig. 4. Schematic depicting the 300-FF-5 Operable Unit geology and proposed treatability test of polyphosphate to sequester uranium.

These activities will be conducted in parallel with a limited field investigation, which is currently underway, to more accurately define the vertical extent of uranium in the vadose zone and in the capillary fringe zone laterally throughout the plume. The treatability test will establish the viability of the method and, along with characterization data from the limited field investigation, will provide the means to determine how best to implement the technology in the field. By conducting the treatability work in parallel with the ongoing limited field investigation, the resulting feasibility study will provide proven, site-specific information to evaluate polyphosphate application and select a suitable remediation strategy for the uranium plume within the feasibility study time frame at an overall cost savings.

## 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<sup>2</sup>. 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 been degraded either by the original process or subsequent transformations in the subsurface to form a co-existing 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 by Truex et al. [28], 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.

A preliminary evaluation of remediation alternatives for the plume [29] drew the following conclusions:

*“The conditions present at the 200 West Area appear favorable to the successful implementation of the MNA [Monitored Natural Attenuation] approach. Application of this technique in conjunction with source-term removal or containment and control in both the vadose zone and the ground water could be a potentially cost-effective strategy. The most significant requirement is to identify and quantify the natural attenuation mechanisms in both the soil and ground water at Hanford.”*

Of the possible natural attenuation mechanisms, biodegradation is not likely to contribute significantly [28]. In contrast, abiotic degradation processes such as hydrolysis and reduction are likely to contribute significantly [28], and, therefore, are important to understand in the context of selecting how active remedies will be applied to the carbon tetrachloride and chloroform plume at Hanford. Previous field and modeling efforts have focused on determining the impacts of other attenuation mechanisms including dispersion and dilution processes and carbon tetrachloride sorption to Hanford sediments [30]. The abiotic degradation processes, however, are not well understood.

Previous determinations of the hydrolysis rate for carbon tetrachloride in water (i.e., homogeneous hydrolysis) have been made [31, 32], but they involved experiments at high temperature ( $>70^{\circ}\text{C}$ ). 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.

To our knowledge, no studies have been made of the possible effects of interactions with solid phases (i.e., heterogeneous effects) on hydrolysis of either carbon tetrachloride or chloroform. A limited body of work exists for other organic compounds at high temperatures. For example, Jeffers et al. [33] attempted to measure the possible effect of mineral surfaces on hydrolysis rate of trichloroethane, trichloroethene, and perchloroethene, and found the rates for these compounds unchanged, even in the presence of sulfide minerals. The possible mechanism by which heterogeneous hydrolysis differs from homogeneous hydrolysis is associated with the sorption of carbon tetrachloride or chloroform to the solid phase. By analogy to heterogeneous catalysis theory, sorption can increase the hydrolysis rate by the immediate release of energy that occurs when the surface complex forms. This energy temporarily raises the local temperature and effectively lowers the activation energy for the reaction. Because amount of sorption is greater at low temperatures, a heterogeneous effect on hydrolysis would be expected to have its greatest impact at low temperatures such as found in groundwater.

The primary objectives of the 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 mineral surfaces on the hydrolysis of carbon tetrachloride at near-ambient temperatures and (3) determine the impact and mechanisms of representative Hanford mineral surfaces on the neutral and base-catalyzed hydrolysis of chloroform at near-ambient temperatures.

## CONCLUSION

Using a peer review process, nine projects have been selected for funding by the US Department of Energy's EM-22 Columbia River Protection Supplemental Technologies Project. These projects are targeted at developing new treatment technologies for four of the major groundwater contaminants at the Hanford site: hexavalent chromium, strontium-90, uranium and carbon tetrachloride. It is anticipated that these new technologies will augment the existing groundwater clean up technologies at Hanford in order to accelerate the time table for achieving the remedial action objectives for the various CERCLA groundwater operable units.

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