

Results from Recent Science and Technology Investigations Targeting Chromium in the 100D Area, Hanford Site, Washington, USA - 10287

Scott W. Petersen*, K. Michael Thompson**, M.J. Tonkin***
* CH2M HILL Plateau Remediation Company, Richland, Washington,
**Department of Energy, Richland, Washington
***S.S. Papadopulos & Assoc., Inc., Bethesda, Maryland

ABSTRACT

Sodium dichromate was used in Hanford's 100D Area during the reactor operations period of 1950 to 1964 to retard corrosion in the reactor cooling systems. Some of the sodium dichromate was released to the environment by spills and/or leaks from pipelines used to deliver the chemical to water treatment plants in the area. As a result, hexavalent chromium [Cr(VI)] has migrated through the vadose zone to the groundwater and contaminated nearly 1 km² of groundwater to above the drinking water standard of 48 µg/L.

Three technology tests have recently been completed in this area to characterize the source area of the plumes and evaluate alternative methods to remove Cr(VI) from groundwater. These are (1) refine the source area of the southern plume; (2) test electrocoagulation as an alternative groundwater treatment technology; and (3) test the ability to repair a permeable reactive barrier by injecting micron or nanometer-size zero-valent iron (ZVI). The projects were funded by the U. S. Department of Energy as part of a program to interject new technologies and accelerate active cleanup.

Groundwater monitoring over the past 10 years has shown that Cr(VI) concentrations in the southern plume have not significantly diminished, strongly indicating a continuing source. Eleven groundwater wells were installed in 2007 and 2008 near a suspected source area and monitored for Cr(VI) and groundwater levels. Interpretation of these data has led to refinement of the source area location to an area of less than 1 hectare (ha, 2.5 acres). Vadose zone soil samples collected during drilling did not discover significant concentrations of Cr(VI), indicating the source is localized, with a narrow wetted path from the surface to the water table.

Electrocoagulation was evaluated through a pilot-scale treatability test. Over 8 million liters of groundwater were treated to Cr(VI) concentrations of ≤ 20 µg/L. The test determined that this technology has the potential to treat Cr(VI) to these low levels, but system reliability and operational complexity rendered electrocoagulation less cost effective than the baseline technology of ion exchange.

Laboratory and field tests were conducted to evaluate the practicality of injecting ZVI into the aquifer to increase the lifespan and effectiveness of an existing permeable reactive barrier. From a database of 30 ZVI materials, 6 were chosen and tested in the laboratory to determine their geochemical and physical performance under simulated 100D aquifer conditions. The best-performing ZVI was injected into the aquifer and met the primary goals of communicating the iron at least 7 meters from the injection point and reducing the aquifer to transform mobile Cr(VI) to trivalent chromium Cr(III), which is effectively immobile in the aquifer.

INTRODUCTION

The Hanford Site is a former nuclear-defense production facility located within the Pasco Basin of south-central Washington State. The Columbia River flows through the northern part of the site and forms much of the site's eastern boundary. This area is underlain by sediments deposited by the Columbia River and by cataclysmic floods of the Pleistocene Epoch. Operations at the site from the mid-1940s to late 1980s involved the production of plutonium in nuclear reactors near the river and in processing facilities located in the central portion of this 1,518 square-kilometer (586 square-mile) site.

The reactors were cooled with water containing hexavalent chromium [Cr(VI)] to retard corrosion. Chromium was delivered to water treatment plants as sodium dichromate in bags, rail cars, barrels, and through local pipelines in a stock solution that was up to 25 wt. % Cr(VI). The solution was diluted so the reactor coolant water contained approximately 700 µg/L hexavalent chromium. Inevitably, some of this chemical was spilled during handling and/or pipeline leaks. Groundwater was contaminated when the chromium migrated through the vadose zone to the groundwater, approximately 25 m (80 ft) below the surface, driven by natural precipitation and/or anthropogenic recharge.

Since the late 1980s, the U. S. Department of Energy has been remediating groundwater and soil at the site under the Comprehensive Environmental Response, Compensation, and Liability Act (CERCLA [1]) regulations [2]. Currently, there are 4 pump-and-treat systems targeting hexavalent chromium contamination. Two of the pump-and-treat systems are in the 100-HR-3 Operable Unit and 2 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.

In fiscal year 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." Nine projects were selected to receive this funding [3], and all have been completed. This paper reports on the results from 3 of the tests, all of which involved Cr(VI) in the southern plume of the 100D Area.

CHROMIUM SOURCE INVESTIGATION

Groundwater investigations beginning in 1999 identified a large Cr(VI) plume in the southwest portion of the 100D Area (Figure 1). Concentrations in the plume have not significantly diminished during the past 10 years, strongly suggesting that there is a continuing vadose zone source supplying contamination to the aquifer [4]. Several likely hexavalent chromium source locations near the proximal portion of the plume have been identified and investigated. These include the 183-DR head house where water-conditioning chemicals including sodium dichromate were handled, and the 100-D-12 waste site where concentrated sodium dichromate was transferred from rail tankers to water treatment facilities through underground pipelines. Vadose zone samples obtained from test pits and boreholes in these areas contained little or no Cr(VI), indicating that these areas did not contribute to groundwater contamination or that Cr(VI) has been washed out of the soil. Because the source of contamination was likely a highly concentrated, dense liquid, it was postulated distribution would occur in a thin, narrow plume

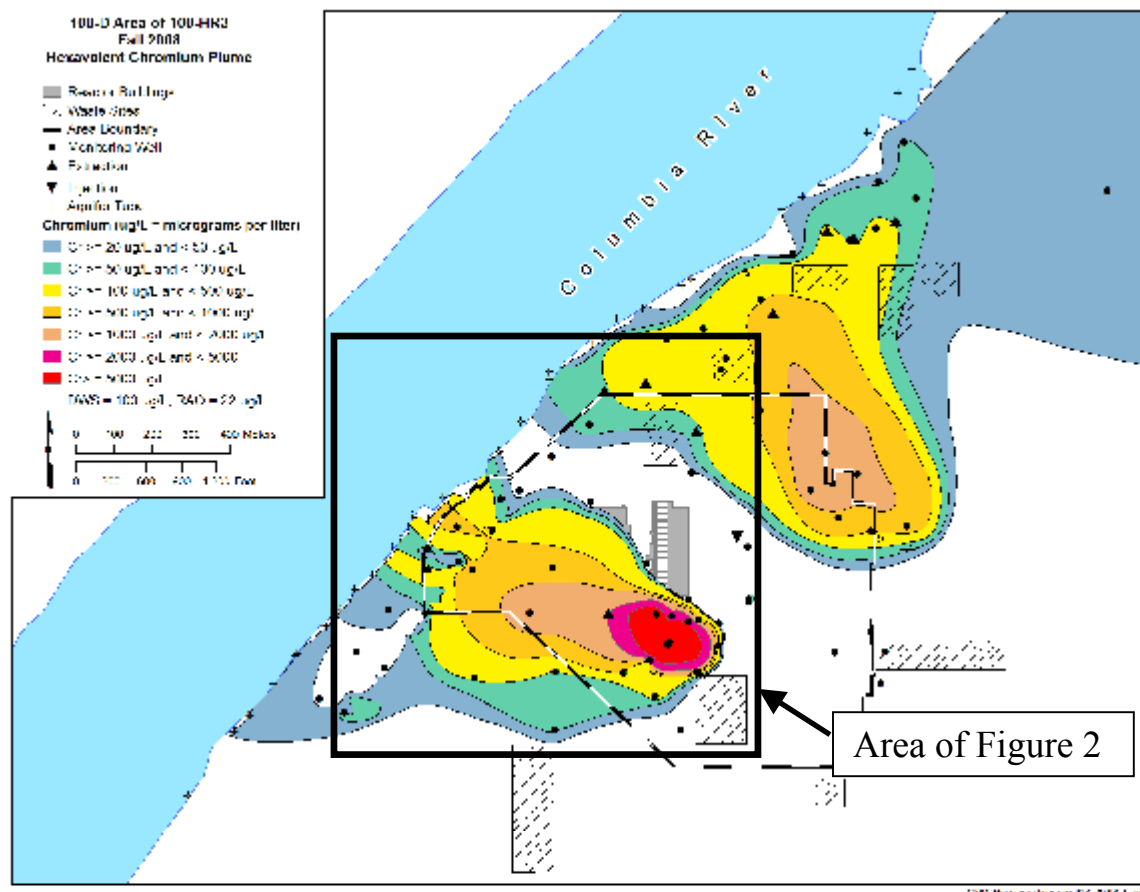


Figure 1. Hexavalent Chromium Plumes in the 100D Area.

through the vadose zone and the probability of intercepting the plume by drilling was remote. Thus, this project focused on obtaining hydrogeologic and geochemical evidence from the aquifer in an attempt to backtrack the contamination to where it enters the aquifer. Evidence from the saturated zone was supplemented by examination and chemical analysis of drill cuttings collected during construction of new groundwater monitoring wells. A full report on this study is available [5].

Methodology

Eleven wells were drilled in the suspected source area (Figure 2). The locations of the first 7 wells, installed in 2007, were chosen based on groundwater analyses from the previous wells in order to best define the highest concentration area of the plume. The last 4 wells, drilled in 2008, were located to refine the area of the source to a 1-hectare (ha, 2.5-acre) area. Soil samples were collected at 1.5-m (5-ft) intervals and analyzed for hexavalent chromium and selected metals. After the wells were completed, they were sampled for field parameters and hexavalent chromium; first every 2 weeks then at 1 month intervals beginning a year into the project. Most of the wells were instrumented with automated water level recording devices to measure

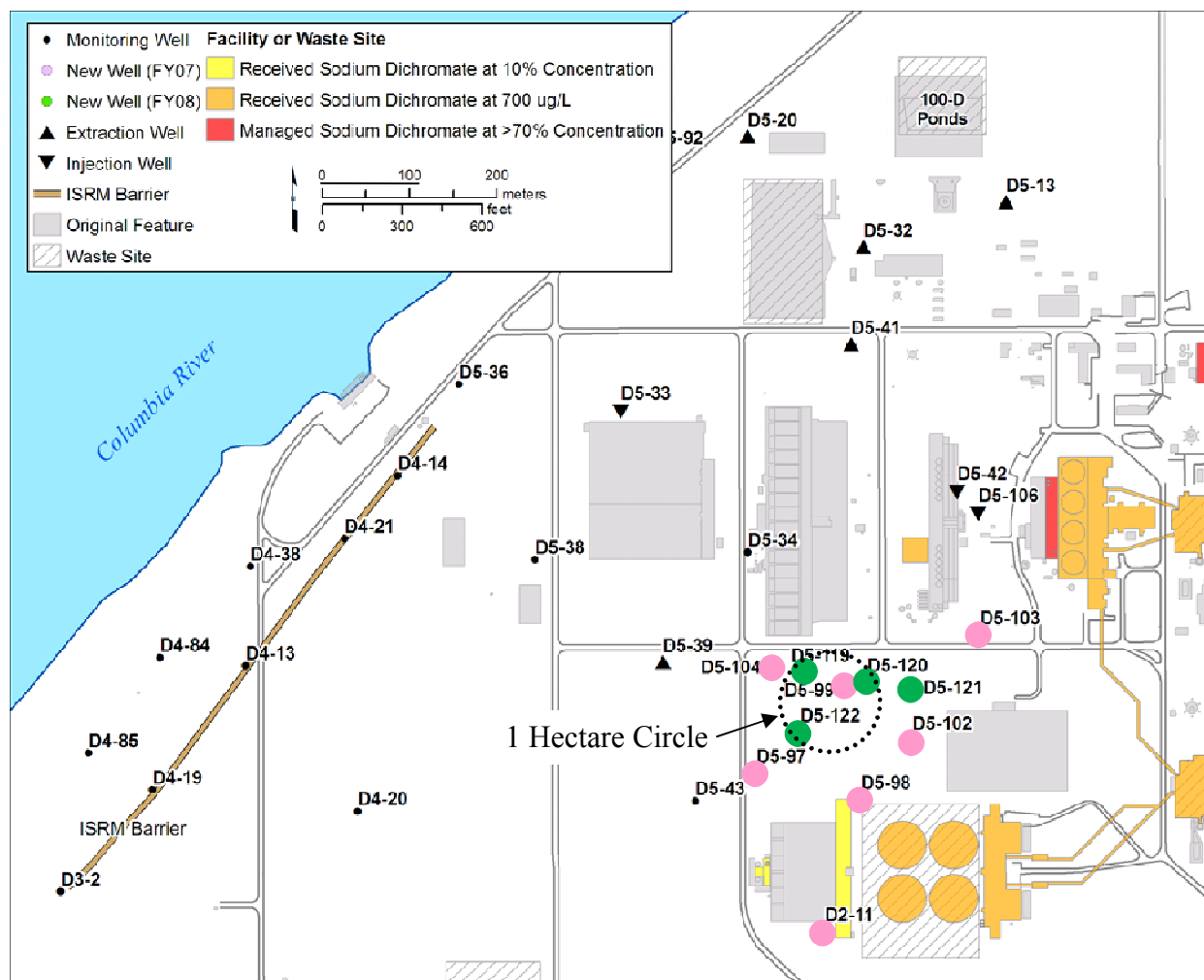


Figure 2. Map Showing Location of Chromium Source Investigation Wells.

elevation of the water table every hour. Six of the wells in the project area were sampled at multiple depths with a Kabis® depth-discrete sampler, after well completion in FY07, to develop vertical profiles of hexavalent chromium concentrations.

Results and Interpretation

Analysis of hexavalent chromium in the wells resulted in the identification of a groundwater hot spot further to the north and east than had previously been identified. This area contains Cr(VI) concentrations over 50,000 µg/L, an order of magnitude higher than found anywhere else in the 100D area or the Hanford site. Evaluation of groundwater levels shows significant variations in groundwater direction and gradient due to large seasonal changes in the Columbia River stage. Groundwater flow response to these changes differs within a few tens of meters in the project area, so that the eastern portion of the hot spot exhibits an extremely shallow gradient with flow predominantly to the north; while the western part of the hot spot flows predominantly to the

Kabis® is a registered trademark of Sibak Industries, San Marcos, California.

west and northwest with a steeper gradient and a velocity of approximately 40 m/year. The seasonal changes also affect Cr(VI) concentrations in some of the hot spot wells, with the contaminant decreasing under the influence of high river stages (after a lag period) and increasing when the river is low.

Most of the vadose zone samples collected during drilling had hexavalent chromium concentrations below the laboratory detection limits (2.1 mg/kg for the first 7 wells and 0.2 mg/kg for the last 4 wells). Twelve samples (from wells 199-D5-120, 199-D5-121, and 199-D5-122) exhibited traces of hexavalent chromium in concentrations ranging from 0.3 to 1.5 mg/kg. One sample (from well 199-D5-120) contained abnormally high (when compared to background) total chromium levels at 54 mg/kg.

The following conclusions can be made based on the data collected from this project.

- The vadose zone source area occurs within a 1-ha circle which encompasses two waste sites suspected to have received Cr(VI).
- The concentrations of hexavalent chromium present at most of the monitoring wells respond to seasonal variations in Columbia River elevation. The highest concentrations follow 2 to 3 months of low river stage, and the lowest concentrations occur several weeks after the springtime high stage of the Columbia River. During this time, water levels in the aquifer in the vicinity of the hot spot change by about 0.5 to 1.0 m (1.6 to 3.3 ft).
- As a result of the seasonal changes in concentration, estimates of the dissolved contaminant mass in the groundwater differ markedly between fall and spring. Because of this ambiguity, it would be difficult to predict the effect of pumping on wells in the vicinity of the hot spot for groundwater remediation. These wells could recover an influent concentration in the higher (50,000 µg/L) or lower (5,000 µg/L) range of concentrations and the concentrations may be expected to change significantly over time. Thus, predictions of mass removal should recognize the high uncertainty.
- The water-level data and apparent hydraulic gradients suggest that a groundwater divide (i.e., saddle point) may exist in the eastern portion of the hot spot. Possible causes for this apparent saddle point may include focused local infiltration (e.g., in open trenches) and lateral heterogeneity, in particular the possible presence of either a coarse-grained channel providing preferential flow or substantial fine-grained materials.
- The apparent gradients suggest that groundwater flow and contaminant migration (west of the apparent saddle point) from the highest contamination area is generally to the west under typical gradients of about 0.0005 to 0.002. Under the assumption that the hexavalent chromium migrates with the groundwater (i.e., is not retarded), and that the hydraulic conductivity is about 50 m/day (164 ft/day), the hexavalent chromium might be expected to migrate at a typical velocity of around 50 m/year (165 ft/yr) to 200 m/year (656 ft/year). This is broadly consistent with the yearly travel distance obtained through the particle tracking analyses.

The principal objective of this investigation was to refine the location of the hexavalent chromium source in the southwestern contaminant plume of the 100D Area. Surface sampling, excavations, and drilling have been, and have remained, ineffective for locating any single

reservoir within or contaminated pathway through the vadose zone. While evidence of minor leaks or spills has been discovered within a few meters of ground surface, no evidence of a major release has been found deeper in the vadose zone. Thus, the origin of the hexavalent chromium contamination remains unknown.

The field data collected to date do not reveal if a significant or active contaminant reservoir remains in the vadose zone, nor do the data reveal the surface or near-surface location of an original leak(s) or spill(s) of sodium dichromate. Concentration data suggest that the 4 high-concentration wells represent the margins of the high-concentration zone. It is reasonable to conclude that these 4 wells effectively constrain the location where hexavalent chromium entered, or continues to enter, the aquifer at the water table. The four wells are easily circumscribed by a 1-ha (2.5-acre) circle.

TESTING ELECTROCOAGULATION TO TREAT HEXAVALENT CHROMIUM

Since the mid-1990s groundwater in the 100D Area has been extracted through pump-and-treat systems to remove mass by ion exchange and control the amount of Cr(VI) entering the Columbia River. This treatment approach was driven by a series of interim action records of decision (RODs) (EPA 1996, 1999). The recent discovery of more extensive and higher-concentration plumes has resulted in the need to improve and accelerate the approach to groundwater cleanup in this area.

Treatment Technology Description

Electrocoagulation (EC) is an alternative to the conventional chemical coagulation and precipitation processes for removing dissolved metals, suspended solids, and colloidal particles from aqueous waste streams. The distinguishing characteristic of EC is the direct application of electric current to the waste stream, which introduces cationic coagulants via electrolytic dissolution of a sacrificial anode. Effluent from the EC is then treated in conventional water purification systems to remove the colloids and precipitants.

The primary purpose of this treatability study was to determine the effectiveness of Cr(VI) removal and the robustness/implementability of an EC system. Secondary purposes of the treatability study were to determine information about derivative wastes and to obtain data applicable to scaling the process from the treatability scale to full scale.

Methodology

The treatment system (Figure 3) performed groundwater extraction and injection, water treatment [Cr(VI) removal], solids-separation/dewatering, and data collection. The design of the EC treatability study involved performing operations in distinct phases: installation, start-up/initial testing, optimization, and treatability testing. The test plan [6] identifies these phases, discusses the operational components of each phase, and details the sampling and analysis procedures associated with relevant portions of the process.

The EC system was designed to perform at a nominal water treatment capacity of 190 L/min (50 gpm), and to be easily set up and decommissioned by prefabricating and containerizing the system to the extent practical. Two existing extraction wells supplied chromium-contaminated groundwater to the EC system, and one new injection well was constructed in an area that had little or no Cr(VI) contamination. The system was automated – recording and responding to temperature, conductivity, and pH of the influent and effluent streams along with well and tank levels, flow rates, pressures, and the operating status of equipment. The control system could automatically start and stop the pumps to maintain the desired flow rate through the system and the proper level in tanks and wells. The control system was designed to allow the EC system to operate unattended during off-shifts (i.e., overnight and through weekends). The system was constructed onsite at the Hanford Site's 100D Area between March 2 and April 2, 2007. Test operations began April 3, 2007 and were terminated October 17, 2007.



Figure 3. Overview Photo of the Installed Electrocoagulation Treatability Test System.

Test Results

A total of 10.3 million L (2.8 million gal.) of groundwater were treated by the test system over the course of the test period [7]. The primary performance objective for this treatability study was to determine the efficiency (effectiveness) of hexavalent chromium removal from the groundwater, with a desired concentration of $\leq 20 \mu\text{g/L}$ Cr(VI) in the effluent prior to reinjection. Hexavalent chromium in the effluent met this performance objective in over 90% of the samples. However, it was not uncommon that the system had to be operated in recycle mode, re-treating the effluent to achieve the performance goal. This need for recycling is a function of EC Unit operational settings and points to issues with system reliability.

A secondary operational objective was to determine the volume and composition of the waste streams to enable proper waste designation. All solid-phase secondary waste streams were found to be below the TCLP limits for the toxicity characteristic and a pH value within the limits for the corrosivity characteristic. Thirty-three 55-gal. drums of solid-phase waste were produced, including consumables (e.g., cartridge filters).

Assessment of operational reliability and safety of the system was another objective of the test. For the continuous operations testing period, the system was not able to operate unattended. Primary, reliability problems involved the necessity to frequently adjust EC unit parameters, inefficiency of the solid separation process, and high effluent iron concentrations which contributed to injection well fouling. The inability to operate unattended was due to the relatively unstable operational conditions that led to control limits being exceeded frequently.

The last operational objective was to assess the overall treatment cost per volume of water treated. The cost of treatment was estimated using the actual cost for the operational and equipment elements of the treatability study and the amount of water treated during continuous operations. Cost elements that were not included for the treatment cost estimate were the injection well, subcontracted technical support, overhead, and burden. The estimated cost per gallon of treatment during this test was \$0.21/L (\$0.78/gal.). Excluding capital costs, the operations cost is \$0.07/L (\$0.28/gal.).

The application of the EC technology for treatment of Hanford groundwater to $\leq 20 \mu\text{g/L}$ Cr(VI) with re-injection of the treated water into the aquifer via a well is a rigorous performance requirement for the EC technology. The EC technology is typically reliable and robust for operations in an industrial setting where effluent standards are higher (e.g., $100 \mu\text{g/L}$), the effluent can be discharged to the sewer rather than injected to a well, and influent chromium concentrations are higher such that the electrodes can be operated more efficiently and solids separation may be more effective.

In summary, the treatability study data suggest that the EC technology has the potential to meet the performance goal for use as the aboveground component of a pump-and-treat system at Hanford, but system operation during the test was problematic. Thus, deployment of this technology to treat groundwater to the low concentrations required for Hanford groundwater is not recommended.

INJECTING ZERO-VALENT IRON TO MEND A PERMEABLE REACTIVE BARRIER

From 1997 to 2002, an innovative permeable reactive barrier was installed in the 100D Area to remediate the southern chromate groundwater plume by reducing Cr(VI) to trivalent chromium [Cr(III)]. This barrier, known as the In Situ Redox Manipulation (ISRM) barrier, was established by injecting sodium dithionite into the aquifer, thereby creating persistent reducing conditions. Although laboratory and field tests indicated that this innovative technology would effectively treat Cr(VI) for nearly 20 years [8], a few of the barrier wells exhibited signs of breakthrough 18 months after treatment. The most probable cause of the premature barrier breakdown was determined to be heterogeneities in the aquifer where laterally discontinuous units with high permeability and lower potential reductive capacity were re-oxidized faster than the less permeable layers.

The project described here tested a technology for increasing the effectiveness of the ISRM barrier by injection of zero-valent iron (ZVI) into the aquifer through an ISRM well, producing a sustaining remediation solution for this area. This work included laboratory testing of different ZVI materials, numerical modeling, and injection of a suitable material into the subsurface.

Methodology

A comprehensive investigation of ZVI products was conducted, including an evaluation of available materials and several different stages of laboratory tests to evaluate their geochemical and injectability properties. This effort was performed to select an appropriate ZVI product for mending the ISRM barrier. The selection process included a literature search, batch screening tests, injection screening tests, and geochemical screening tests.

Batch screening tests were performed on the top 6 materials identified in the literature search to evaluate the ability of each material to create a reducing environment and to reduce hexavalent chromium. The experiments consisted of a 4-hour batch test performed on a mixture of the ZVI material, clean silica sand, and surrogate groundwater containing hexavalent chromium. The results of these tests indicated that all 6 materials successfully reduced the dissolved chromium. These tests were followed by injection tests, which evaluated the ability of the 6 ZVI materials to permeate and deposit throughout the entire cross-section of horizontally placed flow cells. The injection tests also quantified any effects on hydraulic conductivity as a result of injection. Slurries of each material were injected through 2 flow cells packed with a blend of silica sand. Samples of solid cores and flow cell effluent were analyzed for iron to evaluate the depositional characteristics of each ZVI material. From this test, 2 ZVI compounds were determined to be suitable for advanced geochemical and flow cell injection tests.

The geochemical column screening tests were conducted using surrogate groundwater containing approximately 600 µg/L Cr(VI). This solution was injected through vertical columns for approximately 20 pore volumes (PVs). The columns were filled with sand containing 3 concentrations of ZVI: 1.5 wt%, 0.15 wt%, and 0.015 wt%. The materials were evaluated on their ability to reduce hexavalent chromium without producing unwanted byproducts (e.g., ammonia). Approximately 40 PVs of surrogate groundwater were passed through each column, and effluent samples were taken at 6 different times during testing. Advanced injectability tests were then performed on both compounds to evaluate hydraulic head losses caused by their injection into sand – and to develop a mathematical expression for ZVI deposited as a function of injection time, distance from the injection point, and ZVI fluid velocity. Testing was performed using 3-m (10-ft)-long, 7.8-cm (3.1-in)-inside-diameter transparent pipes packed with very coarse sand and configured for horizontal flow. Slurries of each ZVI formulation were injected into 8 flow cells at 4 different flow rates. Hydraulic head measurement and fluid samples were taken along the length of the flow cell, and samples were analyzed for total iron. The mass of deposited iron in each respective segment of a flow cell over each time interval was calculated using analytical results for iron and a mass balance approach. Using data from the column tests, numerical modeling was used to predict the behavior of ZVI fluid injected into high-conductivity sediments in the ISRM barrier.

From the advanced testing, RNIP-M2 was identified as the superior material. Computer modeling was completed using the results of the advanced flow-cell injection to optimize field injection activities. After completing laboratory testing and modeling, a field injection test was performed in well 199-D4-26, located within the ISRM barrier (Figure 4), over days in August 2008. Approximately 370,970 L (98,000 gal) of a RNIP-M2 slurry were injected successfully into the well during the field injection test. Six months after the test was completed, a new

borehole was drilled 7 m from the injection well to evaluate the extent of nZVI injection. Eleven split-spoon samples were collected and analyzed for iron and other constituents. This borehole was completed as a groundwater monitoring well.

Results and Interpretation

The laboratory tests identified the compound RNIP-M2¹ as being superior to the others with respect to reactivity, injectability, and minimum influence on hydraulic conductivity. The modeling predicted that the optimal injection rate would be of 53 L/min (14 gpm). At this rate approximately 4 g/kg of ZVI would be deposited 7 m (23 ft) from the injection well.

The goal of the field injection test was to place sufficient ZVI into the more permeable portions of the barrier to a distance of 7 m (23 ft) radially from the injection well in order to reduce hexavalent chromium concentrations in the groundwater [9]. Based on the data that were gathered before, during, and after field injection testing, the following observations were made [10]:

- A minor amount of pressure increase (i.e., increase in head) was necessary to maintain a constant flow rate of 53 L/min (14 gpm). The increase amounted to 2.5 psi (1.8 m [5.75 ft] of water) over a 5-day period.
- Slug testing performed on the injection well before and after the injection determined that the nZVI mixture caused a decrease in hydraulic conductivity of the aquifer material immediately around the well by a factor of 2.7.
- Based on visual observations of the water sampled from nearby monitoring wells, the injection of nZVI material influenced the nearest monitoring wells, with effects observed in a well located 3 m (9.8 ft) downgradient 16 hours after injection started, and 35 hours after injection started in a well located 3 m (9.8 ft) upgradient.
- Monitoring data were consistent with the visual observations made during the injection. Temperature and pH increased in 3 of the nearest monitoring wells. The oxidation-reduction potential (ORP) and dissolved oxygen (DO) measurements showed significant decreases in the 2 closest monitoring wells, indicating that nZVI was influencing the geochemistry in the immediate area around the wells. No significant changes in ORP or DO were observed in monitoring wells 12.8 m (42 ft) away, indicating that the iron depositional front had not advanced that far.

Eleven split-spoon samples of aquifer material were collected from the verification borehole and analyzed for iron and other constituents. This borehole was completed as a groundwater monitoring well. Results showed that approximately 6 g/kg of ZVI was successfully deposited in a high-conductivity layer at least 7 meters from the point of injection.

¹ RNIP-M2 is a trademark of Toda Kogyo Corporation, Hiroshima, Japan.

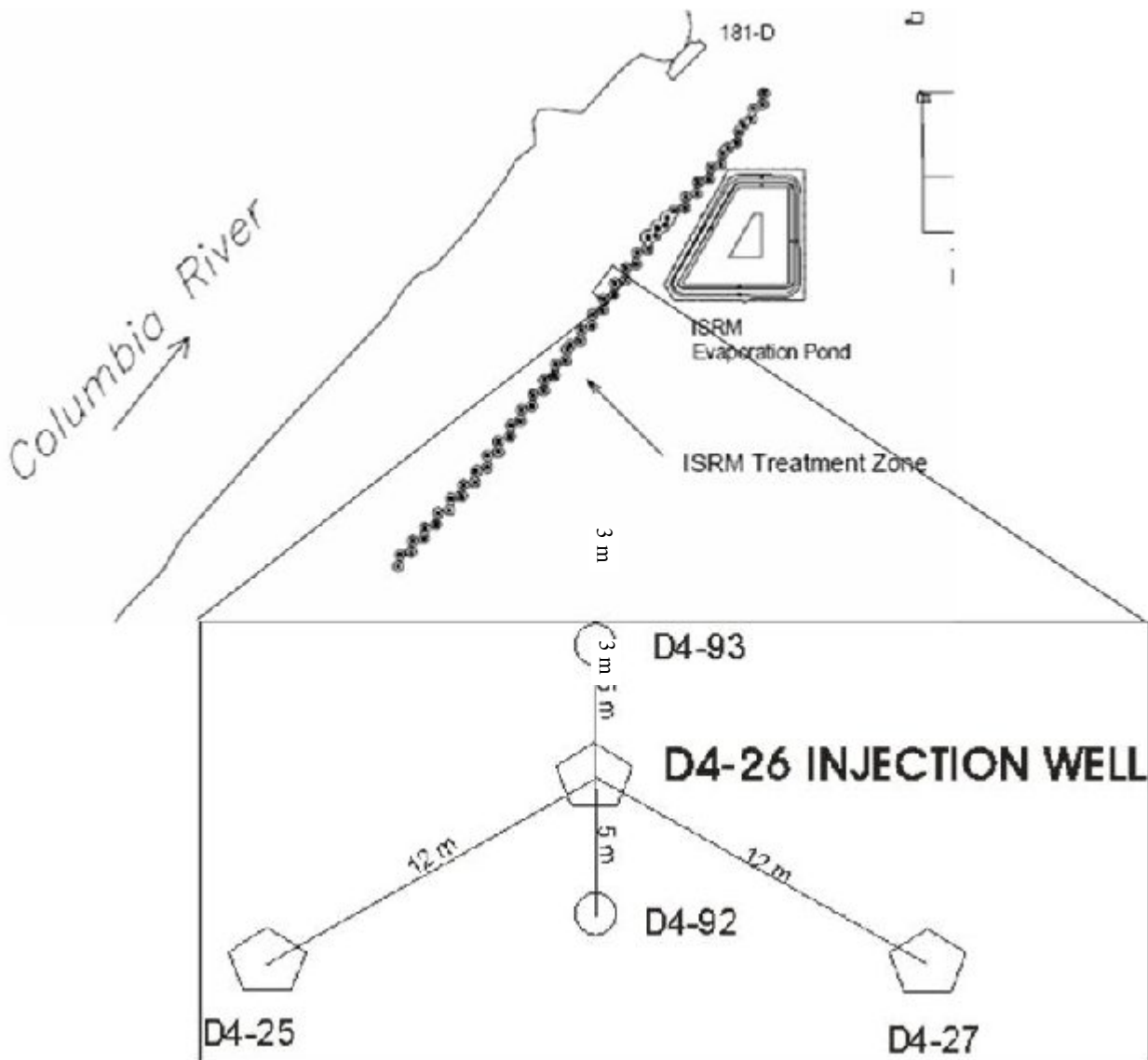


Figure 4. Well Location Map for the Zero-Valent Iron Injection Test.

REFERENCES

1. CERCLA – “Comprehensive Environmental Response, Compensation, and Liability Act,” Public Law 96-510, as amended, 94 Stat. 2767, 42 USC 9601 et seq. (1980).
2. 40 CFR 300, “National Oil and Hazardous Substances Pollution Contingency Plan,” Code of Federal Regulations, as amended.
3. K.M. THOMPSON R.B. ROWLEYS.W. PETERSEN J.S. FRUCHTER, “Supplemental Groundwater Remediation Technologies to Protect the Columbia River at the Hanford Site, Washington - An Update,” WM2008 Symposium, Phoenix, AZ (2008).
4. DOE/RL-2006-74, 2007, “Field Investigation Plan for the Southwestern Chromium Plume in the 100-D Area,” Rev. 0, U.S. Department of Energy, Richland Operations Office, Richland, Washington (2007).
5. DOE/RL-2009-92, “Report on Investigation of Hexavalent Chromium Source in the Southwest 100 D Area,” Department of Energy, Richland, WA (2009).
6. DOE/RL-2006-70, “Treatability Test Plan for Removal of Chromium from Groundwater at 100-0 Area Using Electrocoagulation,” Rev. 0, U.S. Department of Energy, Richland Operations Office, Richland, Washington (2007).
7. DOE/RL-20086-13, “Treatability Test Report for Electrocoagulation,” Rev. 1, U.S. Department of Energy, Richland Operations Office, Richland, Washington (2009).
8. Williams M.D., V.R. Vermeul, J.E. Szecsody, and J.S. Fruchter, “100-D Area In Situ Redox Treatability Test for Chromate-Contaminated Groundwater.” PNNL-13349, Pacific Northwest National Laboratory, Richland, WA (2000).
9. DOE/RL-2008-49, “Treatability Test Plan for Injecting Zero-Valent Iron Into an In Situ Redox Manipulation Well,” Rev. 0, U.S. Department of Energy, Richland Operations Office, Richland, Washington (2008).
10. DOE/RL-2008-92, “Treatability Test Report for Injecting Zero-Valent Iron Into an In Situ Redox Manipulation Well,” Rev. 0, U.S. Department of Energy, Richland Operations Office, Richland, Washington (2009).