#### Groundwater Remediation at the 100-HR-3 Operable Unit, Hanford Site, Washington, USA - 11507

John L. Smoot\*, F. H. Beibesheimer\*, J. A. Eluskie\*, T. Simpkin\*\*, M. J. Tonkin\*\*\*, and A. Spiliotopoulos\*\*\* \*CH2M Hill Plateau Remediation Company, Richland, Washington 99352 \*\*CH2M Hill, Denver, Colorado \*\*\*S.S. Papadopulos & Associates, Bethesda, Maryland

## ABSTRACT

The 100-HR-3 Groundwater Operable Unit (OU) at the Hanford Site underlies three former plutonium production reactors and the associated infrastructure at the 100-D and 100-H Areas. The primary contaminant of concern at the site is hexavalent chromium; the secondary contaminants are strontium-90, technetium-99, tritium, uranium, and nitrate. The hexavalent chromium plume is the largest plume of its type in the state of Washington, covering an area of approximately  $7 \text{ km}^2$  (2.7 mi<sup>2</sup>) with concentrations greater than 20 µg/L. Concentrations range from 60,000 µg/L near the former dichromate transfer station in the 100-D Area to large areas of 20 to 100 µg/L across much of the plume area. Pump-and-treat operations began in 1997 and continued into 2010 at a limited scale of approximately 200 gal/min. Remediation of groundwater has been fairly successful in reaching remedial action objectives (RAOs) of  $20 \,\mu g/L$  over a limited region at the 100-H, but less effective at 100-D. In 2000, an in situ, permeable reactive barrier was installed downgradient of the hotspot in 100-D as a second remedy. The RAOs are still being exceeded over a large portion of the area. The CH2M HILL Plateau Remediation Company was awarded the remediation contract for groundwater in 2008 and initiated a remedial process optimization study consisting of modeling and technical studies intended to enhance the remediation. As a result of the study, 1,400 gal/min of expanded treatment capacity are being implemented. These new systems are designed to meet 2012 and 2020 target milestones for protection of the Columbia River and cleanup of the groundwater plumes.

# INTRODUCTION

The Hanford Site in Washington State served as the primary plutonium production facility in the United States. The 100-D and 100-H Areas at the Hanford Site contain three of the nine plutonium production reactors constructed at Hanford. These are the D reactor, one of the original three reactors constructed during World War II, and the DR and H reactors, which were the first reactors constructed following the initiation of the Cold War in 1947 [1,2,3]. These reactors used sodium dichromate in their cooling water to prevent corrosion of the tubes within the reactor pile. Cladded fuel slugs were loaded into the front side of the reactor and discharged on the back side of the reactor into a water-filled fuel storage basin that allowed the slugs time to cool thermally and radioactively. Approximately 25,000 gal/min of water containing 2 mg/L of sodium dichromate was sent through the tubes in the pile during the early years of operations<sup>1</sup> for cooling [4]. The sodium dichromate prevented corrosion during this process. As reactor operations continued, engineers optimized the operating concentration at approximately 700  $\mu$ g/L in the cooling water. Until 1953, the sodium dichromate was shipped to the site in bags and mixed on site;

<sup>&</sup>lt;sup>1</sup> D Reactor operated from December 17, 1944 to June 26, 1967. DR Reactor operated from October 3, 1950, to December 30, 1964. H Reactor operated from October 29, 1949, to April 21, 1965.

subsequently, a 70 molar stock solution was delivered to the site by rail to save money and mixed to the operating concentration. Releases of large volumes of cooling water from basins and trenches, in combination with point sources of stock solution from rail car unloading facilities and leaks in distribution piping, resulted in contamination of a large portion of the groundwater and the vadose zone in the 100-D and 100-H Areas with hexavalent chromium.

Consequently, the 100-D and 100-H Areas were designated under the CERCLA program. The 100-DR-1, 100-DR-2, 100-HR-1 and 100-HR-2 Soil Operable Units (OU) were designated along with the 100-HR-3 Groundwater OU. Despite the name, the 100-HR-3 OU includes both the 100-D and the 100-H Areas. The OU includes the northern-most portion of the Hanford Site and includes the intervening space that contains the tip or Horn of the Hanford Site. Under the Tri-Party Agreement [5] between the U.S. Department of Energy (DOE), the U.S. **Environmental Protection Agency** (EPA), and the Washington State Department of Ecology (Ecology), Ecology is the lead regulator on the 100-HR-3 OU (Fig. 1).

#### HYDROGEOLOGIC SETTING

The Hanford Site consists of the plio-pleistocene Hanford formation overlying the Ringold Formation,



### Fig.1. Location of the 100-HR-3 OU [6]

which overlies the Columbia River Basalt Group. The aquifer in the 100-HR-3 OU is underlain by the Ringold upper mud (RUM) unit. The surface of the RUM is characterized by local depressions and ridges with relief on the order of several meters; there is a broader east-west trending high in the RUM along the north side of the Horn several hundred meters south of the river. Overlying the RUM in the 100-D Area is the Ringold E unit that constitutes much of the saturated zone and then the Hanford formation that comprises the vadose zone. Further east across the Horn and 100-H Area the Ringold E has been eroded and the Hanford formation unconformably overlies the RUM where it makes up both the aquifer and vadose zone. Consequently, the aquifer is marked by a facies change along the east side of the 100-D

Area wherein it transitions from Ringold E to the Hanford formation to the east (Fig. 2). The Ringold E is somewhat more heterogeneous than the Hanford formation with a hydraulic conductivity on the order of 30 ft/day versus approximately 200 ft/day in the Hanford formation [22].





Groundwater flows toward the Horn and the northern tip of the site from the 200 Area to the south. Groundwater flows north from an elevation of 121 to 122 m in the 200-East Area through the Gable Gap across a broad plain with a low gradient through 120 m to approximately 118 m at the 100-D Area with a significant increase in gradient to the east over to 100-H Area at approximately 116 m. Consequently, the 100-D Area is marked by lower gradients and an inflection point as water flowing into the Horn turns towards the lower water levels at 100-H.

Groundwater flow also is shaped by the annual and diurnal cycles of flow in the Columbia River that causes river stage changes up to 3 m annually; daily fluctuations on the order of 2 m are observed depending upon requirements at dams upstream.

# NATURE AND EXTENT OF CONTAMINATION

Contamination in the 100-HR-3 OU consists primarily of hexavalent chromium with lesser amounts of nitrate and localized strontium-90 in the 100-H Area. A remedial investigation/ feasibility study [6,7] currently is in progress in the 100-HR-3 OU that will lead to the final Record of Decision (ROD). The focus in this paper is the hexavalent chromium remediation under the interim RODs [8,9]. Hexavalent chromium is found in groundwater from the 100-D Area across the Horn to 100-H Area (Fig. 3). Since remediation activities began following the 1996 interim ROD, an additional area of contaminated groundwater has been found in the southwest 100-D Area [10]. Concentrations range from 70,000 µg/L in



#### Fig. 3. Hexavalent Chromium Concentrations in Groundwater at the 100-HR-3 OU

a local area at 100-D in the vicinity of the old sodium dichromate rail transfer station to broad areas less than 100  $\mu$ g/L across the Horn into 100-H [11]. There is a zone of relatively clean water that divides the plume in the 100-D Area in the vicinity of the 182-D Reservoir, a water supply structure that provides emergency fire suppression and special process water to the Hanford Site as a secondary supply to the 182-B Reservoir.

The hexavalent chromium groundwater contamination is divided geographically in to four regions: 1) the D South plume, 2) the D North plume, 3) the Horn plume, and 4) the H plume. The present-day expression of these plumes represents the culmination of anthropogenic and natural processes over a period of 65 years at the 100-D Area and approximately 55 years at the 100-H Area; the area is characterized by hexavalent chromium entering the environment at or near land surface and subsequently migrating through the vadose zone and groundwater to the Columbia River. Additional amounts of hexavalent chromium were discharged directly to the Columbia River via large outfall pipes following passage through the reactors and a period of time in cooling ponds. Of the remnants of hexavalent chromium that are observed in the field today, the largest concentrations are observed in a groundwater "hotspot" area at the D South plume where concentrations have approached 70,000  $\mu$ g/L.

The exact nature and extent of hexavalent chromium in the vadose zone is not well understood; most of the characterization and remediation activities in the vadose zone have focused on radioactive constituents. Evidence has been obtained for additional hexavalent chromium in the vadose zone by the cognizant contractor, Washington Closure Hanford (WCH). In places where the vadose zone has been shielded from deep percolation by vegetation cover, consolidated or very fine-grained materials, or concrete and asphalt at the surface, hexavalent chromium is likely to remain in the soil column. In places

where the surface has been disturbed and gravelly with no plant cover, a significant portion of the annual precipitation is likely to have infiltrated through any mobile hexavalent chromium in the soil column and leached it down into the aquifer. This is consistent with studies at the Pacific Northwest National Laboratory [12], which suggest that approximately 95 percent of the hexavalent chromium is flushed out of the vadose zone in one or two pore volumes taken together with another series of studies at PNNL that indicate that deep percolation through disturbed surfaces at Hanford may approach 75 percent of the annual precipitation of approximately 6 inches [13,14,15]. More study is necessary to understand the nature and extent of the hexavalent chromium contamination in the area; additional characterization is being conducted in FY 2011 to fill this data gap through a remedial investigation/feasibility study [7].

There are several different source terms for the hexavalent chromium that must be integrated to understand its present-day distribution in the environment. During the early years of operation (1944-53), the sodium dichromate was delivered to the site in dry form in bags and mixed on site to form the 2 mg/L level in the cooling water for the reactors. Given the high level of throughput, large groundwater mounds formed in the areas adjacent to the reactors. Beginning in 1953, the concentrated sodium dichromate stock solution was utilized for several years. By the time operations began at H reactor in 1956, operational experience indicated that 700  $\mu$ g/L provided sufficient chromium protection and less concentrated solutions were used. Consequently, groundwater contamination at lower concentrations is observed at 100-H. In addition, there have been the leaks and spills related to the sodium dichromate stock solution and the dichromate distribution piping system. Finally, there are a number of other sites in the vicinity of the reactors where sodium dichromate was released to the environment through either planned or unplanned releases.

In 1967, an infiltration test was conducted at a trench east of the 107 DR retention basin in the northeast portion of the 100-D Area. The test was conducted from March 7 to June 26, 1967, during which time  $3.4 \times 10^9$  gal of reactor effluent infiltrated through the trench bottom at an average rate of 1,500 gal/min/ft<sup>2</sup>. Groundwater mounding of approximately 3 m (10 ft) occurred in the vicinity of the trench generating a vertical downward gradient and enhanced radial flow inland and across the horn [2].

# REMEDIATION

In 1996, a ROD was issued for the 100-HR-3 OU [8], which provided for the application of a pump-andtreat remedy to treat the hexavalent chromium plume for the purposes of protecting the river and providing information that would lead to the final remedy. In response, a relatively small system was developed called the HR-3 pump-and-treat system was designed to treat the known extent of the plume at that time [16,17]. A pair of 100 gal/min trains containing ion exchange resin were placed in the old warehouse building at 100-H, which pumped from 6 extraction wells at H and injected into 3 wells at H and also included 4 wells from the north part of 100-D along the river. This D water was injected at H. A regenerable ion exchange resin is utilized at this plant, which is shipped off site and cleaned and returned. This system has been reconfigured several times over the years and has done a reasonable job of remediating the far eastern extent of the contamination in the OU.

Further characterization and monitoring of the 100-D portion of the OU revealed high concentrations in the southwest portion of the 100-D Area [10]. Two actions occurred in response to these findings: 1) a ROD Amendment was issued in 2000 [9] that authorized the use of an in-situ redox manipulation (ISRM) barrier in the D South plume, and 2) a second pump-and-treat system was constructed. The DR-5 pump-

and-treat system was established in 2002 to treat these high-concentration zones. The system is small, consisting of 4 extraction wells and 1 injection well.

The Ambient Water Quality Standard for hexavalent chromium in Washington State is  $10 \mu g/L$ . A dilution attenuation factor (DAF) of 1:1 is allowed for compliance in the Interim ROD; consequently, 20  $\mu g/L$  is the prescribed compliance level in the aquifer.

Both the pump-and-treat and the ISRM continue to operate. Portions of the ISRM Barrier continue to function well while other portions have experienced breakthrough [18]. The thickness of the aquifer tends to decrease to the northeast along the barrier. As the aquifer thickness decreases, the reactive capacity also decreases as the aquifer discharge is forced through a smaller thickness of the aquifer more rapidly. The thinnest portion of the aquifer is downgradient of the D South "hotspot."

In 2007, Ecology published a paper that described the state of the Hanford Site groundwater remediation strategy, the lessons learned, and the path forward [19]. In this paper, Ecology concluded that pump-and-treat systems such as those in 100-HR-3 "...provided a meaningful approach to address certain contaminants" with the caveat that the deployment "...was too small in scale" and that efforts to deploy innovative technologies and scale-up approved remedies was hampered by budget constraints.

Shortly thereafter, several events occurred that enabled more aggressive remediation at the Hanford Site. CH2M Hill Plateau Remediation Corporation (CHPRC) was awarded the contract that includes groundwater cleanup at the Hanford Site, target milestones to protect the Columbia River by 2012 and cleanup the contamination plumes by 2020, along with the passage of the American Recover and Reinvestment Act (ARRA) of 2009 [20]. A remedial process optimization (RPO) was initiated in October of 2008 following award of the contract to CHPRC.

The RPO efforts have focused on the expansion of the remedial systems to achieve the RAOs within specified timeframes. The primary objectives for the RPO designs are (a) to prevent the discharge of hexavalent chromium to the Columbia River at concentrations exceeding those considered protective of aquatic life in the river and riverbed sediments by the year 2012; and (b) aquifer restoration inland by attaining the Washington State Standard of 48  $\mu$ g/L by the year 2020. The objectives related to achieving river protection by 2012 and target cleanup levels by 2020 will be met, at a minimum, by pumping groundwater from existing and proposed extraction wells located within and around the contaminated areas and removing hexavalent chromium from the groundwater by treatment at ex situ facilities.

Groundwater flow and contaminant transport modeling was performed to calculate appropriate pumping rates for injection and extraction wells to achieve the RPO objectives. A groundwater flow model was developed that encompasses 100-K, 100-N, 100-D, and 100-H Areas to support design of pump-and-treat interim remedies and to evaluate the performance of the pump-and-treat systems.

The groundwater flow model was developed to simulate the operations of the pump-an-treat systems at the OUs. Model development was based on various sources of information including the Model Data Package [21] developed for that reason by CHPRC for each OU. The modeling is documented in a technical memorandum [22]. The model was calibrated using continuous water level data from monitoring wells in the 100-K, 100-D, and 100-H Areas from January 2006 through June 2009. Particle tracking was implemented to develop "capture efficiency" maps to depict likely system performance by

estimating hydraulic containment extent under transient conditions. A contaminant transport model was then developed to simulate the migration of hexavalent chromium in the 100 Areas, using a dual-domain approach that describes advective transport in the mobile domain and mass-transfer between the immobile and mobile domains. The model timeframe was extended to facilitate comparative predictive simulations of various remedial alternatives for each OU.

During the initial stages of the RPO effort, an expanded pump-and-treat system at 100-HR-3 was developed that included 47 injection and extraction wells, focused primarily on meeting the 2012 river protection milestone. However, this initial stage modeling clearly showed additional system expansion was required to meet the 2020 aquifer cleanup milestone. The extraction/injection well configuration was expanded and additional modeling was conducted to optimize the well field and to develop a design that has a reasonable likelihood of meeting both the river protection and aquifer restoration goals based on our best available understanding of the hydrogeology of the system.

The resulting pump-and-treat system design consists of 70 "new" and 33existing extraction and injection wells for a total capacity of 1,400 gal/min. Under the proposed well configuration most extraction wells are designed to operate at 15 to 20 gal/min with most injection wells operating at 40 to 60 gal/min. Contaminated water will be treated at two new plants, the DX plant in the 100-D Area with a capacity of 600 gal/min and the HX plant in the 100-H Area with a capacity of 800 gal/min. The DX plant is on line as of December 2010 with the HX plant following later in 2011. The system is designed to provide hydraulic gradient control for plume containment and expedited mass removal.

The expected remediation based on these modeling design studies is shown in Fig. 4 for 2012 and 2020. The remediated plume configurations suggest that the pump-and-treat system design at DX and HX will be able to achieve the target milestones. Drilling of the new extraction and injection wells is complete and the well development data suggests that the planned pumping scenarios are achievable.



Fig. 4. Projected Remediation in Groundwater, 2012 (top) and 2020 at the 100-HR-3 OU

## IMPLEMENTATION CONSTRAINTS

There are a number of interesting cultural, environmental, and fiscal constraints involved in a project of this nature. The 100-HR-3 OU is located in a culturally sensitive and environmentally sensitive area. Several fortuitous events came together to allow the funding for the project to proceed.

The northern portion of the Hanford Site has a number of culturally sensitive sites predominantly relating to historical Native American usage of the land. The 100-D and 100-H Areas contain a number of sites that were historically inhabited by the local tribes. These include fishing grounds, villages, burial sites, and spiritual sites. Many of these places are in close proximity to the Columbia River; consequently, placement of wells very close to the river is difficult.

The area also is marked by a number of Bald Eagle roosting areas, particularly in the zone north of the 100-H Area. During the eagle roosting season, from November to March each year, well drilling and other disturbances are severely limited to approximately 4 hours in the middle of the day; therefore, rates of progress during this time are limited.

These systems were funded with a combination of baseline and ARRA funding to complete the array of design, construction, and well-drilling activities. The RPO design was completed prior to the signature of the ARRA by President Obama in February 2009; therefore CHPRC had an implementable plan that was ready for engineering, procurement, and construction. Subsequently, funding came together to allow for initiation of the project.

### DISCUSSION AND CONCLUSIONS

Active remediation of groundwater is ongoing in the 100-HR-3 OU. Two remedies are in place under interim RODs: pump-and-treat and the in situ redox manipulation barrier. CHPRC is significantly expanding the pump-and-treat from approximately 200 to 1,400 gal/min. Extensive design and analysis work suggests that a network of approximately 100 extraction and injection wells feeding two pump-and-treat plants provides a reasonable approach to meeting 2012 and 2020 milestones.

Additional design work was conducted to develop an optimized solution that could meet the needs of both target milestones. It became clear that it was necessary to inject into the interior of the large diffuse plume in order to divide the plume into smaller pieces that could be remediated more quickly. An important design consideration was to ensure that injected water developed gradients that would set up a capture zone to capture displaced contaminated groundwater in downgradient extraction wells.

Contaminated water will be treated at two new plants, the DX plant in the 100-D Area with a capacity of 600 gal/min and the HX plant in the 100-H Area with a capacity of 800 gal/min. The DX plant is on line as of December 2010 with the HX plant following later in 2011.

In summary, extensive analyses have been conducted of the likely performance of the DX and HX pumpand-treat systems. These analyses suggest that the systems will be capable of meeting 2012 and 2020 target milestones.

#### REFERENCES

- 1. M.S. GERBER, *Legend and Legacy: Fifty Years of Defense Production at the Hanford Site*, WCH-MR-0293, Rev. 2, Westinghouse Hanford Company, Richland, Washington (1992).
- 2. WCH-SD-EN-TI-181, Rev. 0, *100-D Area Technical Baseline Report*, Westinghouse Hanford Company, Richland, Washington (1993).
- 3. BHI-00127, Rev. 0, *100-H Area Technical Baseline Report*, D.H. DeFord, M.W. Einan, Bechtel Hanford, Inc., Richland, Washington (1995).
- DOE/RL-2001-16, Rev. 0, *Historic American Engineering Record B Reactor (105-B Building)* HAER No. WA-164, U.S. Department of Energy, Richland Operations Office, Richland, Washington (2001).
- 5. Ecology, EPA, and DOE, 1989, *Hanford Federal Facility Agreement and Consent Order*, 2 vols., as amended, Washington State Department of Ecology, U.S. Environmental Protection Agency, and U.S. Department of Energy, Olympia, Washington.
- 6. DOE/RL-2008-46, Rev. 0, *Integrated 100 Area Remedial Investigation/Feasibility Study Work Plan*, U.S. Department of Energy, Richland, Washington (2010).
- DOE/RL-2008-46-ADD1, Rev. 0, Integrated 100 Area Remedial Investigation/Feasibility Study Work Plan, Addendum 1: 100-DR-1, 100-DR-2, 100-HR-1, 100-HR-2, and 100-HR-3 Operable Units, U.S. Department of Energy, Richland Operations Office, Richland, Washington (2010).
- EPA/ROD/R10-96/134, Record of Decision for the 100-HR-3 and 100-KR-4 Operable Units Interim Remedial Actions, Hanford Site, Benton County, Washington, U.S. Environmental Protection Agency, Washington State Department of Ecology, and U.S. Department of Energy, Olympia, Washington (1996).
- 9. EPA/AMD/R10-00/122, Interim Remedial Action Record of Decision Amendment for the 100-HR-3 Operable Unit, Hanford Site, Benton County, Washington, U.S. Environmental Protection Agency, Region 10, Seattle, Washington (1999).
- DOE/RL-2009-92, Rev. 0, Report on Investigation of Hexavalent Chromium Source in the Southwest 100-D Area, U.S Department of Energy, Richland Operations Office, Richland, Washington (2009).
- DOE/RL-2008-42, Rev. 0, Hydrogeological Summary Report for 600 Area Between 100-D and 100-H for the 100-HR-3 Groundwater Operable Unit, U.S. Department of Energy, Richland, Washington (2009).
- PNNL-17674, Geochemical Characterization of Chromate Contamination in the 100 Area Vadose Zone at the Hanford Site, Pacific Northwest National Laboratory, Richland, Washington (2008).
- 13. G.W. GEE, *Recharge at the Hanford Site: Status Report*, PNL-6403, Pacific Northwest National Laboratory, Richland, Washington (1987).
- 14. G.W. GEE, M.J. FAYER, M.L. ROCKHOLD, and M.D. CAMPBELL, "Variations in Recharge at the Hanford Site," *Northwest Science*, 66(4):237-250 (1992).
- G.W. GEE, P.J. WIERENGA, B.J. Andraski, M.H. YOUNG, M.J. FAYER, and M.L. ROCKHOLD, "Variations in Water Balance and Recharge Potential at Three Western Desert Sites," *Soil Science Society of America Journal*, 58(1):63-72 (1994).

- 16. DOE/RL-96-84, Rev. 0 and Rev. 0-A, *Remedial Design and Remedial Action Work Plan for the 100-HR-3 and 100-KR-4 Groundwater Operable Units' Interim Action*, U.S. Department of Energy, Richland Operations Office, Richland, Washington (2003).
- DOE/RL-96-90, Rev. 0, Interim Action Monitoring Plan for the 100-HR-3 and 100-KR-4 Operable Units, U.S. Department of Energy, Richland Operations Office, Richland, Washington (1997).
- DOE/RL-2008-10, Rev. 0, In Situ Redox Manipulation (ISRM) Annual Report Fiscal Year 2007, U.S. Department of Energy, Richland Operations Office, Richland, Washington (2008).
- D. GOSWAMI, J. HEDGES, and C. WHALEN, "Initial Sitewide Groundwater Remediation Strategy of the Hanford Site, WA: It's Application, Lessons Learned and Future Path Forward," *Proceedings of the Waste Management 2007 Conference*, February 25 – March 1, 2007, Tucson, Arizona (2007).
- 20. American Recover and Reinvestment Act of 2009, (Pub. L. 111-5).
- 21. SGW-40781, Rev. 0, *100-HR-3 Remedial Process Optimization Modeling Data Package*, CH2M Hill Plateau Remediation Company, Richland, Washington (2009).
- 22. SGW-40044, Rev. 1, 100-HR-3 Remedial Process Optimization Modeling Technical Memorandum, CH2M Hill Plateau Remediation Company, Richland, Washington (2009).
- DOE/RL-2010-11, Rev. 1, Hanford Site Groundwater Monitoring and Performance Report for 2009, Volumes 1 &2, U.S. Department of Energy, Richland Operations Office, Richland, Washington (2010).