

## **Application of Remedial Process Optimization for Chromium Remediation at the Hanford Site, Washington, USA – 9277**

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### **ABSTRACT**

Remedial Process Optimization (RPO) tools provide a systematic approach for evaluating and improving existing site remediation systems to increase the likelihood of meeting the remedial objectives at an optimized cost. These tools have been applied on the interim remedial actions currently under way at the 100 Areas of the Hanford Sites. This paper discusses the general approach for the application of RPO, as well as providing information on the site-specific application at Hanford 100 Areas.

### **INTRODUCTION**

Hexavalent chromium in groundwater is a major environmental concern in the river corridor at the Hanford Site. Interim action remediation systems have been underway at Hanford since 1996 to address these concerns. These systems are designed to reduce the migration of chromium to the Columbia River and to clean up the plume. They consist of pump and treat approaches with series of extraction and injection wells, with the extracted water treated using ion exchange technology. The remediation systems have been effective in removing 838 kilograms (1,830 lbs) of hexavalent chromium, but room for optimization exists. The Department of Energy (DOE) began efforts in 2008 to optimize these remedial systems using a set of Remedial Process Optimization (RPO) tools.

### **REMEDIAL PROCESS OPTIMIZATION BACKGROUND**

RPO tools provide a systematic approach for evaluating and improving site remediation systems. Many of the RPO tools available were initially developed by federal agencies including the DOE, Air Force, Army, and Navy. They were developed to help improve on the overall performance of the numerous active remediation systems that were being operated by the federal government. For example, as of 2006, the US Air Force had 119 operating pump and treatment systems with average life time cost of \$7.8 million. RPO tools are focused on improving the performance of the system in terms of meeting their objectives, as well as reducing the overall costs to the government. A number of guidance documents on these tools are available [1, 2, 3, 4].

RPO tools can be classified into three general areas of emphasis:

1. Optimization of the remedial strategy and technology

2. Optimization of ongoing remediation system operations and maintenance (O&M)
3. Optimization of long term monitoring and reporting

The first area of emphasis can be thought of as addressing the effectiveness of the current remediation strategy and/or technology. The basic question to be asked is, are we using the best approach to cost effectively meet the remedial objectives? Are there ways to build on the existing approach with different technologies to improve the remedies cost effectiveness? The activities in this process can include:

- Review, and if necessary, refine the Conceptual Site Model (CSM): Involves review of existing and new data, and updating the site understanding, including source area delineation and chemical fate and transport evaluation.
- Evaluate the performance of the existing system: Includes evaluation of trend data to evaluate the performance of existing remedies and the ability of the system to meet the remedial objectives.
- Evaluate remedial action objectives: Includes a review of existing decision documents, and other agreements between the site owner and regulators, or other stakeholders. Changes in site use or site data may result in changes in the remedial objectives.
- Review and screening of potentially applicable technologies: Streamlined screening of potentially applicable technologies for the contaminants of concern, with the list of technologies narrowed down to the few most applicable.
- Develop alternatives from the screened technologies: Develop complete alternatives by combining technologies (including existing systems) to potentially achieve the remedial objectives.
- Develop conceptual designs and conceptual level cost estimates for the alternatives: Conceptual designs and costs estimate are developed to allow the alternatives to be compared.
- Decision analysis or similar tools to select the preferred alternative: Involves the use of various levels of decision making tools to select preferred alternative.
- Technology testing: Perform laboratory or field pilot testing as necessary, to obtain performance and design information, which will allow refinement of the selection process.

The results of this process will potentially end in a change or upgrade to the existing remedial system or technologies. To be able to implement such a change may require that the regulatory documents (such as a record of decision (ROD)) be revised. There are a number of approaches to making such modifications in regulatory documents that vary in complexity and time to

implement (some as much as a year). These factors need to be taken into account in the evaluation of alternatives.

The second area of emphasis of RPO tools involves a detailed evaluation and optimization of the ongoing remedial actions. For pump and treat systems, this typically involves a detailed evaluation of the above ground treatment system as well as the groundwater pumping systems and equipment. Issues that are evaluated include possible enhancements to the unit processes being used, enhancements to the instrumentation and control systems, optimization of the staffing approach, and improvement to the preventative maintenance and spare parts systems. All of these issues are reviewed with the concept of optimizing both the performance and costs of the systems.

The third area of emphasis of RPO tools involves optimizing the long term groundwater monitoring costs. These costs can be substantial for systems that operate many years into the future, and even for remedial actions that include monitored natural attenuation. It is often possible to reduce the monitoring costs as stable, long term operations are undertaken.

## **OVERVIEW OF THE HANFORD 100 AREA**

The 100 Area of the Hanford site contains nine retired plutonium production reactors, numerous support facilities, and solid and liquid waste disposal sites. Reactor operations required large quantities of cooling water. Sodium dichromate (a corrosion inhibitor) was added to the water before it passed through the cooling system. The water was generally diverted to large retention basins for cooling before being returned to the Columbia River. These retention basins leaked in many locations. Spills of high concentration sodium dichromate that was shipped to the site may also have occurred during unloading and transport around the site. The 100 Area includes four operable units (OUs) that have hexavalent chromium as their primary contaminant of concern. Two of these OUs have hexavalent chromium concentrations that warrant active remedial measures. They have plumes with concentrations greater than 20 ug/l that are approximately 9 square kilometers.

Interim action remediation systems have been installed at the two OUs, starting in 1996. These systems are based on pump and treat technology, using a series of extraction wells. Five groundwater treatment systems are currently in place to treat the extracted groundwater. The treatment systems use ion exchange as their primary unit process. The treated water is re-injected. The treatment capacity of these systems is currently 1,450 gpm.

The interim actions were installed under a series of interim action Records of Decisions (RODs). A final Remedial Investigation/Feasibility Study process is currently underway in parallel with these interim remedial actions, with a final ROD due in 2012.

The remediation action objectives (RAOs) defined in these interim action RODs include:

- Prevent unacceptable risk to human health or ecological exposure to surface water containing contaminants above federal and state standards. An aquatic receptor exposure point of concern is within the river substrate at depths up to 18 inches (46 centimeters), where

embryonic salmon and fry could be present during parts of the year. Groundwater discharge impacts achieving this objective.

- Prevent unacceptable risk to human health from ingestion of and incidental exposure to groundwater containing contaminant concentrations above federal and state standards.

More specific objectives have also been defined in the Tri Party Agreement (TPA) which is an agreement between the DOE, US EPA, and the Washington State Department of Ecology. The TPA was first signed in 1989, and was recently amended in 2009. The current TPA has two key milestone targets that significantly impact implementation and optimization of the interim remedial actions in the hexavalent chromium OUs:

- River Protection: DOE shall take actions necessary to contain or remediate hexavalent chromium groundwater plumes in each of the 100 Area NPL Operable Units such that ambient water quality standards for hexavalent chromium are achieved in the hyporheic zone and river water column, by December 31, 2012.
- Plume Remediation: DOE shall take actions necessary to remediate hexavalent chromium groundwater plumes such that hexavalent chromium will meet drinking water standards in each of the 100 Area NPL Operable Units, by December 31, 2020.

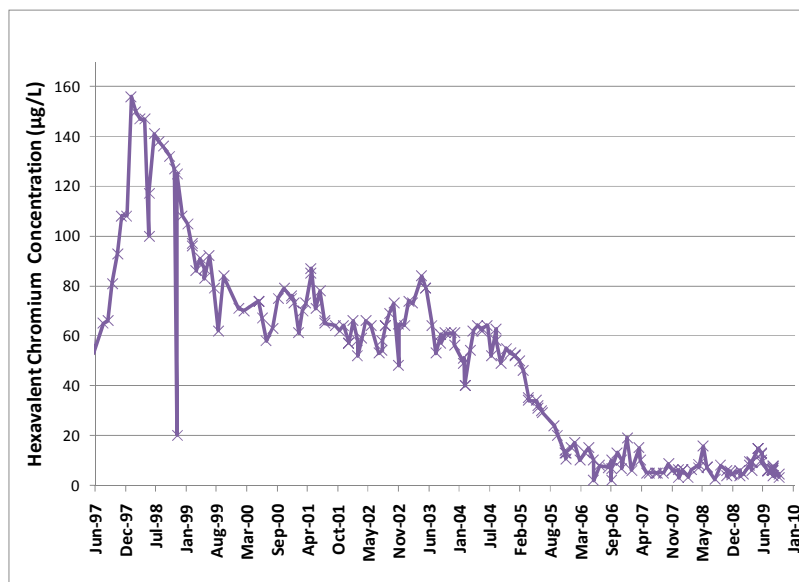
The interpretation of these two milestones is critical and evolving. It drives the monitoring program that will be used to judge the performance of the remedial systems, which in turn will drive the remedial systems implemented.

## **OPTIMIZATION OF REMEDIAL STRATEGY AND TECHNOLOGY**

The steps discussed above for the optimization of the remedial action strategy were undertaken for the 100 Area OU. These were done in conjunction with a number of actions that are currently ongoing. Key findings of these activities in these steps are discussed below.

**CSM Refinement:** The conceptual site model is continuing to evolve as more data is gathered but it includes key factors such as the impacts the seasonal and diurnal changes in River stage have on groundwater flow and concentrations, the presence of vadose zone hexavalent chromium contamination in a few locations that may serve as a long term source of contamination, and the possible presence of hexavalent chromium contamination in the deeper, lower permeability zones.

**System Performance Evaluation:** The operation of the existing pump and treatment facilities have been successful in greatly reducing concentrations of hexavalent chromium, where adequate numbers of extraction wells have been installed and no major sources of ongoing contamination are present. Figure 1 illustrates the reduction in chromium concentration for the 100-H area, where the pump and treat system has been in operation since 1997. Concentrations appear to be plateauing in some of the wells.



**Figure 1. Change in Hexavalent Chromium Concentrations Since System Start, 100-H, Well 199-H4-5**

**Technology Screening:** Remedial technologies potentially applicable for hexavalent chromium were screened. The most promising technologies included pump and treat, and in situ reduction (either chemical, biological, or a combination of biological and chemical).

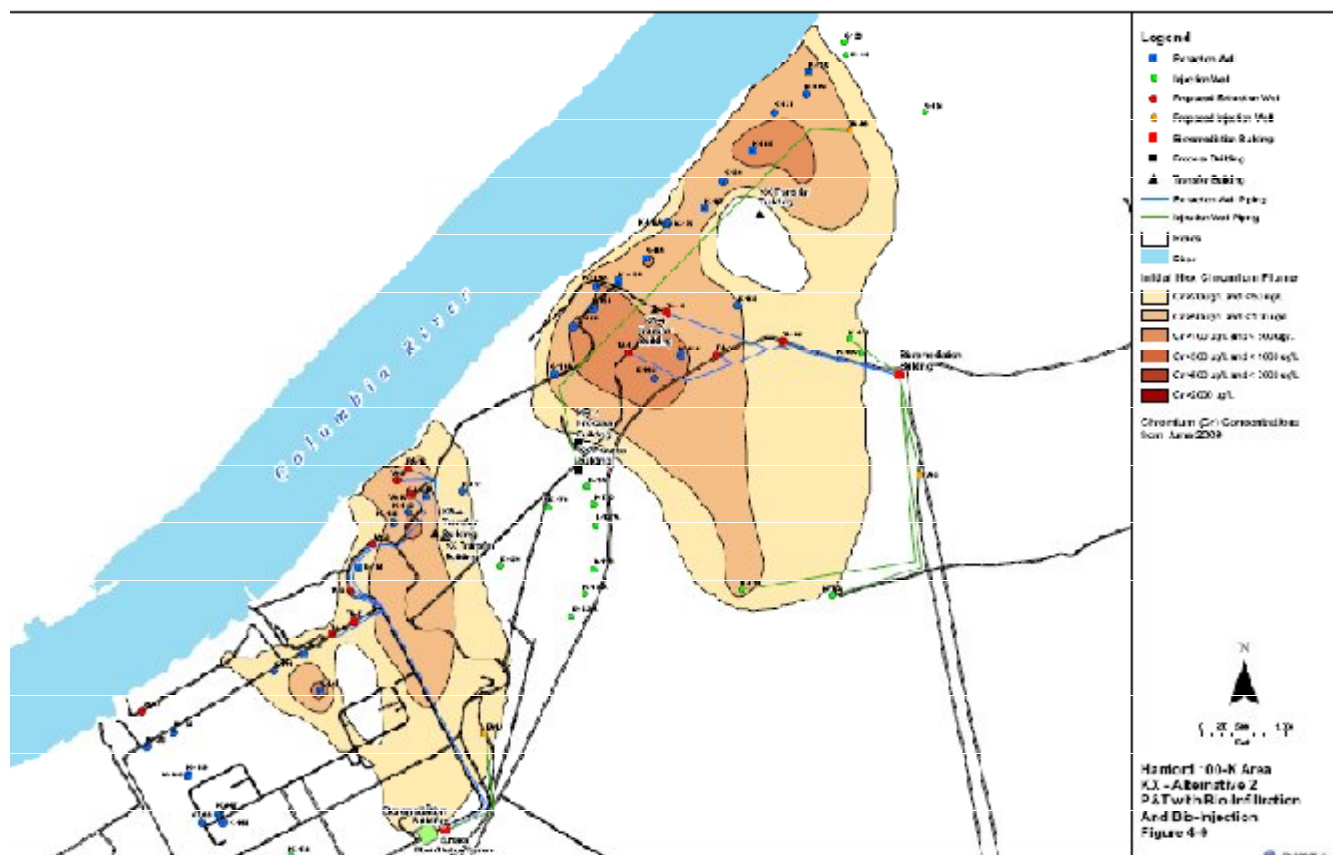
**Alternative Development:** These technologies were assembled into alternatives, with components that focused on the both the 2012 objective of river protection and the 2020 objective of plume remediation. The alternatives considered various combinations of continued pump and treat and bioremediation or in situ chemical reduction.

**Groundwater Modeling:** Modeling of groundwater flow and the transport of hexavalent chromium (CrVI) was used to evaluate various conceptual remedy designs. The model was constructed using versions of MODFLOW [5], MODPATH [6] and MT3DMS [7] specifically approved for use at the Hanford site, this transient model was developed to encompass several OUs along the River Corridor to integrate remediate decision making throughout the RPO effort. Modeling was undertaken in a stepwise manner: first, flow and particle tracking analyses were used to compare the approximate extent of hydraulic capture developed by several potential remedies. These simulations were used to identify and rank candidate extraction and injection well locations and rates. Next, the reactive transport of CrVI was simulated for those potential remedies that showed merit in terms of shorter-term remedial objectives, to contrast the likely effectiveness of each remedy in meeting longer term aquifer restoration goals. Throughout this process, emphasis was placed on animated graphical post-processing of model results, to facilitate discussion with regulators and stakeholders.

A recent uncertainty analysis conducted using the flow-and-transport model identified that the sustainability of proposed pumping rates within this relatively thin water table aquifer may be the single largest factor in achieving the hydraulic containment desired to protect the Columbia River. As a result, dynamic remedy implementation is expected. Development of the

groundwater model is ongoing, with the intent that modeling can continue to support ongoing RPO, particularly as additional data on aquifer response become available during remedy start-up.

**Decision Analysis:** The decision-making was relatively clear cut for the two OUs evaluated. Plume containment with pump and treat using lines of extraction wells was the only alternative that could be installed in a timely fashion in order to have a chance of achieving the River Protection objective by 2012. Figure 2 illustrates the extraction well net work for the 100-K OU, along with an alternative that includes the addition of bioremediation. For the most part, the plume containment systems will be expansions of the existing interim remedial actions. In addition to having much of the infrastructure in place, the regulatory mechanisms were also in place with the interim action RODs. A ROD amendment or explanation of significant difference will be required for almost any other alternative other than pump and treat. The first phase of upgrades to the existing remediation systems is currently underway to achieve the 2012 objective. 25 new extraction and 8 new injection wells are being installed and an additional 600 gpm treatment capacity to bring the total capacity of the ion exchange systems to 2,050 gpm.



**Fig. 2. Example of Alternative 2 for the 100-K OU (Pump and Treatment with Bioremediation)**

For the plume remediation objective, it appears that coupling pump and treat with future bioremediation may be the most cost effective approach. The pump and treat systems using ion

exchange have relatively high operations costs with the long term operations required. Bioremediation approaches can reduce the operations costs and can also increase the certainty of achieving the objectives by addressing the source areas more aggressively. The bioremediation approaches being considered include a surface infiltration to treat vadose zone source contamination, in situ groundwater treatment using recirculation of an organic substrate like ethanol, and a semi-passive bioreactor with a solid organic media as an alternative to ion exchange. Including bioremediation has the potential to reduce the net present value by \$20 million compared to a pump and treat system alone.

### **OPTIMIZATION OF SYSTEM O&M**

RPO efforts for the O&M of the existing treatment systems have focused on a number of areas with the objective of improving performance, reliability and reducing costs. One major activity has been the optimization of the resin used for the ion exchange systems. The management of the resin is the major cost driver in the life cycle costs of these systems. A resin test skid was constructed and a series of three test runs have been conducted on seven different resins under various conditions. Figure 3 shows the test skid in operation.



***Fig. 3. Resin Test Skid in Operation***

The resin skid was designed to simulate conditions typical of the lead vessel in a full-scale Hanford Site treatment facility. The skid is capable of simultaneous evaluation of up to six IX resins for their ability to remove chromium from groundwater. During the evaluation, site-specific groundwater is passed through the resin columns from top to bottom and individual feed streams can be modified (e.g., the pH adjusted) to test the resins under varying conditions. Sample ports at the effluent end of each resin column are used to determine the resin's current performance. Pumps and valves control flow through each test resin and prevent backflow or cross-contamination between the test resins.

Linear flow rates during the testing were maintained at rates similar to full-scale facilities. This ensured that groundwater to resin bead (or granule) contact times were kept similar. Dowex

21K, the resin currently used in most of the full scale pump and treat facilities at Hanford for chromium removal was used in each test as a control to validate the comparison of results from the test skid to full-scale operations. The number of bed volumes to breakthrough for the test skid differed by approximately 10 percent from the full-scale systems, confirming that the test skid was correctly designed to simulate the lead vessel of a typical Hanford site facility.

The results of the testing indicated that several of the resins have a higher capacity for chromium removal than Dowex 21K (pH ~7.5 operating condition). Purolite A500 (pH ~7.5 operating condition), (the resin used in the DR-5 facility at Hanford) performed best of the regenerable resin's tested with approximately twice the capacity of Dowex 21K. ResinTech SIR-700 and ResinTech WBG30-B, operated at pH 5 have shown chromium removal efficiencies of at least an order of magnitude greater than the Dowex 21K baseline in two separate tests without showing signs of breakthrough. These resins have been selected for continued testing with groundwater from other portions of the Hanford site based on their superior performance during testing with D area groundwater. Evaluations of process alternatives were performed incorporating the results of the resin testing. These evaluations indicated that savings of as much as 50% could be achieved from new systems over existing technology. This approach has been adopted for new systems as a direct result of the resin testing.

The second area of O&M optimization focus has been on the reliability of the existing system. CH2M HILL brought in O&M experts to perform an independent review of the operations. The approach for this review was to study the existing and planned facilities looking for ways to mitigate the effects of failures on operations and maintenance. The review team looked at the preventative maintenance program, the level of equipment redundancy, the spare parts program, and the instrumentations and control systems available.

The team found most systems to be in good working order, but also found room for possible improvement. The site maintains a good data base and warehouse of spare parts and maintenance records. One critical recommendation was to evaluate the balance between stocking critical spares and replacements for equipment versus having redundant systems. In some cases, it is more economically feasible to install a backup system or to redesign the system to mitigate consequences of a failure rather than have a large stock of spare parts. For example, if a pump failure will cause significant downtime, even with a replacement in stock, it may make sense to install a backup system. Operations will be interrupted for a few minutes while the backup system kicks on compared to the extended time needed to remove and replace failed equipment if no backup system is present. Understanding the consequences of having the system out of operation is important for this analysis.

## **OPTIMIZATI~~N~~ OF LONG TERM MONITORING**

The efforts toward optimizing the monitoring and reporting have not been geared to optimize existing monitoring programs, but more toward designing new, cost effective monitoring programs for the expanded remediation systems. A key to this is to target the monitoring programs to the most significant remedial action objectives. For the River Projection, 2012 objective, the monitoring programs have been focused on providing reliable data on plume containment as well as on cleanup of the hyporheic zone in the river. The plume containment



monitoring program will use a multiple-lines-of-evidence approach that will focus on detailed evaluations of hydraulic data including:

- The presence, extent and persistence of reversed (landward) hydraulic gradients (i.e., from the Columbia River toward monitoring wells near the line of extraction wells)
- The extent of hydraulic capture as determined using:
  - An auto-calibrated water level mapping technique that combines kriging with analytic elements and particle tracking to prepare capture frequency maps (CFMs)[8].
  - The numerical flow and particle tracking model, described above, following calibration to the hydraulic response of the aquifer to stresses associated with remedy operation.

The monitoring program for monitoring the cleanup of the hyporheic zone is more complicated since sampling in this zone is not a standard practice in the industry and the variations in the river stage complicate the analysis. The river stage varies based on releases from the upstream dam. There are major seasonal variations (as much as 5 m) but also daily variations, as much as 1 m. These variations in river stage result in a complicated pattern of groundwater/river water interaction. During high stage, clean river water flows into the hyporheic zone resulting in low concentrations. During low river stage, contaminated groundwater flows into the hyporheic zone resulting in higher concentrations. Time dependent or composite sampling might be the best approach. However, it is also difficult and expensive to acquire hyporheic zone samples, so that some type of cost effective compromise is required. As more is learned about the groundwater/river interaction, the monitoring program will likely require additional optimization.

## **DISCUSSION**

RPO tools, as discussed here, provide an efficient and effective method to evaluate and optimize the remediation system in use at a site. They should be implemented on a periodic basis to allow continued optimization throughout the life of the remediation.

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