

Advances in Hexavalent Chromium Removal at Hanford – 12416

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ABSTRACT

Chromium was used as a corrosion inhibitor in the reactor cooling water and was introduced into the groundwater at Hanford as a result of planned and unplanned discharges from reactors during plutonium production since 1944. Beginning in 1995, groundwater treatment methods were evaluated leading to the use of pump and treat facilities with ion exchange using Dowex 21K, a regenerable strong base anion exchange resin. This required regeneration of the resin which is currently performed offsite. Resin was installed in a 4 vessel train, with resin removal required from the lead vessel approximately once a month. In 2007, there were 8 trains (32 vessels) in operation. In 2008, DOE recognized that regulatory agreements would require significant expansion in the groundwater chromium treatment capacity. Previous experience from one of the DOE project managers led to identification of a possible alternative resin, and the contractor was requested to evaluate alternative resins for both cost and programmatic risk reductions. Testing was performed onsite in 2009 and 2010, using a variety of potential resins in two separate facilities with groundwater from specific remediation sites to demonstrate resin performance in the specific groundwater chemistry at each site. The testing demonstrated that a weak base anion single use resin, ResinTech SIR-700, was effective at removing chromium, had a significantly higher capacity, could be disposed of efficiently on site, and would eliminate the complexities and programmatic risks from sampling, packaging, transportation and return of resin for regeneration. This resin was installed in Hanford's newest groundwater treatment facility, 100-DX which was started in November, 2010, and used in a sister facility, 100-HX, started up in September of 2011, increasing chromium treatment capacity to 25 trains (100 vessels). This resin is also being tested in existing facilities that utilize Dowex 21K for conversion to the new resin. This paper will describe the results of the testing, performance in the facilities, continued optimization in the pump and treat facilities, and the estimated savings and non-tangible benefits of the conversion.

INTRODUCTION

The Hanford site, approximately 586 square miles located in south central Washington State, was chosen in 1943 as part of the Manhattan project for production of plutonium for the national defense mission. The site was chosen because it was close to the established electrical infrastructure from the Grand Coulee dam, was sparsely populated, considered stable geologically, and had a large amount of cold water available from the Columbia River [1].

Cooling water taken from the Columbia River made a single pass through the reactor and was sent to concrete cribs and basins to allow heat and short lived radionuclides to decay prior to being returned to the river.

Over the years, additional reactors were built. A total of 8 single pass reactors were constructed and operated at Hanford between 1944 and 1971, all using the same once through cooling and sodium dichromate as a corrosion inhibitor. Plutonium production continued into the 1980's and ended with the cold war. In the 1990's the work at Hanford has been characterizing, removing, treating and disposing of contamination from past operations.

Much of the land surrounding the Hanford site is very porous. Leakage of concentrated sodium dichromate from underground piping and other accidental spillage resulted in substantial quantities of chromium finding their way into the soil and over time moving downward into groundwater, and eventually with the groundwater into the Columbia River.

Chromium contamination

Hexavalent chromium on the Hanford site is primarily found near the reactor sites. It is estimated that a 2.0 km² (0.8 mi²) has contamination at concentrations greater than 100 µg/L [2]. Peak concentrations of 55,600 µg/L have been measured near the D and DR reactors. A substantial additional area has contamination below 100 µg/L.

DISCUSSION

Following the shift from plutonium production to site cleanup in the early nineties, a pilot plant was constructed to evaluate the use of ion exchange as a means of remediating the chromium in the groundwater on site. The initial studies used a variety of ion exchange resins available at the time and resulted in a determination that ion exchange could be used.

A type I strong base anion resin was chosen for the full scale facilities constructed in the HR-3 and KR-4 operable units. Initially a 400 gpm plant was constructed (HR-3) to treat the largest area of contamination near the D and H reactors. A 200 gpm plant was also built near the K reactors with operation commencing in 1997.

Control of the contaminant plumes is accomplished using a combination of extraction wells and injection wells. Contaminated groundwater is extracted from near the Columbia River and pumped to ion exchange facility for treatment. Following treatment the water is sent to a series of injection wells upgradient of the plume. This approximates a closed loop system where the injection water drives the contaminants toward the extraction wells.

As more information about the size of the contamination was gathered a series of expansions and continued testing of additional technologies have been implemented.

Pump and treat capacity near the K reactors was expanded from 200 gpm in 1997 to 1100 gpm in 2009 with the addition of two additional facilities.

Additional pump and treat capacity around the D and DR reactors began in 2004 with a 50 gpm pilot scale facility (DR-5) that is able to regenerate resin in vessel.

Another innovative treatment technology was also employed in this area. It is known as the ISRM (In-Situ Redox Manipulation) barrier. This barrier consisted of a closely grouped network of wells that had sodium dithionite injected into them to create a reducing environment, converting hexavalent chromium to trivalent chromium, which is immobile in Hanford soils and greatly reducing the amount of chromium reaching the Columbia River. A portion of the barrier failed to stop the flow of chromium prompting the expansion of pump and treat capacity to 600 gpm beginning in late 2010.

Hanford ion exchange vessel design

Ion exchange vessels for chromium treatment have employed the following design philosophy, the only exception being the DR-5 pilot scale plant. The system is modular, utilizing groups of four vessels or “trains” rated at 100 gpm. To expand capacity additional trains are added rather than changing the size of the vessels. Each vessel has an 80 ft³ capacity for ion exchange resin. Each of the four vessels in a train are in active operation in a lead-lag1-lag2-polish configuration (Figure 1).



Figure 1. Modular 100gpm ion exchange “train”

Resin is removed when the lead vessel reaches capacity for chromium or the polish vessel effluent is greater than 10 µg/L.

The four bed system has proven to be a predictable and forgiving system. Consistency in the vessel design between facilities allows for operational flexibility, since the operators can switch between facilities without extensive retraining.

Over the years several modifications or changes were implemented to aid the dependability of the system. Initially the lead vessel was operated in a sacrificial mode. This was due to concerns that uranium and other radionuclides may accumulate on the resin presenting a transportation risk. During this time the lead vessel would be left in service for six months prior to removal, sampling and disposal. The remaining vessels would be rotated between lead, lag, and polish positions based on chromium breakthrough. Evaluation of sample results showed this as an unnecessary precaution and operation shifted to rotating all four vessels allowing for increased loading of the resin prior to regeneration.

Containers appropriate for offsite transport of the resin for regeneration and a system to load/unload the resin efficiently were also implemented to minimize the need to handle the resin and to speed the changing of resin from the vessels.

Metering pumps to add sulfuric acid for pH adjustment of the influent water were also developed to maintain influent water at pH 7 were implemented to minimize mineral scaling that would develop on the resin bed and distributors that would cause additional strain on the system pumps.

Resin regeneration

The primary method used for treatment of spent strong base anion resin at the Hanford site has been off site regeneration. This method is simple for plant operation but requires extensive sampling and analysis to ensure that the resin meets all shipping requirements. This requires a large investment in resin due to the long turnaround time as the resin is sampled, shipped, regenerated, shipped back and placed into service. Several variations of onsite regeneration have been tested over the years.

Regeneration at a facility onsite was performed using sodium sulfate leaving the resin in the sulfate form (as opposed to the chloride form normally received from offsite). This resin had approximately 80% of the capacity as the resin in the chloride form. Additionally, the facility did not have the capacity to regenerate all of the resin needed to eliminate offsite regeneration.

A pilot scale facility (DR-5) was also operated from 2004 to 2010 that used in vessel regeneration. This process used sodium chloride to strip the chromium from the resin. Sodium dithionite was used to convert the hexavalent chrome (anionic) to trivalent chrome (cationic). Hydrochloric acid was used in a second step to condition the resin. Phosphoric acid was used on the regenerant wastewater solution to precipitate the

chrome, followed by sodium hydroxide to increase the pH and aid precipitation and settling. The precipitated chrome was separated by a filter press.

Bench scale testing

In 2008, plans to expand the pump and treat capacity near the D and H reactors were being finalized. With this impending expansion, the decision to re-evaluate the ion exchange resin and regeneration process was made. A test skid was procured that allowed for six resins to be tested simultaneously using a one inch diameter column with a bed depth of up to 48 inches. The columns had individual feed tanks and pumps allowing for pH and flowrate to be varied individually (Figure 2).



Figure 2. Resin test skid.

Beginning in March of 2009, seven different resins were tested. They included several strong base resins (including the resin's currently being used onsite), a styrenic weak base resin, as well as granular and bead forms of an epoxy polyamine weak base resin.

The initial testing showed results similar to the operating facilities for the strong base resins at pH around 7, confirming the validity of the test skid as a method of evaluating

resin performance. Tests were performed with the epoxy polyamine resins operated at reduced pH (5) showed exceptional affinity for chromate (Orange dots in figure 3).

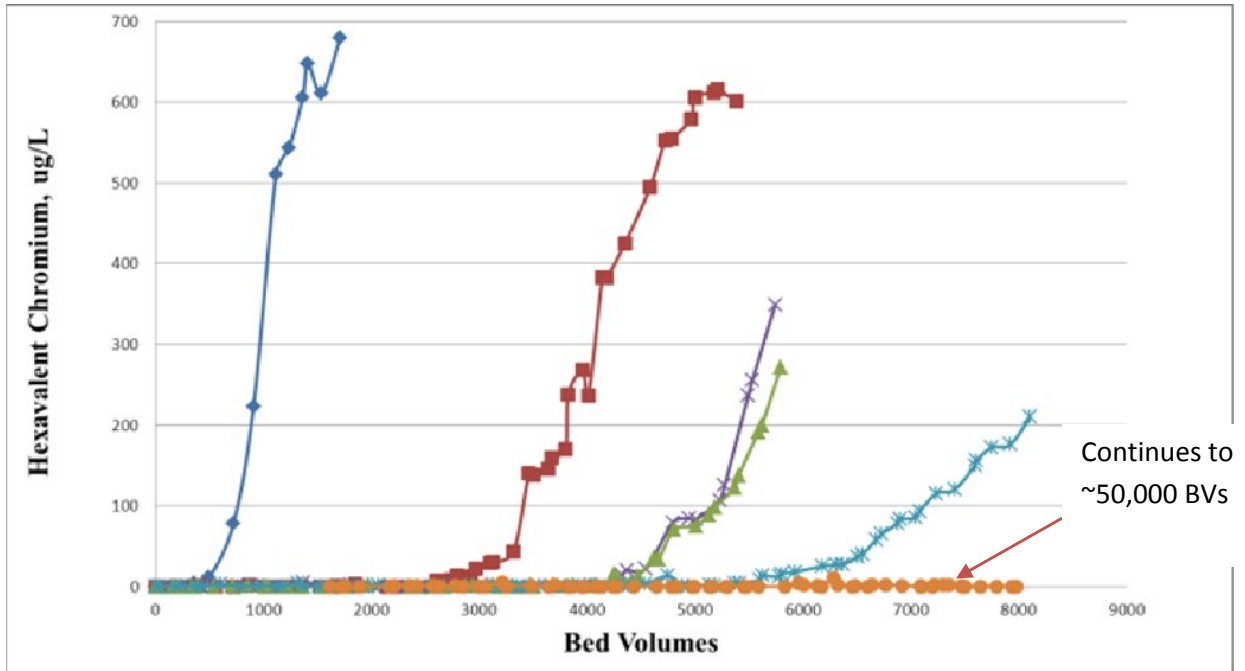


Figure 3. Initial results from resin testing

The initial test column of this resin lasted through the entire duration of the initial test series (almost nine months) without nearing capacity. The performance of this test column shifted the focus of the testing to learn more about this resin and evaluating if the switch to this resin would be the right choice for use at Hanford. Additional columns with much smaller bed depths were tested in an attempt to reach capacity of the resin. None of the tests were able to reach the total capacity of the resin, an idea about when the vessels would begin to allow chrome leakage into the lag vessels was determined (approximately 65,000 BVs when influent concentration averaged 1200 $\mu\text{g/L}$ hexavalent chromium).

Epoxy polyamine resin (ResinTech SIR-700)

Making the switch to a weak base epoxy polyamine resin would require some significant changes to the way ion exchange resin is handled on site. This type of ion exchange resin is granular rather than spherical.

The facility would require systems to deliver acid and caustic to adjust the pH of the groundwater being treated. These systems would also require bulk deliveries of chemicals due to the increased use rates needed to reach lower pH's. Additionally the type of coating inside the vessels was changed to one more appropriate to use in acidic conditions. Cathodic protection was also added to the design of new vessels to add an additional layer of protection against corrosion.

The granular shape (instead of the typical bead shape) of the best performing resin tested generates increased differential pressure across the resin potentially increasing pumping costs and requiring reevaluation of the sizing of the feed pumps. Concerns about loading and unloading of the resin, resulted in a test to load resin into and out of one of the existing vessels to determine if the existing sluicing mechanisms would work. The test was successful, and no discernible difference was noted by the operators performing the work. New vessels also have had four air ports added to the bottoms of the vessels to aid the removal of the resin.

Since the resin cannot be regenerated for reuse, a disposal path is required. To dispose of the resin onsite it must meet certain requirements to be accepted at the disposal facility onsite. Samples of the resin from testing were analyzed to determine if any additional treatment would be required for disposal. The results of these tests showed that the resin would potentially require stabilization (i.e. grouting) to meet TCLP for total chrome. The initial sample indicated stabilization would be required. Later samples, that were taken from resin samples with even higher chrome loading met requirements for disposal onsite.

Additionally these tests showed that more than 90% of the chrome on the resin was in the trivalent form rather than hexavalent form. This helped to confirm that the exceptional capacity of the resin is due to more than simple ion exchange. Testing showed the resin had more than an order of magnitude greater capacity than any of the other resins tested [3].

The mechanism is believed to be ion exchange followed by reduction with the resin matrix and precipitation inside the resin matrix. This hybrid property appears to be both flow and pH sensitive in that the rate at which chromate is reduced to trivalent chrome is slower at higher pH.

pH Testing – An effective operating range for the new resin was determined through a set of bench scale tests. Very small volumes of resin were added to beakers of highly contaminated groundwater and stirred to ensure mixing. Hexavalent chromium concentrations were measured daily and water was replenished until the resin was unable to remove additional chrome. The results shown in Table 3 indicated that the resin capacity decreased substantially when the pH was greater than 6. Additional testing with larger resin volumes and samples measured every minute to more closely simulate normal operation showed a decrease in the rate of chrome removal at pH's above 6.5 as well.

Additional column testing was performed at a facility in the K area with both sulfuric acid and with hydrochloric acid to determine if there was an advantage in operating capacity to using one acid over the other. Very little difference was noted [4]. This round of testing at much lower influent hexavalent chromium concentrations (approximately 50 µg/L) showed that the resin had potential to last 200,000 BVs or more without reaching capacity.

Initial results with epoxy polyamine resin

With questions about the epoxy polyamine resin answered, the decision to use the resin in the newest pump and treat facility was made. The resin was loaded into the vessels and operation began without pH adjustment due to schedule constraints and positive short term testing in the test skid. Operation without pH adjustment occurred for about 100 bed volumes over the course of several weeks. More than a week after the start of operation with pH adjustment chrome leakage was detected in the effluent of the lead vessel (Figure 4).

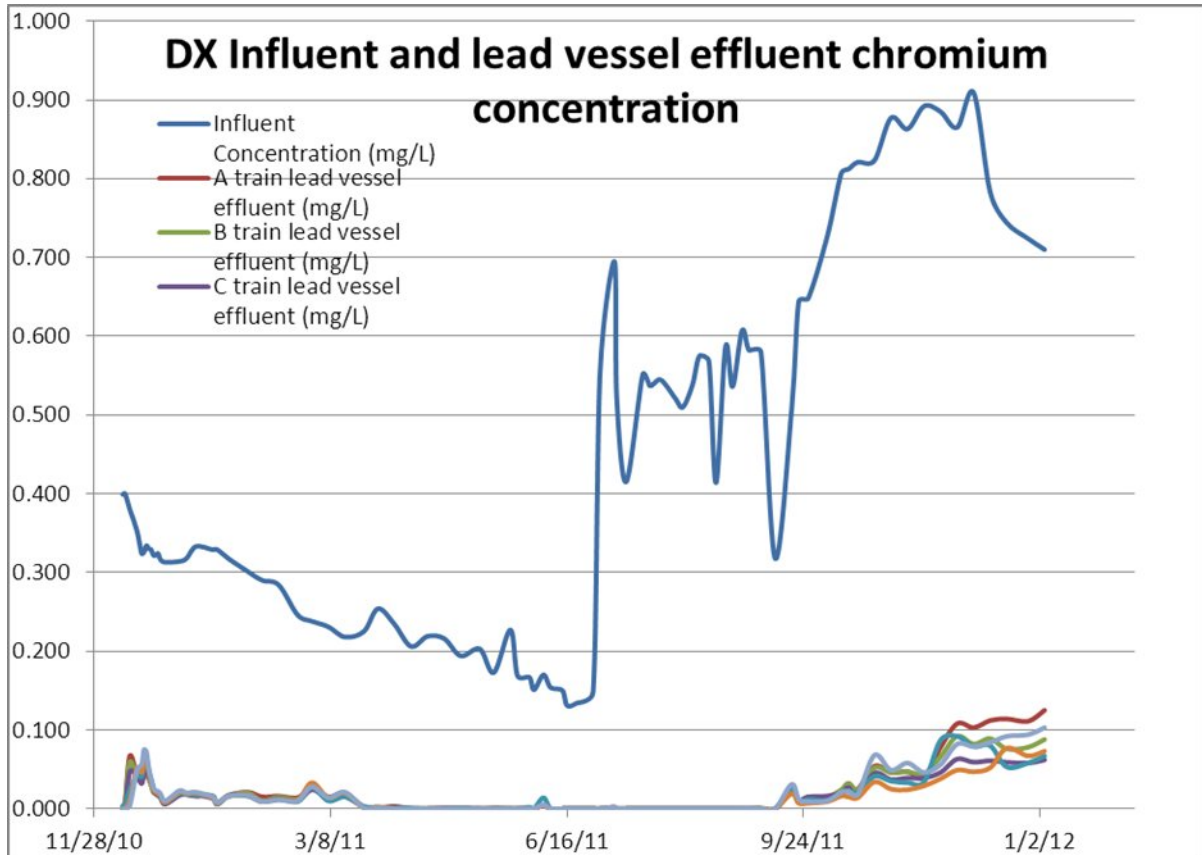


Figure 4. DX Lead vessel effluent

Lead vessel effluent values peaked several days later before stabilizing near 10-20 $\mu\text{g/L}$ (influent was about 325 $\mu\text{g/L}$). During this time the effluent required little to no caustic to return the pH back to neutral. Initial operation stripped the pH buffering capacity of the resin leaving few active sites available for ion exchange. A week after the peak in lead column effluents, a much smaller peak in the lag-1 vessels occurred as the resin was re-acidified. Once the caustic use increased to the expected levels the chromate leakage stabilized and was limited to the lead vessel only. After 2 months of operation the leakage from the lead vessels dropped below detectable levels (5 $\mu\text{g/L}$) and has stayed below detection until September 2011. As of December 2011, the resin has processed

about 75,000 BVs, removed more than 460 kg (1014 lbs) of chromium with 10-20% of the influent concentration bleeding through onto the lag-1 resin bed.

After several months of operation, differential pressure across the resin beds began increasing to higher levels than expected increasing with each subsequent vessel in series. Inspection of the resin beds showed a layer of resin fines had built up on the top of each of the lag-1, lag-2, and polish vessels. Periodic backwashing of the vessels, since they had been exposed to little or no chromate returns pressures to normal. During subsequent vessel loading at the H and K area facilities, the resin was backwashed more thoroughly. These two facilities have not experienced the high vessel differential pressures over 4+ months of operation. Additionally when the new facility near the H reactor was started, a change to three vessels in service at any one time was made at all facilities using SIR-700 resin to reduce pumping costs since the resin is proving to be so much more effective than the strong base resins previously used.

Cost effectiveness

Along with resin testing, life cycle cost estimates were prepared for the facility built near the D reactors. This estimate used the strong base resin with offsite regeneration as a baseline and compared this with the most effective strong base resin regenerated both on and off site, and the single use epoxy polyamine resin. Resin life for the epoxy polyamine resin was assumed to be 40,000 bed volumes (very conservative) due schedule constraints requiring the estimates to be prepared in parallel to the resin testing. These life cycle costs showed that the epoxy polyamine resin to be the most cost effective option saving almost \$20 million over the 11 year lifespan of the facility. This is roughly equal to the cost of construction of the facility.

With the successful implementation of epoxy polyamine resin at the D and H area facilities, the next step is to evaluate the conversion of the remaining facilities near the K reactors to this resin. To do this a test is being performed at the smallest facility to determine whether the existing simple acid injection system is capable of maintaining a desirable pH for use with the new resin. Monitoring of the vessel wall thickness will determine the suitability of the liner for use in an acidic environment. Operation with smaller volumes of resin per vessel is also being evaluated as an alternate method to reduce pressure loss across the resin bed. It is also beneficial to increase the headspace for backwashing since the vessels do not have an upper distributor that would prevent resin carry over in the event backwashing was too vigorous (newly constructed facilities have upper distributors that match the lower distributors to eliminate this concern.

REFERENCES

1. The Hanford Story video, (2011)
http://www.hanford.gov/c.cfm/video/tags.cfm/The_Hanford_Story
2. Hanford Site CERCLA Five-Year Review, (2011), DOE-RL-2011-56

3. Neshem, D (2010). Resin Evaluation and Test Report to Support DX Treatment System. SGW-41642, Rev. 1
4. Neshem, D (2010). K Area Chromium Resin Test Report. SGW-46070, Rev. 0