

# Efficiencies and Optimization of Weak Base Anion Ion-Exchange Resin for Groundwater Hexavalent Chromium Removal at Hanford – 14202

Prepared for the U.S. Department of Energy  
Assistant Secretary for Environmental Management

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### Efficiencies and Optimization of Weak Base Anion Ion-Exchange Resin for Groundwater Hexavalent Chromium Removal at Hanford – 14202

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#### ABSTRACT

The U.S. Department of Energy's (DOE's) contractor, CH2M HILL Plateau Remediation Company, has successfully converted a series of groundwater treatment facilities to use a new treatment resin that is delivering more than \$3 million in annual cost savings and efficiency in treating groundwater contamination at the DOE Hanford Site in southeastern Washington State.

During the production era, the nuclear reactors at the Hanford Site required a continuous supply of high-quality cooling water during operations. Cooling water consumption ranged from about 151,417 to 378,541 L/min (40,000 to 100,000 gal/min) per reactor, depending on specific operating conditions. Water from the Columbia River was filtered and treated chemically prior to use as cooling water, including the addition of sodium dichromate as a corrosion inhibitor. Hexavalent chromium was the primary component of the sodium dichromate and was introduced into the groundwater at the Hanford Site as a result of planned and unplanned discharges from the reactors starting in 1944. Groundwater contamination by hexavalent chromium and other contaminants related to nuclear reactor operations resulted in the need for groundwater remedial actions within the Hanford Site reactor areas.

Beginning in 1995, groundwater treatment methods were evaluated, leading to the use of pump-and-treat facilities with ion exchange using Dowex™<sup>a</sup> 21K, a regenerable, strong-base anion exchange resin. This required regeneration of the resin, which was performed offsite. In 2008, DOE recognized that regulatory agreements would require significant expansion for the groundwater chromium treatment capacity. As a result, CH2M HILL performed testing at the Hanford Site in 2009 and 2010 to demonstrate resin performance in the specific groundwater chemistry at different waste sites. The testing demonstrated that a weak-base anion, single-use resin, specifically ResinTech SIR-700®<sup>b</sup>, was effective at removing chromium, had a significantly higher capacity, could be disposed of efficiently onsite, and would eliminate the complexities and programmatic risks from sampling, packaging, transportation, and return of resin for regeneration.

Based on the positive testing results, the ResinTech SIR-700 resin was used in the newly constructed DX groundwater treatment facility, which began operations in November 2010. The higher capacity of the resin was confirmed and use of the resin expanded to all of Hanford Site pump-and-treat facilities treating hexavalent chromium. Conversions were completed in 2012. Operation at various pH levels is being evaluated for further optimization. This paper describes the performance of the facilities, the continued optimization and efficiencies of the pump-and-treat facilities, and the estimated savings and other benefits associated with the use of the new resin.

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<sup>a</sup> Dowex™ is a trademark of The Dow Chemical Company, Midland, Michigan.

<sup>b</sup> ResinTech® is a registered trademark of ResinTech Inc., West Berlin, New Jersey.

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### INTRODUCTION

Each of the 5 chromate groundwater pump-and-treat remediation systems at the Hanford Site has been converted from strong-base anion resin to weak-base anion resin. The transition has been smooth and very cost effective.

The first system designed to use weak-base anion resin, DX, still has the original resin in service (startup December 2010). The lead vessels have exceeded 200,000 bed volumes of throughput, and approximately 2.7 kg (6 lb) of chromium (as Cr) per cubic foot have been removed. The successful performance of the weak-base resin has been duplicated at four other chromate groundwater pump-and-treat remediation facilities at the Hanford Site. The conversion of the weak-base anion resin remediation systems will enable the U.S. Department of Energy (DOE) to cost effectively meet its regulatory commitments, which include the following goals: (1) protect the Columbia River from groundwater contaminated with hexavalent chromium exceeding aquatic protection standards and, (2) restore the groundwater to its beneficial use.

To accomplish these goals, the focus of the pump-and-treat remedy has transitioned from construction and startup activities to that of system optimization. These activities include extracting groundwater from contaminant “hot spots,” providing more uniform capture along the shoreline of the Columbia River, removing contaminant mass from groundwater plumes, and improving the effectiveness of operational performance and cost.

A significant pump-and-treat operation challenge is related to the close proximity of the hexavalent chromium groundwater plumes to the Columbia River. Upstream dams are used to generate electricity, control seasonal flooding, and protect aquatic habitat, and the dams significantly impact river-stage levels. These transient river-stage effects cause significant fluctuations in groundwater levels, requiring adjustment in pumping rates at impacted extraction well locations in order to maintain adequate flow rates.

The performance of the pump-and-treat systems is evaluated frequently within an annual reporting period to maximize the rate that hexavalent chromium is removed and to meet the river protection and groundwater remediation goals. By frequently evaluating pump-and-treat system performance, the cleanup time frame is optimized, resulting in maximum performance and minimal operating costs.

An excellent example of the use of the evaluation and optimization process to increase performance and contribute significant cost savings was DOE's decision to convert from strong-base to weak-base anion resin (epoxy polyamine resin). The results of the technical evaluation process for this substantial performance improvement results in lower cost, supports DOE's groundwater cleanup goals, and will enable successful and timely completion of the groundwater remedy.

### SITE HISTORY AND SOURCES OF GROUNDWATER CONTAMINATION

The Hanford Site, part of the DOE's nuclear weapons complex, encompasses approximately 1,500 km<sup>2</sup> (586 mi<sup>2</sup>) along the Columbia River in southeastern Washington State (Fig. 1). In 1943, the federal government took possession of the Hanford Site to build the world's first large-scale plutonium-production reactor, which was used to manufacture plutonium for the Trinity Test and the bomb that was dropped on Nagasaki, Japan during World War II in 1945. During

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the Cold War period (1945 through 1991), the federal government built a total of nine reactors to produce weapons-grade plutonium. A total of eight single-pass reactors were constructed and operated at the Hanford Site between 1944 and 1971, all using the same, once-through cooling and sodium dichromate as a corrosion inhibitor [1].

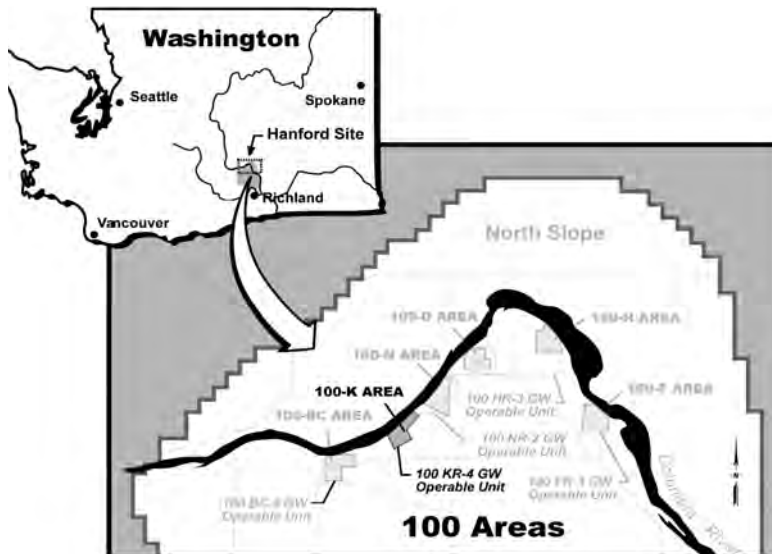


Fig. 1. Location of the Hanford Site in Washington State.

The Hanford Site was chosen because it was close to the established electrical infrastructure from the Grand Coulee Dam, was sparsely populated, was considered stable geologically, and had a large amount of water available from the Columbia River that could be used for cooling the nuclear reactors.

During reactor operations, chemical and radioactive waste was released into the environment and contaminated the soil and groundwater beneath portions of the Hanford Site. Since the 1990s, DOE has worked to remediate this contamination.

Groundwater contaminated with hexavalent chromium resulted from engineered releases of conditioned cooling water and from leakage and spills of concentrated sodium dichromate solution. Since the geology of the Hanford Site is very porous, the contaminated groundwater then migrated to the Columbia River.

### TREATMENT OF CHROMIUM CONTAMINATION

Hexavalent chromium contamination at the Hanford Site is primarily found near the reactor sites. It is estimated that 0.75 km<sup>2</sup> (0.29 mi<sup>2</sup>) of groundwater exhibited contamination at concentrations greater than 100 µg/L [2]. A peak concentration of 69,700 µg/L was measured near the 105-D and 105-DR Reactors in 2010. An area greater than 8 km<sup>2</sup> (3 mi<sup>2</sup>) exhibited contamination above 20 µg/L.

Control of the contaminant plumes is accomplished hydraulically, using a combination of extraction wells and injection wells, along with periodic realignment of wells. Contaminated groundwater is extracted from downgradient wells near the Columbia River and pumped to the ion-exchange facility for treatment. Following treatment, the water is sent to a series of injection

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wells upgradient of the plume. Injection water drives the contaminants toward the extraction wells to accelerate remediation.

Comparison of the plume maps from 2009 and 2012 clearly shows the effectiveness of the treatment process at the Hanford Site's 100-D and 100-H Areas (Fig. 2). The extent of the hexavalent chromium plume and the maximum observed concentrations have been substantially reduced as a result of system modifications.

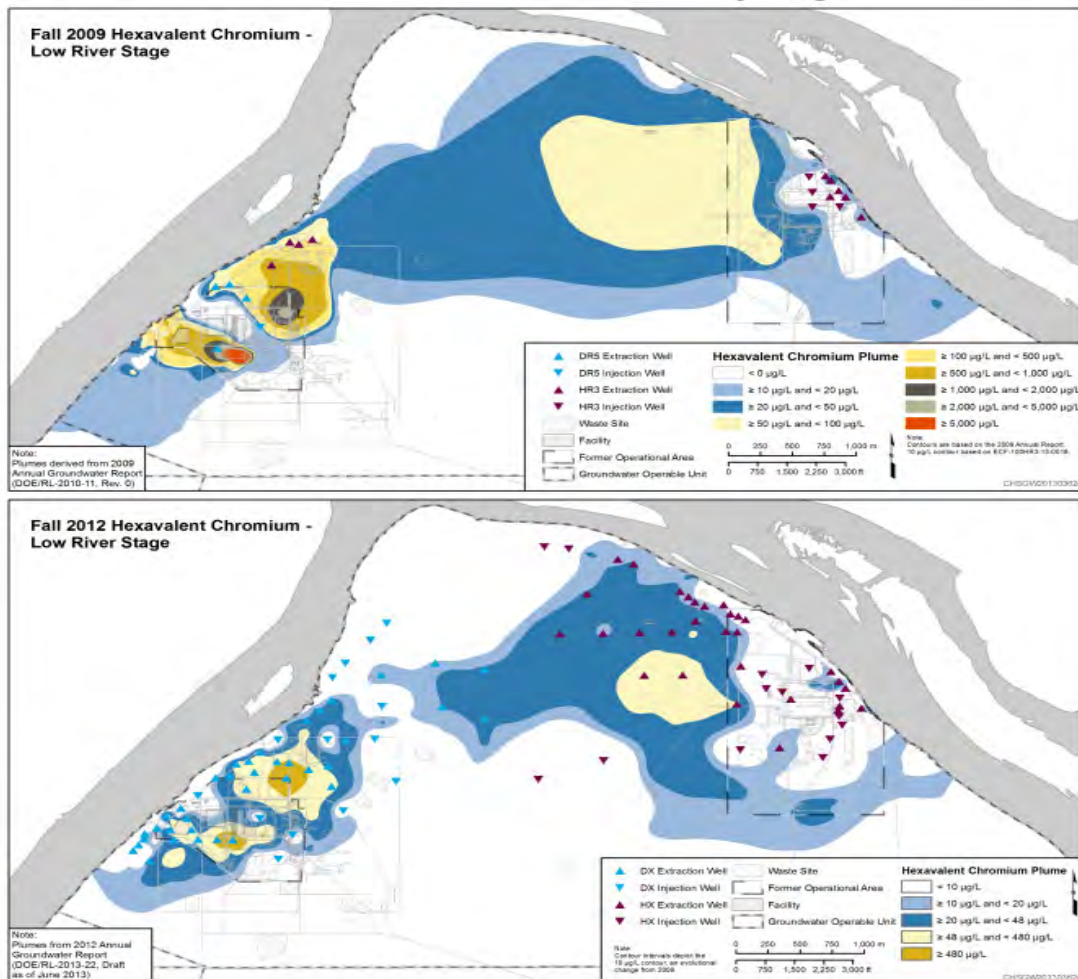


Fig. 2. Comparison of Hexavalent Chromium Plumes, 2009 and 2012.

### Original System Design

All of the ion-exchange vessels for chromium treatment initially employed the following design philosophy. The systems are modular, using groups of four vessels, or a "train," rated at 379 L/min (100 gal/min). To expand capacity, additional trains are added rather than changing the size of the vessels. Each vessel has an 2.3 m<sup>3</sup> (80 ft<sup>3</sup>) capacity for ion-exchange resin. Each of the four vessels could assume any part of a train; the positions being lead, lag-1, lag-2, and polish configuration. The position of each vessel was determined by manual valving. Each vessel could also be bypassed.

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Fig. 3. Ion Exchange trains at DX pump-and-treat

The original four-vessel systems were developed for strong-base anion resin used for chromate removal. The strong-base resins worked well and provided predictable results but had limited throughput, resulting in frequent resin changeouts. Regeneration of the strong-base anion resin was problematic, requiring a high level of regulatory scrutiny prior to offsite shipment, in addition to considerable personnel labor. These costs and difficulties were the drivers behind the conversion to use of a weak-base anion resin.

The original design concept has proven to be a predictable and robust system for the weak-base anion resin. It has provided substantial flexibility in configuration following the conversion. This includes the ability to double the treatment throughput capacity by splitting the trains into two, two-vessel trains (i.e., lead and lag vessels) if needed. Consistency in the vessel design and system controls allows for operational flexibility because the operators can rotate between facilities without extensive retraining.

With replacement of the strong-base with weak-base anion resins, the resin service life is substantially increased and the frequency of resin changeouts correspondingly reduced. Resin changeouts have not been required since conversion of the systems. The hexavalent chromium breakthrough from the lead vessel is predictable, easily measured, and increases very slowly over time. The effluent concentration from the lag vessel remains well below the current regulatory limit for injection to the aquifer. Typically, effluent concentrations from the lag vessel are near the limit of detection (approximately 1  $\mu\text{g/L}$  with current colorimetric analysis methods).

The demonstrated effectiveness of the resin has allowed the option of decoupling the lag-2 and polish vessels and using them as an additional lead/lag pair. This performance improvement would allow doubling the treatment capacity of each facility, if needed, for the remediation effort. This modification results in large increases in facility throughput, with little additional capital cost and minimal increase in operating cost.

### The Question of pH Adjustment

For maximum resin performance, the weak-base anion resin requires that the influent water pH be adjusted to an acidic level to achieve maximum hexavalent chromium removal. Acid pH adjustment of influent and alkaline pH adjustment of effluent water increase the operating costs.



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However, an advantage of the weak-base anion exchange resin is that it exhibits a two-step retention for hexavalent chromium: (1) the chromate/dichromate ions are captured and sorbed to the resin by anion exchange, and (2) the sorbed hexavalent chromium is reduced to trivalent chromium on the resin. The rate of sorption, as well as the overall sorption capacity of the resin is sensitive to solution pH and to flow rate (i.e., relative residence time). The influent pH of 5.0 was selected for this application based on measurements during resin testing (TABLE I).

TABLE I. Results of SIR-700 pH evaluation

Solution pH	Chromium Absorption (mg)	Relative Capacity
5.0	57.0	1.00
5.5	44.3	0.78
6.0	43.6	0.77
6.5	24.3	0.43
7.0	17.5	0.31
8.0	11.2	0.20

Not all weak-base resins exhibit this secondary capture mechanism (i.e., dichromate reduction) and, in particular, the use of styrenic-based weakly basic anion resins show capacities no higher (and in some cases lower) than the original strong-base anion resins used at the Hanford Site.

Two new groundwater pump-and-treat facilities, DX and HX, with a capacity to treat up to 5,300 L/min (1,400 gal/min), were designed to remediate the hexavalent chromium plume (Fig. 2). The design included modifications to incorporate the weak-base anion resin. Groundwater treated through the resin was to be operated within an influent pH range of 5 to 5.5 to optimize resin performance and achieve the maximum resin service life. The system was designed to include alkaline adjustment of the pump-and-treat effluent to ensure minimal impact to aquifer chemistry and injection well performance. The typical aquifer pH is around 7.

The DX facility was the first of the two new systems to be placed in operation. Based on the exceptional performance of the weak-base anion resin at the DX pump-and-treat facility (based on one year of operational data), additional testing was recommended and performed at the KW facility. The KW facility was modified to use weak-base anion resin and incorporated influent pH adjustment to achieve optimal resin effectiveness. Test results indicated that the weak-base anion resin effectively removed hexavalent chromium from groundwater at this location.

### Testing of Weak-Base Anion Exchange Resins at Higher pH Ranges

Based on successful implementation of the weak-base resin at the first three locations, the two remaining pump-and-treat facilities (KX and KR-4) were modified to operate with weak-base resin. At these locations, influent pH adjusted from the optimum performance range of 5.0-5.5 to approximately 6.7 (pH) was evaluated to test the effect on chromium sorption and relative capacity of the resins in a full-scale application. At this higher influent pH, the weak-base resin proved to perform better than expected. The resin has been in place for over 1.5 years without a resin changeout. Effluent concentrations remain well below regulatory standards operating in this higher pH range. Use of the weak-base anion resin has avoided over 75 resin bed changeouts in the K area compared to the previous strong-base anion resin. The better-than-expected performance is believed to be due to relatively low hexavalent chromium concentrations in groundwater at these locations.

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Overall, conversion from strong-base to weak-base anion exchange resin has proven to be a cost-effective modification for the Hanford Site pump-and-treat systems. The pH influent testing indicates better-than-expected resin performance, resulting in substantial lifecycle operation and maintenance cost savings.

### Testing to Extend Weak-Base Anion Exchange Resin Service Life and Performance

To extend the service life of the weak-base resin used in facilities with the higher operational pH, two methods were developed. The first, stand time or vessel idle time, isolates the vessel to increase residence time. This allows the reduction reaction to “catch up” in the vessel from operation at the higher pH. The second method, acid conditioning, operates a series of vessel trains at reduced pH, accelerating the reduction reaction, converting hexavalent chromium to trivalent chromium.

The above methods for resin conditioning were initiated after using the weak-base anion exchange system for approximately one year, operating at a pH of 6.7. Hexavalent chromium concentrations from effluent from individual lead vessels began to increase from nondetectable levels to 10 µg/L. The influent concentration at these pump-and-treat facilities was approximately 30 µg/L.

As described above, two methods were tested to restore the performance of the resin. One method allows resin to set in place, with no flow through the treatment vessels for a period of time to allow the hexavalent chromium sorbed on the resin surface to convert to low-solubility trivalent chromium, thus restoring a portion of the anion sorption capacity of the resin. This phenomenon was observed at the KW pump-and-treat system when the resin trains were split to increase throughput. Prior to splitting the treatment trains, the effluent concentrations leaving the lead vessel were increasing. Following the offline period (i.e., no flow through the vessels) to perform the treatment train modification, resin in the affected vessels was observed to exhibit hexavalent chromium removal consistent with the treatment efficiency encountered at initial startup.

The second method developed is an acid conditioning method, implemented at the KX facility in March 2013. This method temporarily decreases the pH through the vessels to accelerate the conversion of hexavalent chromium to trivalent chromium; re-establishing low to nondetect effluent concentrations of hexavalent chromium for injection to groundwater.

Based on test results, both stand time and acid conditioning methods may be viable methods to extend the life of the weak-base anion resin while operating the pump-and-treat systems above optimal resin performance pH levels. Additional monitoring will be necessary to fully assess the degree of performance extension and the cost effectiveness of the methods.

### TREATMENT SYSTEM PERFORMANCE DATA

The following graphs (Figs. 4, 5, 6, 7, and 8) present a summary of the performance data from the various facilities. The HX, KR, KX, and KW facilities are currently operating at a pH of approximately 6.7. Additional testing is being performed to determine if an even higher pH can be tolerated, provided that resin conditioning steps are employed.

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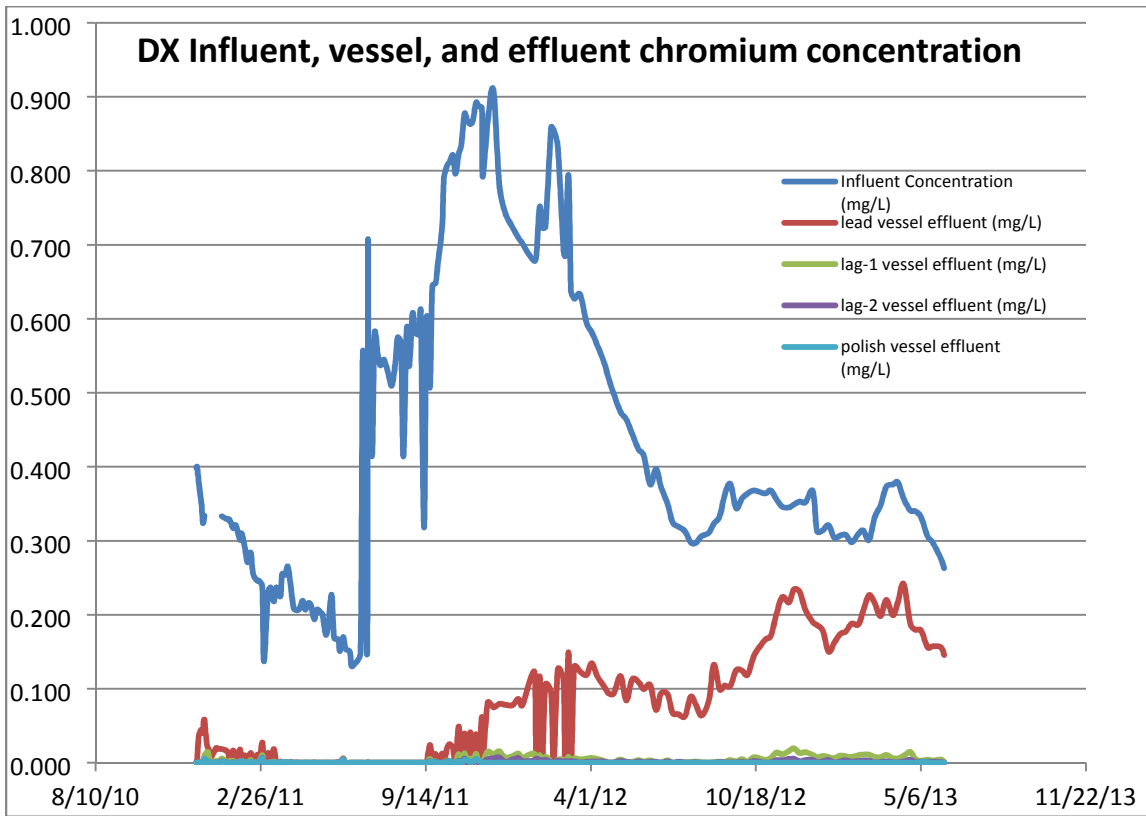


Fig. 4. Summary of Performance Data for the DX System.

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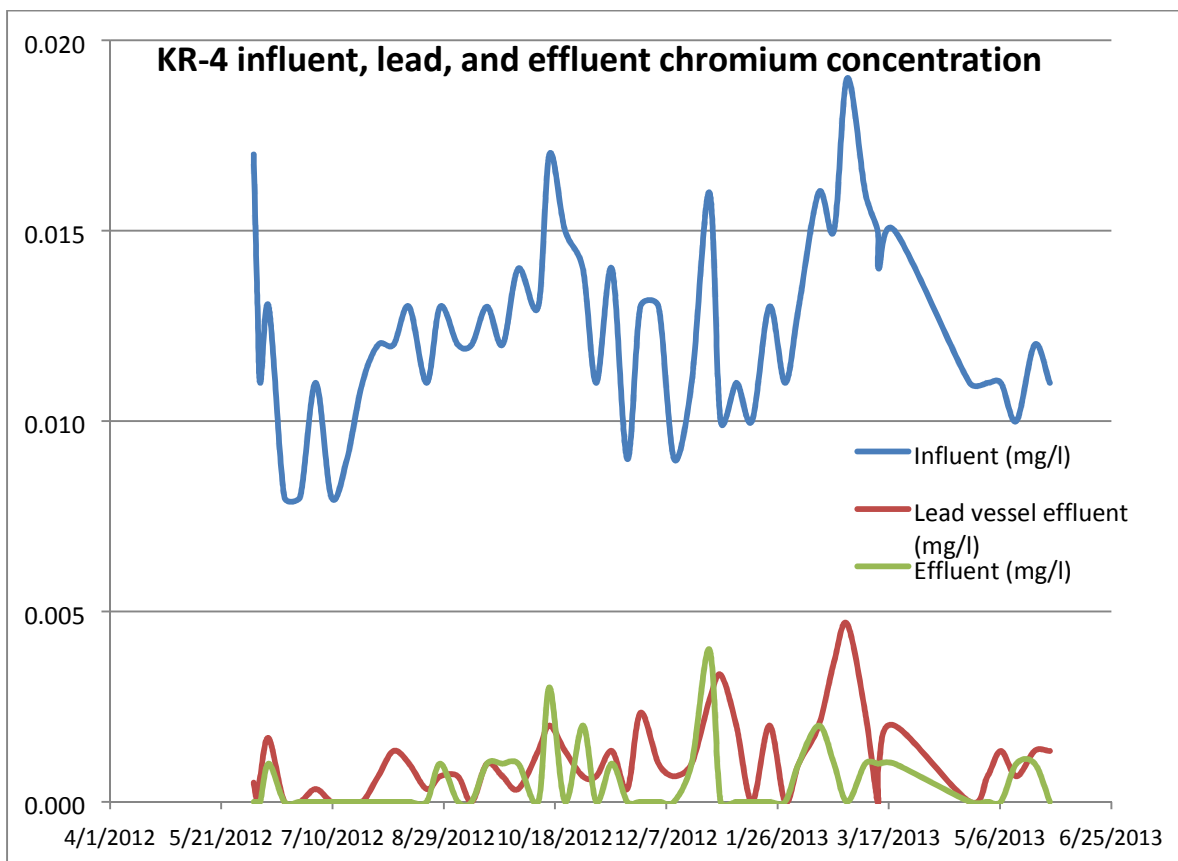


Fig. 5. Summary of Performance Data for the KR-4 System.

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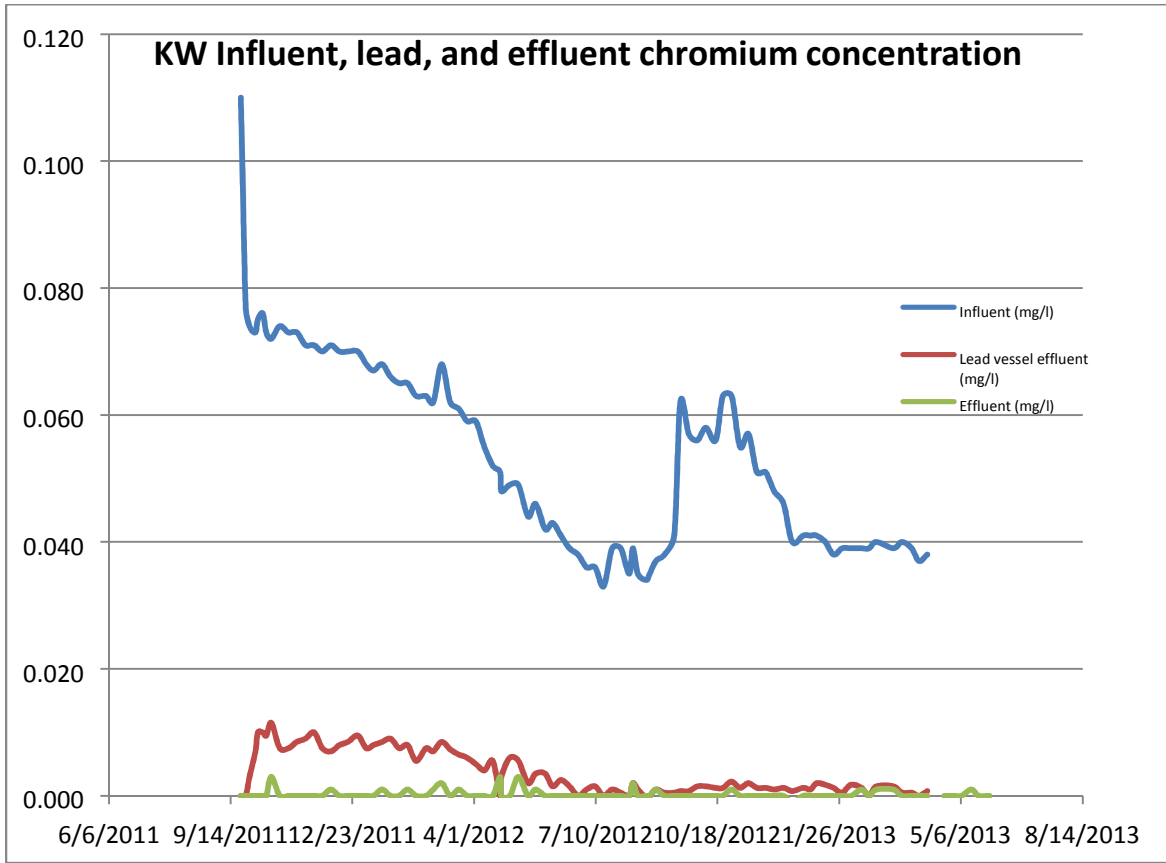


Fig. 6. Summary of Performance Data for the KW System.

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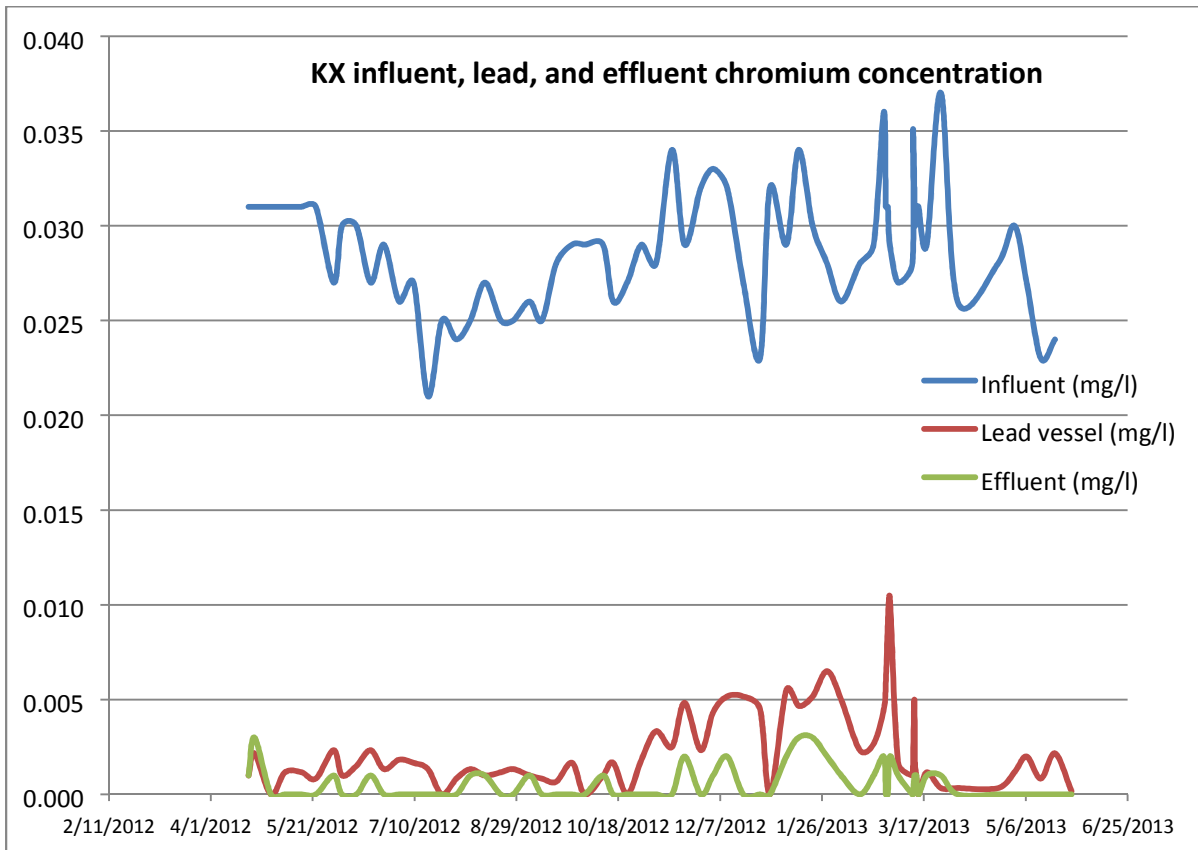


Fig. 7. Summary of Performance Data for the KX System.

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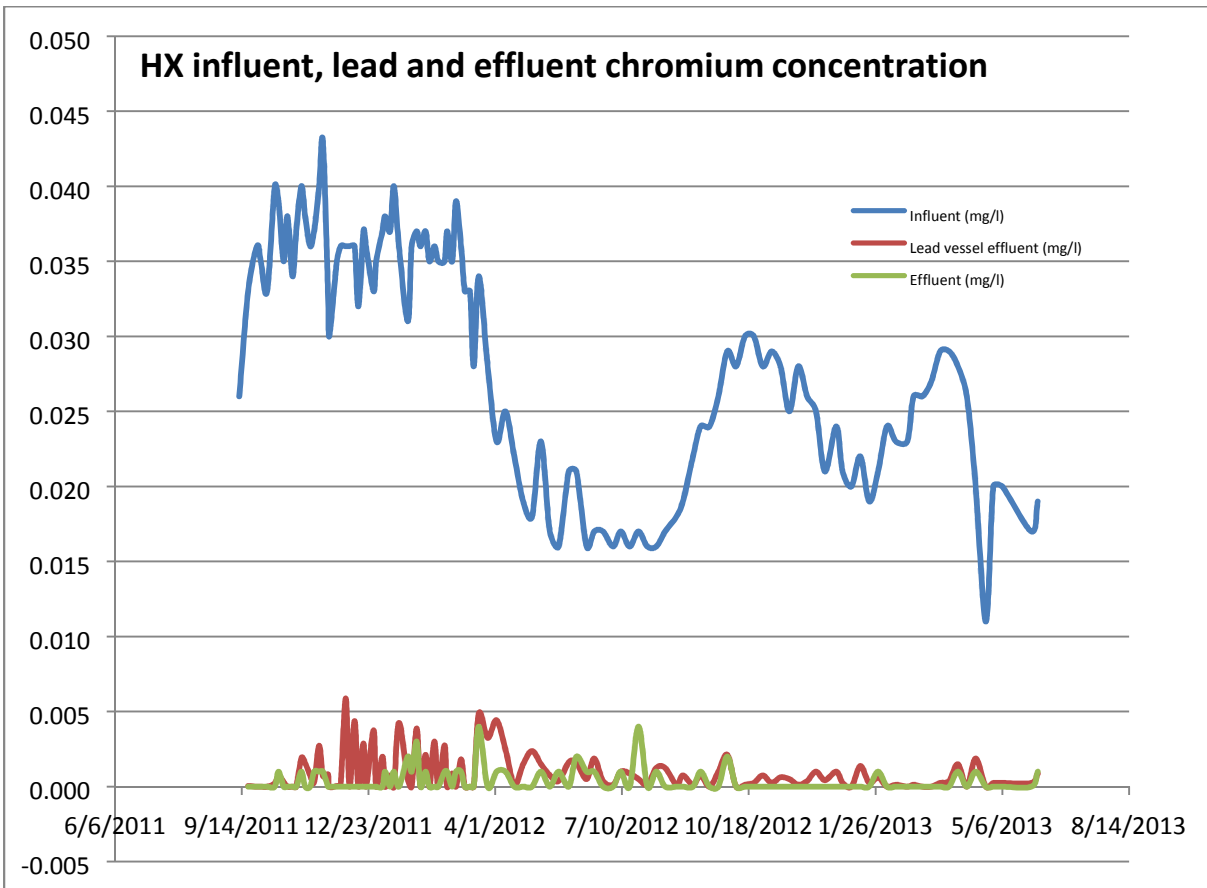


Fig. 8. Summary of Performance Data for the HX System.

### SUMMARY

During the previous 3 years, considerable optimization of the groundwater hexavalent chromium removal systems at the Hanford Site has occurred. These activities, particularly implementation of the weak-base anion exchange (epoxy polyamine) resin, have resulted in substantial remedial system performance improvements and cost reductions. Most of the ion-exchange treatment trains will be reconfigured from four vessels into dual vessels (lead/lag vessel configuration) as system capacity is needed. The pH of the influent water has been increased to 6.7 at most facilities without significant deterioration in hexavalent chromium removal efficiency or reduction in resin longevity. The approaches identified for reconditioning resin have demonstrated the ability to restore efficiency of hexavalent chromium removal of the lead vessels with minimal additional labor.

As a result of design modifications and the conversion to weak-base anion resin, it is estimated that more than 600 resin changeouts have been avoided during the last 2.5 years for groundwater treatment facilities along the Columbia River compared to the previous strong-base anion resin. This translates into significant lifecycle cost savings for remediation of the hexavalent chromium groundwater plumes at the Hanford Site.

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