

ION-EXCHANGE RESIN FOR REMOVING HEXAVALENT CHROMIUM FROM GROUND WATER
AT TREATMENT FACILITY C: DATA ON REMOVAL CAPACITY, REGENERATION EFFICIENCY,
AND OPERATION

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ABSTRACT

Lawrence Livermore National Laboratory (LLNL) is operated for the Department of Energy by the University of California. In July 1987, LLNL was placed on the National Priorities List based on the presence of volatile organic compounds (VOCs) in ground water. The July 1992 Record of Decision stipulates air stripping for treatment of VOCs and ion-exchange to treat chromium in the ground water for Treatment Facility C (TFC). TFC, which was activated in October 1993, was designed to treat influent ground water at 60 gpm with concentrations of hexavalent chromium averaging 30 ppb. The ion exchange system removes the hexavalent chromium to below its limit of detection (2 ppb). The resin used is a strongly basic Type I quaternary ammonium anion exchange resin with a styrene-divinylbenzene copolymer gel matrix. The total hexavalent chromium removed from the ground water as of October 8, 1995 was 660 grams. An initial operating capacity was achieved of 6.4 grams CrO_4^{2-} removal per ft^3 of resin, but this was observed to vary over the next two years. Variation was observed in the rate of breakthrough. The regeneration process was optimized to minimize waste produced and maximize regeneration of the resin. Elevated levels of chloride, sulfate, nitrate, potassium, and uranium have been observed in the regeneration waste. Because of the potassium and uranium content, the regenerated waste had to be disposed of as mixed waste.

¹Lawrence Livermore National Laboratory, *Draft Remedial Design Report No. 2 for Treatment Facilities C and F*, (UCRL-AR-112814 dr), May 10, 1993.

INTRODUCTION

Lawrence Livermore National Laboratory (LLNL) is operated for the Department of Energy by the University of California. In July 1987, the LLNL Livermore site was placed on the National Priorities List based on the presence of volatile organic compounds (VOCs) in ground water. The July 1992 Record of Decision (ROD) stipulates air stripping for treatment of VOCs and ion-exchange to treat chromium in the ground water for Treatment Facility C (TFC). TFC was activated in October 1993.

TFC is designed to treat influent ground water at 60 gpm with concentrations of total VOCs at an average of 130 ppb, and hexavalent chromium at an average 30 ppb.¹ TFC discharges the ground water to a surface arroyo under the Waste Discharge Requirement Order No. 91-091. Under this agreement, the effluent limitation for total VOCs is 5 ppb, and for hexavalent chrome is 11 ppb. Air stripping removes the VOCs to below the limit of detection in ground water (0.5 ppb). The ion exchange system removes the hexavalent chromium to below its limit of detection (2 ppb). Table 1 shows the averaged influent concentrations of VOCs to be remediated at TFC.

Table 1. Maximum and average expected influent concentration of expected VOCs to be remediated by Treatment Facility C. The maximum design flow rate at the facility is 60 GPM.

Constituent	Maximum Influent	Average Influent	Effluent discharge requirements
Perchloroethylene (PCE)	6	5	4
Trichloroethylene (TCE)	25	20	5
1,1-dichloroethylene (1,1-DCE)	3	2	5
Chloroform	4	3	5
Trichlorotrifluorethane (Freon 113)	125	100	5
Total VOCs	163	130	5
Hexavalent chromium	50	30	5

TFC was constructed inside a permanent building, which is shown in Figure 1. Submersible pumps extract the ground water from well fields located near the building. Inside the facility, the ground water is filtered to remove particulate and sediment to a nominal 5 microns, then passed through two tank-type air strippers in series, where the VOCs are removed and collected onto vapor-phase granular activated carbon. The ground water then travels through two columns, connected in series, that are filled with ion exchange resin. After passing through both ion exchange columns, the treated ground water is discharged to a surface arroyo. The air stripping and ion exchange equipment inside the facility is shown in Figure 2.



Figure 1. Treatment Facility C is designed for long term operation and is constructed inside a permanent building.



Figure 2. TFC uses air stripping to remove VOCs and ion exchange to remove hexavalent chromium from ground water.

The two ion exchange columns each contain 30 ft³ of resin. They are part of a larger system called the hexavalent chromium removal unit (HCRU). The HCRU has an internal programmable logic controller (PLC). Both normal water processing and the regeneration sequence are automatically sequenced by the PLC. Process hardware consists of a batch tank, pump, sand filter, ion exchange columns, and valving and piping for treated water. The HCRU also contains a salt tank, pump, and separate piping for regenerating the resin. (Refer to Figure 3.) Regeneration is counterflow to the process flow direction. During normal processing, the effluent ground water is sampled in between the columns for hexavalent chrome. When the level between the two columns exceeds 11 ppb, the upstream column is regenerated and returned to service as the downstream column. In this way the freshly regenerated resin serves as the back-up column.

The purpose of this study was to examine ways we could improve the efficiency of the HCRU, in normal water processing, and in regeneration.

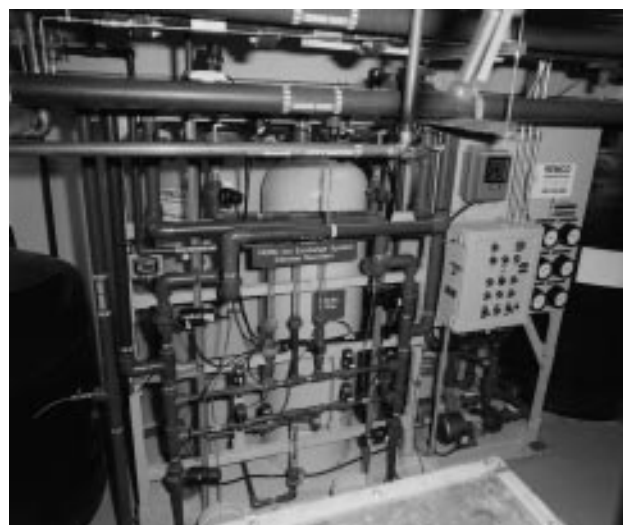


Figure 3. The ion exchange process is housed in a fully automated self-contained system called the hexavalent chromium removal unit.

CHROMIUM REMOVAL FROM THE GROUND WATER

The resin used was Purolite® A-600, a strongly basic Type I quaternary ammonium anion exchange resin with a styrene-divinylbenzene copolymer gel matrix. It has a nominal capacity of 1.5 eq/L of resin bed. The study using this particular resin covered three years of operation, and the total hexavalent chromium removed from the ground water as of October 1995 was 660 grams. This resin is used in the chloride form, where chloride is the mobile ion

which is exchanged for a mobile counterion in the ground water.

The average influent chromium level is 0.034 mg Cr(VI)/L present as the CrO_4^{2-} anion. Other anions and cations present in the TFC influent ground water at the milligram/liter level are bicarbonate (290 mg/L as CaCO_3), chloride (100), nitrate (24), sulfate (38), magnesium (21), calcium (60), and sodium (130). The pH is 7.3, and the total dissolved solids are 560 mg/L.

Before selection for the field, this resin was tested at LLNL using ground water similar to that at TFC in a bench-top test.² The bed volumes (BV) of water treated before effluent chrome levels exceeded 11 ppb were 4860. The results were not as promising as the results from Clifford's study using a Scottsdale, Arizona well, in which 20,700 BV were treated before effluent chrome levels exceeded 10 ppb.³ It is suggested in Reference 2, that at low levels of Cr concentration, the bed volumes scale linearly with sulfate concentration. The sulfate concentration in Clifford's study was one-fifth the sulfate concentration in the bench-top test.

An empirical model to predict the number of bed volumes treated before the effluent reaches 11 ppb Cr is as follows:

$$BV = \frac{0.0593(\text{Cr})^{-0.257}}{(\text{SO}_4) + (\text{Cr})} \quad (1)$$

where the concentrations of sulfate and chromium are expressed in molarity. An assumption is that the concentrations of bicarbonate, chloride, and nitrate only slightly perturb the sulfate/chromium equilibrium, while concentration of sulfate, because of its relatively high selectivity, will have a larger effect.⁴

Figure 4 shows the initial breakthrough of hexavalent chromium in between the columns, plotted against the model given in Eq. (1). The influent sulfate concentration was statistically analyzed, and the breakthrough curves for plus and minus one standard deviation for sulfate concentration are also plotted. As shown, the actual breakthrough matched the prediction given in Eq. (1) to within one standard deviation of influent sulfate levels.

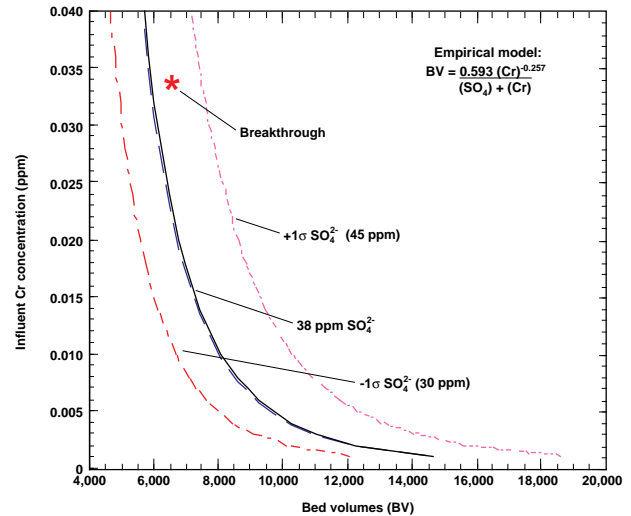


Figure 4. Empirical model for bed volumes treated before the effluent reaches 11 ppb Cr to the concentrations of sulfate and chromium, expressed in molarity. The actual breakthrough matched the model to within one standard deviation of sulfate concentration.

The multicomponent ion exchange effects are made evident by pH swings in brand-new resins and in a resin column freshly regenerated. Initially the pH swings low (4.8) as the bicarbonate ions are removed from the water. Since the bicarbonate ion is less preferred than the presaturant ion, it will have a gradual breakthrough, and the pH will gradually approach influent pH levels (7.3). If chromatographic peaking were to occur, where the least preferred species is concentrated in the column, and at some time exits the column in concentrations exceeding the influent concentrations, the pH could also increase above 7.3. We have observed such pH behavior at TFC. For two columns with new, unused Type II strongly basic gel anion exchange resin, nearly 36,000 gallons (80 BV) of ground water were passed through the two columns before the effluent rose to above our lower discharge limit of 6.5. (Refer to Figure 5.)

²Richard A. Torres, *Removing Hexavalent Chromium from Subsurface Waters with Anion-Exchange Resin*, (UCRL-ID-114369, June 1995).

³Dennis A. Clifford, (1990) in *Water Quality and Treatment*, Chapter 9, Ed. 4, Pontius, F. Ed., McGraw Hill, New York.

⁴Torres, p. 9.

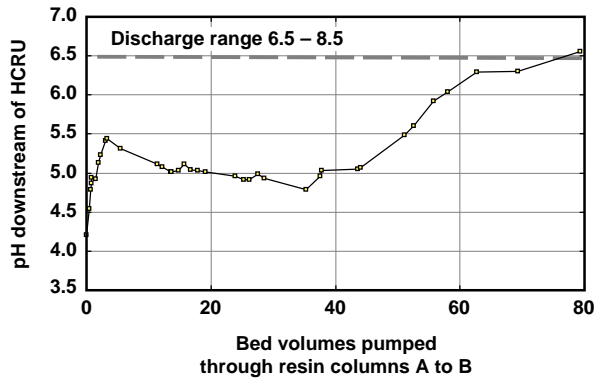


Figure 5. Effluent pH as a function of bed volumes treated. The resin is Purolite® A-300E, a Type II strongly basic anion exchange resin. Two columns with 30 ft³ of resin each are configured in series. The limiting range for pH discharge at LLNL is 6.5-8.5.

HEXAVALENT CHROME REMOVAL CAPACITY AT TFC

The amount of water treated by the upstream column at TFC when the HCRU was first put on-line was 7,173 BV before exceeding 11 ppb at the effluent. This translates to an operating capacity of 6.4 g CrO₄²⁻ removal per cubic feet of resin. At this point the column was regenerated and put back in service in the downstream position. The amount of water treated before the effluent of the upstream column again exceeded 11 ppb was 6,646 BV, or 4.6 g CrO₄²⁻ /ft³ of resin. Over the three years of operation, the average operating capacity was 5.4 g CrO₄²⁻ /ft³ of resin.

The capacity of the resin columns varied from 0.1 to 6.4 g CrO₄²⁻ /ft³ of resin. It is hypothesized that in some regenerations, the columns had broken through prematurely due to channeling caused by particulates in the resin. The particulates may be precipitates of calcium carbonate from the ground water, and water insolubles from the salt used in regeneration. For these regenerations, the capacity was small. The average capacity of 5.4 g CrO₄²⁻ /ft³ of resin did not include the regenerations that had appeared to have broken through prematurely. Refer to Table 2 and Figure 6.

Table 2. Hexavalent chromium removal capacity tabulated by regeneration date and column at TFC.

Regeneration date	Column	TFC cumulative water treated by column (× 10 ⁶ gallons)	Bed volumes (BV)	Capacity (µg Cr VI /ft ³ resin)
8/2/94	B	1.61	7,172	6.4
11/21/94	B*	1.86	1,132	0.7
4/13/95	B	2.92	4,694	5.7
6/8/95	B*	2.94	115	0.3
9/6/95	B*	2.96	63	0.5
1/26/95	A	1.49	6,646	4.6
3/9/95	A*	1.53	162	0.1
6/27/95	A	2.85	5,897	4.9
9/7/95	A*	3.18	1,457	1.0
Average				5.4

* These regenerations not included in average

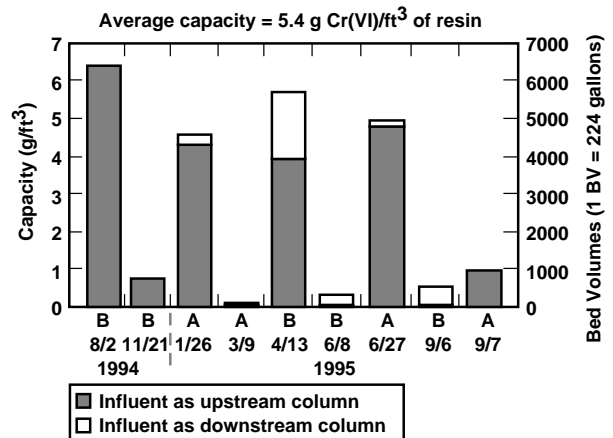


Figure 6. Capacity of ion exchange columns at time of regeneration. The source of the Cr(VI) is also indicated, whether it is from influent water in the upstream position, or loaded onto the column when in the downstream position. The amount of Cr(VI) loaded on in the downstream position is an important factor to consider in management of the ion exchange resin.

RATE OF BREAKTHROUGH

The first time the columns experienced breakthrough of chromium, the number of bed volumes required for the effluent to increase from 3 to 11 ppb was 840 BV. Other regenerations for which we had more than two data points to describe the breakthrough curve had volumes of 635 and 1290. More study needs to be done to demonstrate whether the rate of breakthrough is constant over the life of the resin. Both the expected capacity and expected breakthrough bed volumes are important to know in planning for monitor sampling of the HCRU. (See Figures 7 and 8.)

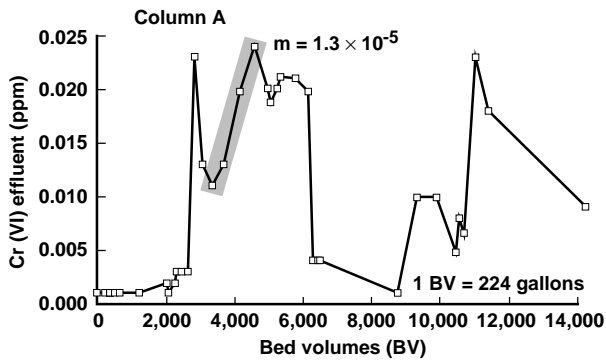


Figure 7. Breakthrough of column A plotted against bed volumes treated. Breakthrough volume is calculated when Cr(VI) levels in the effluent rise from 3 to 11 ppb. The detection level for Cr(VI) is 2 ppb, and the LLNL discharge limit is 11 ppb.

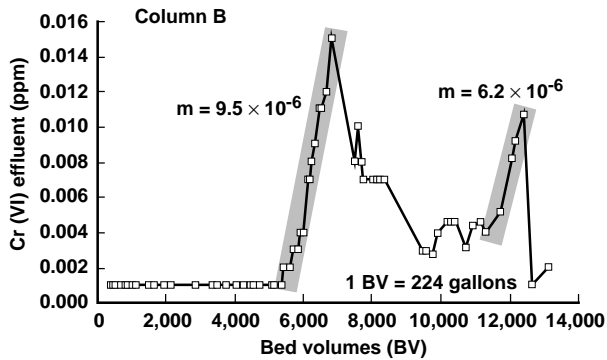


Figure 8. Breakthrough of column B plotted against bed volumes treated. Breakthrough volume is calculated when Cr(VI) levels in the effluent rise from 3 to 11 ppb. The detection level for Cr(VI) is 2 ppb, and the LLNL discharge limit is 11 ppb.

REGENERATION

Regeneration is counterflow to the process flow direction. (Refer to Figure 9.) The regeneration process was optimized to minimize waste produced and maximize regeneration of the resin. In our bench top tests, it was determined that NaOH was not necessary to achieve good regeneration, thus regeneration at TFC is done with NaCl alone. After an initial backwash to fluff the bed, a 3.2 molar or 15.8% NaCl solution is injected at 0.2 gpm/ft³. Approximately 450 gallons of brine or approximately 2 bed volumes is used to regenerate one 30 ft³ resin column. The total rinse volume is about 470 gallons or about 2 bed volumes. The initial, displacement rinse, together with the regenerate solution, is disposed of as waste. To insure the rinse amount was adequate, the residual NaCl in the rinse water was measured with a chloride meter. After approximately 380 gallons, the residual NaCl concentration in the rinse water was below 1%.

We have calculated the regeneration efficiency as the ratio of the chrome eluted off the columns to the total chrome loaded onto the columns. The regeneration efficiency at the first regeneration of column B was 27%. Later, the cumulative regeneration efficiency for both columns combined approached 90%. (Refer to Figure 10.) The concentration of the NaCl and the amount of salt solution injected through the columns were increased until the regeneration efficiency was optimized for the existing HCRU.

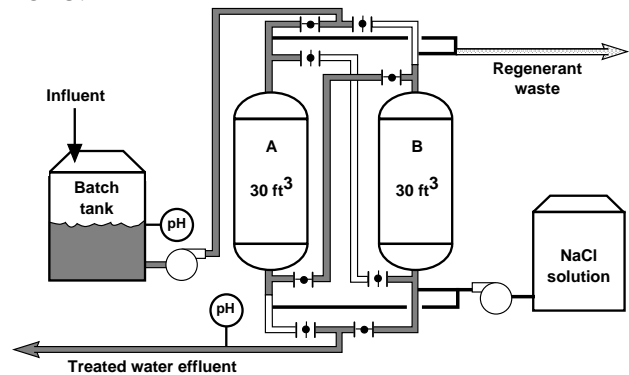


Figure 9. Schematic representation of the process flow and regeneration at TFC.

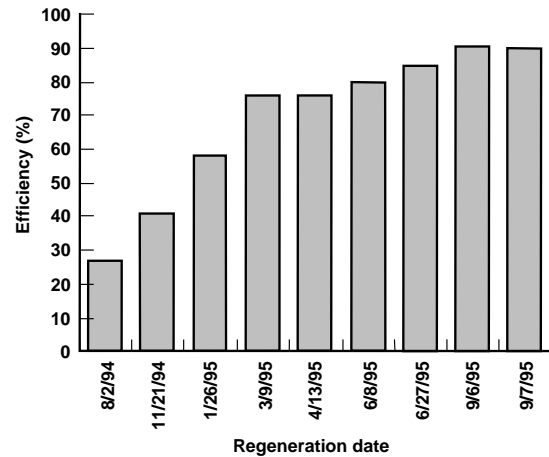


Figure 10. Efficiency of regeneration at TFC. Efficiency is defined as grams of chromium eluted off the resin during regeneration divided by grams of chromium loaded onto the resin in service.

OTHER ANIONS REMOVED BY THE RESIN

Results of regenerant solution analyses along with the chromate analyses show increased concentrations of chloride, sulfate, and nitrate, as compared to their concentrations in the influent ground water, with chromium having the largest increase. There was no arsenic in the regeneration solutions that we tested. We have also seen

levels of potassium⁴⁰ and uranium. We believe the potassium and uranium to be naturally-occurring in our ground water. The presence of both of these contaminants resulted in the regeneration waste having to be disposed of as mixed waste. When the resin was removed it was also treated as mixed waste.

COST

The HCRU was contracted to an external supplier. The HCRU, including the initial resin, cost \$150 K. The estimated yearly cost to operate the HCRU are as follows: Salt, \$1K; resin replacement, \$6K; filter, valve, pump maintenance, \$2K, and waste disposal, \$19K.

STATUS

We have replaced the strong base Type I Purolite[®] A-600 resin with Type II Purolite[®] A-300E resin. This resin is less selective, and we are studying the capacity, regeneration efficiency, and rate of breakthrough to see if the Type II resin is more efficient in our ground water.

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