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Environmental Protection Department
Environmental Restoration Division

Removing Hexavalent Chromium from Subsurface Waters with Anion-Exchange Resin

June 1995

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Introduction

Some subsurface waters at Lawrence Livermore National Laboratory (LLNL) are contaminated with volatile organic compounds (VOCs). Hexavalent chromium, Cr(VI), is also present in the ground water; however, the source of the Cr(VI) may be natural. The Cr(VI) still must be treated if brought to the surface because its concentration exceeds discharge standards. We are planning facilities for removing the VOCs and Cr(VI) to a level below the discharge standards. The planned treatment includes the following steps:

- Pumping the water to the surface facility.
- Purging the VOCs with air and absorbing them on activated carbon. The VOCs in LLNL's subsurface waters are primarily chlorinated organic solvents, such as dichloroethylene (DCE), trichloroethylene (TCE), perchloroethylene (PCE), and chloroform ($CHCl_3$). Contamination levels range from tens to thousands of parts per billion.
- Filtering the water.
- Passing the water through anion-exchange resin to remove the Cr. The Cr in LLNL subsurface waters occurs almost entirely as Cr(VI), which exists as the chromate anion, CrO_4^{2-}, at environmental pH. Cr levels range from tens to hundreds of parts per billion.
- Discharging the treated water into the local arroyos. The relevant discharge criteria are 5 ppb total VOCs, 11 ppb Cr(VI), and pH between 6.5 and 8.5, inclusive.

This report describes laboratory experiments undertaken to learn how the proposed treatment facility can be expected to operate. The laboratory results are expected to supply vendors with the detailed performance specifications needed to prepare bids on the Cr removal portion of the treatment facility. The treatment facility is expected to process 60 gallons per minute (gpm) of water by stripping VOCs with 720 standard cubic feet per minute (scfm) of air and removing Cr(VI) with 60 ft^3 of resin.

Experimental Methods

We used water from well MW-4 in our experiments. The water was collected in 5-gal plastic carboys, which were precleaned by rinsing with dilute nitric acid, deionized water, and, finally, with the wellwater itself, before being filled. Samples of water from wells P-701, MW-351, and MW-361 were analyzed for comparison. These smaller samples were collected in glass bottles after rinsing the bottles with the wellwater.

VOC Removal

VOCs were purged by bubbling air through the water until a 90/1 air/water volume ratio was reached. (This 90/1 volume ratio is used in currently operating treatment facilities at LLNL for removing VOCs.) Typically, 2 L/min of air were bubbled through 20 L of water for 16 hours. The air was presaturated with water vapor (by bubbling it through laboratory water) to avoid evaporating significant amounts of water. The air was introduced at the bottom of the sample container through a fritted-glass impinger, which produces a stream of fine bubbles. The height of water above the impinger was 25 cm or greater.

Filtration

Table 1 outlines the conditions for each resin experiment. Complete data are contained in Appendix A.

Water for Cr-1, -2, -3, and -7 was filtered through glass frits. A coarse frit was used for Cr-1 and -2, while medium frits were used for Cr-3 and -7. In addition, for Cr-1, -2, and -3, the gravity-feed reservoir contained a polymer frit with a nominal pore size of 20 to 35 µm. The presence of this additional frit was overlooked during the course of Cr-1 analysis, although it caused no difficulty. For Cr-2, the flow rate gradually decreased, and finally stopped altogether as the reservoir-frit became plugged with solids. Cr-2 tests showed that the flow was blocked in the reservoir and not the column. After Cr-3 tests, the gravity-feed reservoir was replaced with a plastic syringe barrel, eliminating the extra frit. For Cr-4, -5, and -6, the water was filtered through Whatman 541 filter paper, which has a nominal pore size of 20 to 25 µm.

Cr(VI) Removal

Puralite A600 anion-exchange resin was used for all experiments. This resin is a strongly basic tetraalkylammonium resin with a styrene-divinylbenzene copolymer gel matrix. It has a nominal capacity of 1.5 eq/L of resin bed. After measuring the desired 3.5 mL of resin bed in a 5-mL graduated cylinder, the resin was transferred to a Bio-Rad Econo-column (0.7 cm ID × ~9 cm). The resin was used in the chloride form, except for Cr-3 and Cr-7, which used resin in the hydroxide and sulfate forms, respectively.

Experimental flow rates were 1.2 mL/min (2.6 gpm/ft^3) except for Cr-6, which had a flow rate of 2.3 mL/min (4.9 gpm/ft^3). We used higher flow rates than the 1 gpm/ft^3 planned for the actual treatment facility to shorten the experiments as much as possible. However, the flow rates are still within the supplier's recommended operating conditions of 1 to 5 gpm/ft^3 of resin bed.

To further decrease experimental time, most of the experiments involved water in which the Cr(VI) concentration was elevated above natural levels by the addition of potassium dichromate. In

Table 1. Conditions for Cr(VI) removal in resin experiments.

	Cr (ppb)	pH adjustment	Resin form
Cr-1	**3,100**	**Yes**	**Chloride**
Cr-2	**3,010**	**No**	**Chloride**
Cr-3	**32**	**No**	**Hydroxide**
Cr-4	**35,600**	**No**	**Chloride**
Cr-5	**35,600**	**No**	**Chloride**
Cr-6	**35**	**No**	**Chloride**
Cr-7	**3,010**	**No**	**Sulfate**

these cases, the Cr(VI) spike solution was adjusted to pH 8 before adding it to the wellwater. Addition of the Cr spike caused only ~1% dilution of the native wellwater. The VOCs were stripped after the addition of the Cr spike.

Figure 1 shows components of the anion-resin chromatography system, which included (A) a container of wellwater, (B) a 25-mL autoburet, (C) a 10-mL gravity-reservoir, (D) the 3.5-mL anion-resin column, and (E) a fraction collector. The autoburet, which automatically filled when it was empty, dispensed wellwater at the chosen flow rate from a carboy into the gravity reservoir. The height of the reservoir was adjusted until the rate at which it emptied equaled the rate at which the autoburet filled the reservoir. The column effluent was directed to a fraction collector to allow for automatic, timed sample collection.

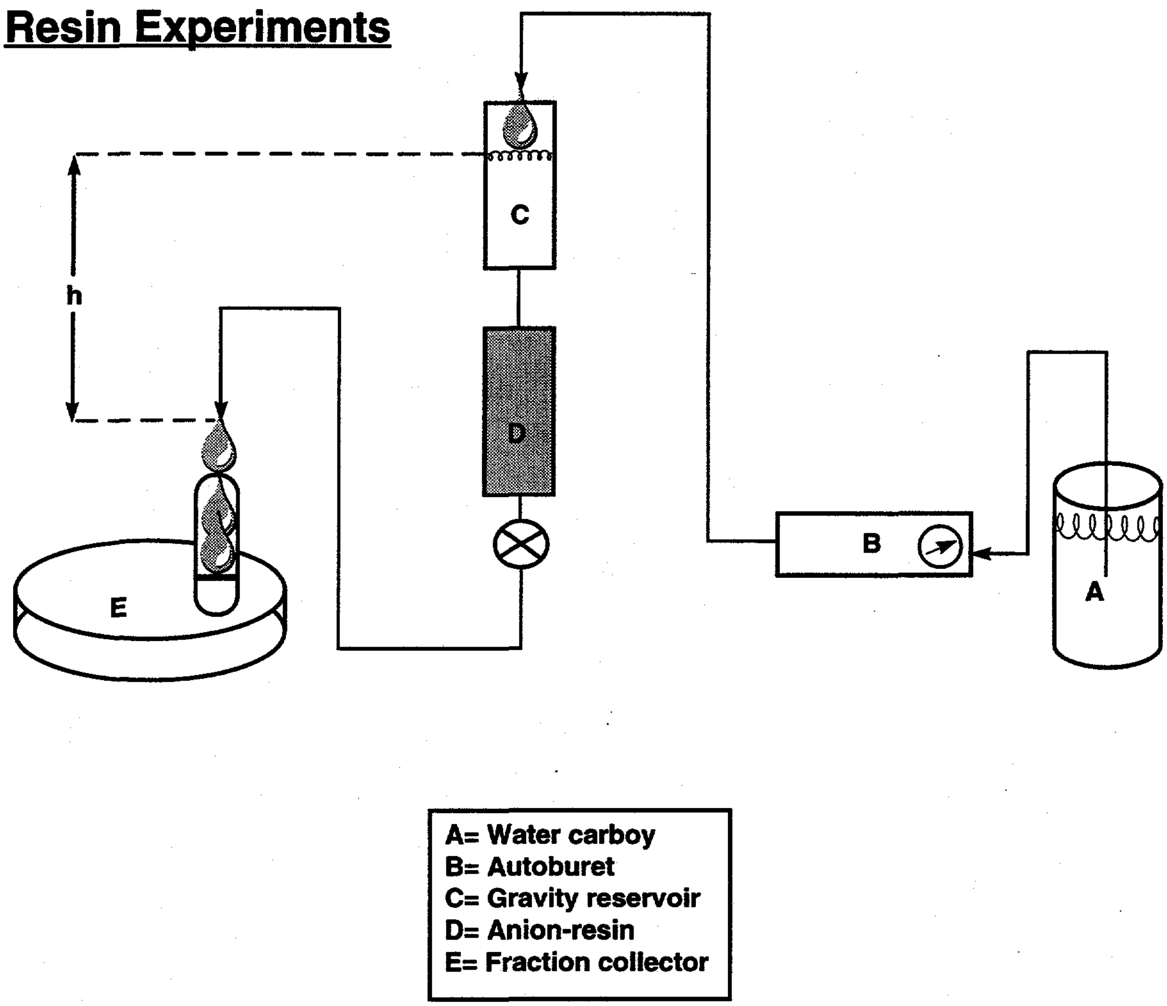

Figure 1. Components of the anion-resin chromatography system: (A) container of wellwater, (B) autoburet, (C) gravity reservoir, (D) resin column, and (E) fraction collector. The difference in heights (h) between the liquid level in C and the effluent point at E determines the flow rate through the column.

Measurements

The following analytical measurements (and techniques) were used for samples generated during the experiments.

- Total Cr, calcium (Ca), magnesium (Mg), and silica (Si) at parts per million (ppm) levels by Inductively Coupled Plasma Emission Spectroscopy (ICP-ES).
- Total Cr at ppb levels by Graphite Furnace Atomic Absorption Spectroscopy (GF-AA).
- Cr(VI) by colorimetry with diphenylcarbazide reagent (EPA Method 7196) using a colorimeter with a 5-cm path-length fiber-optic dipping probe.
- Total chloride (Cl^-), nitrate (NO_3^-), and sulfate (SO_4^{2-}) at ppm levels by ion chromatography (IC).
- Total carbonate (CO_3^{2-}) and bicarbonate (HCO_3^-) at ppm levels by potentiometric titration.
- Total inorganic/organic carbon at ppm levels by Total Carbon Analyzer.
- pH was measured with glass/calomel reference electrodes calibrated operationally with commercially available pH 4 and pH 7 buffers.
- VOCs by purge-and-trap gas chromatography-mass spectroscopy (GC-MS).

Results and Discussion

MW-4 wellwater has the following characteristics from samples measured during this work: pH 7.8 to 8.0, 35 ppb Cr, 62 ppm Ca, 22 ppm Mg, 15 ppm Si, 360 ppm bicarbonate, 110 ppm chloride, 22 ppm nitrate, 45 ppm sulfate, and ~30 ppb total VOCs (85% TCE.) The pH and total carbonate concentrations can vary slightly with the age of the sample, and in particular with whether it has been allowed to outgas; the pH increases and the total carbonate decreases slightly on standing. The VOC levels are also slightly lower than in samples measured directly at the well.

VOC Removal

One experiment was performed to measure the effect of the stripping duration on both the pH and the stripping efficiency. Results are summarized in Table 2.

Obviously, the 90/1 air/water volume ratio is not necessary for VOC removal. A ratio between 10 and 15 is probably sufficient.

Table 2. VOC stripping efficiency as a function of air/water ratio.

Stripping ratio	pH	VOC (ppb)
0	7.83	30
8	8.52	1
20	8.81	ND
50	8.98	ND
90	9.00	ND

These data also show that the laboratory stripping process raises the pH of the water significantly above the discharge limit. The increase to pH 9 was seen consistently in all of the experiments (except for the one in which extra acid was added.) The existing LLNL treatment facilities that strip with an identical air/water ratio reportedly do not exceed pH 8.5. The stripping efficiency in the laboratory is probably greater than the field operation because of smaller bubbles (and larger surface area) in the laboratory.

pH Adjustment

Carbonate concentrations in wellwater were measured by pH titration with HCl titrant. When both carbonate and bicarbonate occur together in solution, the titration curve shows two equivalence points. The first, at pH 8.5, occurs when all of the carbonate has been titrated to bicarbonate; the second, at pH 4.6, occurs when the bicarbonate (from the partially titrated carbonate and the initial untitrated bicarbonate) has been titrated to dissolved carbon dioxide. Titrations of native MW-4 water, which has an initial pH of <8.5, therefore, have a single equivalence point, corresponding to 360 ppm of bicarbonate. After the laboratory stripping process, the water has a pH of 9.2. Therefore, in stripped water, a small fraction of the total carbonate occurs as carbonate, while the bulk occurs as bicarbonate. From the two equivalence points found in the titrations with HCl, the stripped MW-4 water has 32 ppm of carbonate and 290 ppm of bicarbonate. This is 10% less total carbonate than that found in the native water. Therefore, native MW-4 water when exposed to ambient temperature and pressure is slightly supersaturated with respect to carbonate. If the increase to pH 9 were to occur in the treatment facility, then a plant operating at 60 gpm would require only 0.03 gpm of 1 M HCl to titrate the 32 ppm of carbonate to pH 8.5.

Filtration

The high carbonate and Ca/Mg concentrations, coupled with the fact that pH increases as the water is stripped, makes the precipitation of $Ca(Mg)CO_3$ likely. Analytical data (from Appendix A) show that Mg concentrations in the column effluents are constant in all of the experiments (except for Cr-3, which will be discussed later). However, Cr-2, -5, and -6 show that the Ca concentration decreases as the experiments proceed. This is consistent with the roughly 10-fold decrease in solubility of $CaCO_3$ compared to $MgCO_3$. Therefore, the column of resin acts as a finer filter than the 20- to 35-μm filters used in the experiments.

The accumulation of solids in the resin column can be minimized by:

- *Filtering the water to tighter tolerances.* The water in Cr-7 was filtered through a medium glass frit. After filtration, it had the smallest Ca concentration, which remained constant throughout the experiment. More work is required to quantitatively determine the maximum pore size such that influent and effluent Ca concentrations are constant.
- *Acidifying the water before the stripping process to eliminate the bulk of the carbonate.* The water in Cr-1 was acidified with HCl to remove 90% of the carbonate. Filtering the acidified water did not change the Ca concentration, which remained constant throughout the experiment.

Separate experiments (Table 3) show that adding HCl to the native wellwater before stripping removes carbonate on an equimolar basis.

Table 3. Effect of HCl on total carbonate. Observed ratio= $[TIC]/[TIC]_0$ as measured on TIC analyzer. Calculated ratio = $1-([HCl]/[TIC]_0)$.

Observed ratio	Calculated ratio
0.003	–0.014
0.050	0.053
0.087	0.101
0.145	0.154
0.184	0.200
1.000	0.984

Although the accumulation of precipitate in the chloride-form resin does not appear to decrease the performance of new resin, we have no data on the continued reuse of the resin. As a minimum requirement, there should be a means of vigorously backwashing the column with water to help dislodge any precipitate.

Effluent pH

In all experiments, the initial effluents from the columns had a lower pH than the influent solutions. The pH decreases because the resin initially removes a large fraction of the total carbonate present in the water. As the bicarbonate is displaced from the resin by the more tightly bound chloride, nitrate, and sulfate anions, the pH increases, gradually approaching the influent pH. From Cr-6, the test of the chloride-form resin with native MW-4 water, the effluent reaches pH 6.5 after ~20 bed volumes of water have been treated. For the proposed treatment facility, this is equivalent to 1,200 ft^3 (9,000 gal) of water from the first 2.5 hours of operation. There are several options for handling this water. It can be:

- *Recycled* through the resin until the pH reaches pH 6.5.
- *Diluted* with fresh effluent in a holding/mixing tank until the pH reaches pH 6.5.
- *Adjusted* to pH > 6.5 with sodium bicarbonate or sodium hydroxide solution in a holding/mixing tank. The use of sodium bicarbonate solution, which naturally has pH 8.3, would prevent overshooting pH 8.5. However, a solution of sodium hydroxide with the same molar concentration as the sodium bicarbonate solution requires only half the volume.

Cr(VI) Removal

In general, an ion-exchange reaction can be written as:

$$RX + Y = RY + X , \tag{1}$$

where *R* denotes the resin phase. This reaction has an equilibrium constant:

$$K_{eq} = \frac{[RY][X]}{[Y][RX]} , \tag{2}$$

where $[RY]/[Y]$ and $[RX]/[X]$ are the distribution coefficients for the anions between the resin and solution phases. Therefore,

$$[RY] = K_{eq} \frac{[RX][Y]}{[X]} \; . \tag{3}$$

For a two-component system, the amount of anion Y held by the resin is directly proportional to the equilibrium concentration of Y, and inversely proportional to the equilibrium concentration of the competing anion X. When the resin concentrations are expressed in units of moles per gram, the distribution coefficients are denoted by K_d. When the resin concentrations are expressed in units of moles per volume, the distribution coefficients are denoted by D_V. $D_V{}^Y$ is a measure of when the anion Y will "break through" into the effluent from a resin column. The value of $D_V{}^Y$ is equivalent to the number of bed volumes of solution that pass through the column before the concentration of anion Y in the effluent reaches one-half of the influent concentration. When $D_V{}^Y$ is large:

$$D_V^Y = \frac{K_{eq} R_t}{[X] + K_{eq}[Y]} \; , \tag{4}$$

where R_t is the total number of equivalents per milliliter of bed volume. Eq. (4) predicts that for sufficiently small concentrations of Y (when the product K_{eq} $[Y]$ is small compared to the concentration $[X]$), $D_V{}^Y$ is independent of $[Y]$. It also predicts how $D_V{}^Y$ varies when the product K_{eq} $[Y]$ is not negligible.

The wellwater, however, is not a two-component system. The bicarbonate, chloride, nitrate, and sulfate anions all compete with chromate for exchange sites on the resin. An increase in the concentration of any of these anions can be expected to decrease the Cr distribution coefficient, and the amount of water that can be treated before Cr breakthrough occurs.

Furthermore, the anions have varying selectivities for the resin. The preference of the resin for the anions is expected to be:

OH^- (0.09) < HCO_3^- (0.32) < Cl^- (1.0) < NO_3^- (3.8) << SO_4^{2-} (> 10^2) < CrO_4^{2-} (>10^3).

The numbers in parentheses are the equilibrium constants for Eq. (2) relative to chloride as the competing anion (Marhol, 1982). They indicate the relative preference, affinity, or selectivity of the resin toward different anions. (The sulfate and chromate numbers are guesses.) This ordering is inversely correlated with increasing hydrated radii for ions of like charge, and directly correlated with increasing total charge. The ordering is confirmed in our resin experiments.

Anion analyses of the fractions collected during the resin experiments show that bicarbonate is eluted first, followed successively by chloride, nitrate, sulfate, and chromate. (Macroscopic amounts of free hydroxide can not exist in solutions that contain bicarbonate.) Because of this ordering, an increase in nitrate concentration would decrease the Cr distribution ratio more than a comparable increase in chloride concentration, and an increase in sulfate concentration would have the largest effect.

As mentioned previously, acidifying the water before the stripping process prevents the accumulation of solids (presumably $CaCO_3$) in the resin column. Experiments with Cr-1 and Cr-2 differed only in that the water for Cr-1 was acidified with HCl to remove ~90% of the total carbonate. Table 4 shows the breakthrough volumes for nitrate, sulfate, and chromate found from these two experiments. The breakthrough volumes are those required to reach 11 ppm and 22 ppm (50% of the influent concentrations) for nitrate and sulfate, respectively, and 11 ppb for Cr.

Table 4. Total bed volumes of water treated before breakthrough of nitrate, sulfate, and chromate.

	Nitrate	Sulfate	Chromate
Cr-1	359	590	955
Cr-2	457	728	1,380
Cr-2/Cr-1	1.3	1.2	1.4

For Cr-1, the influent concentrations of bicarbonate and chloride were 37 and 300 ppm, respectively, whereas in Cr-2 they were 290 ppm and 110 ppm, respectively. The concentration ratios (Cr-1/Cr-2) are 0.13 and 2.6 for bicarbonate and chloride, respectively. Since the resin is more selective toward chloride, the increase in chloride concentration offsets the decrease in bicarbonate concentration, causing breakthrough to occur sooner in the acidified water.

Our test with native MW-4 wellwater (Cr-6) showed that 4,860 bed volumes were treated before the effluent Cr concentration reached 11 ppb. Maureen Ridley and Roger Martinelli of LLNL's Environmental Restoration Division performed a similar experiment with A600 resin and MW-4 native wellwater. In the Ridley-Martinelli experiment:

- The water was not filtered or air stripped.
- A flow rate of 1 gpm/ft^3 of resin bed was used for the bulk of the experiment; however, the flow rate was increased to 2 gpm/ft^3 near the end of the experiment.

Ridley and Martinelli found that 43 L (6,140 bed volumes) of water were treated before the effluent Cr concentration reached 11 ppb. This was disturbing, because the volume was ~26% greater than the amount of water treated in Cr-6. However, we measured the amount of resin they actually had in their column and found it to be 8.5 mL rather than 7.0 mL. This means 43/0.0085 = 5,060 bed volumes of water were treated, which is only 4% more than in Cr-6. This suggests that Cr removal is not substantially affected over the range of flow rates (1 to 5 gpm/ft^3 of resin bed) recommended by the supplier.

A proposed arrangement for the treatment facility has half the resin in service, while the other half is being regenerated. A facility operating at 60 gpm with 60 ft^3 of resin requires half of the resin to be regenerated every 12.6 days.

Because other wells at LLNL show higher concentrations of Cr than MW-4, a means of predicting the resin performance as a function of Cr concentration would be useful. The water for experiments Cr-2, Cr-5, and Cr-6 had identical anion compositions except for the influent Cr concentrations. Table 5 shows the total volume of water treated in these experiments before the effluent Cr concentration reached 11 ppb.

Table 5. Total bed volumes of water treated before chromium breakthrough.

	Influent Cr (ppb)	Bed volumes
Cr-6	35	4,860
Cr-2	3,010	1,380
Cr-5	35,600	334

An empirical model that fits the MW-4 data in Table 5 is:

$$BV = \frac{0.0593(\mathrm{Cr})^{-0.257}}{(\mathrm{SO_4})+(\mathrm{Cr})} , \tag{5}$$

which relates the number of bed volumes treated before the effluent reaches 11 ppb Cr to the concentrations of sulfate and chromium (expressed in molarity). An implicit assumption in the use of a two-component model such as Eq. (5) is that the concentrations of bicarbonate, chloride, and nitrate only slightly perturb the sulfate/chromium equilibrium. Except for the fractional power Cr concentration dependence, Eq. (5) has the same form as Eq. (4). However, the bed volumes are not identical to the volume distribution coefficient, $D_V{}^Y$, of Eq. (4). Rather than referring to a volume where the effluent concentration is a constant fraction of the influent concentration, the bed volumes refer to an absolute concentration of 11 ppb Cr in the effluent. The ratios of the 11 ppb Cr effluent to the influent concentrations are 0.31, 3.6×10^{-3}, and 3.1×10^{-4} for Cr-6, -2, and -5, respectively. Empirically, a power dependence on the influent Cr concentration seems to correct for the different extents of breakthrough in the three experiments.

Alternatively, we can fit the data directly to Eq. (4), but include a normalization factor, *N*, to correct the different extents of breakthrough:

$$D_V^Y = \frac{K_{eq}R_t}{[X]+K_{eq}[Y]}N . \tag{6}$$

The data in Table 5 for MW-4 wellwater fit equally as well with K_{eq} = 3.04, and R_t = 0.75 mmoles Y^{2-}/mL resin bed (from the suppliers specifications). The normalization factor is *N*=1 for the native wellwater and *N*=0.38 for the two experiments with spiked Cr.

Clifford (1990) describes the use of strong base styrene-divinylbenzene anion resin to remove Cr(VI) from a Scottsdale, Ariz., well. The Arizona wellwater had the following characteristics: pH 7.6, 42 ppb Cr, 19 ppm Ca, 28 ppm Mg, 15 ppm Si, 244 ppm bicarbonate, 24 ppm chloride, and 9 ppm sulfate. The resin treated 20,700 bed volumes of water before the effluent reached 10 ppb. The performance predicted by Eq. (5) is 23,100 bed volumes to reach 11 ppb Cr; the performance predicted by Eq. (6) is 19,000. Both models are equally good at predicting the results of the Scottsdale test. In both cases, since the Cr concentration is so low, the bed volumes scale linearly with the sulfate concentration.

Eq. (6) intuitively seems more reasonable. The magnitude of the selectivity coefficient, K_{eq}, for Cr with respect to sulfate is a reasonable one. However, we realize the futility of trying to choose a model with so little data.

Resin Regeneration

One vendor recommended using sodium hydroxide to regenerate the resin, and even suggested that it was necessary for efficient regeneration. The vendor also suggested using the regenerated resin in the hydroxide form. We disagreed with these recommendations because:

- The resin has the least affinity for hydroxide of all the anions.
- The use of anion resin in the hydroxide form would undoubtedly cause the effluent pH to greatly exceed the upper pH discharge limit, since every anion removed from the water would be replaced by a hydroxide ion.

The results of Cr-3 demonstrate that the hydroxide resin is not suitable for use in the treatment facility. The MW-4 effluent from such a resin has a pH of 12. Furthermore, the flow rate fails catastrophically after only 89 bed volumes of water have been treated. Tests showed that the flow was blocked in the resin column and not in the gravity reservoir. A comparison of analytical data from Cr-3 and Cr-6 shows carbonate being held more strongly by the hydroxide-form resin. Furthermore, unlike the Cl-form resin, the hydroxide-resin removes silica. Also in contrast to the behavior found with Cl-resin, the effluent from the hydroxide-resin has a greatly reduced Mg concentration. The Ca concentration decreases gradually; however, it abruptly decreases just before the flow rate stops. The decreases in concentration of Ca and Mg are probably due to $CaCO_3$ and $Mg(OH)_2$ precipitation, although Mg and Ca silicates are also insoluble.

Table 6 summarizes our results from regenerating the columns used in Cr-4 and -5 with NaCl alone. We regenerated the resin by adding separate 5-mL portions of 1 M NaCl to the resin, until a total of five additions had been made. We allowed 30-minute contact times between each addition of NaCl. Each addition corresponds to one equivalent of NaCl for each equivalent of exchange capacity. Flow rates through the resin were 0.3 mL/min, which corresponds to 0.6 gpm/ft^3 of resin. (The supplier recommends regenerant flow rates of 0.2 to 0.5 gpm/ft^3 of resin.)

The total recovery based on the influent Cr concentration and the total amount of water passed through the resin columns was 101% and 106%, for Cr-4 and Cr-5, respectively.

From the data in Table 6, we conclude that regeneration with 3 equivalents of NaCl for each equivalent of resin is adequate for recovering >98% of the Cr. Regenerating 30 ft^3 of resin with 3 equivalents of 1 *M* NaCl will produce a total of 1,010 gal of Cr-containing waste.

More concentrated NaCl can regenerate the resin adequately with less total volume of regenerant. We treated the resin used in Cr-6 in two steps with 3.5 mL of 1.5 M NaCl. Each addition corresponds to 1 equivalent of NaCl per resin equivalent. The total volume of waste from such a process is 50%

Table 6. Cr recovery from the columns used in Cr-4 and Cr-5 in each regeneration step.

Addition	Cr-4 (%)	Cumulative (%)	Cr-5 (%)	Cumulative (%)
1	2.2	2.2	22.1	22.1
2	84.5	86.7	70.5	92.5
3	11.7	98.4	5.7	98.3
4	1.2	99.7	1.2	99.4
5	0.3	100.0	0.6	100.0

less than using three additions of 1 *M* NaCl. Table 7 summarizes our results. Flow rates through the resin were identical to those described previously. The total recoveries based on the influent Cr and sulfate concentrations were 105% and 91%, respectively.

We conclude that when regenerating with 1 equivalent of NaCl per step, the efficiency of regenerating in two steps with 1.5 M NaCl is not significantly different from regenerating in three steps with 1.0 *M* NaCl. For regenerating 30 ft^3 of resin, 450 gal of Cr-containing waste will be produced with 1.5 M NaCl, whereas 1,010 gal will be produced with 1.0 *M* NaCl.

Table 7. Regeneration of the column used in Cr-6 with 1.5 *M* NaCl.

Addition	Cr (%)	Cumulative (%)	Sulfate (%)	Cumulative (%)
1	12	12	72	72
2	85	97	27	99
Rinse	2	99	0.3	99

Recommendations

- From a practical point of view, it is not important to be able to accurately model the column behavior at high (ppm) Cr influent levels, since LLNL waters have Cr concentrations that range from tens to hundreds of parts per billion. However, an experimental measurement with MW-4 wellwater containing ~300 ppb Cr would be useful to validate the predicted performance of the resin. The choice of ~300 ppb would fill in the gap between 35 ppb and 3,010 ppb. It could also help in determining whether Eq. (5), (6), or some other equation, is the correct model to use. Eqs. (5) and (6) predict that 2,780 and 1,800 bed volumes, respectively, of MW-4 wellwater with 300 ppb Cr could be treated before the effluent reached 11 ppb Cr.
- Well P-701 will be the initial source of water for Treatment Facility C; wells MW-351 and MW-361 are candidates for remediation at Treatment Facility D. Results of anion analyses of these waters are shown in Table 8. In particular, MW-351 has twice the sulfate concentration of MW-4. Assuming the same initial Cr concentration, Eq. (4) predicts the A600 resin could treat 2,490 bed volumes. Therefore, a facility treating MW-351 water would require half the resin to be regenerated every 6.5 days.
- The Arizona study by Clifford (1990) found that a macroporous resin treated 65% more water than the comparable gel resin before Cr breakthrough occurred. If the regeneration frequency

Table 8. Anion concentrations in LLNL wells.

Well No.	HCO_3^- (ppm)	Cl^- (ppm)	NO_3^- (ppm)	SO_4^{2-} (ppm)
MW-4	360	110	22	45
MW-351	250	73	25	88
MW-361	520	110	45	20
P-701	400	95	24	35

required by A600 resin is too short, the use of a macroporous resin might be beneficial. However, the macroporous resin was more difficult to regenerate than the gel resin. They recovered 89% of the Cr from a gel-type resin with 3.1 equivalents of 1 *M* NaCl. However, they recovered only 67% of the Cr from a macroporous resin with 3.6 equivalents of 1 *M* NaCl.

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Appendix A

Appendix Table 1. Data from experiments with A600 resin.

Experiment	Cr (ppb)	pH adjustment	Resin form
Cr-1	3,100	Yes	Chloride
Cr-2	3,010	No	Chloride
Cr-3	32	No	Hydroxide
Cr-4	35,600	No	Chloride
Cr-5	35,600	No	Chloride
Cr-6	35	No	Chloride
Cr-7	3,010	No	Sulfate

Appendix Table 2. Analytical data for Cr-1 experiment.

Sample	Bed vol.	Rate (g/min)	pH	Cr (ppb)	Ca (ppm)	Mg (ppm)	Si (ppm)	CO_3 (ppm)	Cl (ppm)	NO_3 (ppm)	SO_4 (ppm)
1001	0	0	8.0	3098	61.7	21.8	15.5	36.7	295	21.8	44.4
1101	7	0.795	5.1	0	62.2	21.7	14.7	1.7	374	0.0	0.0
1102	12	0.638	5.6	0							
1103	20	0.730	6.1	0				2.4			
1104	28	0.764	6.7	2				5.4			
1105	37	0.725	7.3	0				12.1			
1106	46	1.135	7.6	3				20.5			
1107	56	1.163	7.7	0							
1108	65	1.162	7.8	0							
1109	75	1.169	7.9	0							
1110	84	1.162	8.0	0	62.4	22.1	15.5	0.0	350	0.0	0.0
1111	93	1.172		0							
1112	103	1.165		4				35.3			
1113	112	1.169		0							
1114	121	1.165		0							
1115	131	1.165	8.0	0				36.5			
1116	140	1.165		0							
1117	149	1.165		0							
1118	159	1.165		2							
1119	170	1.369		0				38.3			
1120	179	1.175	8.0	2	61.7	22.2	15.3		345	0.0	0.0
1121	188	1.177		0							
1122	198	1.173		0							
1123	207	1.172		0							
1124	216	1.175		2				38.3			

Appendix Table 2. (Continued)

Sample	Bed vol.	Rate (g/min)	pH	Cr (ppb)	Ca (ppm)	Mg (ppm)	Si (ppm)	CO_3 (ppm)	Cl (ppm)	NO_3 (ppm)	SO_4 (ppm)
1125	226	1.170	8.0	0							
1126	235	1.173		0							
1127	245	1.168		0							
1128	254	1.171		0							
1129	263	1.170		0				38.8			
1130	273	1.165	8.0	0	62.9	22.0	15.7		345	2.1	0.0
1201	295	1.067	8.0	0							
1202	319	1.148		0							
1203	343	1.146		0							
1204	367	1.144	8.0	0	62.5	22.0	15.6	38.0	340	12.3	0.0
1205	392	1.159		0							
1206	416	1.148		0							
1207	440	1.149		0							
1208	466	1.236		0	62.1	21.7	15.5	36.9	327	30.1	2.4
1209	491	1.171		0							
1210	516	1.167		0							
1211	540	1.164		0							
1212	565	1.160		0	62.0	21.7	15.4	36.9	329	33.5	17.2
1213	590	1.164		0							
1301	625	1.155		0							
1302	661	1.154		2	62.3	21.8	15.5	37.0	304	27.9	40.9
1303	697	1.152		0							
1304	734	1.152		3							
1305	770	1.158		4	62.2	21.8	15.4	37.1	309	24.6	48.0

Appendix Table 2. (Continued)

Sample	Bed vol.	Rate (g/min)	pH	Cr (ppb)	Ca (ppm)	Mg (ppm)	Si (ppm)	CO_3 (ppm)	Cl (ppm)	NO_3 (ppm)	SO_4 (ppm)
1306	808	1.176		5							
1307	845	1.169		7							
1308	881	1.141		8	63.0	22.1	15.7	37.5	305	24.8	49.6
1309	918	1.165		10							
1310	955	1.182		11				37.6			
1311	970	1.184		11	60.3	21.1	15.0		300	24.1	47.2

Appendix Table 3. Analytical data for Cr-2 experiment.

Sample	Bed vol.	Rate (g/min)	pH	Cr (ppb)	Ca (ppm)	Mg (ppm)	Si (ppm)	CO_3 (ppm)	Cl (ppm)	NO_3 (ppm)	SO_4 (ppm)
1902	0	0	9.1	2980	60.0	22.5	15.6	290			
2601	0	0	8.9	3070	43.7	23.1	15.9	287			
2001	36	1.150	7.0	3	59.2	22.9	15.5	24	369	0.0	0.0
2002	73	1.156	7.5	0	59.6	23.4	15.9	136			
2003	110	1.156	7.7	0	38.3	23.2	15.9	225			
2004	147	1.160	8.0	0				273	205	0.0	0.0
2005	183	1.156	8.2	0	41.3	22.8	15.7				
2006	220	1.146	8.3	0							
2007	255	1.129	8.4	0	39.0	22.6	15.6	297	166	0.0	0.0
2008	290	1.105	8.4	0							
2009	313	1.086	8.5	0							
2101	348	1.099	8.5	0				286	153	0.9	0.0
2102	382	1.061		0							
2103	414	1.027	8.5	0	28.9	22.5	15.7				
2104	446	1.001		0					130	9.4	0.0
2105	477	0.979	8.6	0							
2106	510	0.975		0							
2107	545	0.950	8.6	0	34.0	22.7	15.6		126	26.4	0.0
2108	581	0.927		0							
2109	617	0.922	8.7	0							
2110	652	0.907		0					122	34.7	5.4
2111	686	0.883	8.7	0							
2201	720	0.892		0	37.8	22.2	15.2				
2202	754	0.881	8.7	0				281	114	29.6	30.6
2203	787	0.840		0							

Appendix Table 3. (Continued)

Sample	Bed vol.	Rate (g/min)	pH	Cr (ppb)	Ca (ppm)	Mg (ppm)	Si (ppm)	CO_3 (ppm)	Cl (ppm)	NO_3 (ppm)	SO_4 (ppm)
2204	817	0.781	8.7	0							
2205	850	0.296	8.7	0					113	24.2	45.0
2206	856	0.179		0	24.1	22.2	15.5				
2701	883	1.171		0	42.1	22.7	15.5		115	24.6	47.9
2702	919	1.169	8.6	0							
2703	955	1.169	8.6	0							
2704	991	1.168		0	41.7	23.0	15.8		112	23.7	49.9
2705	1027	1.173	8.7	2							
2706	1063	1.169	8.6	2							
2707	1099	1.161		2	41.5	22.9	15.7		113	23.7	48.8
2708	1131	0.994	8.6	3							
2801	1164	0.966	8.6	3							
2802	1204	0.706		2	36.8	21.2	14.6	261	105	21.6	44.8
2803	1239	0.263	8.7	2							
3301	1264	1.214		5	25.0	22.4	15.5				
3302	1299	1.168		6							
3303	1334	1.166		7							
3304	1354	1.168		9	22.9	22.3	15.6				

Appendix Table 4. Analytical data for Cr-3 experiment.

Sample	Bed vol.	Rate (g/min)	pH	Cr (ppb)	Ca (ppm)	Mg (ppm)	Si (ppm)	CO_3 (ppm)	Cl (ppm)	NO_3 (ppm)	SO_4 (ppm)
4101	0	0	8.9	32	53.5	24.0	16.4	288.3	116	22.0	46.1
4102	10	1.175	12.1	0	45.9	3.0	0.0	1.9	1	0.0	0.0
4103	19	1.140	12.2	0	47.4	1.5	0.0				
4104	28	1.154	12.2	0	44.1	1.9	0.0	2.8	1	0.0	0.0
4105	37	1.133	12.2	0	39.8	1.8	0.0				
4106	47	1.147	12.2	0	38.2	1.8	0.0	3.1	1	0.0	0.0
4107	57	1.251	12.2	0	36.8	2.6	0.0	2.9	1	0.0	0.0
4108	66	1.147	12.1	0	35.1	3.0	0.0				
4109	75	1.101	12.0	0	6.9	3.1	0.5	23.3	1	0.0	0.0
4110	82	0.943	11.9	0	4.9	2.9	1.3	31.8			
4111	89	0.414	11.4	0	4.5	2.1	6.5		11	0.0	0.0

Appendix Table 5. Analytical data for Cr-4 experiment.

Sample	Bed vol.	Rate (g/min)	pH	Cr (ppb)	Ca (ppm)	Mg (ppm)	Si (ppm)	CO_3 (ppm)	Cl (ppm)	NO_3 (ppm)	SO_4 (ppm)
4204	0	0	9.0	35600	44.2	23.2	15.9	259.3			
4301	7	1.136	4.4								
4302	14	1.154	5.4	0							
4303	22	1.168	6.5								
4304	29	1.161	7.3	0							
4305	36	1.166	7.5								
4306	44	1.166	7.7	0							
4307	51	1.177	7.8								
4308	58	1.173	7.8	0							
4309	66	1.132	7.9								
4310	73	1.132	8.1	0							
4311	80	1.214	8.2								
4312	88	1.173	8.1	0							
4313	95	1.214	8.3								
4314	103	1.223	8.2	0							
4315	110	1.164	8.3								
4316	118	1.159	8.3	0							
4317	125	1.164	8.3								
4318	132	1.164	8.4	0							
4319	140	1.168	8.3								
4320	147	1.168	8.4	0							
4321	154	1.168	8.5								
4322	162	1.168	8.4	0							
4323	169	1.168	8.4								
4324	176	1.168	8.5	0							

Appendix Table 5. (Continued)

Sample	Bed vol.	Rate (g/min)	pH	Cr (ppb)	Ca (ppm)	Mg (ppm)	Si (ppm)	CO_3 (ppm)	Cl (ppm)	NO_3 (ppm)	SO_4 (ppm)
4325	184	1.168	8.5								
4326	191	1.168	8.5	0							
4327	198	1.168	8.6								
4328	206	1.164	8.6	0							

Appendix Table 6. Analytical data for Cr-5 experiment.

Sample	Bed vol.	Rate (g/min)	pH	Cr (ppb)	Ca (ppm)	Mg (ppm)	Si (ppm)	CO_3 (ppm)	Cl (ppm)	NO_3 (ppm)	SO_4 (ppm)
4204	0	0	9.0	35600	44.2	23.2	15.9	259.3			
4901	18	1.153	7.1	2	42.5	22.4	14.8	5.8			
4902	37	1.151	7.5	0							
4903	55	1.142	7.7	0							
4904	75	1.213	7.9	0	42.4	23.2	15.7	156.8			
4905	93	1.136	8.0	0							
4906	111	1.147	8.0	0							
4907	130	1.153	8.1	0							
4908	149	1.213	8.2	0	40.7	23.1	15.6	247.4			
4909	168	1.174	8.5	0							
4910	186	1.171	8.5	0							
4911	205	1.164	8.5	0				257.1			
4912	223	1.136	8.5	0	35.8	22.9	15.6				
4913	242	1.191	8.5	2							
4914	261	1.194	8.6	0							
5001	280	1.179	8.7	3							
5002	298	1.162	8.7	3	33.2	22.9	15.6	278.0			
5003	316	1.171	8.8	9							
5004	334	1.172	8.9	11	28.7	22.8	15.6				
5005	352	1.167	9.0	22							
5006	370	1.166	9.1	29							
5007	388	1.168	9.1	47							
5008	406	1.171	9.1	61	24.4	23.0	15.8				

Appendix Table 7. Analytical data for Cr-6 experiment.

Sample	Bed vol.	Rate (g/min)	pH	Cr (ppb)	Ca (ppm)	Mg (ppm)	Si (ppm)	CO_3 (ppm)	Cl (ppm)	NO_3 (ppm)	SO_4 (ppm)
5502	0	0	9.1	35	43.8	23.7	16.1	252.8	114	23.9	44.3
6800	0	0.000		34	37.7	23.7	16.1	264.4	115	25.3	45.0
5503	9	2.197	4.6	0	50.9	22.5	14.7		339	0.0	0.0
5504	19	2.292	6.4	0				6.3			
5505	30	2.298	7.1	0							
5506	50	2.311	7.6	0	56.0	24.0	16.3				
5507	69	2.311	7.8	0				117.5	284	0.0	0.0
5508	89	2.315	8.0	0							
5509	121	2.300	8.1	0							
5510	152	2.311	8.3	0	47.4	23.8	16.1	226.6	200	0.0	0.0
5511	184	2.298	8.3	0							
5512	215	2.272	8.5	0				236.1	171	0.0	0.0
5513	247	2.326	8.5	0							
5514	279	2.334	8.5	0	35.0	23.0	15.9		155	0.0	0.0
5515	311	2.327	8.5	0				252.1			
5516	342	2.296	8.6	0							
5517	373	2.262	8.6	0	30.6	23.2	16.0				
5518	405	2.313	8.6	0					138	2.8	0.0
5601	471	2.293	8.7	0							
5602	536	2.295	8.8	0	28.8	23.2	15.9		131	8.4	0.0
5603	601	2.280	8.8	0							
5604	668	2.325	8.7	0							
5605	722	2.267	8.7	0	30.5	23.4	16.1		126	28.1	4.0
5606	894	2.290	8.7	0					124	34.2	12.2
5701	1030	2.276	8.6	0					116	28.9	32.6

Appendix Table 7. (Continued)

Sample	Bed vol.	Rate (g/min)	pH	Cr (ppb)	Ca (ppm)	Mg (ppm)	Si (ppm)	CO_3 (ppm)	Cl (ppm)	NO_3 (ppm)	SO_4 (ppm)
5702	1166	2.269	8.5	0	37.6	23.5	15.9		114	24.5	43.7
5703	1374	2.256	8.5	0					114	21.1	45.0
5801	1829	2.274	8.5	0					113	20.6	44.5
5802	2300	2.283	8.5	1	37.0	23.4	15.9		115	23.1	44.0
5901	2761	2.292	8.6	2					116	21.0	45.1
5902	3206	2.291	8.6	3	34.3	23.3	15.9		115	22.0	44.3
6101	3673	2.295	8.6	5							
6102	4079	2.296	8.7	7	34.9	23.5	16.0		116	21.7	44.8
6201	4562	2.179	8.6	9							
6301	4858	2.302	8.6	11	34.9	23.7	16.0		116	25.4	45.0
6302	5049	2.307	8.6	13							
6401	5526	2.304	8.6	15					116	25.3	44.6
6402	5674	2.262									
6404	5696	1.242		17							
6405	5759	1.209		17							
6406	6097	1.207		19	33.0	23.5	15.9		116	25.4	44.8
6501	6374	1.207		20							
6502	6666	1.206		23	32.4	23.4	15.9		116	25.3	44.9
6601	7065	1.205		24							
6701	7234	1.209									
6801	7408	1.208		32							
6802	7705	1.206		32							
6901	7898	1.208		32							
6902	8209	1.206		32							
7001	8353	1.208									

Appendix Table 8. Analytical data for Cr-7 experiment.

Sample	Bed vol.	Rate (g/min)	pH	Cr (ppb)	Ca (ppm)	Mg (ppm)	Si (ppm)	CO_3 (ppm)	Cl (ppm)	NO_3 (ppm)	SO_4 (ppm)
7501	0	0.000	8.6	2970	34.4	23.1	15.9	233.4	0	0.0	0
7601	9	1.176	3.5	0	33.5	22.5	14.1	4.7	0	0.0	424
7602	30	1.228	8.0	0				126.7			
7603	62	1.215	8.5	0	34.4	23.2	15.5		19	0.0	216
7604	93	1.218	8.5	0				213.0			
7605	124	1.218	8.6	0							
7606	155	1.212	8.6	0	34.2	23.1	15.7	226.5	98	0.0	89
7607	187	1.213	8.6	0							
7608	218	1.210	8.6	0	34.4	23.1	15.8	234.5	106	0.0	72
7609	249	1.217	8.6	0							
7610	280	1.221	8.7								
7611	312	1.217	8.6	0	33.9	23.0	15.6	231.6	107	3.9	63
7612	343	1.212	8.6								
7701	375	1.252	8.7	0							
7702	407	1.254	8.7								
7703	439	1.244		0							
7704	471	1.237	8.7		32.7	22.8	15.5		105	17.3	51
7705	503	1.225		0							
7706	534	1.217	8.7								
7707	565	1.213		0							
7708	596	1.213									
7709	627	1.212	8.7	0	33.8	23.1	15.7		107	22.9	48
7710	659	1.213									
7711	690	1.201		0							
7712	720	1.201	8.7								

Appendix Table 8. (Continued)

Sample	Bed vol.	Rate (g/min)	pH	Cr (ppb)	Ca (ppm)	Mg (ppm)	Si (ppm)	CO_3 (ppm)	Cl (ppm)	NO_3 (ppm)	SO_4 (ppm)
7713	751	1.199		0							
7714	782	1.210	8.7		33.1	22.8	15.7		107	22.5	46
7715	813	1.209		0							
7716	845	1.213									
7717	876	1.212	8.7	2							
7718	907	1.207									
7719	938	1.220	8.7	2	32.8	23.0	15.7		106	22.6	46
7801	970	1.235									
7802	1002	1.227	8.7	2							
7803	1033	1.220		3							
7804	1064	1.216	8.7	3							
7805	1095	1.213		3							
7806	1109	1.226	8.7	3							