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Laboratory Study on Regeneration of Spent DOWEX 21K 16-20 Mesh Ion Exchange Resin

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Abstract: Currently the effort to remove chromate from groundwater in the 100K and 100H Areas uses DOWEX 21K 16 - 20. This report addresses the procedure and results of a laboratory study for regeneration of the spent resin by sodium hydroxide, sulfuric acid, or sodium sulfate to determine if onsite regeneration by the Effluent Treatment Facility is a feasible option.

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1. INTRODUCTION

Currently the pump and treat effort to remove chromate [Cr(VI)] from groundwater in the K and H areas located in the 100 Area of the Hanford Site uses DOWEX 21K™[1] 16-20 mesh anion exchange resin (hereinafter referred to as DOWEX 21K). The pump and treat unit is composed of four resin columns (approximately 80 ft^3 each); column 1 is a sacrificial column that is currently not regenerated (sent to burial), and columns 2, 3, and 4 are in a lead, lag, and polish configuration. The resin in columns 2, 3, and 4 is currently sent offsite to Minnesota for regeneration. The DOWEX 21K is a Type I strong base anion exchange resin. The Type I resins have the following structure (Schweitzer 1997):

$$R\text{- }CH_2\text{-}N^+\text{ - }(CH_3)\ OH^-$$

According to the literature, ions of higher charge are preferentially exchanged over ions of lower charge, but there are exceptions. One example is the divalent CrO_4^{-2} ion, which has a lower exchange preference than do the monovalent I^- and NO_3^- ions (Weber 1972). However, Letterman (1999) states that CrO_4^{-2} ion has a much higher affinity to resin than even SO_4^{-2}, and Lee and Lin (1999) report that the selectivity of the CrO_4^{-2} ion over the SO_4^{-2} ion is 10.98 times as great on a Type I strong base, 8% cross-linked anion exchange resin.

A portion of the spent resins are currently shipped offsite for regeneration. These resins are regenerated with a 10% sodium chloride solution. Regeneration with sodium chloride at the onsite facility [200 Area Effluent Treatment Facility (ETF)], is not possible due to concerns with corrosion of the stainless steel. The contradictory literature for chromate, sodium hydroxide, sulfuric acid, and sodium sulfate makes it necessary to conduct laboratory testing to determine a viable regeneration process for the spent resins.

This report is executed under RPP-PLAN-31627, *Test Plan for the Regeneration of DOWEX 21K 16–20 Mesh Anion Spent Resin for the Effluent Treatment Facility.*

2. PROCEDURE AND RESULTS

This section describes the regeneration attempts with sodium hydroxide, sulfuric acid, and sodium sulfate. Initially, the number of bed volumes (BV) used to elute the resin were recommendations from the DOW Chemical Company. In all cases, the resin was sluiced into the column and allowed to settle. Water was drained so the meniscus was just touching the top of the resin column. The eluant would then be pumped into the column at the requisite flow rate. All chrome or sulfate results presented were accomplished using the HACH 8023[2] method.

[1] DOWEX™ is a registered trademark of DOW Chemical Company, Midland, Michigan.
[2] HACH is a trademark of HACH Company, Loveland, Colorado.

2.1. SODIUM HYDROXIDE REGENERATION TESTS

A 10-mL BV of spent resin supplied by Fluor Hanford, Inc. groundwater was used to test the efficacy of using a 4% NaOH and a higher ionic strength of 10% NaOH at a flow rate of 2 BV/hr, downflow followed by a slow DI water rinse. Chrome(VI) concentration was determined at the end of 3 BV, followed by 30 BV of 0.5 M sodium sulfate to strip any remaining chromate from the resin. During the water rinse, pH was recorded up to the amount of BV that yielded a pH in the range of 7 to 8. See Table 1.

Table 1. Result of 4 and 10% Sodium Hydroxide Elution.

BV = 10-mL DOWEX 21K 16-20		
	4% NaOH	10% NaOH
BV eluant	3	3
Cr(VI) mg/L	2.6	10
Cr(VI) mg	0.078	0.3
BV wash to pH 7-8	5	9
BV Na_2SO_4	30	30
Cr(VI) mg/L	4.3	5
Cr(VI) mg	1.29	1.5
Total Cr(VI), mg Eluted	1.37	1.8

2.2 SULFURIC ACID REGENERATION TESTS

A 10-mL BV of the spent resin was eluted with 4% sulfuric acid for 5 BV. Since the amount of Cr(VI) eluted from the column using sulfuric acid was negligible, it was decided to follow the sulfuric acid with a 4% NaOH elution to convert the resin to the hydroxide after an acid wash as specified by DOW recommendations. See Table 2.

Table 2. Result of the 4% Sulfuric Acid and Sodium Hydroxide Elution.

BV = 10-mL DOWEX 21K 16-20		
	4% H_2SO_4	4% NaOH
BV eluant	5	2
Cr(VI) mg/L	0.25	5
Cr(VI) mg	0.0125	0.1
BV DI water wash	3	
30 Minute 4% NaOH Soak and Rinse		
BV eluant		1
Cr(VI) mg/L		2.5
Cr(VI) mg		0.025
0.5 M Na_2SO_4		
BV eluant	30	
Cr(VI) mg/L	2.4	
Cr(VI) mg	0.72	
Total Cr(VI), mg eluted	0.86	

2.3 SODIUM SULFATE REGENERATION TESTING

Since the literature has indicated that the chromate ion is preferred over the sulfate ion on Type I strong base anion exchange resins, it was decided to attempt a regeneration using an eluant of sodium sulfate. The first test carried out was an equilibrium of the spent resin against a control of deionized (DI) water and several molar concentrations of sodium sulfate. The results are presented in Table 3. This data indicates that varying concentrations of sodium sulfate was effective. Based on this data a decision was made to conduct the remaining testing with 0.5 M sodium sulfate. Additionally, this concentration of sodium sulfate can be produced at the 200 Area ETF.

Table 3. 0.5 M Sodium Sulfate Elution.

Na_2SO_4 Equilibrium	
Eluant	Cr (VI)/g dry resin (mg)
DI water	6.2E-04
0.3 M Na_2SO_4	3.5E-01
0.5 M Na_2SO_4	3.9E-01
0.7 M Na_2SO_4	4.4E-01
1.0 M Na_2SO_4	3.8E-01

2.4 SODIUM SULFATE ELUTION TEST

An experiment was carried out using 0.5M sodium sulfate against a 10-mL resin BV; the flow rate was at 1 BV/hour, and samples were taken every 0.5 BV. The results are presented in Table 4. The purpose of this test was to verify the capacity of the sodium sulfate to remove chromate.

Table 4. Elution Using 0.5 M Sodium Sulfate.

BV = 10-mL DOWEX 21K 16-20				
BV	mL	Cr(VI) mg/L	Cr(VI) (mg)	Cumulative Cr(VI) (mg)
0.5	5	2.9	0.0145	0.015
1.0	5	12	0.06	0.075
1.5	5	16	0.08	0.155
2.0	5	19	0.095	0.250
2.5	5	18	0.09	0.340
3.0	5	16	0.08	0.420
3.5	5	16	0.08	0.500
4.0	5	16	0.08	0.580
4.5	5	10	0.05	0.630
5.0	5	13	0.065	0.695
Deionized Water Wash				
6	60	0.02	0.001	0.001
Final Elution 0.5 M Na_2SO_4				
20	200	1	0.2	0.2
			Total Cr(VI)	0.900

Even though the elution was terminated after 5 BV due to time limitations, this experiment verified that a sodium sulfate was effective on removing Cr(VI) and therefore is under consideration by the ETF.

2.4.1 Comparison of Siemens and Sodium Sulfate Regenerated Resin

Based on the previously described testing, it has been shown that sodium sulfate can regenerate the resin. The next step was to conduct a comparison between sodium sulfate regenerated resin and Siemens regenerated resin. This comparison was conducted by using a Cr(VI) spiked groundwater sample through single columns.

The groundwater was spiked to 1.25 mg/L Cr(VI), calculated, and was verified at a concentration of 1.2 mg/L using the HACH™ method 8023. Although the other ions present in the groundwater were not adjusted, it should be noted that Cr(VI) was the primary ion of interest and the concentration gave an equivalent of 30 BV to 1 BV.

Figure 1 presents the challenge results. Note that even with the adjusted concentration of chrome, neither resin approached breakthrough; defined as $C/C_O = 0.5$. The initial sodium sulfate sample data lagged due to problems with the flow equalizer. The pH of the effluent was checked during the test and was between 7.0 and 7.5 for both columns. The x axis indicates two jumps at 1500 BV and 6600 BV, due to overnight run times.

Some residual chrome in the effluent is expected due to the chrome rich influent and the lack of the sacrificial column. Because of this, the data in Figure 1 shows a positive slope for both the Siemens and sodium sulfate regenerated resin. This leakage is approximately 20 ppb for both resins.

The performance of both resins was better than expected, and as a result the test duration did not exceed the plan because breakthrough was not attained. The test continued until the entire available volume of spiked solution was used. The test duration was comparable to 13,000 BVs, or 8 million gal of groundwater.

To present the data in a slightly different way, Figure 2 shows a linear representation of the data to also indicate the 5 ppb limit for the last resin column.

Figure 1. Siemens and Sodium Sulfate Resin Challenge.

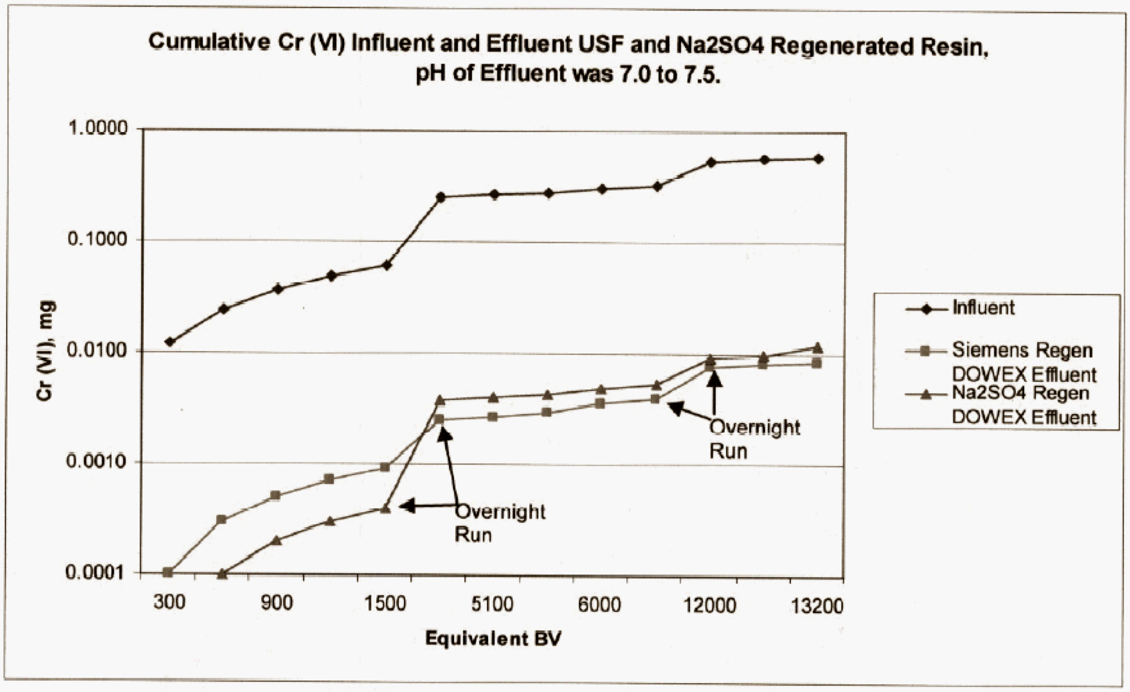
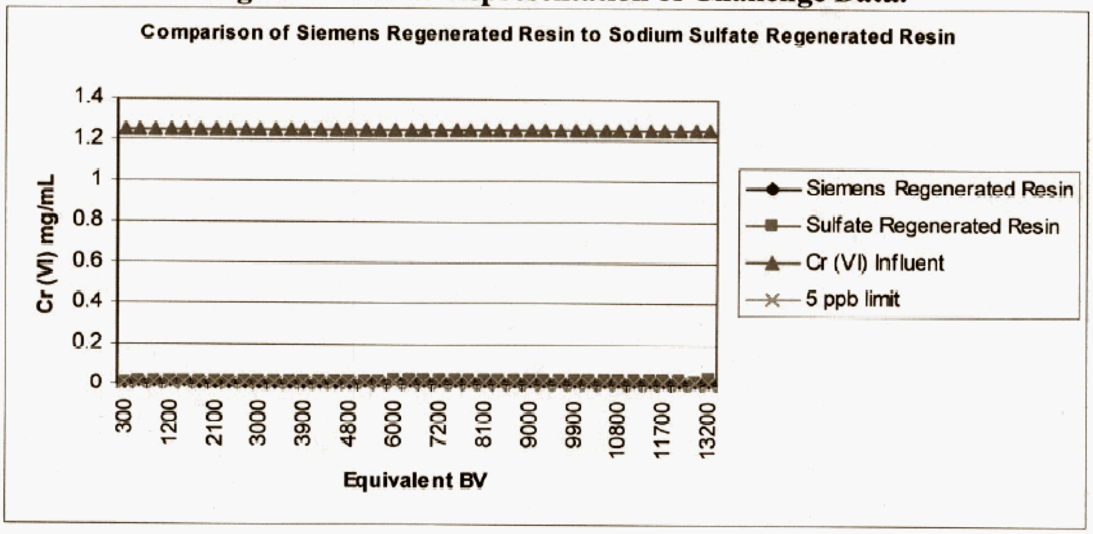


Figure 2. Linear Representation of Challenge Data.



The mass balance for the Siemens and sodium sulfate resin challenge is presented in Table 5. This data shows that the resins were challenged with 0.58 mg of Cr(VI) and 0.56 mg was removed for an difference of 3.5%.

Table 5. Mass Balance of Chrome(VI).

	Siemens Resin	Sodium Sulfate Regenerated Resin
Total Cr(VI) = 0.58	0.29	0.29
Cumulative effluent, mg	0.0083	0.0118
Column wash, mg	0.252	0.286
Sum each column	0.26	0.30
Sum columns	0.56	

2.4.2 Chrome (VI) Residual and Capacity of Sodium Sulfate Regenerated Resin

A final experiment was carried out with sodium sulfate regenerated resin. The purpose of this test was to estimate the chromate residual and capacity of the sodium sulfate regenerated resin. In this test spent resin was slurred into a 10-mL BV column, and regeneration was carried out with 0.5 M sodium sulfate. The Cr(VI) eluted from the column was measured using the HACH™ 8023 method. The column was washed with 10 BV of DI water and then divided into two 4-mL BV columns with separate pumps. One column was eluted with 0.5 M sodium sulfate and the other with 10% sodium chloride to determine residual chromate. From the column eluted with sodium chloride, sulfate was determined using the HACH™ spectrophotometric sulfate method. This data was used to calculate the resin capacity.

Table 6 shows the results of the 10-mL BV primary elution. Samples were taken every 1.5 BV. It should be noted here that the spent resin used had more chromate per unit volume than had been encountered before, a total of 4.35 mg for 10 mL of resin; all previous testing indicated much lower levels of chromate were on the resin. This suggests that there is a significant variability in the resin utilized in this testing.

Table 6. Sodium Sulfate Elution at 1.5 BV/hour.

BV = 10-mL DOWEX 21K 16-20				
Sample No.	L	Cr(VI) mg/L	Cr(VI) mg	Cumulative
1	0.015	40	0.6	0.6
2	0.015	50	0.75	1.35
3	0.015	40	0.6	1.95
4	0.015	40	0.6	2.55
5	0.015	40	0.6	3.15
6	0.015	40	0.6	3.75
7	0.015	40	0.6	4.35

After washing with 10 BV of DI water, the resin was split into two 4-mL BV columns with dedicated pumps. The one column was stripped using sodium sulfate, the other using 10% sodium chloride. The results of the final strip and the residual meq/ml from the column are presented in Table 7.

The results of this test indicate that the capacity of the sodium sulfate regenerated resin is 1.13 meq/ml; this compares very well to the advertised capacity of 1.2 meq/ml (Table 8).

Table 7. Residual Chrome(VI) and Sulfate.

Second Elution (Chrome (VI) Strip), Each BV = 4 mL				
Eluant	L	Cr(VI) (mg/L)	Cr (VI) (mg)	meq/mL
0.5 M Na_2SO_4	0.12	0.7	0.084	0.00081
10% NaCl	0.12	0.8	0.096	0.00092

Table 8. Resin Capacity Based on a 10% Sodium Chloride Eluant.

Eluant	L	SO_4 mg/L	SO_4 mg	Resin capacity (eq/L)
10% NaCl	0.12	1800	216	1.125[a]

[a] Note that the resin is advertised at having 1.2 eq/L capacity.

The results indicate that the residual chromium level on the sodium sulfate resin is 0.00081 meq/ml. This is slightly higher than the current groundwater requirement of 0.00026 meq/ml. As mentioned previously, the resin utilized in this test had significantly higher levels of chromium than any previously seen in the laboratory testing program. A lower chromium residual level would have been possible if the regeneration test would have continued beyond 10 BV (an additional 1 to 2 hr).

3. CONCLUSIONS AND RECOMMENDATIONS

The primary conclusion from the data presented above is that regenerating resin using 0.5 M sodium sulfate is efficacious. It was not within the scope of this study to optimize a process but is merely a collection of data through a series of experiments to show that onsite regeneration is feasible. If desired, further detailed experiments could be carried out to converge on an optimal set of vectors.

The most telling experiment was that of the comparison between the sulfate regenerated resin and the Siemens regenerated resin. Both resins tracked and performed well. It must be remembered that the challenge was not optimal as to the lead, lag, and polish resin columns. The challenge incorporated groundwater and those competing ions that an upfront sacrificial column would (or should) remove. It would be fair to state that if the challenge water was the composition contacted by the lead or lag columns, there probably would not have been leakage exhibited by either regenerated resin.

It is the conclusion and recommendation that onsite regeneration by the ETF is not only feasible but is practicable. It is beyond the scope of this laboratory study to consider economics, but it would seem that onsite regeneration giving faster turnaround, more responsive to the onsite customer, transportation cost savings, etc., would be a positive impact on the budget for the groundwater effort.

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