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Project Summary

Removal of Chromium from Ion Exchange Regenerant Solution

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A pilot study in Scottsdale, AZ, determined that chromate could be efficiently removed from groundwater using chloride-form anion exchange resin. A typical run length exceeded 30 days after which the column could be regenerated with 3-5 bed volumes of 1 N (6%) NaCl. The purpose of the present study was to establish means of removing the chromate (Cr(VI)) from the spent regenerant solution, thus rendering it a non-toxic brine. In this bench-scale study, the Cr(VI) was reduced to Cr(III) and then precipitated as $Cr(OH)_3(s)$. Sulfite, hydrazine, and ferrous sulfate were tried as reductants. Sulfite and hydrazine operated best at pH < 2 while ferrous sulfate performed well in the neutral pH range. Sludges from all of the reduction processes settled well and settling was improved with increasing NaCl concentration. All three sludges passed the extraction procedure (EP) toxicity test when evaluated for chromium leachability. Ferrous sulfate reduction proved to be the lowest cost treatment method for the regenerant brine. For a 4 MGD treatment system utilizing 70% bypass flow and reducing the chromium from the 0.050 mg/L to 0.035 mg/L in the blended product water, the spent regenerant brine treatment cost was quite low—$1.50/million gal of product water. For a 0.1 MGD treatment system, the corresponding cost was $4.60/million gal of product water. These estimates include only the costs for ferrous sulfate and $Cr(OH)_3$ sludge landfilling. Pilot-scale studies of the entire chromate ion exchange removal system including brine treatment and possible reuse are recommended before a full-scale system is designed.

This Project Summary was developed by EPA's Water Engineering

Introduction

Hexavalent chromium of natural origin is found in the ground water in several Arizona locations. In one such location, a 75-mi^2 area in Paradise Valley encompassing Scottsdale, AZ, the highest concentrations exceed 0.05 mg/L, the maximum contaminant level (MCL) for chromium in drinking water as specified by the U.S. Environmental Protection Agency (EPA). Three of Scottsdale's 10 city water supply wells were found to exceed the MCL for chromium, and several more were just below the limit. Because these chromium-contaminated wells constituted a major portion of the Scottsdale water supply, it was considered important that their use be continued. In most cases blending with low Cr(VI) wells was possible to meet the MCL. Looking to the future and the possibility that the marginal wells could eventually exceed the MCL for chromium, treatment by ion exchange and desalting processes were studied for Cr(VI) reduction.

EPA-funded, pilot-scale chromate removal studies performed by the University of Houston (UH) in the UH/EPA Mobile Drinking Water Treatment Facility showed that excellent Cr(VI) removal was obtained by ion exchange using a macroporous strong-base anion resin in the chloride form. However, this treatment process generated a waste brine containing 1.5%-12% NaCl and 100-400 mg/L Cr(VI). In order to dispose of this potentially toxic brine, it was necessary to evaluate means of removing the Cr(VI)

and rendering it non-toxic. The detoxified brine could then be disposed of in an evaporation pond or the local sanitary sewer. It also would have a reuse potential.
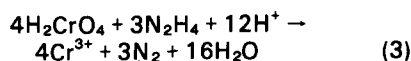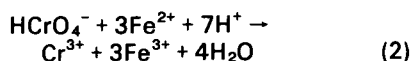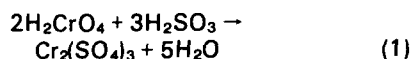
The bench-scale study of Cr(VI) removal from brine described in this report included three phases: (1) evaluation of reducing agents and optimum pH conditions for the reduction of Cr(VI) to Cr(III), (2) determination of optimum conditions for precipitation of Cr(OH)$_3$(s), and (3) an economic evaluation of the process including reduction and precipitation.

Experimental Details

Optimum pH, Reductant Dosage, and Reaction Time

Jar Tests—

Acidic sulfite, ferrous iron, and acidic hydrazine were tried as reductants. The reduction reactions of Cr(VI) to Cr(III) using these reagents are shown below.

$$2H_2CrO_4 + 3H_2SO_3 \rightarrow$$
$$Cr_2(SO_4)_3 + 5H_2O \qquad (1)$$

$$HCrO_4^- + 3Fe^{2+} + 7H^+ \rightarrow$$
$$Cr^{3+} + 3Fe^{3+} + 4H_2O \qquad (2)$$

$$4H_2CrO_4 + 3N_2H_4 + 12H^+ \rightarrow$$
$$4Cr^{3+} + 3N_2 + 16H_2O \qquad (3)$$

In the three reactions above, pH adjustment to 8.3 following the reduction resulted in the formation of a Cr(OH)$_3$(s) precipitate, which was flocculated, settled, and dewatered. Ferrous iron was used in the neutral to alkaline pH range and the precipitate formed during the reduction step contained both Cr(OH)$_3$(s) and Fe(OH)$_3$(s).

All of the experiments in this study were 750-mL jar tests conducted at room temperature (22° to 25°C) with an initial Cr(VI) concentration of either 100 mg/L or 364 mg/L. Reagent grade chemicals dried at 105°C were used for all the test procedures. In the jar tests, solutions of Cr(VI) in 2.0 M or 1.0 M NaCl brines were reduced to Cr(III) following the addition of sodium sulfite, ferrous sulfate, or hydrazine. The composition of the artificial ion-exchange regenerant solution is shown in Table 1. It is based on the composition of an actual spent-regenerant solution from the Scottsdale pilot study. A magnetic stirrer was used to rapidly mix the samples at 150 rpm for 5 min during addition of the reductant. Then the pH of the Cr(III) solution was

Table 1. Makeup of the Artificial Ion Exchange (IX) Spent Regenerant Solutions for Us in Cr(VI) Removal Experiments

	364 mg/L Cr(VI); 2 M NaCl		100 mg/L Cr(VI); 1 M NaCl	
	mg/L	meq/L	mg/L	meq/L
Cations				
Na^+	47,725	2,075	24,725	1,075
K^+	273	7	75	1.9
Total Cations	47,998	2,082	24,800	1,076.9
Anions				
$Cr_2O_7^{2-}$	757	7	208	1.9
Cl^-	71,000	2,000	35,500	1,000
HCO_3	4,575	75	4,575	75
Total Anions	76,332	2,082	40,283	1,076.9
TDS	124,329		65,083	

Note: Potassium (K) was in the artificial spent regenerant solution because it was made u, from $K_2Cr_2O_7$. Potassium would not be in a typical spent regenerant solution and it presence here is considered unimportant.

increased to 8.3 by the addition of either NaOH or Ca(OH)$_2$ while the solution was rapidly mixed on the magnetic stirrer for approximately 5 additional min. The Cr(III) solutions were then flocculated by mixing at 40 rpm for 20 min. Finally, the samples were allowed to settle quiescently for at least 2 hr. The experimental system is shown in Figure 1.

At the end of the settling period, a supernatant sample was collected, filtered through a 0.45 μm membrane filter, acidified with HNO$_3$ to a pH < 2.0, and then stored in a plastic bottle at 4°C. The concentration of total chromium in each sample was analyzed with a Perkin-

Elmer Model 5000 graphite furnac atomic adsorption spectrophotomete (GFAAS) with Zeeman backgroun correction.*

Optimization Tests—

Jar tests using varying stoichiometri amounts of sodium sulfite and ferrou sulfate were conducted to determine th optimum dosage. The dosages used wer 0.0, 0.75, 1.0, 1.25, 1.5, 1.75, and 2.(times the theoretical stoichiometri amount (SA). A higher level of hydrazin
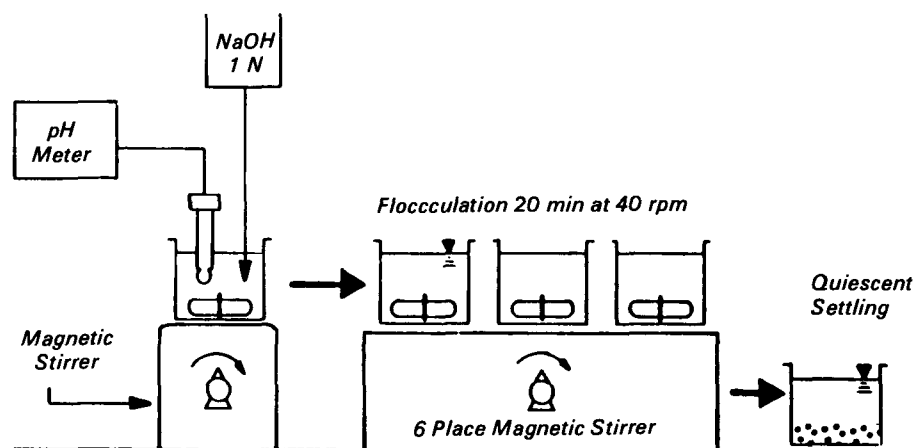
Figure 1. Jar test experimental apparatus schematic.

was used because literature supplied by the manufacturer, Olin Chemical Company, indicated that 3 times the SA of hydrazine would be required to give nearly complete chromium reduction within 2 hr. Thus, hydrazine dosage was not optimized.

Solution pH's during the reduction reaction were next optimized by adjusting the pH of the chromium solution to 1.2, 2, 3, 4, 5, or 6 prior to the addition of the hydrazine or sodium sulfite. Information obtained from the literature had suggested that the reduction of Cr(VI) by ferrous sulfate would be in the neutral pH range. Therefore the pH's of the Cr(VI) solutions prior to ferrous sulfate addition were adjusted to 5, 6, 7, 8, 9, or 10.

The reaction times for the three reductants were then optimized by reducing the Cr(VI) for varying periods of time: 0.25, 0.5, 1, 2, 3, 4, 5, and 6 hr. Both optimum and non-optimum concentration of hydrazine, sodium sulfite, and ferrous sulfate were used. Finally, the effect of the solution NaCl concentration on the Cr(VI) removal was determined by performing the tests with artificial spent regenerants containing varying amounts of NaCl. The brine concentrations used in the tests were 0.0, 0.1, 0.25, 0.5, 1.0, or 2.0 M NaCl. Optimum reductant dosages and more than sufficient reaction times were used.

Sludge Testing Procedures

The gravity-settled $Cr(OH)_3(s)$ or $Cr(OH)_3(s)$ + $Fe(OH)_3(s)$ sludges were dewatered by either centrifugation or filtration. A weighed sample of the centrifuged or filtered chromium sludge was dried at 105°C for 48 hr and cooled in a dessicator. The dried sludge was then weighed and the percentage of solids in the dewatered sludge was determined by difference.

The various sludges were tested for Cr(total) leachability using the extraction procedure (EP) toxicity test as specified by EPA. Briefly, the procedure comprises the extraction of a 100-g sample of centrifuged or filtered sludge at pH 5 in the presence of an acetate buffer. The extraction period is 24 hr, during which the sludge buffer mixture is continually stirred.

Results and Discussion

Optimization Test Results

Figure 2 shows that the optimum dosage for both sodium sulfite and ferrous sulfate was approximately 1.25
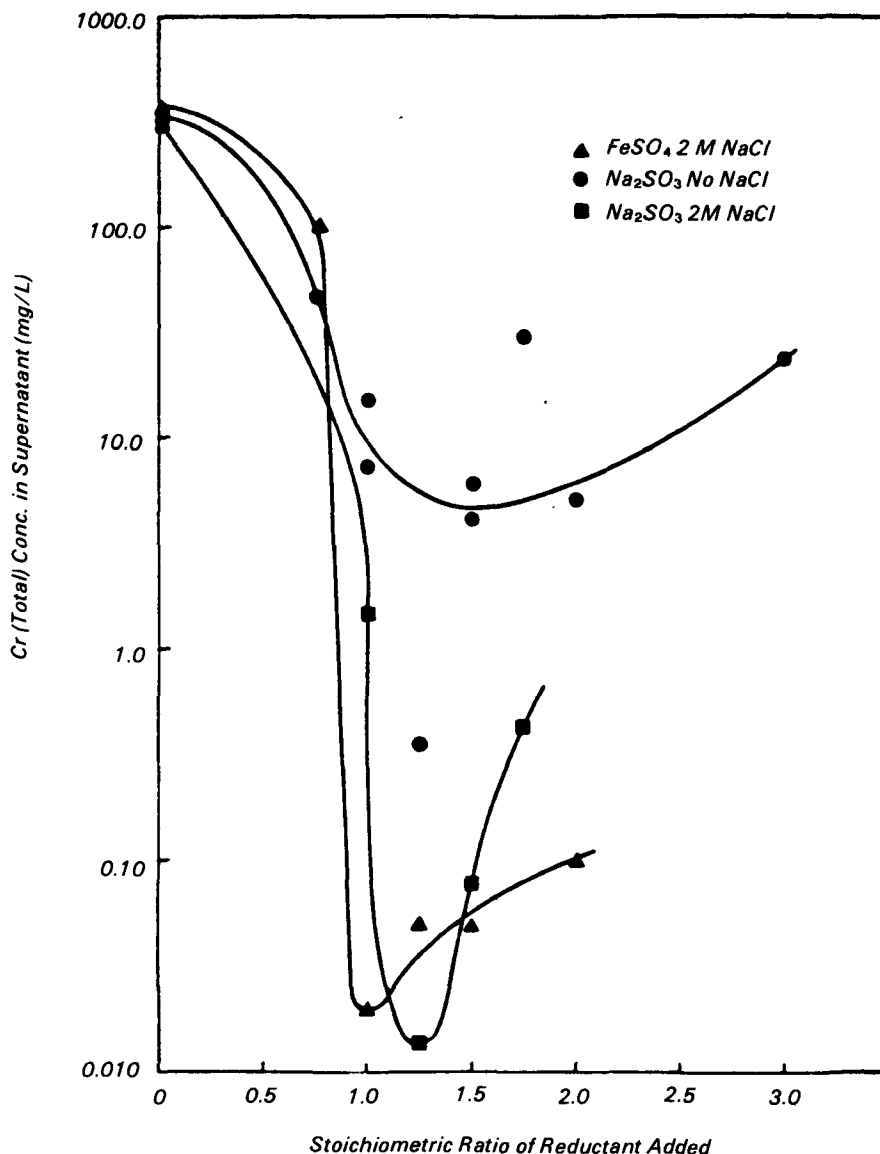

Figure 2. The effect of stoichiometric reductant concentration on residual Cr(total) concentration during Na_2SO_3 and $FeSO_4$ reduction. All test solutions contained 364 mg/L Cr(VI). All supernatant samples were filtered through a 0.45 μm membrane filter.

times the stoichiometric amount (SA). As mentioned previously, the minimum hydrazine concentration was not optimized but was estimated to be 3 times the SA. The initial pH of the solutions prior to sodium sulfite or hydrazine addition was found to be an extremely important factor in hexavalent chromium reduction and removal. Figures 3 and 4 show that there was > 99.9% chromium reduction and removal (following pH adjustment and sedimentation plus filtration of Cr(OH)₃(s)) if the initial pH was ≤ 2. With an initial pH in the range of 2-4, there was no less than 80%

reduction and removal of Cr(VI) from the test solutions.

Regarding the reaction time required at pH ≤ 2, hexavalent chromium was completely reduced, as evidenced by an overall 99.9% removal of total chromium, in less than 15 min with sodium sulfite, and in less than 1 hr with hydrazine. If the solution pH was greater than 2 prior to hydrazine or sodium sulfite addition, increasing the reaction time did not increase the amount of Cr(VI) reduced and subsequently removed as Cr(III).

Figure 5 shows that, for optimum Cr(VI) reduction by ferrous sulfate, pH should
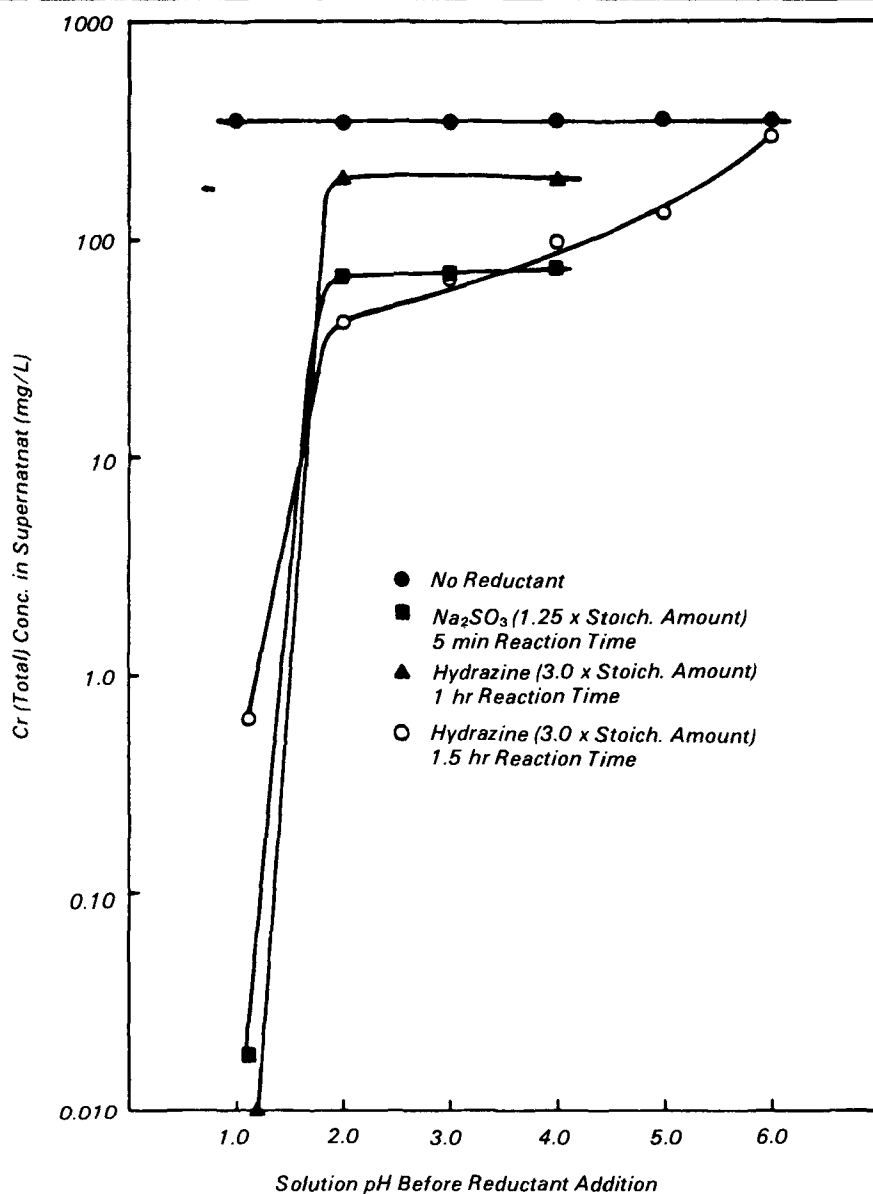
Figure 3. *The effect of pH on the efficiency of Cr(VI) reduction by Na₂SO₃ or N₂H₄. All test solutions contained 364 mg/L Cr(VI) and 2 M NaCl. All supernatant samples were filtered through a 0.45 μm membrane filter.*

Legend in figure:

- ● No Reductant
- ■ Na₂SO₃ (1.25 x Stoich. Amount) 5 min Reaction Time
- ▲ Hydrazine (3.0 x Stoich. Amount) 1 hr Reaction Time
- ○ Hydrazine (3.0 x Stoich. Amount) 1.5 hr Reaction Time

Y-axis: Cr (Total) Conc. in Supernatnat (mg/L)

X-axis: Solution pH Before Reductant Addition

reduction by sulfite or hydrazine. Addition of 13-133 mg/L alum to the test beakers increased the rate of settling of the Cr(OH)₃(s) sludge following sulfite reduction, but it still settled significantly slower than the Fe(OH)₃(s) + Cr(OH)₃(s) sludge.

Gravity settling for 4 days gave sludges with less than 8% solids except for the sludge containing CaCO₃(s), which gave 12% solids consisting mostly (91%) of CaCO₃(s). Centrifugation at 3,000 rpm for 10 min gave better dewatering sludges, i.e., from 12% to 17% solids for the Cr(OH)₃(s) and Cr(OH)₃(s) + Fe(OH)₃(s) sludges, respectively. The best dewatering technique proved to be filtration. The Cr(OH)₃(s) and Fe(OH)₃(s) + Cr(OH)₃(s) sludges had approximately 20% solids. The Cr(OH)₃(s) sludge containing 45% CaCO₃(s) could be dewatered to a final concentration of 28% solids, while the sludge containing 91% CaCO₃(s) dewatered to approximately 53% solids. All of the sludges produced firm, easy-to-handle filter cakes.

All of the Cr(OH)₃(s) or Cr(OH)₃(s) + Fe(OH)₃(s) sludges generated during the Cr(VI) reduction procedures proved to be non-hazardous as judged by the EP Toxicity Test results. The amount of Cr(total) that leached out of the Cr(III) sludges (without CaCO₃(s) added) during the EP Toxicity Tests was in the range of 0.02 to 1.0 mg/L. These levels are significantly lower than the allowable limit of 5.0 mg/L Cr(total). Addition of CaCO₃(s) to the Cr(OH)₃(s) sludges was detrimental in that higher, but still acceptable, levels of Cr(total) were leached out of the sludges.

Costs for Chemical Treatment and Sludge Disposal

Scottsdale well #32, producing 2,700 gal/min (3.89 MGD), has a chromium concentration of 0.042 to 0.049 mg/L. Since the MCL is 0.05 mg/L, partial treatment of the raw water by strong-base anion exchange may eventually be required. The following assumptions were used to size the ion exchange (IX) unit required for Cr(VI) removal by chloride-form anion exchange.

1. The concentration of Cr(VI) rises to 0.05 mg/L.

2. Bypass blending is used, and the ion-exchange (IX) column effluent water contains an undetectable level of Cr(VI).
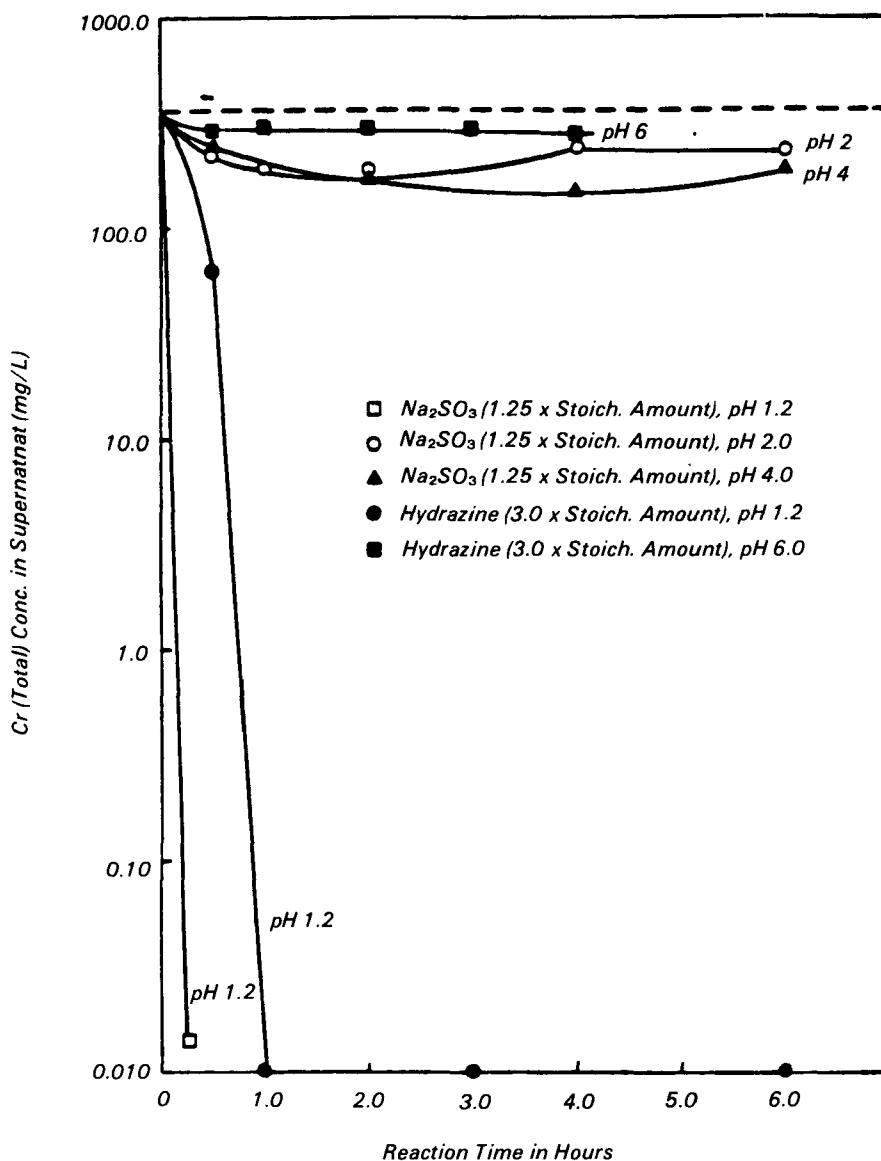
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be in the range of 5-8. As with optimum dosages of sulfite and hydrazine, greater than 99.9% of the Cr(VI) was removed as Cr(OH)₃(s) from the pH adjusted, settled, and filtered solution.

Sodium chloride in the test solutions clearly improved the formation and settling properties of the Cr(OH)₃(s) floc formed using either sodium sulfite or hydrazine as the reductant. In contrast, very small Cr(OH)₃(s) floc particles formed in deionized water solutions, and significant turbidity remained in the supernatant solution after settling. The same was true of the deionized water system when ferrous sulfate was used as the reductant, but the presence of a large quantity of readily settleable ferric hydroxide floc rendered the enhancing effect of the NaCl less important.

Sludge Test Results

The Fe(OH)₃(s) + Cr(OH)₃(s) sludge produced in the tests using ferrous iron as the reductant settled much faster than the Cr(OH)₃(s) sludge produced following

Figure 4. The effect of solution pH (before reductant addition) on the kinetics of Cr(VI) reduction with SO_3^{2-} or N_2H_4. All test solutions contained 364 mg/L Cr(VI) and 2 M NaCl. All supernatant samples were filtered through a 0.45 μm membrane filter.

Legend in figure:

□ Na_2SO_3 (1.25 x Stoich. Amount), pH 1.2
○ Na_2SO_3 (1.25 x Stoich. Amount), pH 2.0
▲ Na_2SO_3 (1.25 x Stoich. Amount), pH 4.0
● Hydrazine (3.0 x Stoich. Amount), pH 1.2
■ Hydrazine (3.0 x Stoich. Amount), pH 6.0

Axis labels: Cr (Total) Conc. in Supernatnat (mg/L) ; Reaction Time in Hours

3. The allowable Cr(VI) concentration in the effluent blended water (raw + IX treated) is 70% of the MCL, i.e., 0.035 mg/L.

4. The IX resin is regenerated after treating 25,000 BV of raw water.

5. Regeneration of the resin bed is accomplished using 5 BV of 1.0 N NaCl and 5 BV of rinse water for a total of 10 BV of spent regenerant solution.

Based on the above assumptions, 30% of the raw water must be treated by ion exchange while the other 70% can be bypassed and blended with the treated water.

Two cases with differing flow rates were analyzed. The first case is that of a well with a capacity of 3.89 MGD (2,700 gal/min) like Scottsdale Well #32. The second case is representative of a smaller community, with a similarly contaminated well having a flow rate of 0.1 MGD (69 gal/min). In both cases, an empty bed contact time (EBCT) of 2-min

(3.74 gal/min ft³) was chosen for the optimum design flow rate because it is near the high end of the acceptable flow rates (1-5 gal/min ft³) recommended by ion exchange resin manufacturers. Using a 2-min EBCT for the 3.89 MGD well yields approximately 61,000 L of spent regenerant solution containing approximately 100 mg/L Cr(VI), while the 0.1 MGD well yields approximately 1,580 L of a similar spent-regenerant solution. In both cases, the ion exchangers would need to be regenerated only once in 35 days. With such a long run, prefiltration or occasional backwashing would be required to prevent IX column plugging.

The laboratory test results for reduction of 100 mg/L Cr(VI) under optimum conditons were extrapolated to estimate the amounts of chemicals necessary to treat the 1,580 L (417 gal) and the 61,000 L (16,200 gal) volumes of regenerant solution.

The costs of reducing the Cr(VI) to Cr(III) with subsequent removal from the large and small volume regenerant solutions are shown in Tables 2 and 3. The tables list the costs for the acidic sulfite and ferrous iron methods of Cr(VI) reduction. The relative costs of removing the Cr(VI) from the two different size systems are shown graphically in Figure 6. Cr(VI) reduction using $FeSO_4$ is more economical than that using Na_2SO_3, principally because the sulfite reduction method requires larger quantities of acids and bases (relatively expensive) for pH adjustment than the ferrous iron method. In fact, the major expense for sulfite treatment is for pH adjustment, while the major cost for Fe(II) treatment is due to the amout of ferrous iron required to reduce the Cr(VI) to Cr(III). $FeSO_4$ is more cost effective in dollars spent per kg Cr(VI) removed than Na_2SO_3 for both the 0.1 MGD and the 3.89 MGD well systems.

Another consideration in addition to the cost of Cr(VI) reduction is the ease of handling the chromium sludge produced. Using $FeSO_4$ as the reductant also has the added advantage of producing a heavier, quicker settling $Cr(OH)_3(s)$ + $Fe(OH)_3(s)$ sludge. The much larger volume of sludge produced using $FeSO_4$ does cost more to dispose of but the sludge disposal costs are insignificant compared to the chemical costs.

Conclusions and Recommendations

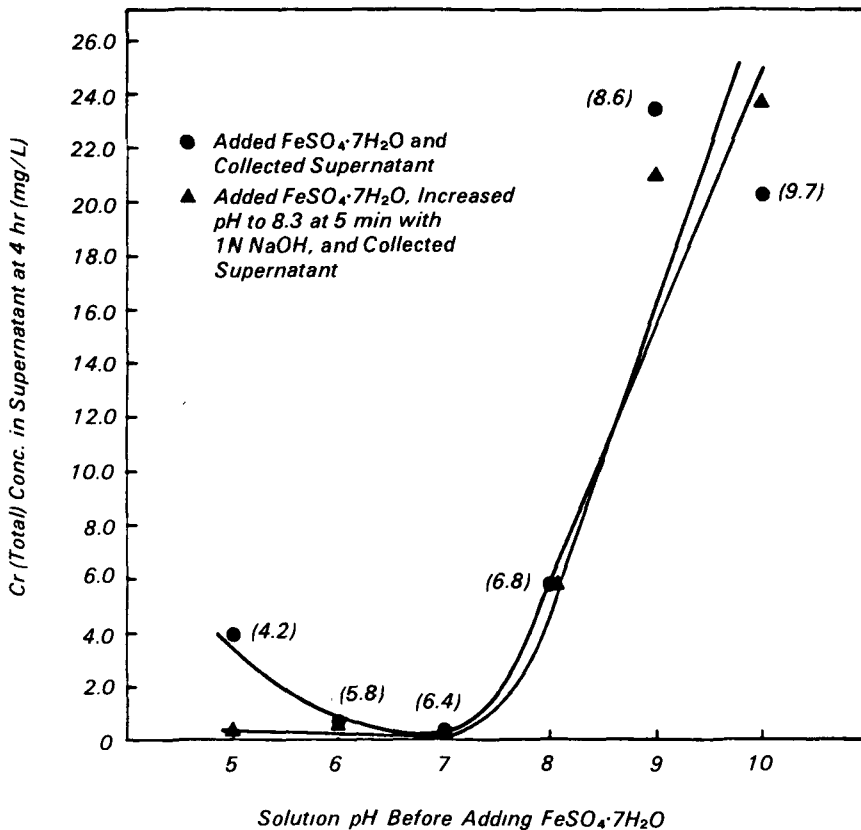Acidic sulfite, ferrous iron, and hydrazine are capable of reducing

Figure 5. *Effect of initial pH (pH 5, 6, 7, 8, 9, 10) on reduction of Cr(VI) FeSO₄. 1.25X stoichiometric amount FeSO₄. All solutions contained an initial 100 mg/L Cr(VI) concentration, 1 M NaCl, 75 meq/L HCO₃. All supernatant samples were filtered through a 0.45 μm membrane filter.*

Table 2. *Chemical and Disposal Costs for Treating 61,000 L Spent Regenerant Solution* (Large Community Case)*

Item	Reduction by Na₂SO₃	Reduction by FeSO₄
Wt. Filtered Sludge 20% Solid, kg	81	363
Chemical Cost, $	121.91	56.39
Cost to Dispose of Sludge	0.51	2.30
Chemical + Disposal Costs		
Total, $	122.42	58.69
$ / 1,000 gal product H₂O	0.003	0.0015

*Assumptions include: 3.89 MGD product water; 70% bypass flow; 0.05 mg/L Cr(VI) in feed and 0.035 mg/L Cr(VI) in blended water; 2 min EBCT; 25,000 BV run length (34.7 days); 10 BV of spent regenerant solution containing 100 mg/L Cr(VI). Capital and labor costs are not included and sludge disposal costs do not include transportation.

hexavalent chromium (Cr(VI)) to trivalent chromium (Cr(III)) providing the dosage, pH, and reaction time are properly controlled. The optimum dosage of both sodium sulfite and ferrous sulfate was 1.25 times the theoretical stoichiometric amount. Hydrazine dosage was not optimized. Rather, it was used at a 3-

times-stoichiometric concentration 1 reduce the time required for Cr(V reduction. For hydrazine and sodiul sulfite, the optimum solution pH for th chromium reduction reaction was les than 2.0. Ferrous sulfate gave goo reduction of Cr(VI) to Cr(III) if the solutio pH was between 5 and 8. The Cr(VI) wa reduced to Cr(III) in less than 15 mi when using sodium sulfite or ferrou sulfate, and in less than 1 hr usin hydrazine, when all reduction reaction occurred at optimum conditions.

The presence of NaCl in the regenerar solution gave better Cr(OH)₃(s) flo formation and decreased floc settlin times following pH adjustment to 8.3 fc all three reductants. Even though th NaCl concentration varied among th regenerant solutions, there was alway good floc formation when the solutio contained from 0.25 to 2.0 M NaCl (1.5% 12% NaCl). The voluminous amount c Fe(OH)₃(s) floc present when ferrou sulfate was used as the reductant als increased the Cr(OH)₃(s) floc size an decreased the settling time.

Using NaOH or Ca(OH)₂ for adjustmen of the solution pH to 8.3 gave equall good Cr(OH)₃(s) floc formation in the la test procedures. However, lime i preferred for the pH adjustment becaus it costs less and tends to precipitat anions like fulvates and humates tha could possibly complex the Cr(III) an prevent complete Cr(OH)₃(s) precipitatior from occurring.

Upon filtration, the sludges from the sulfite, Fe(II), and hydrazine treatment all had similar filter cake properties an contained approximately 20% solids. The filter cakes without CaCO₃(s) added easily passed the EP Toxicity Test b having much less than 5.0 mg/L tota chromium in the leachate. Sludge containing added CaCO₃(s) leached more chromium but still passed the test.

Regarding spent-regenerant treatmen and disposal costs, reduction usinc FeSO₄ will be less expensive than sulfite reduction for both small (0.1 MGD) anc large (3.89 MGD) installations. For a large installation utilizing ferrous sulfate reduction, the estimated cost fo chemicals and landfilling was $1.50/ million gal while it was $4.60/million gal for a small installation. (Hydrazine treatment costs were not evaluated because, although technically feasible, it is a potential human carcinogen and most probably would not be used.) The cost estimate was based on treating 30% of the flow at an EBCT of 2 min and a total run length of 25,000 BV, i.e., 35

Table 3. *Chemical and Disposal Costs for Treating 1,500 L Spent Regenerant Solution* (Small Community Case)*

Item	Reduction by Na_2SO_3	Reduction by $FeSO_4$
Wt. Filtered Sludge 20% Solid, kg	2.10	9.40
Chemical Cost, $	5.28	4.80
Cost to Dispose of Sludge	0.01	0.06
Chemical + Disposal Costs		
Total, $	5.29	4.86
$\dfrac{\$}{1,000\ gal\ product\ H_2O}$	0.0050	0.0046

*Assumptions include: 0.1 MGD product water; 70% bypass flow; 0.05 mg/L Cr(VI) in feed and 0.035 mg/L Cr(VI) in blended water; 2 min EBCT; 25,000 BV run length (34.7 days); 10 BV of spent regenerant solution containing 100 mg/L Cr(VI). Capital and labor costs are not included and sludge disposal costs do not include transportation.

days to chromate breakthrough. The cost advantage for ferrous iron reduction is mainly due to lower chemical costs. Sodium sulfite is a less expensive reductant than ferrous sulfate but the total chemical costs for sulfite reduction include large amounts of acid and base for pH control. In both cases, the estimated cost of the non-toxic sludge disposal was less than 4% of the total treatment and disposal costs. Thus, the four times greater amount of sludge produced using $FeSO_4$ does not significantly impact the cost of treatment plus disposal.

Recommendations

For a large Cr(VI)-contaminated well like Scottsdale Well #32, the following simple cost-effective procedure for treatment and disposal is recommended for the spent ion-exchange regenerant using a batch reactor-settler.

1. Add approximately 1.3 times the SA of $FeSO_4$ and adjust pH to 5-7 using acid or base if necessary.

2. Mix rapidly for 30-60 sec and then mix slowly (flocculate) for 20-30 min.

3. Settle for 2-24 hr.

4. Filter the supernatant.

5. Filter or centrifuge the sludge.

6. Dispose of the filtrate into the sanitary sewer or an evaporation pond.

7. Dispose of the non-toxic filter cake ($Cr(OH)_3(s) + Fe(OH)_3(s)$) in a landfill.

Before implementation on a municipal scale, the entire chromate removal process, including chloride-form anion exchange followed by spent regenerant treatment using ferrous sulfate, should be demonstrated over a period of at least 1 yr on a pilot scale. During this time, tests should be performed on reuse of the spent regenerant following Cr(VI) reduction and removal.

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Thomas Sorg is the EPA Project Officer (see below).

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