

California Water Service, Willows Proposition 50, Chapter 6(b), Grant Number P50-1110002-290

***Strong Base Anion Exchange Treatment and Brine Minimization
for Hexavalent Chromium Removal***

Final Report

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1.0 Executive Summary

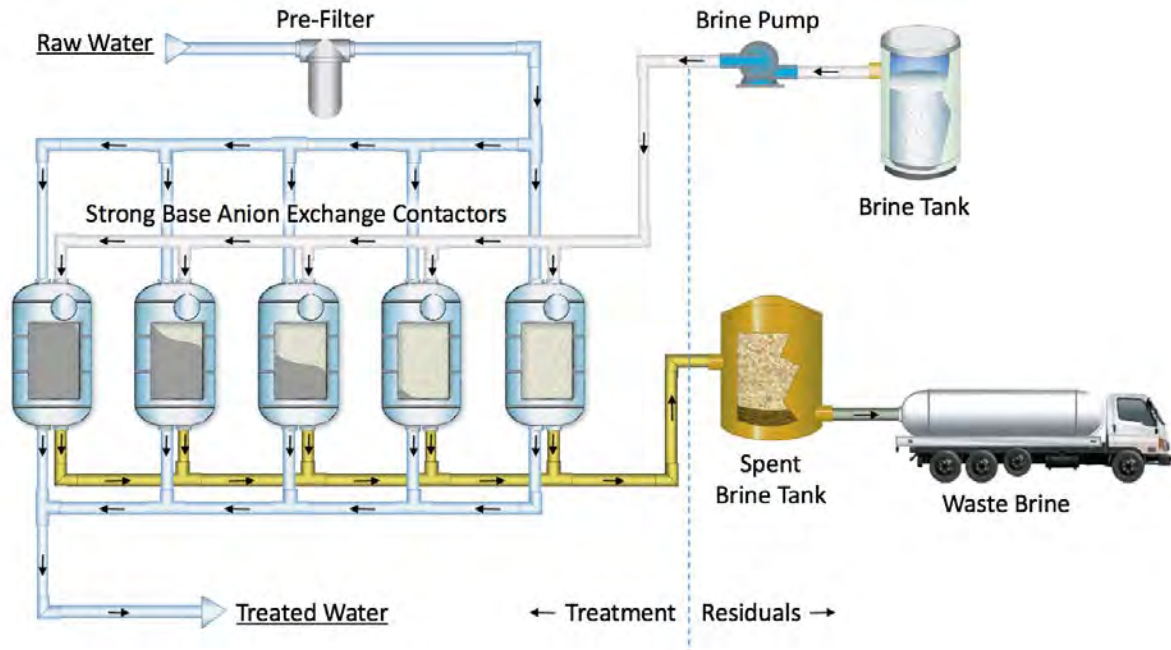
Introduction

On July 1, 2014, the California State Water Resources Control Board (SWRCB) Division of Drinking Water (DDW) finalized a Maximum Contaminant Level (MCL) for hexavalent chromium [Cr(VI)] of 10 µg/L. California Water Service (Cal Water) owns and operates several drinking water systems that were impacted by the Cr(VI) MCL. Every well in the Cal Water Willows system, total of 8 wells, had Cr(VI) over the MCL and would require treatment to remain active. In 2013, given the understanding of the Best Available Technologies (BATs) at the time, regenerable strong base anion exchange (SBA-IX) was identified as the most cost-effective treatment approach.

SBA-IX treatment has been implemented by water utilities for nitrate, arsenic, perchlorate, and other groundwater contaminant treatment. SBA-IX for Cr(VI) removal can operate in a regenerable or single-use mode. Figure 1 presents a typical regenerable SBA-IX treatment system comprised of a pre-filter, pressure vessels or contactors filled with anion exchange resin, and regeneration equipment including a brine tank and pumps. Typical regenerable SBA-IX treatment systems utilize multiple contactors operated in a staggered sequence. As depicted in Figure 1, each contactor is progressively loaded with the contaminant of concern, i.e. Cr(VI).

Regenerable mode SBA-IX commonly employs sodium chloride (NaCl), typically greater than 10% solution strength, to regenerate the spent resin. Multiple bed volumes (BV), typically 3 to 5 BV for the Cal Water systems, of the regenerant are used to restore the exchange capacity. Waste brine quantity and quality characteristics (e.g., salinity, metals and radionuclides), and geographical location can affect the feasibility and costs of disposal. In the absence of the ability to dispose of the spent brine to a brine line, the regenerant brine will require off-site disposal as a hazardous waste, due to elevated concentrations of hexavalent chromium and other competing contaminants such as selenium. Therefore, management of regenerant brine presents challenges for utilities using this treatment approach.

Figure 1 Regenerable SBA-IX treatment schematic



Objectives

In 2014, Cal Water received a \$5M Proposition 50, Chapter 6b grant to assist with the construction and implementation of SBA-IX treatment units for the Willows system, which is an economically disadvantaged community. Since Cal Water was the first utility in California to install permitted, full-scale SBA-IX systems for Cr(VI) treatment, a portion of the Proposition 50 grant funding was designated to validate system performance and investigate strategies to optimize the process not only for the Cal Water Willows system, but also for other Cr(VI) impacted systems. Because brine management comprises the majority of the SBA-IX O&M costs, advances in brine treatment and reuse, such as segmented regeneration and membrane filtration of brine waste, have the potential to significantly decrease costs of Cr(VI) treatment with SBA-IX. Moreover, the development of more efficient SBA-IX resins could further increase performance and decrease brine waste volumes, resulting in additional cost savings. The overarching goal of this Proposition 50 research is to understand the cost implications of advances in SBA-IX brine minimization with state-of-the-art brine treatment technologies, reuse schemes, and newly developed SBA-IX resins. The findings demonstrate that implementing SBA-IX could enable Cr(VI)-impacted utilities to comply with the Cr(VI) MCL of 10 µg/L more affordably than was originally estimated when the MCL was established.

The primary objectives for this project, which were carried out through bench- and pilot-scale research and full-scale monitoring, are:

1. Validate and compare full-scale SBA-IX performance of the Cal Water Willows system to literature and pilot results
2. Investigate opportunities for process optimization and spent brine minimization
3. Identify conceptual SBA-IX capital and O&M cost savings through advances in bench and pilot research
4. Document full-scale SBA-IX implementation successes and challenges

5. Conduct preliminary investigation of stannous chloride application for Cr(VI) treatment

These objectives are addressed in the following sections.

Results

Extensive bench-, pilot-, and full-scale SBA-IX testing was conducted to meet the primary objectives detailed above. Key results from pilot testing are summarized below.

Resin Loading

From previous 2014 pilot testing, Purolite A600E 9149 was found to be the best performing resin of those screened at Willows Station 9 achieving nearly 12,000 BV prior to reaching an 8 µg/L treatment threshold. Subsequent pilot- and full-scale performance of the A600E 9149 resin in 2015 – 2016 achieved approximately 6,000 BVs prior to the 8 µg/L threshold, demonstrating lower Cr(VI) removal capacity for the resin installed and utilized later. Although an increase in nitrate has been observed between the 2014 to 2016 pilot studies, this increase is not expected to decrease performance to the extent that has been experienced.

In addition, since the initial 2014 pilot testing that identified A600E 9149 as the best performing resin, several new resins have been developed or identified as potentially having greater Cr(VI) exchange capacity. As part of this Proposition 50 pilot research, three new resins were screened for their Cr(VI) removal performance. Two resins, the CalRes 21117 and Lewatit XREA 783 resins, achieved approximately 3 to 4 times higher capacity for chromium removal than that of Purolite A600E 9149. Knowing that regeneration and subsequent management and disposal of the regenerant brine comprises the bulk of SBA-IX operational costs, increased resin capacity is perhaps the simplest way to improve overall efficiency and reduce costs.

Regeneration

In 2015, three full-scale SBA-IX systems were installed in the Cal Water Willows District using equipment provided by Ionex SG. Initially the Willows SBA-IX systems implemented a conventional regeneration protocol prior to transitioning to the proprietary Ionex SG segmented regeneration, in order to reduce the volume of spent brine and subsequent O&M costs. The segmented regeneration approach concentrates the Cr(VI)-laden brine fraction and can potentially reduce brine volumes requiring disposal by 80% or greater. Profiling of full-scale conventional and Ionex SG segmented regenerations successfully demonstrated full-scale SBA-IX operation over multiple loading cycles.

Additional bench and pilot testing was conducted to investigate brine minimization and process optimization. Use of alternative regenerants, such as sodium bicarbonate and sodium sulfate, was demonstrated but would result in increased volume of spent brine for hazardous disposal. Direct brine reuse, up to three cycles, was also successfully demonstrated. In addition, bench testing of brine treatment methods such as chemical precipitation, electrocoagulation, nanofiltration (NF), modified activated carbon, and photocatalyst resulted in chromium and co-contaminant removal below the RCRA hazardous waste levels. Further pilot testing of NF successfully demonstrated up to three cycles of NF brine treatment and reuse. These regeneration approaches provide opportunities for O&M cost savings through spent brine minimization and/or treatment to render brine non-hazardous for disposal.

Conclusion

From the time Cal Water began evaluating Cr(VI) treatment methods in 2013 to full-scale implementation of seven SBA-IX systems at well sites in the Dixon and Willows Districts in 2015, advances in SBA-IX technology from bench- and pilot-scale research as well as a competitive bid process resulted in significant capital and O&M cost savings. In 2013, for SBA-IX treatment of four wells in the Willows District, Cal Water initially presented an estimated \$17.0 M capital and \$360 K O&M annually to City Council. Since the original 2013 cost estimates, an approximate 60% costs saving has been realized with updated estimates of approximately \$10 M capital with \$100 K in O&M annually. The cost burden of treatment was further offset for Willows by the Proposition 50 grant program which allocated \$5 M of which 90% was allocated to treatment installation. As demonstrated through bench and pilot testing, there are additional opportunities for further capital and O&M cost reduction through selection of an appropriate resin with higher Cr(VI) capacity and optimization of the regeneration approach.

2.0 Introduction

On July 1, 2014, the California State Water Resources Control Board (SWRCB) Division of Drinking Water (DDW) finalized a Maximum Contaminant Level (MCL) for hexavalent chromium [Cr(VI)] of 10 µg/L. The Cr(VI) MCL triggered implementation of quarterly compliance monitoring at individual water sources that are over the MCL or entry points to the distribution system after treatment. Compliance with the MCL is determined by a running annual average of quarterly samples. This new standard is substantially lower than the federal MCL of 100 µg/L for total chromium and California's total chromium standard of 50 µg/L, which continues to remain in effect.

Unlike federal drinking water regulations, the California Cr(VI) regulation did not include an implementation schedule and required water utilities to begin sampling no later than six months after the finalization of the rule (January 1, 2015). The lack of an implementation schedule resulted in many utilities not being able to maintain compliance. To provide relief to these utilities, Senate Bill No. 385 (SB 385), was signed into law on September 4, 2015. SB 385 provides a grace period until January 1, 2020 for public water systems to achieve compliance.

California Water Service (Cal Water) owns and operates several drinking water systems that were impacted by the Cr(VI) MCL. Every well in the Cal Water Willows system, total of 8 wells, had Cr(VI) over the MCL and would require treatment to remain active. In 2013, Cal Water conducted a desktop water supply and treatment technology screening study, which concluded that four wellhead treatment systems would be required to satisfy the water supply needs of the district, while the remaining four wells were placed in stand-by. Given the understanding of the Best Available Technologies (BATs) at the time, strong base anion exchange (SBA-IX) was identified as the most cost-effective treatment approach.

2.1 Objectives

In 2014, Cal Water successfully pursued a \$5M Proposition 50, Chapter 6b grant to assist with the construction and implementation of their SBA-IX treatment units for the Willows system, which is an economically disadvantaged community. In addition to supporting the construction of one of the first SBA-IX installations specific for Cr(VI) treatment, a portion of the Proposition 50 grant funding was designated to investigate strategies to optimize the process and minimize the volume of hazardous regenerant brine produced. The primary objectives for this project, including bench- and pilot-scale research detailed by task in Section 5.0 Research Plan, are listed below.

1. Validate full-scale SBA-IX performance for the Cal Water Willows system
2. Investigate opportunities for process optimization and spent brine minimization
3. Identify conceptual SBA-IX capital and O&M cost savings through advances in bench and pilot research
4. Document full-scale SBA-IX implementation successes and challenges
5. Conduct preliminary investigation of stannous chloride application for Cr(VI) treatment

As Cal Water was the first utility in California to install permitted full-scale SBA-IX systems for Cr(VI) treatment, Objective 1 is validation of full-scale SBA-IX performance when compared to literature and pilot results. To advance the state of SBA-IX research and investigate potential cost savings for utilities considering SBA-IX treatment, Objectives 2 and 3 are bench- and pilot-scale research into process optimization and spent brine minimization, as well as its associated capital and O&M cost implications. In

addition to process validation and optimization, Objective 4 is documentation of the successes and challenges of full-scale SBA-IX implementation, which are detailed in Appendix B.

Based on previous research and its ability to effectively treat Cr(VI)-laden spent brine, Objective 5, a preliminary investigation of stannous chloride application, was added to the original test plan as an alternative Cr(VI) treatment method. A description of the stannous chloride treatment approach, background literature, and bench test results are included in Appendix A.

2.2 Strong Base Anion Exchange (SBA-IX) Overview

2.2.1 SBA-IX Loading

SBA-IX has been implemented by drinking water utilities with nitrate, arsenic, perchlorate and other groundwater contaminants, and, as such, has been researched extensively. During water treatment, anions in the water are transferred to the solid phase of the resin by replacing anions with less affinity for the resin.

The affinity of select anions relative to chloride is shown in Table 1. Anions with a higher relative affinity are better held on the resin, and will subsequently be more efficient to treat. For example, chromium is held relatively well on the resin (100 times better than chloride), while nitrate has a lower affinity of 3.2. In the case of Willows Station 9, nitrate breakthrough was typically observed before 1,000 bed volumes (BV) with chromium breakthrough between 6,000 to 10,000 BV for the Purolite A600E 9149 resin partly because of nitrate's lower affinity.

In addition to relative affinity, the concentration of competing anions is important in predicting loading performance. For the Cal Water Willows District, nitrate and sulfate occur at concentrations approximately 1,000 times higher than that of chromium, which allows them to compete for the same sites by mass action.

Table 1 Anion affinities for anion exchange resin relative to chloride. Adapted from American Water Works Association (1999)

Compound	Relative Affinity
Uranium ($\text{UO}_2(\text{CO}_3)_3^{4-}$)	3,200
Perchlorate (ClO_4^-)	150
Chromium VI (CrO_4^{2-})	100
Sulfate (SO_4^{2-})	9.1
Arsenic (HAsO_4^{2-})	4.5
Nitrate (NO_3^-)	3.2
Chloride (Cl^-)	1.0

A photograph of Purolite A600E 9149 SBA-IX resin is shown in Figure 2. The SBA-IX resin is made of crosslinked co-polymers of polystyrene and divinylbenzene (Purolite 2017). Different functional groups can be added to the resin matrix for selectivity of specific ions. Positively charged functional groups are

Figure 2 Photograph of Purolite SBA-IX resin

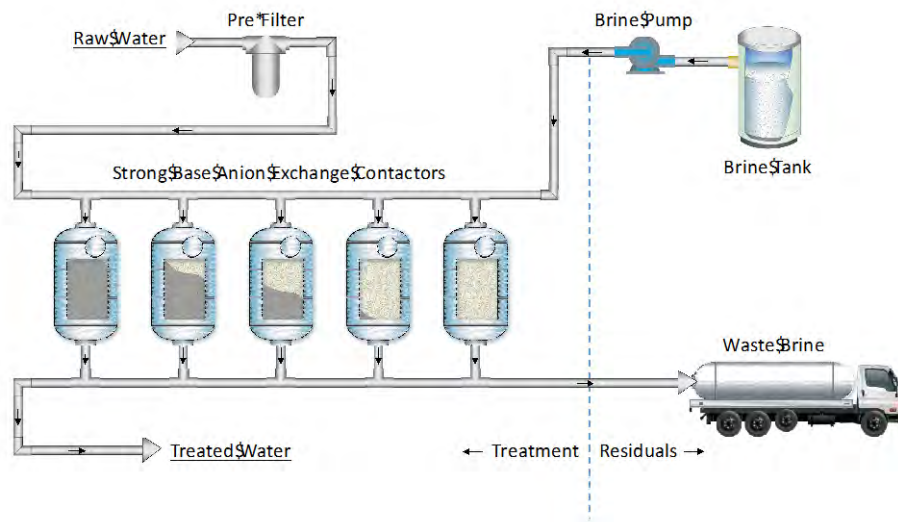


added to hold anions by electrostatic attraction, which is, in most cases a reversible reaction. Two types of resin are relevant for Cr(VI) treatment (Type 1 and Type 2). The difference between Type 1 and Type 2 resins is related to the resin's quaternary amine group. A Type 1 resin has three methyl groups, while one of the methyl groups for Type 2 resins is replaced with ethanol (Brandhuber et al. 2004). As a result, these structural differences result in Type 1 resins being more chemically stable, while Type 2 resins typically have slightly greater capacity and regeneration efficiency.

The regenerable SBA-IX process is shown schematically in Figure 3. Raw water is first pre-filtered to protect the resin bed from

particulate fouling. Unlike weak base anion exchange, the functional groups of SBA-IX resins remain ionized over a wide pH range so there is not a requirement for pH depression for operation (American Water Works Association 1999). Once pre-filtered, the water passes through pressure vessels containing SBA-IX resin where competing anions are exchanged with anions with lower affinities. Following the ion exchange step, the treated water is typically disinfected prior to entering the distribution system.

Figure 3 Regenerable SBA-IX process flow diagram



2.2.2 SBA-IX Regeneration

When the exchange sites are occupied with the target contaminant and other anions, the resin is said to be exhausted and requires regeneration (Brandhuber et al. 2004). Regeneration is accomplished by using a 1.5% (0.25M) to 12% (2M) sodium chloride (NaCl) solution to impart a concentration gradient to replace the contaminant anions on the resin with chloride (Siegel and Clifford 1988). Multiple bed volumes (BV), typically 3 to 5 BV for the Cal Water systems, of the regenerant are used to restore the exchange capacity. For Cr(VI) treatment, the spent brine will be hazardous and therefore management of regenerant brine presents challenges for utilities using this treatment approach.

Brine management options include waste volume reduction using drying beds, trucking to an off-site approved disposal location, ocean discharge through a coastal pipeline, deep well injection, and advanced treatment. Waste brine quantity and quality characteristics (e.g., salinity, metals and radionuclides), and geographical location can affect the feasibility and costs of these disposal options. Proximity and access to off-shore disposal options, such as a brine line to the ocean, can be a significant factor in determining the burden of brine disposal.

In the absence of the ability to dispose of the brine to a brine line, the regenerant brine requires off-site disposal as a hazardous waste, due to elevated concentrations of hexavalent chromium and other competing contaminants such as selenium. The Resource Recovery and Conservation Act (RCRA) hazardous waste classifications for heavy metals of concern, including chromium, are given in Table 2 (40 CFR 261.24). The low-level radioactive waste limit for uranium (Title 10 CFR 61.55) and the CA non-RCRA hazardous soluble threshold limit concentration (STLC) for vanadium (Title 22 66261.24) are also included in the table.

Table 2 RCRA heavy metal hazardous waste classification

Heavy Metal	Hazardous Waste Classification (mg/L)
Arsenic	5.0
Barium	100.0
Cadmium	1.0
Chromium	5.0
Lead	5.0
Mercury	0.2
Selenium	1.0
Silver	5.0
Uranium	0.05% by weight ¹
Vanadium	24 ²

¹Nuclear Regulatory Commission low-level radioactive waste (Title 10 CFR 61.55)

²CA non-RCRA hazardous waste STLC limit (Title 22 66261.24)

2.2.3 Chromatographic Peaking

Chromatographic peaking during SBA-IX treatment has been observed in drinking water applications (Clifford et al. 1987, McGuire et al. 2006). Chromatographic peaking occurs when anions with lower affinities are removed and subsequently displaced by more-preferred anions. This phenomenon results in a short term concentration increase. In addition to the target anion, in this case Cr(VI), non-target anions including bicarbonate, nitrate, phosphate, and sulfate are all simultaneously removed by the SBA-IX resin. In testing conducted at Glendale, CA, nitrate and sulfate peaking occurred at approximately 410 and 450 BVs respectively, with hexavalent chromium breakthrough occurring later at 1,900 bed volumes (McGuire et al. 2006). The peak concentrations observed were three to four times greater than the raw water concentrations.

In cases where a higher concentration of a contaminant such as arsenic or nitrate coexists with Cr(VI), short term releases of arsenic or nitrate greater than the MCL can occur due to chromatographic peaking. For treatment facilities with multiple treatment vessels, loading can be staggered to lower the peak in the treated water via blending from each of the vessels. Additionally, as peaking has been noted to occur consistently, the control unit can be preprogrammed to lower the flow from an individual vessel during the bed volume range in which peaking typically occurs. An online analyzer can also be installed to continuously monitor the concentration of the treated water, and turn off the well and SBA-IX unit at predetermined set-points.

3.0 Willows Water System Background

Prior to 2015, the Willows district was supplied by eight groundwater wells that contained average Cr(VI) concentrations between 12 and 17 µg/L. As noted above, it was determined Willows could meet their water supply needs with SBA-IX treatment at four of their wells. The remaining four wells are reserved for stand-by operations. A map of active and stand-by wells in the Willows district is given in Figure 4, and a summary of the water quality of the wells requiring treatment is provided in Table 3.

Figure 4 Map and layout of Cal Water Willows District Wells

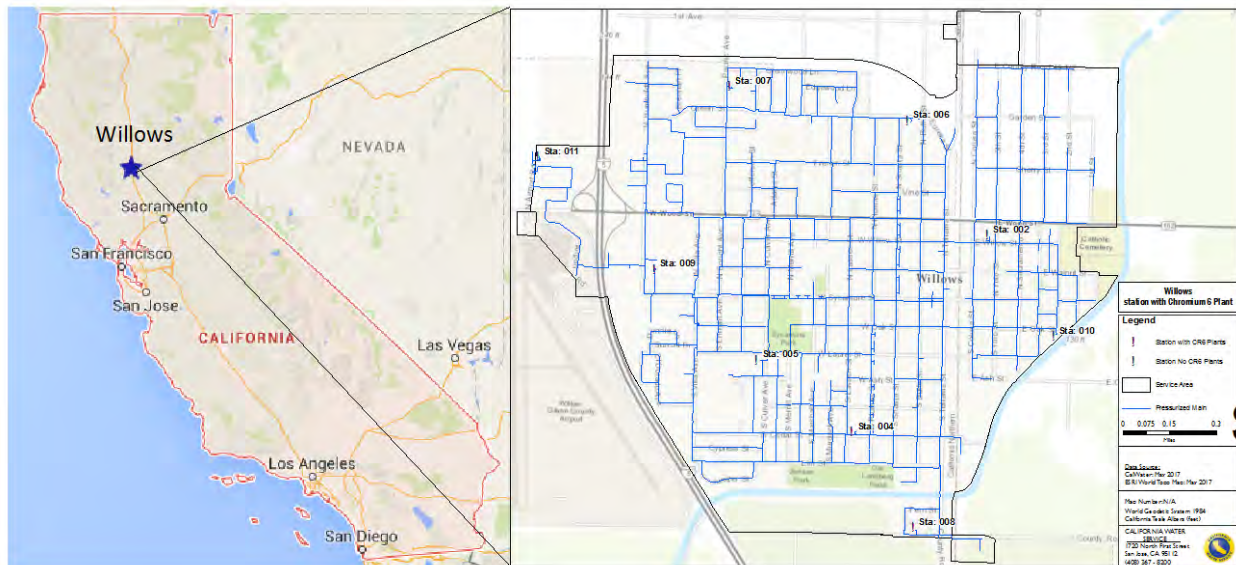


Table 3 Average water quality summary (2006-2016) for treated wells

Well	Design Flow (gpm)	Cr Total (µg/L)	Cr(VI) (µg/L)	Alkalinity as CaCO ₃ (mg/L)	Nitrate as NO ₃ -N (mg/L)	Sulfate (mg/L)
4	500	22	18	233	2.1	42
7	525	12	12	206	2.0	14
8	1,400	19	15	239	1.6	31
9	650	17	16	223	3.1	54

3.1 2014 Pilot Testing

In 2014, Cal Water conducted extensive SBA-IX pilot testing in Willows to inform the design process. Site-specific pilot testing was necessary to identify the best performing SBA-IX resin and to better understand the impact of empty bed contact time (EBCT) and hydraulic loading rate (HLR) on process performance (Gorman et.al., 2016, Li et.al, 2016).

Results from the resin screening at Willows station 9 are shown in Figure 5. In this example, four resins; Purolite A600E 9149, ResinTech SBG1, Sybron GW66 and DOWEX SAR were evaluated and the Purolite product was found to have the greatest performance. Based on these results, Purolite A600E 9149 was specified for use in the full-scale SBA-IX system.

Figure 5 Willows Station 9 pilot resin screening results

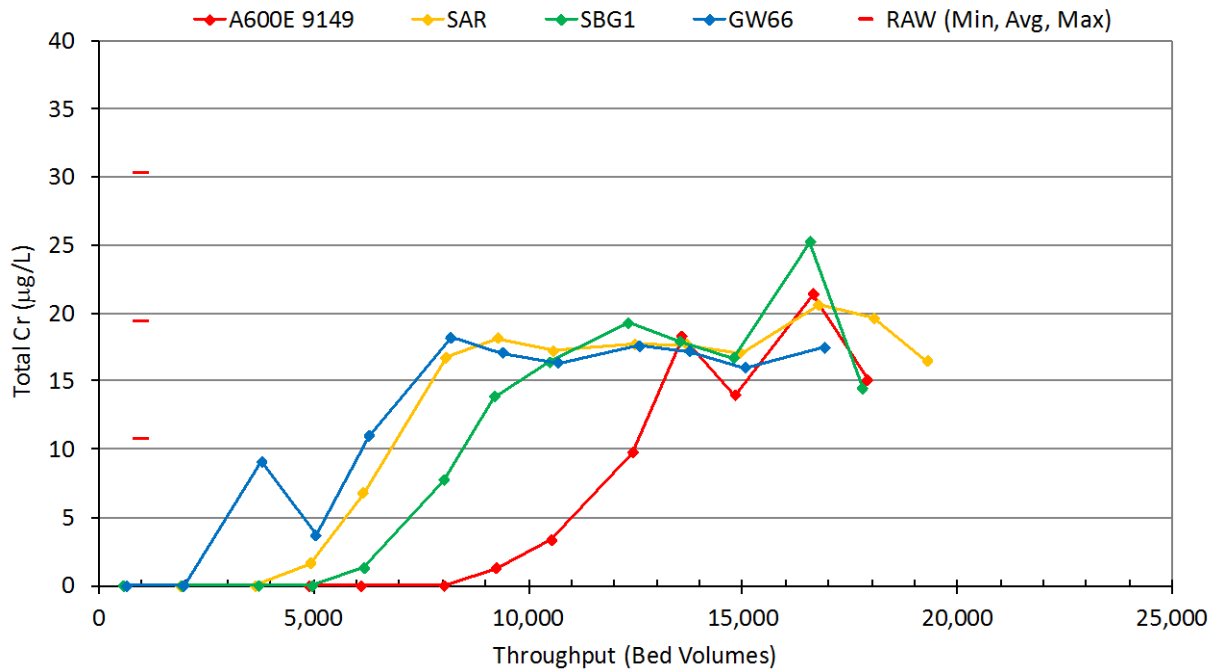
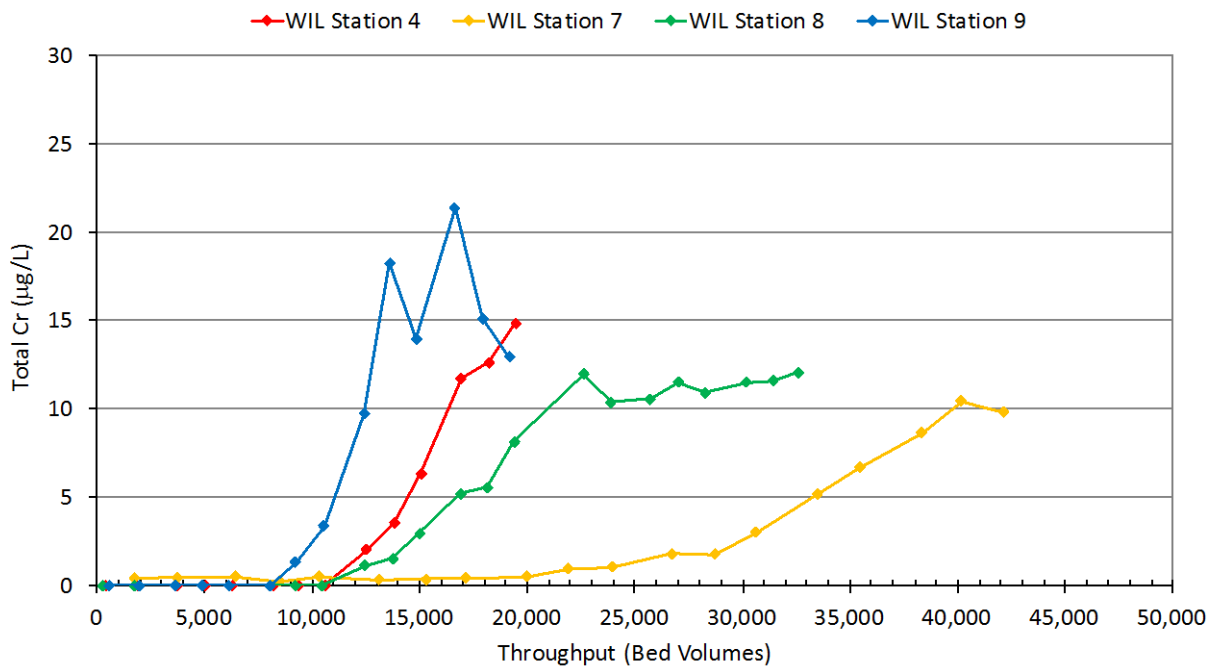


Figure 6 details the pilot-scale performance of Purolite A600E 9149 for each of the sites tested. Of the four stations, Station 9 demonstrated the fastest Cr(VI) breakthrough which results in the most frequent regenerations. Because of this factor, Station 9 was selected as the primary location for the Proposition 50 pilot-scale and full-scale demonstration testing activities as it allowed for expediting the research plan detailed in Section 5.0 Research Plan.

Additional key conclusions from the initial pilot testing are described in 4.0 Literature Review. Process efficiencies demonstrated from the initial pilot testing coupled with a competitive bidding process, saved the Willow's district approximately \$7 Million on the implementation of SBA-IX treatment when compared to original cost estimates.

Figure 6 2014 pilot performance of Purolite A600E 9149 at all Willows well sites



3.2 Full-scale Implementation

Based on the 2014 pilot testing results and SBA-IX performance estimates including maximum headloss, HLR and EBCT ranges were specified for each site. Detailed water quality and performance estimates included in the procurement documents are given in Table 4 and Table 5, respectively. After a competitive bidding process, Ionex SG was selected to provide the SBA-IX equipment and provide operation services for at least the first year.

In an effort to provide other utilities with information regarding the implementation of SBA-IX for Cr(VI) treatment, several round table discussions with Cal Water, Ionex SG, and Corona personnel were held in 2016 to document the successes and challenges faced throughout the design, permitting, installation, and operation of SBA-IX treatment units. This detailed information can be found in Appendix B: Full-scale – Successes and Challenges.

Table 4 Willows Station 9 average water quality (2006-2016)

Parameter Description	Units	Count	Average	Minimum	Maximum
Alkalinity (total) as CaCO ₃	mg/L	3	223.33	210	240
Arsenic	µg/L	3	0.90	0	2.7
Calcium	mg/L	3	30.33	25	34
Chloride	mg/L	3	14.67	14	16
Hexavalent chromium [Cr(VI)]	µg/L	12	15.92	12.2	17
Hardness (total) as CaCO ₃	mg/L	3	183.33	150	210
Iron	µg/L	12	4.85	0	24.1
Manganese	µg/L	12	0.11	0	0.4
Nitrate as NO ₃ -N	mg/L	10	3.10	2.61	3.61
pH measured in the field	STD U	31	7.91	7.5	8.4
pH measured in the laboratory	STD U	3	8.20	8	8.3
Selenium	µg/L	3	2.50	0	7.5
Silica ¹	mg/L	9	26.00	25	27
Specific conductance (E.C.)	US	3	586.68	560	610
Sulfate	mg/L	3	54	48	62
Temperature	°C	18	18.61	14	26
Total chromium	µg/L	29	17.38	12	24.718
Total filterable residue measurement at 180°C ¹	mg/L	14	327.57	270	370
Total organic carbon ¹	mg/L	9	0.00	0	0
Turbidity measured in laboratory	NTU	12	0.08	0	0.3
Uranium	pCi/L	10	0.66	0	0.786
Vanadium ¹	µg/L	2	10.50	10	11

¹ No results since 2006

Table 5 Willows full-scale SBA-IX treatment design

Willows Station	4	7	8	9
Well capacity (gpm)	500	525	1,400	650
SBA-IX system Flow Rate (gpm)	500	525	1,400	650
Planned Utilization	30%	32%	34%	30%
Number of treatment vessels	4	4	8	4
Diameter of treatment vessels (ft)	4	4	4	4
EBCT (min)	3.10	2.95	2.22	2.39
HLR (gpm/ft ²)	9.9	10.4	13.8	12.9

4.0 Literature Review

As mentioned above, SBA-IX is a process where anions in the water are transferred to the solid phase of the resin by replacing anions with less affinity from the resin. Raw water is first pre-filtered to protect the resin bed from particulate fouling. Once pre-filtered, the water passes through pressure vessels containing SBA-IX resin where competing anions are exchanged for less preferred anions. Following the ion exchange step, the treated water is typically disinfected prior to entering the distribution system. Refer to Section 2.2 Strong Base Anion Exchange (SBA-IX) Overview above for further description of SBA-IX loading, regeneration, and chromatographic peaking.

4.1 SBA-IX for Cr(VI) Treatment

A 2004 AWWA Research Foundation tailored collaboration, resulting from increased public concern over low-level concentrations of Cr(VI) in drinking water, investigated several treatment technologies including SBA-IX for Cr(VI) removal (Brandhuber et al. 2004). Bench-scale testing of anion exchange resins using water from Glendale, CA demonstrated significantly increased Cr(VI) capacity compared to that of adsorptive medias, as well as effective Cr(VI) removal at an empty bed contact time (EBCT) of 2.5 minutes.

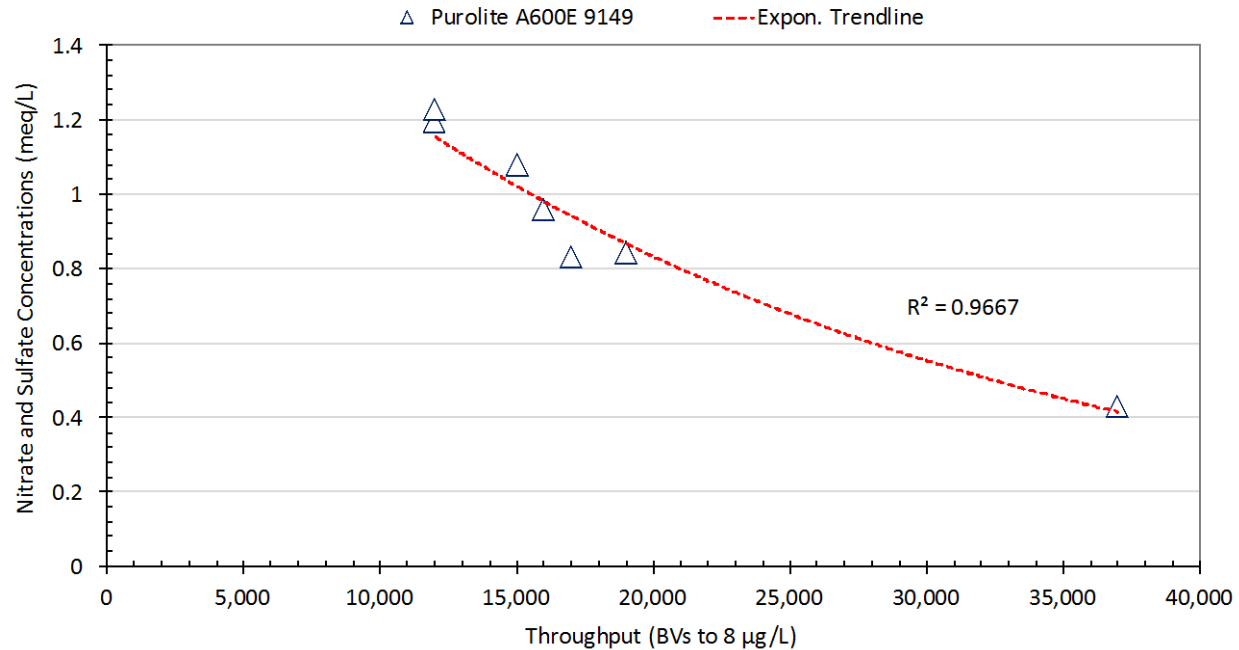
Additional bench-tests conducted using 10 different Cr(VI)-impacted source waters, as part of Water Research Foundation (WRF) Project #4450, demonstrated significantly increased, an order of magnitude, throughput prior to regeneration for Cr(VI) SBA-IX treatment in comparison to nitrate treatment systems (Najm et al. 2014). The research also concluded that SBA-IX performance is correlated to raw nitrate and sulfate concentrations, with low nitrate and sulfate water resulting in the highest throughput prior to a Cr(VI) breakthrough of 1 µg/L.

In 2013, WRF tailored collaboration #4488 further investigated bench- and pilot-scale testing of SBA-IX for Cr(VI) removal using water from the Soquel Creek Water District (Seidel et al. 2014). An initial bench-scale screening at an HLR of 5.5 gpm/ft² resulted in near identical chromium breakthrough curves for EBCTs of 45 and 90 seconds, but the 30 second EBCT was not as effective for Cr(VI) removal.

In 2014, and as mentioned above in Section 3.0, extensive SBA-IX pilot testing was also conducted at seven Cr(VI)-impaired Cal Water well sites to optimize the SBA-IX treatment process and lower expected capital and O&M costs. Four different resins were screened at each Dixon and Willows well site, at an HLR of 15 gpm/ft² and EBCT of 2.25 min, with the ability to test lower EBCTs of 45 and 90 seconds. For all sites, the Purolite A600E 9149 was identified as the best performing resin, achieving between 12,000 to 40,000 BVs of treated water prior to an 8 µg/L chromium breakthrough. Increased HLR testing was also conducted for the Purolite A600E 9149 resin, and an EBCT of 45 seconds and HLR up to 30 gpm/ft² were demonstrated to be adequate for chromium removal. This allows for installation of less capital equipment and a smaller footprint, although increases in HLR correspond to increases in operational costs due to higher pumping costs (Gorman et al. 2016, Li et al. 2016).

The 2014 pilot testing results, in agreement with results from the WRF Report #4450, also concluded that competing anions such as sulfate and nitrate influence Cr(VI) removal performance, more so than the raw water Cr(VI) concentration (Najm et al. 2014, Gorman et al. 2016). To illustrate this point, Figure 7, adopted from Gorman et al. 2016, shows the Purolite A600E 9149 throughput in terms of BVs to an 8 µg/L treatment threshold plotted against the raw water chromium, sulfate, and nitrate concentrations expressed in milliequivalents per liter for each of the wells tested.

Figure 7 Purolite A600E 9149 throughput as a function of raw nitrate and sulfate concentrations (Gorman et al., 2016)



4.2 Brine Regeneration and Minimization Optimization

Due to Cr(VI)-laden brine management comprising a majority of the SBA-IX O&M costs, research into regeneration optimization as well as brine minimization has been conducted with the intent to reduce the overall volume of brine for hazardous disposal. Proprietary regeneration methods have also been developed by technology providers to concentrate and reduce the total BVs of brine for disposal. Examples include a cascading approach patented by Envirogen Technologies and the segmented regeneration and sulfate return approach patented by Ionex SG and implemented in the Cal Water Willows District, which is described further in Section 6.0 Results.

In addition to regeneration optimization, brine reuse or recycle of spent Cr(VI)-laden brine in lieu of fresh brine is another approach for brine minimization. Brine reuse work conducted in Albuquerque, NM, in a drinking water SBA-IX arsenic treatment application, demonstrated 20 reuses at the pilot scale (Clifford et al. 2003). The salt strength was adjusted to 1 M (5.8 %) NaCl for each reuse, and the brine was not treated prior to remove arsenic. Although sulfate accumulation occurred (starting at about 25,000 mg/L and peaking at about 145,000 mg/L), the BV to arsenic breakthrough was not significantly shortened at the higher sulfate concentrations.

Cr(VI)-laden brine reuse minimization pilot research conducted in Glendale, CA, investigated brine recycle using varying concentrations, 6% or 26%, of NaCl brine (McGuire et al. 2006). Multiple cycles of brine reuse were conducted using 5 BV of recovered brine. The research concluded a regenerant brine of 6% NaCl was insufficient to fully regenerate SBA-IX. With a 6% NaCl brine solution, the BV to breakthrough during treatment declined from 1,900 BVs with fresh regenerant to less than 500 BVs after the first recycle pass. Further treatment capacity reduction after subsequent regeneration cycles was also noted. Increasing the sodium chloride concentration from 6% to 26% improved performance; however, the Cr(VI)

exchange capacity continued to diminish after subsequent cycles. Unlike arsenic-exhausted resin, in which 20 cycles of brine reuse was successfully demonstrated by Clifford et al., significantly diminished exchange capacity was observed after only three cycles for chromium-exhausted brine. In this instance, the diminished capacity was attributed to sulfate accumulation in the brine.

Investigation of eight consecutive rounds of direct brine reuse was also conducted as part of Water Research Foundation Report #4488 (Seidel et al. 2014). Although brine reuse resulted in loss of some resin Cr(VI) capacity, no significant decrease in performance after eight rounds was observed. In each case, at least 15,000 BV was observed prior to Cr(VI) breakthrough to 8 µg/L. Additional brine reuse pilot research conducted in 2014 using Cr(VI)-impaired groundwater from several Cal Water well sites, demonstrated comparable results to fresh brine regeneration up to seven consecutive rounds of brine reuse (Li et al. 2016b). While multiple rounds of direct brine reuse have been successfully demonstrated at the pilot-scale, unanswered questions regarding competing anion accumulation and chromatographic peaking served as the basis for brine reuse pilot research conducted as part of this Proposition 50 project.

Additional SBA-IX brine reuse and minimization research was conducted by Water Quality & Treatment Solutions, Inc. in 2015 as part of the Water Research Foundation Project #4556 (Najm et al. 2017). Of the five consecutive direct brine regenerations conducted, diminished performance was observed after two consecutive cycles, which corresponds to a spent brine volume reduction of 50% compared to that of fresh brine regeneration. Increased raw water sulfate levels of 170 mg/L, compared to lower sulfate concentrations of 50 mg/L, correlated to diminished performance and decreased chromium recovery over multiple cycles of brine reuse.

In addition to direct brine reuse, brine treatment technologies including use of chemical reductants such as ferrous sulfate have been investigated to render spent brine non-hazardous and reduce the overall volume of brine for disposal. The technologies evaluated for brine treatment include chemical reduction and precipitation of Cr(VI) and other potentially hazardous constituents (WRF Project 4488, Li et al. 2016), adsorption (WRF Project 4488), and physical separation. Detailed literature review of each brine treatment approach is given in Section 6.3 Brine Treatment.

5.0 Research Plan

The goal of this Proposition 50 research effort is to understand the cost implications of advances in SBA-IX treatment: specifically, brine minimization approaches including an assessment of alternative resin screening, brine treatment and reuse, and alternative regenerants. Additionally, the loading capacity and regeneration efficacy of newly formulated resins were evaluated. Refer to Section 2.1 for a list of the research objectives.

5.1 Research Tasks

A Research Plan (Plan) was submitted to the Department of Water Resources (DWR) and DDW in September 2015 for review and approval. The original Plan reflected the current state-of-the-science with respect to Cr(VI) SBA-IX treatment. The Plan has since been amended to include additional developments since it was initially drafted, including screening of additional SBA-IX resins and use of alternative regenerants.

The primary research tasks completed during this Proposition 50 project are summarized in Table 6. Tasks are numbered per the initial 19 tasks detailed in the Plan, which can be referenced in Appendix C. Amended Tasks 20 to 22 were conducted in lieu of original Tasks 10, 14, and 15, and are described below:

Task 20 – Stannous Chloride Treatment: This task investigates the ability of stannous chloride to treat unchlorinated and chlorinated water via hexavalent chromium [Cr(VI)] reduction. Stannous chloride literature, experimental method, and bench test results can be found in Appendix A.

Task 21 – Alternative Resin Screening: This task investigates the Cr(VI) removal capacity of recently developed resins that have been engineered specifically for Cr(VI) removal. Each resin screened is benchmarked against the Purolite A600E 9149 resin which, to date, has demonstrated the greatest Cr(VI) capacity in most waters that have been tested.

Task 22 – Alternative Regeneration with Sodium Sulfate and Bicarbonate: This task will investigate the performance of alternative regenerants including sodium sulfate and sodium bicarbonate. Pilot regeneration using Purolite A600E 9149 resin with sulfate and bicarbonate is conducted to determine alternative regenerant efficacy.

Table 6 Summary of Proposition 50 research tasks

Task	Description
<i>Full-scale demonstration</i>	
1	Testing to determine if a 9.9 to 13.9 gpm/ft ² Hydraulic Loading Rate (HLR) is adequate during non-regeneration conditions
2	Testing with 1.8 to 2.3 minutes Empty Bed Contact Time (EBCT) at full scale
3	Demonstration of Cr(VI) removal with multiple regenerations
4	Testing to determine if pilot scale BV to breakthrough correlate with full scale results
5	Start-up documentation of successes and challenges
6	Evaluate efficacy of ICP-MS with High Matrix Introduction (HMI) to analyze high TDS liquid wastes
7	Profile individual column loading
8	Profile individual column regeneration
9	Characterization of the Ionex SG segmented regeneration
<i>Bench-scale brine treatment</i>	
11	Sodium chloride brine jar testing
12	Other brine treatment
<i>Pilot testing</i>	
12	Other brine treatment (nanofiltration)
13	Direct brine reuse
21	Alternative resin testing
22	Alternative regeneration with sodium sulfate and bicarbonate
<i>Communication and reporting</i>	
16	Quarterly update reports
17	Webinars
18	Final written report
19	Ongoing communication with Cal Water and DDW
<i>Alternative Cr(VI) treatment</i>	
20	Bench-scale stannous chloride investigation

5.2 Experimental Design

As described above, different phases of research were conducted at either full-, pilot-, or bench-scale. The following section describes the experimental set-up, data collection, sampling, and analytical methods used throughout the course of the research.

5.2.1 Full-scale Demonstration

Validation of full-scale SBA-IX performance was conducted using Willows Station 9 Vessel 2. Tasks 1, 2, and 7 were accomplished through full-scale profiling of Vessel 2 loading, while Tasks 3, 4, 8, and 9 were achieved via profiling of four rounds of Vessel 2 regeneration. Task 5, documentation of full-scale implementation successes and challenges, is further detailed in Appendix B: Full-scale Success and Challenges.

SBA-IX pilot testing was conducted at Willows Station 9 with two different pilot systems. The alternative resin screening and alternative regenerant testing, Tasks 21 and 22, were conducted using four two-inch

diameter panel mounted PVC columns. Raw water filled a 5,000-gallon break tank and then was pumped to each of the columns. The break tank allowed for non-stop operation of the columns without running the wells continuously which expedited the collection of data and analysis of results. The column panels are equipped with a prefilter, feed pump and four two-inch columns. Each column is equipped with flow control, flow isolation, pressure monitoring, flow totalizer and four individual sample ports. An example photograph of a representative installation is provided in Figure 8.

Alternative resin and alternative regenerant regeneration testing was conducted on-site at Station 9 using the two-inch columns. A low-flow peristaltic pump was used for brine flow control, with conductivity, pH, and brine samples taken manually. Full description of the of the regeneration test conditions is given in Section 6.2 SBA-IX Regeneration.

Figure 8 Resin screening pilot columns



Tasks 12 and 13, brine treatment and brine reuse, were investigated using three four-inch diameter pilot columns (IXP) leased from Ionex SG. Each IXP column, filled with Purolite A600E 9149 resin, were loaded until Cr(VI) breakthrough at Willows Station 9 and then transported to the Ionex SG facility located in Davis, CA for regeneration. Images of the IXP columns and the Ionex SG regeneration facility are shown in Figure 9. The IXP regeneration test conditions are described later in Section 6.2 SBA-IX Regeneration.

Figure 9 (a) IXP pilot columns and (b) Ionex SG regeneration facility



5.2.2 Bench-scale Testing

In January 2016, bulk brine, including the rinse fraction, from full-scale regeneration at Willows Station 9 was collected and shipped to research partners at University of California Davis (UC Davis), University of California Riverside (UC Riverside), ToxSorb, Baker Corporation, and the United States Bureau of Reclamation (USBoR) Water Treatment Group to conduct bench-scale brine treatment testing. Chemical precipitation bench testing was conducted by Corona staff in conjunction with UC Davis, while preliminary results for other brine treatment methods were received from each research partner respectively. A summary of the brine treatment technologies investigated and associated research partners is given in Table 7.

Table 7 Brine treatment technologies

Technology	Research Partner
Chemical Precipitation	UC Davis
Electrocoagulation	Baker Corporation
Modified Activated Carbon	ToxSorb
Nanofiltration	USBoR
Photocatalyst	UC Riverside

5.2.3 Data Collection

5.2.3.1 Full-scale Demonstration

Treated water from Vessel 2 was sampled every 500 BVs profiling vessel loading and subsequent chromium breakthrough. For regeneration, three cycles of conventional regeneration and one cycle of the Ionex SG segmented regeneration were profiled by collecting samples every 0.2 BV. Only one segmented regeneration was profiled due to delays in the transition from conventional to segmented regeneration. A summary of the full-scale sampling locations and frequency is given in Table 8.

Table 8 Willows Station 9 sampling locations and frequencies

Matrix	Sample Locations	Description	Sample Events	Sampling Frequency
Treated Water	SBA-IX Vessel 2	Treated water from individual SBA-IX column	2	Every 500 BV between regenerations
	SBA-IX Vessel 2	Effluent brine from individual column conventional regeneration	3	Every 0.2 BV for 5 BV
	SBA-IX Vessel 2	Effluent brine from individual column segmented regeneration	1	Every 0.2 BV for 7 BV

5.2.3.2 Pilot-scale Testing

The 2-inch columns were monitored and sampled three times a week by Cal Water operators during the resin screening and adjustments to the flow rate were made as necessary. During regenerations, total metals, nitrate, and sulfate samples were collected by Corona staff every 0.2 BV. Flow rate was manually measured every bed volume and adjusted as needed. A summary of the 2-inch column sampling plan is shown in Table 9 .

Table 9 Two-inch column data collection

Matrix	Sample Locations	Parameters Monitored	Sampling Frequency
Treated Water	Raw	Pressure, total metals	Three times a week
	Individual column effluent	Pressure, flow rate, total flow, total metals	Three times a week
Spent Brine	Individual column effluent	Total metals, nitrate, sulfate, conductivity	Every 0.2 BV during regeneration

For the IXP columns, treated water samples were collected at 10,000 BV to confirm total chromium breakthrough. A 10,000 BV set-point was selected as it represents the set point for full-scale regeneration. After regeneration, the IXP columns were also sampled during the first 1,000 BV to profile potential chromatographic peaking of nitrate and other contaminants.

Similarly, the IXPs were sampled every 0.2 BV during regeneration. Bulk brine was also collected before and after regeneration for characterization. During investigation of brine treatment and reuse, additional brine samples were taken to profile the treatment process. A summary of the IXP column sampling plan is provided in Table 10.

Table 10 IXP column data collection

Matrix	Sample Locations	Parameters Monitored	Sampling Duration/Frequency
Treated Water	Raw	Total metals, nitrate, sulfate	First 1,000 BV during loading
	Column effluent	Total metals, nitrate, sulfate	First 1,000 BV during loading; Cr breakthrough confirmation at 10,000 BV
Spent Brine	Individual column effluent	Total metals, nitrate, sulfate, conductivity	Every 0.2 BV during regeneration
	Bulk brine	Total metals, nitrate, sulfate conductivity	Fresh and spent brine characterization pre/post regeneration

5.2.3.3 Bench-scale Testing

As noted above, several research partners participated in the bench-scale brine treatment investigation. Each partner provided detailed experimental protocols and results. Validation samples representing the optimal results from each treatment approach were sent to UC Davis for analysis via inductively coupled plasma mass spectrometry (ICP-MS). The analytical methods are described in further detail below.

5.2.4 Analytical Methods

All samples from the full-scale demonstration as well as bench and pilot testing were sent to UC Davis for analysis. For cost savings, total chromium was used as a surrogate for Cr(VI), as historical water quality for Station 9 indicated total chromium is primarily present as Cr(VI). The total metals samples were analyzed via ICP-MS, while the nitrate and sulfate samples underwent flow injection analysis (FIA). The treated water nitrate standards are acidified below a pH of 2 and analyzed within the holding period, as specified by EPA Method 353.2.

For ICP-MS, treated water and brine samples are analyzed in separate batches, and a helium (He) collision cell is used to reduce polyatomic interferences. The ICP-MS instrument is also tuned before each batch run to automatically adjust lens positions to optimize performance.

In general, for QA/QC, duplicate samples were within 10% of each other and measured values for matrix spikes achieved 80% to 120% recovery. In addition, several standards, including NIST 1643f with a maximum known value deviation of 10%, were used. Duplicates and matrix spikes are prepared for every tenth sample. Repeat samples were also analyzed between batches to ensure integrity of results across

multiple batches. Several differences in analytical methods for treated water and brine samples are detailed below.

For treated water samples:

- Samples were prepared undiluted in 15 mL polypropylene disposable centrifuge tubes
- 0.12 mL of concentrated nitric acid was added for metals digestion
- An internal standard of 1 ppm Scandium, Germanium, Yttrium, Indium, and Thulium at 16x dilution was used

For brine samples:

- The ICP-MS was conditioned using a 10x dilution of Agilent 6020 Interference Check Solution A (ICSA). This prevents signal variations due to salt build-up on the cones during a run
- All samples were diluted at least 100x using a 1% nitric acid solution in 15 mL polypropylene disposable centrifuge tubes
- For samples diluted 500x or greater, dilutions were prepared in 50 mL centrifuge tubes to prevent inaccuracies associated with small volume dilutions
- An internal standard of 10 ppm Scandium, Germanium, Yttrium, Indium, and Thulium at 16x dilution was used
- An additional external standard, ICSZ, was also checked every 10 samples with measured values to be within 10% of the first measured ICSZ value

All runs that did not meet the QA/QC were reanalyzed.

5.2.4.1 High Matrix Introduction (HMI)

As part of the Proposition 50 research, a new ICP-MS using the High Matrix Introduction (HMI) analytical method was implemented with the intent to better characterize metals in brine solutions. Traditional analytical methods for metals in brine solutions using ICPMS are negatively impacted by high salt concentrations; samples for traditional ICPMS are frequently diluted more than 20 times to lower the salt concentration, reducing the accuracy and sensitivity of the analytical method. The goal of implementation and validation of the new ICPMS using HMI was to enable higher sensitivity and better characterization of metals.

Using a set of 83 brine samples, including duplicates, the samples were analyzed via ICP-MS with and without HMI. For the traditional ICP-MS analysis, a dilution factor of 100x was used. For the ICP-MS with HMI, the samples were prepared using 10x dilution, with 13 samples prepared using a 100x dilution and 2 samples using a 200x dilution. In each scenario, the run was stable and the instrument passed QA/QC checks for most elements.

Comparison of the traditional ICP-MS results with the results from ICP-MS HMI analysis at 100x and 200x dilutions, yielded chromium concentrations within 0.5 to 14 percent of each other. At the 10x dilution, the ICP-MS with HMI instead yielded chromium concentrations well below the traditional ICP-MS results, with only one sample being within a 10% difference. On average, the ICP-MS HMI with 10x dilution resulted in chromium concentrations 30% below the corresponding traditional ICP-MS results.

Although there is little variation between the traditional ICP-MS and ICP-MS with HMI results at a 100x dilution, the 10x dilution resulted in significant variance. This discrepancy at lower dilutions may be

attributed to higher background salt concentrations, which may impact the ability of the plasma to fully ionize the molecules, resulting in a lower signal. As a result, all brine samples were prepared using a minimum 100x dilution and analyzed using the traditional ICP-MS method. Due to the high dilutions in this instance, it is unclear if the ICP-MS with HMI would have offered any benefits to this research project.

6.0 Results

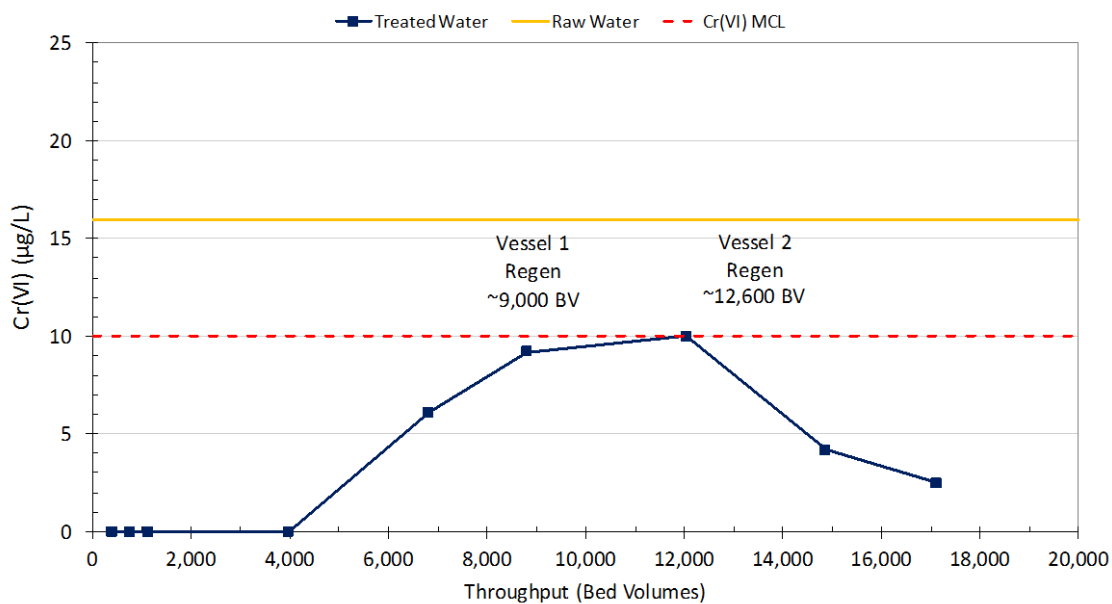
As previously described, two primary goals of the Proposition 50 research are to validate full-scale SBA-IX performance for Cr(VI) treatment, with respect to loading and regeneration, and to investigate opportunities for process optimization and spent brine minimization. The results from full-scale demonstration and pilot research are detailed below in the following sections.

6.1 SBA-IX Loading

6.1.1 Station 9 Full-scale Start-up

Start-up of a full-scale SBA-IX treatment system at Willows Station 9, consisting of four SBA-IX vessels, began in September 2015 with an average September to October daily run time of 23 hours at 461 gpm. Illustrated in Figure 10, at start-up, the blended effluent yielded approximately 12,000 BVs prior to exceeding the 10 µg/L Cr(VI) MCL. This initial breakthrough to 8 µg/L at approximately 7,200 BVs is substantially less than what was observed in the 2014 pilot testing (Figure 11).

Figure 10 Station 9 SBA-IX system blended effluent during start-up



Regeneration of each individual SBA-IX vessel was staggered, beginning with Vessel 1 regeneration at approximately 9,000 BV. At 12,300 BV, blended treated water reached the Cr(VI) MCL of 10 µg/L due to Cr(VI) breakthrough of Vessels 2, 3, and 4. Vessel 2 underwent conventional regeneration at 12,620 BV, resulting in the decreased effluent Cr(VI) concentrations in the blended effluent, as depicted in Figure 10.

With the exception of the SBA-IX system start-up, all vessels are regenerated prior to 10,000 BV to avoid Cr(VI) breakthrough in the blended treated effluent. Later sampling of Station 9 treated water, in November and December 2016, yielded Cr(VI) concentrations well below the MCL of 10 µg/L.

6.1.2 Purolite A600E 9149

In other applications for Cr(VI) treatment, the SBA-IX process was shown to be scalable and reproducible given consistent water and resin quality (Seidel et. al, 2014). Average Willows Station 9 raw water quality

parameters known to have an impact on SBA-IX performance from 2014, when the initial piloting was conducted, and 2016 are given in Table 11. As seen in the table, sulfate concentrations are consistent with an increase of 1.3 mg/L as N nitrate.

Table 11 Average raw water quality summary for Willows Station 9

Pilot Period	Testing	Cr Total (µg/L)	Cr(VI) (µg/L)	Alkalinity as CaCO ₃ (mg/L)	Nitrate as NO ₃ -N (mg/L)	Sulfate (mg/L)
2016		13.3 ¹	16	225	4.2 ¹	50
2014		19.4 ¹	16	214	2.9	49

¹Calculated from samples collected by Corona during pilot testing

As noted above in Section 3.0 Willows Water System Background, the Purolite A600E 9149 was found to be the best performing resin of those screened at Willows Station 9 achieving nearly 12,000 BV prior to reaching an 8 µg/L treatment threshold for Station 9. With that said, the pilot- and full-scale performance of A600E 9149 resin when compared to previous 2014 pilot results, illustrated in Figure 11 and Figure 12, respectively, show an overall decrease in the resin's Cr(VI) removal capacity. Although an increase in nitrate has been observed between the 2014 to 2016 pilot testing, this increase is not expected to decrease performance to the extent that has been experienced.

Figure 11 Pilot-scale performance of A600E 9149 resin (2014-2016)

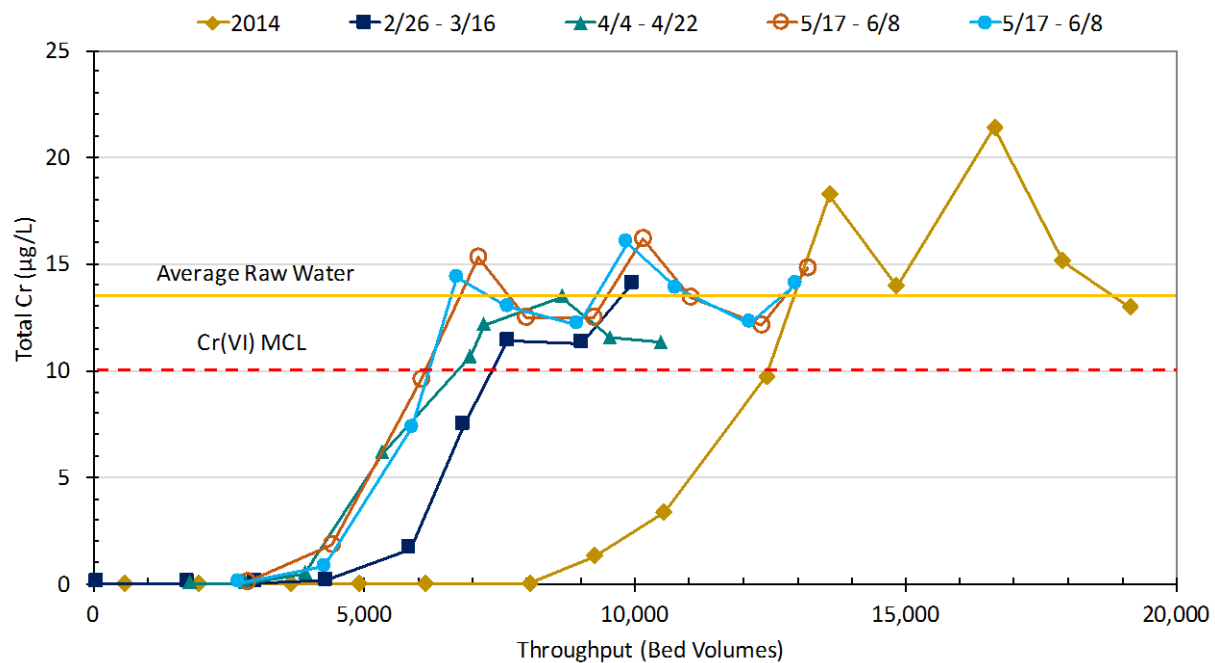
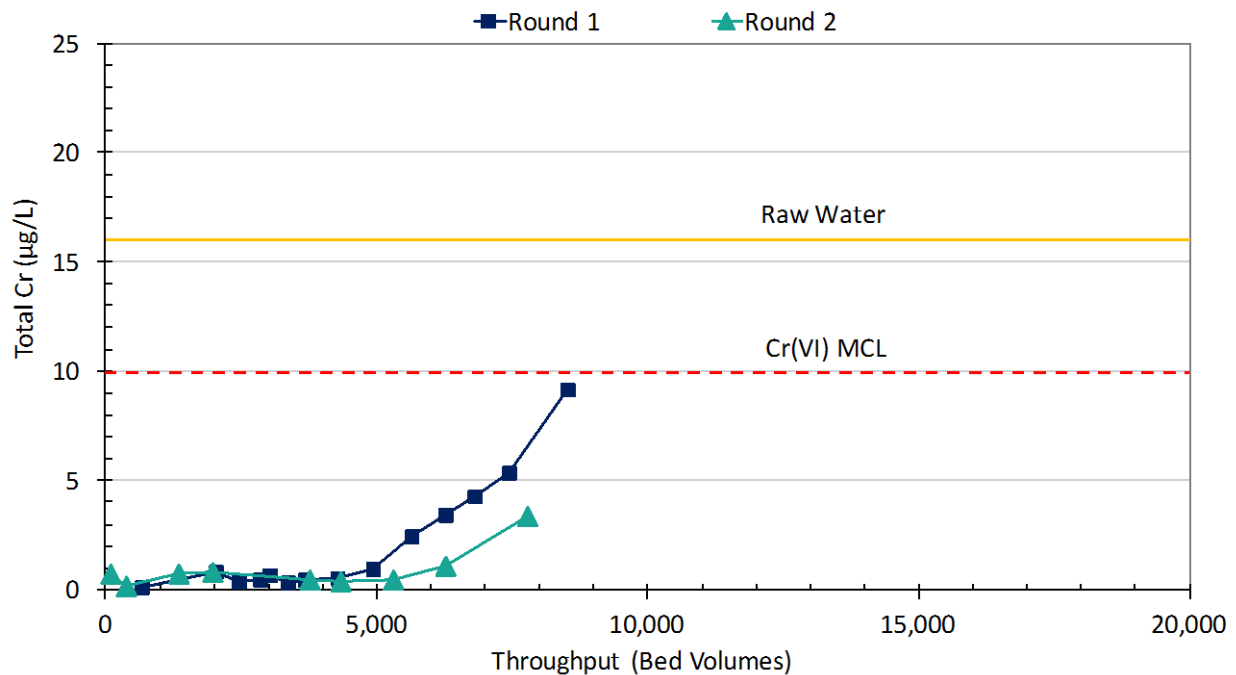


Figure 12 Willows Station 9 Vessel 2 full-scale performance of A600E 9149 resin



As shown in Figure 12, two rounds of loading for Vessel 2 were documented with Vessel 2 approaching the Cr(VI) MCL at approximately 8,500 BV, a decrease in resin performance compared to the 2014 pilot results. Additional pilot-scale resin screening of the A600E 9149, conducted on the 2-inch diameter pilot columns, also yielded decreased performance over multiple loading cycles as seen in Figure 11. Profiling of the A600E 9149 resin performance occurred over several months using virgin resin for each loading cycle, eliminating the influence of regeneration on resin performance. In these scenarios, total chromium breakthrough to the 10 µg/L MCL occurred earlier between 5,000 to 7,000 bed volumes.

The observed decrease in performance from the 2014 pilot- to full-scale has also been reported for other systems Cal Water operates. To determine the variation between resin batches, an additional round of screening was conducted using a new batch of A500E 9149. In this case, total chromium breakthrough was once again observed at 6,000 BV. A collaborative investigation with Purolite has been initiated to identify the cause of decreased A600E 9149 performance.

6.1.3 Alternative Resin Testing

Since the initial 2014 screening, several new resins have been developed or identified as potentially having greater Cr(VI) exchange capacity. Knowing that regeneration and subsequent management and disposal of the regenerant brine comprises the bulk of SBA-IX operational costs, improvements to resin capacity is perhaps the simplest way to improve overall efficiency and reduce costs.

For the resin screening conducted as part of this research, the Purolite A600E 9149 was used to benchmark the performance of other resins tested. A summary of the resins screened during this research, as well as resins screened as part of the 2014 pilot testing, is provided in Table 12. Regeneration of the A600E 9149 resin has been proven effective in previous pilot testing (Seidel et al., 2014), while

regeneration capability of the CalRes 21117 and Lewatit XREA 783 were investigated as part of this Proposition 50 pilot research.

Table 12 Summary of resins screened

Manufacturer	Resin	Date Screened	NSF Certified
Purolite	A600E 9149	2014, 2016	Yes
ResinTech	SBG1	2014	Yes
DOW	SAR	2014	Yes
LANXESS Sybron	GW66	2014	Yes
Calgon	CalRes 2117	Feb – Mar, 2016	No
DOW	PWA17	May – Jun, 2016	Yes
LANXESS Sybron	Lewatit XREA 783	May – July, 2016	Yes
Purolite	D5886	July – Nov, 2016	No

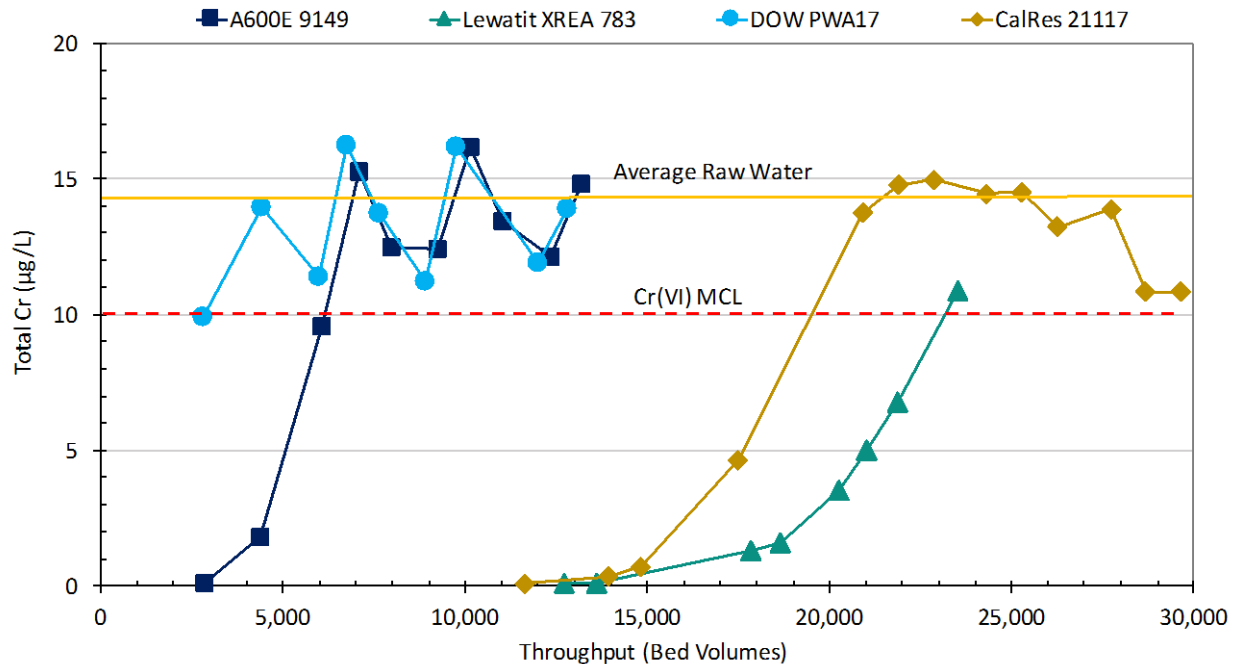
The resins provided were screened using 2-inch diameter columns located on-site at Willows Station 9. Table 13 details the resin screening test conditions. A hydraulic loading rate (HLR) of 15 gpm/ft² and empty bed contact time (EBCT) of 135 seconds were targeted to replicate the 2014 pilot testing conditions. For each round of resin screening, A600E 9149 resin was included as a baseline. All resins were evaluated on throughput prior to chromium breakthrough, as well as regeneration performance, discussed later in Section 6.2 SBA-IX Regeneration.

Table 13 Resin screening pilot conditions

Column Parameter	Unit	A600E 9149	CalRes21117	PWA17	Lewatit XREA 783
Diameter	in.	2.0	2.0	2.0	2.0
Volume	gal.	0.72	0.69	0.78	0.27
Empty Bed Contact Time (EBCT)	sec.	137	127	142	135
Hydraulic Loading Rate (HLR)	gpm/ft ²	15	15	15	15

The performance of the Purolite A600E 9149, Dow, LANXESS Sybron and Calgon resins screened is detailed in Figure 13. Breakthrough curve of Purolite D5886 resin is not given, due to limited volume of resin for screening and resulting lower EBCT of 45 seconds. Preliminary screening of the D5886 resulted in similar chromium breakthrough to that of the A600E 9149 resin.

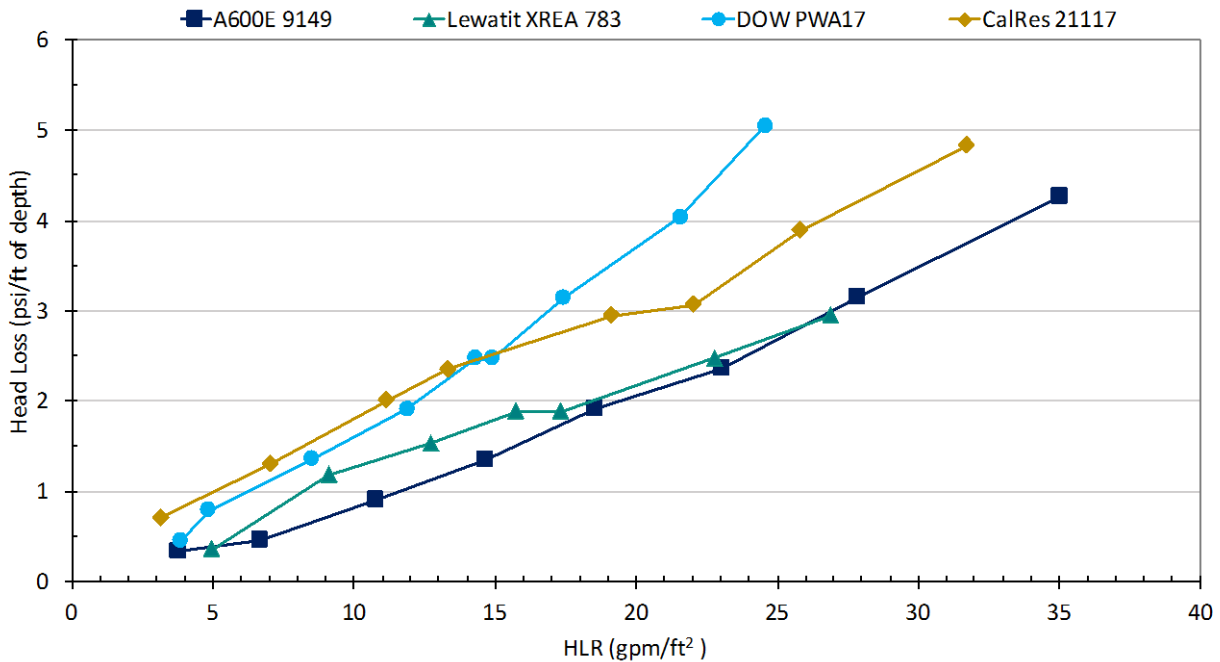
Figure 13 Comparative performance resins screened



Shown in Figure 13, in comparison to the Purolite A600E 9149, the CalRes 21117 and Lewatit XREA 783 resins achieved an approximately 3 to 4 times higher capacity for chromium removal. The DOW PWA17 resin resulted in near immediate breakthrough, and it is speculated that the resin was not properly hydrated prior to testing. A subsequent sample of properly conditioned resin was tested in a later round of resin screening, which resulted in the same immediate chromium breakthrough.

In addition to resin capacity, the head loss as a function of HLR was investigated for each alternative resin, as shown in Figure 14. The DOW PWA17 resin resulted in the steepest head loss for increasing HLR, with the remaining resins yielding an incremental head loss of 1 psi per foot of resin depth for a HLR increase of 10 gpm/ft². At the pilot testing HLR condition of 15 gpm/ft², the starting head loss for the DOW PWA17 and CalRes 21117 resins were approximately 60% greater than the Purolite A600E 9149.

Figure 14 Alternative resin head loss as a function of HLR



6.2 SBA-IX Regeneration

For the purposes of this Proposition 50 research and Cal Water full-scale operation, conventional regeneration is defined as co-current regeneration using 3 to 4 bed volumes of 2 M NaCl brine (116.9 g/L NaCl with an approximate conductivity of 120 mS/cm) followed by a 2 BV soft water rinse.

Initially the Willows SBA-IX systems implemented a conventional regeneration protocol prior to transitioning to the proprietary Ionex SG segmented regeneration, detailed further in Section 6.2.3 IonexSG Segmented Regeneration. The full-scale performance of Station 9 Vessel 2 conventional regeneration is used as the benchmark for regeneration performance of alternative resins and regenerants.

6.2.1 Full-scale Conventional Regeneration

Full-scale Station 9 Vessel 2 conventional regeneration with sodium chloride was profiled three times, every third regeneration, after start-up. A summary of each regeneration profiled is provided in Table 14. The intent of this monitoring was to document full-scale contaminant elution and regeneration performance over multiple cycles. For this project, successful demonstration is defined as recovery of anions as to not have a discernable impact on the subsequent loading cycle.

Table 14 Willows Station 9 Vessel 2 regeneration profiling summary

Parameter	Unit	Regeneration 3	Regeneration 6	Regeneration 9
Date		December, 2015	March, 2016	June, 2016
Vessel		2	2	2
Throughput prior to regeneration	BV	12,620	9,800	8,307
Total regeneration sample time	BV	3.8	4	4
Sample frequency	BV	0.2	0.2	0.2
Total Cr, final brine sample	mg/L	0.60	0.19	0.24

The total chromium [used as a surrogate for Cr(VI)], sulfate, nitrate, chloride, and conductivity results from regeneration profiling for regenerations 3, 6, and 9 are shown in Figure 15, Figure 16, and Figure 17, respectively. For each figure, the brine and rinse fractions are denoted by the black dashed line. In each case, the sulfate was eluted first from the resin followed by chromium and then nitrate. As anions are exchanged with chloride ions, the chloride concentration increases slowly through the regeneration process until it ultimately approaches a value equal to that of the unused brine which indicates the regeneration is nearing completion.

In addition to chromium, sulfate, and nitrate, other contaminants such as vanadium, uranium, selenium, and arsenic are also removed via the SBA-IX process. These co-contaminants compete with chromium for sites on SBA-IX resin. The co-contaminant elution curves are shown in Figure 18. Note in Figure 18, the y-axis has been adjusted to show greater resolution of the co-contaminants. The uranium and vanadium peak concentrations are between 15 to 20 mg/L, significantly lower than the peak chromium elution at 120 mg/L, indicating less accumulation of these contaminants during loading due to low-level raw water concentrations.

Figure 15 Full-scale conventional regeneration 3 profiling (December 2015)

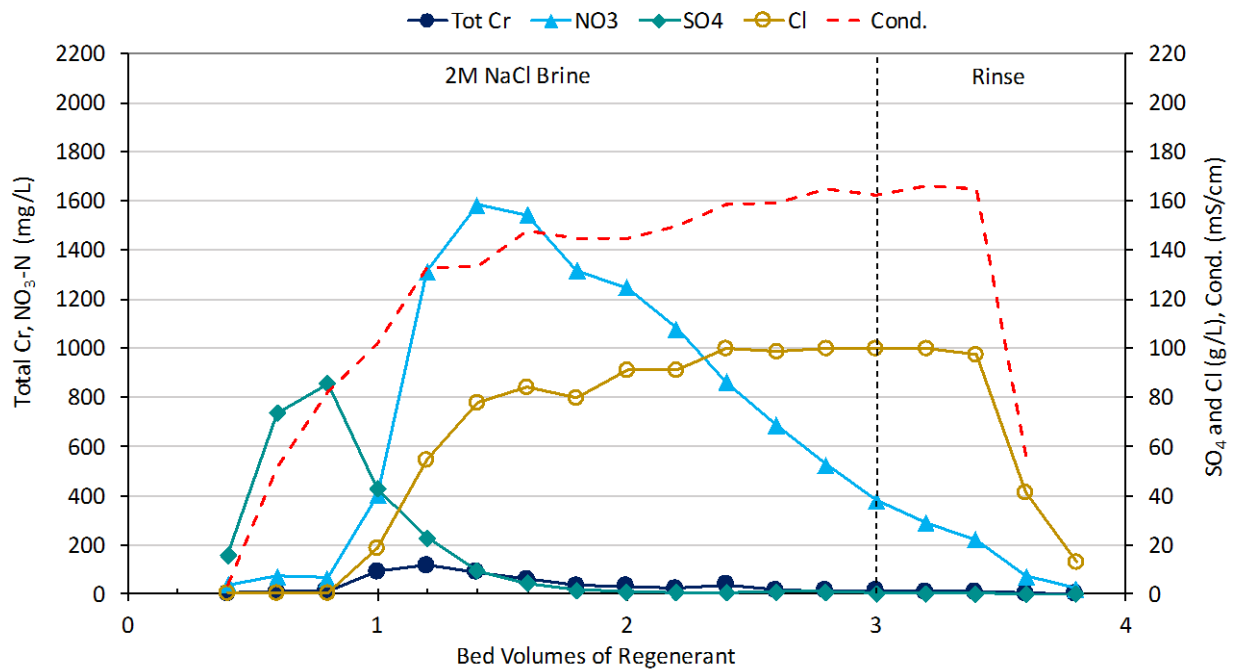


Figure 16 Full-scale conventional regeneration 6 profiling (March 2016)

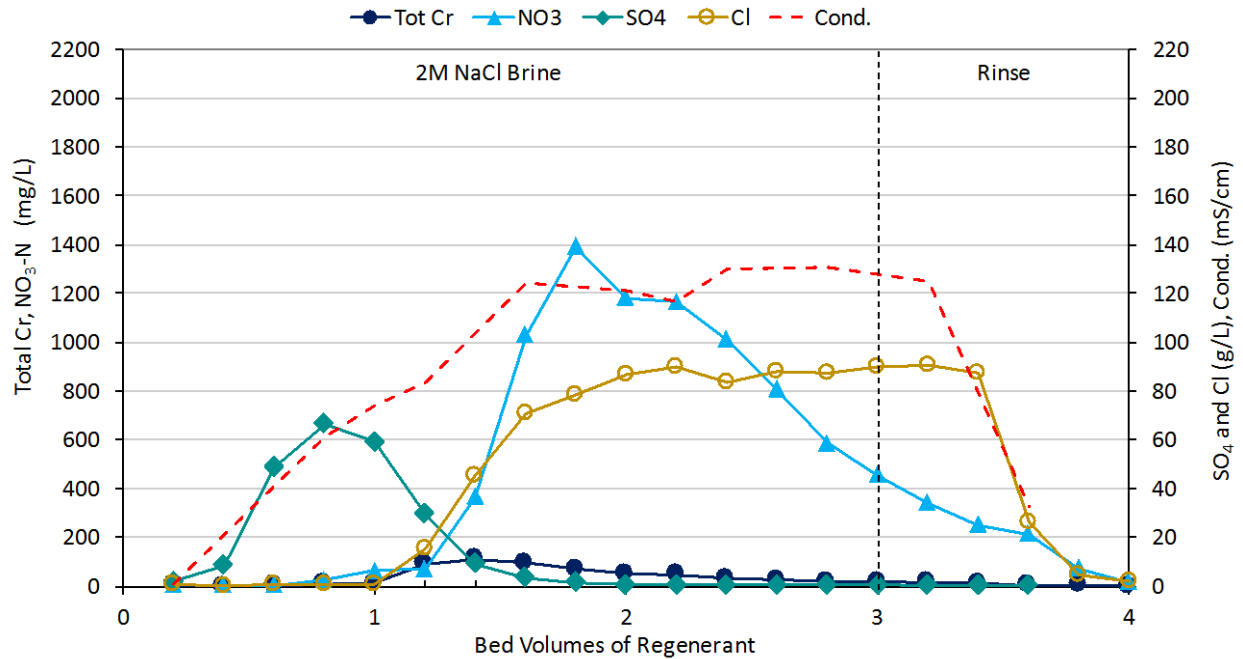


Figure 17 Full-scale regeneration 9 profiling (June 2016)

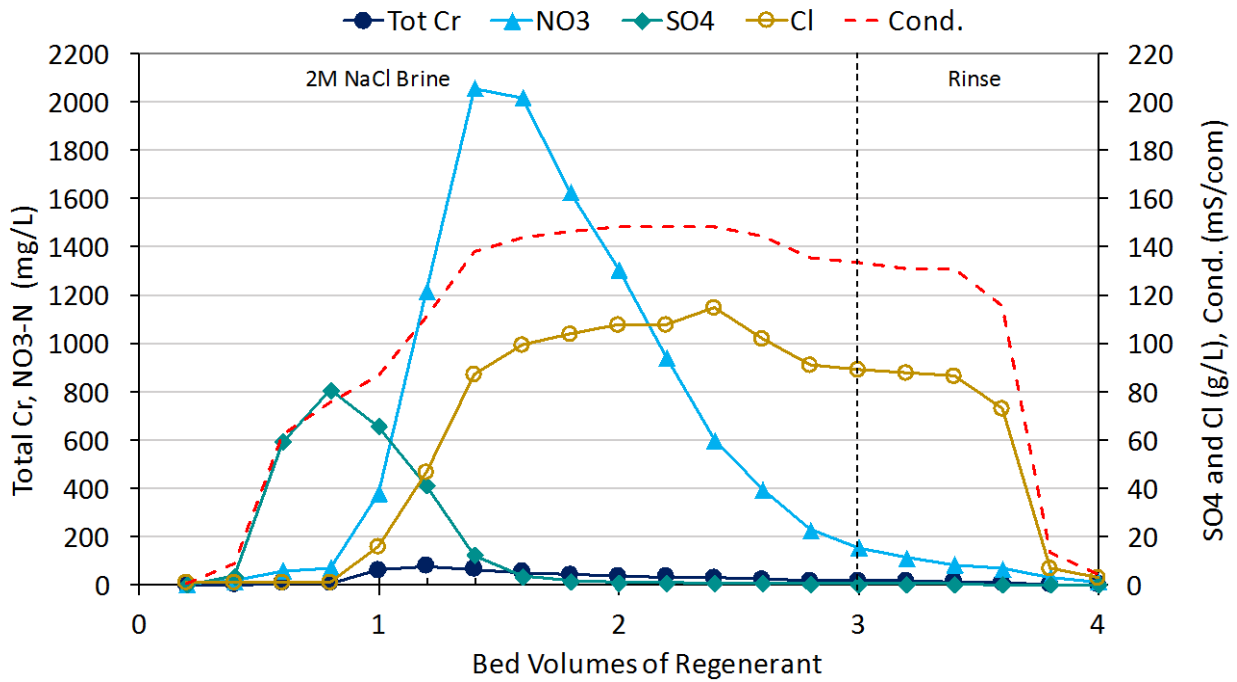
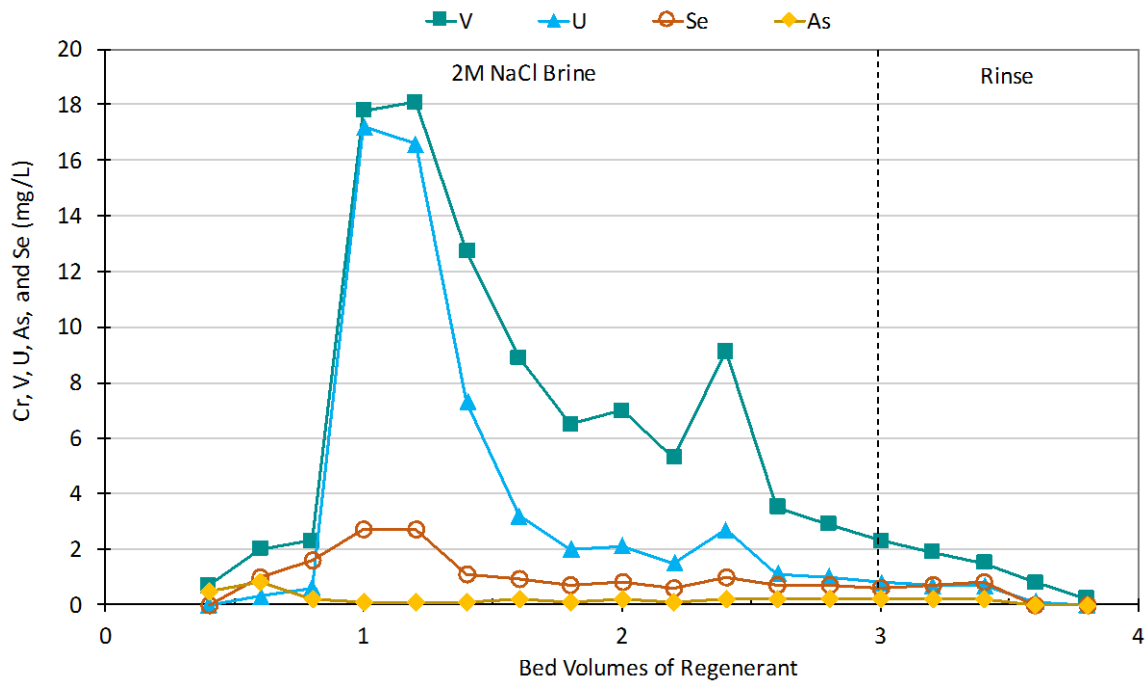


Figure 18 Full-scale regeneration showing the elution of 3 micro-contaminants (December 2015)



Total chromium results for regenerations 3, 6, and 9 shown in Figure 15, Figure 16, and Figure 17, respectively, are also illustrated in Figure 19 with the y-axis having a maximum of 140 mg/L for better resolution; the comparison of all three regenerations show similar total chromium elution curves, with

peak chromium concentrations varying between 80 to 120 mg/L. The lower chromium peak for Regeneration 9 in June 2016 can be attributed to early regeneration at 8,307 BV.

A summary of the total mass of chromium, sulfate, nitrate, and additional metals eluted during each regeneration, calculated using the Riemann Summation Method, is given in Table 15. For most analytes, including total chromium, sulfate, and nitrate, the relative standard deviation (RSD) for the three different regenerations is below 15%, with 7.3% deviation for chromium. Large standard deviations between 34% to 48% for arsenic and selenium can be attributed to analytical error caused by low concentrations near the detection limits. Overall, regenerations were consistent and resulted in similar chromium, and other anions, elution.

Figure 19 Comparison of full-scale regeneration profiling

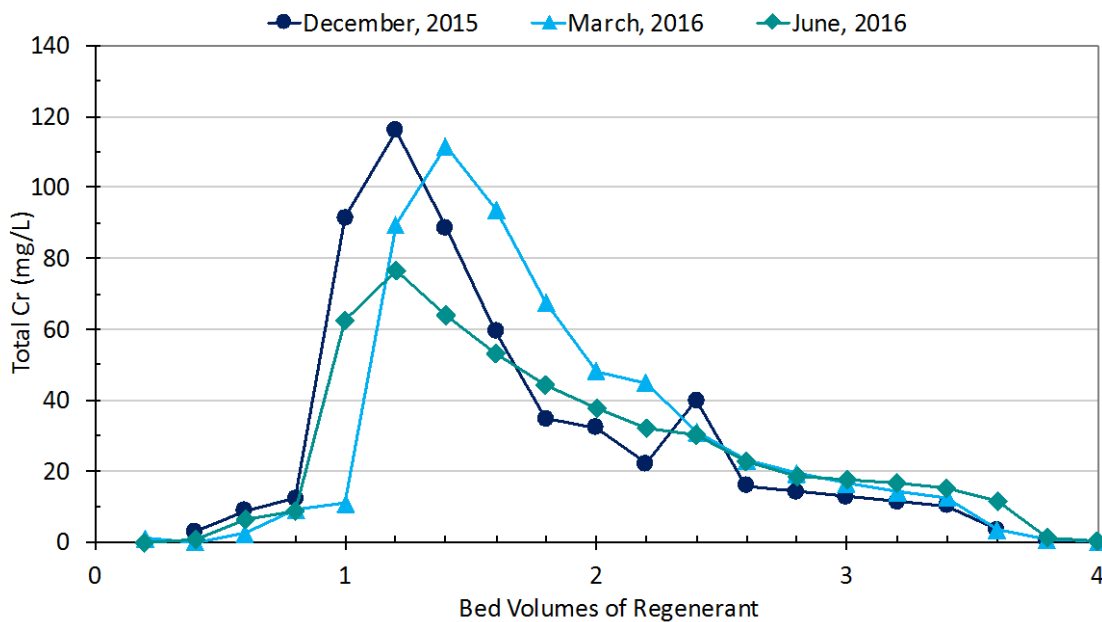


Table 15 Total mass of contaminants eluted during vessel regeneration

Analyte	Unit	Regeneration 3	Regeneration 6	Regeneration 9	% RSD
Total chromium	g	170	176	153	7.3
Sulfate	kg	81.9	68.2	80.4	9.6
Nitrate	kg as N	3.5	2.7	3.3	13.8
Arsenic	g	1.2	0.7	0.5	47.8
Selenium	g	4.9	2.7	2.9	34.1
Uranium	g	17.0	14.6	14.9	8.4
Vanadium	g	30.6	26.6	25.5	9.7

6.2.2 Alternative Resin Regeneration

Regeneration of the alternative resins, described above in Section 6.1.3 Alternative Resin Testing, was investigated to determine regeneration efficiency and its impact on O&M costs. The Purolite A600E 9149

resin is certified for regenerable SBA-IX systems, while successful regeneration of the Lewatit XREA 783 and Calgon CalRes resins have not been demonstrated over multiple loading cycles to date.

All three resins were regenerated in the 2-inch pilot columns using a modified conventional regeneration approach of 3.5 to 4.5 BV of 2M NaCl brine followed by a water rinse. The extended BV of NaCl brine is to ensure complete chromium elution during regeneration, as the Calgon and LANXESS resins demonstrated twice the chromium capacity compared to the A600E 9149. The regeneration approach for each resin is further specified in Table 16. Regeneration of the DOW PWA17 resin was not conducted due to almost immediate chromium breakthrough during loading.

Table 16 Pilot resin regeneration conditions

Parameter	Unit	A600E 9149	CalRes 2117	Lewatit XREA 783
Date		May, 2016	May, 2016	July, 2016
Bed volumes of 2 M NaCl brine	BV	3.5	3.5	4.5
Bed volumes of rinse	BV	2	2	2
Sample frequency	BV	0.2	0.2	0.2
Total Cr in final sample	µg/L	0.021	0.004	0.004

Conductivity, and chromium, nitrate, sulfate, and chloride elution curves during regeneration of the A600E 9149, CalRes 21117, and Lewatit XREA 783 resins are presented in Figure 20, Figure 21, and Figure 22, respectively. For each figure, the brine and rinse fractions are denoted by the black dashed line. The A600E 9149 elution curve is consistent with the full-scale regenerations profiled at Station 9, as shown in Figure 15, Figure 16, and Figure 17, while the CalRes and Lewatit resins resulted in higher chromium peaks and broader elution tails which are suspected to be due to increased chromium loading.

Figure 20 Pilot-scale conventional regeneration of Purolite A600E 9149 resin

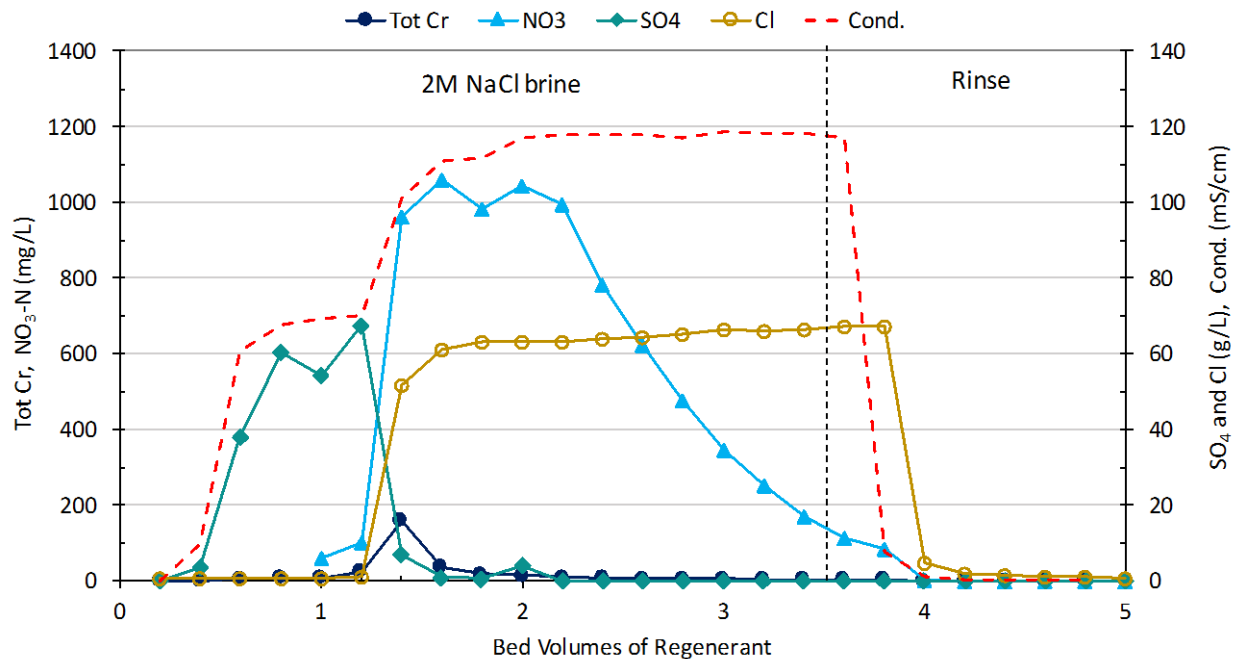


Figure 21 Pilot-scale conventional regeneration of Calgon CalRes 21117 resin

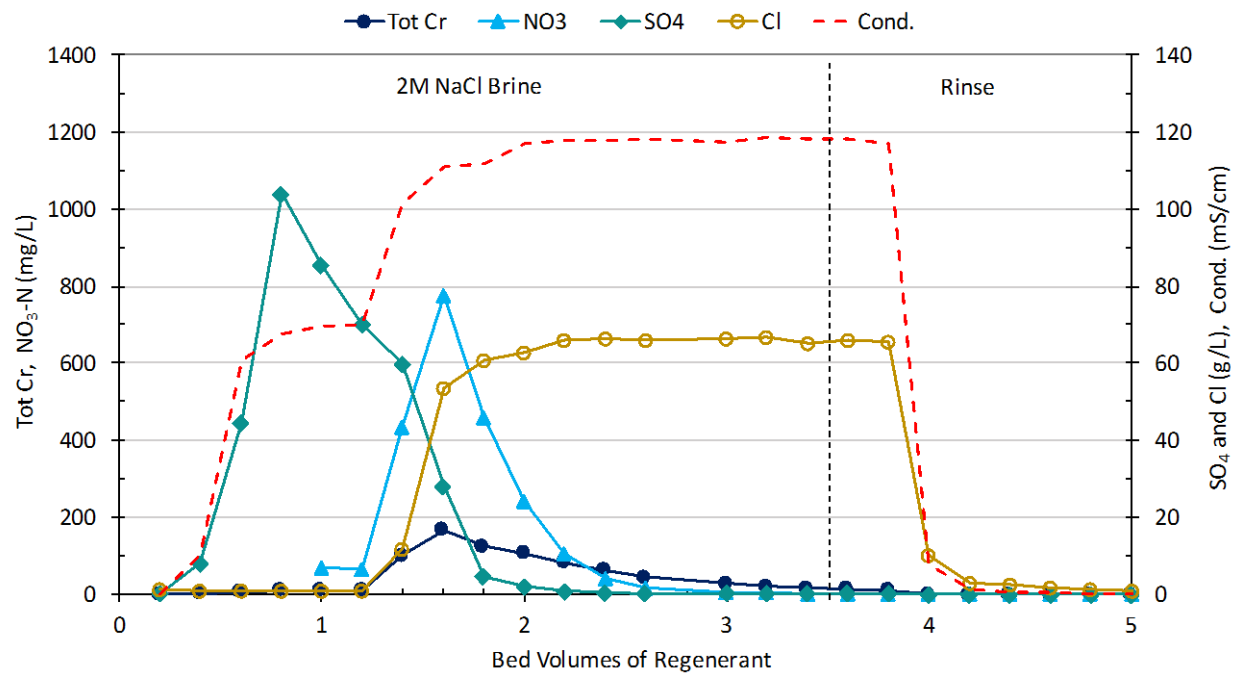
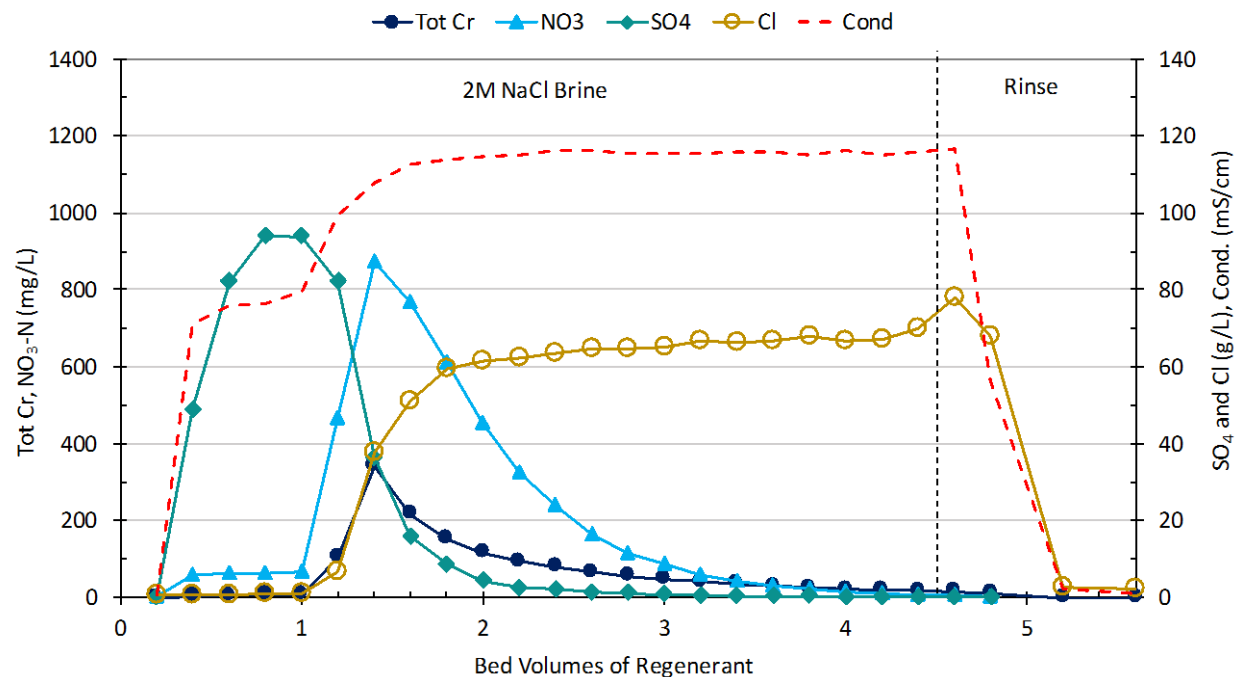


Figure 22 Pilot-scale conventional regeneration of LANXESS Sybron Lewatit XREA 783 resin



A comparison of the total chromium loaded and subsequently eluted during regeneration for each resin is shown in Table 17. Regeneration of both the A600E 9149 and Lewatit XREA 783 resins resulted in approximately full chromium elution. In comparison, regeneration of the CalRes resin yielded only 73.3% chromium removal and could have benefited from a higher strength brine solution or an additional

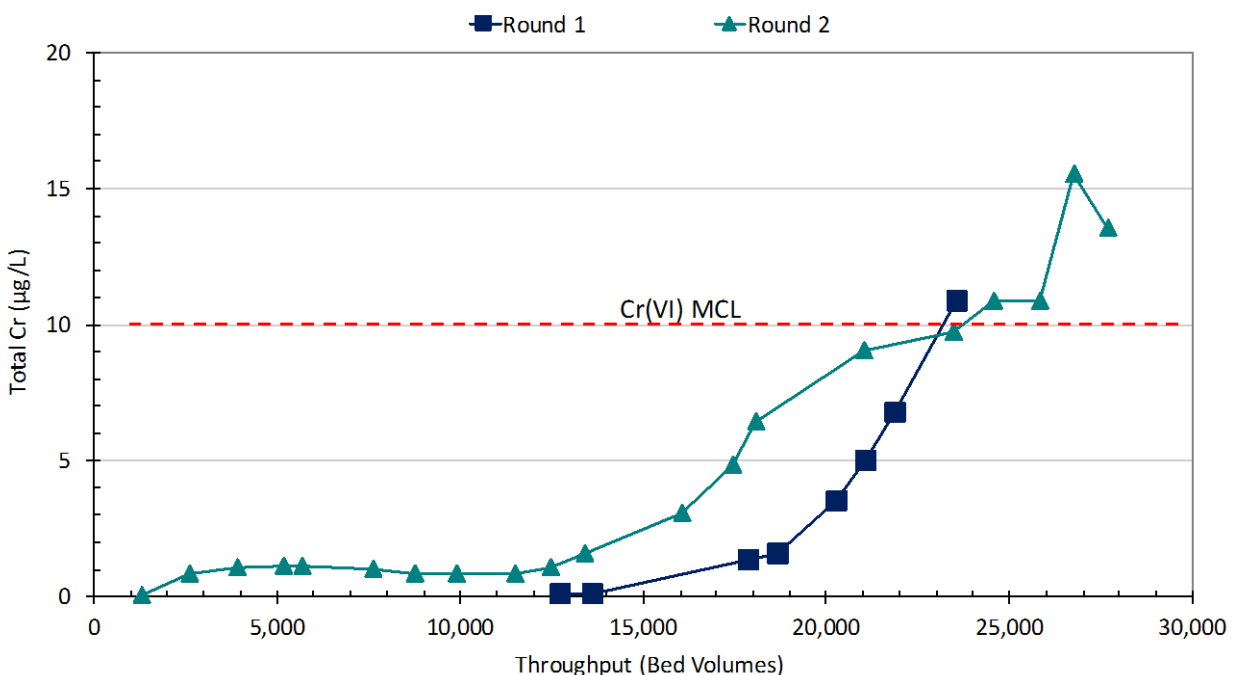
regeneration bed volume of NaCl brine like the Lewatit XREA resin, which was regenerated for 4.5 BVs instead of 3.5 BVs.

Table 17 Comparison of alternative resin regeneration

Analyte	Total Cr Loaded (g Cr/L resin)	Total Cr Eluted (g Cr/L resin)	Percent Cr Recovered (%)
A600E 9149	0.063	0.068	108.0
CalRes 21117	0.218	0.160	73.4
Lewatit XREA 783	0.300	0.309	103.0

A comparison of Lewatit XREA 783 chromium breakthrough curves before and after regeneration is shown in Figure 23. Although both rounds of loading resulted in chromium concentrations approaching the Cr(VI) MCL around 25,000 BV, the second round of resin loading resulted in earlier chromium breakthrough. After regeneration, the Lewatit resin reached the Cr(VI) 8 µg/L threshold approximately 4,000 BV earlier than the virgin resin suggesting regeneration did not meet the success criteria defined above in Section 6.2.1 Full-scale Conventional Regeneration. Additional rounds of resin regeneration and loading using a higher strength brine solution or extended regeneration approach will be conducted by LANXESS Sybron conducted to determine potential use as a regenerable resin.

Figure 23 Lewatit XREA 783 resin loading after regeneration



6.2.3 IonexSG Segmented Regeneration

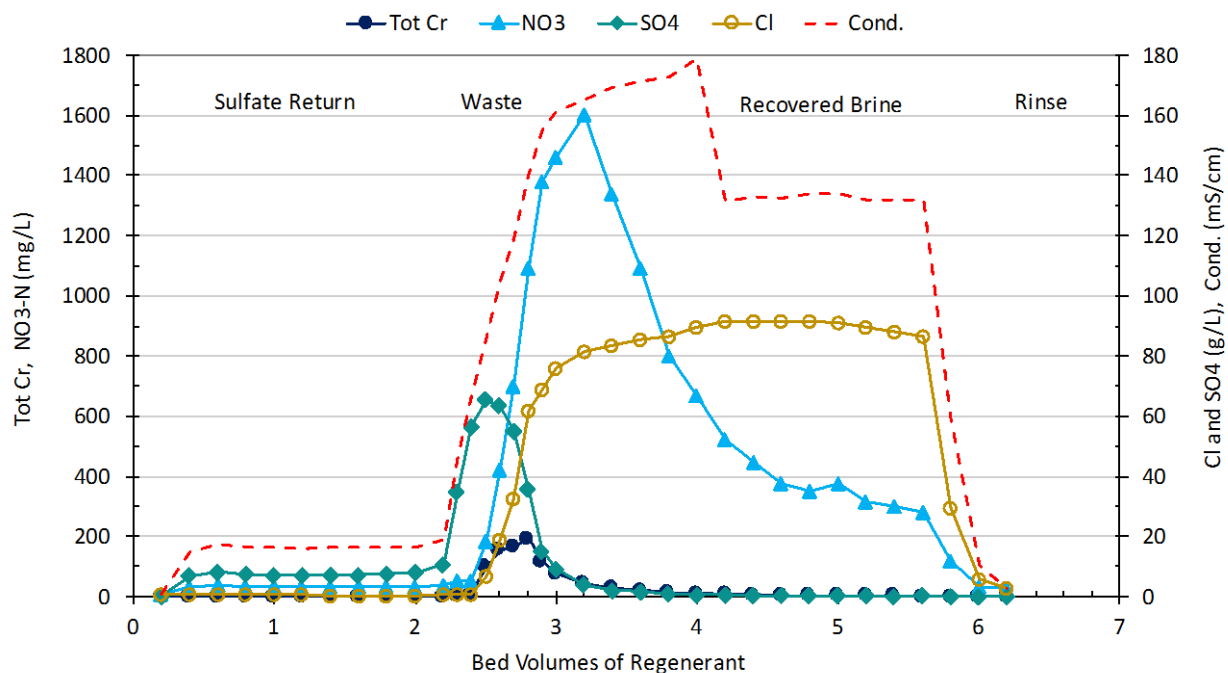
Previous research has shown that the bulk chromium is eluted in a fraction of the total regeneration (Seidel et al. 2014, Waite 2015). Researchers and technology providers have suggested that this portion of the regeneration could be isolated for disposal, while the remainder of the brine could be collected for

potential reuse. To reduce the cost of waste brine disposal, all Cal Water Willows well sites are in the process of implementing a proprietary segmented regeneration approach, designed by Ionex SG. This approach has been in operation for two years at a Soquel Creek Water District full-scale SBA-IX demonstration plant and Ionex SG has been successful at demonstrating a similar segmented process for nitrate SBA-IX applications. For Cr(VI) treatment, the segmented regeneration can potentially reduce brine volumes requiring disposal by 80% or greater.

In recent small-scale proof of concept studies at Dixon 9-01, which has an average influent Cr(VI) concentration of 21.9 µg/L, Ionex SG has shown the Cr(VI) fraction of the waste can be isolated to approximately 0.5 BV during a 7 to 8 BV regeneration cycle.

Initial transition from traditional to segmented regeneration began at Willows Station 9 in September, 2016. The IonexSG segmented regeneration produces three brine fractions and a rinse segment. The first Station 9 segmented regeneration is illustrated in Figure 24.

Figure 24 Willows Station 9 first segmented regeneration (September, 2016)



Depicted in Figure 24, the initial portion of the brine, labeled 'Sulfate Return' and shown in purple, is a lower concentration salt solution that removes the majority of the sulfate from the resin. The second step, highlighted in yellow, is a higher concentration salt solution that contains the concentrated Cr(VI) fraction. The third step, shown in red, is the recovered brine segment. The final step, shown in blue, is a rinse step.

The rinse is reused in the next regeneration to create the sulfate return fraction. Ideal operation feeds the sulfate return portion into the untreated water at the top of SBA-IX treatment. This sulfate-laden lower concentration brine requires full characterization before considering reintroduction to the treatment process. A portion of the recovered brine is reused to make the more concentrated chromium-laden waste in the next regeneration, while the remainder is reused as recovered brine during the subsequent

regeneration. A flow diagram illustrating the recycling of recovered brine and rinse fractions is given in Figure 25. The chromium laden brine fraction is the only waste product.

Comparison of the Ionex SG segmented approach to conventional regeneration at Willows Station 9 is given in Figure 26. As shown in the figure, the segmented regeneration results in a more concentrated chromium elution curve.

Figure 25 Segmented regeneration brine reuse flow diagram

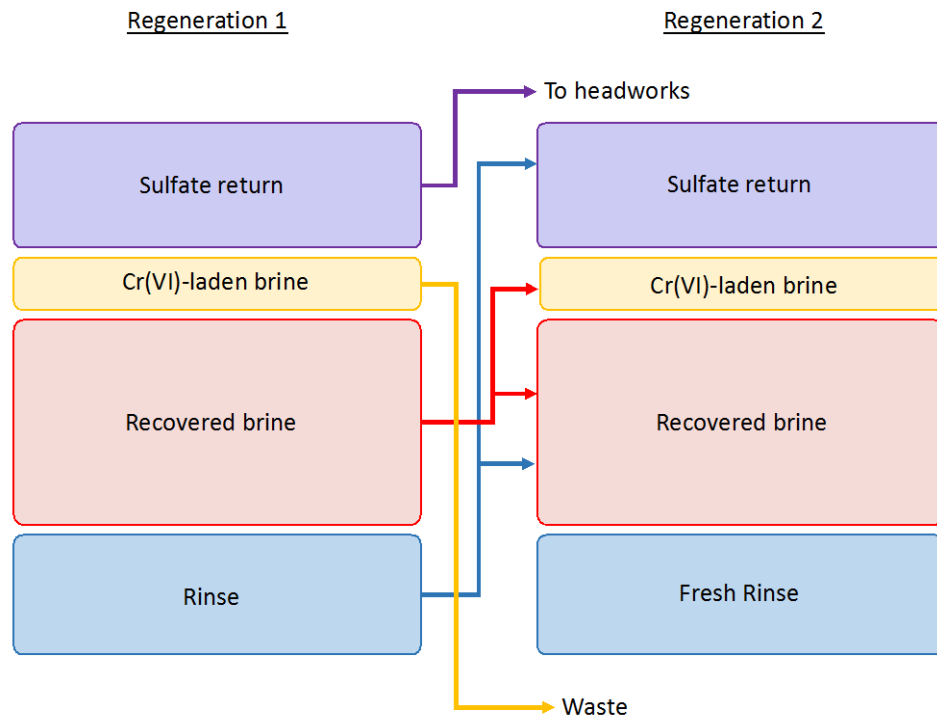
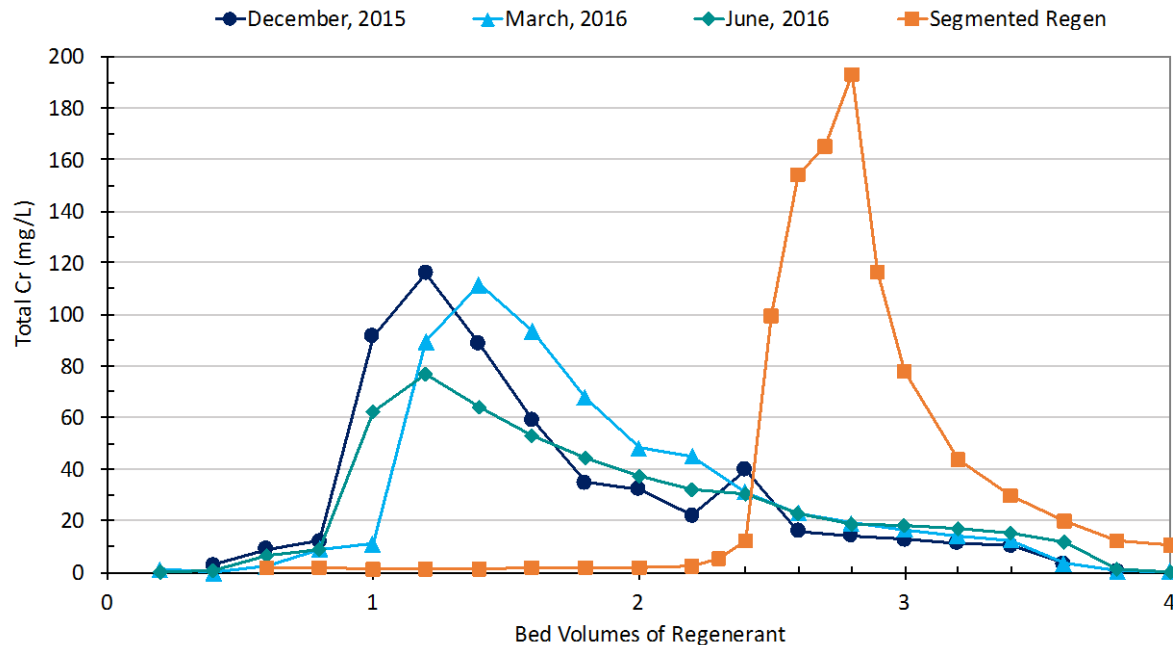


Figure 26 Comparison of Willows Station 9 segmented and conventional regeneration



Before implementing brine reuse and sulfate return, several series of Station 9 segmented regenerations will be profiled to characterize the brine fractions. Once implemented, the IonexSG segmented regeneration with sulfate return could result in reduction of 80% of waste brine for disposal, significantly lowering O&M costs.

6.2.4 Alternative Regenerant Testing

When Cal Water was considering Cr(VI) treatment for their Dixon district, there was concern about increased chloride in the finished water due to release of chloride as a function of the exchange process. As a result, the use of alternative regenerants, including sodium bicarbonate and sodium sulfate were considered. If effective, these regenerants would release either bicarbonate or sulfate as the co-ion as opposed to chloride.

From a statewide perspective, if the resulting brine waste could be rendered non-hazardous through treatment, described further in Section 6.3 Brine Treatment, there may be increased potential for local sewer disposal.

To better understand the efficacy of alternative regenerants, sodium sulfate (NaSO_4) and sodium bicarbonate (NaHCO_3) were used to regenerate 2-inch pilot-scale columns loaded with Purolite A600E 9149 to allow for direct comparisons to a chloride-based regenerant. Table 18 details the alternative regenerant testing conditions. It should be noted that bicarbonate and sulfate regenerants require a larger volume of brine to effectively regenerate the resin (12 BV and 8 BV including rinse respectively) as opposed to the 3.5 BV for chloride.

Table 18 Alternative regenerant testing conditions

Parameter	Unit	NaCl	NaHCO ₃	NaSO ₄
Resin		A600E 9149	A600E 9149	A600E 9149
Resin volume	gal	0.72	0.73	0.69
Concentration	% w/w (g/L)	12 (120)	9 (90)	14 (140)
Bed volumes of regenerate	BV	3.5	10	6
Bed volumes of rinse	BV	2	2	2
Flow rate	BV/hr	2	3	2

The resulting elution curves for regeneration of Purolite A600E 9149 resin with chloride, bicarbonate, and sulfate are presented in Figure 27, Figure 28, and Figure 29, respectively. Pilot column regeneration of A600E 9149 with sodium chloride was conducted for direct comparison of alternative regenerants and validation of pilot regeneration with full-scale results. All three regeneration profiles are depicted on the same scale, 12 bed volumes of regenerant. For the total chromium and nitrate concentrations, a maximum y-axis value of 160 mg/L is used for resolution of the elution curves. Full nitrate elution during the chloride regeneration is given in Figure 31 below. For the sulfate regeneration, the sulfate elution curve is not profiled as it cannot be distinguished from the sulfate regenerant.

Figure 27 Pilot-scale regeneration with sodium chloride

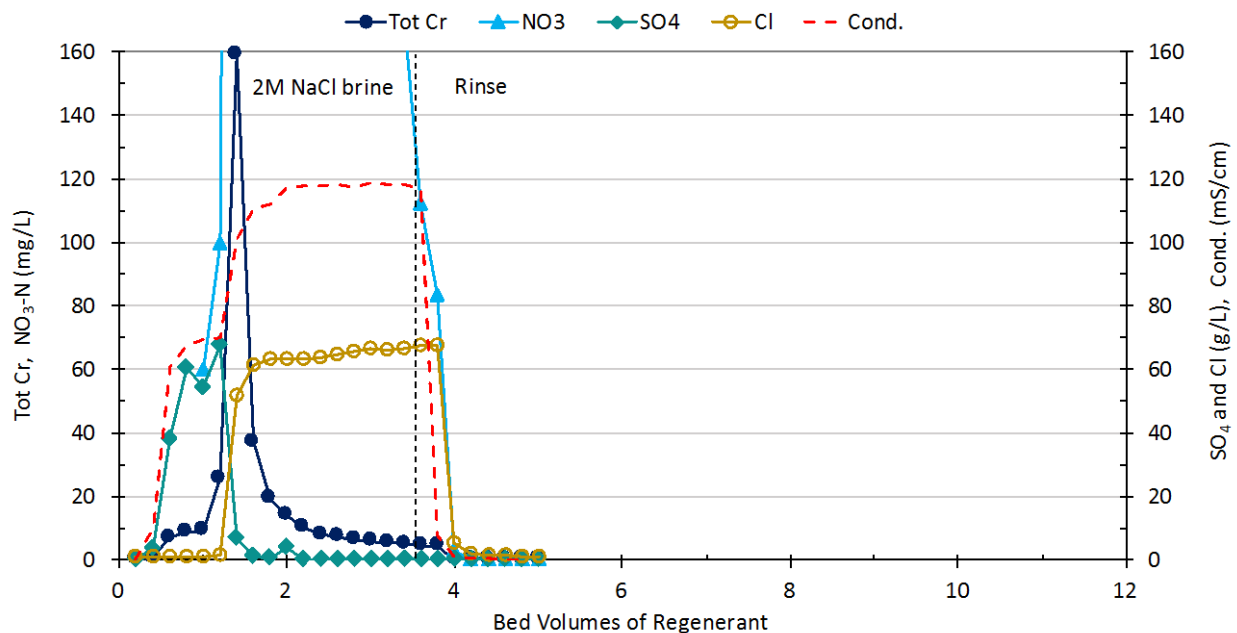


Figure 28 Pilot-scale regeneration with sodium bicarbonate

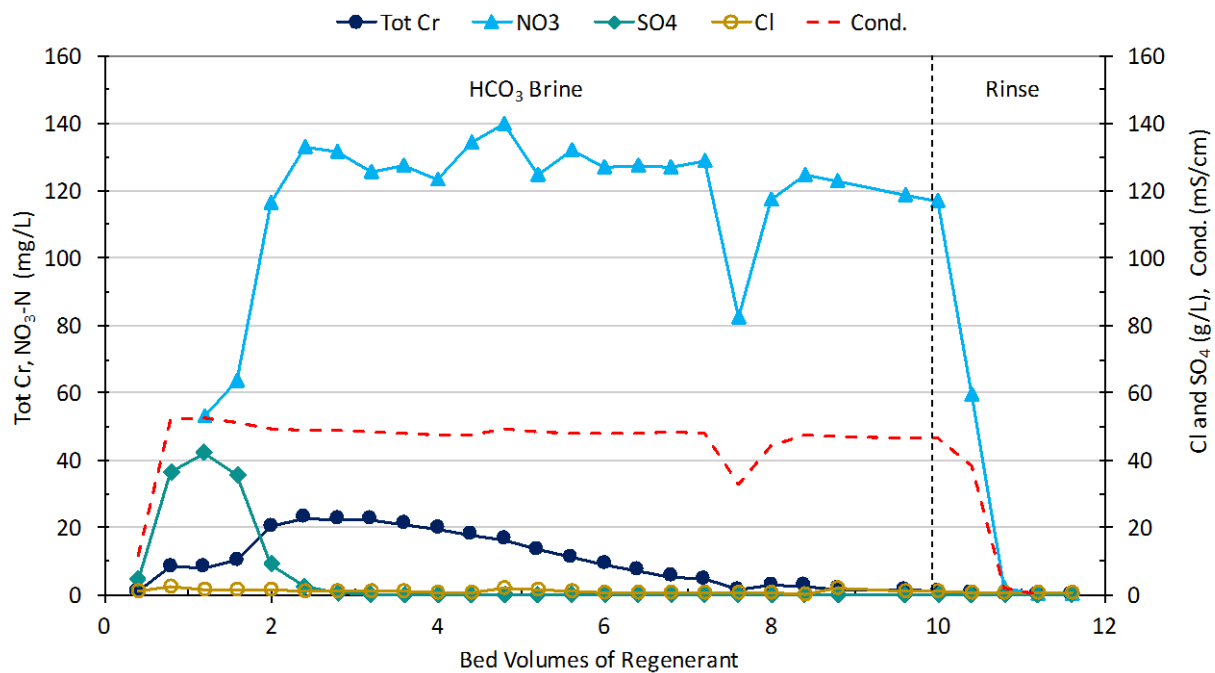
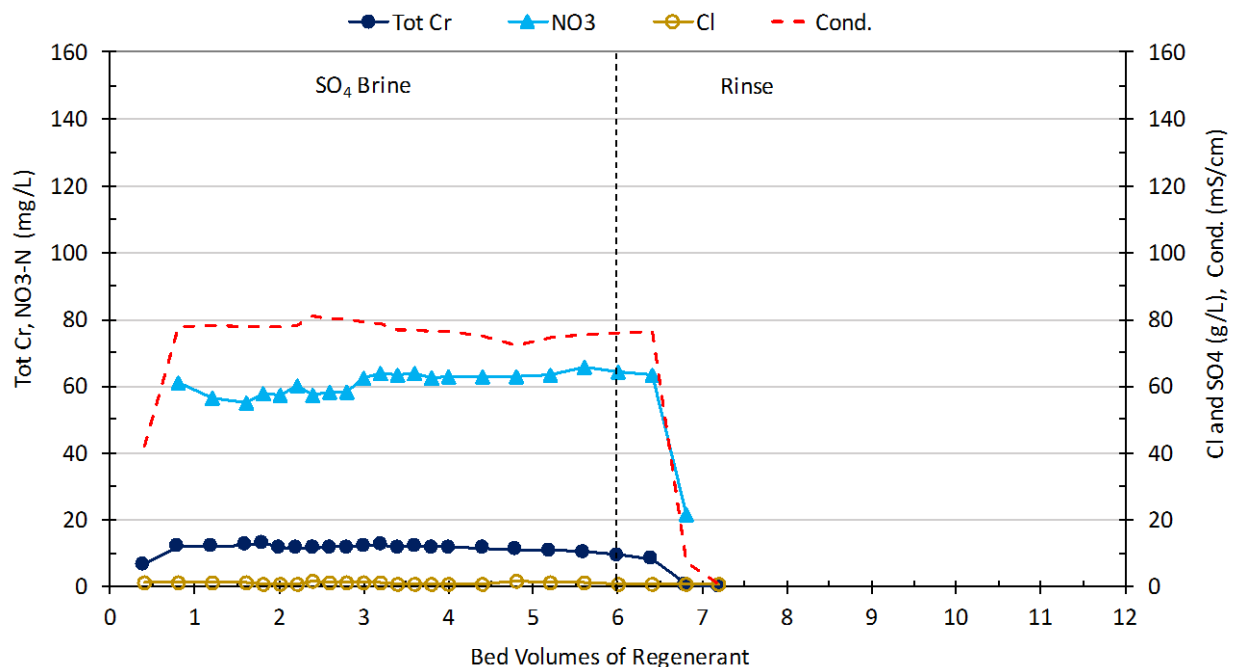


Figure 29 Pilot-scale regeneration with sodium sulfate

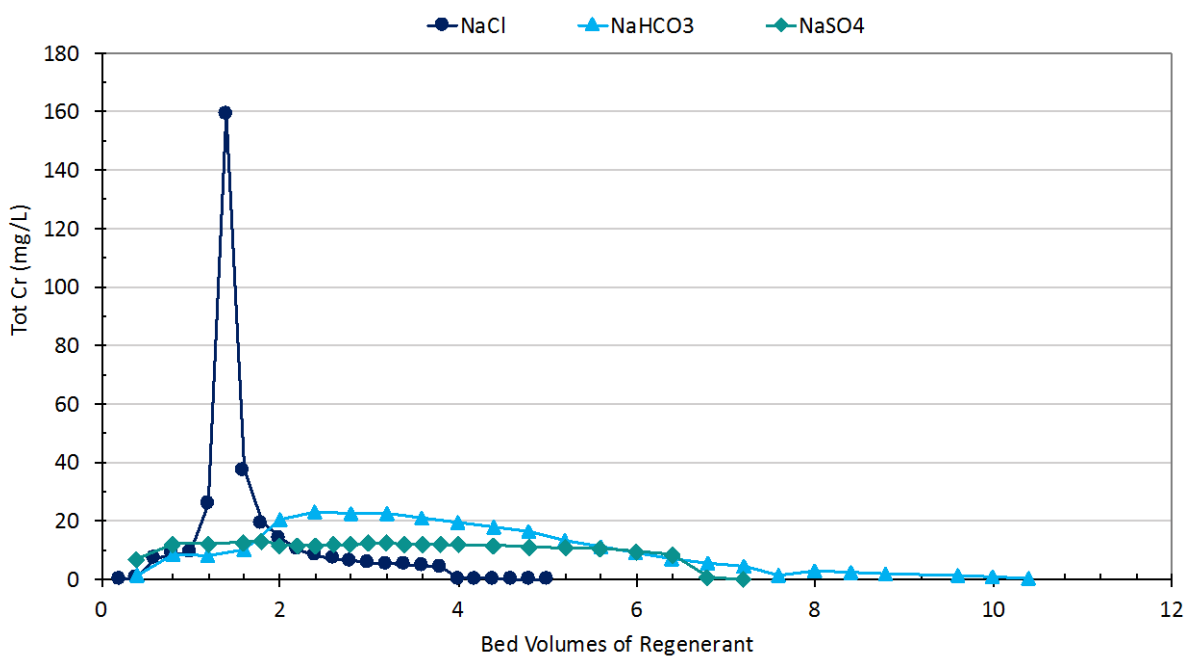


As seen in Figure 28 and Figure 29, the bicarbonate and sulfate based regenerants result in protracted elution curves when compared to both the pilot (Figure 27) and full-scale (Figure 15 through Figure 17) chloride regenerations. This is largely because chloride is a more effective regenerant due to its size, charge density, and increased solubility. In this case, the larger volume of bicarbonate and sulfate brine required

for complete chromium elution would result in increased O&M costs for hazardous brine disposal, as the bulk brine waste chromium concentrations exceeded the RCRA 5 mg/L limit for both regenerants.

To further illustrate this point, Figure 30 shows a comparison of the chromium elution for a chloride, bicarbonate, and sulfate regeneration. As seen in the figure, the chloride regeneration results in a condensed chromium peak being eluted from the resin. In contrast, the elution of chromium with the alternative regenerants is drawn out for much of the duration of the regeneration. Since the alternative regenerants produce a larger volume of waste and the chromium cannot be concentrated into a small fraction of the brine, their applicability is likely limited to places with chloride discharge challenges, where treatment and subsequent sewer disposal can be realized.

Figure 30 Comparison of Cr elution with chloride, bicarbonate, and sulfate regenerants at the pilot-scale



It should also be noted, as depicted in Figure 31, that the bicarbonate and sulfate regenerants result in less nitrate elution during regeneration. A summary of total chromium and nitrate eluted during each regeneration is given in Table 19. Although each regenerant showed effective chromium recovery, the bicarbonate and sulfate regenerants eluted only 70% and 23% of nitrate, respectively, when compared to the chloride regeneration. Nitrate accumulation on the resin could result in decreased chromium capacity or nitrate peaking during reloading.

Figure 31 Comparison of nitrate elution with chloride, bicarbonate, and sulfate regenerants

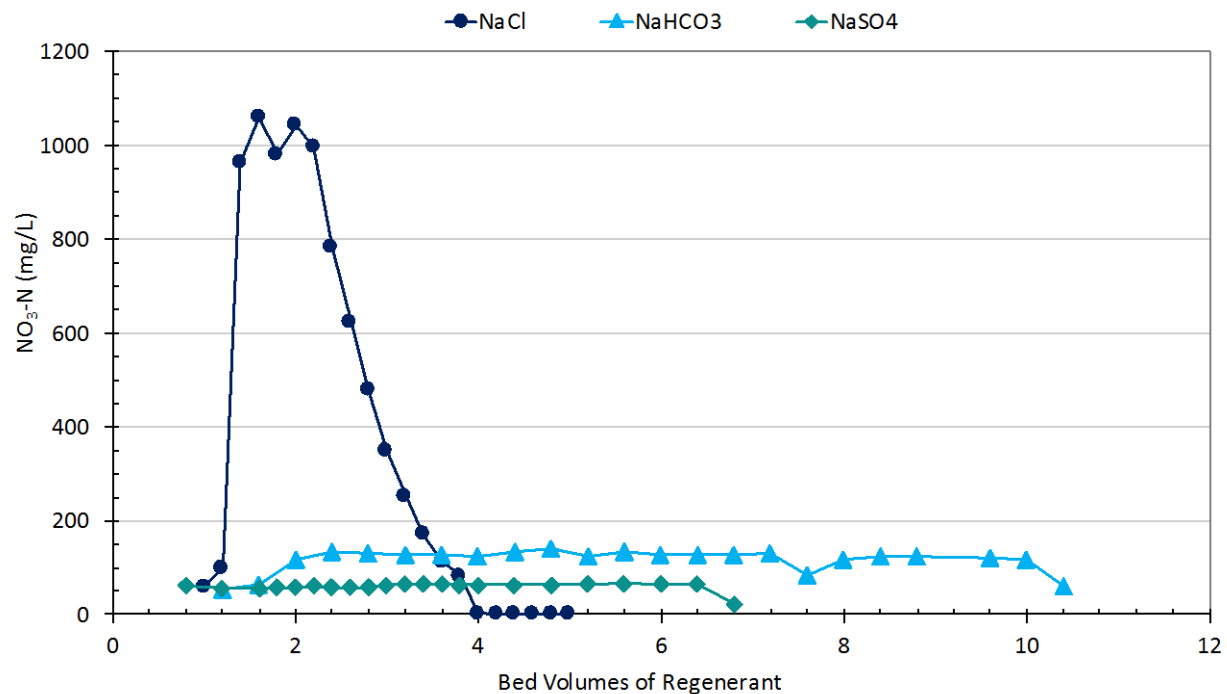


Table 19 Summary of alternative regenerant performance

Parameter	Unit	NaCl	NaHCO ₃	NaSO ₄
Chromium				
Total Cr loaded	mg Cr/L of resin	62.9	80.8	72.7
Total Cr eluted	mg Cr/L of resin	67.6	101.5	69.7
Percent elution	%	108	126	96
Nitrate				
Total nitrate eluted	mg NO ₃ /L of resin	1,603	1,125	377

6.2.5 Direct Brine-Reuse and Mixed-Bed Regeneration

As previously mentioned, the Ionex SG segmented regeneration approach, which is currently being implemented by Cal Water at all Willows well sites, results in a concentrated Cr(VI)-laden fraction of brine waste, minimizing the volume of hazardous waste brine for disposal and allowing for the remaining brine to be reused. For other California utilities opting to implement conventional regeneration direct brine reuse could provide significant cost savings.

Three regeneration approaches, using fresh brine, direct brine reuse, and a mixed-bed preceding regeneration, were investigated using the IXP columns and Purolite A600E 9149 resin. For each approach, an extended conventional regeneration of 4 BV of 2 M NaCl followed by a 2 BV soft water rinse was used. Regeneration with fresh brine was intended to replicate full-scale demonstration, and the spent brine was directly reused in the next column regeneration. After regeneration with spent brine and subsequent

loading, a second round of direct brine reuse was conducted. In both regenerations, additional NaCl was added to the spent brine prior to use, in order to bring conductivity up to the desired 120 mS/cm.

For the mixed-bed regeneration, resin was slurried out of the pilot column, mixed, and then reloaded prior to regeneration with fresh brine. This is intended to simulate off-site regeneration, where spent resin is collected from several columns and regenerated at a centralized location. A summary of each regeneration approach is given in Table 20.

Table 20 Pilot regeneration testing conditions

Parameter	Unit	Fresh Brine	Direct Brine Reuse Round 1	Direct Brine Reuse Round 2	Mixed Bed
Column volume	L	10	10	10	10
Resin		A600E 9149	A600E 9149	A600E 9149	A600E 9149
Total volume treated water	BV	10,377	10,200	10,445	10,105
Effluent Cr before regeneration	µg/L	18.7	13.8	14.4	15.4
Bed volumes of 2 M NaCl brine	BV	4	4	4	4
Bed volumes of rinse	BV	2	2	2	2
Sample frequency	BV	0.2	0.2	0.2	0.2
Final Cr after regeneration	mg/L	0.07	0.05	0.06	0.09

6.2.5.1 Direct Brine Reuse

Elution curves from regeneration using fresh brine and the first and second trials of direct brine reuse are shown in Figure 32, Figure 33, and Figure 34, respectively. The pilot-scale conventional regeneration using fresh brine is consistent with full-scale performance as seen in Figure 15 through Figure 17.

Figure 32 Pilot-scale conventional regeneration with fresh brine

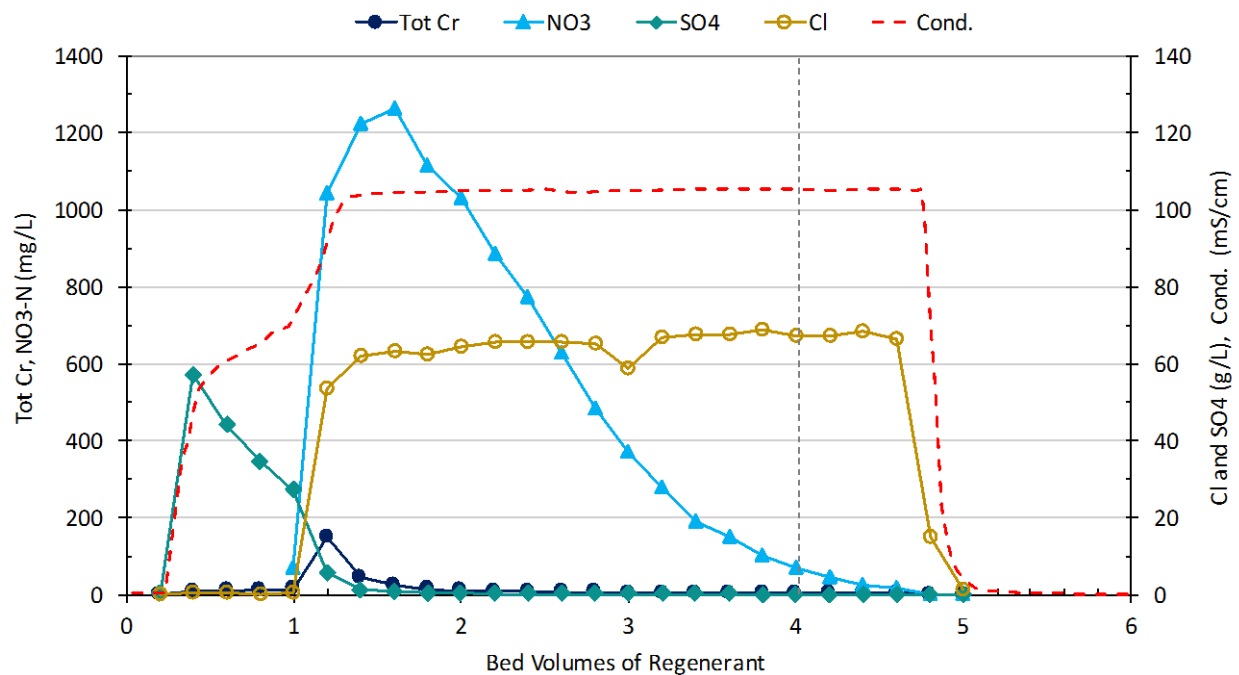


Figure 33 Pilot-scale conventional regeneration with first round of direct brine reuse

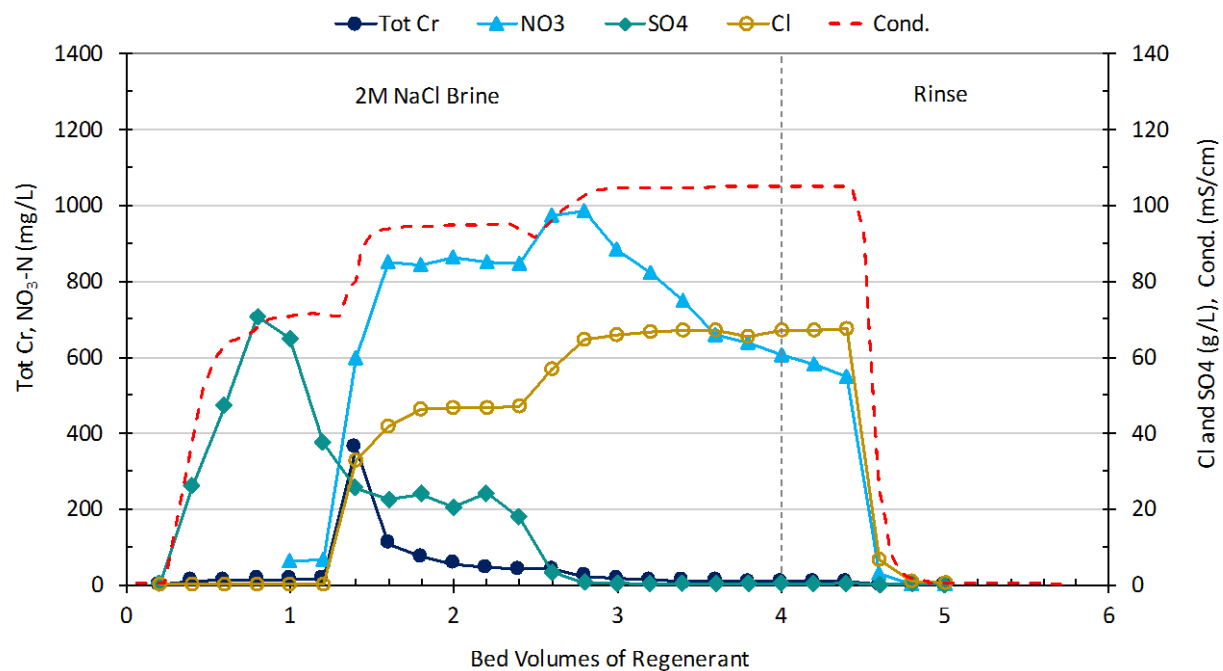
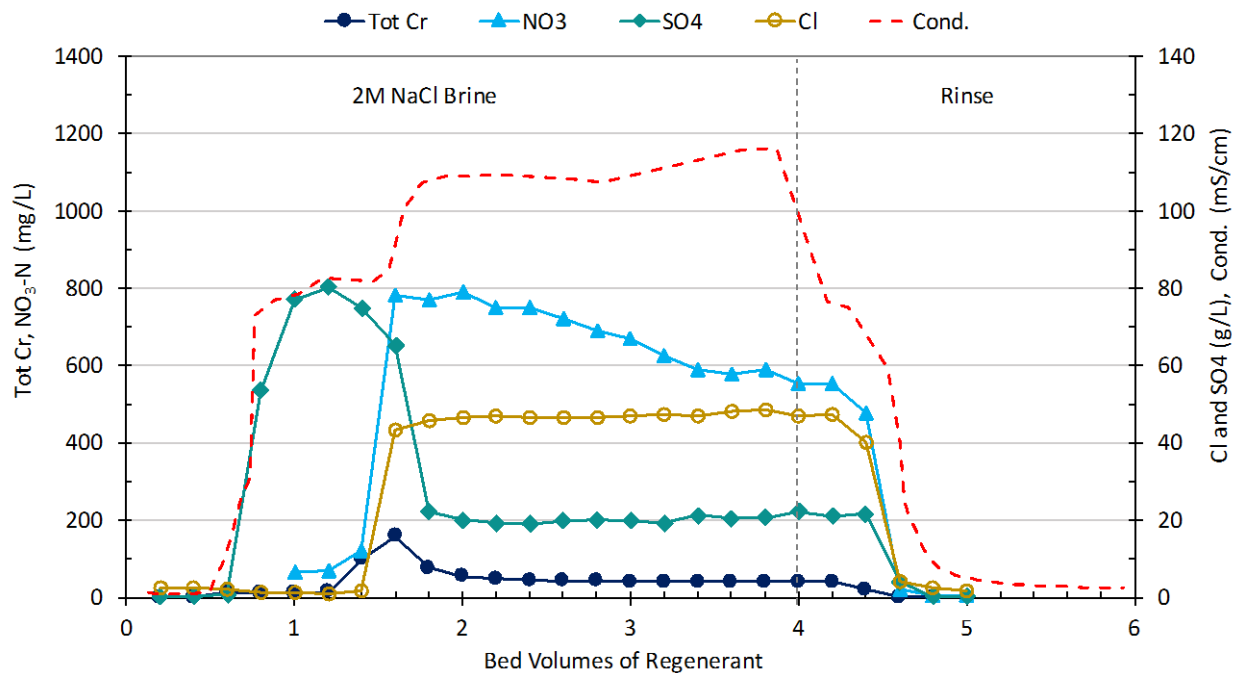


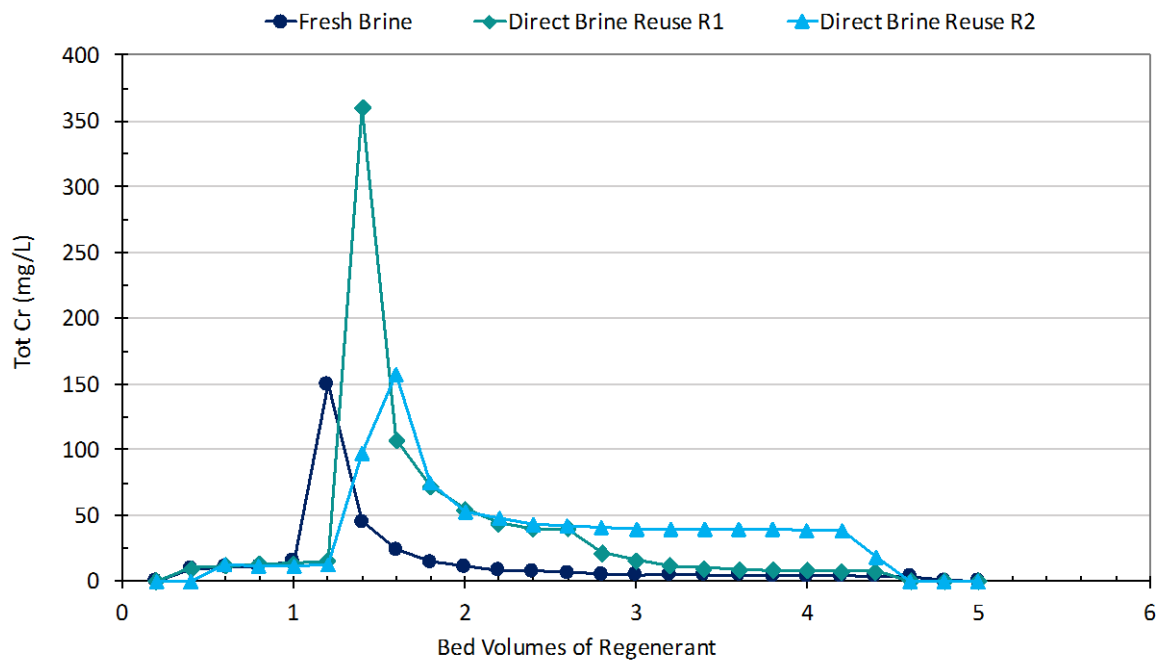
Figure 34 Pilot-scale conventional regeneration with second round of direct brine reuse



The first round of regeneration with direct brine reuse resulted in a peak total chromium elution of 360 mg/L, more than twice that of fresh brine regeneration. In comparison, the second round of direct brine reuse yielded the same peak total chromium elution as fresh brine, but with a broader elution curve. For the first round of direct brine reuse, sulfate and nitrate elution curves are drawn out for one additional bed volume due to high background concentrations of both constituents. In the second round of direct brine reuse, sulfate has an elevated 'floor' of 20 g/L while chloride concentrations never reach 60 g/L (Figure 34), whereas chloride concentrations exceed 60 g/L during the fresh brine regeneration and the first round of direct brine reuse as shown in Figure 32 and Figure 33, respectively, indicating sulfate displacement is still occurring.

Comparison of the total chromium elution, at a higher resolution between 0 to 400 mg/L, using fresh and reused brines is given in Figure 35. As seen in the figure, the initial direct brine reuse resulted in a peak chromium concentration more than double that of regeneration with fresh brine. While the peak chromium concentration during the second round of brine reuse is similar to the fresh brine regeneration, the second round of brine reuse also resulted in an elevated chromium 'floor' of chromium up to 50 mg/L.

Figure 35 Comparison of total chromium elution using fresh brine and during direct brine reuse



6.2.5.2 Mixed-Bed Regeneration

The mixed-bed regeneration with fresh brine profile, presented in Figure 36, is comparable to the full-scale demonstration. Both the sulfate and nitrate elution curves occur at the same point in the regeneration cycle and have similar peak concentrations when compared to the fresh brine regeneration. As seen in Figure 37, total Cr elution for the mixed-bed regeneration begins slightly earlier than the fresh brine and direct brine reuse regenerations, possibly due to changes in resin exchange profile from extensive mixing.

Figure 36 Pilot-scale conventional regeneration with mixed bed

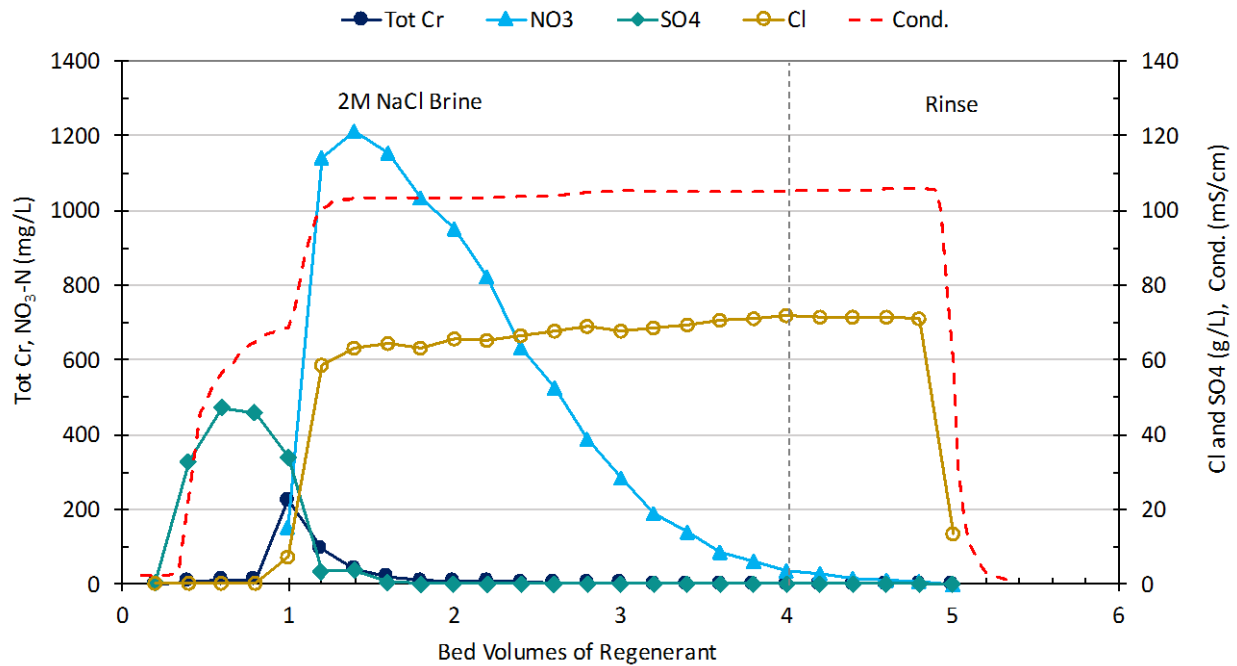
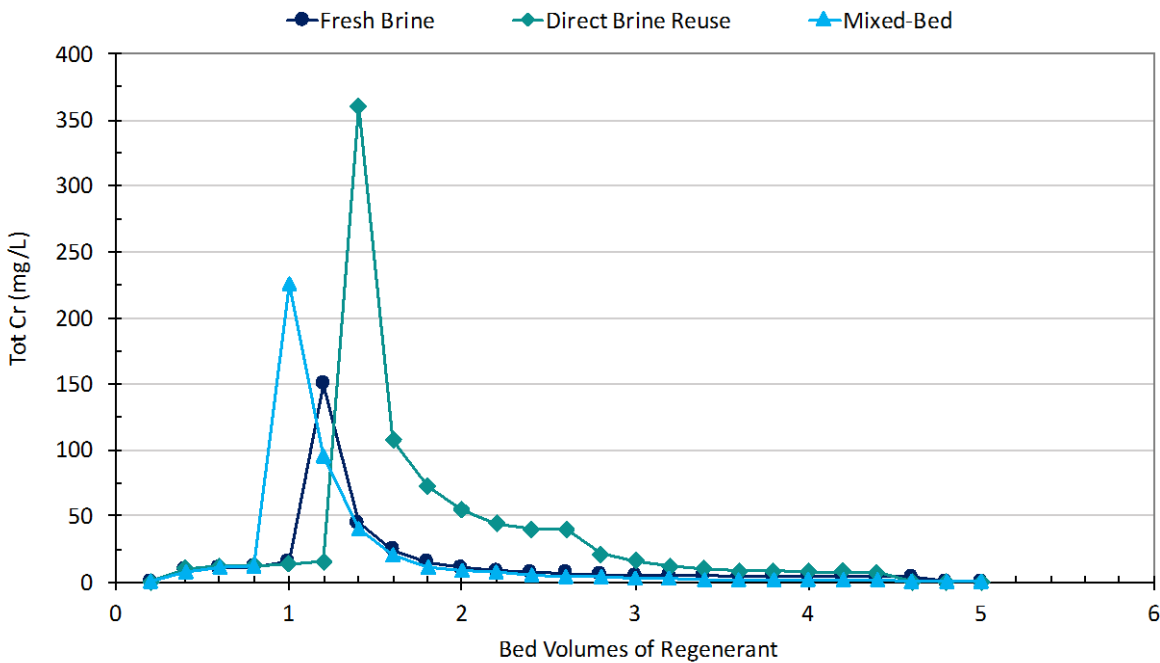


Figure 37 Comparison of total Cr elution from conventional, direct brine reuse, and mixed-bed regeneration



6.2.5.3 Nitrate Peaking

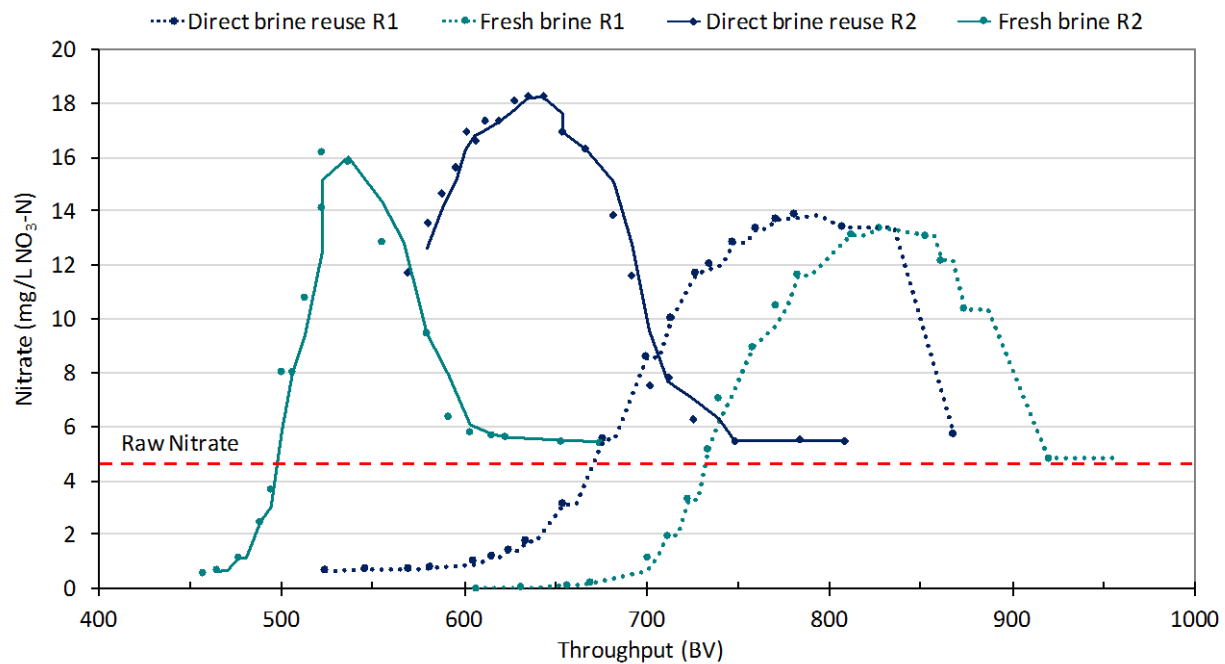
Nitrate chromatographic peaking during SBA-IX loading occurs when nitrate anions are replaced by a more preferred anion resulting in nitrate anions exiting the SBA-IX resin bed at high concentrations. Typically, treated water nitrate peaks from SBA-IX are expected to be approximately two to three times the influent

concentrations (McGuire et al. 2006). Previous pilot-scale studies concluded nitrate peaking often occurs at approximately 1,000 BV. Field sampling was conducted during the first 1,000 BV to determine the impact of brine reuse on nitrate peaking.

Nitrate peaking curves for the fresh brine and direct brine reuse regenerated columns are given in Figure 38. Data points are laboratory results gathered from grab samples, while the solid and dotted lines represent two period moving averages. As shown in the figure, the direct brine reuse regeneration did not result in greater nitrate peaking compared to the fresh brine regeneration and nitrate peaks over four times the raw water concentration were observed.

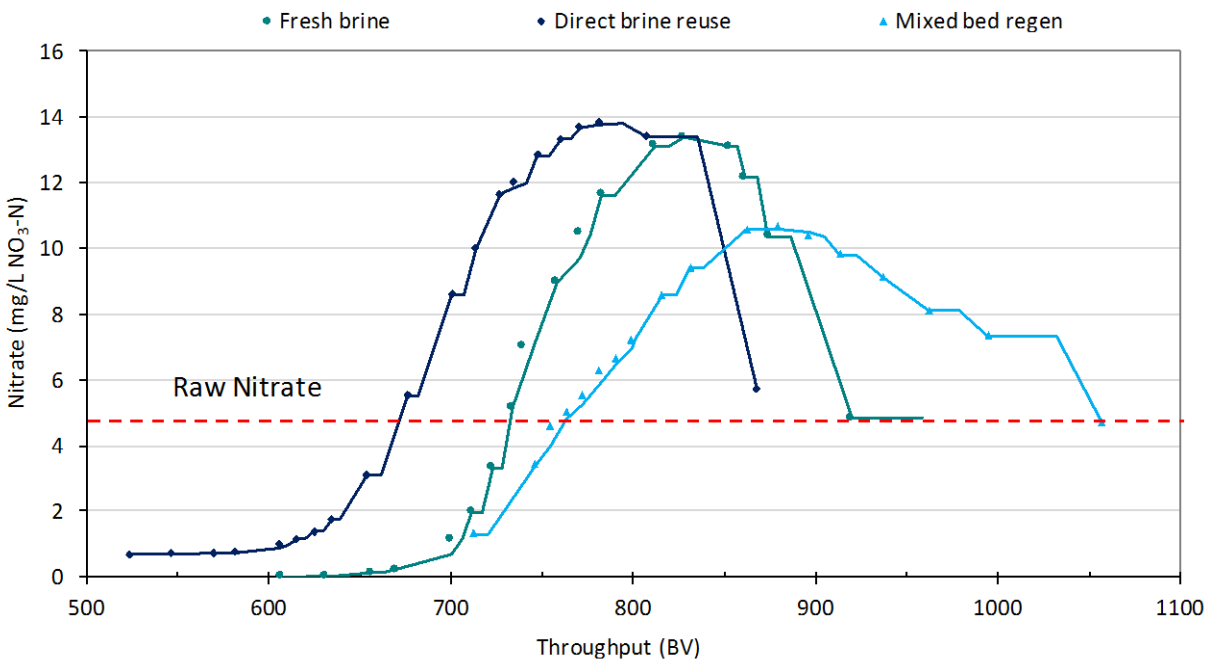
It should also be noted that nitrate peaking during the second round of both fresh brine as well as direct brine reuse occurred approximately 200 to 300 bed BV earlier than that of the first round. This could be attributed to partial elution of nitrate during regeneration, suggesting an incomplete regeneration.

Figure 38 Direct brine reuse nitrate peaking



For the mixed-bed regeneration, Figure 39 depicts nitrate peaking of the conventional, direct brine reuse, and mixed-bed regenerated IXP columns, analyzed at the laboratory. The mixed-bed regenerated column resulted in a prolonged nitrate elution curve while the fresh brine and direct brine reuse regenerated IXP columns eluted nitrate concentrations exceeding the California MCL of 10 mg/L as NO₃-N. Depending on the raw water nitrate concentration, a mixed bed regen could also result in prolonged nitrate MCL violation.

Figure 39 Nitrate peaking of regenerated pilot columns measured in lab via FIA analysis



In order to prevent a nitrate MCL violation, Cal Water and Ionex SG have implemented three strategies to minimize nitrate concentrations:

1. SBA-IX vessel regenerations are staggered which prevents peaking from occurring simultaneously between columns.
2. When an individual column is at the BV range associated with nitrate peaking, flow is reduced, resulting in a greater dilution of the peaking vessel.
3. An online nitrate analyzer was installed at well sites with high raw water nitrate concentrations to monitor treated water nitrate concentrations and subsequently shut down the well if nitrate concentrations approach the MCL. The analyzer is programmed to set off a low-level alarm at a nitrate concentration of 8.5 mg/L as N and subsequently shutdown the well if the effluent concentration reaches 9 mg/L as N.

6.3 Brine Treatment

Waste brine from SBA-IX regeneration is classified as a California Hazardous and Resource Conservation and Recovery Act (RCRA) hazardous waste with respect to Cr(VI) concentrations. Depending on the SBA-IX regeneration approach, bulk Cr(VI) concentrations can approach or exceed 1 g/L, and disposal of the waste brine governs operational costs. If the brine can be rendered non-hazardous through on-site treatment, disposal costs could be significantly decreased. It should be noted, that full-scale brine treatment would trigger additional permit requirements through the California Department of Toxic Substance Control (DTSC).

As mentioned above in Section 4.0 Literature Review, technologies evaluated for brine treatment include chemical reduction and precipitation of Cr(VI) and other potentially hazardous constituents (WRF Project 4488), adsorption (WRF Project 4488), and physical separation. For each potential brine treatment approach, technology developers were asked to conduct bench scale brine treatment to evaluate the

feasibility of each approach. Below is an overview of brine treatment technologies and conventional regeneration brine treatment results provided by the technology developers.

6.3.1 Brine Treatment Background

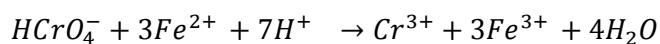
6.3.1.1 Chemical Treatment of Regenerant Brine

The process of removing hexavalent chromium [Cr(VI)] by reduction to trivalent chromium [Cr(III)] and subsequent coagulation and precipitation has a long history of use in industrial treatment of Cr(VI)-laden wastes. The regenerant brine can be treated through this process to remove the Cr(VI) rendering it non-hazardous. Siegel and Clifford (1988) conducted bench-scale experiments with different reductants to evaluate their performance in reducing Cr(VI) to Cr(III) and to determine the optimal conditions for precipitation of Cr(OH)_{3(s)}. The results showed that acidic sulfite, ferrous sulfate and hydrazine are all capable of reducing Cr(VI) to Cr(III); however, ferrous sulfate was the only reductant that did not require pH adjustment for the reduction reaction to proceed and did not require additional chemical feed to achieve precipitation. In addition to ferrous and sulfite, listed as a permit-by-rule (PBR) chemicals for Cr(VI) reduction, polysulfide and stannous were also tested in this work as possible chemical brine treatment options. Chemical brine treatment for chromium removal, using each of these chemicals, is discussed below.

6.3.1.1.1 Ferrous

Reduction with ferrous sulfate has been investigated as a primary treatment and removal method in low level (µg/L) Cr(VI) applications (Qin et al. 2005, McGuire et al. 2007) and as a brine treatment alternative (Siegel and Clifford 1988). Cr(VI) reduction coupled with ferrous [Fe(II)] oxidation requires a 3:1 molar ratio of Fe:Cr to reduce Cr(VI) as characterized in Equation 1. Subsequently, the chromium, along with ferric hydroxide precipitate out of solution. As such, the experimental protocol developed for this study bracketed ferrous doses around the theoretical molar dose ratio of 3:1.

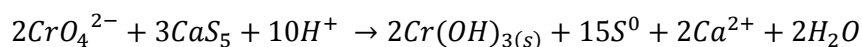
Equation 1. Ferrous reduction of Cr(VI)



6.3.1.1.2 Polysulfide

In the industrial and remediation settings, polysulfide has been used to remove Cr(VI) from chromite ore waste and contaminated groundwater (Graham et al. 2006, Wazne et al. 2007a, 2007b). Removal of chromium from SBA-IX waste brine has been tested at bench-scale with optimal performance at pH 8 to 10.3 (Pakzadeh and Batista 2011), and is currently employed at full-scale SBA-IX treatment systems in the Coachella Valley Water District and the Cal Water Las Lomas 303 well site. Cr(VI) reduction coupled with polysulfide oxidation requires a 3:2 molar ratio of CaS₅:Cr to reduce and subsequently precipitate chromium, characterized in Equation 2. Therefore, the experimental protocol developed for this study bracketed polysulfide doses around the theoretical molar dose ratio of 3:2.

Equation 2. Polysulfide reduction of Cr(VI)

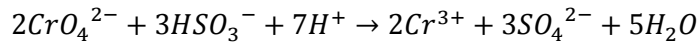


6.3.1.1.3 Bisulfite

Bisulfite was tested at pilot-scale for Cr(VI) removal in a drinking water application in Glendale, CA (McGuire et al. 2006). Although the reduction was complete, the removal of the total chromium was incomplete ranging from 39 to 50% in the best treatment scenario. Cr(VI) removal from chromium plating

facilities uses bisulfite for reduction of Cr(VI) to Cr(III) at a pH of 2 to 3, followed by pH adjustment to a pH between 7 and 9.5 to facilitate precipitation (Cushnie 2009). The pH was not adjusted in this experiment because one anion exchange vendor had proposed using bisulfite without pH adjustment for brine treatment. Cr(VI) reduction with bisulfite oxidation requires a 3:2 molar ratio of $\text{SO}_3\text{:Cr}$ to reduce and subsequently precipitate chromium, characterized in Equation 3.

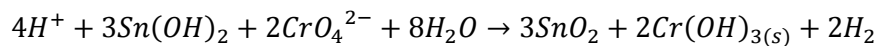
Equation 3. Bisulfite reduction of Cr(VI)



6.3.1.1.4 Stannous

Stannous chloride, SnCl_2 , is a reducing agent conventionally utilized as a NSF 60 approved corrosion inhibitor in drinking water systems. Acting as a free electron donor, stannous chloride reduces hexavalent chromium Cr(VI) to Cr(III). Reduction of Cr(VI) by stannous chloride is given in Equation 4. Previous research conducted on Cr(VI) reduction in drinking water, in Glendale, CA, demonstrated rapid stannous chloride reduction of Cr(VI) (Brandhuber et al. 2004, Lai and McNeill 2006). Based on this previous research, stannous showed promise as a reductant for brine treatment that would not require pH adjustment. Cr(VI) reduction coupled with stannous oxidation requires a 3:2 molar ratio of Sn:Cr to reduce and subsequently precipitate chromium and is characterized in Equation 4.

Equation 4. Stannous reduction of Cr(VI)



6.3.1.2 Physical separation¹

Nanofiltration (NF) is a pressure driven membrane separation process that uses semipermeable membranes with an effective pore size of between 1 and 10 nm to reject large ions while allowing permeation of small monovalent anions (Crittenden et al. 2012). In contrast, reverse osmosis (RO) membranes reject nearly all solutes and ultrafiltration (UF) membranes reject suspended solids but allow permeation of all salts (Metcalf & Eddy and AECOM 2014). NF membranes typically have a negative surface charge that enhances rejection of anionic compounds such as sulfate or Cr(VI) as chromate (CrO_4^{2-}) (Hafiane et al. 2000, Oatley et al. 2012, Mohammad et al. 2015, Pérez-González et al. 2015b). Due to their unique characteristics, NF membranes have the potential to selectively reject Cr(VI) and allow passage of sodium chloride (NaCl) from SBA-IX waste brine and allow for onsite reuse of the brine for SBA-IX resin regeneration.

NF membranes have been used to selectively remove Cr(VI) from low ionic strength waters and have achieved high Cr(VI) rejection using both ceramic and polymeric NF membranes (Brandhuber et al. 2005, Pugazhenthai et al. 2005, Yoon et al. 2009). In low ionic strength waters, increased Cr(VI) rejection has been observed above a pH of 7 due to an equilibrium shift in Cr(VI) speciation from bichromate (HCrO_4^-) to chromate (Muthukrishnan and Guha 2008). Increasing ionic strength tends to decrease rejection by depressing the membrane surface charge (Hafiane et al. 2000, Yoon et al. 2009). Decreased Cr(VI) rejection can also be caused by concentration polarization (CP) which is enhanced by increasing transmembrane pressure and / or decreasing membrane crossflow velocity (Tabakci et al. 2008). The relationship between Cr(VI) rejection, NF membrane operational parameters, and bulk water chemistry is

¹ Provided by the US Bureau of Reclamation, Water Treatment Group. Denver, CO

well documented for low ionic strength waters and is in accordance with CP and electrical double layer theories (Hafiane et al. 2000, Brandhuber et al. 2005, Lv et al. 2008, Muthukrishnan and Guha 2008, Yoon et al. 2009, Anupam et al. 2015).

Specialty membranes have been developed to treat industrial wastewaters containing Cr(VI) with an effective pore size matched to the hydrated radii of sulfate and chromate, thereby enhancing chromate and sulfate rejection (Wang and Chung 2006). Other NF membranes have been produced with low surface roughness, and therefore a lower fouling propensity, and used for Cr(VI) treatment of industrial waters (Wang 2007). Polymer enhanced membrane filtration processes using p-Sulfonated Calix[4]arene as a Cr(VI) specific complexing agent can form stable complexes even in the presence of competing ions at one or two orders of magnitude greater molarity than Cr(VI). Once formed, the complexed Cr(VI) is well removed by loose NF membranes and other solutes are allowed to permeate through the membrane (Tabakci et al. 2008). Hexadecylpyridine chloride and hexadecylpyridine bromide have also been used to complex Cr(VI) but not for NF pretreatment (Bohdziewicz 2000, Woo and J 2015). Despite development of specialized membranes and membrane processes for Cr(VI) removal, other alternative technologies, such as SBA-IX, are typically implemented for municipal Cr(VI) treatment due to cost and operational considerations (Seidel et al. 2013). NF technology could be used to reduce the volume of SBA-IX waste brine requiring disposal and to produce a treated brine stream onsite for reuse during subsequent SBA-IX regenerations.

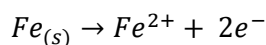
NF membranes have been used to remove anionic organic carbon from high ionic strength SBA-IX waste brines produced during sugar refining while allowing monovalent salts to pass through into the treated permeate (Meadows and Wadley 1992). NF treatment of SBA-IX waste brines from sugar processing has achieved up to a 77% reduction in salt consumption and a 90% reduction in water consumption, when the treated permeate was reused in the refinery process (Meadows and Wadley 1992, Cartier et al. 1997, Salehi et al. 2011). In some cases UF membranes were used to achieve 50% removal of color, and 90% removal of chemical oxygen demand (COD) from SBA-IX waste brines (Cox 1980, Wilson and Percival 1990). It is important to note that studies focused on the sugar refining industry evaluated rejection of organic dyes, which were larger than the chromate anion. Cr(VI) rejection from SBA-IX waste brine using NF could be substantially different from organic carbon rejection using NF due to the smaller size and higher charge of chromate ions and differences in solution composition and pH.

NF treatment of Cr(VI) containing SBA-IX waste brines has the potential to reduce the cost of SBA-IX treatment by reducing the volume of waste brine that must be disposed of and by recovering sodium chloride for reuse during future regenerations. Anecdotal evidence from similar studies that evaluated NF treatment of RO concentrates for selective sulfate rejection suggest that NF treatment of Cr(VI) containing SBA-IX waste brine is possible. Perez-Gonzalez et al. (2015) used NF membranes to selectively reject between 75% and 96% of sulfate from RO concentrates, while recovering sodium and chloride for later use during acid / alkali production (Pérez-González et al. 2015a, 2015b). The concentrates evaluated by Perez-Gonzalez et al. had ionic strengths between 1.0 M and 1.5 M compared to SBA-IX waste brines which typically range between 1.5 M and 2.0 M (Gorman et al. 2016a, Li et al. 2016). The results from Perez-Gonzalez et al. (2015) indicate that NF treatment of Cr(VI) containing SBA-IX waste brines should allow for waste volume minimization and onsite brine reuse due to the physical similarities between sulfate and chromate (e.g., charge, mass, and hydrated radius), and similarities in ionic strength between RO concentrates and SBA-IX waste brines.

6.3.1.3 Electrocoagulation

Electrocoagulation, dating back to 1906, is the use of an applied electrical current for removal of inorganic contaminants from drinking water or wastewater (Dieterich 1906). Chromium removal, using electrocoagulation, has been demonstrated in treatment of metal plating waste (Akbal and Camcı 2011), wastewater (Gao et al. 2005) and synthetic solutions (Bazrafshan et al. 2008). Equation 5 shows the production of ferrous iron in the electrocoagulation process (Parga et al. 2005). After ferrous iron is produced, Cr(VI) is reduced to Cr(III), as in Equation 1 (Parga et al. 2005). Insoluble trivalent Cr(III) hydroxide complexes can be subsequently removed from solution via sedimentation and filtration.

Equation 5. Ferrous iron production in the electrocoagulation process



6.3.1.4 Photo-catalyst²

In recent years, the application of a titanium dioxide (TiO₂) photocatalyst for Cr(VI) removal has drawn some attention (Liu et al., 2014; Stancl et al., 2015; Testa et al., 2004). In particular, P25, a commercialized TiO₂ material, has been applied due to its mixed anatase and rutile phases, which facilitate the hole-electron separation and suppress charge carrier recombination upon UV irradiation (Munoz and Domenech, 1990; Ku and Jung, 2001; Lin et al., 1993; Testa et al., 2001). However, the interfacial electron transfer process is several orders of magnitude slower than the electron-hole recombination in commercialized TiO₂ materials (Hoffmann et al., 1995). Consequently, electrons become less available for reductive water treatment. To make TiO₂ more effective in releasing electrons, prior studies added organic chemicals (e.g., oxalic acid, methanol and formic acid) or inorganic ions (e.g., S²⁻, I⁻ and IO₃⁻) as external hole scavengers to TiO₂ suspension and sacrificially consumed the holes generated from the valence band of TiO₂ (Doudrick et al., 2013; Rengaraj et al., 2007; Tan et al., 2003; Galińska and Walendziewski, 2005). As a result of the scavenging effect, electron-hole recombination is suppressed and more electrons are freely released from TiO₂ to reductively remove contaminants, including nitrate, chromate, selenate, bromate and perchlorate (Doudrick et al., 2013; Yang et al., 2013; Rengaraj et al., 2007; Tan et al., 2003; Marks et al., 2016). However, because of inefficient hole trapping by external hole scavengers, an excess amount of sacrificial organic or inorganic compounds is required to achieve a high hole-scavenging efficiency (Shkrob et al., 2004). This leads to chemical residuals in treated water and make it undesirable for drinking water applications.

To increase the hole trapping efficiency and eliminate the external addition of sacrificial hole scavengers, the design of a catalyst with an internal hole-scavenging capacity is highly advantageous for reductive Cr(VI) treatment. Internal hole scavengers that are covalently bonded or chemisorbed on TiO₂ surface can highly enhance the hole transfer across the interface to the trapping molecules and produce long-lived electrons. Prior studies demonstrated that scavengers with poly-hydroxyl moieties covalently bonded on TiO₂ surface served as efficient internal hole traps upon photo-excitation of the catalyst, and the hole-scavenging efficiency was associated with hydroxyl groups chelated on TiO₂ surface (Du et al., 2007; Shkrob et al., 2004). This novel design of TiO₂ catalyst with internal hole-scavenging capacity can highly inhibit electron-hole recombination process and preferentially release a large quantity of electrons for

² Provided by Dr. Haizhou Liu, Ph.D., University of California, Riverside

surface reduction. However, this designing concept for the TiO₂ catalyst has not been reported for photocatalytic Cr(VI) removal.

The objectives of this study were to synthesize a new TiO₂ photo-catalyst that possesses a high internal hole-scavenging capacity and to apply it for reductive Cr(VI) removal in diverse water chemical conditions. Diethylene glycol (DEG) was chosen as the internal hole scavenger, because it has hydroxyl groups that can chelate uncoordinated Ti atoms and be chemically bonded on TiO₂ surface. Covalently-bonded DEG molecules serve as hole-trapping molecules and favor fast scavenging of photo-generated holes upon photoexcitation of TiO₂. In addition, the mechanism and kinetics of Cr(VI) removal were investigated, with emphasis on the effects of catalyst dosage, pH and the presence of background ions.

6.3.1.5 Modified Activated Carbon

Carbon that has been altered to remove inorganic contaminants is referred to as Modified Activated Carbon (MAC). There are many methods for carbon modification, including chemical, physical and biological (Bhatnagar et al. 2013). For this project ToxSorb, LTD. (ToxSorb) brand MAC was tested. The ToxSorb patent indicates that the carbon can be chemically modified by either a cationic or anionic chelant to cause adsorption of heavy metals (Rytwo and Gonen 2009). MAC has previously been demonstrated for chromium removal in water with very high chromium concentrations (Monser and Adhoum 2002, Mohan and Pittman Jr. 2006, Liu et al. 2007, Rytwo and Gonen 2009).

6.3.2 Results

As mentioned above, full-scale conventional waste brine from Willows Station 9 was collected and sent to all included research projects for bench-scale brine treatment. Water quality of the brine collected is given in Table 21. Results detailed below are collated from all research partners, with duplicate samples sent to UC Davis for result validation. The criteria for successful brine treatment is removal of heavy metals (e.g. chromium and selenium) below the RCRA hazardous waste levels, detailed in Table 21.

Table 21 Bulk full-scale conventional brine characterization

	Concentration (mg/L)						
	Total Cr	Arsenic	Selenium	Vanadium	Uranium	Sulfate	Chloride
Waste Brine	34.1	0.2	0.9	5.6	3.3	18,000	49,300
RCRA Hazardous Waste	5.0	5.0	1.0	24	0.05% by wt.	-	-

6.3.2.1 Chemical Precipitation

In January, 2016, preliminary chemical precipitation jar testing was conducted using conventional regeneration brine and four chemical reductants: stannous chloride (stannous), ferrous chloride (ferrous), sodium bisulfite (bisulfite), and calcium polysulfide (polysulfide). Chromium reduction equations for each chemical reductant are detailed above in Equations 1 through 4.

For each jar test, 1 L of conventional brine containing 36 mg/L of total Cr (30 mg/L Cr(VI)) was dosed with a chemical reductant. Immediately following chemical dosing, the jar was mixed at 200 rpm for 2 minutes, followed by 10 minutes at 100 rpm, and one hour of sedimentation. A summary of the jar testing doses is provided in Table 22.

Table 22 Chemical precipitation jar-testing doses

Chemical Reductant	Estimated ¹ Stoichiometric Dose Ratio [reductant]:[Cr(VI)]	Actual Stoichiometric Dose Ratio [reductant]:[Cr(VI)]	Dose (mg/L)
Stannous	0.25	0.26	42.3
	0.5	0.52	84.6
	1	1.03	169.3
	2	2.06	338.5
Ferrous	0.5	0.55	121.6
	1	1.11	243.3
	2	2.22	486.6
	4	4.44	973.2
Bisulfite	0.5	0.55	49.9
	1	1.11	99.9
	2	2.22	199.8
	4	4.44	399.5
Polysulfide	0.5	0.55	96.2
	1	1.11	192.3
	2	2.22	384.7
	4	4.44	769.3

¹Estimated stoichiometric dose calculated using total Cr concentration as a surrogate for Cr(VI)

Initial results, given in Figure 40 after the hour sedimentation period, show full reduction of Cr(VI) between a 2 to 2.5 stoichiometric dose ratio of reductant to Cr(VI) for stannous, ferrous, and polysulfide. Detailed in Figure 41, both stannous and ferrous achieved approximately 95% total chromium removal at a stoichiometric dose ratio of 2:1 and 0.45 µm filtration. It should also be noted that at this stoichiometric dose ratio and pore size, filtered total chromium concentrations were below the RCRA hazardous waste level of 5.0 mg/L.

At a higher stoichiometric dose ratio of 4.5:1, the bisulfite only achieved a 50% reduction and no total chromium removal post filtration. Due to its efficacy at reducing and removing chromium, as well as its lower costs compared to stannous chloride, ferrous is demonstrated to be the most viable reductant for chemical precipitation treatment of waste brine. Further research on dose and filtration optimization is needed to refine the potential of ferrous application for brine treatment.

Figure 40 Cr(VI) results for bench-scale jar testing of chemical reductants

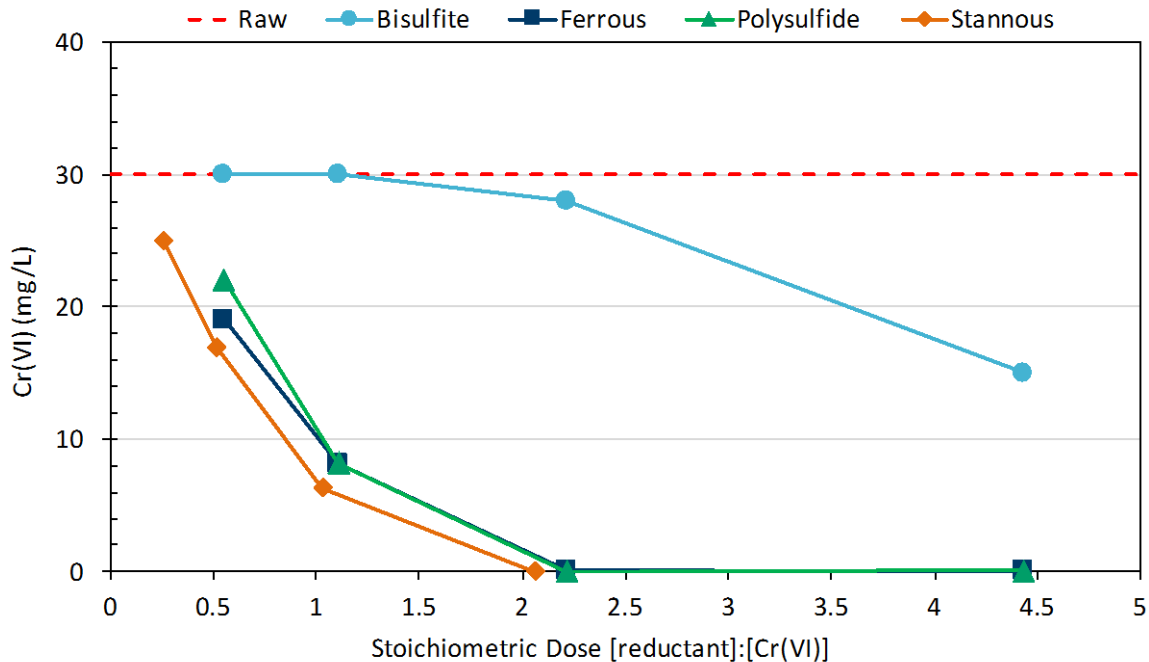
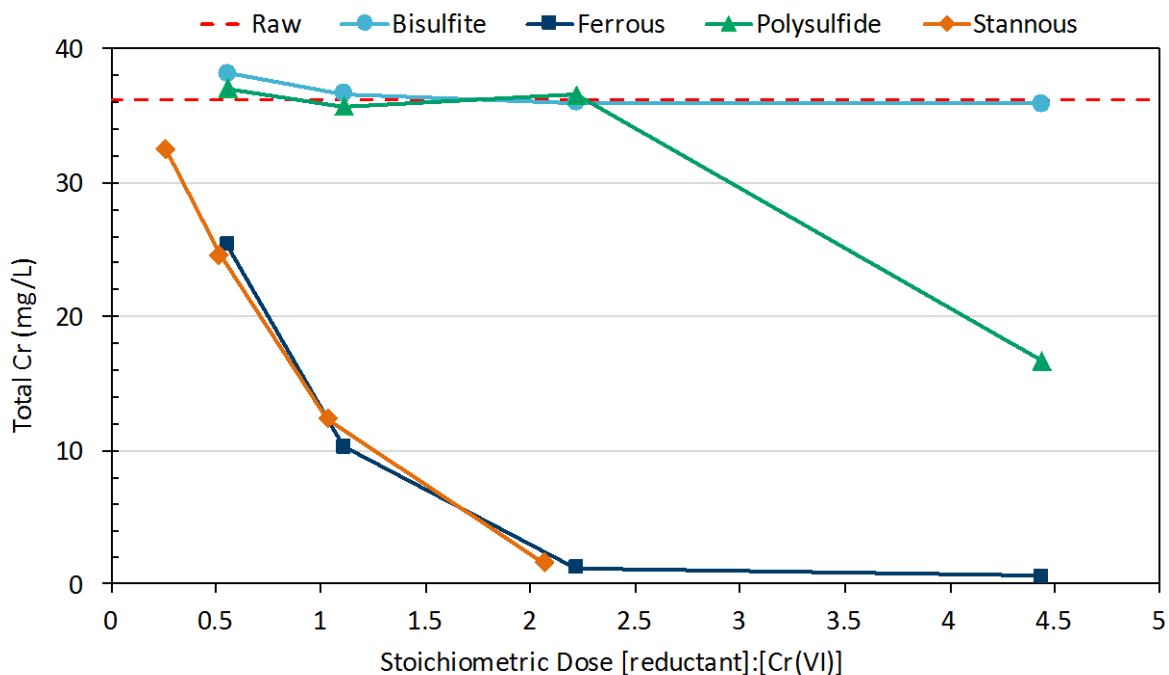


Figure 41 Filtered (0.45 µm) total Cr results for bench-scale jar testing of chemical reductants



6.3.2.2 Nanofiltration (NF)

The bench-scale NF treatability study, conducted by the USBOR, investigated treatment of 14 L of brine over a 24-hour period. Per method provided by the USBOR, brine was circulated through three lab-scale

SEPA membrane cells containing NF membranes at a constant driving pressure of 250 psi. Bench tests were terminated once the observed flux rate was reduced to 3% of the original flux.

Permeate results for nanofiltration bench tests conducted by the USBoR are shown in Table 23. Up to approximately 70% recovery, NF treatment resulted in Cr(VI) below the 5 mg/L RCRA hazardous limit. In addition to Cr removal, 99% selenium removal was also observed. Above a 70% recovery, rejection rate of chromium anion began to decrease.

Table 23 Permeate concentration as a function of batch recovery

Analyte	Raw	Recovery (%)					
		0	28	50	70	82	88
Sodium (mg/L)	41,073	33,095	33,603	35,007	36,247	38,414	41,634
Chloride (mg/L)	51,403	50,274	51,400	52,892	54,156	55,056	54,069
Total Cr (mg/L)	30.5	2.03	2.18	3.11	6.51	18.69	41.85
Arsenic (mg/L)	0.1	0.00	0.00	0.00	0.01	0.02	0.04
Selenium (mg/L)	0.6	0.05	0.05	0.06	0.1	0.23	0.26
Uranium (mg/L)	3.1	0.06	0.02	0.03	0.06	0.17	0.46
Vanadium (mg/L)	5.0	0.77	0.86	1.17	2.15	4.74	7.96
Alkalinity (mg/L CaCO ₃)	2,200	1,280	1,420	1,640	2,070	2,550	2,790

Additional bench testing of NF at the 70% recovery is given in Table 24. As shown in the table, 70% recovery resulted in approximately 90% rejection of chromium, selenium, and arsenic, with approximately 99% rejection of uranium. The concentrate yielded total chromium of 75.4 mg/L and would have to undergo hazardous waste disposal. Further testing of NF treatment based on percent recovery or osmotic pressure setpoints is required to optimize concentrate volume for disposal and ensure chromium remains below the 5 mg/L hazardous waste level.

Table 24 Characterization of permeate with 70% recovery

Analyte	Raw	Permeate	Concentrate	% Rejection
Sodium (mg/L)	41,073	34,319	51,449	16.4
Chloride (mg/L)	51,403	52,037	46,244	1.22
Total Cr (mg/L)	30.5	3.07	75.4	89.9
Arsenic (mg/L)	0.1	<0.01	0.27	90.0
Selenium (mg/L)	0.6	0.06	1.4	90.0
Uranium (mg/L)	3.1	0.04	8.0	98.7
Vanadium (mg/L)	5.0	1.13	11.5	77.4
Alkalinity (mg/L CaCO ₃)	2,200	1,555	3,200	29.3

6.3.2.3 Electro-coagulation

Two rounds of bench-scale electro-coagulation treatability tests were conducted by Baker Corps. ICP-MS results for both tests are given in Table 25. In both scenarios, treated chromium concentrations ranged between 0.1 to 0.15 mg/L, due to the formation of insoluble metal hydroxides. Little to no selenium removal occurred with concentrations close to the 1.0 mg/L RCRA hazardous waste level. In addition, iron from the anodes and cathodes was present in the treated water and could lead to fouling of SBA-IX resin and decreased performance during brine reuse.

Table 25 Electrocoagulation brine treatment results

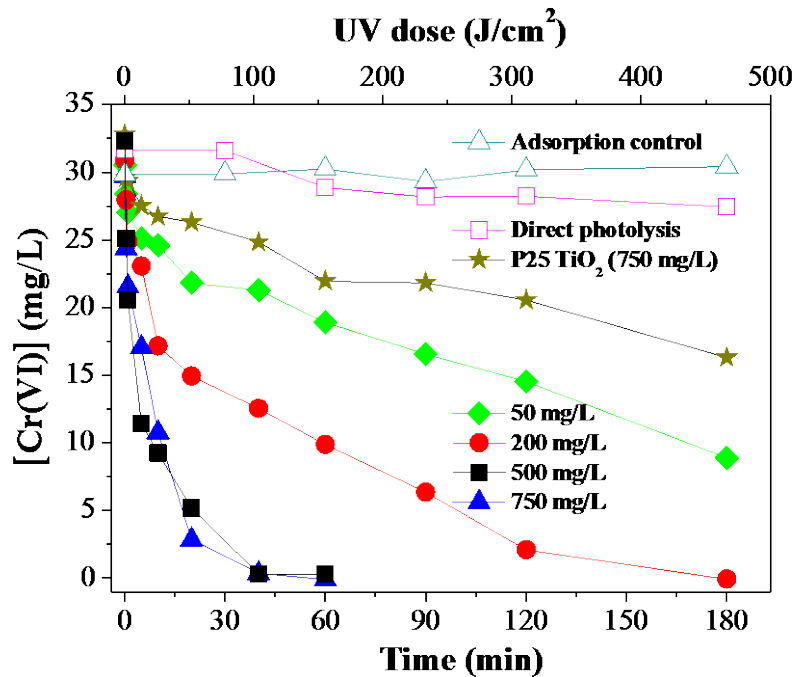
Analyte	Unit	Waste Brine	Test 1	Test 2
Total Cr	mg/L	34.1	0.14	0.11
Arsenic	mg/L	0.2	0.08	0.12
Selenium	mg/L	0.9	0.83	0.98
Vanadium	mg/L	5.6	0.15	0.06
Uranium	mg/L	3.3	2.81	0.66
Sulfate	mg/L	18000	-	-
Chloride	mg/L	49300	-	-
Iron	mg/L	-	0.2	0.3

6.3.2.4 Photo-catalyst

Bench tests of chromium reduction using varying doses of TiO₂ photocatalyst and UV strength were conducted by the Liu research group at UC Riverside. The relationship of Cr(VI) reduction to UV strength, photocatalyst dose, and contact time is depicted in Figure 42, provided by Dr. Haizhou Liu. As shown in the figure, full Cr(VI) reduction was achieved within one hour for TiO₂ doses above 500 mg/L. At a lower TiO₂ dose of 50 mg/L, 50% reduction was noted after 180 minutes. It should also be noted that only Cr(VI)

reduction, not total chromium removal, is shown. Subsequent filtration of the Cr(III) hydroxide complexes is required for chromium removal.

Figure 42 Cr(VI) reduction by TiO₂ (Liu, 2016)



Overall, the 750 mg/L of TiO₂ nanocrystals resulted in the best Cr(VI) reduction within 30 to 60 minutes. Analysis of the treated brine via ICP-MS for the 750 mg/L of TiO₂ dose and 42 mW/cm² irradiation with a medium pressure UV lamp for 90 minutes is given in Table 26. After 90 minutes, the catalyst was separated by a 25 nm membrane to quench the reaction. Shown in Table 26, the filtered TiO₂ photocatalyst bench tests achieved 99.5% total chromium removal. Despite this, only partial (approximately 50%) selenium and uranium removal occurred.

Table 26 Brine treatment with 750 mg/L TiO₂ nanocrystals

Analyte	Unit	Waste Brine	TiO ₂ treatment	% Removal
Total Cr	mg/L	34.1	0.15	99.6
Arsenic	mg/L	0.2	0.01	95.0
Selenium	mg/L	0.9	0.45	50.0
Vanadium	mg/L	5.6	0.03	99.5
Uranium	mg/L	3.3	1.49	54.8
Chloride	mg/L	49,300	40,659	17.5

6.3.2.5 Modified activated carbon (MAC)

Eight cycles of MAC brine treatment were conducted in series by ToxSorb using 50 mL batch samples of brine and 2 g of MAC. Brine pH was reduced to 2 using HCl prior to beginning bench tests. The MAC was

run in 2 modes, reduction and adsorption, depending on the goal of treatment to either reduce or remove the Cr(VI) respectively. Spent MAC can be regenerated using a HCL acidic solution.

Table 27 depicts effluent results for all reduction and adsorption batch tests. Shown in the table, Cr(VI) results for each test were ND, with effluent total chromium concentrations between 0.3 to 2.7 mg/L for the adsorption tests. In comparison, the reduction mode fully reduced, but did not remove, the Cr(VI). pH adjustment to 9.5 using NaOH was required to achieve Cr(III) precipitation.

Table 27 MAC results for reduction and adsorption modes

Analyte	Unit	Effluent cycle							
		Waste Brine	Reduction Mode					Adsorption Mode	
			2	3	4	5	6	1	7
Total Cr	mg/L	34.1	27.39	13.30	16.78	7.28	10.25	0.32	2.65
Cr(VI)	mg/L	34.1	ND	ND	ND	ND	ND	ND	ND
Arsenic	mg/L	0.2	0.09	0.04	0.04	0.04	0.04	0.03	0.02
Selenium	mg/L	0.9	0.72	0.55	0.68	0.53	0.70	0.62	0.55
Vanadium	mg/L	5.6	3.01	0.52	0.71	0.54	0.61	0.02	0.09
Uranium	mg/L	3.3	0.82	0.26	0.55	0.53	0.64	0.01	0.06
Sulfate	mg/L	18000	-	-	-	-	-	-	-
Chloride	mg/L	49,300	54,394	53,935	54,575	54,773	54,335	54,011	54,353

6.3.3 Brine Treatment Summary

To summarize, all brine treatment approaches investigated could remove chromium to below the 5 mg/L RCRA hazardous waste level, as shown in Table 28. Despite this, only the nanofiltration achieved full selenium removal; chemical precipitation, MAC, and TiO₂ photocatalyst processes resulting in only 50% removal.

Table 28 Performance summary of brine treatment methods

Analyte	Unit	Treatment Method					
		Waste Brine	Ferrous (2:1)	Electro-coagulation	MAC	NF	Photo-Catalyst
Total Cr	mg/L	34.1	1.2	0.137	0.321	3.07	0.15
Arsenic	mg/L	0.2	0.0	0.084	0.034	<0.01	0.01
Selenium	mg/L	0.9	0.4	0.83	0.622	0.06	0.45
Vanadium	mg/L	5.6	0.7	0.149	0.025	1.13	0.03
Uranium	mg/L	3.3	3.2	2.813	0.007	0.04	1.49
Chloride	mg/L	49,300	50,338	-	54,011	52,037	40,659

Due to NF's ability to remove both chromium and selenium, as well as its low estimated costs for full-scale implementation, discussed later in Section 7.0, NF brine treatment was selected for additional pilot-scale testing of brine treatment and reuse.

6.3.4 NF Treated Brine Reuse

NF brine treatment followed by reuse was investigated at pilot-scale by Corona and the USBoR. Three IXP pilot columns were loaded at Willows Station 9 and spent conventional brine was collected for NF treatment. Following NF treatment and subsequent IXP regeneration, the combined spent NF treated brine and rinse fraction were once again collected for treatment and reuse. In total, three consecutive rounds of NF treatment and brine reuse were tested. Summary of NF pilot testing conditions are given in Table 29. Because NF treatment was conducted using the combined spent brine and rinse fractions, a total of 6 BVs, no fresh brine was required to make-up for loss of brine as concentrate. Additional NaCl was added to NF treated brine to meet an approximate conductivity of 120 mS/cm prior to regeneration.

Table 29 NF brine treatment and reuse pilot testing conditions

Parameter	Round 1	Round 2	Round 3
Regen brine fraction (BV)	4	4	4
Regen rinse fraction (BV)	2	2	2
Source of brine for NF treatment	Station 9 Waste Brine	Round 1 Waste Brine	Round 2 Waste Brine
Volume waste brine treated (L)	60	60	60
Permeate volume (L)	40	40	40
Recovery (%)	67%	67%	67%

Based on bench test results indicating an optimal 70% recovery of brine prior to a 5 mg/L chromium passing the membrane, 60 L of mixed brine and rinse waste underwent NF treatment to yield 40 L (4 BV) of permeate for subsequent IXP regeneration. All three rounds of NF treatment, shown in Table 30, resulted in chromium below 5 mg/L and complete removal of sulfate, arsenic, selenium, and uranium. No nitrate was removed during NF treatment. Elution curves for the first, second, and third round of consecutive IXP regenerations using NF treated brine are given in Figure 43, Figure 44, and Figure 45 respectively.

Table 30 NF brine treatment results

Contaminant	Round 1		Round 2		Round 3	
	Raw	Permeate	Raw	Permeate	Raw	Permeate
Total Cr (mg/L)	26.91	4.07	15.18	3.82	21.20	2.13
Nitrate as N (mg/L)	290	252	318	332	478	412
Sulfate (g/L)	32	1	11	2	16	0
Arsenic (mg/L)	0.11	0.00	0.08	0.02	0.12	0.00
Selenium (mg/L)	0.53	0.04	0.36	0.10	0.56	0.06
Uranium (mg/L)	2.14	0.02	1.83	0.20	3.14	0.01
Vanadium (mg/L)	3.29	1.09	3.33	1.29	5.12	1.47

Figure 43 First round of NF brine treatment and reuse

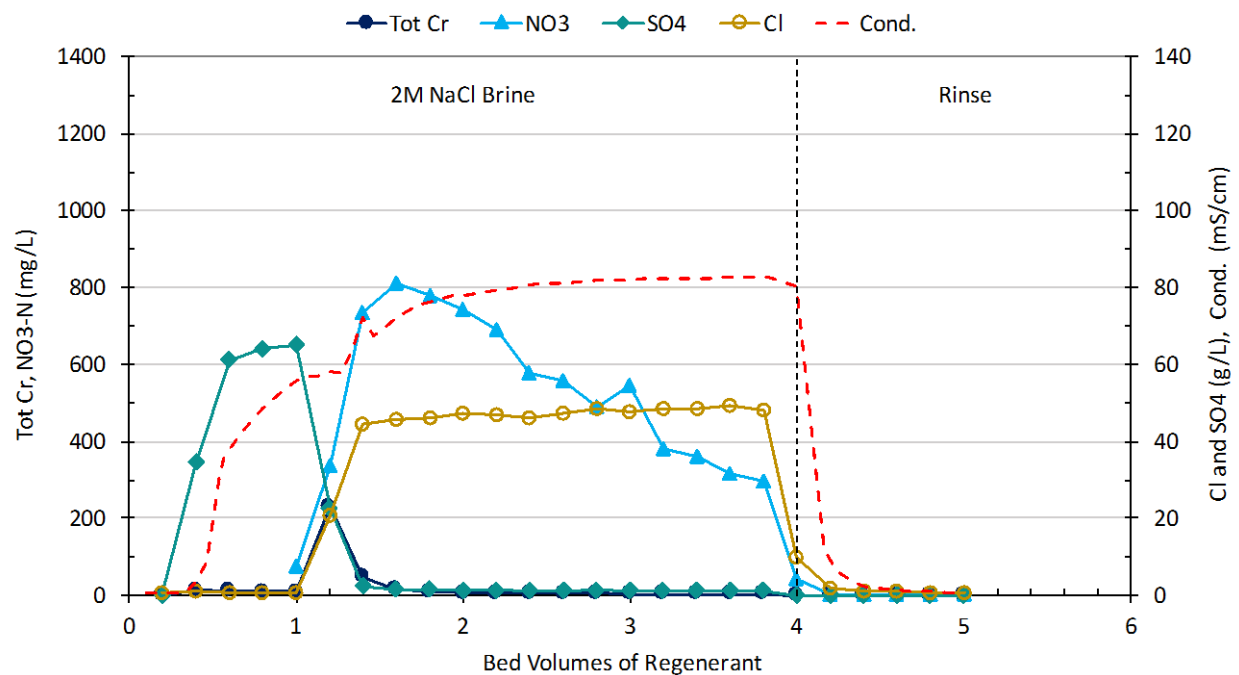


Figure 44 Second round of NF brine treatment and reuse

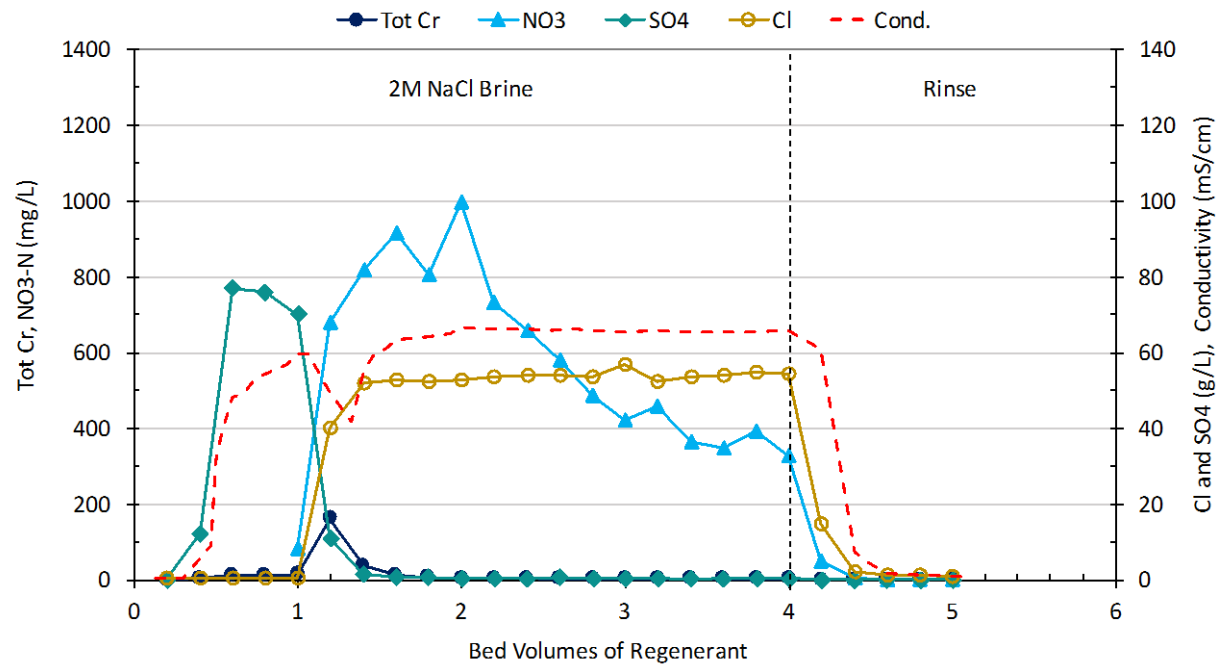
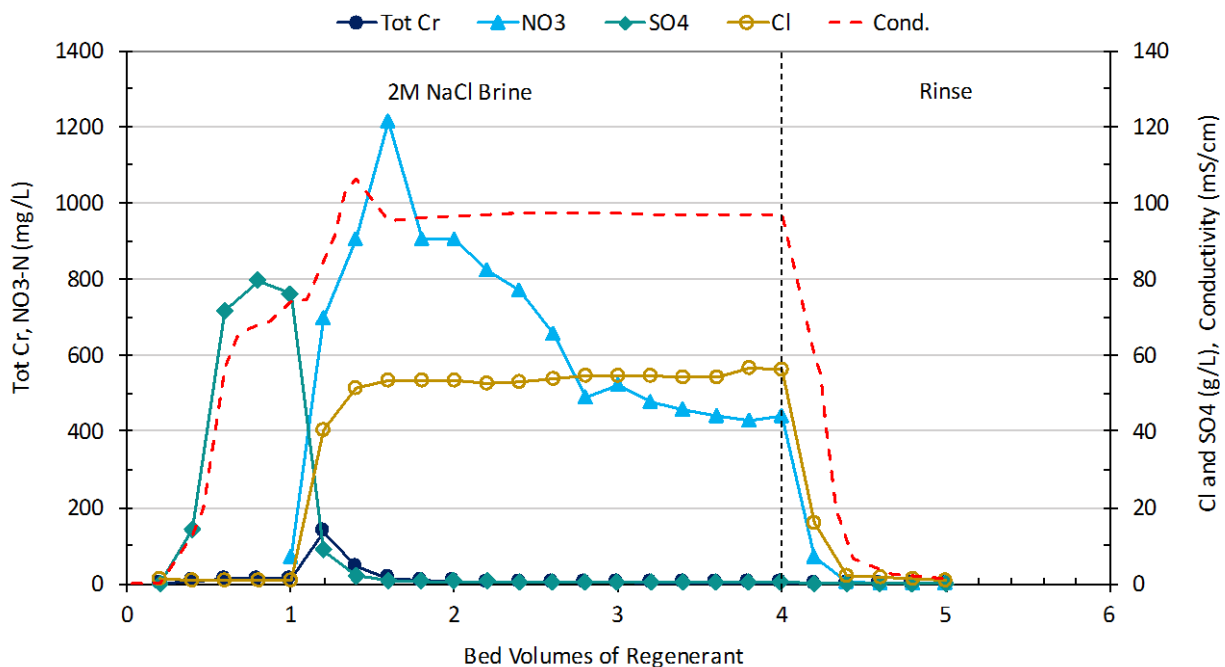


Figure 45 Third round of NF brine treatment and reuse

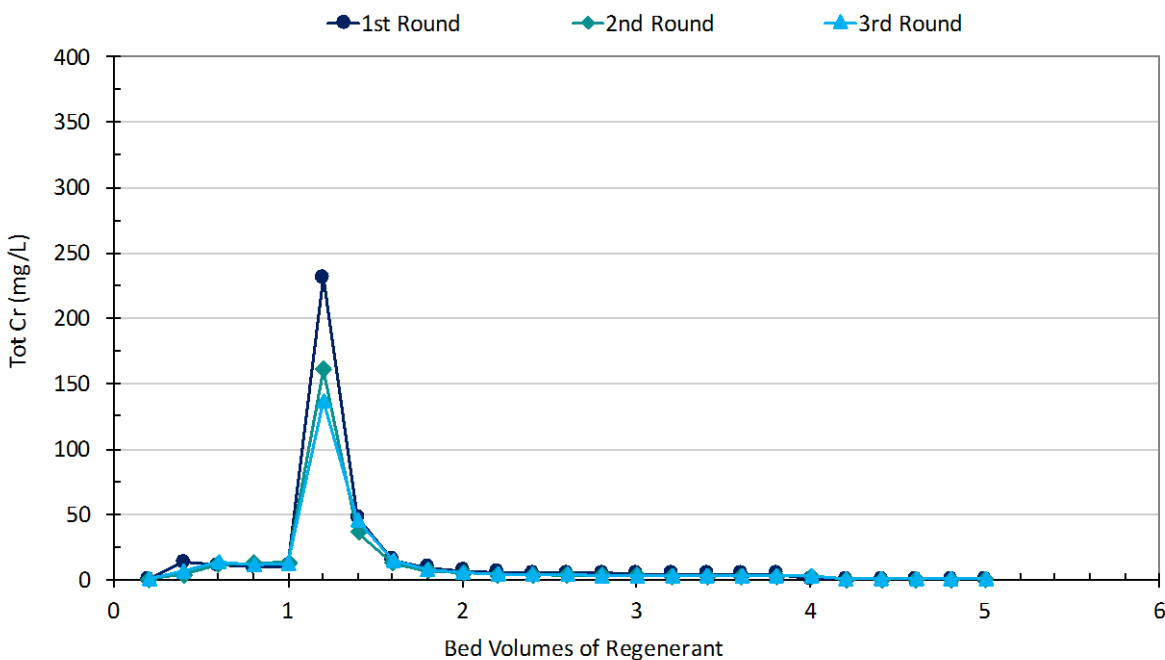


As shown in the figures above, conventional regeneration with NF treated brine resulted in a peak chromium elution between 150 to 220 mg/L, with the highest concentration occurring for the first round of NF treatment. In addition, the chromium floor for all three rounds did not rise after peaking, unlike

results for serial direct brine reuse. Low conductivity results for the second round of brine reuse is attributed to an air pocket formation in the analyzer at 1.4 BV.

Direct comparison of chromium elution curves for all three rounds of regeneration is given in Figure 46. Due to consistent elution curves and no nitrate, sulfate, and micro-contaminants accumulation on the resin over multiple rounds of regeneration, NF treatment and brine reuse was successfully demonstrated for three rounds. Additional regeneration testing is needed to determine the viability of subsequent rounds of brine treatment and reuse.

Figure 46 Total chromium elution for direct brine reuse

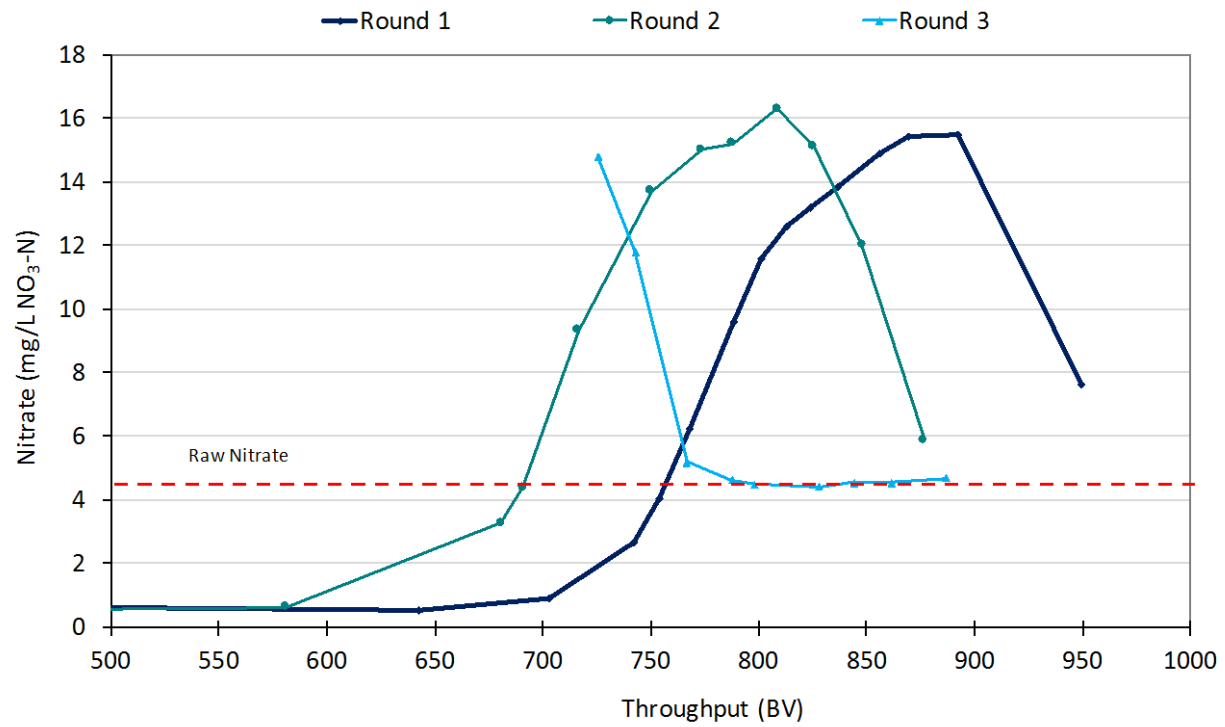


In addition to regeneration profiling, all IXPs were monitored for the first 1,000 BVs after regeneration to profile potential nitrate chromatographic peaking. Refer to Section 4.0 Literature Review or Section 6.1 SBA-IX Loading for further background of chromatographic peaking. As detailed above in Section 6.0, treated water profiling of pilot columns that underwent direct brine reuse resulted in increased nitrate concentrations during chromatographic peaking.

Nitrate peaking curves for the three rounds of NF treatment and brine reuse are shown in Figure 47. Peak nitrate concentrations for Rounds 1 and 2 were between 15 to 16 mg/L, approximately 3.5 to 4 times higher than raw influent concentrations.

In addition, similar to direct brine reuse discussed in Section 6.2, each subsequent round of NF treatment and brine reuse resulted in earlier chromatographic peaking, with Round 3 peaking occurring before 700 BV. This could be . For full-scale implementation of NF treatment and brine reuse, due to varying occurrence of chromatographic peaking, an online nitrate analyzer would allow for better monitoring and control of nitrate concentrations in the blended treated water immediately after regeneration.

Figure 47 NF-treated brine reuse nitrate peaking



7.0 Costs

From the time Cal Water began evaluating Cr(VI) treatment methods in 2013 to full-scale implementation in 2015 of seven SBA-IX systems at well sites in the Dixon and Willows Districts, advances in SBA-IX technology from bench- and pilot-scale research as well as a competitive bid process resulted in significant capital and O&M cost savings. This chapter details SBA-IX original predictive costs, actual full-scale implementation costs, and potential cost savings to the Willows District resulting from this Proposition 50 funded research.

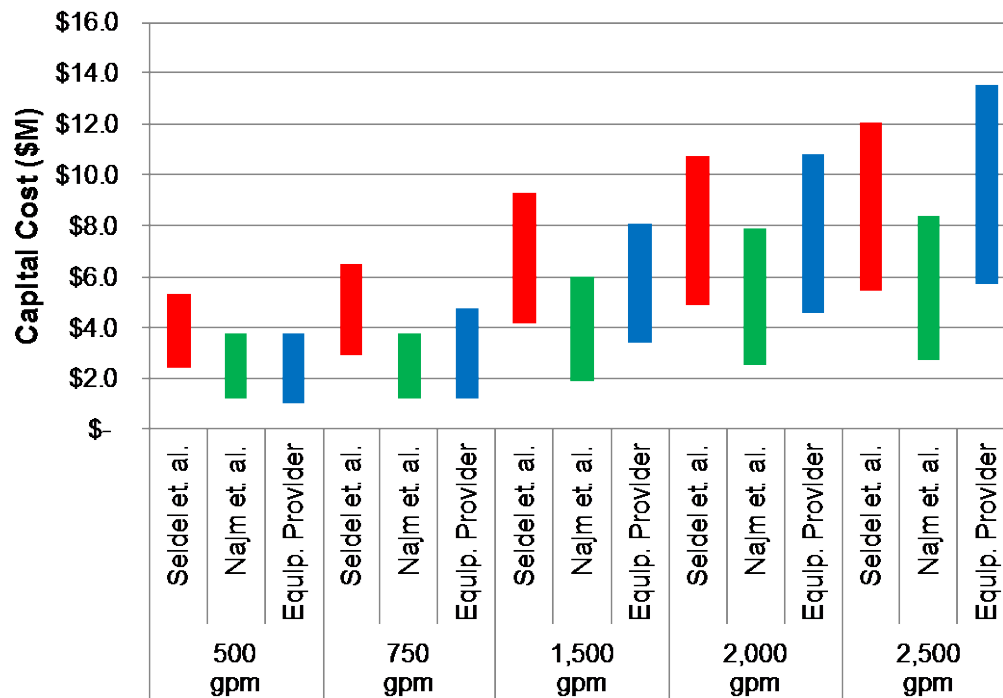
In addition, brine optimization and reuse research conducted as part of this project resulted in approaches that could further decrease O&M costs as described below. For this analysis, O&M costs for conventional brine disposal are used as a baseline to assess the potential savings.

7.1 Full-scale Predictive Costs

As part of a 2013 joint Water Industry Technical Action Fund (WITAF) and Water Research Foundation Project #4432, national and California treatment costs, including SBA-IX, to comply with a Cr(VI) MCL were investigated (Seidel et. al, 2013). Later Water Research Foundation Project #4450, further investigated the impact on water quality on Cr(VI) removal efficiency and cost, resulting in the creation of the online Cr(VI) Removal from Groundwater Cost Calculator (Najm et. Al, 2014).

A range of 2013 predictive Cr(VI) treatment capital costs for SBA-IX by well capacity, based on the WRF Report #4432, WRF Report #4450, and vendor input, is shown in Figure 48. Estimates for a well site with design capacity of 2,000 gpm are between \$2.0 M to \$11.0 M. In 2013, for SBA-IX treatment of four wells in the Willows District, Cal Water initially presented an estimated \$17.0 M capital and \$360 K O&M annually to City Council. Cost estimates were refined following the 2014 pilot testing. The process improvements learned from those efforts reduced the estimated capital and annual O&M costs to \$10 M and \$100 K, respectively.

Figure 48 Predictive SBA-IX capital costs (Jacobs, 2013)



7.2 Full-scale Implementation Costs

Construction and implementation of SBA-IX treatment systems at all four Willows well sites began in 2015 with Willows Station 9 completed in September 2015. The installed capital costs for each well divided by category through December 2016 are shown in Table 31.

Table 31 SBA-IX implementation costs for all Willows well sites (December, 2016)

Category	Total Costs by Category (\$k)			
	Well 4	Well 7	Well 8	Well 9
Installation/ Construction	\$515	\$322	\$639	\$409
Electrical and I&C	\$6	\$10	\$86	NA ¹
General Site Civil	\$7	\$7	\$7	\$7
Overhead and Profit	\$264	\$211	\$288	\$267
Contingency	\$0	\$66	\$0	\$0
Planning / Engineering	\$54	\$102	\$142	\$92
Construction Admin	\$11	\$8	\$8	\$8
Capital Interest	\$8	\$40	\$21	\$16
Equipment	\$563	\$398	\$863	\$548
Labor	\$107	\$103	\$201	\$124
Total	\$1,535	\$1,267	\$2,254	\$1,472

¹Information not available

7.3 Pilot Research Cost Optimization

In addition to the capital costs savings demonstrated in full-scale implementation, conceptual O&M cost savings could be realized through brine treatment and optimization. As mentioned above, hazardous brine disposal dominates the SBA-IX operational costs. The following sections discuss the development of the capital and operational costs associated with treatment and disposal of the brine.

The level of accuracy for the cost estimates corresponds to a Class 4 Estimate as defined by the Association for the Advancement of Cost Engineering (AACE) International. This level of engineering cost estimating is generally made with limited information, including process block diagrams, preliminary equipment lists, and indicated layout, and it is appropriate for feasibility study evaluations. Cost estimates prepared at this level of engineering are considered to have an accuracy range of +50/-30 percent.

It should also be noted that the costs detailed below are the capital and O&M costs associated with brine treatment and disposal, and do not represent the entire SBA-IX treatment process. Capital costs shown are add-on brine treatment equipment to the existing Willows Station 9 SBA-IX system. O&M costs are inclusive of electricity, chemical consumption, media replacement, and residuals disposal associated with brine treatment.

7.3.1 Basis of Conceptual Cost Estimates

Three different scenarios were considered for the brine waste. The three options are detailed below in Table 32. Option 1 refers to disposal of hazardous brine from conventional or Ionex SG segmented regeneration with no brine treatment. Options 2 and 3, brine treatment with and without reuse, are considered for the brine treatment methods detailed above in Section 6.3 Brine Treatment. For the purposes of this report, Options 1, 2, and 3 are referred to as ‘None,’ ‘Disposal,’ and ‘Reuse’ in the summary cost figures below.

Table 32 Description of brine treatment alternatives

Option	Title	Summary	Description
Option 1	“None”	No treatment	All brine waste is disposed as hazardous liquid waste. Includes both conventional and Ionex SG Segmented regeneration
Option 2	“Disposal”	Treatment with disposal	All brine waste is treated. Precipitated solid residuals are disposed as hazardous solid waste, while liquid residuals are disposed of as hazardous liquid waste. Treated liquid is disposed as non-hazardous liquid waste.
Option 3	“Reuse”	Treatment with reuse	All brine is reused for three cycles of brine treatment and subsequent regeneration. Precipitated solids are disposed as hazardous solid waste. Treated liquid after the 3 rd round of regeneration is disposed as non-hazardous liquid waste

All calculations were based on the following assumed operating parameters, similar to that of Willows Station 9. This is equivalent to a 650 gpm well with 38% utilization and SBA-IX system with Purolite A600E 9149 resin:

1. 8,200 gallons of conventional brine waste is generated during each month.
2. The chromium concentration of untreated brine waste is 34.1 mg/L.
3. 100% of waste brine, including the fresh water rinse, will undergo brine treatment.
4. For Option 3, the treated brine waste will be reused for three cycles prior to disposal.

Capital and annual O&M costs were solicited from each brine treatment research partner using the same operating parameters detailed above. All results are normalized, and an installed capital cost multiplier of 3.0625 was used. The following sections further detail the cost assumptions for each brine treatment method.

7.3.2 Sodium Chloride Costs

The conventional brine regeneration uses a 2 M sodium chloride solution. For Option 1 and Option 2, no treatment and treatment and disposal, the sodium chloride required for generation of 2 M brine is constant each month.

Because sodium chloride is not completely consumed during brine regeneration, Option 3 results in some conserved sodium chloride for subsequent regeneration cycles in which the treated brine waste is reused. Sodium chloride costs for Option 3 is the salt make-up required for treated brine to reach a 2 M concentration. For Options 1 to 3, the cost of sodium chloride is assumed to be \$0.12/lb³.

7.3.3 Disposal Costs

Disposal is responsible for the majority of operational costs associated with brine waste treatment and disposal. Detailed below are the disposal options:

For Option 1, all brine waste produced is RCRA hazardous waste due to the raw brine waste's exceedance of the Total Threshold Limit Concentration (TTLC), 5 mg/L, for chromium concentration in California. Therefore, all brine waste produced must be disposed at an estimated cost of \$1.50/gal.⁴

For Option 2, all liquid brine waste produced after treatment is non-RCRA hazardous waste because the treated brine waste does not exceed the TTLC. All liquid and solid residuals from the brine are assumed to be classified as RCRA hazardous waste. Therefore, the treated liquid is disposed at an estimated non-hazardous cost of \$0.15/gal,⁵ while the resulting liquid and solid waste must be disposed at an estimated cost of \$1.50/gal and \$1.70/lb. respectively.⁶

For Option 3, treated liquid brine waste produced is disposed of as non-RCRA hazardous waste. Year-round, all residuals from the treatment processes are assumed to be classified as RCRA hazardous waste and must be disposed of accordingly. Refer to Option 2 disposal costs above.

³Estimate from Ionex SG quote for SBA-IX, 2016

⁴ Liquid RCRA hazardous waste disposal estimate from Ionex SG, 2014

⁵ Liquid non-RCRA hazardous waste disposal estimate from East Bay MUD, 2014

⁶ Adapted from cost estimates in "Hexavalent Chromium Treatment Residuals Management," ACWA, 2012.

7.3.4 Brine Reuse Cost Assumptions

Direct brine reuse and NF brine treatment and reuse pilot testing conducted as part of this project demonstrated successful brine reuse for three cycles of conventional regeneration. Option 3, assumes three cycles of brine treatment and reuse, which corresponds to a time frame of four months. The treated waste will be disposed as non-hazardous liquid waste, and a fresh brine solution will be used for the next brine regeneration.

7.3.5 Brine Reuse Storage Cost Assumptions

As mentioned above, potential savings derived from brine optimization are based upon add-on equipment costs to an existing SBA-IX system. It is assumed the SBA-IX system has a brine storage tank with capacity to store brine prior to treatment or disposal. Capital costs for an additional 2,500-gallon tank for treated brine storage and an additional brine pump is included for each brine treatment option evaluated. For separation of the Cr(VI)-laden or rinse fraction, similar to the Ionex SG segmented approach, 10% increased capital costs for additional brine storage and instrumentation compared to that of SBA-IX with conventional regeneration is used.

7.3.6 Chemical Precipitation Cost Assumptions

Treatment of the brine waste by chemical precipitation was evaluated using three chemicals that are all effective precipitants of chromium: ferrous chloride (Ferrous), stannous chloride (Stannous), and calcium polysulfide (Polysulfide).

Previous laboratory jar testing of each reductant determined appropriate stoichiometric dose ratios for each chemical and effluent chromium and reductant concentrations. Refer to Section 6.0 for bench-scale performance of chemical precipitation.

Precipitated solids (residuals) quantities are estimated from a mass balance using the generalized redox equations for each reductant, which can be referenced in Section 6.3 Brine Treatment. Several assumptions were made for the mass balance calculations:

1. All ferrous iron added to the brine waste for Ferrous treatment is assumed to be converted to ferric hydroxide, and removed as solid residuals. 1 mg/L-Fe of ferrous iron dose was assumed to generate 1.9 mg/L of ferric hydroxide solids⁷.
2. All stannous chloride added to the brine waste for stannous treatment is assumed to be converted to stannic hydroxide, Sn(OH)_4 , and removed as solid residuals. 1 mg/L-Sn of stannous dose was assumed to generate 1.6 mg/L of stannic hydroxide solids⁸.
3. All calcium polysulfide added to the brine waste for Polysulfide treatment is assumed to be converted to sulfur, S, and removed as solid residuals. 1 mg/L of calcium polysulfide sulfur dose was assumed to generate 0.8 mg/L of sulfur based solids⁹.
4. Chromium removed from the brine waste, as demonstrated by the laboratory jar testing, was assumed to be converted to chromium(III) hydroxide, Cr(OH)_3 , and removed as solid residuals.
5. Solids from turbidity in the water are low and ignored in the mass balance calculation.
6. The residuals moisture content was assumed as 98%, which is typical of settled solids.

⁷ "Hexavalent Chromium Treatment Residuals Management", ACWA, 2012.

⁸ Calculated based the stoichiometric relationship for oxidation of stannous chloride to stannous hydroxide.

⁹ Calculated based the stoichiometric relationship for oxidation of polysulfide, CaS_5 , to elemental sulfur.

Table 33 shows relevant parameters to chemical precipitation costing. Estimates for chemical stock concentrations and prices were provided by manufacturers. Using a stoichiometric dose ratio of 2, identified as the optimal dose ratio from jar testing described in Section 6.3 Brine Treatment, ferrous is the most cost effective reductant with annual ferrous chemical costs less than \$300. In comparison, annual stannous chloride costs are approximately \$15,926 as stannous is significantly more expensive per unit of active chemical than that of ferrous.

Table 33 Key operational parameters and chemical prices for ferrous, stannous, and polysulfide treatment

Parameters	Ferrous	Stannous	Polysulfide
Stoichiometric dose ratio	2.2	2.1	4.5
Dose (mg/L)	660	390	887
Chromium concentration of treated waste (mg/L)	1.2	1.6	16.7
Iron concentration of treated waste (mg/L)	9.5	0.3	-
Stoichiometric oxygen requirement for iron oxidation (g/L)	1.3	0.04	-
Unit cost of precipitant (\$/gal) ¹⁰	\$0.87	\$20.73	\$7.55
Quantity of residuals produced (lb)	1,812	1,537	2,652
Annual cost of chemical precipitant	\$297	\$15,926	\$13,194

As residual iron is present in treated waste for chemical precipitation using ferrous, an aerator is required for Option 3 to oxidize remaining iron before the treated waste is reused for brine regeneration. Chlorine is not considered for residual iron oxidation as chlorine is known to have adverse effects on SBA-IX resin stability. A two-horsepower aerator would be appropriate to deliver the stoichiometric oxygen requirement for iron oxidation. Costs of electricity requirements for aeration, \$0.13/kWh based on average CA rates, are included in cost estimates.

7.3.7 MAC Cost Assumptions

MAC capital and O&M cost estimates to treat 2,000 gallons of conventional brine were provided by ToxSorb. The anticipated treatment rate is 3.3 gpm resulting in treatment of spent brine from an individual SBA-IX vessel, 2,000 gallons, in less than a day. The treatment system assumes two 10 ft³ vessels with MAC media replacement every 1.5 months. Spent media is regenerated with media replacement, transportation, and regeneration at a central facility managed by ToxSorb. Thus, no hazardous residuals are produced onsite. This maintenance, media, and additional chemical costs are packaged as part of an annual O&M service agreement. For this analysis, the O&M service agreement costs are labeled as part of annual media costs.

¹⁰ Estimates are for the following: 30% ferrous chloride from Kemira, 5% stannous chloride from Guard Products Inc., and 5% calcium polysulfide from Envirogen Technologies.

7.3.8 Electrocoagulation Cost Assumptions

Capital and O&M costs for brine treatment via electrocoagulation were provided by BakerCorp. Capital equipment includes one Kaselco EC system, chemical feed systems, and post-treatment solids handling. Consumables include polymer addition for coagulation and replacement of steel electrodes within the reactor. For residuals management, a 30% solids concentration prior to disposal is assumed. Electricity requirements are also included in annual O&M costs.

7.3.9 Nanofiltration Cost Assumptions

Nanofiltration cost estimates were provided by the USBOR. Capital cost estimates assume a NF filtration unit with two membrane modules, ¾ HP motor pump, and valving for flow control. NF elements have a replacement frequency of five years. Based on bench- and pilot-scale testing conducted by Corona and the USBOR, a design recovery of 70% is assumed. The concentrate produced will be disposed of as a hazardous RCRA liquid. Electricity requirements are also included in annual O&M costs.

7.3.10 Other Considerations

As it is still an emerging technology, full-scale cost estimates for brine treatment using the TiO₂ photocatalyst were not pursued. Combinations of several brine treatment methods were also investigated. These scenarios are described below:

1. Direct brine reuse for three regeneration cycles. After the third regeneration, hazardous waste brine will be treated via chemical precipitation (ferrous) prior to disposal. This allows the waste brine to be disposed as non-hazardous.
2. Combination NF and chemical precipitation brine treatment. Waste brine from regeneration will first undergo NF treatment. Because disposal of hazardous liquid residuals is costlier than disposal of solid residuals, the concentrate from NF treatment will be treated via ferrous addition prior to disposal.

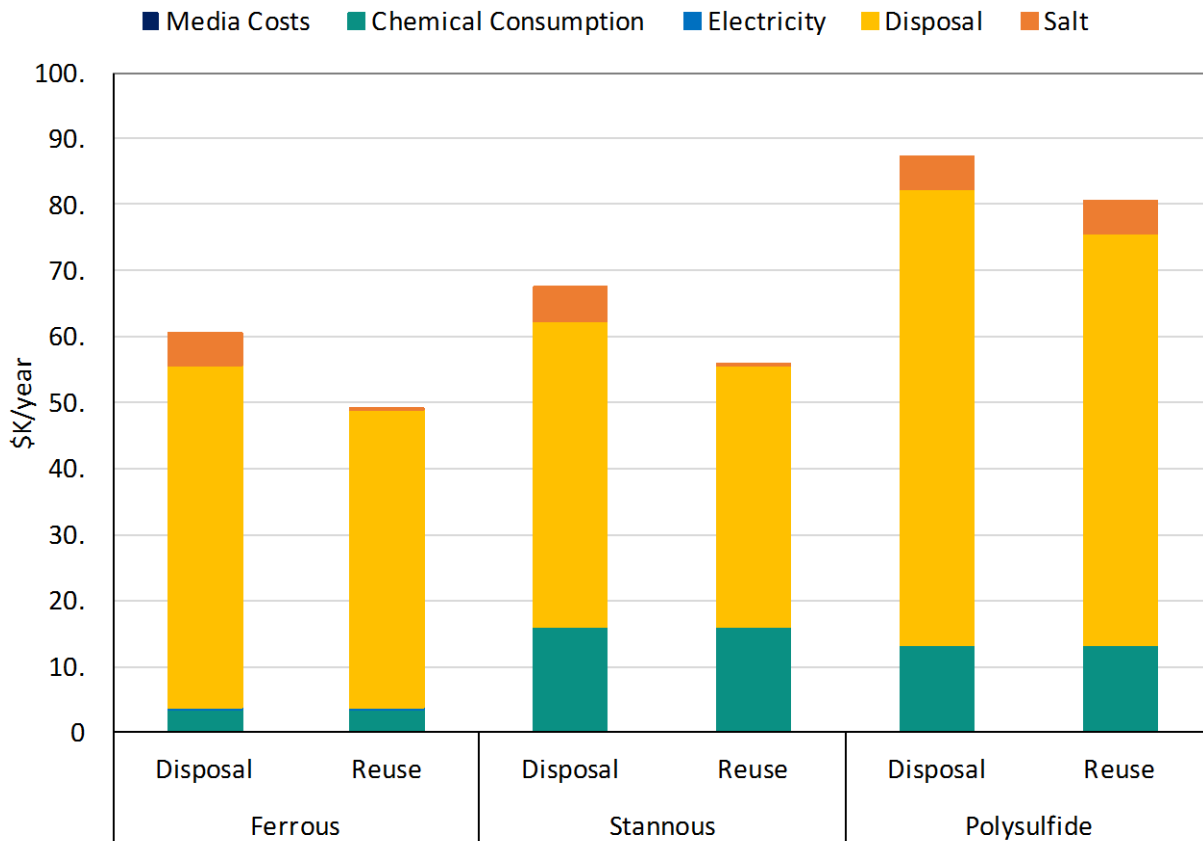
It should be noted that only the direct brine reuse and NF brine treatment have been validated on the pilot scale.

7.3.11 Brine Treatment Cost Summary

As noted above, O&M costs associated with conventional regeneration is used as the benchmark for the direct brine reuse and brine treatment scenarios evaluated. For monthly disposal of 8,200 gallons of hazardous brine, annual conventional brine disposal and chemical costs are approximately \$153 K. For the Ionex SG segmented regeneration approach, sulfate return and fractioning of the Cr(VI)-laden portion, reduces annual O&M costs to \$45 K.

For chemical precipitation, annual O&M costs for the three chemical reductants, ferrous, stannous, and polysulfide, shown in Figure 49, range between \$49 K to \$87 K per year. Due to the lower stoichiometric dose ratio required for chromium removal below the 5 mg/L RCRA level as well as decreased costs compared to that of stannous, ferrous is shown to be the most cost efficient chemical reductant for brine treatment. Thus, comparison of chemical precipitation to other brine treatment methods assumes ferrous as the reductant.

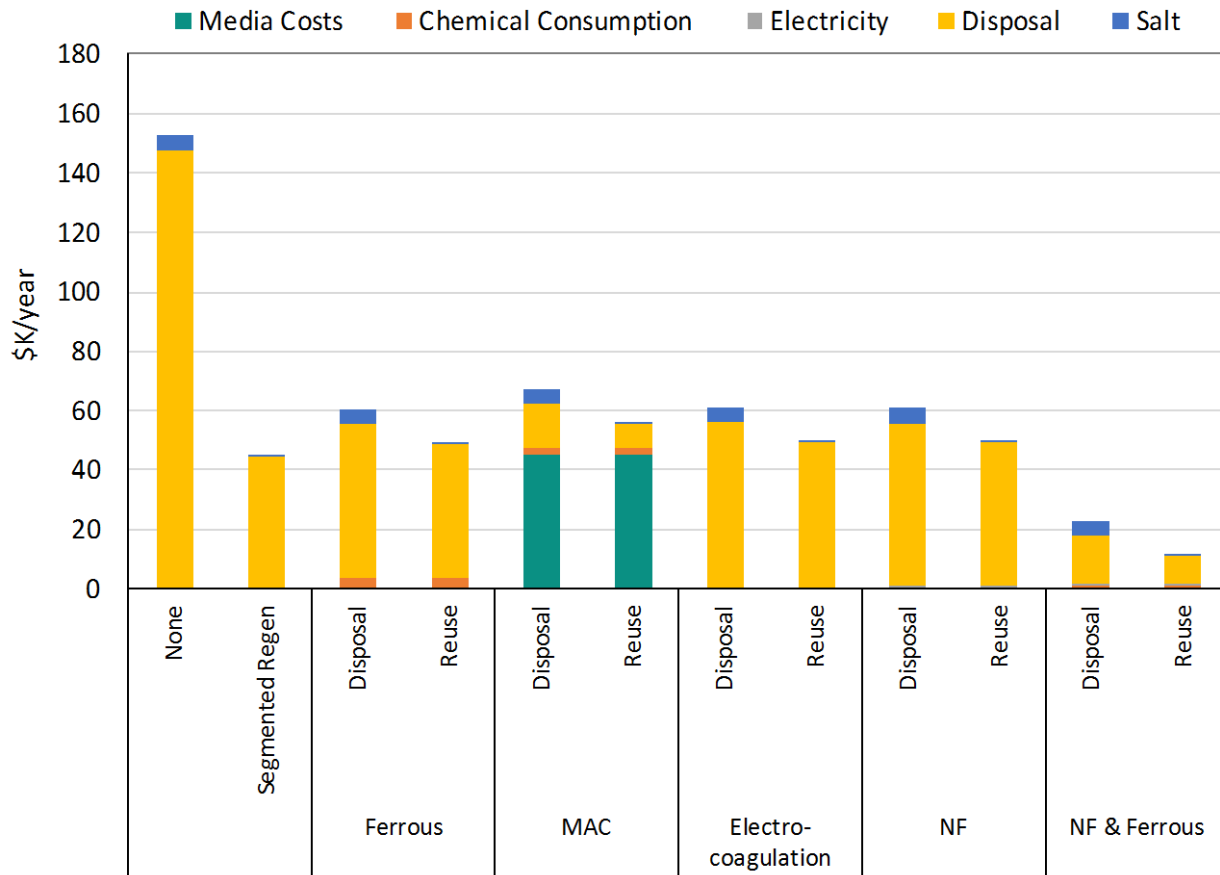
Figure 49 Chemical precipitation O&M cost estimates



The annual O&M and capital costs for all brine treatment costs are provided in Figure 50 and Figure 51, respectively. O&M costs associated with conventional and segmented regeneration approaches are also included in Figure 50 for comparison. The O&M cost estimates for the ferrous, MAC, and NF brine treatment range between \$49 K to \$67 K annually with brine disposal representing the largest portion of the costs. For MAC, as noted above, media replacement, regeneration, and hazardous brine disposal are lumped together under an annual media service agreement. Electrocoagulation, as well as, combination NF and ferrous brine treatment resulted in the lowest operational costs due to a lower volume of hazardous solids for disposal.

Detailed in Figure 50, some reduction in O&M costs, approximately \$10 K annually, could be made via brine reuse for all treatment systems. These savings would further increase with additional cycles of brine reuse prior to disposal. While brine reuse could reduce O&M costs there may be a trade-off with increased operational complexity and permitting of a brine reuse system.

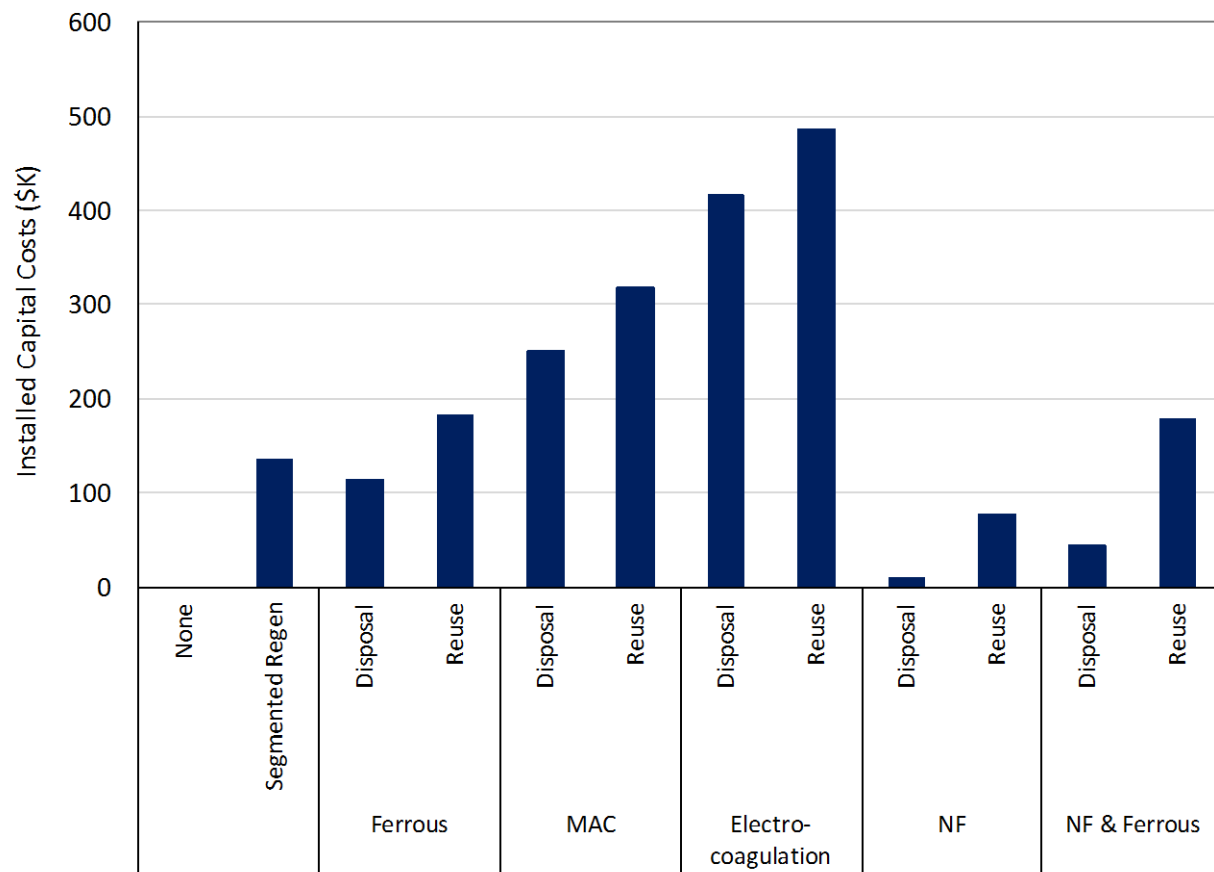
Figure 50 Brine treatment O&M cost estimates



Detailed in Figure 51, the MAC and electro-coagulation brine treatment systems resulted in the highest installed capital cost estimates between \$250 K and \$485 K. The NF brine treatment system has the lowest installed capital cost estimates, below \$77 K for NF treatment and reuse, and the NF unit also results in the smallest footprint for space-constrained sites. A combined NF and chemical precipitation treatment system, using ferrous to treat NF concentrate, has an installed capital cost estimate of approximately \$44 K for treatment only.

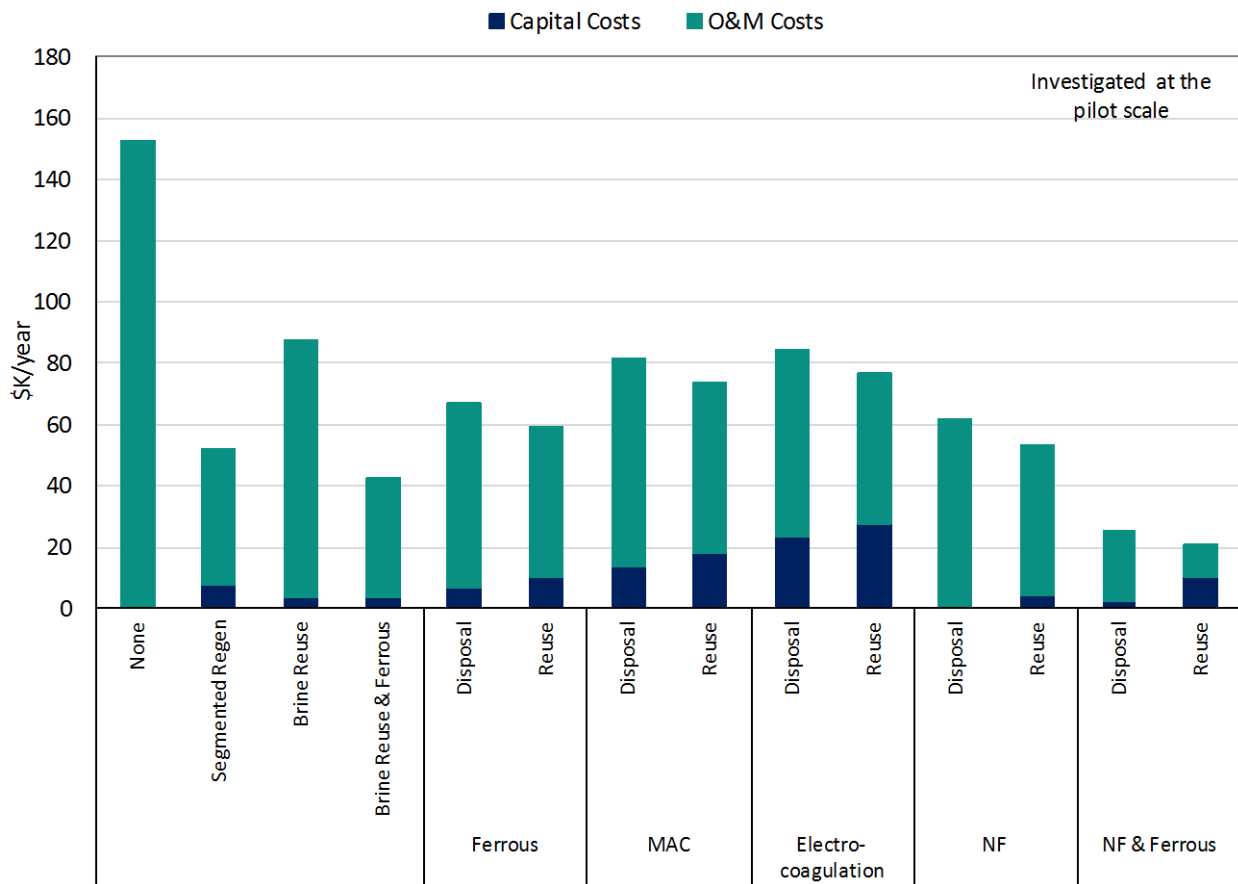
As mentioned above, the capital equipment for all systems include treatment equipment, chemical storage, chemical feed systems, and, if applicable, solids handling. The installed capital costs do not reflect costs for any additional housing structure if needed. For this cost estimate, installed capital costs associated with conventional and segmented regeneration approaches are not considered as only add-on capital costs to an existing SBA-IX system are incorporated.

Figure 51 Brine treatment installed capital costs



Derived from the installed capital and annual O&M costs, Figure 52 details the 20-year annualized costs, interest rate of 1.2%, for all brine treatment methods evaluated. O&M costs associated with conventional regeneration, Option 1 or “None”, as well as the Ionex SG segmented regeneration, refer to Section 6.2 SBA-IX Regeneration, are used as the baselines for treatment evaluation. The treatment technology that has been tested at pilot-scale at Willows Station 9 is highlighted by the grey box. Brine reuse with all other treatment technologies have not been demonstrated beyond bench-scale.

Figure 52 20-year annualized costs



Shown in Figure 52, all brine treatment methods result in lower 20-year annualized costs compared to conventional regeneration. Due to increased capital costs, MAC and electrocoagulation offer the lowest cost savings compared to conventional regeneration. Brine reuse with ferrous treatment prior to disposal, as well as combined NF and ferrous treatment have the most potential for cost savings, but as mentioned above, have not been successfully demonstrated at the pilot-scale. For all brine treatment methods, brine reuse prior to disposal offers some cost savings at the expense of increased operational complexity.

The proprietary Ionex SG segmented regeneration, currently used at all Willows stations, resulted in a 20-year annualized cost of \$52 K, a 66% reduction compared to the conventional regeneration. Of the two treatment methods successfully demonstrated at the pilot-scale, brine reuse and NF treatment, NF has the lowest 20-year annualized cost of \$53 K to \$61 K. Direct brine reuse may face public perception and permitting challenges as concentrations of chromium in the reused brine will exceed the 5 mg/L RCRA limit.

In conclusion, NF brine treatment was proven to be an effective brine treatment method to reduce O&M costs associated with conventional regeneration. Although direct brine reuse was successfully demonstrated and offers an approximate 40% cost savings, reuse of hazardous brine could present permitting challenges. For utilities with SBA-IX systems that do not opt to implement the proprietary Ionex

SG segmented regeneration, NF is the least complex demonstrated treatment method with the highest cost savings potential.

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Appendix A:
Stannous Chloride Application for Cr(VI) Treatment

Introduction

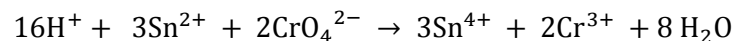
Investigated as part of a 2003 Water Research Foundation bench-scale evaluation of Cr(VI) treatment options (Brandhuber et al. 2004), Cr(VI) reduction by stannous chloride is a potential low capital cost solution to gain reliability and use of current standby wells. Bench-scale investigation of stannous chloride application with and without chlorine was investigated using two waters: Willows Station 9 and water from the San Andreas Mutual Water Company (SAMWAC) located in the Central Coast, CA. In comparison to Cal Water Willows District, San Andreas Mutual Water Company is an unchlorinated small groundwater system. The intent of evaluating both chlorinated and unchlorinated water is if preliminary bench tests of chlorinated water result in significant chromium reoxidation back to Cr(VI), stannous chloride could still be a viable option for small unchlorinated groundwater systems.

Results from the preliminary stannous chloride bench tests are detailed below. It should be noted that since the initial bench tests, additional bench, pilot, and full-scale demonstration testing have been conducted at other water systems. This research was not conducted in collaboration with this Proposition 50 project and the data is not included as part of this Final Report.

Background

Stannous chloride, SnCl_2 , is a reducing agent conventionally utilized as a NSF 60 approved corrosion inhibitor, up to 0.6 mg/L-Sn, in drinking water systems. There are neither federal nor state limits for tin in drinking water. Acting as a free electron donor, stannous chloride reduces Cr(VI) to trivalent chromium [Cr(III)], which is regulated under the total chromium MCL of 50 $\mu\text{g/L}$. Reduction of Cr(VI) by stannous chloride is given in Equation 1.

Equation 6 Stannous chloride redox reaction



Previous research conducted on Cr(VI) reduction in drinking water, in Glendale, CA, demonstrated stannous chloride reduction of Cr(VI) within the first sampling time of 30-40 minutes (Brandhuber et al. 2004). Bench tests were conducted on DI, synthetic, and Glendale water with Cr(VI) concentrations spiked to 100 $\mu\text{g/L}$. Table 34 and Table 35 show a summary of the experimental parameters and Cr(VI) concentration reduction, respectively, from the Brandhuber et al. (2004) research. Further bench tests of alternative reductants on DI and Glendale water also concluded stannous chloride is a more effective reductant compared to sulfides and sulfites (Lai and McNeill 2006).

Table 34 Summary of experimental parameters from the Brandhuber et al. 2004 work

Experimental Parameters	Value
Cr(VI) concentration ($\mu\text{g/L}$)	100
Stannous chloride dose (mg/L Sn)	0.82
Stoichiometric dose ratio ([Sn]:[Cr(VI)])	3.57

Table 35 Summary of Cr(VI) reduction from the Brandhuber et al. 2004 work

Matrix	% Cr(VI) Reduction Range
DI water	98 – 100
Synthetic water	30 - 60
Glendale water	30 - 50

Objectives

Initial bench-scale experiments investigating stannous chloride reduction of Cr(VI) were conducted with water from Willows Station 9 and SAMWAC. Bench tests were designed to meet the following three objectives:

1. Investigate reaction kinetics of Cr(VI) reduction via stannous chloride
2. Characterize chromium particulate formation
3. Determine the impact of chlorination on Cr(VI) reduction and chromium filtration

Objective 1, investigation of the reduction reaction kinetics, is accomplished through stannous chloride application to two different waters at varying doses. As mentioned above, previous research has demonstrated the reduction reaction occurring within the first sampling time of 30 to 40 minutes (Brandhuber et al. 2004, Lai and McNeill 2006). The new SafeGuard™ III Duo Cr(VI) Analyzer, described further below, allows for better resolution of the dose-response curve with a shorter sampling time of 5 to 10 minutes. Description of the stannous doses investigated are detailed below in Methods and Materials.

Characterization of chromium particulate formation, Objective 2, is achieved through treated water filtration at varying time intervals and filter sizes. For Willows Station 9 water, 0.45 µm syringe filtration as well as 6 µm and 50 µm gravity filtration of stannous treated water at 15 minutes, 1 hour, 24 hours, and 5 days were conducted. Varying filter sizes are intended to characterize particulate formation and determine the potential for chromium accumulation in the distribution system. Finally, as part of Objective 3, a bench test of chlorinated water was conducted for Station 9 water, using the same filter sizes and sampling times as that of Objective 2.

Materials and Methods

A summary of the bench test conditions for all three objectives is given below in Table 36. For Objectives 2 and 3, two control tests, one with no chemical addition and one with only chlorine addition, were used for comparison to stannous treated samples. Unfiltered and filtered total chromium and tin samples were sent to Eurofins Eaton Analytical for analysis.

Table 36 Bench test conditions for Objectives 1 to 3

Objective	Water	Raw Cr(VI) (µg/L)	Stannous Dose (mg/L-Sn)	Chlorine Dose (mg/L)	Filter Size (µm)	Sample Times
1. Investigation of Reaction Kinetics	SAMWAC	17	0.6, 0.3, 0.15	0	-	-
	Willows Station 9	13	0.15	0	-	-
2. Characterization of Particulate Formation	Willows Station 9	16	0.6	0	Unfiltered, 0.45, 6, 50	15 min, 1 hr, 24 hrs, 5 days
		16	0	0	Unfiltered, 0.45, 6, 50	15 min, 1 hr, 24 hrs, 5 days
3. Impact of Chlorination	Willows Station 9	16	0	1.0	Unfiltered, 0.45, 6, 50	15 min, 1 hr, 24 hrs, 5 days
		16	0.6	1.0	Unfiltered, 0.45, 6, 50	15 min, 1 hr, 24 hrs, 5 days

For all bench tests detailed above, stannous chloride was dosed via Eppendorf pipette and mixed for 20 seconds on a stir plate. For bench testing with chlorinated water, 1 mg/L of chlorine was dosed immediately after the initial mixing period. After chlorination, treated water was mixed for an additional 20 seconds via stir plate.

Figure 53 SafeGuard™ III Duo Cr(VI) Analyzer

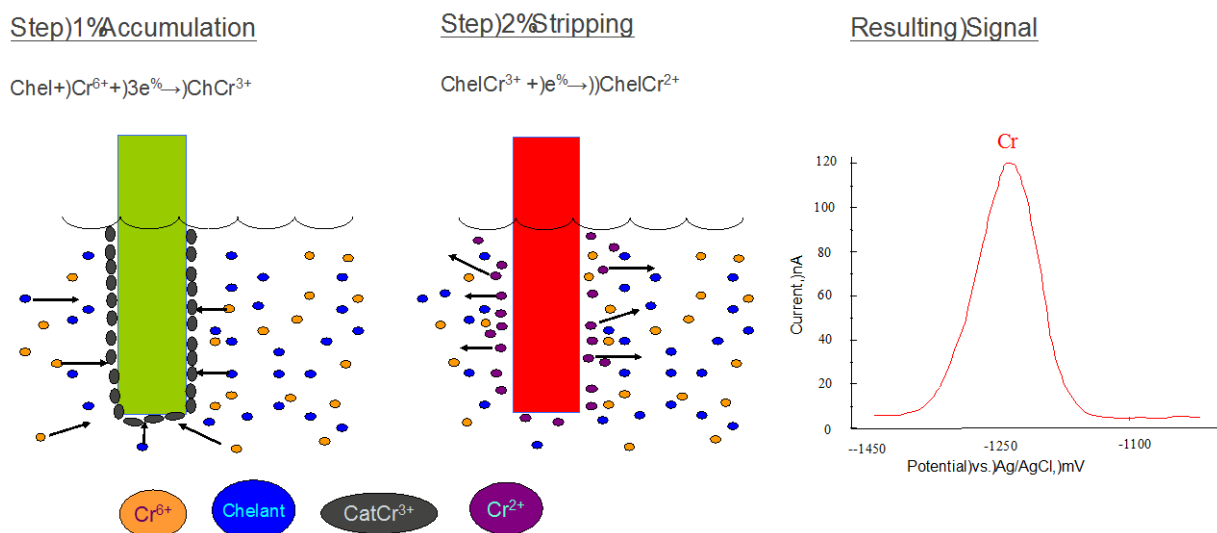


The reaction kinetics studies were conducted at the Aqua Metrology Systems (AMS) Laboratory, in Sunnyvale California, with the use of the SafeGuard™ III Duo Cr(VI) Analyzer (SafeGuard) to quantify Cr(VI) reduction. A photograph of the instrument can be seen in Figure 53. This instrument allows for near real-time analysis of hexavalent chromium, which is necessary to determine the kinetics of the chromium reduction. For each bench test, initial SafeGuard grab samples were collected five minutes after stannous dosing.

The SafeGuard utilizes a Catalytic Adsorptive Stripping Voltammetry method. Voltammetry measures electric current through an electrode at specific potentials. Cr(VI) reacts with a chelating agent which accumulates on the surface of an electrode as chelated Cr(III). Then a current is applied to convert and strip the chelated Cr(III) from the surface. The current needed to strip off the chromium is proportional to the concentration. A

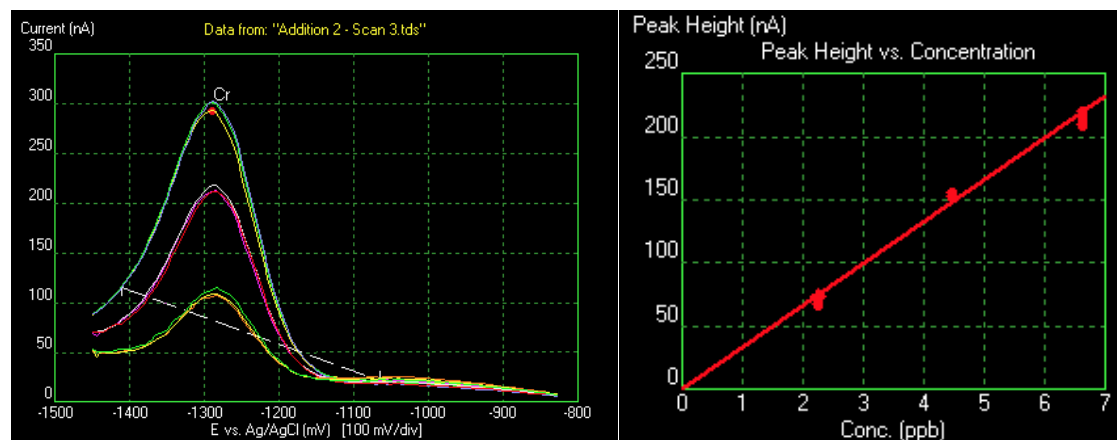
diagram of the stripping voltammetry method, courtesy of AMS, is shown in Figure 54.

Figure 54 Diagram of stripping voltammetry method, courtesy of AMS



An example of the Cr(VI) standard scans and resulting calibration curve are shown in Figure 55. For this testing, a quick analysis method was used, which measures the peak current to strip Cr(VI) in approximately 5 to 7 minutes per sample. In order to determine Cr(VI) reduction within the first 10 minutes, the instrument was not calibrated for each sample and relative results rather than quantitative results are presented below.

Figure 55 SafeGuard calibration curve scans and resulting calibration curve, courtesy of AMS



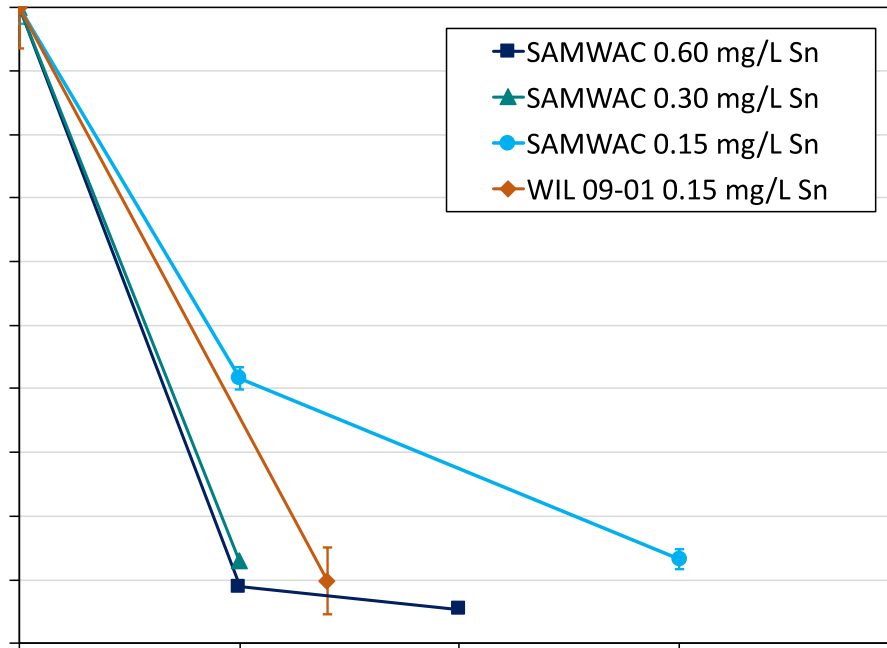
Results

Objective 1. Investigation of Reaction Kinetics

As mentioned above, previous research into the reaction kinetics of stannous chloride reduction of Cr(VI) was limited by an extended analysis time of 30 to 40 minutes. For this technology to be relevant to drinking water applications, it is important to gain a better understanding of the reaction rate and dose-response mechanism. The required reduction time and stannous dose to achieve full Cr(VI) reduction will have significant impact on the anticipated capital and O&M costs.

Shown in Figure 56 is the percent reduction in the measured Cr(VI) peak from the SafeGuard analyzer as compared to the corresponding raw Cr(VI) results prior to stannous addition. A chromium peak of 100% represents the raw water concentration, while a 10% chromium peak corresponds to a 90% Cr(VI) reduction. Results from both Willows Station 9 and SAMWAC bench tests are given.

Figure 56 Percent reduction in Cr(VI) peak from the quick SafeGuard analysis

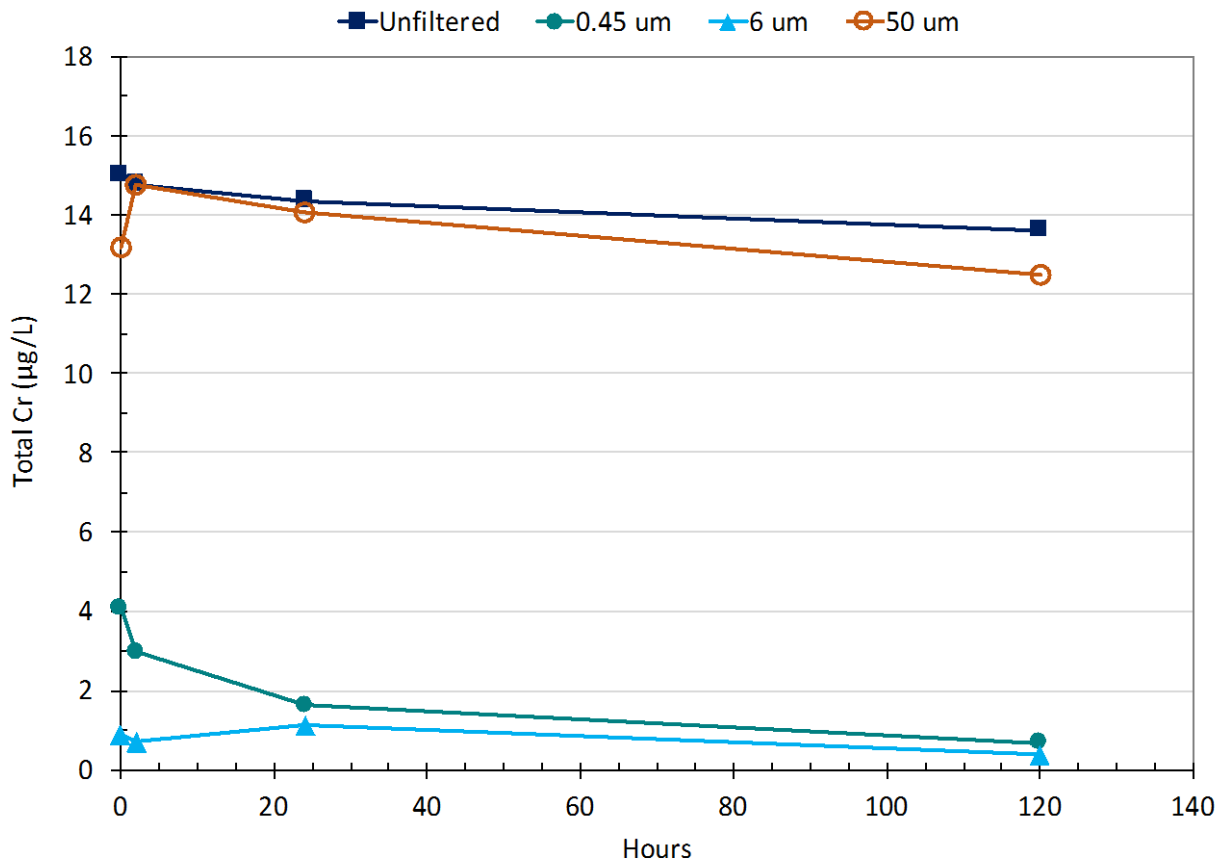


For the Station 9 water as well as SAMWC water with stannous doses of 0.3 mg/L-Sn or 0.6 mg/L-Sn, the first sample yielded an approximate 90% reduction in the relative Cr(VI) peak. In comparison, the SAMWC bench test with the lowest stannous dose, 0.15 mg/L-Sn, showed incomplete reduction at 5 minutes, with 90% reduction at about 15 minutes. Thus, at a higher stannous dose the reduction reaction is finished within the first sample time of approximately five minutes. To determine the dose-response mechanism of stannous chloride, bench testing with lower stannous doses, less than 0.15 mg/L-Sn, is required.

Objective 2. Characterization of Chromium Particulate Formation

This experiment expands on the existing research demonstrating that reduced Cr(III) is less soluble than Cr(VI) and forms a solid that can be filtered. Using the maximum NSF approved dose of 0.6 mg/L-Sn, bench testing of unchlorinated Willows Station 9 water was conducted. The unfiltered and filtered performance of Station 9 treated water with 0.6 mg/L-Sn is given in Figure 57.

Figure 57 Total chromium results for filtered unchlorinated water with a 0.6 mg/L-Sn dose



As shown in Figure 57, the 50 µm filter size resulted in no removal of chromium precipitate, however the 0.45 and 6 µm filters successfully removed chromium from stannous treated water to below the 10 µg/L MCL. In addition, as shown in the figure, both unfiltered and filtered total chromium concentrations were stable between one to five days.

It should also be noted that the 0.45 µm filter performed worse than the 6 µm filter at the early sample times of 15 minutes and 1 hour. This may be due to the 0.45 µm syringe filtration occurring in under 1 minute, whereas the 6 µm gravity filtered samples took approximately 20 minutes to filter, allowing more time for particle formation.

In general, the unchlorinated Station 9 results yielded increased chromium removal with stannous chloride compared to the Brandhuber et. al (2004) work. This may be due to the increased stoichiometric tin: chromium dose ratio used and/or water quality differences.

Objective 3. Impact of Chlorination on Cr(VI) Reduction and Particulate Formation

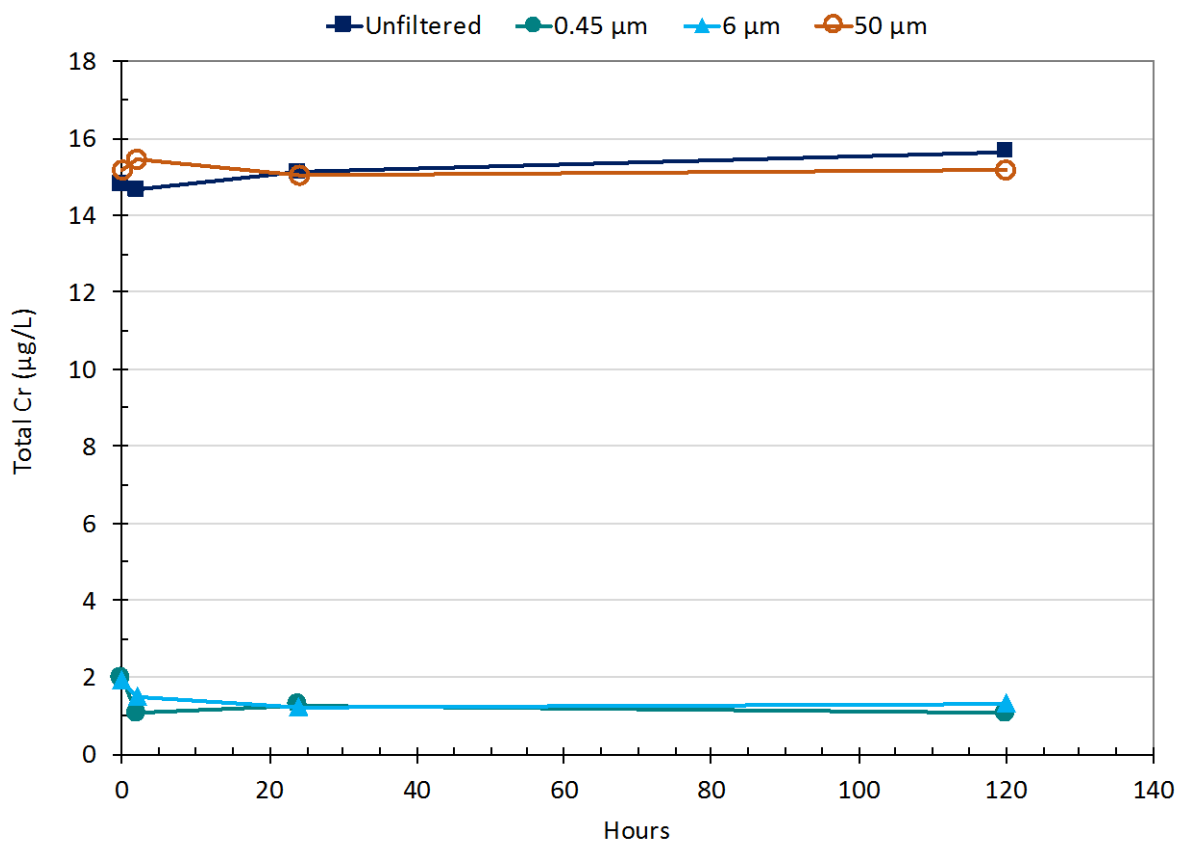
The results of the control tests, raw and chlorinated water without stannous addition are presented in Table 37. Filtration of raw Station 9 water did not result in any chromium removal. Similarly, chlorine addition did not result in any changes in Cr(VI) or total chromium concentration in any of the filtered or unfiltered samples. This demonstrates that the removal of chromium is due to stannous treatment and subsequent filtration.

Table 37 Untreated Well 9 and Well 9 with chlorine only filtered sample chromium concentrations

Treatment	Unfiltered		0.45µm filter		6µm filter		50µm filter	
	Cr(VI) (µg/L)	Tot. Cr (µg/L)	Cr(VI) (µg/L)	Tot. Cr (µg/L)	Cr(VI) (µg/L)	Tot. Cr (µg/L)	Cr(VI) (µg/L)	Tot. Cr (µg/L)
Untreated Station 9	16.0	15.6	16.0	15.6	16.0	16.3	16.0	16.0
Station 9, 1 mg/L Chlorine	16.0	15.8	16.0	15.4	16.0	15.3	16.0	15.7

Given in Figure 58 are total chromium results for unfiltered and filtered Station 9 treated water with a stannous dose of 0.6 mg/L and chlorine dose of 1 mg/L. Similar to the unchlorinated bench tests, total chromium concentrations for the unfiltered and filtered samples remained stable over the course of five days. The 0.45 µm and 6 µm filters resulted in over 85% removal of total chromium within the first sample time of 15 minutes, while the 50 µm filter showed no total chromium removal.

Figure 58 Total chromium results for filtered and unfiltered chlorinated water with a 0.6 mg/L-Sn dose



Based on the difference between the 0.45 µm filter performance for unchlorinated versus chlorinated water, as shown in Figure 57 and Figure 58 respectively, chlorine addition appears to enhance coagulation

and improve the filterability of the chromium solid. Although, total chromium concentrations for the unfiltered and filtered samples at 5 days were on average 0.5 µg/L higher than that of the unchlorinated bench test. This may be attributed to partial reoxidation of Cr(III) back to Cr(VI).

Appendix B:
Full-scale – Successes and Challenges

As one of the first utilities in the state to implement Cr(VI) treatment, Cal Water was faced with many unique challenges. Coupled with being among the first to install SBA-IX treatment for Cr(VI) removal, Cal Water also undertook a very aggressive timeline in order to meet compliance prior to the finalization of the Cr(VI) MCL. Overall, the effort to install SBA-IX at multiple sites on a short timeline was successful. The construction projects took a remarkable level of coordination between the various departments in Cal Water, vendors, contractors, sub-contractors and regulatory agencies.

This section of the report covers the successes and the challenges that were experienced during the planning, procurement, permitting, engineering, installation, and operations of the full-scale systems. In general, this section primarily focuses on the Cal Water Willows District SBA-IX treatment systems, although other SBA-IX systems in Dixon and Salinas are referenced for comparison. It should also be noted that this section does not provide a full account and timeline of the project, but is intended to provide relevant experience and lessons learned to assist other utilities considering SBA-IX treatment.

Planning

Cal Water made a corporate level decision to stay in compliance with the Cr(VI) MCL, which required collection of the first compliance sample on or before January 1, 2015. Compliance is based on the running average concentration over four quarters. For wells with Cr(VI) concentrations above the MCL, the length of time before the system was considered out of compliance was based on the raw Cr(VI) concentration. A well with Cr(VI) above 40 µg/L is considered out of compliance after the first quarter, as averaging that high concentration with any level of Cr(VI) measured in the next three quarterly samples would result in a value above the MCL. If the first compliance sample results in Cr(VI) under the 10 µg/L, compliance sampling is not required until the follow year. Refer to Table 38, which shows an example of how the chromium concentration impacts how quickly a given system is out of compliance. The data in red indicates which sample puts the system out of compliance.

Table 38 Example data to show how compliance with the MCL depends on concentration

	Q1 Jan. 1, 2015	Q2 Jun. 2015	Q3 Sept. 2015	Q4 Dec. 2015
System A	8			
System B	10	11	11	12
System C	15	16	14	15
System D	22	21	23	22
System E	45	40	44	43

For System E, the first sample was collected on January 1st, 2015 and the concentration was 45 mg/L. This result puts the system out of compliance because even if the next three quarters had non-detectable levels, the average would be 11.25 mg/L, which is over the MCL. While System E would be out of compliance in January 2015, System D would not be out of compliance until June of 2015 due to lower average Cr(VI) concentrations.

As detailed above in Table 38, Willows wells have Cr (VI) concentrations in the teens. Thus, the wells would have been out of compliance by either the third quarter or fourth quarter of 2015. In anticipation of the MCL, Cal Water began planning efforts in 2011 that included a treatment technology assessment for the impacted wells. This assessment identified which wells would require treatment at different MCLs, and gave a range of costs to treat the identified wells.

Pilot testing

For each well requiring treatment, onsite pilot testing was conducted to investigate the impact of resin selection, HLR, and EBCT at each site. Refer to Section 3.0 Willows Water System Background and Section 4.0 Literature Review above for further description and results of the 2015 pilot testing. The testing was conducted concurrently with the development of procurement documents, and the results from the testing were used to inform the design and operations of the full-scale facilities. Additionally, the results were used to refine performance estimates and project full-scale operational costs.

Cal Water's direct involvement with pilot testing helped alleviate their concerns with the full-scale treatment approach. Knowledge regarding HLR, EBCT, and resin selection gained during pilot testing allowed Cal Water to be very specific in the procurement documents, which significantly reduced the cost of treatment as detailed above in Section 7.0 Costs.

Regulatory Planning

In efforts to keep the project on schedule with respect to permitting, Cal Water initiated conversations with state and local regulators early in the planning. Since Cal Water is a private water utility, the rates are regulated by the California Public Utilities Commission (PUC). Cal Water was the first utility in the state to get a memorandum (memo) account approved through the PUC to track and ultimately recover the costs associated with Cr(VI) treatment. The memo account became effective in June 2014. A negative declaration was filed and accepted for California Environmental Quality Act (CEQA). National Pollutant Discharge Elimination System (NPDES) permits were obtained from the City in a timely fashion for all of the pilot-scale discharges as to not impact schedule.

DDW chose to issue a formal Letter to Operate rather than a permit amendment. This gives DDW time to evaluate the performance of the treatment units and decide what requirements need to be included in the permit amendment.

Legislative Action

Cal Water staff worked with the California Water Association (CWA) and the Association of California Water Agencies (ACWA) to develop legislation that allowed for a compliance period with the Cr(VI) MCL. Cal Water met with each state Assemblyperson and Senator for the impacted districts to help them understand the financial impacts of this regulation, and why legislation was needed to allow water systems time to evaluate alternatives and install treatment.

The outcomes of this effort ultimately resulted in the passing of Senate Bill (SB) 385 which extended the compliance deadline to January 1, 2020 if a compliance plan was submitted by May 1, 2016 and updated quarterly. Despite these efforts, Cal Water successfully maintained compliance without the need for the extension afforded by SB 385.

Procurement

The site-specific performance estimates specified in the procurement documents were based on the initial pilot testing and included estimates for maximum head loss and HLR and EBCT ranges. Vendors were also provided an O&M table to complete, including specification of brine waste generation percentage and salt usage. This ensured that the bids were comparable, and clearly indicated the design estimates for HLR and EBCT, which was beneficial to Cal Water as well as the bidders.

Performance Guarantees

The successful bidder was required to operate the system for a minimum of one year to ensure accurate operations and maintenance estimates and ease the SBA-IX operation transition for Cal Water staff. The operations and maintenance fees are contractually fixed for a 2-year term, with a fixed monthly service fee and additional costs for consumables. Cal Water can go to mediation if a vendor does not meet contract terms as well as withhold funds if a vendor does not meet performance specifications.

Cal Water looked at the historical water quality of all wells to receive treatment to determine if changing nitrate concentrations are expected, and did not find increasing concentrations at any of the sites. Other utilities would benefit from looking at performance guarantees in the long term, and accounting for changing water quality conditions. Not designing for increasing nitrate, for example, can lead to the undersizing of equipment. While the equipment will perform as expected in the short-term, it may have excess operations and maintenance costs as water quality changes.

Cost

The original cost estimate for treatment at all Willows sites was \$17M for the capital installation, with an annual operations and maintenance expense of \$360K, which would have resulted in an estimated 126% rate increase. Due to the applied research conducted, Ionex segmented regeneration, and the competitive bidding process, the overall capital cost for all Willows sites was reduced to just over \$10M, with an annual operations and maintenance expense of \$100K. Proposition 50 grant funding covered \$4.4M of the full-scale installation costs for Willows, which is classified as a disadvantaged community. The overall reduction in cost to the community was a huge success.

Permitting

The City of Willows does not have a city engineer on staff, and the outside engineering firm was not a participant in many of the early meetings where Cal Water spent time getting the buy-in of City staff. Caution on the part of the outside engineering firm resulted in a 6-month delay in permitting due to potential hazard and safety unknowns associated with this treatment. This resulted in a City requirement for brine and waste brine tanks to have built-in secondary and tertiary containment for all Willows sites. Further description of tertiary containment permitting challenges is given below.

In general, it would be very helpful for the utilities, vendors and DDW to standardize permitting, procurement specifications, and operations plans. This could be accomplished by DDW. In the UK, the process is more standardized which creates efficiencies. Another possibility is for DDW to certify equipment for the removal of certain contaminants, similar to the certification process that exists for in-home treatment units.

Tertiary Containment Requirement

At all of the Willows sites, the brine and waste brine tanks do not meet a 20-foot separation from the property line as specified by the City. Both types of tank are double walled and have secondary

containment built-in, but there was no secondary containment for the pipelines carrying brine. Because of these two issues, the City required the installation of tertiary containment. The tertiary containment was added after full-scale start-up, as permitting was not completed until after construction was underway. The brine and waste tanks without and with concrete tertiary containment at Station 9 are shown in Figure 59 and Figure 60 respectively. The concrete berm is able to catch overflow spills, spills on broken pipelines, or spills due to leaking valves or connections, offering additional advantages over the built-in secondary tank containment. Not all cities may require tertiary containment; Dixon, for example, did not.

Figure 59 Brine tank and waste brine tank with secondary containment



Figure 60 Brine tank and waste brine tank with tertiary containment



Engineering and Installation

Construction on such a tight timeline lead to a variety of challenges. There were delays in acquiring necessary equipment, such as new well pumps, panel boards and treatment equipment. Many sites also required power upgrades, resulting in delays. Described below are engineering and installation challenges and successes relevant to site access, equipment selection and installation, controls, and communication between parties.

Site Access

In the case of regenerable SBA-IX treatment, the brine tanks and waste brine tanks need to be accessed regularly. Refer to Figure 59 for a photo showing the brine tank in the foreground, and the waste brine tank in the background. Solid salt is delivered to the sites by truck and pneumatically transferred into the brine tank. Waste brine, in the case of all Willows sites, is hauled away by trucks for offsite treatment. For both of these purposes, there must be an unobstructed path to the tanks and pull through access should be provided whenever possible. In some areas, the brine hauling trucks can be full size semi-trucks, which are up to 73 feet long. Cam lock fittings are used to vacuum the hazardous waste from the waste brine tank to the truck and address spill concerns.

The transportation of the hazardous brine is a key cost driver. As a result, it is more cost effective for the tanker to leave full. This can be done by sizing the waste brine tanks to store waste brine from multiple regenerations. Note that the waste brine maximum storage time on a given site per RCRA is 90 days, which may dictate hauling frequency. Although combining loads from different sites within a utility could significantly decrease costs, the combination of hazardous waste from different sources is not allowed. Utilities with brine waste classified as non-hazardous should consider combining waste from different well sites into the same tanker truck to reduce hazardous brine transportation costs.

Ion Exchange Vessels Storage

The ion exchange vessels at the Willows sites are in cargo containers which makes the vessels difficult to access for maintenance. On some of the smaller space-constrained Cal Water sites, the brine and waste tanks would also have to be moved with a forklift or other large equipment in order to access the cargo containers. A rolling fence is one option for providing access around the existing tanks.

In addition to poor maintenance access, the design of the cargo containers contains a 3-foot wide panel that could be removed to allow mechanical access. Although there was sheet metal shroud around the area, an incident at a Dixon site arose when an individual broke into the container through this access point. It would be better to have flanged fittings flush with the external portion of the cargo containers, to allow a spool piece to connect the units and eliminate the need for sheet metal covers. Another option is to have a building rather than cargo containers. All of the sites are equipped with gates and fencing. There are no cameras or motion activated lighting at the sites.

Ionex is moving away from cargo containers and constructing permanent buildings with larger diameter vessels. Fewer vessels result in less moving parts that can fail, but would require larger regeneration tanks. As this was one of the first full-scale SBA-IX treatment units to remove Cr(VI) in drinking water, there was a lack of knowledge regarding how well larger diameter vessels would perform. Subsequent work has demonstrated that large diameter vessels have the same performance as smaller diameter vessels (personal communication Phil Chandler 9/9/16).

One a positive note, the cargo container design separates the IX resin vessels from the brine regeneration system, which limits the corrosion of the painted metal components due to salt. Cargo containers also increased the speed of permitting, as they were considered temporary structures.

Brine and Waste Brine Tanks

Materials Selection

The original brine lines were PVC which could be accidentally broken and cause a release of brine or waste. Some of these lines have now been changed to Hastalloy, which is a corrosion resistant metal alloy pipe. Hastalloy is costly compared to other materials, however, it is not broken as easily as PVC. The tertiary containment, as mentioned above, also adds an additional level of safety to the brine and waste storage facility.

Tank Connections

All Willows sites have tank level pressure transducer lines and PVC lines through the bottom of the brine and waste brine tanks. Figure 61 shows an example of a pressure transducer line entering the bottom of the brine tank. If one of these connections were to accidentally break, there would be a discharge of brine or hazardous waste. In lieu of the current configuration, these lines could be run into the top of the tank to prevent damage to the equipment or accidental discharges.

Figure 61 Example of a connection to the brine tank



Air Compressor

Ionex SG utilizes pneumatic valves and an “air hold down” system during regeneration that require the use of an air compressor. The original air compressor, shown in Figure 62, was undersized, had a low capacity, regularly overheated, and no drier. Air Driers remove humidity present in the ambient air to prevent maintenance issues associated with corrosion. A new compressor, shown in Figure 63, was purchased that has larger capacity, a drier, and produces better quality compressed air. The increased capacity resulted in less start/stop cycles due to increased storage for air.

Figure 62 Original air compressor



Figure 63 New air compressor



Controls and Programming Challenges

The well permissive signal interface is the biggest area for controls improvement. The permissive signal interface is a controls system which requires specified conditions to be met throughout the treatment system prior to initiating any process change, such as well start-up and shut-down. Faulty signal communication and/or lack of interface fail safes between the treatment system and well can result in incidents such as treatment equipment damage and emergency well shut-down.

It would have been helpful to have a meeting between all parties including the utility, engineers, vendors, and construction personnel to discuss, agree upon, and document the controls and protections earlier in the construction process. Each condition should have been tested at start-up more thoroughly to verify proper communication between the well and the treatment unit.

High Pressure Incident

In February 2016, one of the Dixon sites had a high pressure event that lead to failure of the treatment equipment. A valve situated between the treatment unit and entry point to the distribution system was accidentally closed. When the well was turned on, the high pressure alarm failed because of a clogged pressure sensor. This lead to over pressurization of the treatment unit. Ultimately, some of the PVC joints failed and resin was released on site. There was no high pressure signal in the Ionex unit connected to the Cal Water controls. Subsequently, the controls have been changed to allow communication between the Ionex controls and the Cal Water controls.

Communication

As with any project, communication is incredibly important. Having multiple vendors, permitting agencies and sites adds to the importance of clear and timely communication. Cal Water staff provided specific suggestions for improving multi-party projects:

- Have a clear check-list of what needs to be delivered and what has been completed at any given time.
- Communication should be tracked in one unified document.
- Use schedule tracking tools to insure that milestones have been reached.
- Have clear and agreed upon testing with clearly-stated acceptable results and response to unacceptable results.
- Clear communication with contractors on what tasks have been assigned to sub-contractors.
- Plan changes need to be managed properly.
- Have a single project delivery partner.
- Have an experience design build firm.
- Hazard and operability checklists should have clear implementation on controls.
- Hold regular project calls with all relevant parties.
- Clear delineation of responsibilities between all parties.

Operations

Remote Data Access

For water system control, Cal Water uses a Supervisory Control and Data Acquisition (SCADA) system. In the past, the SCADA system was accessible through an online interface. Computers were available at the local offices for access, which was not very convenient for the operators out in the field. One significant improvement to SCADA access, implemented during the construction of the treatment units, is SCADA access on portable tablets. This allows operators to look at each treatment unit and make changes while they are out in the field.

Discharge

The pump at Willows Well 8 was changed out so that the well could produce more water. After the installation, the well needed to be run to waste for water quality testing. Across the street from the site

is an outfall into a drainage ditch. In the past, high flow volume had caused scouring issues, so rip-rap and large rocks were installed for erosion prevention. Figure 64 is a photograph of these improvements.

Figure 64 Photo of improvements to the discharge area



Bacterial Growth

Preventing bacteriological issues at start-up requires a multi-pronged approach. Any well that is oil lubricated should be converted to a water lubrication before installing treatment. Oil lubricated pumps, especially those that have used food grade oil, are associated with bacterial growth in wells due to increased assimilable carbon (LeChevallier, 1993). All of the oil should be bailed out and the well casing should be cleaned. Willows Station 4 is currently undergoing this process, and all other Willows wells were water lubricated prior to initiating the project.

Before treatment installation, wells should be tested for bacteria by a quantitative total coliform method and Heterotrophic Plate Count (HPC). All pipes and vessels should be disinfected and tested in accordance with the current AWWA standard. Any bacterial presence in the well should be addressed before installing treatment because the bacteria can colonize the resin, which is challenging to address. Bacterial presence on the resin can result in periods of non-operation and lost water, because of running to waste. Some DDW offices will allow a treatment unit to run to system as long as Total Coliform/*Escherichia Coli* (TC/EC) is negative and HPC present is below 500 CFU/mL. Running to the system as much as possible is an effective method for eliminating HPC growth within filter beds.

It would be helpful for DDW to establish a statewide standard on how long SBA-IX treatment units are allowed to be stagnant before they must be run, and also a minimum run time. Two resin manufacturers recommend running wells with treatment at least once in a 24-hour period.

Water Hammer

Sudden pressure changes are experienced in the distribution system after the start-up of some wells. This is commonly referred to as water hammer. Willows Station 8 is currently experiencing water hammer issues due to start/stop operations. Prior to installation of treatment, the production capacity of that well was increased to provide additional treated supply, although this is thought to not be directly influencing the issue. Cal Water staff have suggested several solutions to address water hammer, including:

- Soft start and smart controller
- Variable frequency drive motor on the well
- Pump-control valves for gradual flow increases
- Surge tank in front of SBA-IX
- Installation of a device to measure and record water hammer on resin units

To date, a soft starter has been installed at Station 8 with negligible benefit. Cal Water is currently evaluating the installation of a Variable Frequency Drive (VFD) to address the water hammer.

Waste Disposal

One unique feature of the Ionex treatment approach is the engineered waste path for the Cr(VI) laden brine. Initially Ionex investigated treatment and disposal of brine at conventional facilities, such as East Bay Municipal Utility District wastewater treatment plant. Another treatment and disposal option is Cr(VI) recovery from the waste brine, resulting in its classification as a non-hazardous waste after treatment. In both cases, the waste brine is still transported off-site as a hazardous material. Ultimately, Ionex elected to transport the brine to the Phibro-Tech facility in Santa Fe Springs, California. Phibro-Tech has an existing process to recover Cr(VI) for beneficial reuse and render the brine non-hazardous prior to disposal.

Nuisance to Neighbors

Wells can be the source of noise that is irritating to nearby neighbors. The usual well noises are those caused by vertical turbine pumps and back-up generators. Additional noise contributing sources include the use of an air compressor required for the operation of the pneumatic valves. The delivery of salt and brine hauling also require large trucks. Often well sites are located in neighborhoods and the truck traffic can be an annoyance to nearby residences.

Full-scale Operations in the Salinas Area

For comparison to the Ionex SG SBA-IX systems installed at four Willows wells sites: In the Salinas area, Envirogen SBA-IX units were installed at two locations. These units have been meeting the performance specifications for headloss. Although waste generation is approximately 40% greater than what was committed in the initial contract, the bed volumes to breakthrough are consistent with modeled predictions, with no impacts on effluent water quality.

Brine treatment

The Envirogen brand SBA-IX treatment units were installed with a brine processing unit (BPU) to treat the liquid hazardous waste brine to non-hazardous. The resulting solids are hazardous according to the California specific Total Threshold Limit Concentration (TTLC) procedure. The BPU removes chromium from the waste brine via chemical precipitation with calcium polysulfide, which is an NSF 60 approved chemical that does not require pH adjustment. The waste brine is then disposed of as non-hazardous material. Although Envirogen had successfully used calcium polysulfide at other sites, the higher

concentrations of calcium polysulfide used at the Salinas locations produced a strong hydrogen sulfide odor in the enclosed space containing the BPU. Additional ventilation has been added to remedy this issue.

SBA-IX Full-scale Performance

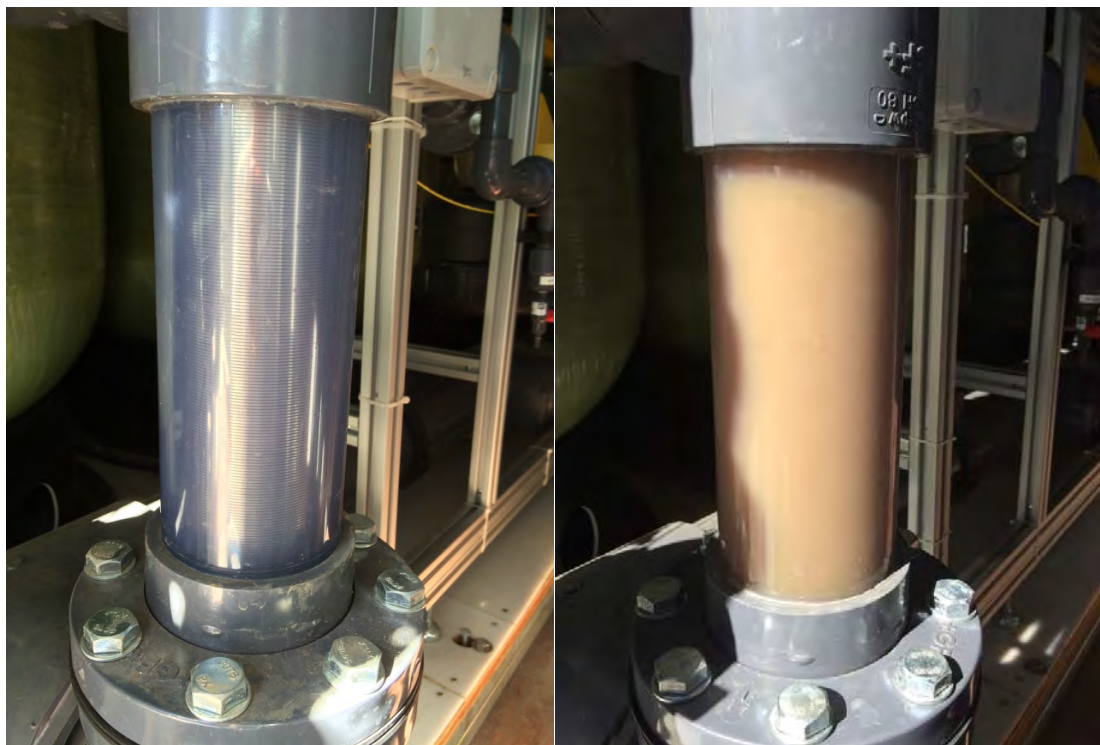
Resin Performance

For Willows Station 9 at the full-scale and in the most recent round of pilot-scale tests, the Purolite A600E 9149 has not been performing as well as in the initial pilot studies. Refer to Figure 11 above, where the original pilot bed volumes to breakthrough was approximately 10,000, while the most recent pilot study resulted in an average 6,000 bed volumes to the 8 µg/L treatment threshold. This is discussed in further detail in the Section 6.1 SBA-IX Loading, and Purolite is currently investigating the discrepancy.

Resin Loss

Ionex equips each resin vessel with a resin trap to prevent offsite resin release. Figure 65 shows two photos from Station 9 that highlight the importance of resin traps in the design of SBA-IX systems. In this instance, as seen in Figure 65, it is believed the column valve was closed before the isolation valve, which caused brief pressure transients that pulled resin out of the bottom of the column. A recent software change has increased time delay so now the outlet valve closes before inlet valve. Since the software change there have not been any resin loss incidences. The vessels that had this issue will be inspected for mechanical damage.

Figure 65 Station 9 resin trap with no resin, on the left, and full of resin, on the right



Head Loss

Prior to treatment installation, several of the wells had issues with sand and silt production. On an ion exchange treatment unit, it is standard to install a pre-filter to catch particulates before they can go into

the resin. A photo of several bag filters after use can be seen in Figure 66. Initially, the wells were equipped with 50 µm bag filters. Fines that are small enough to pass through the filters became lodged in the distribution laterals and in the resin bed adding to the high differential pressure. The size gradation of the solids should have been characterized prior to installation of the treatment units.

Some sites have experienced higher than expected differential pressure through the treatment unit. Fifteen psi was the expected headloss. At Station 7 in Dixon, the headloss has been as high as 50 – 60 psi, resulting in less production. The design flow is about 1,400 gpm and the well is currently operating at 900 gpm. Three contributing factors have been identified: fine particles were not being captured by the bag filter, the filter did not seat into the housing properly, and the resin at some sites required re-grading. This resulted in material bypassing the filter and being strained on the surface of the resin bed.

Figure 66 Bag filter photo



Re-grading the ion exchange beds is a process where the beds are backwashed with treated water to lift up the resin and let it stratify by size. The fine sediment that went through the bag filters will also be removed. Challenges to re-grading result from the cargo containers providing limited access to the SBA-IX vessels and the current design of the vessels that does not allow for significant bed expansions.

Sites experiencing headloss challenges were backwashed to remove the sediment that has accumulated in the resin and to re-grade the resin bed. Cal Water sites that have been through this process and it has improved the headloss, at least temporarily. The differential pressure before re-grading at Dixon Station 1 was 30 psi and after re-grading, it was 15 psi. In addition, at all sites, 5 micron filters were installed at the beginning of September, 2016 to increase particle capture pre-SBA-IX.

Appendix C:
Proposition 50 Research Plan

California Water Service, Willows Proposition 50, Chapter 6(b), Grant

Research Plan for Project Number P50-1110003-290

July 2, 2015

Prepared by Corona Environmental Consulting, LLC

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Introduction

On April 15, 2014 the Division of Drinking Water (DDW) issued a final Maximum Contaminant Level (MCL) for hexavalent chromium [Cr(VI)] at 10 µg/L. Every well (total of 8 active wells) in the Cal Water Willows system contains Cr(VI) over the draft MCL, and will require treatment to remain active. Cal Water is currently proceeding to implement four full-scale strong-base anion exchange (SBA-IX) treatment systems in the Willows district.

Since California is the first state to have a Cr(VI) MCL, Cal Water will be among the first to implement full scale Cr(VI) treatment using strong base anion exchange (SBA-IX). As such, many questions need to be confirmed regarding treatment performance, reliability, and operability, as well as waste generation, handling, and disposal.

In 2013, Cal Water conducted a desktop water supply and treatment technology screening study, which concluded that four wellhead treatment systems would be required to satisfy the water supply needs of the district, while the remaining four wells will be placed in stand-by. In each case, SBA-IX was identified as the most cost effective treatment approach when compared to other promising technologies, namely reduction/coagulation/filtration (RCF) and weak base anion exchange (WBA-IX).

SBA-IX treatment has traditionally been implemented by water utilities, including Cal Water, for nitrate, arsenic, perchlorate, and other groundwater contaminant treatment. illustrates a simplified SBA-IX treatment process schematic.

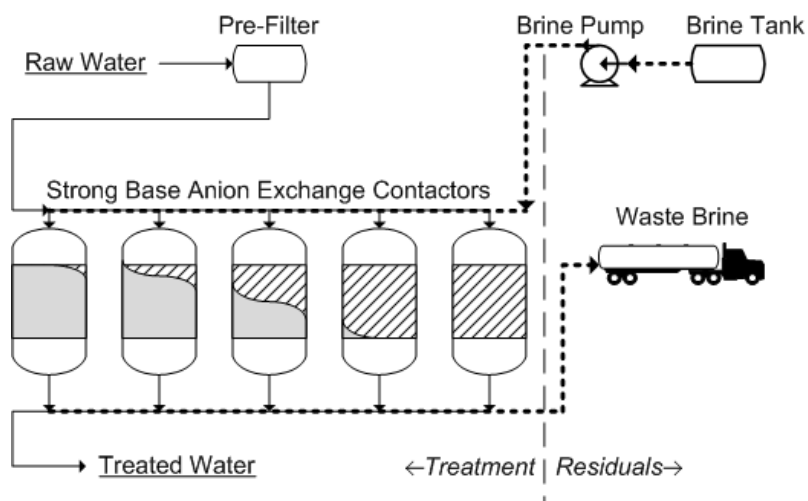


Figure 1 Typical SBA-IX treatment process schematic

As compared to WBA-IX, SBA-IX has the benefit of being able to operate without pH depression, which eliminates the need for acid and caustic chemical feed and storage systems on-site. Additionally, pH depression for WBA-IX is challenging and costly for water supplies such as those in Willow with relatively high alkalinity.

The disposal of the regenerant brine is often the greatest challenge to implementing SBA-IX treatment systems. Waste brine is anticipated to contain Cr(VI) concentrations ranging from 25 mg/L to greater than 800 mg/L and chloride concentrations of 25-60 g/L. Other co-contaminants removed by the SBA-IX process (e.g. arsenic, vanadium, selenium, uranium) can also accumulate in the waste brine. An

important aspect of research will be to track these micro-contaminants through the treatment and regeneration process. Previous bench- and pilot-scale investigations have shown the accumulation of these co-contaminants in the regenerant brine while their concentration in the source water was below the detection limit.

Disposal options depend on the availability high strength liquid waste discharge (e.g. >25 g/L chloride) and metals disposal limits (e.g. total and/or Cr(VI)). In the absence of a brine line for ocean discharge or acceptable local wastewater discharge, waste brine is typically trucked off-site for disposal.

Since the waste brine will contain greater than 5 mg/L Cr(VI), the current California threshold for hazard classification, the waste brine must either be a) treated and/or managed at a brine disposal facility, or b) treated to render it non-hazardous with the resulting treated brine disposed of at a brine disposal facility and the solids disposed of at an appropriate non-RCRA California hazardous waste facility or LLRW facility depending hazard characterization. At this point in time, Cal Water anticipates disposing of the SBA-IX brine waste or other treatment residuals at approved disposal facilities.

While physically very similar to SBA-IX systems for nitrate removal, the cost of SBA-IX for Cr(VI) treatment is expected to be significantly lower due to the efficiency of the Cr(VI) removal process. SBA-IX systems that target nitrate removal are typically regenerated after only 500 to 1,000 bed volumes (BVs) of treatment. Pilot scale testing in Willows has indicated that 12,000 to over 40,000 BVs of treatment can be achieved before regeneration.

In addition to supporting the construction of what will be among the first SBA-IX installations specific for Cr(VI) treatment, a central focus of this Proposition 50 project is investigating strategies to reduce the overall volume of spent brine. This objective will be met through both full- and pilot-scale regeneration optimization and brine minimization research.

The lessons learned from the design and permitting phase of the project will be summarized in a report format so that they can help other California utilities navigate this process. The findings of the regeneration optimization and brine minimization research will also be disseminated, assisting utilities select the most appropriate technology for treatment.

Research Team

This research will be led by Corona Environmental Consulting on behalf of California Water Service. Tarrah Henrie will serve as project manager with technical oversight from Dr. Chad Seidel. Craig Gorman and Eli Townsend will support technical delivery of the research. Cal Water staff involved in the project include Robert Thompson, Sophie James, and Geoff Fulks. Mike Waite and Phil Chandler of IonexSG will support IonexSG relevant aspects of the full-scale demonstration and pilot-scale testing.

The research team will also include support from other partners. Dr. Peter Green and graduate students at the University of California, Davis will provide analytical support. Portions of the brine treatment will be conducted by Dr. Miguel Arias-Paic at the U.S. Bureau of Reclamation and Dr. Haizhou Liu at the University of California, Riverside.

Communication Partner

The California/Nevada section of AWWA is interesting in participating in, supporting, and advertising the Task 17 webinars that are proposed to distribute the results of this research.

Pilot Testing Key Conclusions

Cal Water conducted extensive SBA-IX pilot testing in Willows in an attempt to optimize the treatment process, and lower both capital and operational costs. Based on the pilot testing, several key design parameters were established. Please refer to the report titled “California Water Service Company: Summary of Site Specific Testing of SBA-IX Treatment for Cr(VI) at the Dixon and Willows Districts” for a much more detailed discussion of the results of the bench and pilot scale testing.

1. Four different resins were tested. At each of the wells tested in Dixon and Willows, the Purolite A600E/9149 resin had the best chromium removal performance.
2. Between 12,000 and 40,000 bed volumes (BVs) of water were treated prior to 8 ug/L chromium breakthrough.
3. A shortened Empty Bed Contact Time (EBCT) of 90 seconds was adequate to provide chromium removal. This was used during pilot testing to demonstrate breakthrough in a shorter period of time compared with longer EBCT conditions (greater than 2 minutes) traditionally used at full-scale.
4. Traditional Hydraulic Loading Rate (HLR) for regenerable SBA-IX is 5 gpm/ft². A higher HLR allows for a smaller footprint, installation of less capital equipment, and provides a substantial cost savings. Pilot testing successfully demonstrated that HLRs up to 30 gpm/ft² could achieve the same Cr(VI) removal as compared with the traditional 5 gpm/ft²; albeit with higher pressure drop across the resin bed and corresponding increases in operational costs due to higher pumping costs.
5. Nitrate and sulfate concentrations in the raw water correlate with how many bed volumes of treatment are achieved before chromium breakthrough. As expected higher nitrate and sulfate concentrations lead to fewer bed volumes to chromium breakthrough.
6. Bicarbonate was demonstrated for chromium regeneration as compared to traditional chloride regenerant. The bicarbonate regeneration was shown to take more than 10 BVs, which is significantly more than the BVs required with chloride regeneration. At this time regeneration with bicarbonate is technically possible, but not economically favorable.
7. Efficiency gains due to this pilot testing and the competitive bidding process have saved the Cal Water Willow’s district approximately \$7 Million, as compared to the original cost estimates.

Research Plan Discussion

There are two categories of SBA-IX research that will be investigated during this project: full scale demonstration and pilot scale testing.

The goal of the full scale demonstration is to determine how closely the full scale performance matches the pilot scale testing, and look at the performance of full scale treatment over a nine month period. Since the Willows full-scale SBA-IX units are among the first to be installed in the nation for Cr(VI) drinking water treatment, this is an excellent opportunity to document performance and start-up issues.

It is anticipated that this information will be useful for many other utilities considering Cr(VI) treatment using SBA-IX.

Additional pilot scale testing targets the goal of further reducing the operations and maintenance costs by minimizing the amount of waste brine produced. Research will be conducted on two styles of regeneration: IonexSG segmented regeneration and conventional regeneration. IonexSG is the vendor selected by Cal Water for the full scale installations in Willows. Since Cal Water and other water systems may elect to install conventional SBA-IX, this research aims to minimize conventional regeneration waste volumes as well.

Full Scale Research

Tasks 1 – 5 Full Scale Demonstration

Previous pilot testing investigated and confirmed several key design parameters subsequently used in the full scale design. This portion of the research is designed to compare the full scale treatment to the pilot scale results from phase 1 of the pilot work. These tasks will begin with the start-up of treatment at Willows Well 9-01 and will be tracked for 9 months.

Task 1 - For the full scale demonstration, HLRs of 9.9 to 13.9 gpm/ft² during normal running conditions and 13.3 to 17.2 gpm/ft² during regeneration will be tested. This is a higher HLR than traditionally used with SBA-IX treatment.

Task 2 - The full scale units are designed with an EBCT between 1.8 and 2.3 minutes. The adequacy of the EBCT will be demonstrated.

Task 3 – Although pilot testing did examine performance to complete chromium breakthrough it is expected that slightly fewer bed volumes of treatment will be achieved with each regeneration. There are anions that are so tightly held on the resin that they do not come off during regeneration. It is important to understand how the treatment performance will change over time. The number of BVs to breakthrough will be tracked for multiple regeneration cycles.

Task 4 – At pilot scale, for Well 9-01, about 12,000 BV of water were treated before the Cr(VI) concentration reached 8 µg/L. The goal is to determine if the pilot scale results accurately predict the full scale results, so that other water systems can better understand how much to trust pilot scale results.

Task 5 – The start-up of any new treatment system can be expected to face some delays and challenges. For all four of the Willows wells to be treated with SBA-IX for Cr(VI), the challenges and solutions will be documented. Documenting the start-up phase issues will help other water systems anticipate, avoid and better prepare for the challenges.

Task 6 Analytical Method Validation

Traditional analytical methods for metals in brine solutions using ICPMS are negatively impacted by high salt concentrations. Samples are frequently diluted more than 20 times to lower the salt concentration. Unfortunately this reduces the accuracy and sensitivity of the analytical method. Recent advances with ICPMS using High Matrix Introduction (HMI) offers the opportunity to directly analyze brine solutions without dilution; however these approaches have not yet been utilized or validated for ion exchange

brine solutions. In order to better characterize metals in brine solutions throughout this research, the new ICPMS using HMI analytical method will be implemented and validated.

Tasks 7 and 8 Individual Column Breakthrough and Elution

In some ways these two tasks are a more detailed examination of Task 3. Task 3 will look at how the performance of the overall treatment unit changes over time.

Task 7 - Three times during the first 9 months of treatment the same ion exchange column will be monitored closely for breakthrough. This detailed examination of performance may enhance our understanding of the overall performance. Breakthrough curves will be developed and prepared.

Task 8 - Three times during the first 9 months of treatment the same ion exchange column will be monitored closely during regeneration to understand when, and at what concentrations the anions are coming off the resin. Elution curves will be developed and compared.

Task 9 and 10 Sulfate Return

There are three brine segments, and a rinse segment produced by an IonexSG style regeneration as illustrated in Figure 1. The initial portion of the brine is a lower concentration salt solution that removes the majority of the sulfate from the resin (shown in purple window). The second step is a higher concentration salt solution that removes the Cr(VI) (shown in yellow window). Third is the recovered brine segment (shown in red window). The final step (shown in blue window) is a rinse step. The rinse brine is reused in the next regeneration to create the sulfate laden brine. Eventually the goal is to trickle the sulfate portion of the lower concentration salt solution brine into the untreated or treated water. This sulfate-laden lower concentration brine requires characterization before considering reintroduction to the untreated or treated water. Recovered brine is reused to make the chromium laden waste in the next regeneration, and is also reused as recovered brine during the subsequent regeneration. The chromium laden brine fraction will be the only waste product. Pilot scale brine treatment and reuse will determine if it may be possible to treat and reuse this portion of the brine.

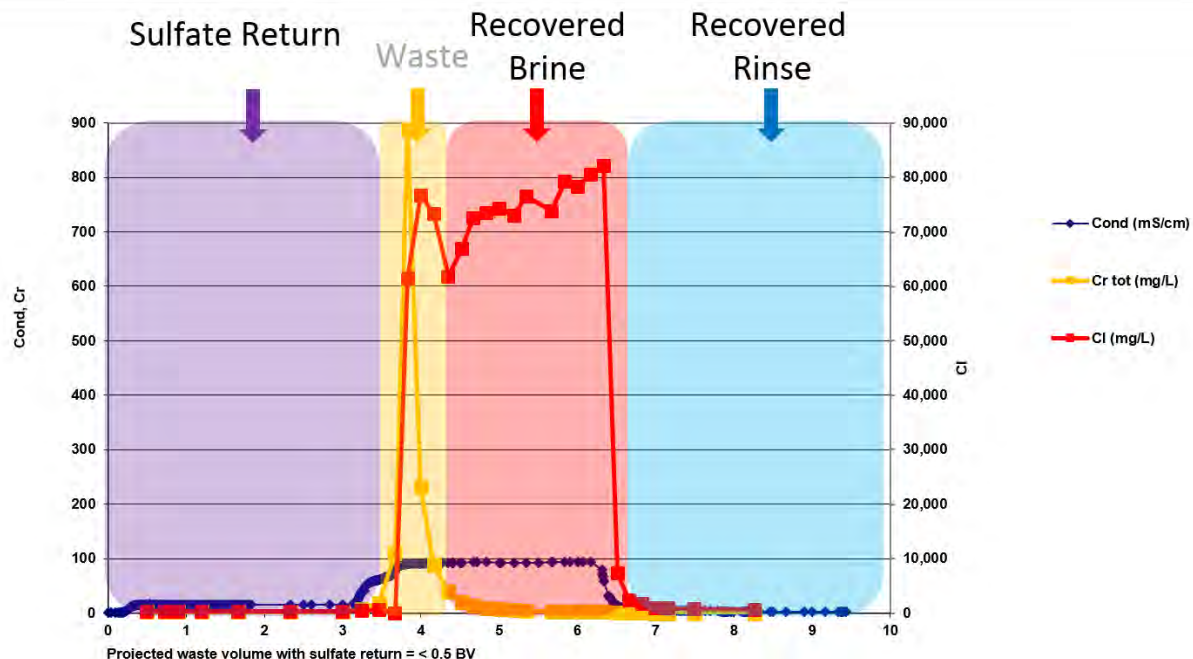


Figure 2 IonexSG style regenerations brine fractions

Task 9 - During chromium removal many other anions are simultaneously removed, including nitrate, sulfate, arsenic, uranium, selenium and vanadium. Anions that are not even detectable in the raw water can accumulate at on the resin in higher concentrations. The sulfate return segment of the brine needs characterization to understand the micro-contaminants that may be coming off the resin along with the sulfate and support Division of Drinking Water (DDW) approval to return the sulfate return fraction to the untreated or treated water. Time series characterization of the sulfate return, as well as bulk sampling, will be conducted to examine their water quality.

IonexSG can model the expected sulfate return water quality. The model will be compared to the measured concentrations of anions in the sulfate return.

Task 10 – If DDW approves full scale implementation of sulfate return, extensive testing of the sulfate return portion of the brine will be conducted at all 4 wells. Treated water will also be tested to verify the predicted water quality.

Pilot Scale Testing

Task 11 and 15 Chemical Treatment of Chloride and Bicarbonate Brine

Spent regenerant brine will be chemically treated to precipitate chromium and determine if the resultant supernatant can be reused. For other locations with potential direct sewer discharge, brine treatment may have applicability to onsite waste treatment, so that the resulting liquid waste is non-hazardous.

Bench-scale testing of chemical precipitation of brine solutions will be comprised of a series of jar tests to be conducted at the University of California, Davis. The Cr(VI) treatment efficacy of 4 precipitant chemicals, namely ferrous sulfate/chloride, sodium dithionite, sodium bisulfite with and without pH adjustment, and calcium polysulfide will be tested. A summary of the proposed precipitants is provided in Table 1, including the technology provider that has proposed the approach and if the precipitant is a DTSC Permit by Rule listed Cr(VI) reductant. These precipitants have been selected for testing based upon peer-reviewed literature, past testing results (e.g. ferrous sulfate testing of regenerant brine as a part of the Soquel Creek Water District Water Research Foundation Tailored Collaboration Project #4488), and technology provider recommendations.

Table 1 Summary of precipitants to be tested

Precipitant	Technology Provider	DTSC Permit by Rule Listed Cr(VI) Reductant
Ferrous Sulfate or Ferrous Chloride	NA	Yes
Sodium Dithionite	Ionex SG	No
Sodium Bisulfite	Ionex SG	Yes
Sodium Bisulfite w/ adjusted pH	Evoqua	Yes
Calcium Polysulfide	Envirogen	No

For each chemical precipitant, a range of 4 doses will be tested at ambient pH unless otherwise directed by the technology providers. Samples pre- and post- chemical addition will be collected for laboratory analysis for Cr(VI), total chromium, arsenic, selenium, vanadium and uranium. A mass balance approach will be taken to estimate the solid waste profile.

Task 11 – Chemical precipitation treatment and testing will be completed using the sodium chloride brines for both the IonexSG style and the conventional style regeneration. For the IonexSG style regeneration, only the chromium laden portion of the brine will be tested.

Task 15 – Chemical precipitation treatment and testing will be completed using the sodium bicarbonate brine produced by the conventional style regeneration in phase 1 pilot testing of the research.

Task 12 Other Brine Treatment

In addition to the chemical brine treatment methods that will be tested, six other treatment methods will be evaluated, in conjunction with our research partners. For the IonexSG style regeneration, only the chromium laden portion of the brine will be treated.

Table 2 Additional brine treatment methods

Treatment method	Who will test the treatment method
Membrane treatment	Dr. Miguel Arias-Paic, Bureau of Reclamation
Chemical removal of CrVI, followed by membrane treatment	Dr. Miguel Arias-Paic, Bureau of Reclamation
TiO ₂ brine treatment	Dr. Haizhou Liu, University of California at Riverside
Adsorbant media - Toxsorb	Corona
Adsorbant media - Tusaar	Corona or Tusaar

Nanofiltration membrane treatment offers the potential to separate larger mono and multivalent anions such as Cr(VI), sulfate and nitrate from the chloride ions used for regeneration. Given the relatively infrequent regeneration frequency for SBA-IX Cr(VI) treatment, nanofiltration membrane treatment would require a small treatment system operating at a moderate recovery (e.g. 50-80%) to produce a high quality recovered chloride brine.

Chemical treatment, with ferrous chloride, before the membrane may remove much of the chromium, and increase the chloride concentration. Although a 2 step brine treatment process may be too complicated for field application it worth understanding the options available.

Treatment with titanium dioxide (TiO₂) is an interesting new technology. At this time the media is not NSF approved, and is not ready for full scale application. The media can be prepared with a magnetic iron based center.

Toxsorb and Tusaar are modified granular activated carbons that are used to remove high concentrations of metals in industrial applications.

Samples pre- and post- brine treatment will be collected for laboratory analysis for Cr(VI), total chromium, arsenic, selenium, vanadium and uranium. A mass balance approach will be taken to estimate the solid waste profile.

Task 13 Micro-contaminant Concentrations as a Result of Brine Reuse

The most significant cost savings left for SBA-IX treatment of Cr(VI) is minimizing the amount of waste generated. The IonexSG style regeneration has already made tremendous progress on that front. At Willows well 9-01, the treatment unit will treat about 12,000 BV before breakthrough. The waste rate is estimated to be about 0.5 BV, if sulfate return is allowed. This is a 0.004% waste rate. Brine treatment and reuse could lower this even more.

Potentially, the more significant waste rate reduction will be for the conventional style regeneration. The waste rate for conventional regeneration is estimated to be about 0.03% for well 9-01.

For the Ionex style, regeneration it will be necessary to make sure that pilot brine has similar quality to full scale brine. Since there is not a full scale conventional SBA-IX treatment unit, the pilot unit brine will not be compared to a full scale brine.

Brine reuse will be demonstrated at pilot scale. The brine will be treated to remove Cr(VI), by the method determined to be the best in the brine treatment portion of the study. Micro-contaminants and anions will be analyzed after each reuse. The brine will be reused at least 2 times. The untreated and treated water will also be analyzed after regeneration to look for any changes in water quality as a result of brine reuse.

The full scale untreated brine will be characterized for each of the Willows sites.

Task 14 Chloride regeneration, followed by bicarbonate rinse

During phase 1 of the pilot research, sodium bicarbonate was tested as an alternate regenerant to sodium chloride. Many wastewater plants cannot accept additional chloride. While it was clear that

treated chloride waste brine could not be discharged to sewer, an additional concern was that the very small increase in chloride in the treated water could prevent the permitting of the full scale SBA-IX treatment using a chloride brine. Bicarbonate regeneration would avoid potential sewer implications with increased chloride concentrations. However, while bicarbonate can be used as a regenerant, it takes many more BVs of regenerant than chloride to remove the chromium as compared in Figure 2.

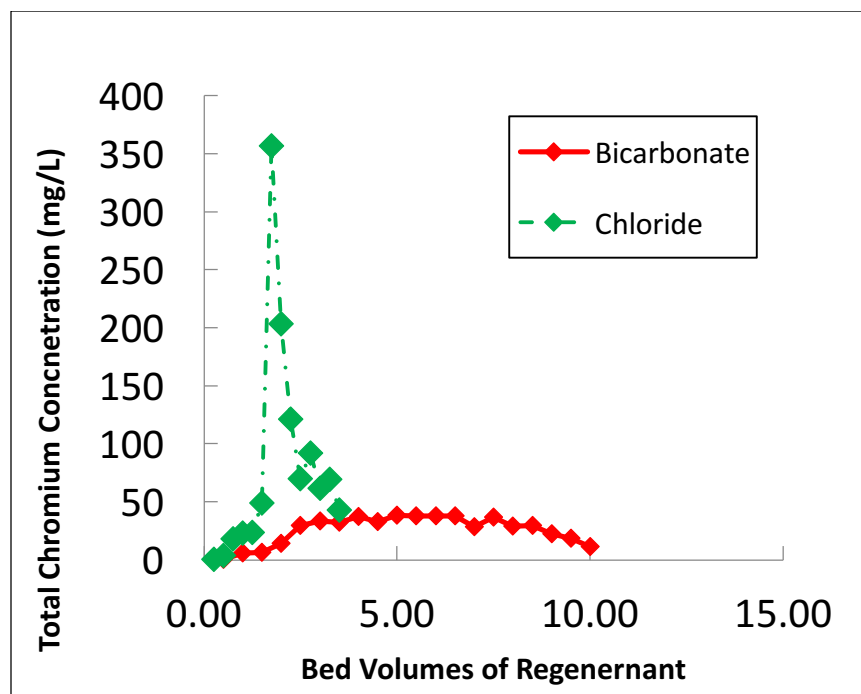


Figure 3 Bicarbonate regeneration, compared to sodium chloride regeneration

As an alternative, another option that may give water utilities the efficiency of sodium chloride regeneration, and minimize the chloride in the finished water is to first regenerate with sodium chloride, and then rinse with bicarbonate. This method will be tested at pilot scale. The bicarbonate will be reused at least two times. Micro-contaminants and anions will be characterized in the used brine and treated water.

Communication and Reporting

Tasks 16 and 18 Quarterly Progress Reports and Final Report

Quarterly reports and a final report are requirements of the Proposition 50, Chapter 6(b) funding agreement. The first quarterly report is due 3 months after the research plan is approved. The quarterly reports will be structured so that they can be compiled into the final report. Corona is responsible for the reporting. Cal Water will provide information on the full scale start-up issues and performance.

Task 17 Webinars

Four webinars are planned to communicate the pilot, and full scale research with the Division of Drinking Water engineers and drinking water utilities. The California Nevada section of AWWA is

interested in partnering on the webinars for utilities. Each of the webinars is planned to be about two hours long.

The goal is to record the webinars for utilities, and to make them available on demand, for free. The DDW website, and others, can then link to this resource.

The first two webinars will be held in the fall of 2015. The goal is to discuss the various Cr(VI) treatment technologies, including WBA-IX, Reduction/Coagulation/Filtration and SBA-IX. The results of the pilot scale work to date will also be presented. The webinar for the Division of Drinking Water will be very technical in nature. The webinar for water systems will have a practical tone, and will be targeted to small water systems with Cr(VI) issues.

The last two webinars will be held at the conclusion of the project. The new full scale treatment results will be presented, along with the results of the new pilot scale research.

Task 19 Communication with DDW and Cal Water

Regular meetings will be held with Cal Water Operations staff, Water Quality staff, and Engineering staff during the duration of the research. Corona will take the lead on the meetings. Corona will also take the lead on communication with the DDW staff, including Eugene Leung and the local Associate, District and Regional Engineers. Cal Water will be informed of all communications with DDW.

Prop 50 Research Plan Overview

Table 3 Full scale demonstration summary

Full Scale Demonstration	
Task #	Task Description
1	Determine if a 9.9 to 13.9 gpm/ft ² HLR is adequate during non-regeneration conditions
2	Test 1.8 to 2.3 minutes EBCT at full scale
3	Demonstrate Cr(VI) removal with multiple regenerations
4	Determine if pilot scale BVs to breakthrough correlate with full scale results
5	Start-up documentation (challenges)
6	Develop and validate a method to analyze the high sodium chloride and sodium bicarbonate liquid wastes.
7	Individual column breakthrough curves on one column, on run 1, 5 and 10 (this may be modified to 1, 3 and 6 to meet the timeline)
8	Individual column elution curves on one column, on run 1, 5 and 10 (this may be modified to 1, 3 and 6 to meet the timeline)
9	<p>Characterization of the sulfate portion of the brine for the Ionex style regeneration</p> <p>9.1 The sulfate laden portion of the brine will be characterized, with an end goal of DDW allowing this portion of the weak brine solution to be slowly trickled into the untreated or treated water</p> <p>9.2 Time series sampling and holding tank (homogenized) sampling</p> <p>9.3 Theoretical calculations of the anion concentrations of the treated water with and without the sulfate portion will be provided</p> <p>9.4 Weekly anion analysis, and micro-contaminant analysis will be conducted on the treated water with the sulfate feed, if this process is implemented at full scale. These additional weekly analyses will be conducted for one month to validate the theoretical concentrations</p>
10	If full scale brine reuse is allowed by DDW based upon pilot scale research, then the reused brine will be analyzed for relevant micro-contaminants and anions.

Table 4 Pilot scale research summary

Task #	Ionex Style Regeneration	Conventional Regeneration Approach
11	<p><i>Sodium chloride brine jar testing</i></p> <ol style="list-style-type: none"> 1. Jar testing with 4 chemicals will be conducted. 2. The resultant supernatant will be analyzed to determine if it has been made into a non-hazardous waste. 3. A mass balance approach will be used to estimate characteristics of the solid waste. 	<p><i>Sodium chloride brine jar testing</i></p> <ol style="list-style-type: none"> 1. Jar testing with 4 chemicals will be conducted. 2. The resultant supernatant will be analyzed to determine if it has been made into a non-hazardous waste. 3. A mass balance approach will be used to estimate characteristics of the solid waste.
12	<p><i>Other treatment of brine</i></p> <ol style="list-style-type: none"> 12.1 The treated portion, and the resultant waste will both be characterized, if possible. If not enough solid waste is generated then a mass balance approach will be used. 12.2 Membrane treatment 12.3 Chemical removal of CrVI, followed by membrane treatment 12.4 TiO₂ brine treatment 12.5 Adsorbant media (Toxsorb, Tusaar) 	<p><i>Other treatment of brine</i></p> <ol style="list-style-type: none"> 12.1 The treated portion, and the resultant waste will both be characterized, if possible. If not enough solid waste is generated then a mass balance approach will be used. 12.2 Membrane treatment 12.3 Chemical removal of CrVI, followed by membrane treatment 12.4 TiO₂ brine treatment 12.5 Adsorbant media (Toxsorb, Tusaar)
13	<p><i>Understanding micro-contaminant concentrations as a result of brine reuse</i></p> <ol style="list-style-type: none"> 13.1 Make sure that pilot brine has similar quality to full scale brine. 13.2 At the pilot scale brine reuse will be demonstrated. The brine will be treated to remove Cr(VI), by the method determined to be the best in the brine treatment portion of the study. The brine will be reused at least 2 times. 13.3 Micro-contaminants will be analyzed after each reuse. 13.4 The untreated and treated water will also be analyzed after regeneration to look for any changes in water quality as a result of brine reuse. 	<p><i>Understanding micro-contaminant concentrations as a result of brine reuse</i></p> <ol style="list-style-type: none"> 13.1 The pilot brine will not be compared with full scale brine, as this is not the treatment technology that has been implemented in Willows. 13.2 At the pilot scale brine reuse will be demonstrated. The brine will be treated to remove Cr(VI), by the method determined to be the best in the brine treatment portion of the study. The brine will be reused at least 2 times. 13.3 Micro-contaminants will be analyzed after each reuse. 13.4 The untreated and treated water will also be analyzed after regeneration to look for any changes in water quality as a result of brine reuse.

Task #	Ionex Style Regeneration	Conventional Regeneration Approach
	13.5 At full scale the untreated brine will be characterized for each of the Willows sites.	
14		<i>Chloride regeneration, followed by bicarbonate rinse</i> 14.1 Regeneration with sodium chloride to remove chromium followed by bicarbonate rinse, to minimize the change in chloride in the treated water. 14.2 The bicarbonate will be used at least two times
15		<i>Bicarbonate brine jar testing</i> 15.1 Jar testing with 4 chemicals will be conducted. 15.2 The resultant supernatant will be analyzed to determine if it has been made into a non-hazardous waste. 15.3 A mass balance approach will be used to estimate characteristics of the solid waste.

Table 5 Communication plan and reporting summary

Communication and Reporting	
Task #	Task Description
16	Quarterly update reports
17	<p>Webinars</p> <ol style="list-style-type: none"> 1. How many? Four total - pilot results (one for DDW, one for water systems), final results (one for DDW, one for water systems). 2. How long? 2 hours. 3. Topics to present in first webinars: <ol style="list-style-type: none"> a. Cr(VI) treatment overview SBIX, WBIX, RCF/RCOF, chemical reduction (half of the time) b. More specific research 4. When? First two soon, second two after final report. 5. Make available online, for viewing, for free, on demand. DDW to post link. 6. DDW District engineers, and staff engineers webinars – Susan Brownstein. Two hour window available every few months. Eugene to work with the treatment committee. 7. Broader audience – partner with CA/NV AWWA <ol style="list-style-type: none"> a. Small system emphasis
18	Final written report
19	Ongoing communication with Cal Water and DDW

Project Timeline

Table 6 Tasks that begin after the research plan has been approved

		Month after research plan approval														
Task #	Task Description	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15
6	Analytical method development															
15	Bicarbonate brine jar testing															
16	Quarterly progress reports															
17	Webinars															
18	Final report															
19	Project communication															

Table 7 Tasks that begin after full scale treatment start-up

		Month after full-scale startup								
Task #	Task Description	1	2	3	4	5	6	7	8	9
1	Demonstrate 12.9 to 13.9 gpm/ft ² HLR									
2	Demonstrate 1.8 to 2.2 minutes EBCT									
3	Demonstrate Cr(VI) removal with multiple regenerations									
4	Determine if pilot scale BVs to breakthrough correlate with full scale results									
5	Start-up documentation (challenges)									
7	Individual column break through curves on one column – 3 times									
8	Individual column elution curves on one column – 3 times									
9	Characterization of the sulfate portion of the brine for the IonexSG style regeneration									

Table 8 Tasks that begin after pilot start-up

		Month after pilot startup								
Task #	Task Description	1	2	3	4	5	6	7	8	9
11	Sodium chloride brine jar testing									
12	Other treatment of brine									
13	Understanding micro-contaminant concentrations as a result of brine reuse									
14	Chloride regeneration, followed by bicarbonate rinse									

= Critical path item