

**IWC 25-05: Regenerable Activated Alumina
and Hybrid Ion Exchange Resins for the
Removal of Fluoride, Silica, and Arsenate
from High-TDS Sodium Chloride Brines**

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ABSTRACT

This paper presents the findings of two extended column studies evaluating the use of Activated Alumina and a Hybrid Ion Exchange resin for purifying sodium chloride brines. The first study focused on the removal of fluoride and arsenate from a 1% brine using a granular aluminum oxide adsorbent (GAOX) traditionally applied in potable water treatment. The second study examined the removal of silica and arsenate from an 8.7% brine using a hybrid anion exchanger (HAIX) with high selectivity for silica and arsenate, originally developed for nuclear fuel pool water treatment. Each column underwent two regeneration cycles and three exhaustion cycles to assess performance under simulated industrial operating conditions. The results provide insights into the effectiveness, selectivity, and operational feasibility of these treatment technologies for high-TDS brine purification. The study serves as a foundation for full-scale equipment design, and if available, an update on plant design and operational implementation will be presented.

Dedication

This work is dedicated to my friend and mentor, Peter Meyers, whose exceptional intelligence and decades of experience provided the critical insight into the chemistry and practical knowledge of ion exchange resin regeneration that made this process possible. Peter's deep understanding of the fundamental science and unwavering belief in innovative solutions guided us toward success. His mentorship has been invaluable not only in developing these purification technologies, but in teaching us that the most challenging problems often yield to persistent application of sound chemical principles and creative engineering thinking.

Thank you, Peter, for showing that what seems impossible today is tomorrow's standard practice.

Acknowledgments

The author gratefully acknowledges the essential contributions of our project collaborators who made this work possible. Blue Brine provided financial support and technical expertise that enabled this comprehensive column study evaluation. Their commitment to advancing brine purification technologies and willingness to invest in innovative solutions was instrumental in bringing this research to bear.

Sincere appreciation to NORAM Engineering for their expertise in scaling this technology from the laboratory to the pilot plant and ultimately to full-scale industrial implementation. Their engineering insight and process design capabilities have been crucial in bringing this from the lab to the plant.

This collaborative effort demonstrates the power of combining fundamental research, industry partnership, and engineering excellence to solve complex water treatment challenges.

Introduction:

Two column studies were run to simulate the operational performance, resin regeneration and subsequent cycle performance of two ion exchange media for two separate brine purification processes. The two investigations are as follows and will be reported separately.

STUDY 1: Fluoride Removal from Brine with added Arsenate using ResinTech SIR-900 (GAOX)

GAOX is a granular aluminum oxide adsorbent intended for the removal of Fluoride from water. GAOX is also useful for the removal of arsenate, selenate, and lead from water. The application under study is the removal of Fluoride and Arsenic from a high TDS Sodium Chloride brine. Existing application data is traditionally from potable water treatment applications. The experiment is designed to simulate the operating conditions of the customer's product stream.

STUDY 2: Silica Removal from Brine with added Arsenate using ResinTech ASM-125 (HAIX)

HAIX is a HYBRID Anion Exchanger with a high affinity for Silica and Antimony. HAIX is also selective for the removal of arsenate from water. The application under study is the removal of Silica and Arsenic from an extremely high TDS Sodium Chloride brine. Existing application data is traditionally from Nuclear Fuel Pool water treatment applications. The experiment is designed to simulate the operating conditions of the customer's product stream.

STUDY 1: Fluoride Removal from Brine with added Arsenate using GAOX

GAOX is a granular aluminum oxide adsorbent intended for the removal of Fluoride from water. GAOX is also useful for the removal of arsenate, selenate, and lead from water. The application under study is the removal of Fluoride and Arsenic from a high TDS Sodium Chloride brine. Existing application data is traditionally from potable water treatment applications. The experiment is designed to simulate the operating conditions of the customer's product stream.

A 1-inch diameter column filled 24" deep with GAOX contained 312 ml of resin. The initial flow rate was set at 77 ml/min. Over the duration of the study, the flow rate varied by +/- 2 ml/min.

The column was used for all process work including exhaustion, regeneration, and subsequent cycles. Per the initial performance prediction calculations, the bed is expected to run for 800 Bed Volumes.

Samples were taken once per day for the first five days and then four samples a day for the final two days to capture the expected breakthrough. The column did not show any signs of shrink or swell. During the backwash portion of the regeneration, the GAOX appeared to "fluff up" to 25 inches. During the second regeneration, the GAOX packed a little tighter, returning the bed volume to 24 inches.

There were three samples that were contaminated with Iron. Results were recognized and confirmed by re-analysis. Since there is no iron in the system, we believe these are an anomaly or possible sample contamination from other work in this experiment.

Influent Brine Analysis:

66 Gallons of brine was made for each exhaustion run. The synthetic brine was made as follows, targeting 10,000-11,000 ppm of Sodium Chloride (NaCl) containing approximately 4 ppm of Fluoride and 0.1 ppm of Arsenate.

Table 1: GAOX Brine Batch Recipe

Saturated Brine (26.4%)	2	Gallons
DI Water	64	Gallons
Fluoride	998.40	mg Fluoride
Arsenic	24.96	mg Arsenic

Total Gallons: 66 Gallons

NOTE: BRINE Ph must be 5.5 to 6.0, 3 batches made for a total of 198 gallons of brine

The Influent Brine was made in the laboratory and analyzed for metals by ICP-MS and IC. The recipe is as shown below. A total of 198 gallons of brine was made. The brine was analyzed over the course of the run. The brine analysis on Day 1 and Day 18 is shown. The brine analysis for the extension of Run#3 is also listed.

Table 2: Brine Analysis for GAOX study

influent	F (ppm)	As (ppb)	Al (ppb)	Fe (ppb)	NaCl (ppm)	pH	Cond.
Day 1	3.743	84.734	546	<1	11630	5.94	17.36
Day 18	3.77	111.8	6.927	<1	11724	5.94	19.07
Run #3 extension	3.61	108.987	4.363	<5	10109	5.08	15.3
Average	3.76	98.27	276.46	<1	11677.00		

Column Capacity and Leakage Runs

The column capacities have been estimated at 757 bed volumes. The experiment was run to 800 bed volumes and sampling frequency increased to capture the end of the run. The flow rate was ¼ Bed Volume per minute (1.87 gpm per cf, 4-minute EBCT). The actual run time was 3200 minutes, 53.3 hours, 6.67 days. Actual Column Capacity appears to be 600 Bed Volumes.

Table 3: Exhaustion Run

Flow Rate	0.25	Bed Volumes /min (bv/min)
Flow Rate	78	ml/min
Run Length	3200	Min
	53.3	Hours
	6.7	Days

Effluent samples were collected and analyzed for Fluoride, Arsenic, Aluminum and Iron. The effluent pH and conductivity were also measured.

Table 4: Sampling / Test Protocol

Test	Qty	Comment
Test Effluent for F, As, Al, Fe, pH and Conductivity	1	per day for 5 days, collecting the effluent in a batch
	4	per day for days 6 and 7, collecting the effluent in 4 separate batches and test individually

Figure 1: Exhaustion Curves for Fluoride:

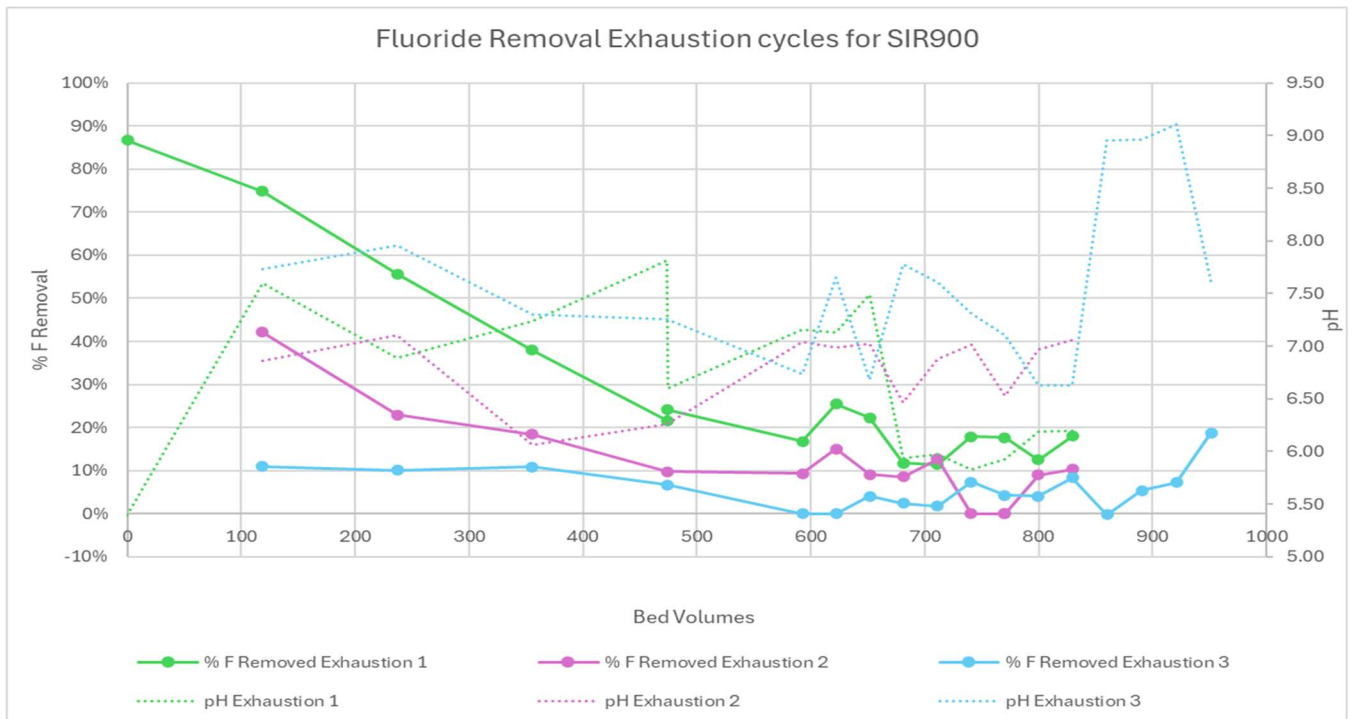
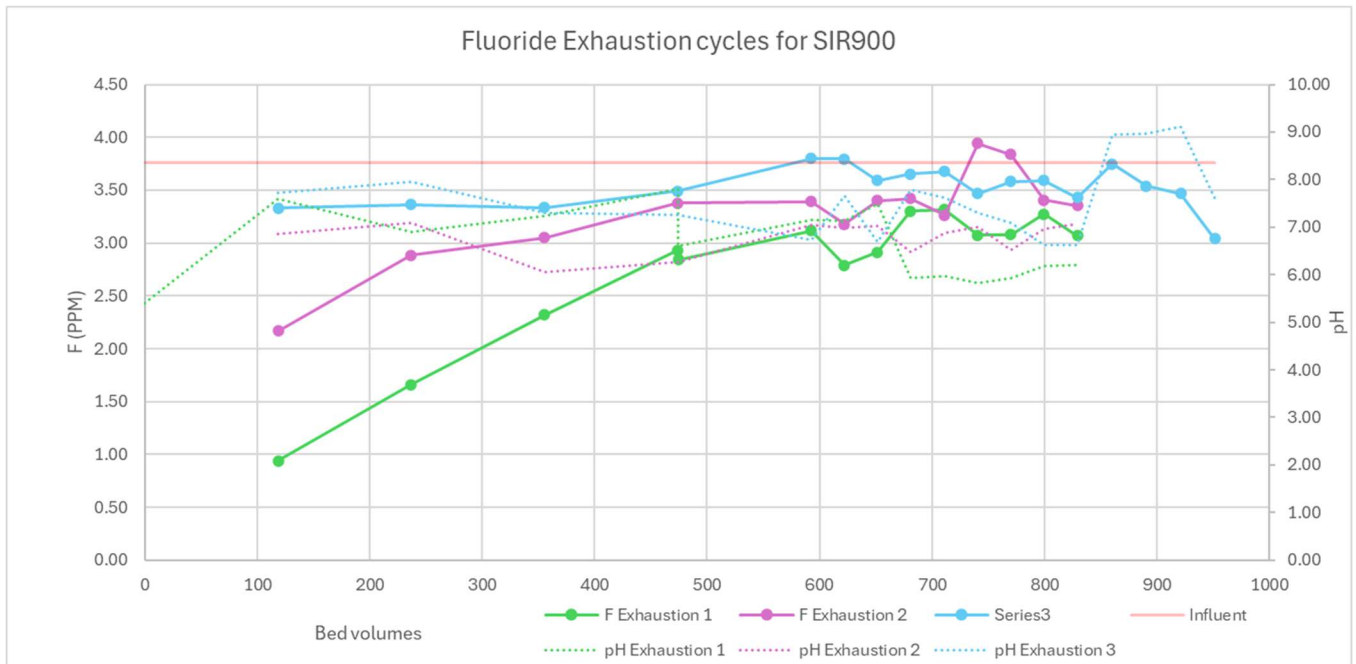
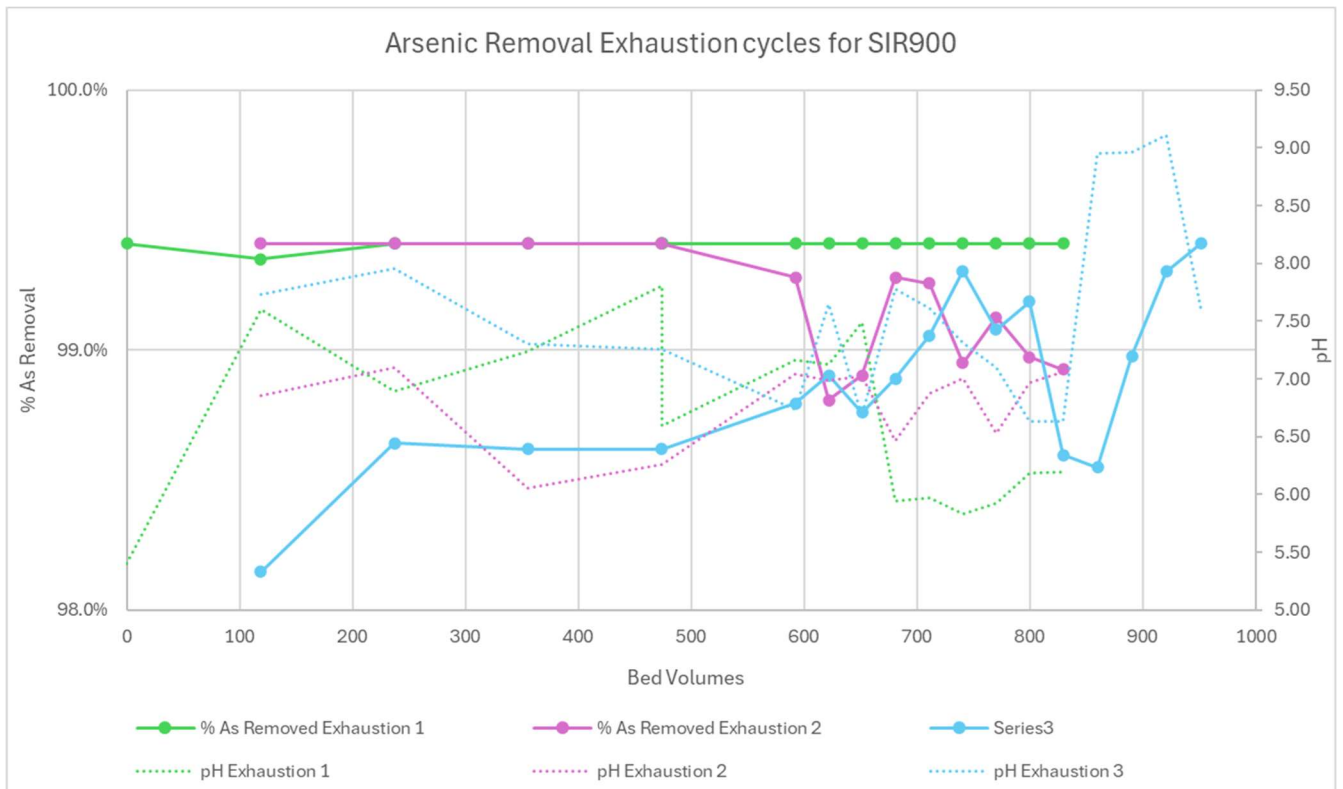
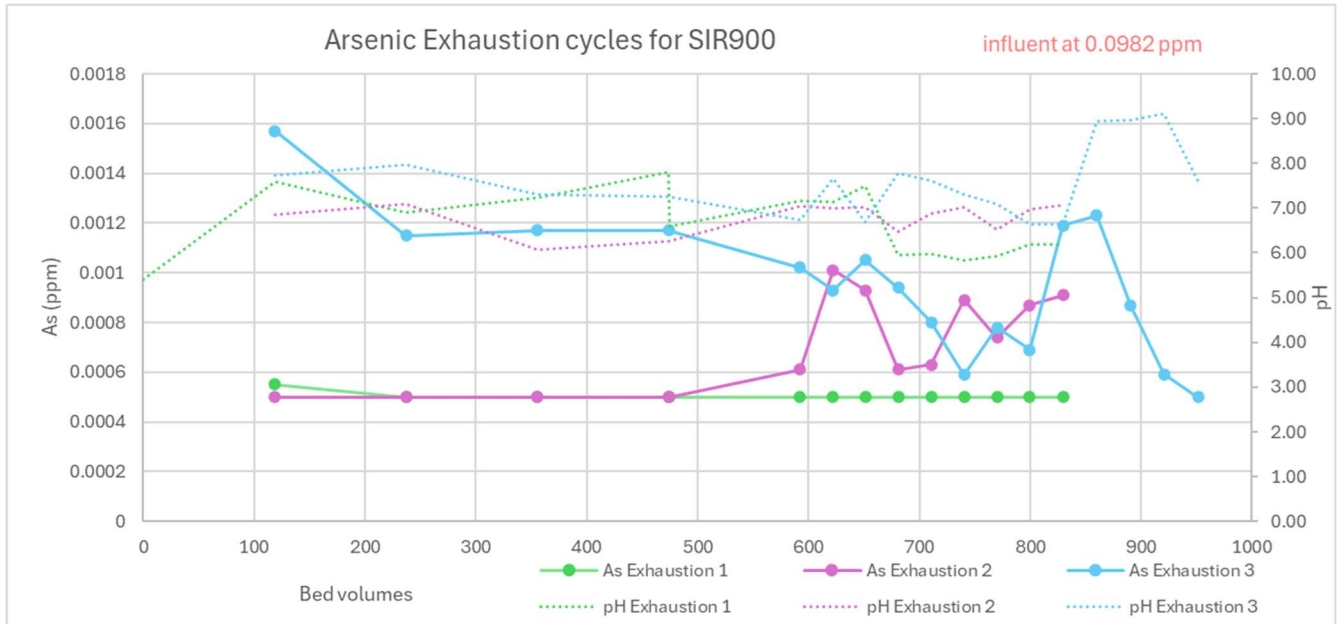


Figure 2: Exhaustion Curves for Arsenic:



Regeneration of the GAOX Column

Regeneration is the reversible exchange of contaminants removed during the service cycle. Regeneration is not a perfect process. Some contaminants will remain on the resin after the regeneration process. Leakage is these residual contaminants coming off the resin at very low levels during the subsequent cycles.

Regeneration of the column will be performed according to the Regeneration Schedule below. The effluent from the NaOH regeneration and displacement rinse will be collected and analyzed for Volume, Fluoride, Arsenic and Aluminum.

- Regeneration Outline
 - Backwash (up flow)
 - Caustic injection, (downflow)
 - Caustic displacement (downflow)
 - Caustic rinse (downflow to effluent pH 9.0 to 9.5)

Table 5: Regeneration Protocol Followed in Study *

Step	Process	flow ml/min	time min	Volume (L)	Comments
1	Sweeten off (fresh water downflow)	89	7	0.624	2, BV
2	Backwash (upflow) 20 mins		10	1.0	50% Expansion
3	Caustic inject (downflow)	13	30	0.39	20.02 g NaOH / ml resin, 4 #/cf NaOH
	Caustic Soak		30	0.38	Liters, 5% NaOH
4	Caustic displacement (downflow)	10	30	0.312	
5	Caustic rinse (downflow) (effluent pH 9.0 to 9.5)	104	30	3.12	
6	Sweeten on (with process liquor) (downflow)	156	4	0.624	

141 Minutes
2.4 Hours
6.45 liters

* Regenerant will be collected and tested for Volume, Fluoride, Arsenic and Aluminum

Detailed Conclusion's:

Fluoride Removal:

The brine was run through the lab column a total of 3 exhaustion and 2 regeneration cycles. Fluoride and Arsenic Effluent Limits were not specified so the results were evaluated as % Removal. The results showed diminishing returns / diminished removal of Fluoride on each subsequent cycle.

The initial results were discussed, and two observations were made that may be degrading the performance of the GAOX for Fluoride removal. First, flow rate may be a contributing / controlling factor due to the high salt content. Experimental flows were 0.246 BV/min or 1.85 gpm/cf. Literature suggests that over 1.0 gpm/cf may negatively affect Fluoride removal performance.

Additionally, the optimal pH for the GAOX is 5.5. A literature review suggests that pH management could yield better results. The average effluent pH was 6.9 with an influent pH of 5.9. There was enough Brine to run an additional 122 Bed Volumes. A decision was made to drop the Brine pH from 5.9 to 5.08 and continue Run #3.

Run #3 had run the entire 829.5 bed volume. No regeneration was done, only a continuation of the run. There was significant improvement in the removal of Fluoride. Fluoride removal started at 0% and improved as the run continued. At the end of the run, 951.5 Bed Volumes, the Fluoride removal had improved to 19% and was trending towards continued improved performance.

Table 6: Summary of Fluoride Removal Over Requested Conditions (Runs 1-3) and with Decreased pH Conditions (Run3, Continued)

Fluoride Removal Performance	Maximum	Minimum	Average	Comments
Run 1	87%	11%	30%	Around 600 Bed volumes the run appeared to be over. This coincided with the peak in Aluminum leakage
Run 2	42%	0%	13%	
Run 3	8%	0%	4%	
Run 3, Continued	19%	0%	8%	Fluoride Performance improved with a reduction in the inlet pH

Arsenic Removal:

Arsenic removal was excellent over the course of all 3 runs. Arsenic / Arsenate removal was 99%. Most of the Arsenic removed by the GAOX remained on the resin after regeneration. Arsenic Appeared to accumulate on the resin during the second cycle. It is anticipated that arsenic will continue to accumulate on the resin over multiple cycles. It is possible that Arsenic will foul the resin or limit the removal capacity of Fluoride.

Table 7: Mass Balance Accounting of Arsenic Loading and Elution

	Cycle 1	Cycle 2
mg Arsenic Removed	21.93	40.40
Eluted	3.46	7.68
Left on the Resin	18.47	32.73

Per the Fluoride optimization theory, the Brine pH was reduced from 5.94 to 5.08 and run #3 was continued. Arsenic Removal improved at the lower inlet pH.

Aluminum Throw and Resin Attrition:

The initial brine had 546 ppb of Aluminum. No Aluminum was added to the brine and the presence of aluminum suggests that perhaps some dust from the GAOX got into the initial brine. Additional brine had to be made for this experiment and the second batch of Brine contained only trace amounts of Aluminum (4.3 t 6.9 ppb). The first data point showed 12,012.6 ppb of Aluminum believed to be dust released into the effluent upon start up. An initial backwash or rinse of the material in the field will eliminate this concern.

There did not appear to be an increase in Aluminum during the first 3 original runs. However, Aluminum did appear to leak upon bed exhaustion for Fluoride around 600 Bed Volumes. The extension of Run #3 where the Brine pH was lowered showed an initial spike in Aluminum that quickly resolved and reduced dramatically. It appears likely that lowering the pH has a beneficial effect on Aluminum leakage.

There was Aluminum lost during the regeneration of the GAOX. A Mass Balance of Aluminum suggested that about .86% of the product is lost for each regeneration resulting in a life span of 117 regenerations.

Table 8: Aluminum Loss During Regeneration

Total Al Lost, mg	Al Lost Per Regen (g)	Bulk Density GAOX /cu ft	mg of GAOX @ Start	% of Material Lost	Number of Column Regens for Absolute Attrition
3,256.67	1.63	38	190	0.86%	117

Further analysis of the regeneration and the Aluminum loss during the various steps shows that 60-70% of the attrition takes place during the Caustic Displacement rinse. It would be worth investigating a process improvement step whereby the caustic concentration is modified to reduce Aluminum loss.

Table 9: Regeneration 1 - Aluminum Lost by Regeneration Step

Regen 1	V (l)	pH	Al (ppm)	mg Al Lost	% of total Aluminum Attrition
SW off	0.71	6.00	16.4	11.61	1%
BW	1	6.33	3.2	3.22	0%
C IN	0.5	6.21	6.5	3.24	0%
C DIS	0.475	12.80	1961.2	931.57	61%
C rinse	3.6	12.32	156.5	563.56	37%
SW on	0.6	7.05	11.3	6.76	0%
TOTAL:				1519.97	100%

Table 10: Regeneration 2 - Aluminum Lost by Regeneration Step

Regen 1	V (l)	pH	Al (ppm)	mg Al Lost	% of total Aluminum Attrition
SW off	0.76	6.91	3.9	3.00	0%
BW	1.91	6.83	3.7	7.10	0%
C IN	0.475	12.86	1023.5	486.16	28%
C DIS	0.31	13.44	3867.4	1198.88	69%
C rinse	3.96	12.17	6.5	25.90	1%
SW `on	0.46	9.77	34.0	15.66	1%
TOTAL:				1736.70	100%

Visual Inspection and Particle Size Analysis:

The GAOX was evaluated before and after the study. There was a noticeable difference in the shape of the particles but there did not appear to be an increase in the -50 MESH fines.

Table 11: Particle Size Analysis of GAOX Fine Mesh Before and After Study

Screen Size	SIR900 New	SIR900 Used
-50	0.1	0.1

On the left is the GAOX starting material (New) before the study was conducted. On the right is the GAOX end material (Used) pulled from the column.

Figure 3: GAOX Microscope Examination Pre/Post Column Study



STUDY 2: Silica Removal from Brine with added Arsenate using HAIX

HAIX is a dual action hybridized resin intended for the removal of antimony from water. HAIX is also useful for the removal of Silica, Arsenic, and radio nuclides from water. The application under study is the removal of Silica and Arsenic from a high TDS Sodium Chloride brine.

Existing application data is traditionally from potable water treatment applications. The experiment is designed to simulate the operating conditions of the customer's product stream.

A 1-inch diameter column filled 24" deep with HAIX contained 312 ml of resin. The initial flow rate was set at 97 ml/min. Over the duration of the study, the flow rate varied by +/- 2 ml/min.

The column was used for all process work including exhaustion, regeneration, and subsequent cycles. Per the initial performance prediction calculations, the bed is expected to run for 217 Bed Volumes.

Samples were taken four times per day for the duration of each cycle to capture the expected breakthrough. The resin bed showed signs of shrinking. The resin bed shrank a maximum of 1 inch at the end of the run. After the regeneration, the HAIX returned to its original bed height of 24 inches.

Influent Brine Analysis:

23.7 Gallons of brine will need to be made for each exhaustion run. The number of runs will need to be defined at the beginning of the experiment to minimize the cost of brine make up and analysis. The synthetic brine will be made as follows, 87,000 ppm, +/- 2,000 ppm of Sodium Chloride (NaCl). The brine will be spiked with 47 ppm, +/- 5 ppm of Silica and .03 to 0.5 ppm of Arsenic. The pH will be 4.5 to 5.5.

Table 12: HAIX Brine Batch Recipe

Saturated Brine (26.4%)	7.2	Gallons
DI Water	17.5	Gallons
Silica	9.83	ml
Arsenic	46.8	mg Arsenic

Total Gallons: 25 Gallons

The influent brine was made in the laboratory (Table-12) and analyzed for metals by ICP-MS to acceptance test prior to starting the evaluations (Table-13). A total of 74.19 gallons of brine was made. The brine used in the run's extension was the same as the other initial runs but with a modification of the influent Brine pH from 5.41 to 8.11

Table 13: Brine Analysis of HAIX Study

	Cond. mS/CM	pH	TDS	Si (ppm)	SiO ₂ (ppm)	As (ppm)	AsO ₄ (ppm)	Fe (ppm)
Target		4.5- 5.5	87,000 +/- 2000	22.0	47.0	0.03- 0.05		
Lab	146.6	5.41	87960	22.0	47.0	0.0395	0.0732	0.150

NOTE: The solution was made with the above recipe with one minor tweak. The order of addition was changed so that the silica was added first, followed by the sodium arsenate, and finally the brine solution. It was found that following the original order of addition created a white flocculent. We tested a small batch with the order below and there was no flocculent formed. All samples generated by this project were analyzed using the prescribed analytical methods. All data was reviewed by the Analytical Manager (TS) and Senior Ion Exchange Technologist (LG).

Column Capacity and Leakage Runs

The column capacities were estimated at 217 bed volumes. The experiment was run to 300 bed volumes to capture the full run. The recommended flow rate of 0.31 Bed Volume per minute (2.32 gpm per cf, 3.2-minute EBCT) was utilized. The estimated run time is 16.0 hours and was broken into 2 days running with 8 hours each day. Effluent samples were collected and analyzed for Silica and Arsenic as follows: 4 per day.

Table 14: HAIX Exhaustion Run Conditions

Flow Rate	0.31	bv/min
Flow Rate	96.42	ml/min
Run Length	967.74	min

Total's: 16.13 Hours
2.02 Days

Effluent samples were collected and analyzed for Silica (SiO₂), Arsenic (As), and Iron (Fe). The effluent pH and conductivity were also measured.

Table 15: Sampling / Test Protocol

Test	Qty	Comment
Test Effluent for SiO ₂ , As, Fe, pH, and Conductivity	4	per day for 2 days, collecting the effluent in a batch

Figure 4: Exhaustion Curves for Silica in HAIX Study:

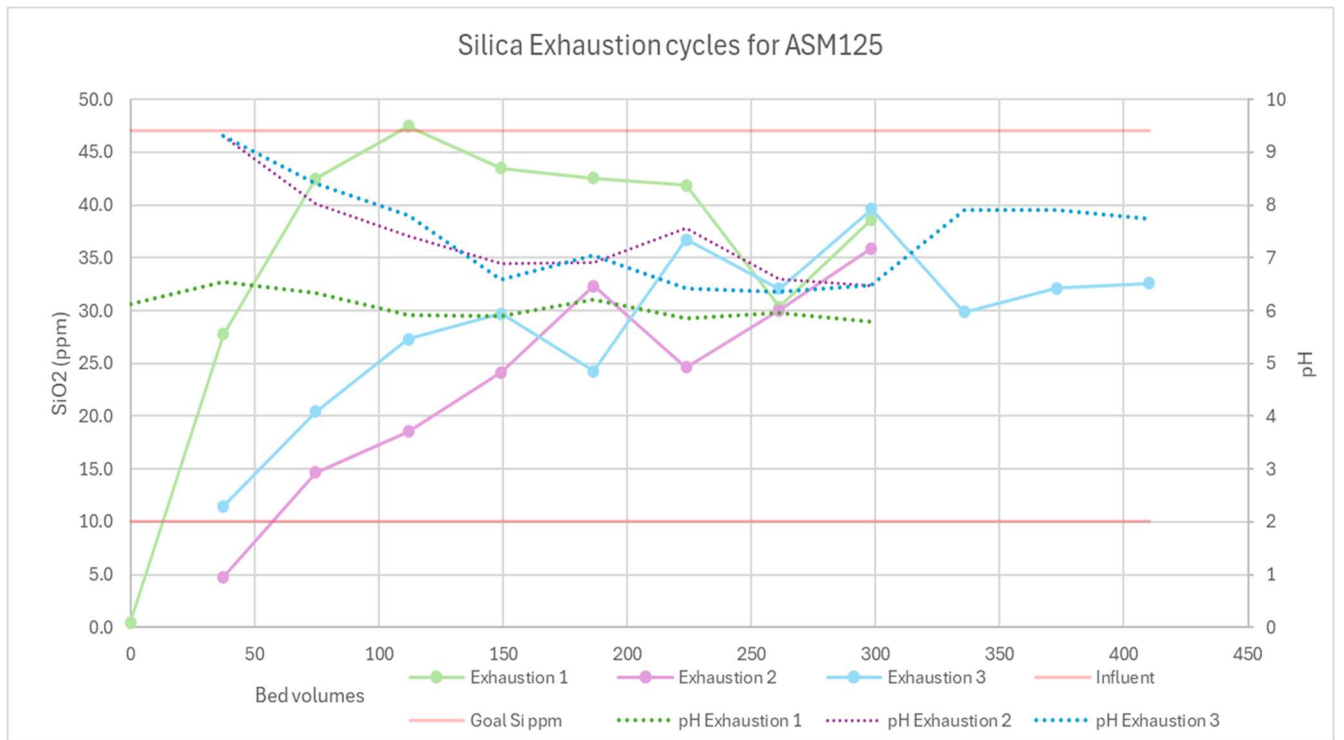
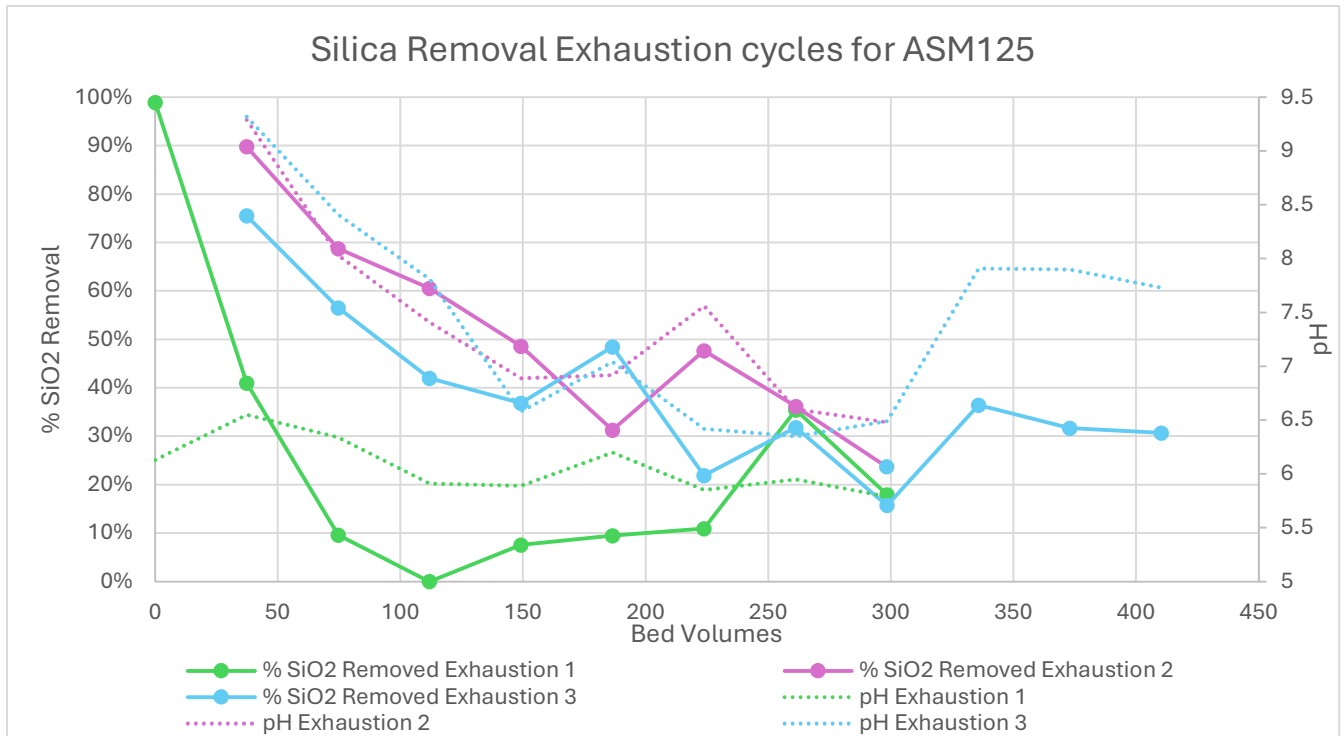
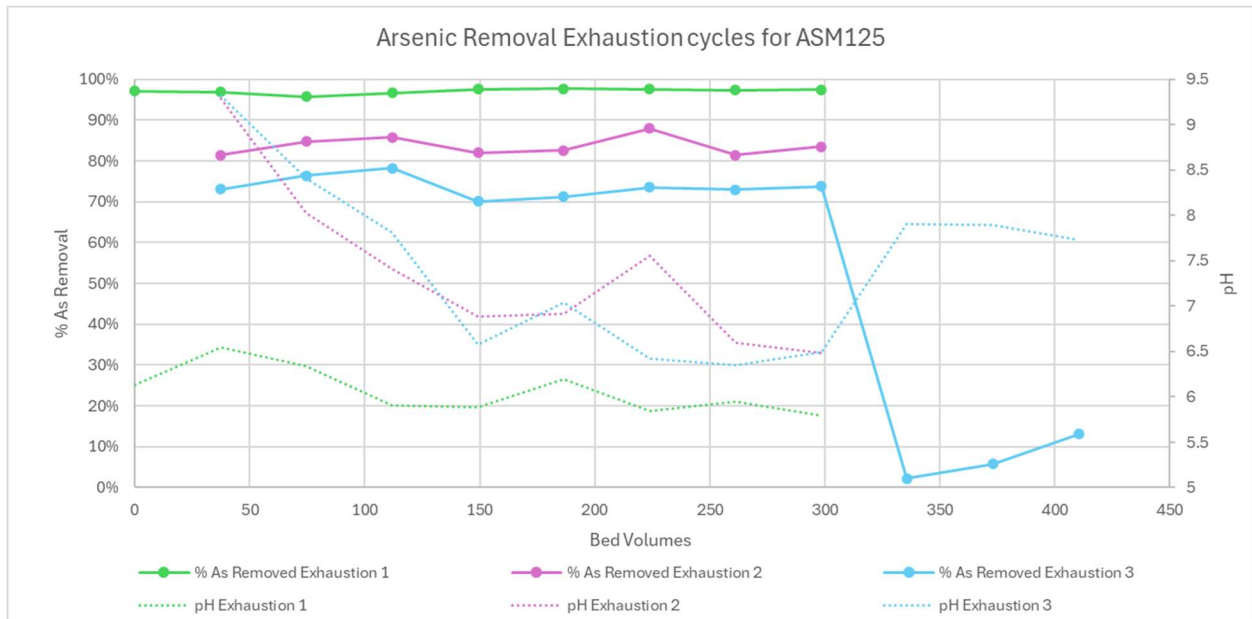
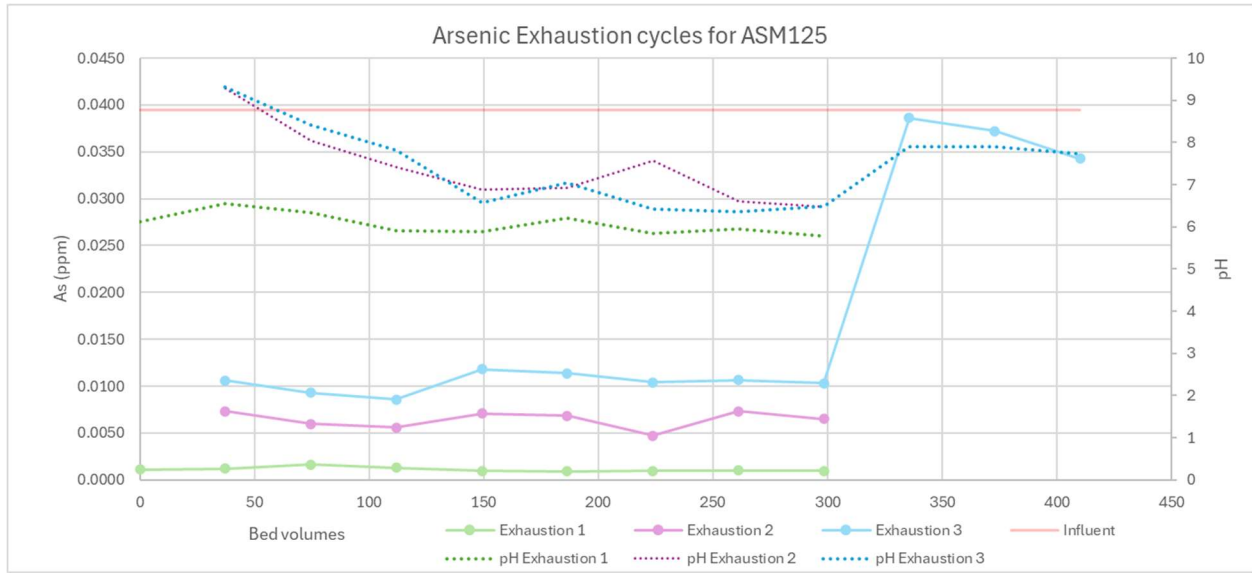


Figure 5: Exhaustion Curves for Arsenic in HAIX Study



Regeneration of the HAIX Column

Regeneration is the reversible exchange of the contaminants removed during the service cycle. The regeneration of Silica from HAIX is a chemically slow and temperature dependent process. HAIX regeneration will require 4% Sodium Hydroxide. The total regeneration procedure will take approximately 6 hours. Some contaminants will remain on the resin after the regeneration process. Leakage is these residual contaminants coming off the resin at very low levels during the subsequent cycles.

Regeneration of the column will be performed according to the Regeneration Schedule below. The effluent from the NaOH regeneration and displacement rinse will be collected and analyzed for Volume, Silica and Arsenic.

- Regeneration Outline
 - Backwash (up flow)
 - Caustic injection, (downflow)
 - Caustic displacement (downflow)
 - Rinse
 - Acid Neutralization

Table 16: HAIX Regeneration Protocol

<u>Step</u>	<u>Process</u>	<u>flow ml/min</u>	<u>time min</u>	<u>Volume</u>	<u>Comments</u>
1	Sweeten off (fresh water downflow)	15.60	30	468.00	1.5, BV
2	Backwash (up flow)		10		50% Expansion
3	Caustic injection #1*	11.88	80	50.05	g NaOH / ml resin
	Caustic injection #2*	11.88	80	0.95	Liters
4	caustic displacement (downflow)	7.80	60	468.00	1.5 BV
5	caustic rinse (downflow) (effluent ph 9.0 to 9.5)	31.20	60	1872.00	6 BV
6	Sweeten on (with process liquor) (downflow)	7.80	30	468.00	1.5 BV

350 Minutes

5.83 Hours

*Total Caustic Dose was 10 # NaOH per cf at 5% concentration. Regenerant will be collected and tested for Volume, Silica and Arsenic.

Silica Removal:

The brine was run through the lab column a total of 3 exhaustion and 2 regeneration cycles. Silica Effluent Limits were specified at 10 ppm, so the results were evaluated in ppm and as % Removal. The results showed that an initial regeneration /preconditioning step is necessary. The two subsequent runs are similar to each other, displaying the same general trends.

Additionally, the optimal pH for the HAIX for Arsenic is <5.5, but a higher pH benefits the uptake of silica. A literature review suggests that pH management would optimize removal of Arsenic or Silica but not both. The average effluent pH was 7.0 with an influent pH of 5.41. There was enough Brine to run an additional 112 Bed Volumes. A decision was made to increase the Brine pH from 5.41 to 8.11 and continue Run #3.

Run #3 had run the entire 298.4 bed volume. No regeneration was done, only a continuation of the run. There was improvement in the removal of Silica and extra capacity was found with the increase in pH. Silica removal started at 16% and improved to 36% then slightly diminished over the rest of the run. At the end of the run, 410.3 Bed Volumes, the Silica removal had settled down to 31% and was trending slightly downwards. The silica was still improved compared to the lower pH.

To achieve the customer-desired level of Silica in their high TDS process liquor the pH of the solution would have to be adjusted upwards. This would increase the uptake of silica by the resin and help achieve a sub 10 ppm Silica level. This would, however, negatively affect the uptake of Arsenic, which is most selective at pH levels below 5.5.

Table 17- Silica Removal Performance Summary

Silica Removal Performance	Maximum	Minimum	Average	Comments
Run 1	99%	18%	26%	Around 150 Bed volumes the run first appeared to be over. Run two and three both appeared to be over at the predicted time of 300 Bed Volumes.
Run 2	90%	24%	51%	
Run 3	76%	16%	41%	
Run 3, Continued	36%	31%	33%	Silica Performance improved with an increase in the inlet pH

Table 18: Mass Balance of silica for ASM125

	Cycle / Run 1	Cycle / Run 2
mg Silica Removed	717.09	2,225.00
mg of Silica regenerated	329.99	1,074.76
Left on the resin	387.10	1,150.24
% Left on the resin	54%	52%

Cycle 2 loaded more silica due to higher pH conditions post regeneration. Cycle 3 had a similar exhaustion profile and loaded more Silica than cycle 1. Cycle 3 was extended and silica loading further improved with a higher inlet brine pH. HAIX was successfully regenerated after each subsequent run. Roughly 50% of the silica was eluted from the resin. Some precipitation of Silica was present in the bed as noted in figure 7, post column visual inspection. As more cycles are conducted silica may potentially foul the resin. Cleaning may be required with vigorous air mixing, backwashing and/or extended caustic regeneration.

Arsenic Removal:

With a lower pH influent, Arsenic removal was great over all 3 runs. Arsenic / Arsenate removal ranged from 99% to 70%. At a higher pH there was a major drop of Arsenic removal. The Arsenic removal dropped from 74% to 7% after the pH was adjusted to optimize for Silica uptake.

Arsenic was not eluted from the resin during the regeneration process. Arsenic accumulated on the resin during each subsequent cycle. It is anticipated that arsenic will continue to accumulate on the resin over multiple cycles. If HAIX is optimized for Arsenic removal for this application, then optimization of the regeneration will need to be conducted to regain Arsenic selective sites on the media. Historically, HAIX is a single use long life arsenic removal media.

Per the Silica optimization theory, the brine pH was increased from pH 5.41 to 8.11 to determine if Silica removal could be improved and to determine the impact on Arsenic removal related to the pH change to develop suggestions for preferred operating conditions.

Table 19: Arsenic Removal Performance of HAIX

Arsenic Removal Performance	Maximum	Minimum	Average	Comments
Run 1	98%	96%	97%	Arsenic removal was stable during each of the runs, across runs arsenic removal slowly decreased.
Run 2	88%	81%	84%	
Run 3	78%	70%	74%	
Run 3, Continued	13%	2%	7%	Arsenic Performance decreases with an increase in the inlet pH

**Table 20: Mass Balance of Arsenic
(Resin Loading and Regeneration Off)**

	Cycle 1	Cycle 2
mg Arsenic Loaded	3.57	3.08
Eluted	0.005	0.005
Left on the Resin	3.56	6.63

Visual Inspection and Particle Size Analysis:

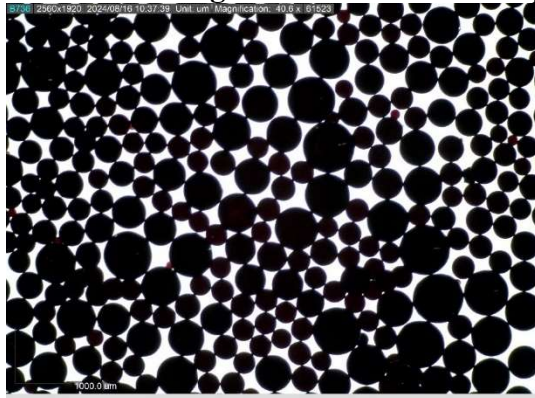
The HAIX was evaluated before and after the study. There was no noticeable difference in the shape of the particles but there appeared to be an increase in the -50 MESH fines. We then rinsed the resin with DI and the -50 was reduced to the same as the starting material. This increase in -50 particles was due to solid silica precipitate being in the bed of the column study after run three.

Table 21: screen size of HAIX before and after column study.

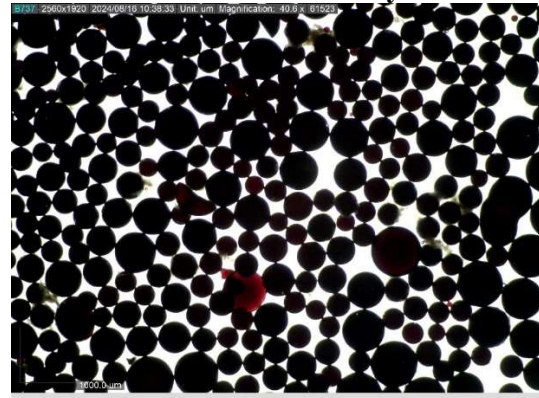
Screen Size	ASM125 SM	ASM125 EM before rinse	ASM125 EM after rinse
+16	0.0	0.00	0.0
+20	2.1	1.47	1.8
+30	22.6	18.05	22.1
+40	60.8	63.57	62.3
+50	13.9	15.40	13.7
-50	0.3	1.52	0.2
EPS	0.37	0.36	0.37
UC	1.41	1.39	1.40

On the left is the HAIX starting material (New) before the study was conducted. On the right is the HAIX end material (Used) pulled from the column.

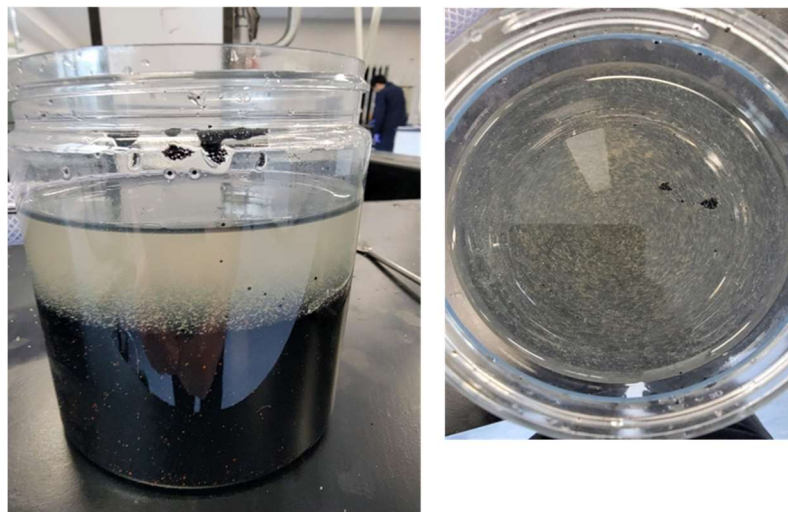
Figure 6: HAIX Microscope Examination Pre/Post Column Study



New (Pre-Column Study)



Used (Post-Column Study)

Figure 7: HAIX visual inspection Post Column Study

When the resin was taken out of the column, there was a slight brown haze in the transfer DI. In the pictures, there appears to be a small amount of precipitate, which looks like the observation made after the first run was completed. This is precipitated Silica.

SUMMARIES

An extended column study was performed utilizing GAOX at 0.25 BV/min contact time utilizing a synthetic brine (TABLE-1) representative of final use conditions. This column study was run over an extended period and the effluent of the column was routinely tested via ICPMS and IC for metals and ion leakage. Additionally, a second column study was completed utilizing HAIX using a different brine (TABLE-12) run at 0.33 bv/min. The resin was used to treat a brine at 47.0 ppm SiO₂ and Arsenic at 0.039 ppm, 39 ppb of Arsenic equates to 72 ppb Arsenate versus the 30-500 ppb experimental design request. The effluent of the column and effectiveness of treatment was determined by ICPMS for metals analysis.

STUDY 1: Fluoride Removal from Brine with added Arsenate using GAOX

Fluoride was removed from the brine. Performance diminished over the 3 runs. Reducing the brine pH improved performance.

Arsenic Removal from the brine was excellent. Arsenic removal dropped off when the brine pH was reduced to improve Fluoride removal performance.

GAOX (Aluminum) was not dissolved during the run, but Aluminum was dissolved during the regeneration. 60% to 70% of the Aluminum loss was during the caustic regeneration / displacement step. This is an area for process improvement.

Optimizing conditions for the removal of Fluoride will negatively affect the removal of Arsenic.

STUDY 2: Silica Removal from Brine with added Arsenate using HAIX

Silica was removed from the brine. A conditioning/initial regen will optimize performance. Increasing the Brine pH improved performance.

Arsenic Removal from the brine was diminished over the three runs. Arsenic removal dropped off when the brine pH was increased to improve silica removal performance.

HAIX did not release iron during the run. No Iron was released from the resin during the regen processes.

Optimizing conditions for the removal of Silica will negatively affect the removal of Arsenic.

Key Results and Conclusions:

1. GAOX was effective at removal of Fluoride up to 600 bed volumes of throughput and then subsequent runs demonstrated a reduction in capacity. Factors influencing the effectiveness of GAOX Fluoride removal can be correlated to the pH and flow rate. This study ran at an inlet pH of 5.94 however further studies on behalf of the client showed that a reduction in pH to 5.08 offered improvement in fluorine reduction. Secondly, the flow rate of 0.246 bv/min (1.85 gpm/cf) was used in this study at the client's request. Further improvement in the GAOX performance based on current literature may be made at a lower flow rate approaching 1 gpm/cf.
2. Arsenic was extremely well removed by the GAOX and never broke through the bed. The regeneration was based solely on the Fluoride Capacity. Arsenic was not eluted during the regeneration and seemed to accumulate on the media.
3. GAOX (Aluminum) was not dissolved during the run, but Aluminum was dissolved during the regeneration. 60% to 70% of the Aluminum loss was during the caustic regeneration / displacement step. Based on the mass balance analysis, each regeneration lost .86% of the media. Estimated life of the media to total loss is 117 regenerations. This is an area for process improvement.
4. HAIX reduced Silica approaching greater than 300 bed volumes utilizing the specified brine and column conditions. A further extension of silica removal capacity was demonstrated at an increased pH of 8.11. HAIX was only effective at meeting the 10-ppm target for a short duration of time immediately after regeneration. To achieve 10 ppm of Silica you would need to raise the pH of the brine to facilitate removal. Even then, your effluent Silica level may be higher than the 10-ppm target. Higher pH negatively affects arsenic removal efficiency.
5. Arsenic removal by the HAIX was constant over the course of each run. Performance seemed to decrease as the pH increased. This was especially noted when the brine pH was adjusted to 8.11 to optimize the silica removal. Arsenic did not seem to elute during the regeneration process. Iron did not leach from the media during any of the runs or regenerations.
6. pH represents a critical process variable for the performance of both GAOX and HAIX. For GAOX, improvements in Fluoride and Arsenic removal are gained at lower pH (ideally pH 5.5). For HAIX, Silica and Arsenic versus pH seem to be inversely proportional. Optimizing one may reduce the performance of the other.
7. HAIX's performance profile for Silica is optimal at pH >8, however it is effective at the pH used in the study (pH 5.41). Precipitated Silica in the bed could be seen and is a potential long-term concern for running at the lower pH.
8. The results of these column studies support that they are viable processes for the purification of the brines. pH control seems to be key in the performance of both media.