THE PERILS OF USING CHLORAMINES FOR PRETREATMENT OF WATER REUSE RO

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Abstract

The use of chloramines has become a standard pretreatment method for biofouling control in water reuse RO. When used in the 2 - 3 ppm range, chloramines have been known to cause only minimal losses in salt rejection, and the benefits are generally believed to far outweigh the risks.

However, in recent years, significant irreversible declines in permeability have been observed at some plants, with no major foulants found on the membrane surface or incoming feed water. These declines were often attributed to irreversible fouling caused by invisible layers of unknown organic compounds in the wastewater effluent feeding the water reuse RO systems. A thorough autopsy and feed water analysis of relatively new water reuse RO plant that was showing an especially severe irreversible decline found no evidence of any type of organic fouling.

A review found several research papers identifying a relationship between dichloramines and loss in membrane permeability. However, at one plant using membranes from 3 different manufacturers and operating at pH \sim 7, trains containing certain models saw an irreversible permeability loss of more than 50% while other trains fully recovered with a high pH CIP. Based on the Cl₂:NH₄ ratios and the operating pH, it was unlikely that any dichloramines were forming at this plant.

Virgin membrane sheet from various manufacturers were evaluated in a cell-test apparatus. The membranes were operated with only NaCl, a bicarbonate buffer, and chloramine at varying pH levels. It was observed that all membranes exhibited a decline in permeability coupled with an improved salt rejection. However, upon cleaning, certain membranes would fully restore to their original performance, while others would show only a temporary improvement and then return to a continued decline in performance.

Streaming potential analysis found that membranes exposed to chloramines had a significantly altered zeta potential as compared to virgin membranes of the same model. A stepwise method combining oxidation with a proprietary chemical CIP was found to fully recover lost membrane permeability, and when placed back in operation, losses in permeability due to chloramine exposure occurred at a far lower rate.

Introduction

As the global demand for clean water continues to grow, membrane-based technologies can provide an energy-efficient means for water desalination, with polyamide thin-film composite (TFC) membranes being the current industry standard for water reuse reverse osmosis (RO). Despite ongoing improvements in membrane technology, biofouling continues to be a major obstacle in optimizing RO system design and operation.

Biofouling increases energy consumption and decreases permeate quality, hindering transport across the membrane and amplifying the effects of concentration polarization (Hoek 2003). Membrane biofouling can be removed with chemical cleanings, but to decrease cleaning frequency, most RO plants will implement pretreatment for their feed water. Sodium hypochlorite is a standard chemical for controlling biological growth, but it is incompatible with most RO membranes. Polyamide membranes are susceptible to halogenation by hypochlorite even at very low doses. Excessive chlorine exposure will cause severe damage to the active polyamide layer of the membrane, eventually resulting in a complete, irreversible loss in salt rejection.

Chloramines have been considered as an alternative to hypochlorite, as one of the few biofouling mitigation solutions that are considered safe within the industry. Monochloramine is commonly accepted as being less damaging to polyamide membranes than free chlorine, though degradation can still occur, leading to losses in rejection (Da Silva 2006). For some water treatment RO plants with severe biofouling issues, the benefits of chloramine dosing can outweigh the risks, especially when moderate rejection losses are acceptable.

In recent years, some water reuse RO plants that use chloramine have started to report losses in membrane permeability and increased energy consumption. These losses have often been attributed to irreversible membrane fouling caused by organic compounds in the wastewater effluent feeding the RO system. However, an in-depth analysis at one plant found no evidence of organic fouling, prompting an investigation into the interaction of the membranes with chloramines.

Case Study: Plant A

A water treatment plant treating tertiary wastewater effluent and maintaining a 3 ppm chloramine residual reported significant issues with four recently installed membrane trains. All trains in this plant were of the same model, referred to as Membrane A. Shortly after installation, the permeability of the new membranes began to rapidly decline. This permeability would initially be recovered with a chemical cleaning-in-place (CIP) procedure but would quickly drop back to pre-cleaning levels. The cleanings showed no apparent impact on the permeability decline trend. The normalized permeability data from one of the RO trains at this plant are presented in Figure 1.



Figure 1: Normalized permeability data from Plant A. Permeability steadily declined and could not be fully restored with traditional cleaning treatments.

A lead element from an affected train was pulled for autopsy, to determine the cause of the permeability loss. Performance tests at the manufacturer's specified testing conditions found the membrane to have a \sim 40% loss in permeability, compared to the manufacturer's wet test (Table 1). The element was only found to have sparce fouling, which could not account for the severe permeability losses. A cell test cleaning study was able to completely remove any remaining foulant, but the performance could not be completely recovered (Table 2).

Analysis of the cleaned coupon by scanning electron microscopy-energy dispersive spectroscopy (SEM-EDS) and Fourier-transform infrared spectroscopy (FTIR) did not identify any fouling that could explain the poor membrane permeability. However, SEM-EDS can only detect elements; thin organic foulant layers can be difficult to differentiate from the polyamide layer of the membrane, as both are carbon-based. FTIR analysis can identify chemical changes to a membrane and organic foulant layers. Unfortunately, FTIR can only resolve deposits that are greater than 0.5 micron in thickness. Due to the apparent absence of foulants, physical and/or chemical changes to the membrane were investigated.

Membrane dehydration can present as poor membrane permeability. A rehydration procedure was performed on cleaned membrane coupons to investigate this possibility. After membrane coupons were treated with an ethanol solution, a modest improvement in permeability was observed. However, as there were no events that could have led to dehydration on all four trains, this possibility was dismissed. The feed stream was tested by gas chromatography-mass spectroscopy (GC-MS) to identify any possible compounds that might cause the poor membrane performance, such as organic solvents. No compounds were identified that could be responsible for the decline.

SEM/EDS/SEI[®] analysis of the membrane cross-section found no evidence of compaction as evidenced by the thickness and porosity of the polysulfone substrate (Figure 2). The membrane manufacturer confirmed our findings with their own analysis.



Virgin Membrane

Autopsied Membrane

Figure 2: Thickness measurement and pore size analysis of polysulfone layer using SEM/EDS/SEI analysis.

All of these results led us to believe the loss in membrane permeability was more likely to be a chemical alteration of the membrane, rather than fouling, compaction, or dehydration. Analysis of a membrane coupon by X-ray photoelectron spectroscopy (XPS) compared against a virgin membrane coupon found chlorine present within the membrane (Figure 3, Table 3). A high-resolution scan of the chlorine peak determined that the chlorine was present as C-Cl (Figure 4). This chlorine peak was not observed in the XPS analysis of a virgin membrane of the same model, indicating that the membrane from Plant A had been halogenated.

These results were shared with the manufacturer of the membrane element. In the subsequent discussions with the manufacturer, dichloramine exposure was proposed as a potential cause for the observed permeability loss.

Similar symptoms of irreversible permeability decline have been observed at other treatment plants. Another tertiary wastewater reuse membrane plant—referred to as Plant B—maintained a chloramine residual of 2.0 ppm for biofouling control. Plant B was using different membrane models than Plant A, but still observed similar permeability losses.

Due to these troubling results, experiments to investigate chloramine interactions with various membrane models were performed.

	Manufacturer Specification (nominal)	Manufacturer QC Result	Performance Test Result (Normalized to 25°C)	%Difference from Manufacturer QC Result
Permeate Flow (GPD)	12100	12625.0	7290.6	-39.75%
Recovery (%)	15.0%	15.7%	9.0%	-39.75%
Flux (GFD)	30.25	31.56	18.23	-39.75%
Specific Flux (GFD/PSI)	0.250	0.261	0.150	-40.00%
Salt Rejection (%) (NaCl)	99.70%	99.70%	99.76%	+0.06%
Flux Normalized Salt Rejection (%)	-	-	99.86%	+0.20%

Table 1: Initial performance results of autopsied membrane from Plant A.

Table 2: Cell test cleaning results of membrane coupons collected from Plant A autopsy.

	Initial Cell Test Performance	High pH: 2% AWC C-227 pH 11.9 35°C For 6 hours	Low pH: 2% AWC C-234 pH 2 26°C For 2 hours	12.5% Ethanol for 1 hour (rewetting)	%Difference Final vs. Manufacturer QC Result	%Change from Initial	Flux Normalized Salt Rejection (%)	%Difference Flux Normalized Rejection Vs. QC Result
Salt Rejection (%)	99.21%	99.24%	99.14%	98.97%	-0.73%	-0.24%	99.13%	-0.53%
Membrane Specific Flux (GFD/PSI)	0.147	0.214	0.185	0.211	-19.39%	+43.32%	N/A	N/A



Figure 3: XPS Survey of cleaned membrane coupon from Plant A autopsy.

Table 3: Atomic percentage of membrane surface from Plant A autopsy.

Element	Ν	С	0	Cl
Atomic %	12.32	69.8	16.28	1.6



Chloramine – Dichloramine Relationship

Chloramines can exist as three different species: monochloramine (NH₂Cl), dichloramine (NHCl₂), and trichloramine (NCl₃). The equilibrium relationship between these chloramine species is described in Eq. 1-3 (Trogolo 2017).

$$NH_{3 ag} + HOCl_{ag} \rightleftharpoons NH_2Cl_{ag} + H_2O$$
(1)

$$NH_2Cl_{aq} + HOCl_{aq} \rightleftharpoons NHCl_{2,aq} + H_2O$$
(2)

$$NHCl_{2 aq} + HOCl_{aq} \rightleftharpoons NCl_{3,aq} + H_2O$$
(3)

Chloramine speciation is typically modeled as being a function of the NH₄:Cl₂ ratio and the solution pH. Monochloramine is generally dominant under neutral and acid conditions. A representation of the distribution of chloramine species is presented in Figure 5. At the typical feedwater conditions for Plant A and Plant B, monochloramine would be the predominant form of chloramine, with very little expected dichloramine formation. Dichloramine has been implicated in membrane halogenation in recent studies (Lee 2020).



Figure 5: Chloramine speciation as a function of pH (El-Chakhtoura 2018).

Polyamide Halogenation

Polyamide membrane chlorination has been thoroughly examined in a variety of different studies, but the observed effects on membrane performance have been inconsistent (Maugin 2013). The interactions between chlorinating species and reverse osmosis membranes are complex and can be influenced by numerous different factors, including polymer chemistry, membrane surface coatings, solution pH, operating pressure, and the presence of catalysts.

It is generally accepted that polyamide can be chlorinated through several reaction pathways, and the varied responses to chlorination can be attributed to the competing effects of the different reactions; however, the relationship between the chemical changes in membrane structure and overall membrane transport properties is not fully understood.

Chloramine Exposure Experiments

To replicate the effects of chloramine exposure in a controlled environment, brackish water reverse osmosis (BWRO) membranes from three different membrane manufacturers were exposed to a controlled concentration of chloramine and regularly tested to examine the effects of the exposure. The exposure experiment was performed at both pH 6.5 and pH 7.0, to investigate the effects of pH.

Virgin membranes samples of three industry standard BWRO membrane were acquired for testing, referred to as Membranes A, B, and C. Membrane A was the model of membrane in use at Plant A. Membranes B and C were models used in Plant B. Flat sheet samples of each membrane were soaked in deionized water to remove any preservatives or residual chemicals from the manufacturing process.

Four coupons of each membrane were mounted in Sterlitech CF42A crossflow filtration cells, and the hydraulic permeability and salt rejection were routinely measured for each membrane coupon. The feed solution was prepared by adding 2,000 ppm of NaCl to deionized water. The solution was circulated through the test cells at a rate of 0.8 gpm and a pressure of 150 psig, adjusted by throttling the bypass and concentrate valves. To maintain a constant temperature throughout the performance tests, the feed solution was cooled with an AquaEuro 1/2 HP Apex Titanium Chiller, set to 25°C. A simplified diagram of this system is shown in Figure 66.



Figure 6: Simplified diagram of the chloramine exposure and performance testing system.

The membrane samples were exposed to a chloramine solution, to recreate the conditions of a full-scale plant in a controlled setting. To accelerate the aging process, the chloramine concentration was increased to 50 ppm.

The exposure was performed at a feed pressure of 150 psig, with 50 ppm of chloramine as Cl_2 and 2,000 ppm of NaCl. Chloramine was formed in situ by combining ammonium sulfate and aqueous sodium hypochlorite at a molar ratio of 3:1 as ammonium and chlorine. To maintain the

pH of the chloramine solution, 100 ppm of a carbonate-bicarbonate buffer were added, dilute hydrochloric acid was added to adjust the solution to the target pH.

Periodically throughout each exposure, membranes were cleaned with a proprietary CIP. Each coupon was cleaned with 2% AWC C-227-LF for 6 hours at pH 12 and 35°C. The high pH cleaning was followed by low pH cleaning with 2% AWC C-209 for 6 hours at 35°C and pH ~2.

Chloramine Exposure at pH 6.5

The first chloramine exposure was performed at pH 6.5. This pH was selected to target the average feed pH of Plant A, as shown Figure 7. The performance of each membrane sample was tested every 250ppm hours of exposure. After a total of 4250 ppm hours the membranes were cleaned with standard AWC C-227 LF and AWC C-209 procedures. The coupons were then operated at standard conditions for 40 hours to determine if a permeability decline would occur after cleaning. These results are presented in Figure 8.



Figure 7: Feed water conditions from Plant A.



Figure 8: Membrane permeability for the initial 50 ppm chloramine exposure at pH 6.5 and after the first cleaning.

Both Membrane A and Membrane C suffered from significant permeability losses over the course of the exposure, while the Membrane B samples showed significantly less decline. After cleaning, each membrane showed significant improvements in permeability. Membrane A rapidly decreased in permeability after cleaning, returning to the pre-cleaning performance. The permeabilities of Membranes B and C initially increased after the cleaning, but rapidly declined over the 40 hours of operation at test conditions. Membrane C returned to its starting performance, while Membrane B displayed an overall increase in permeability.

Chloramine was then reintroduced into the system, and the exposure was continued for an additional 4250 ppm hour, with performance tests every 250 ppm hours of exposure. The permeability over the course of the exposure is displayed in Figure 9.



Figure 9: Membrane permeability during the second 50 ppm chloramine exposure at pH 6.5 and after the second cleaning.

Unlike in the initial exposure, no significant losses in permeability were observed for Membranes B or C. Fluctuations in performance were observed, but overall, the permeability remained stable. After cleaning, the pattern of initial increase and quick decline in permeability was again observed, but the permeability loss occurred at a much slower rate. After 48 hours of operation, Membrane A and Membrane C appeared to have returned to their initial performance, while Membrane B actually had an overall increase in permeability.

The complete performance results of the chloramine exposure experiment at pH 6.5 can be found in Appendix A.

Chloramine Exposure at pH 7.0

A second set of membrane samples were prepared, and exposure experiment was repeated with the same protocol, but instead adjusted to pH 7.0. These results are presented in Figure 10.



Figure 10: Membrane permeability for the chloramine exposure at pH 7.0.

A significant reduction in permeability was observed for Membrane A. Membrane B and Membrane C experienced moderate losses; however, their trends in permeability were less clear. As with the pH 6.5 exposure, the permeability immediately increased after the first cleaning, quickly dropped during the first 48 hours of operation, and stayed relatively stable throughout the second exposure. Again, the complete performance results for this chloramine exposure experiment can be found in Appendix A.

Possible Solutions to Lost Permeability - Oxysperse Treatment

After determining that a standard cleaning protocol would be unable to recover membrane permeability at Plant A, a membrane restoration protocol was investigated.

After a CIP, all of the membranes from a 1st stage pressure vessel were pulled and sent for testing. A replacement set of virgin membranes were installed and monitored. The removed elements were individually performance tested. Each element's initial performance values are recorded in Table 4. Despite having been cleaned at the plant, all membrane were found to be significantly underperforming, with permeabilities far below the listed specifications. Element Number #2 was cut open to confirm that the surface was clean of all foulants as observed in previous tests.

	Manufacturer Specification		Plant A Membranes						
	(nominal)	(minimum)	#1	#2	#3	#4	#5	#6	#7
Permeate Flow (GPD)	12100	10300	6384.1	6399.2	6674.3	5948.8	6529.2	6529.2	6384.1
Recovery (%)	15.0%	12.8%	7.9%	7.9%	8.3%	7.4%	8.1%	8.1%	7.9%
Flux (GFD)	30.25	25.75	15.96	16.00	16.69	14.87	16.32	16.32	15.96
Permeability (GFD/PSI)	0.250	0.213	0.128	0.131	0.134	0.136	0.131	0.143	0.128
Salt Rejection (%) (NaCl)	99.70%	99.50%	99.77%	99.76%	99.78%	99.76%	99.76%	99.79%	99.71%

Table 4: Initial performance results of each element 1st stage vessel from Plant A.

Three different concentrations of Oxysperse were tested, each concentration was used on two elements. After treatment, all six elements were cleaned with a proprietary cleaning procedure. The results of these trials are summarized in Figure 11.



Figure 11: Results of Oxysperse treatment at varying concentrations.

The lowest tested concentration successfully restored the treated membranes to the manufacturer's minimum specification with no significant reduction in salt rejection. At higher Oxysperse concentrations, the permeability continued to increase, though some losses in rejection were observed.

The newly installed virgin membrane elements demonstrated a decline in performance, as was first observed at system startup. The flow rate from the vessel decreased from 30 gpm when first installed, to 22 gpm after 55 days online. See Table 6. After the six elements were treated with Oxysperse and returned to Plant A, they were reinstalled, and their performance was monitored. The treated elements demonstrated a notably slower decline in performance than the untreated elements. See Table 7.

	Manufacturer Specification (Nominal)	Manufacturer Specification (Minimum)	0.5% Oxysperse Average Final Results	0.75% Oxysperse Average Final Results	1.0% Oxysperse Average Final Results
Permeate Flow (GPD)	12100	10285	10871.3	12241.4	12710.9
Permeability (GFD/PSI)	0.250	0.212	0.225	0.255	0.261
Salt Rejection (%) (NaCl)	99.70%	99.50%	99.55%	99.45%	99.35%
Flux Normalized Salt Rejection	99.70%	N/A	99.60%	99.44%	99.31%

 Table 5: Average results for Plant A Oxysperse treatments

Table 6: Single vessel performance of new membrane elementsover 55 days of online time.

New Virgin Membranes						
Date	Feed Pressure (psi)	Feed Temperature (°C)	Single Vessel Flow Rate (gpm)			
23-July 20	136	28	30			
24-July 20	136	28	28.4			
23-Aug 20	139	30	23.2			
28- Sep 20	140	29	21.5			

Table 7: Single vessel performance of Oxysperse treated elementsover 52 days of online time.

Oxysperse Treated Membranes						
Date	Feed Pressure (psi)	Feed Temperature (°C)	Single Vessel Flow Rate (gpm)			
21-Oct 20	119	29	27.3			
22-Oct 20	133	26	27.0			
22-Nov 20	151	24	25.9			
25-Dec 20	154	25	24.8			
17-Jan 20	153	24	24.7			

Zeta Potential and Oxysperse Treatment

To further investigate the theory of chemical modification of the membrane surface, the charging characteristic, or zeta potential, of the membrane was examined.

Zeta potential measurements were performed using SurPASS 3 (Anton Paar) electrokinetic analyzer. The zeta potential was measured across a range of pH values, to observe any shifts to the isoelectric point and quantify the surface charge at a typical feed water pH. The results of the zeta potential analyses are presented in Figure 12.

The zeta potential was measured for a virgin sample of Membrane B and a clean Membrane B sample from Plant B. Zeta potential measurements of the clean membrane samples were found to have significantly different surface charging across the measured pH values than the virgin.

After treating the membrane samples with Oxysperse, the zeta potential of the membrane was found to have been restored back to the virgin-like levels. Additionally, the performance of these membranes was measured, to investigate any relationships between the permeability and zeta potential. The findings of these tests are summarized in Table 8. The Oxysperse concentration was found to correlate with both permeability and zeta potential. With increasing concentrations of Oxysperse, the permeability continued to increase, with some losses in salt rejection.



Figure 12: The Plant B membrane was found to have a significantly stronger negative charge, compared to a virgin membrane of the same model. After the treatment with Oxysperse, the zeta potentials were restored to virgin-like levels.

Sample	Salt Rejection (%)	Permeability (gfd/psi)	Zeta Potential at pH 7 (mV)
Untreated	99.59	0.116	-27.87
0.50% Oxysperse Treated	99.56	0.155	-21.40
0.75% Oxysperse Treated	99.59	0.168	-20.83
1.00% Oxysperse Treated	99.47	0.183	-19.72
Virgin Membrane B	99.60	0.193	-20.47

Table 8: Performance results of Oxysperse treated membranes from Plant B

Discussion

Irreversible Permeability Loss from Chloramine Exposure

The chloramine exposures at pH 6.5 successfully recreated the permeability losses that have been reported by RO plants using chloramine to mitigate biofouling. Furthermore, permeability was initially recovered after cleaning, but quickly dropped within 48 hours of operation, validating the reports from the full-scale plants; however, the permeability did not decline to the same extent.

The loss in permeability observed at Plant A with Membrane A was demonstrated clearly in the initial exposure at pH 6.5. Membrane B did not demonstrate significant declines in permeability during our testing, but Plant B did observe this behavior. In the chloramine exposure at pH 7.0, Membrane A showed a clear decline in permeability. The permeability trends for Membrane B and Membrane C were somewhat less clear.

The observed loss in permeability caused by exposure to chloramines may be attributed to a collapse in the membrane structure by halogenation (Lee 2020) or formation of crosslinking within a membrane (Verbekea 2017). The reactions for polyamide chlorination are known to be strongly pH dependent (Do 2012). Membrane permeability declines have been found to occur more readily under acidic conditions; membrane hydrophobicity also increases when halogenated under more acidic conditions. Under more alkaline conditions, amide bond cleavage reaction is promoted, opening up the membrane and increasing the permeability, and membrane hydrophilicity (Verbekea 2017).

The different observed trends at pH 6.5 and 7.0 could indicate an inflection point for membrane chlorination. At this point, the effects of the competing reactions may be cancelling each other out, though membrane halogenation is still occurring in both cases.

When exposed to the chloramine solution at pH 6.5, all tested membranes showed consistent permeability losses, though the rate of decline varied between membrane models. Since all membrane samples were treated simultaneously, these variations can reasonably be attributed to chemical differences in the membranes themselves. These differences could affect both the way that chlorinating species attack the membrane and the resulting changes in performance.

Effects of Oxysperse Treatment

The Oxysperse treatment and subsequent proprietary cleaning were found to partially restore the permeability of the chlorinated membrane, initially deemed unrecoverable. Increasing the strength of Oxysperse provided additional increases in permeability, at the cost of salt rejection.

The Oxysperse treatment was found to have a significant effect on the surface charge on the membrane, returning the membrane zeta potential to virgin-like levels. This change in charge could provide some explanation for the observed losses in salt rejection. The separation of salt ions from water is mostly charge-based, so a weaker surface charge would reduce a membrane's capacity for salt rejection.

The zeta potential of a surface is understood to be directly correlated to the wettability of a surface (Matteis 2020); with more positive zeta potential, surface hydrophilicity increases. The increased hydrophilicity of the treated membrane can also partially explain the improved membrane permeability. Hydrolysis of excessively crosslinked membranes from low pH halogenation would also explain the improved membrane permeability.

Conclusions

In the past, common wisdom has held that RO plants that treat secondary wastewater experience irreversible losses in membrane permeability. This work demonstrates that exposure to chloramines may be, at least in part, responsible for this decline.

The observed permeability losses in the full-scale plants could be successfully recreated in a laboratory setting with chloramine exposure. The extent of the permeability loss observed in the experiments was less severe than observed onsite. This suggests that other factors or components in the feed water could be influencing the interactions between the chloramines and the polyamide membrane. To investigate the possible compounding effects of feed water on membrane permeability decline, additional chloramine exposures using secondary effluent are currently being pursued.

Due to the interactions between chloramine and polyamide membranes, caution should be taken when considering using chloramine for biofouling mitigation. Different membrane models were found to have drastically different responses to chloramine exposure. Pilot-scale tests may provide additional insight into the effects of chloramine with different membrane models and feed water compositions. Chloramine residuals should be maintained at the minimum dosage required for control, to reduce the risk of chloramine damage.

Oxysperse treatment has shown promising results, both restoring lost permeability and slowing further losses.

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Appendix A: Supplementary Figures

Figure 13: Hydraulic permeability and salt rejection of the sample membranes exposed to 50 ppm of chloramine at pH 6.5. From left to right, this includes initial performance tests, the first chloramine exposure, the first post-CIP operation, the second chloramine exposure, and the second post-CIP operation.



Figure 14: Hydraulic permeability and salt rejection of the sample membranes exposed to 50 ppm of chloramine at pH 7.0. From left to right, this includes initial performance tests, the first chloramine exposure, the first post-CIP operation, the second chloramine exposure, and the second post-CIP operation.