

Effect of a mixture of poly (acrylic co maleic) acid and EDTA on CaCO_3
scale formation on the surface of a RO membrane

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Executive Summary:

Reverse osmosis is one of the main technologies providing human beings water demand. One of the most challenging problems in RO desalination industries is dealing with different kinds of scale formation. Scale formation in Ro plants results in lower plant efficiency and lower recovery, higher energy consumption and higher operational and maintenance cost.

There are several methods to deal with the scale formation problems. One of these methods is using scale inhibition chemicals. Although the environmental effects of using phosphorous based chemicals have been completely proven, these antiscalants are currently the market-dominating chemicals used in this industry. Polycarboxylic based antiscalants are the suggested alternative regarding environmental problems.

This research is mainly focused on evaluating a phosphorous free, polycarboxylic based antiscalant combined with a chelating agent and comparing its performance with a commercially available polycarboxylic based antiscalant, through experimental studies.

Acknowledgements:

I wish to express my deepest gratitude to Dr. Cummings for helping and supporting me through this project. It was a great experience full of academic and spiritual learnings. I would like to pay my regards to the chemical engineering department of BIHE for their supportive attitude. I would also thank Shimifann for helping me with the technical aspects of laboratory equipment. I also thank my family for supporting me.

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Reverse Osmosis in Water Treatment Applications:

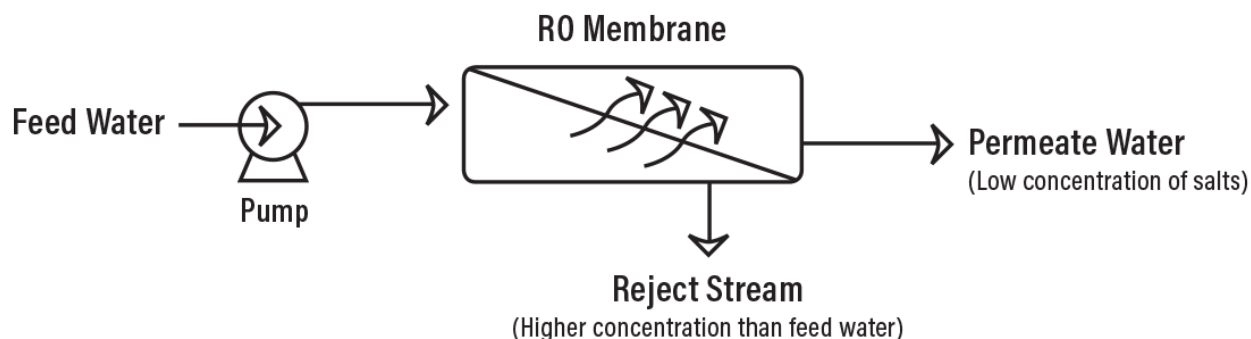
There are many types of equipment involved with water including cooling towers, heat -exchangers and water and wastewater treatment equipment.

Membrane processes (RO, NF & UF) are vastly used in water treatment industries. Reverse osmosis is one of the most used technologies when it comes to desalination.

Reverse Osmosis is a technology that is used to remove a large majority of contaminants from water by pushing the water under pressure through a semi-permeable membrane.

Reverse Osmosis Operation:

Reverse Osmosis works by using a high pressure pump to increase the pressure on the salt side of the RO and force the water across the semi-permeable RO membrane, leaving almost all (around 95% to 99%) of dissolved salts behind in the reject stream. The amount of pressure required depends on the salt concentration of the feed water. The more concentrated the feed water, the more pressure is required to overcome the osmotic pressure.



As it's shown in the figure, feed water during the membrane process is divided into 2 streams: permeate and concentrate.

Permeate stream which is the treated stream has lower TDS (total dissolved solids) than the feed and apparently, the reject stream is more concentrated.

As water permeates through the semi-permeable membrane layer the concentration of water increases and high concentration of water and high pressure of RO operating condition leads to super saturation condition.

Scaling in RO Operation:

In such a condition, scale formation appears among the surface of the membrane which leads to less membrane permeability. So in order to maintain the membrane permeability, plant recovery and permeate flow rate, the higher operating pressure is required which increases energy consumption, scale formation rate and decreases the membrane lifetime that all lead to higher operating costs.

$$\text{Recovery\%} = \frac{\text{permeate flow rate}}{\text{feed flow rate}} * 100$$

Several models are describing how the membrane operation works. One of these models is called Solution-Diffusion (SD). Based on this model flux through the membrane can be calculated as:

$$J = \frac{\Delta P - \Delta \pi}{\mu(R_m + R_c)}$$

where is ΔP average pressure drop across the membrane, $\Delta \pi$ is the osmotic pressure over the membrane, μ is the viscosity for the liquid at hand, R_m is membrane resistance and R_c is fouling/scaling resistance.

Regarding the Solution diffusion model, if the feed water condition is assumed constant, the viscosity and osmotic pressure are constant too. R_m is relative to membrane property. So scaling occurs on the surface of the membrane R_c increases and permeate flux decreases. [1]

Due to operating condition in RO operation, scaling is very common. Major scaling salts are calcium carbonate (CaCO_3), calcium sulfate ($\text{CaSO}_4 \cdot \text{H}_2\text{O}$), barium sulfate (BaSO_4), strontium sulfate (SrSO_4), silicates, calcium phosphate ($\text{Ca}_3(\text{PO}_4)_2$) and alumino-silicates (Al_2SiO_5).

Common Methods to Reduce Membrane Scaling:

To reduce scale formation on the surface of the membrane, 4 common techniques are used:

- Lime Softening that has been largely supplanted by ion exchange technologies in recent years.
- Acid Dosing is an inexpensive way of reducing water scaling potential. In this method, LSI is lowered by decreasing the pH. But this method imposes higher operating costs to desalination plants with high alkalinity feed water and CO_2 production increases permeate conductivity that makes using degasifier equipment necessary. Also, commercially available acids containing metals can increase the risk of membrane fouling.
- Sodium regenerated ion exchange softeners are one of the most widely expanded scale-control methods. But this method imposes significant capital and operational expenses. There are also environmental problems with regeneration brines discharging.
- Antiscalant dosing is a very effective way of controlling scale formation. When it comes to this method, there are many advantages of operational and capital cost reduction and environmental acceptability and safety. [2]

Scale Inhibition Mechanisms

Although there is a minor understanding of fundamental inhibition mechanisms, it's known that scale inhibitors prevent scale formation through combined physical processes including adsorption, nucleation and crystal growth processes rather than chemical reactions. Main mechanisms of scale inhibition are:

- a) The threshold effect: even trace amount of inhibitor can prevent a scale layer from growing or adhering to a flow surface.
- b) Crystal distortion effect: precipitation occurs under a non or low adherent form.
- c) Dispersion: Avoid deposition of the precipitate

*Mostly polymeric antiscalants work through these 3 mechanisms.

- d) Chelation: Removing metal ions through this mechanism. [3] , [4]

Phosphorous Containing Antiscalants:

Polyphosphates, polyphosphonates and polycarboxylic acids are the main popular scale inhibitors. Although phosphate containing additives are vastly used and are pretty efficient in controlling scale precipitation specially CaCO_3 scale, use of high levels of these chemicals are being restricted in terms of release to the environment. [5]

As EPA (U.S Environmental Protection Agency) has claimed, a high concentration of phosphorus which is mostly caused by human activities can increase the growth of algae to the level that ecosystems cannot handle. Increase in algae harm water quality, food resources, and habitats, and decrease dissolved oxygen level which puts fish and other aquatic life in danger. [6]

So, to avoid the mentioned environmental risks, polycarboxylic acids are chosen as the scale inhibitors.

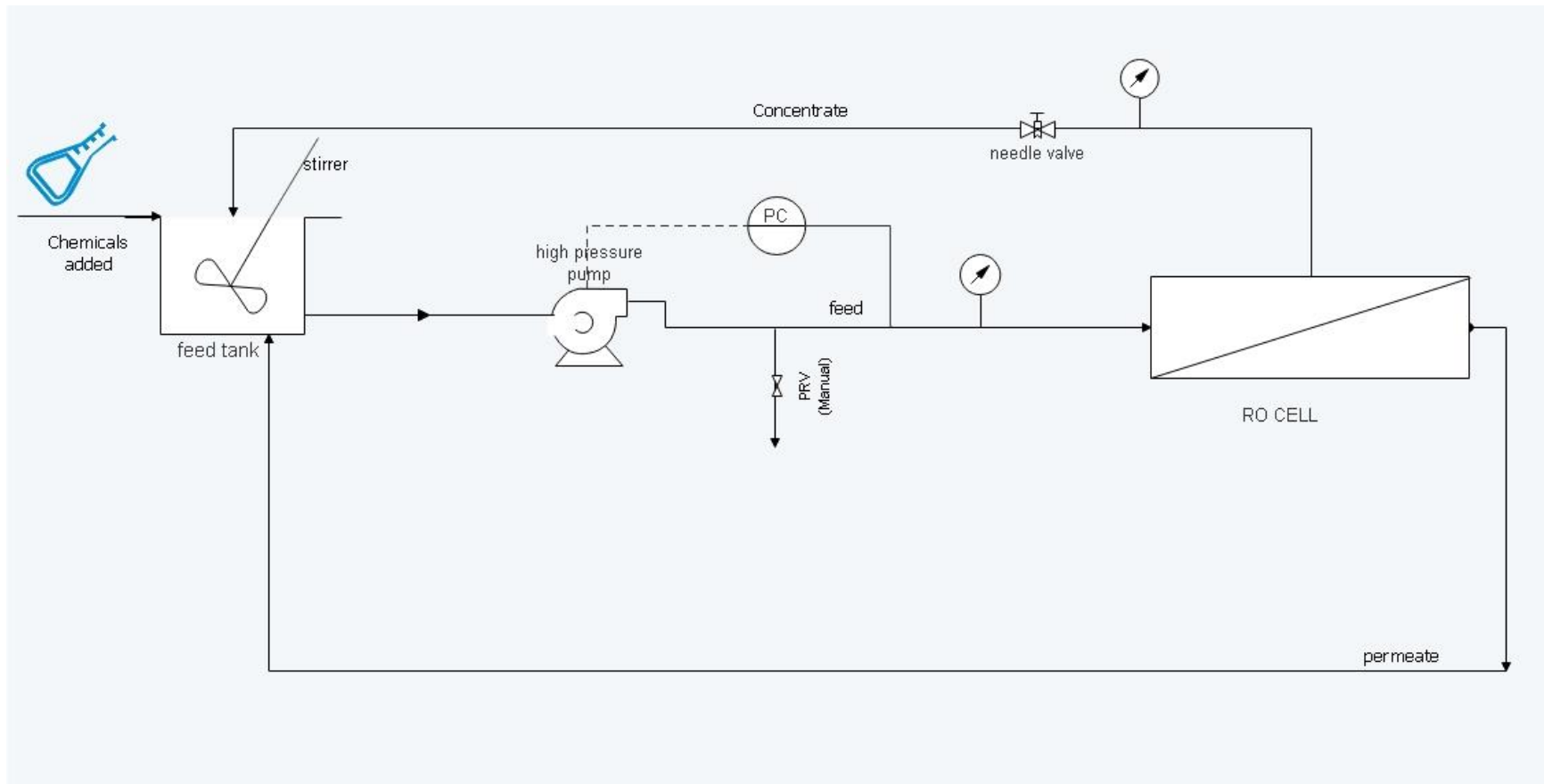
It's known that polycarboxylic acids with molecular weight less than 10000 represent more scale properties rather than high Mw polycarboxylic acids & Mw weight distribution between 500 and 4000 is preferred. [7]

Lab Scale Reverse Osmosis:

To simulate the reverse osmosis process and super saturation condition to monitor scale formation on the surface of the membrane, a lab-scale reverse osmosis system was built.

This set-up is supposed to provide 15 bar pressure to RO membrane sheet.

Process Flow Diagram:



*Flow rates of permeate and reject streams are measured using the volumetric method.

*Concentration of ions are measured with EC-meter.

This system includes:

a- Membrane sheet:

TW30-1812 is selected for this test. Molecular weight cut-off of this membrane is 30 Daltons which is the same MWCO of membranes used in industrial desalination plants.



(MWCO is defined on the basis of 90% rejection of a solute with a particular molecular weight.)

Datasheet of this membrane is provided below:

Product Specifications

Product	Part number	Active area ft ² (m ²)	Feed spacer thickness (mil)	Permeate flow rate gpd (m ³ /d)	Stabilized salt rejection (%)	Minimum salt rejection (%)
BW30-400	98650	400 (37)	28	10,500 (40)	99.5%	99.0%

1. Permeate flow and salt rejection based on the following standard conditions: 2,000 ppm NaCl, 225 psi (15.5 bar), 77°F (25°C), pH 8 and 15% recovery.

2. Flow rates for individual elements may vary but will be no more than 15% below the value shown.

3. Sales specifications may vary as design revisions take place.

4. Active area guaranteed +/-3%. Active area as stated by Dow is not comparable to nominal membrane area often stated by some manufacturers. Measurement method described in Form No. 609-00434.

b- High-pressure pump: to provide RO required pressure a dosing pump that can provide 20 bar is used.

Lara A-Enlsa was selected for this purpose.



c-Pressure Vessel: The stainless steel pressure vessel was used. The membrane was cut into circle shaped pieces to be installed inside the vessel. The PV is actually made of 2 flanges and two O-rings.



This part was pretty challenging. There were 2 major challenges:

1. *Sealing the PV was one of the biggest challenges. As the experiment was supposed to be done at 15 bar, leakage was one of the biggest problems. This problem was solved by adding an extra O-ring.*



To solve this problem different solutions were applied.

- *Doubling and tripling the membranes which didn't work.*
- *Using a polymeric mesh as support that worked for 15 minutes.*
- *Using a SS mesh as support. The interesting experience was that the water pressure squashed the SS mesh. So cylindrical support was used to support the SS mesh and it worked.*



d- Piping and Fittings:

Pneumatic polymeric piping and fittings were used. The problem was that although fittings were supposed to tolerate 20 bar, they failed to operate at 15 bar pressure. So all polymeric fittings were replaced with SS ones.



d- Pressure Switch:

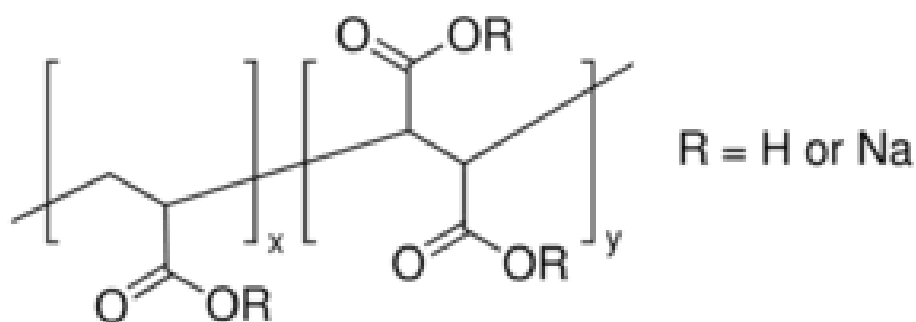
The other problem during the process of testing the set-up was that making the pressure stable was very difficult.

In order to make it easier, a Danfoss pressure switch was used that works as an On/Off controller.



Evaluating a Novel Antiscalant for RO Operation:

Regarding what has been mentioned before, and as study is mainly focused on evaluating a polycarboxylic acid based scale inhibitor that can reduce calcium carbonate scale formation rate and comparing its performance to a commercially available one, poly(acrylic co melic)acid with average molecular weight distribution = 3000 is chosen as a scale inhibitor.



EDTA as a chelating agent is chosen to make the mixture of Antiscalant solution. So chelation is added to polymeric scale inhibition properties.

Material

Poly (acrylic co maleic) acid 50% solution with M_w avg=3000 and EDTA 0.1N solution were respectively obtained from Sigma-Aldrich and Merck.

The purpose of these experiments is to compare the scale inhibition properties of {60% (PAA/MAA 50% wt/wt) + 40%(0.1N EDTA)} mixture to a commercially available one.

But first, the feed water should be prepared.

Feed water preparation:

According to the table below, a challenging water to desalinate like Caspian Sea water will be prepared: [8]

Parameters	Spring	Summer	Autumn	Winter	Years
Temperature (°C)	17.42 ± 0.41 ^c	27.23 ± 0.55 ^a	20.58 ± 0.20 ^b	11.79 ± 0.05 ^d	19.26 ± 0.40
Conductivity (µmos/cm)	15.92 ± 0.14 ^c	19.68 ± 0.20 ^a	17.33 ± 0.08 ^b	14.18 ± 0.01 ^d	16.78 ± 0.14
Turbidity (FTU)	5.98 ± 0.70 ^a	3.55 ± 0.34 ^b	4.76 ± 0.58 ^{ab}	3.81 ± 0.40 ^b	4.52 ± 0.26
Salinity (g/l)	12.22 ± .01 ^c	12.22 ± 0.01 ^c	12.34 ± 0.01 ^b	12.42 ± 0.02 ^a	12.30 ± 0.01
DO (mg/l)	9.49 ± 0.08 ^b	8.68 ± 0.10 ^d	9.17 ± 0.06 ^c	10.56 ± 0.02 ^a	9.48 ± 0.05
pH	8.23 ± .01 ^b	8.42 ± 0.01 ^a	8.07 ± 0.00 ^c	8.06 ± 0.00 ^c	8.19 ± 0.01
Chlorophyll-a (µg/l)	1.09 ± .03 ^b	1.04 ± 0.02 ^b	1.26 ± 0.03 ^a	0.86 ± 0.02 ^c	1.06 ± 0.17
NH ₄ ⁺ (µg/l)	21.28 ± 0.76 ^b	21.23 ± 0.54 ^b	28.12 ± 0.56 ^a	30.01 ± 0.89 ^a	25.18 ± 0.43
NO ₂ ⁻ (µg/l)	0.82 ± 0.05 ^c	0.46 ± .05 ^d	1.20 ± 0.07 ^b	1.61 ± 0.08 ^a	1.02 ± 0.43
NO ₃ ⁻ (µg/l)	23.12 ± 1.10 ^a	13.24 ± 0.82 ^c	19.50 ± 0.92 ^b	22.49 ± 0.57 ^{ab}	19.59 ± 0.50
N.org (µg/l)	309.34 ± 8.96 ^b	235.33 ± 7.94 ^c	294.77 ± 6.48 ^b	363.58 ± 7.90 ^a	300.75 ± 4.87
TN (µg/l)	354.58 ± 9.44 ^b	270.28 ± 8.42 ^c	345.25 ± 7.90 ^b	426.47 ± 7.64 ^a	349.14 ± 5.49
P.min (µg/l)	17.14 ± 0.38 ^c	15.53 ± 0.37 ^d	21.45 ± 0.52 ^b	23.57 ± 0.70 ^a	19.42 ± 0.33
P.org (µg/l)	52.35 ± 1.27 ^b	60.44 ± 1.39 ^a	48.05 ± 0.92 ^c	53.28 ± 0.97 ^b	53.53 ± 0.64
TP (µg/l)	69.50 ± 1.29 ^b	75.97 ± 1.51 ^a	68.12 ± 1.15 ^b	76.86 ± 0.99 ^a	72.61 ± 0.66
SiO ₂ (µg/l)	223.62 ± 7.40 ^b	232.71 ± 6.80 ^b	259.21 ± 5.67 ^a	269.01 ± 7.42 ^a	246.14 ± 3.61

Mean ± SE. Values with different superscripts are significantly different ($P < 0.05$, one-way ANOVA) from each other

N.org organic nitrogen, *P.org* organic phosphorus, *P.min* inorganic phosphorus, *TN* total nitrogen, *TP* total phosphorus, *DO* Dissolved oxygen

To make the feed water susceptible for CaCO_3 scale formation NaHCO_3 and CaCl_2 powder is used and NaCl is used to increase the EC to make the water similar to Caspian Seawater.

LSI value is the key value to determine the scale formation potential of feed water.

LSI:

LSI (Langelier Saturation Index) is an index for quantifying the scaling-corrosion tendency of water. LSI calculation is considered below:

$$LSI = pH - pH_a$$

$$pH_a = (9.30 + A + B) - (C + D)$$

$$A = (\log_{10}[TDS] - 1)/10, \text{ where } [TDS] \text{ is in ppm}$$

$$B = -13.12 \times \log_{10}(^{\circ}\text{C} + 273) + 34.55$$

$$C = \log_{10}[\text{Ca}^{+2}] - 0.4, \text{ where } [\text{Ca}^{+2}] \text{ is in ppm } \text{CaCO}_3$$

$$D = \log_{10}[\text{alkalinity}], \text{ where } [\text{alkalinity}] \text{ is in ppm } \text{CaCO}_3$$

In order to simulate challenging feed water with high scale formation potential, LSI is considered 2.8 : [9]

LSI	Condition
+3.0	Extremely severe scaling
+2.0	Very severe scaling
+1.0	Severe scaling
+0.5	Moderate scaling
+0.2	Slight scaling
0.0	Stable water (no scale)
-0.2	No scale, very slight tendency to dissolve scale

Electro conductivity and pH are respectively 20 mS/cm (TDS= 13298ppm) and pH 8.4. So the LSI will be 2.8.

	<i>Mw</i> (gr/mole)	<i>weight fraction</i> (w/w)			<i>meq</i> /Lit	<i>mg/Lit</i>				
<i>NaHCO₃</i>	84.00	1	Desired <i>LSI</i> = 2.83 @ <i>pH</i> =8.4 So Required: [<i>Ca</i>] = 40 <i>meq/lit</i> [<i>HCO₃</i>] = 40 <i>meq/lit</i>		40	3360.28				
<i>HCO₃</i>	61.01	0.726			40	2440.672				
<i>Na</i>	22.99	0.273			40	919.608				
<i>CaCl₂</i>	110.98	1			40	4439.2				
<i>Ca</i>	40.07	0.361			40	1603.12				
2 * <i>Cl</i>	70.90	0.638			40	2836.08				
<i>NaCl</i>						5499.95				
<i>TDS(ppm)</i>						13299.43				
estimated Electro- conductivity (micro <i>simens/cm</i>)						20348.1279	TDS to EC conversion factor $\cong 1.53$			

[<i>Ca</i>] = [<i>CO₃</i>] : <i>meq/Lit</i>	40
<i>pH</i>	8.35
<i>TDS(ppm)</i> * <i>NaHCO₃</i> & <i>CaCl₂</i> are used to make the solution	13298
$A = (\log_{10}[TDS] - 1)/10$	0.312379
$B = -13.12 \times \log_{10}(^{\circ}\text{C} + 273) + 34.55$	2.088283
$C = \log_{10}[Ca^{+2} \text{ as } CaCO_3] - 0.4$	2.804966
$D = \log_{10}[\text{alkalinity as } CaCO_3]$	3.380284
$pH_s = (9.30 + A + B) - (C + D)$	5.515412
$LSI = pH - pH_s$	2.834588

All the chemicals are obtained from Merck.

So 3.360gr of NaHCO_3 and 4.439gr of CaCl_2 and 5.499gr of NaCl was added to each liter of deionized water to prepare the feed water with $\text{EC}=20.348 \text{ mS/cm}$ ($\text{TDS}=13299.43 \text{ ppm}$) and $\text{LSI}=2.83$ and needed amount of NaOH to reach $\text{pH}= 8.4$

Methods:

To compare the scale inhibition performance, 3 scenarios have experimented. During these experiments, the flow rate of permeate and concentrate streams and EC of permeate are measured.

Then the SEM picture of the surface of the membranes will be compared.

All tests are applied under the below conditions:

- 15 bar feed pressure
- 6 hours of operation
- samples and values are measured per 60 minutes.
- Constant feed water composition (permeate and concentrate streams are recycled to the feed tank so that the concentration is almost constant)

Tests will cover 3 scenarios:

1. Raw water - 2 runs
 2. a Commercial Antiscalant: 8 ppm of Flocon 260. (As Iran's vendor has recommended) - 3 runs
 3. 60% of PAA/PMA 50% wt/wt solution + 40% of 0.1N EDTA solution- 3 runs
- Raw data gathered from experiments are mentioned in **Appendix A**.

Data Analysis Approach:

To analyze the primary data above, 3 system properties, are discussed:

1. $Q/Q_{\max}$: This value shows how the permeate flow rate has changed through time in comparison to the maximum permeate flow rate during the operation.

2. R/R_0 : This value shows how recovery has changed over time.

Recovery: The percent of **recovery** is the percentage of the feed water which becomes product water.

$$\text{Recovery\%} = (\text{Permeate flow rate} / \text{Feed flow rate}) * 100$$

3. Ion Rejection%: Since RO systems are used to remove dissolved salts, measuring salt (ion) rejection is a direct way to monitor the performance. This value shows the quality of desalination process and membrane condition. Salt rejection is the percentage of the feed water TDS that has been removed in the permeate water.

$$\text{Ion Rejection\%} = (1 - \text{EC}_{\text{Permeate}} / \text{EC}_{\text{Feed water}}) * 100$$

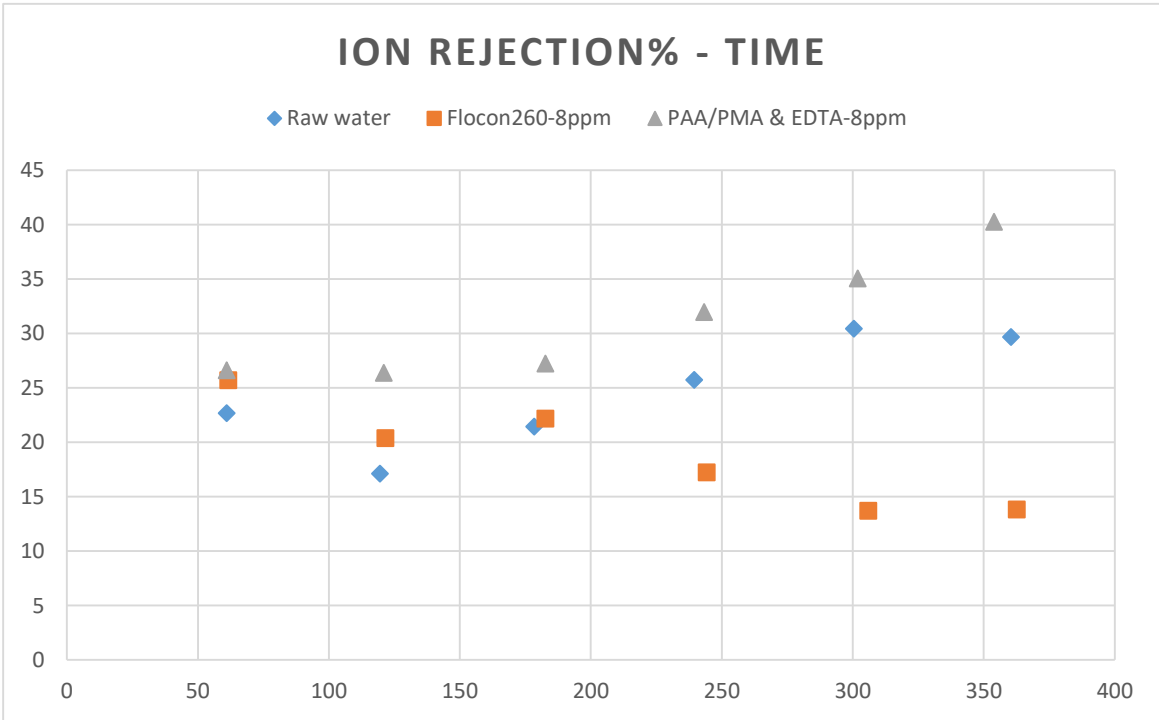
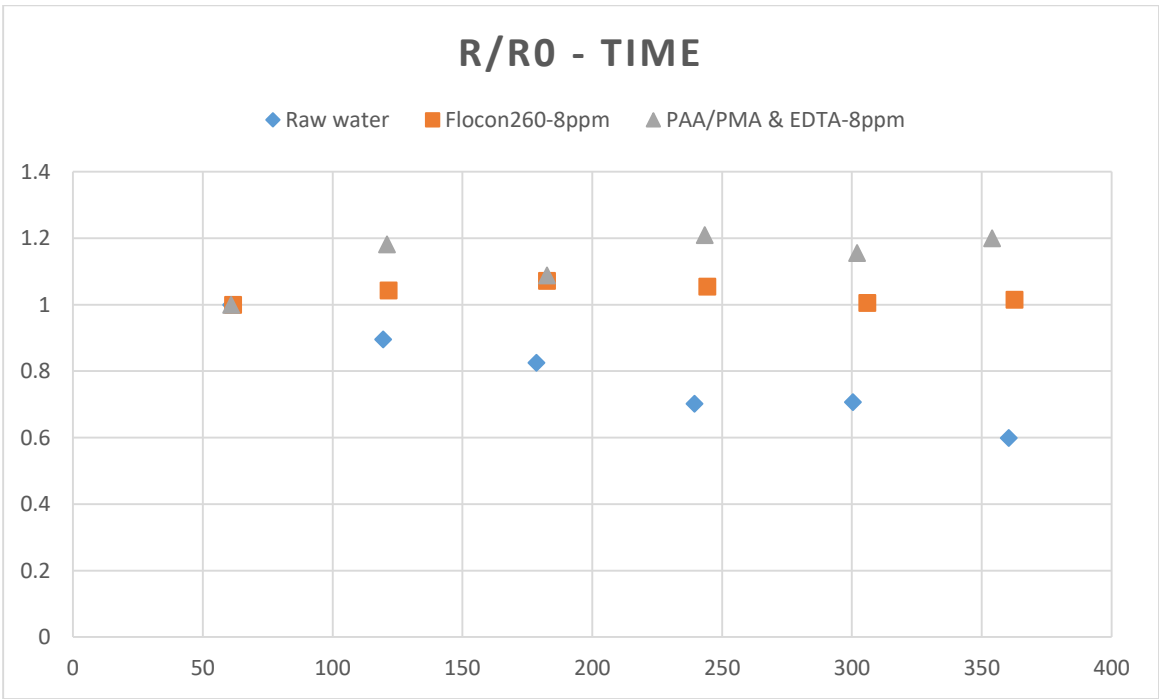
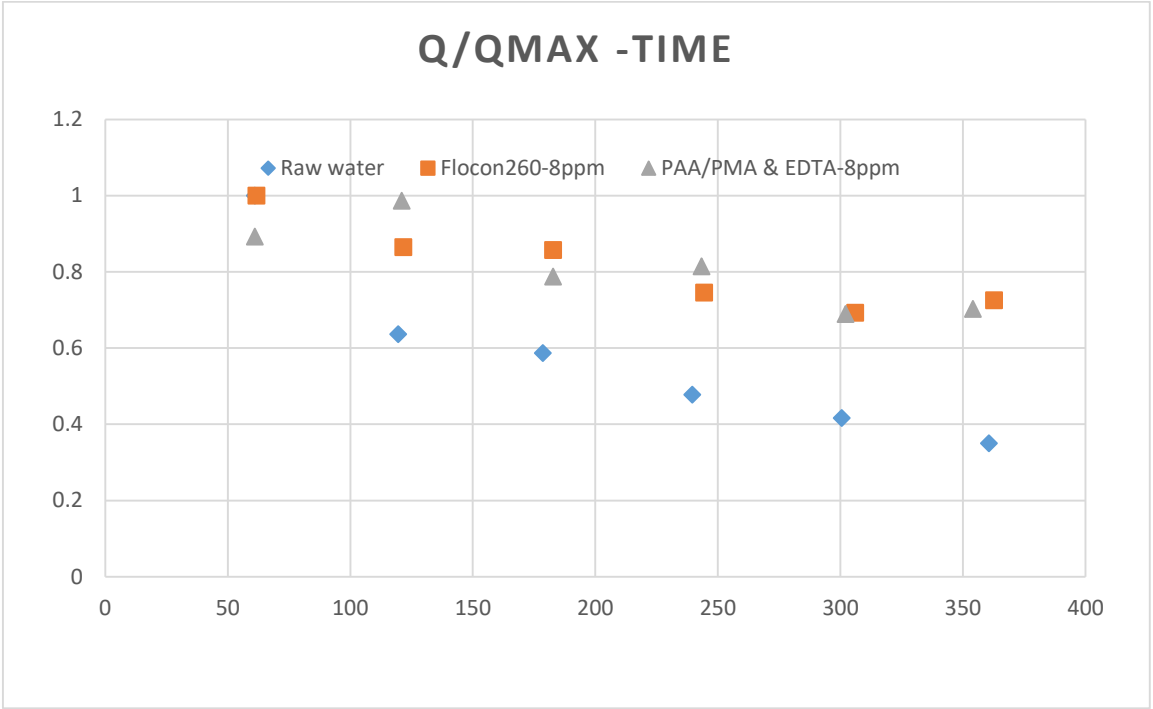
These values will be plotted as variables of time.

Data Analysis and System Properties:

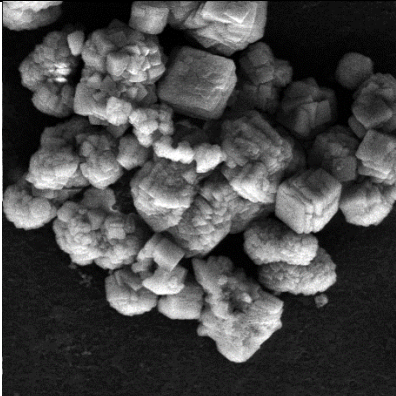
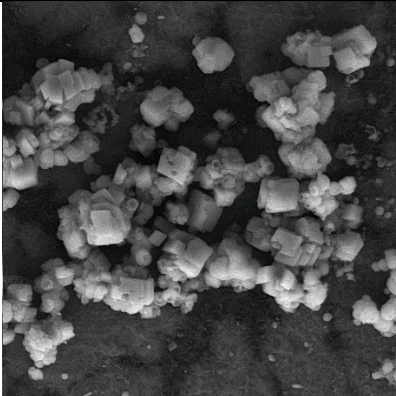
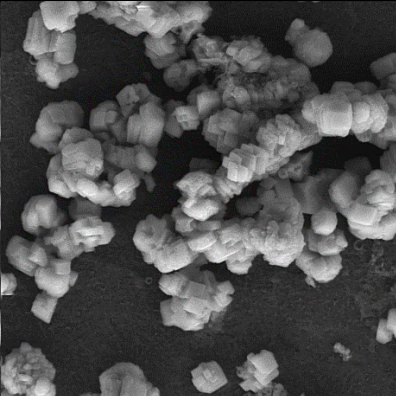
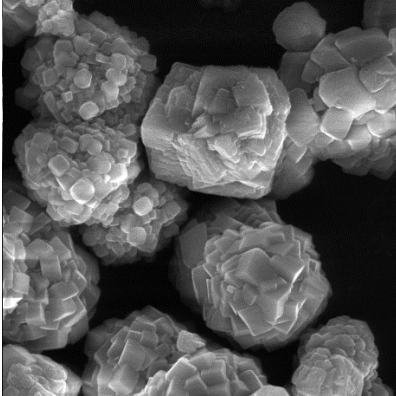
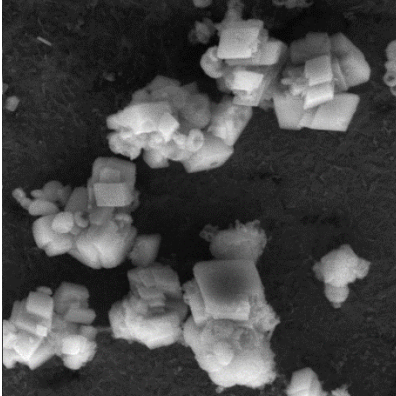
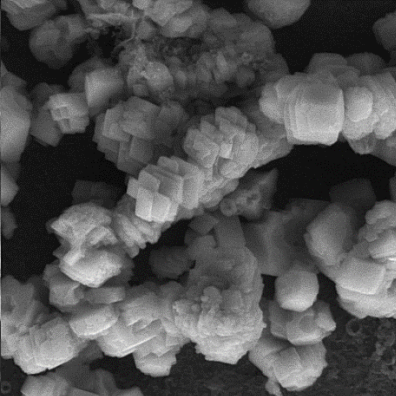
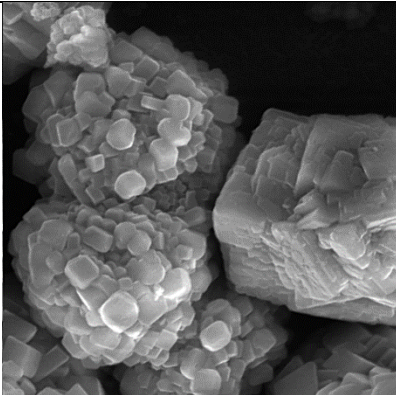
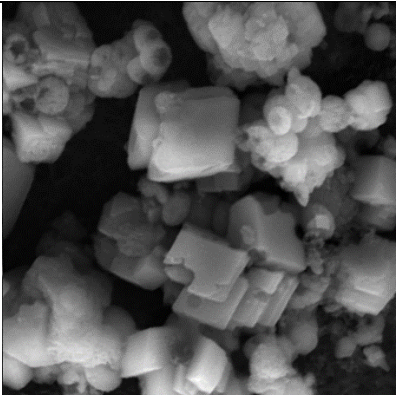
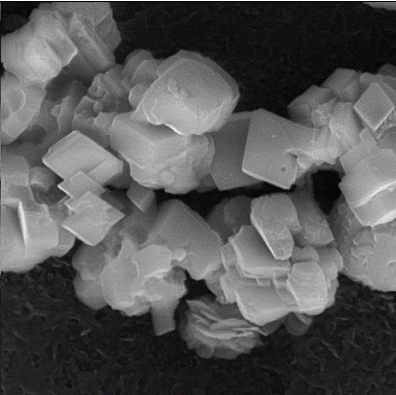
Data Analysis and System Properties data are mentioned in **Appendix B.**

		Time	sys properties			
	Set	Time	Ion Rejection%	recovery %	Q/Q _{max}	R/R ₀
Raw water Average	1	61	22.675	43.790	1.000	1
	2	119.5	17.125	39.229	0.636	0.895
	3	178.5	21.45	36.166	0.586	0.825
	4	239.5	25.75	30.746	0.477	0.702
	5	300.5	30.45	30.949	0.416	0.706
	6	360.5	29.675	26.245	0.350	0.599
8ppm of flocon 260 Average	1	61.667	25.7	49.551	1	1
	2	121.67	20.383	51.684	0.864	1.043
	3	182.67	22.166	53.133	0.857	1.072
	4	244.33	17.25	52.241	0.745	1.054
	5	306	13.716	49.842	0.692	1.005
	6	362.67	13.816	50.280	0.725	1.014
60% PAA/pM A + 40% EDTA average	1	61	26.633	36.822	0.892	1
	2	121	26.4	43.508	0.986	1.181
	3	182.67	27.25	40.057	0.787	1.087
	4	243.33	31.966	44.543	0.814	1.209
	5	302	35.066	42.557	0.688	1.155
	6	354	40.283	44.188	0.702	1.200

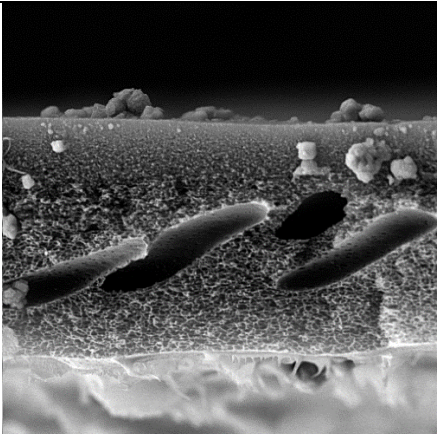
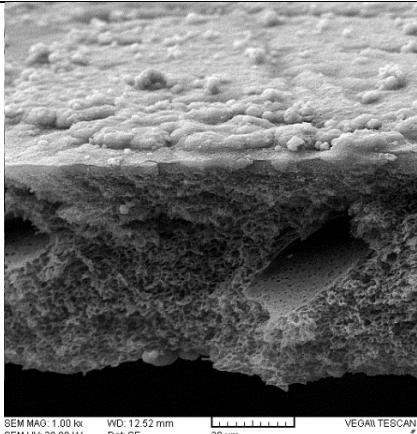
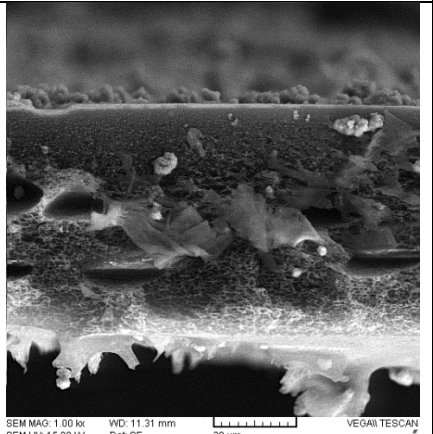
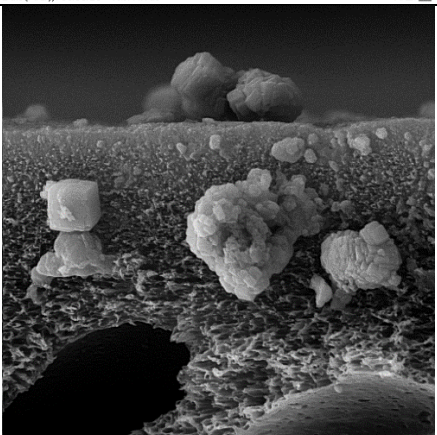
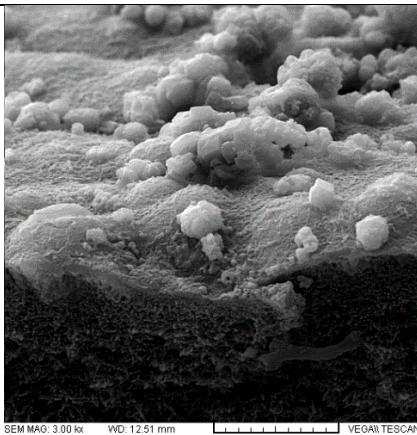
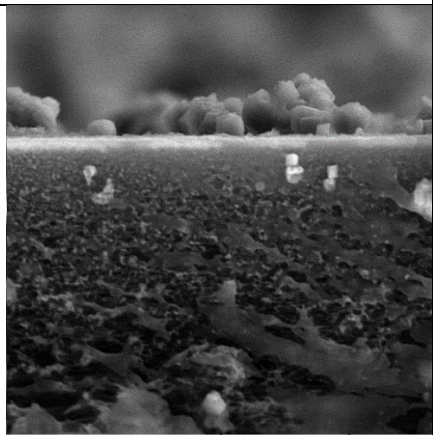
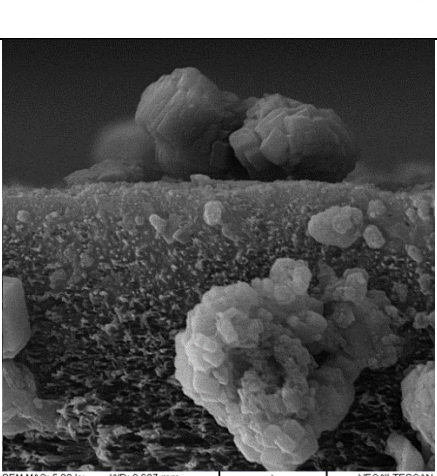
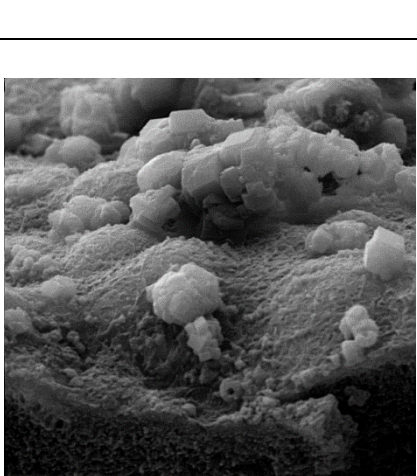
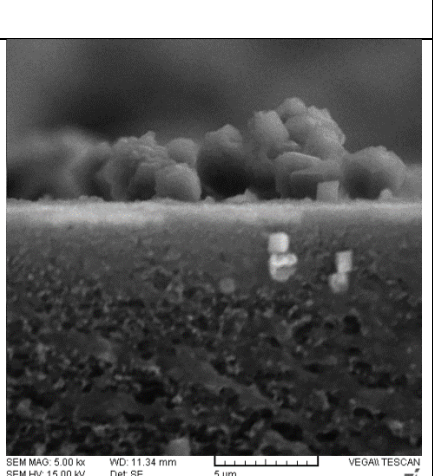
Data Analysis Graphs:



SEM Images:

	Raw water	Flocon 260	60% PAA/MAA + 40% EDTA
10μm			
5μm			
2μm			

Cross Images:

	Raw water	Flocon 260	60% PAA/MAA + 40% EDTA
20µm cross	 SEM MAG: 1.00 kx WD: 9.669 mm SEM HV: 20.00 kV Det: SE Date(m/d/y): 03/03/20 Vac: HiVac VEGAII TESCAN RAZI	 SEM MAG: 1.00 kx WD: 12.52 mm SEM HV: 20.00 kV Det: SE Date(m/d/y): 03/03/20 Vac: HiVac VEGAII TESCAN RAZI	 SEM MAG: 1.00 kx WD: 11.31 mm SEM HV: 15.00 kV Det: SE Date(m/d/y): 02/27/20 Vac: HiVac VEGAII TESCAN RAZI
10µm cross	 SEM MAG: 3.00 kx WD: 9.598 mm SEM HV: 20.00 kV Det: SE Date(m/d/y): 03/03/20 Vac: HiVac VEGAII TESCAN RAZI	 SEM MAG: 3.00 kx WD: 12.51 mm SEM HV: 20.00 kV Det: SE Date(m/d/y): 03/03/20 Vac: HiVac VEGAII TESCAN RAZI	 SEM MAG: 3.00 kx WD: 11.34 mm SEM HV: 15.00 kV Det: SE Date(m/d/y): 02/27/20 Vac: HiVac VEGAII TESCAN RAZI
5µm cross	 SEM MAG: 5.00 kx WD: 9.607 mm SEM HV: 20.00 kV Det: SE Date(m/d/y): 03/03/20 Vac: HiVac VEGAII TESCAN RAZI	 SEM MAG: 5.00 kx WD: 12.51 mm SEM HV: 20.00 kV Det: SE Date(m/d/y): 03/03/20 Vac: HiVac VEGAII TESCAN RAZI	 SEM MAG: 5.00 kx WD: 11.34 mm SEM HV: 15.00 kV Det: SE Date(m/d/y): 02/27/20 Vac: HiVac VEGAII TESCAN RAZI

Technical Conclusion:

As the plots have shown:

- Both commercial and lab-made Antiscalant, increase maintain the permeability of the membrane. The permeability of both has dropped about 30% while the permeability of raw feed water has dropped about 65% which is a significant sign of scaling.
- R/R_0 trend line shows that as the time passes and the system becomes more stable, the recovery% has maintained the same compared to its initial value in commercial A/S, it had a minor increase in lab-made A/S & it had a significant decrease in raw feed water.
- As the system becomes more stable and rejection% of Raw water and lab-made A/S increase through the time, rejection% of commercial A/S decreases and TDS leakage through the membrane has increase which can be the sign of minor membrane damage. SEM pictures show the same problem on the surface of commercial A/S related membrane. As the manufacturer claimed that this product is highly corrosive the minor damage may be caused because of this property.

SEM pictures have shown, both commercial and lab-made antiscalants, decrease the size of CaCO_3 crystals formed on the surface of the membrane. As discussed previously, there are signs of minor membrane damage are in commercial A/S case.

As the $Q/Q_{\max}$ and R/R_0 graphs and SEM picture imply, because of scale formation caused by raw water, R_c (scaling/fouling resistance in the solution diffusion model) is increased which decreases membrane permeability. ($Q/Q_{\max}$ and R/R_0 are relative values to monitor membrane permeability.)

Flocon 260 and the lab-made antiscalant as polycarboxylic based antiscalants, were very effective for controlling the membrane scaling and maintaining the permeability.

The Ion Rejection% graph which shows the quality of the desalination process shows that the chosen commercially available A/S, Flocon 260, has caused minor damages to the surface of the membrane which leads to salt leakage.

So polycarboxylic based antiscalants combined with chelating agents show good scale inhibition properties.

As the lab-made scale inhibitor is a mixture of polycarboxylic acid & EDTA agent, its performance can be explained with the threshold, distortion and dispersion effects (polymeric scale inhibition mechanisms) and chelating mechanism (related to EDTA).

Economic Analysis:

FOB prices

EDTA= 1.3 \$/kg

SHMP=1.145\$/kg

PAA/PMA= 1.5 \$/kg

Flocon 260=1.6 \$/kg

(Required data is mentioned in **Appendix C**)

EDTA pure powder market is 1.3\$/kg makes and PAA/MAA 50% solution market price is 1.2\$/kg.

Density of 0.1N EDTA solution is 1.0177 gr/ml. To make a 0.1N EDTA solution, 18.6gr of pure EDTA powder should be dissolved in each liter of DI water.

So the price of lab-made A/S is:

$$[0.6 * 1.5 \$/\text{kg PAA/MAA}] + [0.4 * ((0.0186 * 1.3 \$/\text{kg EDTA}) / 1.0177)] \\ = 0.909 \$/\text{kg}$$

Flocon 260 market price is 1.6 \$/kg

Assuming 8ppm of SHMP , Flocon 260 & the lab-made AS is required for raw water treatment:

Antiscalant	\$/Kg antiscalant	\$/m³ raw water treatment
SHMP (phosphorus based)	1.1	0.0088
Flocon 260	1.6	0.0128
Lab-made AS	0.909	0.0073

So this lab-made A/S can be a good alternative for both phosphorous based and commercially available antiscalants.

Recommendations:

There are a couple of things that have been missed in this study because of a lack of time.

1. Experiments with other w/w% of PAA/PMA+EDTA will show what the best combination is.
2. Experiments with other feed water pressure will show the effect of pressure on scale formation using this lab-made A/S.
3. Adding a data logger to the system will make the operation easier and lets the researcher runs longer sets of experiments without taking samples manually.
4. Doing experiments with more complicated feed water compositions will produce more reliable results.
5. This study has produced lots of raw data that can be used to show how R_m changes based on SD theory

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Appendix A – Experimental Raw Data

		Time	permeate			concentrate	
	Set	Time (min)	permeate volume (ml)	permeate flow ml/min	permeate Ec - ms	concentrate volume(ml)	concentrate flow ml/min
Raw water 1st run	1	60	50	0.833	17.67	58	0.966
	2	120	32	0.533	17.3	43	0.716
	3	179	29	0.491	16.9	40	0.677
	4	239	24	0.4	15.52	41	0.683
	5	296	20	0.350	14.36	46	0.807
	6	356	17	0.283	14.37	44	0.733
Raw water 2nd run	1	62	45	0.725	13.26	64	1.032
	2	119	26.2	0.459	15.85	47	0.824
	3	178	25	0.423	14.52	57.5	0.974
	4	240	21.4	0.345	14.18	65.7	1.059
	5	305	19.4	0.298	13.46	42	0.646
	6	365	15.68	0.261	13.76	48	0.8
Raw water Average	1	61	47.5	0.779	15.465	61	0.999
	2	119.5	29.1	0.496	16.575	45	0.770
	3	178.5	27	0.457	15.71	48.75	0.826
	4	239.5	22.7	0.372	14.85	53.35	0.871
	5	300.5	19.7	0.324	13.91	44	0.726
	6	360.5	16.34	0.272	14.065	46	0.766

		Time	Permeate			concentrate	
	Set	Time (min)	permeate volume (ml)	permeate flow ml/min	permeate Ec - ms	concentrate volume(ml)	concentrate flow ml/min
8ppm of flocon 260 1st run	1	65	35	0.538	13.23	34	0.523
	2	125	31	0.516	14.22	28	0.466
	3	186	28	0.459	14.5	24	0.393
	4	249	25.2	0.4	16.6	26	0.412
	5	309	20.3	0.338	16.7	23	0.383
	6	369	17.2	0.286	17.01	23	0.383
8ppm of flocon 260 2nd run	1	60	48	0.8	12.35	32	0.533
	2	120	45	0.75	17.45	21	0.35
	3	179	43	0.728	17.9	21.5	0.364
	4	239	37	0.616	17.69	17	0.283
	5	299	36	0.6	18.07	17	0.283
	6	359	34.4	0.573	17.8	17	0.283
8ppm of flocon 260 3th run	1	60	33	0.55	19	54	0.9
	2	120	23	0.383	16.1	44	0.733
	3	183	28	0.444	14.3	44	0.698
	4	245	24.6	0.396	15.36	38.5	0.620
	5	310	25	0.384	17	47	0.723
	6	360	25.5	0.51	16.9	36.5	0.73
8ppm of flocon 260 Average	1	61.667	38.666	0.629	14.86	40	0.652
	2	121.67	33	0.55	15.923	31	0.516
	3	182.67	33	0.544	15.566	29.833	0.485
	4	244.33	28.933	0.471	16.55	27.166	0.438
	5	306	27.1	0.440	17.256	29	0.463

		Time	permeate			concentrate	
	Set	Time (min)	permeate volume (ml)	permeate flow ml/min	permeate Ec - ms	concentrate volume(ml)	concentrate flow ml/min
	6	362.67	25.7	0.456	17.236	25.5	0.465
60%PAA/ PMA + 40% EDTA 1st run	1	60	59.4	0.99	17.67	44	0.733
	2	120	61	1.016	17.3	31	0.516
	3	179	25	0.423	16.9	27.5	0.466
	4	239	36	0.6	15.52	23.5	0.391
	5	296	33	0.578	14.36	20	0.350
	6	356	30	0.5	14.37	20	0.333
60%PAA/ PMA + 40% EDTA 2nd run	1	61	35	0.573	14.05	58	0.950
	2	121	33	0.55	14.81	46	0.766
	3	181	34	0.566	14.7	40	0.666
	4	243	33.6	0.541	14.5	40	0.645
	5	303	21	0.35	13.74	35	0.583
	6	363	25.4	0.423	13.44	33.3	0.555
60%PAA/ PMA + 40% EDTA 3th run	1	62	20	0.322	12.3	110	1.774
	2	122	27.5	0.458	12.05	95	1.583333333
	3	188	29	0.439	12.05	80	1.212
	4	248	25	0.416	10.8	66	1.1
	5	307	24	0.406	10.86	62	1.050
	6	343	14.5	0.402	8.02	35	0.972

		Time	permeate			concentrate	
	Set	Time (min)	permeate volume (ml)	permeate flow ml/min	permeate Ec - ms	concentrate volume(ml)	concentrate flow ml/min
60%PAA/ PMA + 40% EDTA average	1	61	38.133	0.628	14.673	70.666	1.152
	2	121	40.5	0.675	14.72	57.333	0.955
	3	182.67	29.333	0.476	14.55	49.166	0.781
	4	243.33	31.533	0.519	13.606	43.166	0.712
	5	302	26	0.445	12.986	39	0.661
	6	354	23.3	0.442	11.943	29.433	0.620

Appendix B - Data Analysis and System Properties Data:

	Time		sys properties			
	Set	Time	Ion Rejection%	recovery %	Q/Q _{max}	R/R ₀
Raw water 1st run	1	60	11.65	46.296	1	1
	2	120	13.5	42.666	0.64	0.921
	3	179	15.5	42.028	0.589	0.907
	4	239	22.4	36.923	0.48	0.797
	5	296	28.2	30.303	0.421	0.654
	6	356	28.15	27.868	0.34	0.601
Raw water 2nd run	1	62	33.7	41.284	1.000	1
	2	119	20.75	35.792	0.633	0.866
	3	178	27.4	30.303	0.583	0.734
	4	240	29.1	24.569	0.475	0.595
	5	305	32.7	31.596	0.411	0.765
	6	365	31.2	24.623	0.360	0.596
8ppm of flocon 260 1st run	1	65	33.85	50.724	1	0.962
	2	125	28.9	52.542	0.959	0.996
	3	186	27.5	53.846	0.852	1.021
	4	249	17	49.218	0.742	0.933
	5	309	16.5	46.882	0.628	0.889
	6	369	14.95	42.786	0.532	0.811
8ppm of flocon 260 2nd run	1	60	38.25	60	1	1
	2	120	12.75	68.181	0.937	1.136
	3	179	10.5	66.666	0.911	1.111
	4	239	11.55	68.518	0.770	1.141
	5	299	9.65	67.924	0.75	1.132
	6	359	11	66.926	0.716	1.115

8ppm of flocon 260 3th run		Time	sys properties			
	Set	Time	Ion Rejection%	recovery %	Q/Q_{max}	R/R₀
	1	60	5	37.931	1	1
	2	120	19.5	34.328	0.696	0.905
	3	183	28.5	38.888	0.808	1.025
	4	245	23.2	38.985	0.721	1.027
	5	310	15	34.722	0.699	0.915
	6	360	15.5	41.129	0.927	1.084
60%PAA/ PMA + 40% EDTA 1st run	1	60	11.65	57.446	0.973	1
	2	120	13.5	66.304	1	1.154
	3	179	15.5	47.619	0.416	0.828
	4	239	22.4	60.504	0.590	1.053
	5	296	28.2	62.264	0.569	1.083
	6	356	28.15	60	0.491	1.044
60% PAA/ PMA + 40% EDTA 2nd run	1	61	29.75	37.634	1	1
	2	121	25.95	41.772	0.958	1.109
	3	181	26.5	45.945	0.987	1.220
	4	243	27.5	45.652	0.944	1.213
	5	303	31.3	37.5	0.61	0.996
	6	363	32.8	43.270	0.737	1.149
60%PAA/ PMA + 40% EDTA 3th run	1	62	38.5	15.385	0.703	1
	2	122	39.75	22.449	1.000	4.766
	3	188	39.75	26.606	0.958	1.729
	4	248	46	27.473	0.909	1.785
	5	307	45.7	27.907	0.887	1.813
	6	343	59.9	29.293	0.878	1.904

Appendix C – Economical Analysis Data

Home > Weekly Price > EDTA 4NA

EDTA 4NA Price Analysis CAS No.: 13235-36-4 (Update on 2020-03-03)



Reference Price	\$1300/MT (Latest Price)	\$1300/MT (Previous Price)
Change	\$0.0/MT	

Date	Price	Change
2020-03-03	\$1300/MT	\$0.0/MT
2020-02-25	\$1300/MT	\$0.0/MT
2020-02-18	\$1300/MT	\$0.0/MT
2020-02-11	\$1300/MT	\$0.0/MT
2020-02-04	\$1300/MT	\$0.0/MT
2020-01-14	\$1300/MT	\$0.0/MT
2020-01-07	\$1300/MT	\$0.0/MT

⌘ This indicative price is based on market analysis for reference only and should not be used for other commercial purposes.

<https://www.echemi.com/productsInformation/pd20160714155237501-tetra-sodium-edta.html>



Sodium Hexametaphosphate 68% Tech Grade

Views : 🔥 5,159+ **Most Popular**

Read reviews Write a review

FOB Reference Price **\$1,145.00 /ton**
Total FOB Price **\$1,145.00**

Subscribe to Price Alert
 Reference Currency ▼

Select Package Type * Choose an Option...

Quantity: - 1 + Metric Tons

Estimate		
Shipping Cost:		
Country	Port	Calculate
Iran	Bandar Abbas	
Product Name	Containers (FCL)	Price
Sodium Hexametaphosphate 68% Tech Grade	1	\$1,500.00

Countries with no shipping rates: [Contact us](#) for shipping options.

<https://www.echemi.com/productsInformation/pd20160714155237501-tetra-sodium-edta.html>

Copolymer of Maleic and Acrylic Acid(AA/MA)

FOB Reference Price: [Get Latest Price](#)

>=5 Metric Tons

\$1,800.00

Shipping: Support Sea freight

Lead Time:

Quantity(Metric Tons)	1 - 5	>5
Est. Time(days)	7	Negotiable

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Alibaba.com Freight | [Compare Rates](#)

Payments: **VISA** **Online Bank Payment** **T/T** **Pay Later** **WesternUnionWU** **Alibaba.com Logistics** **Inspection Solutions**

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https://www.alibaba.com/product-detail/Copolymer-of-Maleic-and-Acrylic-Acid_60815595577.html?spm=a2700.7724857.normalList.16.16b04b5fEZTfuY&s=p

Copolymer of Maleic and Acrylic Acid

FOB Reference Price: [Get Latest Price](#)

20 - 25 Metric Tons	>=26 Metric Tons
\$1,500.00	\$1,000.00

Shipping: Support Sea freight

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Payments: **VISA** **Online Bank Payment** **T/T** **Pay Later** **WesternUnionWU** **Alibaba.com Logistics** **Inspection Solutions**

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chemical raw materials Copolymer of Maleic and Acrylic Acid scale inhibitor for boiler water

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\$1,000.00 - \$1,400.00 / Metric Ton | 1 Metric Ton/Metric Tons (Min. Order)

MARCH

Featured Product in March Expo 2020

4% OFF Product value more than \$10,000.00, Capped at \$1,000.00 [Get Coupon](#)

Customization: Customized logo (Min. Order: 1 Metric Tons)
Customized packaging (Min. Order: 1 Metric Tons) [More](#)

Samples: \$1,400.00 /Metric Ton | 1 Metric Ton (Min. Order) [Buy Samples](#)

<https://www.alibaba.com/product-detail/chemical-raw-materials-Copolymer-of-Maleic-60756717063.html?spm=a2700.7724857.normalList.67.16b04b5fEZTfuY>



Copolymer of Maleic and Acrylic Acid

FOB Reference Price: [Get Latest Price](#)

\$100.00 - \$120.00 / Metric Ton | 1 Metric Ton/Metric Tons (Min. Order)

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Alibaba.com Freight [Compare Rates](#)

Payments: **VISA** **Online Bank Payment** **T/T** **Pay Later** **WesternUnion\WU**

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<https://www.alibaba.com/product-detail/Copolymer-of-Maleic-and-Acrylic-Acid-2013966975.html?spm=a2700.7724857.normalList.108.16b04b5fEZTfuY>

The screenshot shows the Alibaba.com website interface. At the top, there's a search bar with the text "What are you looking for...". Below the search bar, there's a navigation menu with categories like "Ready to Ship", "Trade Shows", "Services", "Sell on Alibaba", and "Help". The main content area displays a product page for "poly(acrylamide-co-acrylic acid)". The product image shows a white powdery substance being poured from a container. The product details include the FOB Reference Price, quantity ranges (10-21 Metric Tons and >=22 Metric Tons), and prices (\$2,000.00 and \$1,500.00). The page also features a "Trade Assurance" badge, payment options (VISA, Online Bank Payment, T/T, Pay Later, WesternUnion\WU), and a supplier profile for "Yucheng Jinhe Industrial Co., Ltd." with a "Gold Supplier" badge. The supplier profile includes a "Contact Supplier" button, a "Chat Now" button, and a "Browsing History" section. The bottom of the page shows a Windows taskbar with various application icons and the system clock.

<https://www.alibaba.com/product-detail/poly-acrylamide-co-acrylic-acid-62158682659.html?spm=a2700.7724857.normalList.143.35666c558HhXS6>

Flocon[®] 260

www.wateradditives.com



Premium Antiscalant and Antifoulant for Membrane Systems

Description

Flocon 260 is an aqueous solution of a specialised polycarboxylic acid, highly effective in controlling the deposition of inorganic scale forming salts and particulate fouling on membrane surfaces.

- Excellent control of carbonate scales, sulphate and fluoride for cost effective operation
- Effectively control both soluble and insoluble iron
- Effective against silica fouling
- Dispersant
- Compatible with all major membranes
- International potable water approvals

Application

Flocon 260 is an aqueous solution of an organic acid and as such is corrosive in its concentrated form. Corrosion resistant dosing equipment should therefore be used. Examples of suitable materials are 316L stainless steel, or plastics such as GRP, PVC and PE.

The recommended injection point is into the feedwater downstream of any filtration equipment and cartridge filters.

Usage

Flocon 260 is miscible with water in all proportions. It may be applied as the neat product, or as a solution in permeate. Minimum dosing solution strength of 10% w/w is recommended. Flocon 260 should be dosed continuously and proportionately to the feed water flow, to maintain the recommended dose level.

The dose level required is dependent on the quality of the feedwater and the saturation indices of the various scales forming species present in the concentrated brine. Proprietary computer software is used to calculate scaling indices and calculate optimum system recovery. Dose level projections and recommendations are available on request.

*Please consult with your BWA Water Additives representative to determine optimal dosage recommendations for your system.

Packaging / Weight

Pail	55 lb	25 kg
Drum	500 lb	230 kg
IBCs/Totes	2,204 lb	1,000 kg

*Consult your sales representative for availability.

Physical Properties

Appearance	Pale yellow liquid
pH	< 2
Specific gravity at 20/20°C	1.14 to 1.165
Freezing point range	0 to -10 °C

Further details are available in the safety data sheet