

# A NOVEL CALCIUM CARBONATE SCALING MODEL FOR MAXIMUM RECOVERY AND INHIBITOR DOSAGES IN MEMBRANE SYSTEMS

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## **Abstract**

Calcium carbonate ( $\text{CaCO}_3$ ) is the most frequently encountered scale in industrial reverse osmosis (RO) systems. The Langelier Saturation Index (LSI) has traditionally been used to predict antiscalant limits to inhibiting  $\text{CaCO}_3$  scaling, but has been highly unreliable. The lack of reliability of the LSI is in part due to its use of TDS values rather than ionic strength to estimate  $\text{CaCO}_3$  solubility, but mostly because it doesn't consider for ion pairing. Another widely used scale prediction model, the Calcium Carbonate Precipitation Potential (CCPP), accurately predicts the quantity of precipitant in a low ionic strength solution, but cannot reliably predict levels at which antiscalants will fail to inhibit scale; the reason being that severe scaling occurs at very low CCPP values at the upper pH range where the driving force for scale formation is highest. Both calculations are ineffective at reliably predicting antiscalant dosage demands at varying pH levels, however both are commonly used to estimate such dosages in the absence of alternatives.

Antiscalants inhibit crystalline scales like calcium carbonate through threshold inhibition, a mechanism that interferes with the rate of crystal nucleation. A series of lab experiments through the neutral to high pH range validated a relationship between the rate of nucleation and antiscalant demand. This led to the development of a kinetics index used to calculate inhibitor dosages. Furthermore, a saturation calculation using ionic activity and ion complexation was used to predict the maximum saturation that could be controlled by antiscalants regardless of feedwater type. By considering for both carbonate and bicarbonate alkalinity, the calculation was made to be reliable at any pH. Such a calculation was essential for predicting whether pH reduction would be required, and for reliably determining the maximum recovery at which an RO system could be operated. The calculation was converted into an index for ease of use.

It was also recognized that antiscalants were severely limited by calcium and magnesium concentrations when attempting to operate at high recovery or high pH. Calcium and magnesium at high concentrations can form salts with all antiscalants, regardless of whether phosphonate or acrylate based. Higher inhibitor dosages exasperate this phenomenon, frustrating those who adhere to the common engineering practice of applying a safety factor. This creates scenarios where the antiscalant could fail even when a calculated saturation index is well below the maximum limit for a given inhibitor. The failure is twofold; the calcium or magnesium salts act as scales, while the loss of active inhibitor results in  $\text{CaCO}_3$  precipitation. An index was developed to calculate the point of failure for antiscalants at all pH ranges, with different constants applied for different antiscalant chemistries.

Using the three abovementioned indices, the maximum recovery, optimal operating pH, and minimum antiscalant dosage can all be predicted for complex feedwater chemistries.



## Introduction

The most commonly used indices to predict scaling in brackish water reverse osmosis systems (BWRO) are the Langelier Saturation Index (LSI) [1] and the Calcium Carbonate Precipitation Potential (CCPP) [2]. For seawater reverse osmosis systems (SWRO), a modification of the LSI known as the Stiff and Davis index (S&DI) [3] is used; while this should theoretically be more versatile because it uses ionic strength instead of TDS, it has still been shown to be unreliable. Many suppliers of scale inhibitors have written scale prediction software that rely on these values for their dosage calculations.

However, our work has shown that it is impossible to correlate any of these indices to a dosage outside of a very narrow pH range. The dosage required to inhibit scaling for a LSI of 2.3 is completely different at pH 7 as compared to pH 8. Likewise, a CCPP of 500 mg/l at pH 7 would not require the same dosage as a CCPP of 500 mg/l at pH 8. Furthermore, a CCPP of 500 mg/l at pH 9 would be associated with conditions that cause severe scaling and could not be inhibited.

The Stiff and Davis [3] index is widely used for TDS > 10,000 ppm, however, we've found it to be highly misleading in industrial water applications where the water chemistry can be vastly different to that of seawater.

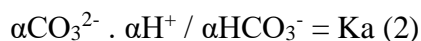
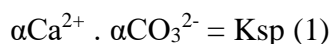
The purpose of this work was to:

1. Create an index that could be used to determine the scaling potential and maximum achievable RO recoveries for any type of water.
2. Identify a useful method to predict antiscalant dosages at any pH and for any water chemistry

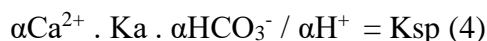
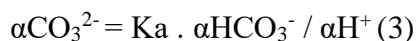
## Background

LSI was originally developed by Langelier [1] in 1936 to establish the pH at which calcium carbonate would precipitate to form a protective layer on iron pipe. This was under the mistaken assumption that passive scales were made up of iron hydroxide co-deposited with calcium carbonate (we now know that it's actually ferrous carbonate that forms).

The LSI is based on the algebraic manipulation of the active ion product for calcium carbonate and that of the dissociation of the bicarbonate ion:



where (2) is rearranged and substituted into (1);



and rearranged to solve for the log activity of the hydronium ion;

$$\alpha\text{H}^+ = \alpha\text{Ca}^{2+} \cdot \text{Ka} \cdot \alpha\text{HCO}_3^- / \text{Ksp} \quad (5)$$

$$\text{Log } \alpha\text{H}^+ = \text{Log } \alpha\text{Ca}^{2+} + \text{Log } \text{Ka} + \text{Log } \alpha\text{HCO}_3^- - \text{Log } \text{Ksp} \quad (6)$$

$$\text{pHs} = - \text{Log } \alpha\text{Ca}^{2+} - \text{Log } \text{Ka} - \text{Log } \alpha\text{HCO}_3^- + \text{Log } \text{Ksp} \quad (7)$$

$$\text{pHs} = - (\text{Log } \gamma \text{Ca}^{2+} + \text{Log } \gamma \text{HCO}_3^-) + \text{Log } (\text{Ksp} / \text{Ka}) - (\text{Log } [\text{Ca}^{2+}] + \text{Log } [\text{HCO}_3^-]) \quad (8)$$

where activity coefficients are replaced with a total dissolved solids (TDS) dependent constant (A) and a temperature correction factor is added for Ksp and Ka values (B), and C and D are calcium and bicarbonate alkalinity values.

$$\text{pHs} = (A + B) - (C + D)$$

$$\text{LSI} = \text{pH} - \text{pHs}$$

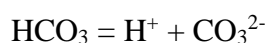
Langelier did not account for ion complexations as little data was available at the time, and computers were not available to perform the non-trivial calculations. However, they would have been likely negligible in the low salinity water for which the LSI was intended.

He used TDS to estimate activity coefficients based on his correlations between TDS and ionic strength for various natural bodies of water. A complete water analysis would be required to calculate ionic strength; this made the use of activity coefficients impractical for a plant operator who had to make regular pH adjustments to maintain a slightly scaling water.

For this reason, Langelier created a table of constants that could be referenced by an operator through a TDS and gave a relatively reliable prediction of the likelihood for calcium carbonate scale to form.

However, the LSI was never meant to be used for RO scaling predictions. Source waters can carry varying degrees of salinity, and high recoveries concentrate them further. Under these conditions, ion complex formation is significant, and reliable activity coefficient calculations are essential for calculating both the ion complex formation and the scale formation potentials. In the case of NF membranes, the preferential rejection of divalent ions further deviates the ratios of dissolved ions from those found in natural bodies of water.

CCPP [3] is a stoichiometrically limited calculation that accounts for the equilibrium of carbonate species in water. When calcium carbonate precipitates, bicarbonate ions dissociate to form more carbonate and hydronium ions to maintain the equilibrium. The increased concentration in hydronium ions results in a pH decrease that is typically observed when calcium carbonate precipitation occurs.



This makes CCPP a very reliable calculation for predicting the quantity of scale that could form under a given condition. The drawback is that a highly saturated water with low calcium concentration may result in a low CCPP value, even when the driving force for scale formation is too high to be controllable by antiscalant. Furthermore, in RO systems, a thin layer of scale covering the membrane surface can be just as disruptive to membrane permeability as a scaling layer that is triple the thickness.

The CCPP is therefore not useful in predicting maximum recovery in a RO system, nor is it in any way related to antiscalant dosage. Scale is controlled primarily by threshold inhibition which acts on a crystal nuclei to prevent its growth into a crystal lattice. The potential for total calcium carbonate precipitation is therefore of little relevance to the dosages of antiscalant required. At best, the CCPP is useful for predicting the severity of differential pressure ( $\Delta P$ ) increases across the last stage of a system if scaling were not controlled.

It was therefore apparent that a saturation-based approach would be more reliable than a quantified precipitation-based approach for predicting maximum recoveries in RO systems. However, in order for the saturation calculation to be useful for a broad range of water chemistries, ion complexes and ion activities had to be considered.

## Experimental Setup

Separate solutions of calcium chloride ( $\text{CaCl}_2$ ) and sodium bicarbonate ( $\text{NaHCO}_3$ ) were prepared using reagent grade salts in batches large enough to perform up to 10 tests. The solutions were then each filtered using a  $0.45 \mu\text{m}$  filter in a vacuum apparatus to remove any insoluble matter. The  $\text{CaCl}_2$  and  $\text{NaHCO}_3$  solutions were heated to exactly  $25^\circ\text{C}$  and mixed together into a glass dish at a controlled rate. The mixed solutions were then continuously stirred on hotplates at 200 rpm for the remainder of the experiment to maintain homogeneity. The hotplates were equipped with a thermocouple to maintain a temperature of  $25^\circ\text{C}$  throughout the experiment.

pH was adjusted to target in one of the solutions using reagent grade hydrochloric acid (HCl) or sodium hydroxide (NaOH). Once the amount of HCl or NaOH required was determined, the bulk solution was adjusted using the same ratio.

Preliminary experiments found significant loss of alkalinity upon mixing of solution, even in the absence of precipitation. This was presumed to be a result of carbon dioxide off-gassing upon mixing of the low pH  $\text{CaCl}_2$  solution with the  $\text{NaHCO}_3$  solution. To ensure accurate interpretation of the results, the alkalinity was therefore always measured by titration upon mixing.

Various antiscalants were tested at various dosages. The initial turbidity readings were collected immediately upon mixing and every 30 minutes thereafter for a total of 2 hours. Turbidity values were compared to those of the filtered anion and cationic solutions. Antiscalant dosages were only considered successful if they prevented turbidity from rising. In some cases, the experiment at any given pH, calcium and alkalinity concentration would have to be repeated several times to optimize the dosage for each of the antiscalants tested. Inevitably,

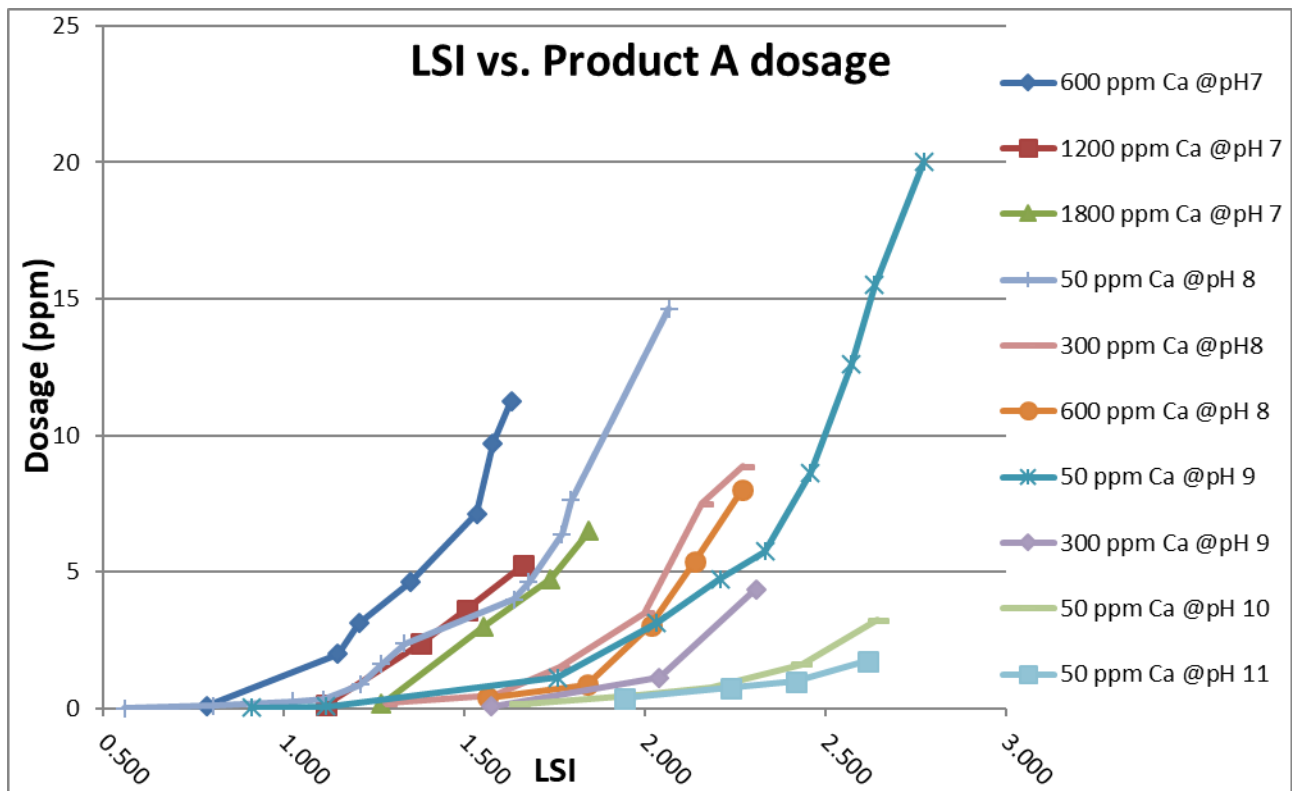


experiments below pH 9 saw a slight increase in pH over the 2 hour period due to CO<sub>2</sub> equilibrating with the atmosphere. For the same reason, experiments at pH 10 and above saw a slight decrease in pH. While these pH changes would normally be considered to be “noise”, we considered this to be an important part of the experiment due to scaling events frequently experienced during concentrate disposal at atmospheric pressure. The goal was to identify a method for calculating antiscalant dosages that would control scale beyond the membrane system.

Experiments were performed at pH 7, 8, 9, 10 and 11. At each pH, multiple values of calcium and alkalinity were tested. In total 130 different combinations were tested, each test being repeated a total of three times to validate the results and identify false values caused by human error.

## Results

The collected data was initially graphed to show dosage vs LSI. It became immediately apparent that there was no consistent relationship between LSI and antiscalant dosage (see Fig.1).



**Fig.1: A plot showing calculated LSI vs. optimal dosages obtained through lab experimentation.**

Dosages were also compared to CCPP values. Due to the computer loops required for calculating CCPP, plotting a graph for all the experimental results would have been overly tedious. However, several data points were selected and are shown in Table 1 to demonstrate the lack of a relationship between CCPP and antiscalant dosage.

The initial goal of this study was to determine whether a reliable saturation calculation could be correlated to dosages. The approach was to use a method first proposed by Larson [4], where all relevant complexes would be calculated and then the activities of the free calcium and carbonate ions would be used to determine the saturation. This has now become the standard method for calculating saturation, and is used by well-known geological software such as PHREEQC. Only complexes for which reliable thermodynamic data was available were considered as follows:

$$[\text{Ca}^{2+}] = [\text{Ca}_T] - \{[\text{CaOH}^+] + [\text{CaCl}^+] + [\text{CaF}^+] + [\text{CaHCO}_3^+] + [\text{CaCO}_3^0(\text{aq})] + [\text{CaSO}_4^0(\text{aq})] + [\text{CaPO}_4^-] + [\text{CaHPO}_4^0(\text{aq})] + [\text{CaH}_2\text{PO}_4^+] + [\text{CaH}_2\text{SiO}_4^0(\text{aq})] + [\text{Ca}(\text{H}_3\text{SiO}_4)_2^0(\text{aq})] + [\text{CaH}_3\text{SiO}_4^+] + [\text{CaNO}_3^+]\} \quad (9)$$

$$[\text{CO}_3^{2-}] = [\text{C}_T] - \{[\text{HCO}_3^-] + [\text{H}_2\text{CO}_3] + [\text{CaHCO}_3^+] + [\text{MgHCO}_3^+] + [\text{BaHCO}_3^+] + [\text{SrHCO}_3^+] + [\text{NaHCO}_3^0(\text{aq})] + [\text{MnHCO}_3^+] + [\text{FeHCO}_3^+] + [\text{CaCO}_3^0(\text{aq})] + [\text{MgCO}_3^0(\text{aq})] + [\text{BaCO}_3^0(\text{aq})] + [\text{SrCO}_3^0(\text{aq})] + [\text{NaCO}_3^-] + [\text{MnCO}_3^0(\text{aq})] + [\text{FeCO}_3^0(\text{aq})]\} \quad (10)$$

$$[\text{Ca}^{2+}] \cdot \gamma_{\text{Ca}^{2+}} \cdot [\text{CO}_3^{2-}] \cdot \gamma_{\text{CO}_3^{2-}} = K_{\text{spCaCO}_3} \quad (11)$$

The equilibrium and solubility constants would be corrected for temperature by utilizing the Van't Hoff equation and the enthalpy of reaction for each association or formation reaction, where:

$$\Delta_r G^\circ = -RT \ln K \quad (12)$$

And

$$\Delta_r G^T = (T/298.15) \Delta_r G^\circ + \Delta_r H^\circ (1 - (T/298.15)) \quad (13)$$

Where;

$\Delta_r G^\circ$  = Gibbs Free Energy of Reaction

$\Delta_r H^\circ$  = Enthalpy of Reaction

R = Universal Gas Constant

T = Temperature (°K)

K = Equilibrium or Solubility Constant

Since activity coefficients were necessary to calculate the complexes, but calculation of complexes were necessary to calculate the ionic strength, multiple iterations were required to determine these codependent values. This was essential because neutral complexes do not contribute to ionic strength, and monovalent complexes would have a lower contribution to ionic strength than the free divalent ions originally considered in the ionic strength calculation.

While the calculations used for saturation were not novel, the equilibrium constants that were selected were those that best fit our experimental data; in many cases those were different from values used in the PHREEQC database; the same was true for activity coefficient parameters that were used. The log of the saturation value was given the name "Calcium Carbonate



Nucleation Index” or CCNI to distinguish it from similar saturation calculations that used different equilibrium constants.

Our experiments used salts of chlorides and sodium, so the formations of those complexes had to be considered in order to determine the ionic strength of the solution. The following complexes were therefore considered in calculating saturations of the experimental solutions:

$$[\text{Ca}_T] = [\text{Ca}^{2+}] + [\text{Ca}^{2+}] + [\text{CaOH}^+] + [\text{CaCl}^+] + [\text{CaHCO}_3^+] + [\text{CaCO}_3^0_{(\text{aq})}] \quad (14)$$

$$[\text{C}_T] = [\text{CO}_3^{2-}] + [\text{HCO}_3^-] + [\text{H}_2\text{CO}_3] + [\text{CaHCO}_3^+] + [\text{NaHCO}_3^0_{(\text{aq})}] + [\text{CaCO}_3^0_{(\text{aq})}] + [\text{NaCO}_3^-] \quad (15)$$

$$[\text{Na}_T] = [\text{Na}^+] + [\text{NaOH}^0] + [\text{NaHCO}_3] + [\text{NaCO}_3^-_{(\text{aq})}] \quad (16)$$

$$[\text{Cl}_T] = [\text{Cl}^-] + [\text{CaCl}^+] \quad (17)$$

$$\text{Saturation} = [\text{Ca}^{2+}] \cdot \gamma_{\text{Ca}^{2+}} \cdot [\text{CO}_3^{2-}] \cdot \gamma_{\text{CO}_3^{2-}} / K_{\text{spCaCO}_3} \quad (18)$$

Table 1 shows a comparison between LSI, CCPP and CCNI vs. the dosage of one of the tested antiscalants. It was apparent that neither supersaturation or precipitation potential could be correlated to inhibitor dosages.

Under these conditions, the CCNI values were consistently lower than those of LSI due to the inclusion of complexes in the calculation. However, the advantages of using the CCNI to predict whether a scaling potential existed become even more apparent in more complex water.

A projection for a seawater plant operating at 45% recovery (Table 2) calculated the following:

CCNI: 0.48

LSI: 1.72

S&DSI: -2.09

The LSI showed an unrealistically high supersaturation while the Stiff and Davis index showed the water to be under-saturated. Since it is known that seawater is oversaturated with calcium carbonate and that calcium carbonate precipitation can occur in the presence of a seed [5], the S&DSI value was also considered to be unreliable.

The CCNI value of 0.48 was below the range at which our experiments found spontaneous nucleation to occur. We found that a minimum 5X saturation was necessary for overcoming the barrier energy for nucleation, and this was in agreement with other work [6]. Seawater also contains natural organic matter (NOM) which has an inhibitory effect on calcium carbonate nucleation [7].



**Table 1: Comparison of some CCPP, LSI, S&DSI, and CCNI values to minimum required dosage for scale inhibition. All values are calculated at 25°C.**

Test pH	Ca <sup>2+</sup>	Na <sup>+</sup>	Bicarbonate Alkalinity, ppm CaCO <sub>3</sub> (by titration)	Carbonate Alkalinity, ppm CaCO <sub>3</sub> (by titration)	Cl <sup>-</sup>	TDS	Ionic Strength	CCPP (mg/l)	LSI	S&DSI	CCNI	Product A Dosage, ppm
7.04	600	226	394	0	1122	2428	0.05	222	0.79	0.68	0.75	0.10
7.03	600	2035	3634	0	1657	8724	0.13	920	1.69	1.41	1.41	Light scaling regardless of dosage
7.06	1800	904	1604	0	3423	8085	0.17	1199	1.84	1.42	1.53	6.50
8.01	50	2864	6018	0	214	10469	0.13	123	1.80	1.56	1.46	7.125
8.02	50	5727	11817	0	293	20487	0.25	124	2.07	1.49	1.51	14.625
8.01	600	345	732	0	1062	2900	0.06	513	2.02	1.91	1.92	3.055
9.06	50	42	76	14	88	282	0.01	18	1.11	1.05	1.25	0.0625
9.02	50	729	1290	260	88	2597	0.04	124	2.20	2.18	1.97	4.75
9.03	300	143	228	86	531	1303	0.03	171	2.27	2.21	2.20	4.375
10.03	50	386	342	482	88	1230	0.03	33	2.67	2.63	2.15	3.25
10.02	50	548	486	698	88	1698	0.03	28	2.80	2.75	2.18	Light scaling regardless of dosage





**Table 2: Water Quality Obtained from Projection for a Seawater RO plant operating at 45% recovery. A temperature of 25 °C was used for the purposes of the projection.**

Cations	Raw	pH Adjusted Feed	Reject	Permeate	Anions	Raw	pH Adjusted Feed	Reject	Permeate
	mg/L	mg/L	mg/L	mg/L		mg/L	mg/L	mg/L	mg/L
Ca <sup>2+</sup>	437.37	437.370	793.51	2.084	HCO <sub>3</sub> <sup>-</sup> Alk (CaCO <sub>3</sub> )	153.18	148.29	246.10	0.97
Mg <sup>2+</sup>	1435.58	1435.580	2604.78	6.554	CO <sub>3</sub> <sup>2-</sup> Alk (CaCO <sub>3</sub> )	11.57	21.41	53.32	0.001
Ba <sup>2+</sup>	0.02	0.020	0.036	0.000	Total Alk (CaCO <sub>3</sub> )	164.757	169.70	299.41	0.98
Sr <sup>2+</sup>	7.64	7.640	13.86	0.036	Orthophosphate (PO <sub>4</sub> <sup>3-</sup> )	0.33	0.33	0.58	0.03
Na <sup>+</sup>	12083.49	12083.485	21915.40	66.71	SO <sub>4</sub> <sup>2-</sup>	2358.94	2358.94	4286.01	3.63
K <sup>+</sup>	401.96	401.960	729.02	2.220	F <sup>-</sup>	0.86	0.860	1.56	0.01
Fe <sub>2</sub> <sup>+</sup>	0.00	0.000	0.00	0.000	Cl <sup>-</sup>	22103.00	22103.00	40091.13	124.32
Fe <sub>3</sub> <sup>+</sup>	0.000	0.000	0.00	0.000	Br <sup>-</sup>	0.32	0.32	0.58	0.00
Al <sub>3</sub> <sup>+</sup>	0.000	0.000	0.00	0.000	SiO <sub>2</sub>	1.00	1.00	1.81	0.01
Mn <sub>2</sub> <sup>+</sup>	0.000	0.000	0.00	0.000	NO <sub>3</sub> <sup>-</sup> - N	0.00	0.00	0.00	0.00
Total Ammonia (NH <sub>3</sub> -N)	0.000	0.000	0.00	0.000	NO <sub>2</sub> <sup>-</sup> - N	0.00	0.00	0.00	0.00
					Total Sulfide (S <sub>2</sub> <sup>-</sup> )	0.00	0.00	0.00	0.00
					B(OH) <sub>3</sub> - B	0.00	0.00	0.00	0.00
					H <sub>3</sub> AsO <sub>3</sub> - As(III)	0.00	0.00	0.00	0.00
pH	8.20	8.20	8.00	7.02	H <sub>3</sub> AsO <sub>4</sub> - As(V)	0.00	0.00	0.00	0.00



However, despite the reliability of the CCNI in determining whether a solution was saturated, it could still not be used to predict antiscalant dosages.

Antiscalants have been postulated to interfere with crystal nucleation by changing the kinetics rather than thermodynamics of crystal growth [8,9]. This suggested that antiscalant dosages would be dependent on the rate of nucleation rather than the saturation of calcium carbonate scale.

Experimentation at variable temperatures also found that dosages increased in very good agreement with calculated rate constant when published values for activation energy and pre-exponential factor for  $\text{CaCO}_3$  nucleation were used. This was further evidence that dosages were most likely correlated to the rate of nucleation.

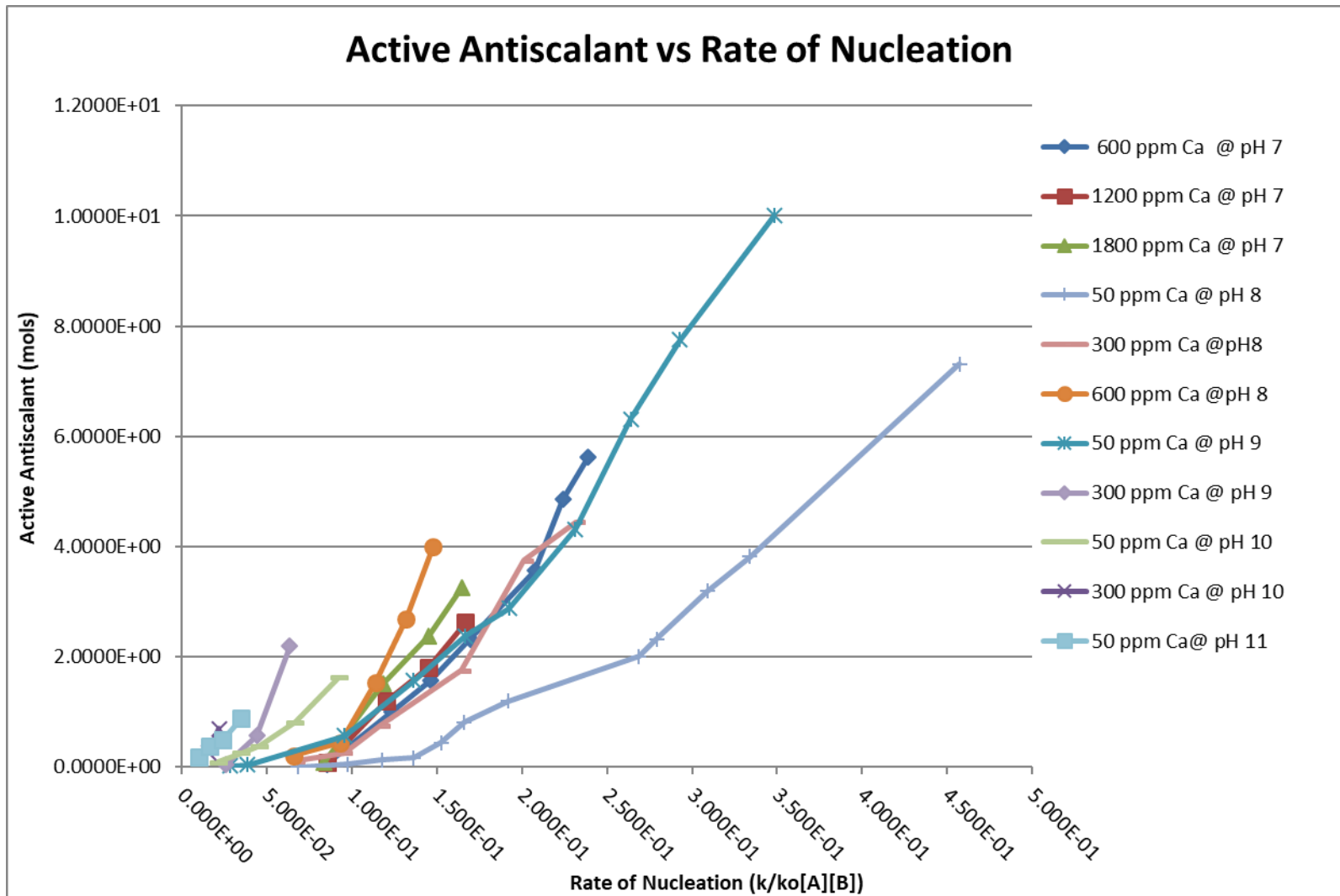
Several models for  $\text{CaCO}_3$  nucleation rate were considered. Many of the models used saturation as a basis for the rate calculation, but those did not correspond well with our data. The best fit was established using a model that accounted for the individual concentrations of Ca and  $\text{CO}_3$ , but had an order of reaction that was unrelated to their stoichiometric relationship (Fig.2). However, despite the fit being far better than that obtained against LSI, there were still some inconsistencies under different conditions.

When the complexation of the antiscalant with sodium and calcium (the only two metals involved in our experiments) was taken into account, the data fit improved significantly. The dosages now showed a very predictable relationship to the rate of nucleation (see Fig.3).

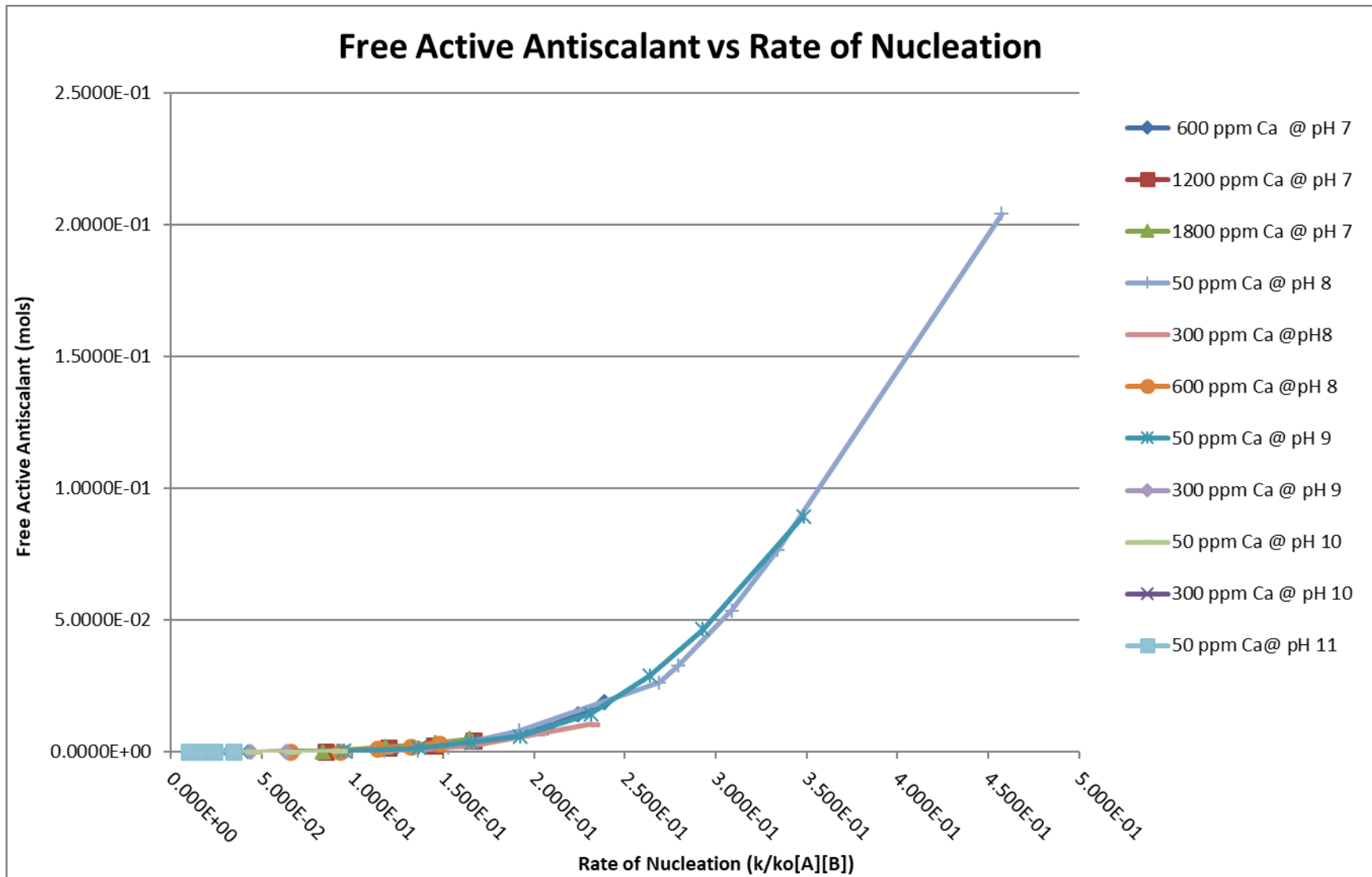
It therefore became evident that only free (uncomplexed) antiscalant ions would act to inhibit scale, and as such, dosages had to account for all cations in solution. Our model was therefore adjusted to account for ligand formation with Na, K, Ca, Mg, Ba, Sr, Fe (II), Fe(III), Mn (II), Al.

A review of the experimental data found that precipitation would sometimes occur at extremely low saturation values. In those cases, there would be no pH decline despite an extremely high turbidity, suggesting that the precipitate did not consist of calcium carbonate. SEM/EDS analysis of the precipitate found that the scales consisted of amorphous calcium salts of the antiscalant, regardless of whether a phosphonate or polymer were used (Fig.4). The precipitations did not occur only when calcium levels were high, but also appeared to form at low calcium concentrations when alkalinity was extremely high. In those cases, other experiments at identical calcium concentrations but lower alkalinity did not show a similar precipitate. This suggested that a calcium-carbonate-antiscalant compound was forming. Furthermore, available  $K_{sp}$  values for calcium-antiscalant salts verified that in all cases, the solutions were undersaturated for those precipitants. When phosphonate antiscalants were tested, the SEM/EDS analyses verified that Ca:P ratios were not consistent with those of the pure calcium phosphonate scales for the phosphonates in question. Similar precipitates were observed in experiments using magnesium, albeit at more severe conditions.





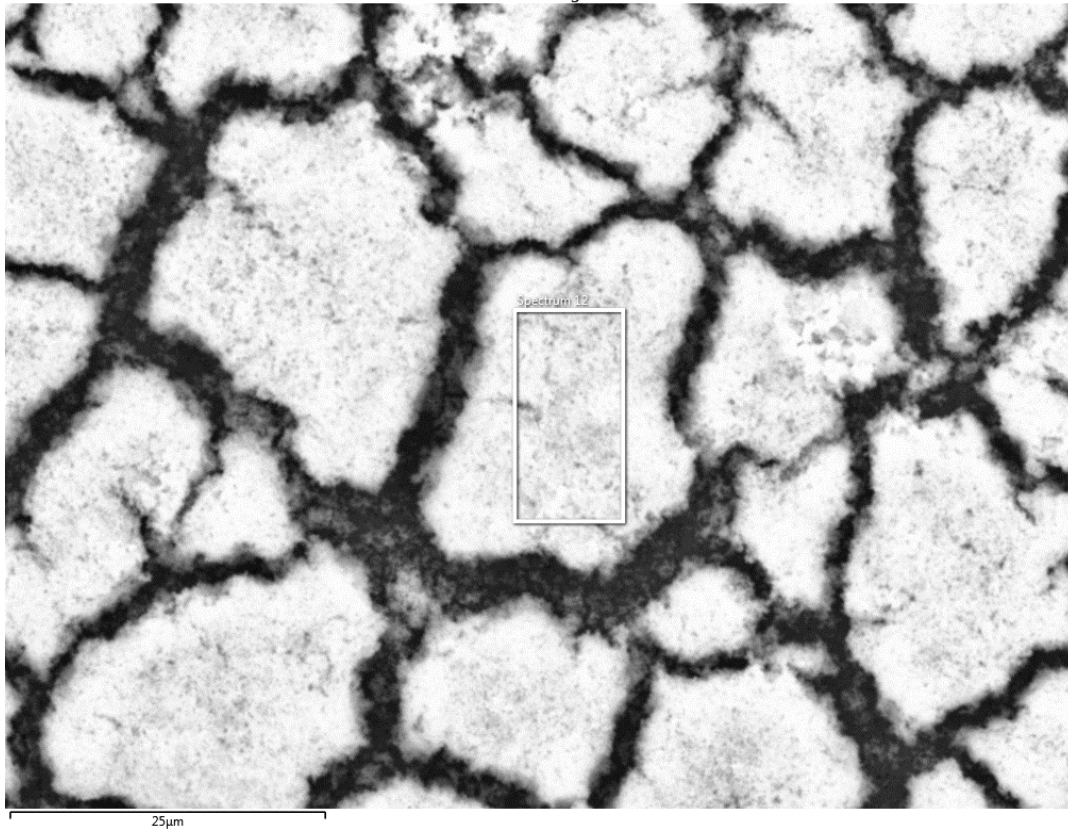
**Fig. 2: Active antiscalant dosage vs calcium carbonate nucleation rate**



**Fig.3: Free active antiscalant dosage vs calcium carbonate nucleation rate**



Electron Image 4

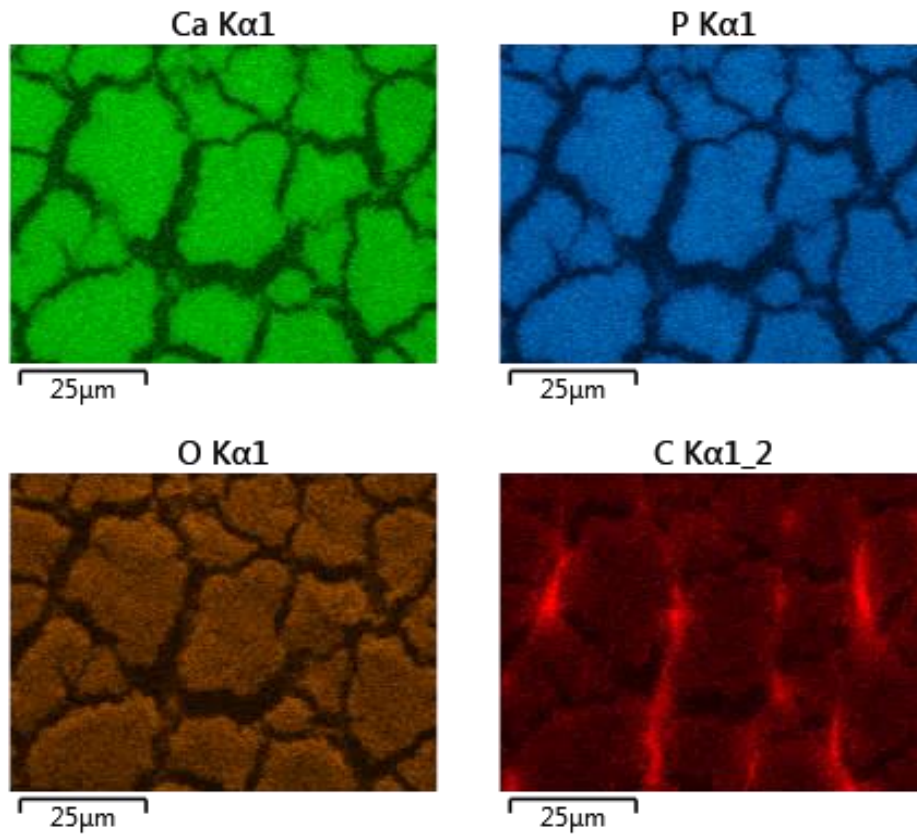


**Fig.4: Calcium-antiscalant salt formed in cases where calcium values were held constant and only alkalinity values were increased. This implied the formation of a complex calcium-carbonate-antiscalant salt.**

**Table 3: The EDS percentages were reported with and without carbon and oxygen. This was due to the large margin of error introduced by elements with an atomic number less than 10.**

Spectrum 12	Atomic %
C	28.02
O	50.65
P	9.24
Ca	12.08
Total	100.00

Spectrum 12	Atomic %
P	42.13
Ca	57.87
Total	100.00



**Fig.5: Calcium-antiscalant salt consisted of an amorphous scale with equally distributed Ca, P, O and C in the elemental map.**

It was apparent that inhibition could not always be correlated to a calcium carbonate saturation index was because the precipitant was not calcium carbonate. It appeared that when a scale could not be controlled, it was either due to under-dosing of antiscalant, resulting in calcium carbonate scale formation, or overdosing of antiscalant where a salt of the antiscalant would form.

It was also apparent that in some cases, overdosing of the antiscalant was inevitable. During our experiments, dosages would be increased with every experiment until a turbidity equivalent to that of deionized water could be achieved. In some cases, a higher dosage would show decreased turbidity with every trial, but after a certain dosage was exceeded, the turbidity would suddenly increase. When even higher dosages were attempted, turbidity values only increased further. In other words, the dosage of antiscalant necessary to inhibit the calcium carbonate scale under those conditions would form a calcium-antiscalant precipitate. It was also observed that calcium carbonate precipitation would eventually follow, since the antiscalant had been removed from solution.

Solubility limits were estimated for the various antiscalants based on the experimental results, as functions of calcium, carbonate and antiscalant concentrations. This resulted in a fairly reliable method for predicting antiscalant failures in RO systems. In order to simplify their use, a constant was added to the log saturation values to achieve a single failure value that could be reported to the user of the Proton<sup>®</sup> scale prediction software. This was named the “Antiscalant Precipitation Index” or API.

## Conclusion

A series of calcium carbonate precipitation experiments were performed at various pH values, calcium and alkalinity concentrations. The results of the experiment found that LSI, S&DSI and CCPP were not useful at predicting antiscalant dosages or maximum RO recoveries. However, the Calcium Carbonate Nucleation Index (CCNI), which considered for ion pairs and ionic activities, could consistently predict calcium carbonate scaling potential for any water chemistry. It was determined that phosphonate-based antiscalants could not control calcium carbonate beyond a CCNI of 2.3, and polymer-based antiscalants were limited to a CCNI of 2.0.

Maximum RO recoveries with respect to calcium carbonate were determined to be primarily limited by the supersaturation of a complex calcium-carbonate-antiscalant salt, as opposed to simple calcium carbonate saturation. These salts were found to form with all antiscalants, regardless of whether they were phosphonate or polymer based. An index, the Antiscalant Precipitation Index (API), was developed and incorporated into the Proton<sup>®</sup> reverse osmosis antiscalant projection software, and used in conjunction with CCNI to predict maximum recoveries.

A review of the experimental data determined that antiscalant dosages had no dependence on saturations, but were instead functions of nucleation kinetics. Incorporation of calculations for cation ligands enabled the free active antiscalant to be correlated to antiscalant precipitation under all test conditions.



In conclusion, no single calculation could be used to predict both antiscalant dosage, and maximum RO recovery. Three separate indices were developed and incorporated into the Proton<sup>®</sup> membrane projection software so they could be used in conjunction.





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