Modeling Scale Inhibitor Upper Limits: In Search of Synergy

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Existing models for calculating the minimum effective dosage for scale control have been applied to industrial and oil field scale control treatment optimization since the 1970s. Standard correlations are routinely used in developing the models.[1,2,3,4,5,6,7] The models typically apply to a single inhibitor. There is a driving force limit for each inhibitor, above which scale control can not be achieved regardless of the inhibitor dosage. Knowing the upper limit is critical for selecting the optimum treatment program and in specifying control limits for a system such as an open recirculating cooling tower or membrane system. Limits for individual inhibitors have been well documented. Studies have been conducted to determine the impact of blending inhibitors on the upper driving force limit. Upper driving force limits, as expressed by calcite saturation ratio, were measured for calcium carbonate inhibition by individual inhibitors and combinations. Results were evaluated and blends found to:

- increase the upper limit above that of either inhibitor when applied alone (synergism),
- decrease the upper limit (antagonism or competitive inhibition), or
- provide an upper limit in between that of the individual inhibitors (equivalent efficacy).

Test methods, data, and correlations are presented and discussed with respect to mechanisms.

How Inhibitors Work

When reactants are mixed, a solution is heated, cooled, undergoes a pressure change or is otherwise perturbed, the impact of the environmental changes is not immediate. A finite time passes before the perturbation affects any susceptible reaction. In the case of scale formation, induction time can be defined as the time before a measurable phase change (precipitation or growth) occurs after perturbation.[4,7] In a pure system, with only the reactants present such as calcium and carbonate, or barium and sulfate, scale formation might proceed as follows:

1) Aqueous calcium carbonate molecules congregate, and form larger and larger clusters.
2) The clusters grow to a critical size and overcome the "activation energy" needed for the change from the "aqueous" to "solid" phase to occur.
3) The phase change is then observed. In the case of $CaCO_3$, pH drops as the salt changes phase, and the induction time can be defined.
4) Crystals will then grow.

Scale inhibitors do not prevent scale. They delay the inevitable. The minimum, effective dose for a given water will prevent scale formation, or growth, until the water has passed through the system. The time until scale formation or growth is initiated is termed induction time. Scale inhibitors are induction time extenders. Untreated, there is a baseline induction time before scale growth occurs ($T_{induction\ 0}$). This baseline induction time decreases as the driving force for scale

formation increases. So induction time decreases as scale driving force like saturation ratio increases.

Equation 1)
$$T_{induction\ 0} = \frac{1}{k\ [x\ Saturation]^{M}}$$

Inhibitors extend this time by interfering with one of the steps in scale formation or growth ($T_{extended}$)

Equation 2)
$$T_{extended} = \frac{[inhibitor]^{N}}{k\ [x\ Saturation]^{M}}$$

where
$T_{induction\ 0}$ is the induction time untreated
$T_{extended}$ is the induction time when treated
inhibitor is the scale inhibitor molar concentration
M is s coefficient related to the number of molecules in a critical cluster
N is s coeficient
k is a temperature dependent rate constant
Saturation is the saturation ratio [8,9,10,11,12] as defined in Table 1.

Induction time has been studied extensively for industrial processes. Original crystallization studies were conducted to maximize production. In the case of sucrose crystallization, the objective is to minimize induction time and maximize crystallization. In the case of scale control, the objective is to extend the induction time until a water has safely passed through the cooling system, or other process adversely affected by scale. The induction time, in the absence of scale inhibitors, has been modeled for common scales, including barite ($BaSO_4$) and calcite ($CaCO_3$). Figures 1 and 2 are derived from this study, and compared to related works.[4]

Figure 1 profiles the untreated induction time for calcite in the practical operational range for calcite of 0 to 150x saturation. This range was chosen because it is the effective range for most scale inhibitors. The 150x saturation level limit is a commonly accepted upper limit for operation with common inhibitors such as phosphonates and polymers. Figure 2 profiles the saturation level range for barite, 0 to 80x saturation.

It should be noted that the induction times for both calcite and barite are several orders of magnitude below the typical residence time in an open recirculating cooling water system, oil field production process, or membrane system. As a result, the use of the thermodynamic saturation

ratios for predicting scale is accurate and an acceptable practice in typical operating ranges for these systems.

Actual induction times in practical operating systems will typically be lower than those of a pure system. Existing "seed" crystals and deposits provide a substrate for crystal growth without the necessity for achieving the "activation energy" for the initial phase change. In other words, it is easier to keep a clean system clean than to keep a dirty system from getting dirtier. Other factors can also decrease induction time. Ideally, studies will incorporate both “seeded” and “unseeded” conditions.

It is imperative that the upper driving force limits for inhibitors be known so that dosages curves and inhibitors are not applied to waters above the point where no dosage of the inhibitor will be effective.

Growth on Existing Substrates

At low saturation ratios, below the critical saturation ratio where seed crystal formation occurs, precipitation occurs by growth at active sites on an existing substrate. For precipitation from a pure solution, the substrate would be the scale of interest. In an operating practical environment such as oil field production, an industrial cooling system or a reverse osmosis unit, the substrate could be any surface where growth might occur.

Seed Crystal Formation and Growth

Above the critical saturation ratio, spontaneous nucleation can occur, followed by growth on the seed crystals. As the degree of supersaturation increases, the rate of seed crystal formation increases.

The Behavior of Inhibitor Blends – Saturation Ratio Limit

Inhibitors have an upper driving force that they can handle. Once this upper limit is reached, even increasing inhibitor dosage drastically will not provide scale control. Inhibitors included in this study are outlined in Table 2. Typical upper limits for single inhibitors are outlined in Table 3.

It has been known that blending inhibitors can increase the upper limit. The combination of a phosphonate and PMA, for example, has been observed to raise the upper limit well above that of the phosphonate alone. Not all combinations or ratios show this positive effect. Possibilities for the impact of inhibitor blends on the upper limit include:

- The limit for the blend would be the lower of the limits for the inhibitors in the blend
- The limit would be a weighted average of the limit for each inhibitor when applied alone.
- The limit would be the higher of the limits for the individual inhibitors in the blend.
- The new limit would be higher than the limit for any of the inhibitors in the blend.

A laboratory study reproduced the impact of polymaleates observed in field applications when blended with PBTC, and for the phosphonate blend of HEDP and ATMP . The study measured the upper saturation ratio limit for calcium carbonate for the individual inhibitors, and when blended in various ratios.. Two solutions where prepared:

- An anion solution of bicarbonate and carbonate.
- A cation solution of calcium.

The scale inhibitor, or blend being tested is included in the anion solution. No inhibitor is added for the blank, untreated, tests.

The test is initiated by mixing the cation and anion solutions. pH is monitored as anion solution is added to the mixture. The additional anion solution increases carbonate, pH, and the calcium carbonate saturation ratio. The upper limit for the inhibitor is indicated by loss of control, and a drop in pH as calcium carbonate precipitates. The solution is also observed for turbidity. Figure 3 profiles a typical plot of pH as the solution is "titrated" to the upper saturation limit for the inhibitor.

Care must be taken in the experimental design so that the solubility of inhibitor salts does not interfere, such as through the formation of Ca-HEDP. The time for the test must also be less than the treated induction time to prevent precipitation other than that from exceeding the upper limit.

Inhibitors discussed in this section are outlined in Table 2.

IN SEARCH OF UPPER LIMIT SYNERGY: RESULTS

PBTC:PMA Combination: The combination of PBTC and PMA demonstrated the most dramatic impact of blending upon the upper saturation limit, as depicted in Figure 5. As the blend ratio in the test goes from polymer only to phosphonate only, there appears to be a drop in the upper limit at high polymer to PBTC ratios, possibly indicating an antagonistic effect when the polymer is the primary inhibitor. The upper limit failure point increases to a maximum at a ratio of 3 to 1 PBTC to polymer, with the upper limit of the higher ratios indicating a synergy between the PBTC and lower levels of PMA. This trend has been observed in field applications.

Antagonism might occur as a result of polymer adsorbing near newly formed active sites and blocking the PBTC from nearby active sites, or by changing the surface charge to decrease attraction. In this case, the upper limit for the blend would be expected to have a lower limit than either inhibitor alone.

Synergy might occur as a result of polymer attaching near newly formed active sites and by changing the surface charge to increase the attraction of PBTC to nearby active sites. In this case, the upper limit for the blend would be expected to have a higher limit than either inhibitor alone.

HEDP:PMA Combination: The combination of HEDP and PMA demonstrated a similar impact trend to the PBTC:PMA blend.on the upper saturation limit, as depicted in Figure 6. As the blend

ratio in the test goes from polymer only to phosphonate only, there appears to be a drop in the upper limit at high polymer to HEDP ratios, possibly indicating an antagonistic effect when the polymer is the primary inhibitor. The upper limit failure point increases to a maximum at a ratio of 3 to 1 HEDP to polymer, with the upper limit of the higher ratios indicating a synergy between the HEDP and lower levels of PMA. The overall impact of blending the phosphonate HEDP with PMA upon the upper saturation limit appears to be less than the PBTC:PMA blend.

HEDP:ATMP Combination: The combination of ATMP and HEDP demonstrated a positive impact upon the upper saturation limit, as depicted in Figure 7. As the blend ratio in the test goes from HEDP only to ATMP only, the upper limit failure point increases to a maximum at a ratio of approximately 1 to 1 HEDP to ATMP, with the upper limit indicating a synergy between the HEDP and ATMP at all ratios.

A similar trend in inhibitor effectiveness was observed in similar studies that demonstrated an increase in percent inhibition for phosphonate blends.[8]

The Behavior of Inhibitor Blends – Inhibitor Solubility

As mentioned as a caveat for test protocols, inhibitor upper limit tests should be conducted in a range where the solubility of the inhibitor will not decrease the limit measured, The formation of salts such as a *Calcium–Inhibitor* or *Iron–Inhibitor* have been known to limit the maximum dosage in a water. Incorporation of copolymer and higher polymers into a blended inhibitor formulation allows the product to function at higher dosages, and has been observed to prevent deposition or inhibitor activation of inhibitor salt solubility limited treatments. A reduction in dosage is not necessarily observed. The added protective polymer allows the original scale inhibitors(s) to function at a higher dosage, a dosage above their normal solubility. Some might term this Synergy. Others may call it Smart Formulating. In either, or both, cases, the end result is the addition of another molecule into the formula allows the inhibitors to function at a higher dosage under the same conditions.

Inhibitor salts can be modelled like any scale. Their solubility, and the inhibitor dosage required to prevent their precipitation or deactivation, can be modelled using the same methods used for mineral scale inhibitors. The degree of supersaturation for the *Metal-Inhibitor* reactant is calculated. Studies can be run to determine the impact of copolymer dosage on *Metal-Inhibitor* induction time and degree of saturation.

CONCLUSIONS

Blending inhibitors can raise the maximum driving force limit where the inhibitor is effective, and demonstrate synergy. Blends can also decrease the upper driving force limit when individual inhibitors compete for active sites or modify seed crystals to interfere with the second inhibitor in a blend. When present, the degree of synergy or antagonism between inhibitors is a function of the ratio of inhibitors. A given blend might be antagonistic at lower ratios, and synergistic at higher ratios.

RECOMMENDATIONS

Inhibitor blends should be evaluated to determine their impact upon the upper limit of effectiveness for the particular inhibitors, and ratio. Limits for individual inhibitors should not be assumed to apply to blends.

FURTHER WORK

Additional inhibitors and blends will be studied using the procedure outlined for measuring the upper saturation ratio limit.

The impact of inhibitor blends upon induction time extension will be studied for inhibitors with existing models (Table 4) and blends until the standard arsenal of phosphonates and proprietary inhibitors has been studied.

Studies for both upper limit and induction time extension will be run in both a “clean” system and when “seeded” with the solid phase of the scale under study.

Scales studied will be expanded to include $CaCO_3$, $CaSO_4*2H_2O$, $BaSO_4$, and where appropriate, $Ca:PO_4$.

As data is available, the laboratory results and trends will be validated to operating industrial systems.

TABLE 1 - SATURATION LEVEL FORMULAS

Calcium carbonate $S.L. = \frac{(Ca)(CO_3)}{K_{sp\ CaCO3}}$

Barium carbonate $S.L. = \frac{(Ba)(CO_3)}{K_{sp\ BaCO3}}$

Strontium carbonate $S.L. = \frac{(Sr)(CO_3)}{K_{sp\ SrCO3}}$

Calcium sulfate $S.L. = \frac{(Ca)(SO_4)}{K_{sp\ CaSO4}}$

Barium sulfate $S.L. = \frac{(Ba)(SO_4)}{K_{sp\ BaSO4}}$

Strontium sulfate $S.L. = \frac{(Sr)(SO_4)}{K_{sp\ SrSO4}}$

Tricalcium phosphate $S.L. = \frac{(Ca)^3(PO_4)^2}{K_{sp\ Ca3(PO4)2}}$

Amorphous silica $S.L. = \frac{H_4SiO_4}{(H_2O)^2 * K_{sp\ SiO2}}$

Calcium fluoride $S.L. = \frac{(Ca)(F)^2}{K_{sp\ CaF2}}$

Magnesium hydroxide $S.L. = \frac{(Mg)(OH)^2}{K_{sp\ Mg(OH)2}}$

Table 2: Inhibitors and Blends Included in the Saturation Limit Evaluation	
Inhibitor	
ATMP	amino tris (methylene phosphonic acid)
HEDP	1-hydroxy ethylidene-1,1-diphosphonic acid
PBTC	2-phosphonobutane-1,2,4- tricarboxylic acid
Enh PMA	polymaleic anhydride, enhanced
ATMP:HEDP blends	
HEDP:PMA blends	
PBTC:PMA blends	

Table 3: Typical Treated Limits Comparison				
SCALE FORMING SPECIE	**FORMULA**	**MINERAL NAME**	**TYPICAL TREATED SATURATION RATIO LIMIT**	**STRESSED TREATMENT LIMIT**
Calcium carbonate	$CaCO_3$	Calcite	125 - 150	200 - 225
Calcium sulfate	$CaSO_4*2H_2O$	Gypsum	2.5 - 4.0	4.0 +
Barium sulfate	$BaSO_4$	Barite	80	80+
Strontium sulfate	$SrSO_4$	Celestite	12	12
Silica	SiO_2	Amorphous silica	1.2	2.5
Tricalcium phosphate	$Ca_3(PO_4)_2$		1500 - 2500	125,000

Table 4: Typical Scale Inhibitor Models Available		
Inhibitor		**Scales Modeled**
ATMP	amino tris (methylene phosphonic acid)	$CaCO_3$, $CaSO_4$, $BaSO_4$
HEDP	1-hydroxy ethylidene-1,1-diphosphonic acid	$CaCO_3$, $BaSO_4$
PBTC	2-phosphonobutane-1,2,4-tricarboxylic acid	$CaCO_3$, $BaSO_4$
HDTMP	hexamthylenediamine tetra(methylene phosphonic acid)	$CaCO_3$, $CaSO_4$, $BaSO_4$
DTPMPA	diethylene triamine penta (methylene phosphonic acid)	$CaCO_3$, $CaSO_4$, $BaSO_4$
PAA	polyacrylic acid	$CaCO_3$, $CaSO_4$, $BaSO_4$
PMA	polymaleic acid	$CaCO_3$, $CaSO_4$
AA-AMPS	acrylic acid-2-acrylamido-2-methylpropane sulfonic acid	$Ca_3(PO_4)_2$, $CaCO_3$
Proprietary copolymers, terpolymers	Various	$Ca_3(PO_4)_2$
Proprietary polymers	Unknown	SiO_2, $MgSiO_3$, $Mg:SiO_3$

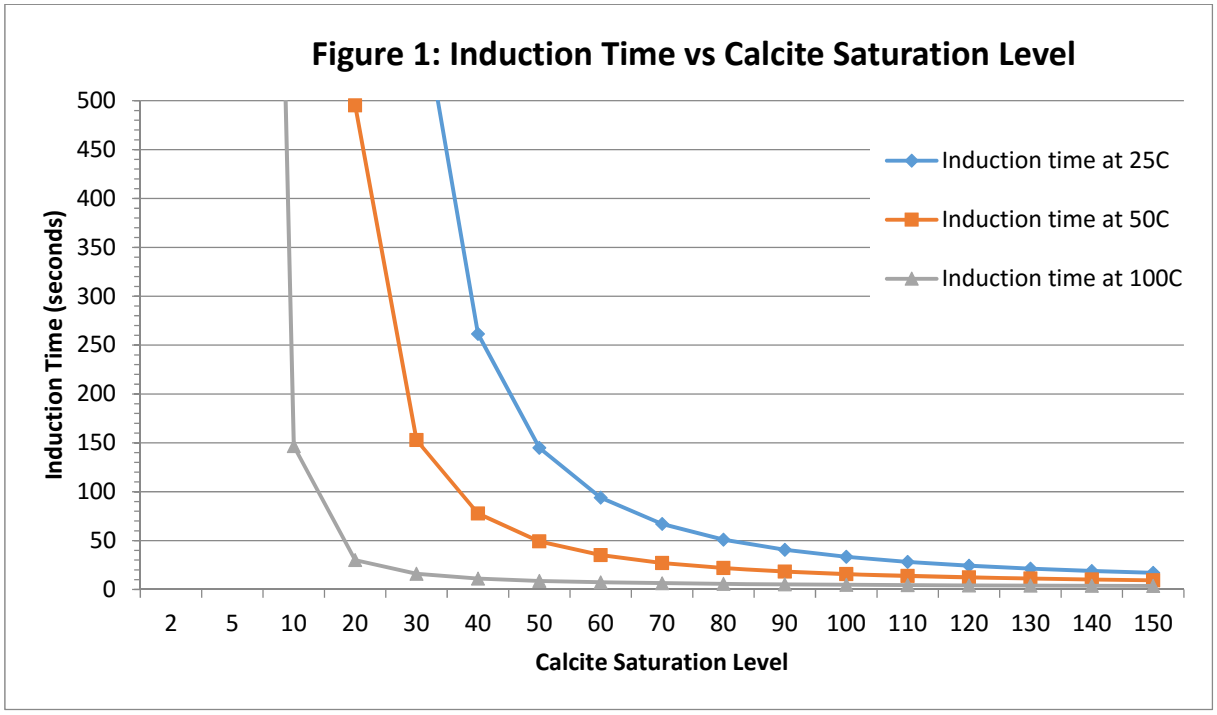


Figure 1: Induction Time vs Calcite Saturation Level
Induction Time (seconds)
500
450
400
350
300
250
200
150
100
50
0
2
5
10
20
30
40
50
60
70
80
90
100
110
120
130
140
150
Calcite Saturation Level
Induction time at 25C
Induction time at 50C
Induction time at 100C

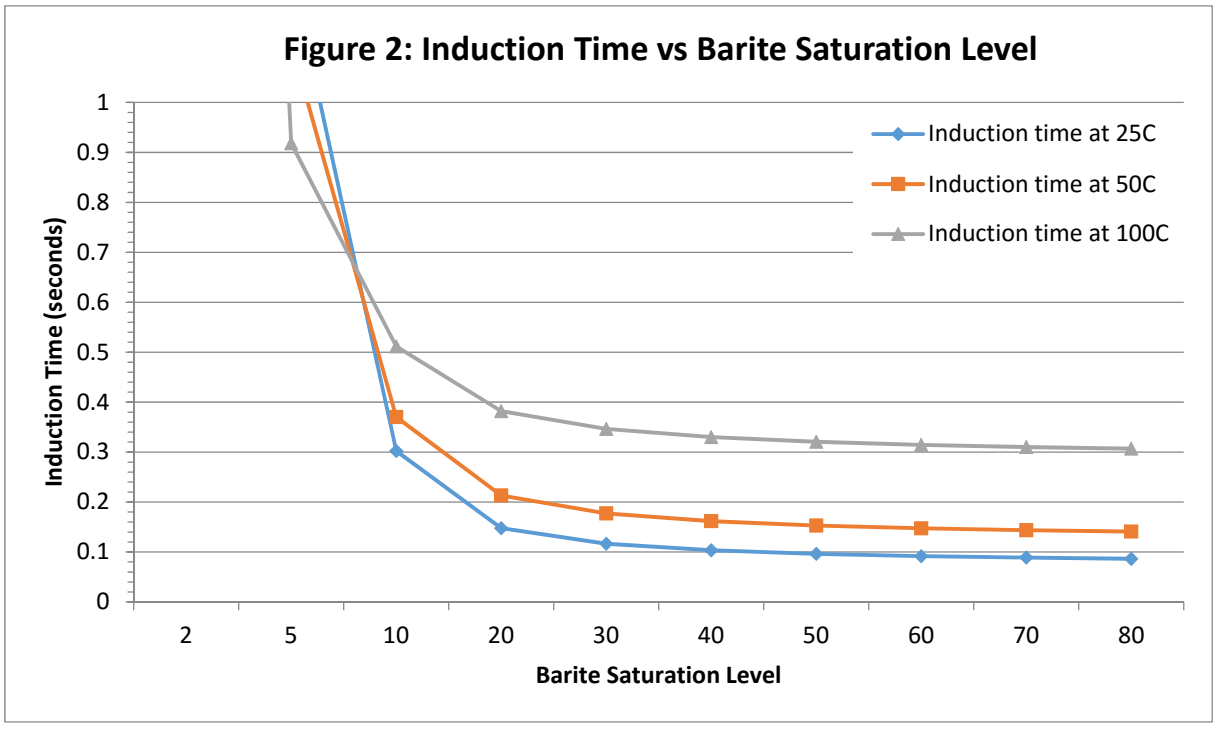


Figure 2: Induction Time vs Barite Saturation Level
Induction Time (seconds)
1
0.9
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
0
2
5
10
20
30
40
50
60
70
80
Barite Saturation Level
Induction time at 25C
Induction time at 50C
Induction time at 100C

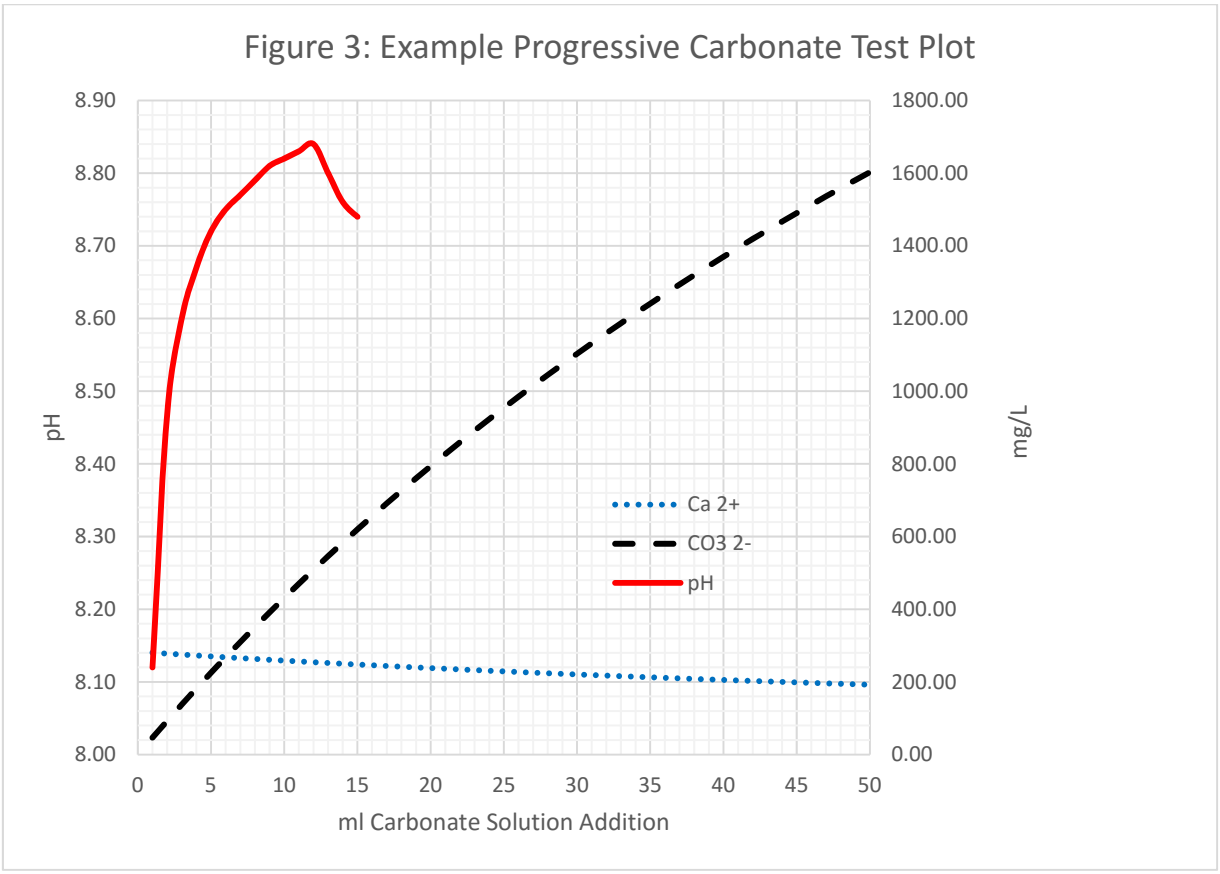


Figure 3: Example Progressive Carbonate Test Plot
8.90
8.80
8.70
8.60
8.50
8.40
8.30
8.20
8.10
8.00
pH
1800.00
1600.00
1400.00
1200.00
1000.00
800.00
600.00
400.00
200.00
0.00
mg/L
0
5
10
15
20
25
30
35
40
45
50
ml Carbonate Solution Addition
Ca 2+
CO3 2-
pH

Figure 4: IMPACT OF POLYMER TO PHOSPHONATE RATIO
Upon Maximum Saturation for Enhanced PMA and PBTC

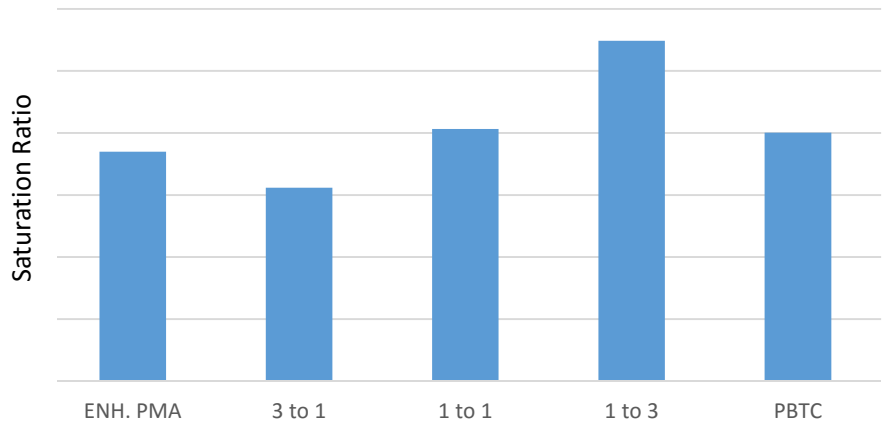


Figure 5:IMPACT OF POLYMER TO PHOSPHONATE RATIO
Upon Maximum Saturation for Enhanced PMA and HEDP

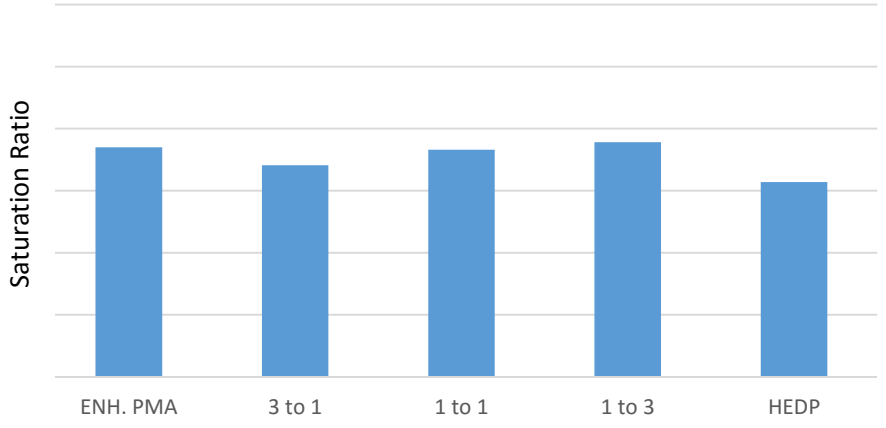
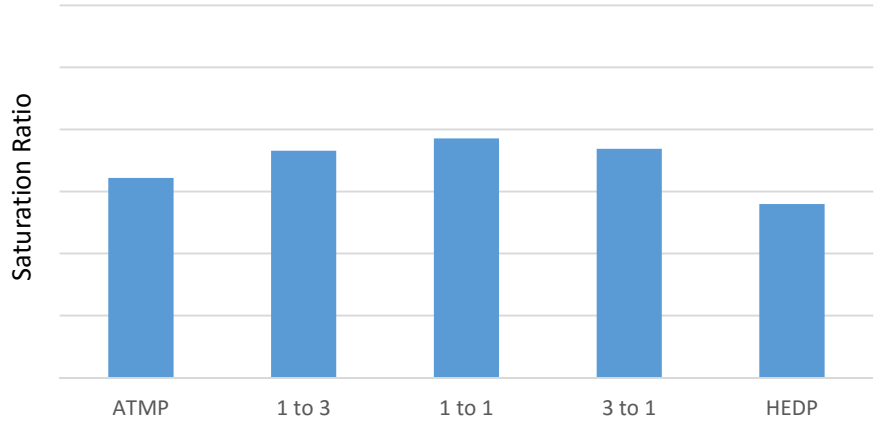


Figure 5: IMPACT OF PHOSPHONATE RATIO
Upon Maximum Saturation for ATMP and HEDP



REFERENCES

[1] Ferguson, R.J., "Developing Scale Inhibitor Models", WATERTECH, Houston, TX, 1992.

[2] Ferguson, R.J., D.A. Weintritt, "Developing Scale Inhibitor Models For Oil Field", NACE, CORROSION 1994, Baltimore, MD.

[3] Ferguson, R.J*., B. R. Ferguson, and R. F.* Stancavage, "Modeling Scale Formation and Optimizing Scale Inhibitor Dosages in Membrane Systems", AWWA Membrane Technology Conference March 30, 2011 Long Beach, CA, USA

[4] Tomson, M.B., Fu, G., Watson, M.A. and A.T. Kan, "Mechanisms of Mineral Scale Inhibition, Society of Petroleum Engineers, Oilfield Scale Symposium, Aberdeen, UK, 2002.

[5] B.W. Ferguson, R.J. Ferguson, "Sidestream Evaluation of Fouling Factors in a Utility Surface Condenser," Journal of the Cooling Tower Institute,2, (1981):p. 31-39.

[6] Ferguson, R.J., Codina, O., Rule, W., Baebel, R., Real Time Control Of Scale Inhibitor Feed Rate, International Water Conference, 49th Annual Meeting, Pittsburgh, PA, IWC-88-57.

[7] Ferguson, R.J., "30 Years of Ultra Low Dosage Scale Control", NACE, CORROSION 2003, San Diego, California

[8] Ferguson, R.J., "The Kinetics Of Cooling Water Scale Formation And Control," Association of Water Technologies Annual Meeting, Association of Water Technologies Annual Meeting, September 14 - 17, 2011 Atlanta, GA, USA

[9] Ferguson, R.J., Computerized Ion Association Model Profiles Complete Range of Cooling System parameters, International Water Conference, 52nd Annual Meeting, Pittsburgh, PA, IWC-91-47.

[10] Ferguson, R.J., A.J. Freedman, G. Fowler, A.J. Kulik, J. Robson, D.J. Weintritt,"The Practical Application of Ion Association Model Saturation Level Indices To Commercial Water Treatment Problem Solving," (Washington, DC: American Chemical Society Annual Meeting, Division of Colloid and Surface Chemistry Symposia, Scale Formation and Inhibition, 1994).

[11] Ferguson, R.J., A Kinetic Model for Calcium Carbonate Scale, CORROSION/84,Paper No. 46, (Houston, TX:NACE INTERNATIONAL 1984).

[12] Ferguson, R.J., "The Impact of Inhibitor Speciation on Efficacy: pH, Ionic Strength and Temperature Impact," Presented at the 2015 Cooling Technology Institute Annual Conference, New Orleans, Louisiana February 9-12, 2015

[13] Griffiths, D.W., Roberts, S.D., and Y.T. Liu, "Inhibition of Calcium Sulfate Dihydrate Crystal Growth by Phosphonic Acids – Influence of Inhibitor Structure and Solution pH," *Society of Petroleum Engineers*, International Symposium on Oil Field and Geothermal Chemistry (1979).