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DEVELOPING REALISTIC SCALE INHIBITOR TEST PROCEDURES
CALCIUM CARBONATE SCALE INHIBITOR TESTING

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ABSTRACT

Various Laboratory test procedures have been used to develop profiles and models of minimum effective dosage as a function of water chemistry, temperature and time. Some procedures provide realistic data, directly applicable to operating systems. Others that have been used and published serve only as generators of marketing data under conditions no sane water treatment chemist would run, with performance no customer would accept. This paper discusses the development of standard test procedures for simulating calcium carbonate scale control in operating systems.

This study and paper is the first in a series on test procedures for calcium carbonate, calcium phosphates, calcium sulfate, barium sulfate, and the elusive culprits silica and magnesium silicate.

INTRODUCTION

Scale inhibitor laboratory testing provides performance and limits data to allow the development of models for:

1) Calculating the minimum effective dosage.
2) Calculating the dissociation profile for an inhibitor and its impact upon scale inhibitor active species.
3) Determining the upper driving force limit for the inhibitor, beyond which even very high dosages do not provide scale control.
4) Determining if an upper limits exists for cations, such as the solubility of calcium phosphonates.
5) Determining if the inhibitor “salts out” at high ionic strength.
6) Determining if separate mechanisms are operative for low and high saturation environments, requiring separate models.

This paper describes the rationale and methodology for developing a test procedure and subsequently a model(s) appropriate to the intended application. Specific comments are made for differences in procedures required for scales, e.g. calcium carbonate versus calcium sulfate.

RATIONALITY

Scale inhibitors do not prevent scale formation or growth. They interfere and delay the inevitable. (At this point, a review of the theory behind scale formation and its control is recommended).[1] Simple inhibitor studies measure the induction time as the degree of supersaturation increases, as inhibitor dosage increases, and as temperature increases. Induction time is the time before a phase change occurs (first crystal), or before growth begins on an existing active site.

Dosages can then be modelled as a function of the time it takes a water to pass through the system, that being the time that scale formation of growth must be inhibited. A critical step in any test procedure is measuring and determining the end point, the time when inhibition is lost.

MODELS DEVELOPED FROM THE DATA

Untreated Induction Time

Induction time has been studied extensively for processes like sucrose production, which rely upon crystallization as a critical step in production. In the case of sucrose production, the objective is to minimize induction time to speed the production process. In the case of scale control, the objective is to increase induction time until scale forming waters have passed through the system, and are no longer a threat to the process or system.[1,2]

$$\text{Time} = \frac{1}{k\,[SR - 1]^{P-1}} \qquad \text{(Eq 1)}$$

where: Time is the induction time
inhibitor is the scale inhibitor molar concentration
k is a temperature dependent rate constant
SR is the saturation ratio
P is the number of molecules in a critical sized cluster

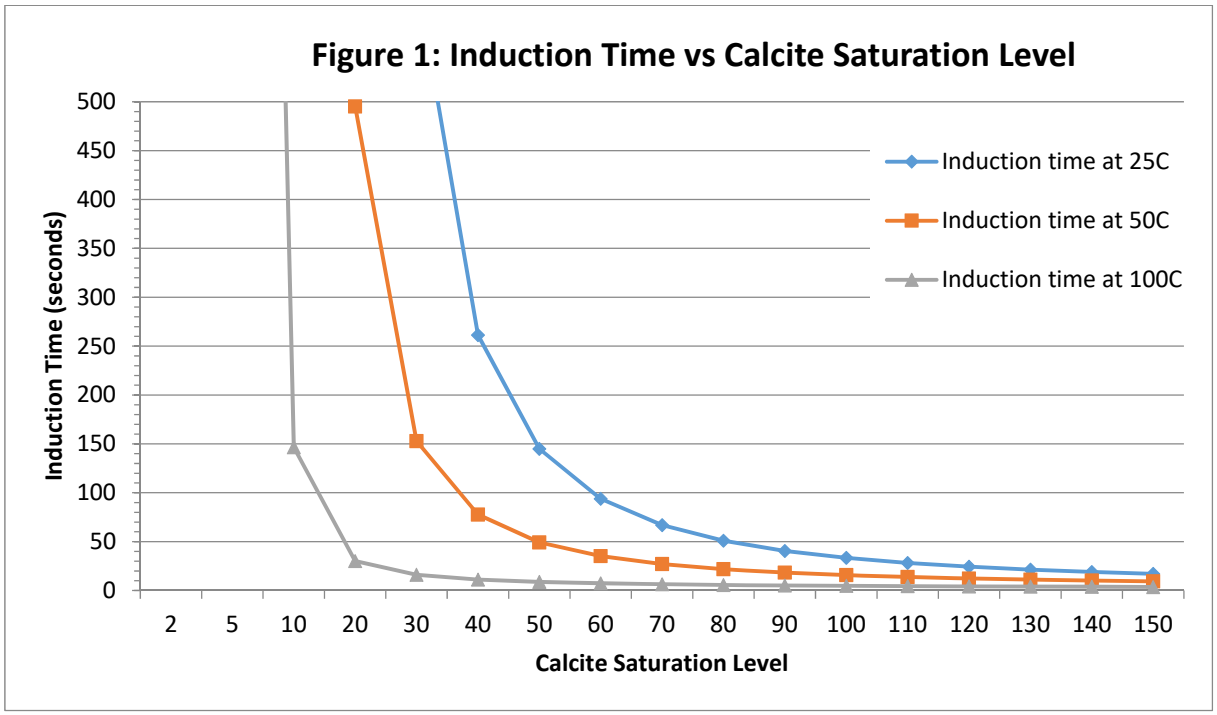
Other correlations for untreated induction time are in similar format. Tomson and Kan use the following or a variation.[3, 4]

$$\text{Time} = 10^{(a_0 + a_1/SI + a_2/T + a_3/(T \times SI))} \qquad \text{(Eq 2)}$$

where: Time is the induction time in seconds
T is temperature in degrees Kelvin
SI is the base 10 log of saturation ratio, also termed Saturation Index
$a_0 - a_3$ are empirical coefficients

Other induction time models have also been proposed and used to model the scale formation process.[5,6]

Figure 1 depicts and untreated induction time profile for Calcite.



Minimum Effective Dosage

Minimum effective dosage is defined for this paper as the dosage required to extend induction time until water has passed through the system, and where scale deposition from the water is no longer a threat to the system and process. Models used to estimate the minimum effective dosage incorporate those for untreated induction time and extend them to include the impact of inhibitor formation upon induction time.

$$\text{Time} = \frac{[\text{inhibitor}]^{M}}{k\,[SR - 1]^{P-1}} \qquad \text{(Eq 3)}$$

where: Time is the induction time
inhibitor is the scale inhibitor molar concentration
k is a temperature dependent rate constant
SR is the saturation ratio
P is the number of molecules in a critical sized cluster

Kan and Tomson[3] have proposed and implemented the use of a model in the format of the ratio between the desired treated induction time and the calculated untreated induction time.

$$b_{inh} = 10^{(B_0 + B_1 \times SI + B_2/T + B_2 \times pH + B_4 \times \log R_{inh})} \quad \text{(Eq 4)}$$

$$C_{inh} = (1/ b_{inh}) \times \log (t_{inh}/t_0) \quad \text{(Eq 5)}$$

where: t_{inh} is the desired treated induction time in Seconds
t_0 is the calculated untreated induction time in Seconds
C_{inh} is the scale inhibitor concentration in mg/L
T is the temperature in degrees Kelvin
SI is the log 10 of saturation ratio, also termed Saturation Index
$B_0 – B_4$ are empirical coefficients

Other models for minimum effective dosage incorporate the same critical parameters:

- Saturation Ratio as a driving force
- Temperature as it affects rate, independent of impact upon saturation
- Time

These parameters are of paramount importance in the experimental design for collecting data for the models. Other models also incorporate pH or pKa' to define the "active" inhibitor concentration, which is described in detail later in the paper. [5, 6, 7]

DETERMINING THE LOSS OF CONTROL END POINT

Old test procedures would sample an inhibited solution after twenty four (24) hours, or some other set time period. Analysese would be run for critical reactants (e.g. Ca, Alkalinity), and a percent inhibition calculated. Analytical sampling is inconvenient when inhibition versus time is studied. Reference parameters versus time are measured to indicate the loss of control. pH, for example, drops in a calcium carbonate solution as precipitation begins. A plot of pH versus time can be evaluated to determine the $CaCO_3$ induction time end point. pH does not work as an end point for many other scales, such as calcium sulfate, and barium sulfate. Turbidity increases as control is lost. Techniques, such as the use of a quartz crystal microbalance are also available to quantitatively measure deposition.

Analytical Testing: Many scale tests results are presented in the form of % inhibition, which might be defined as the percent retention of reactants. For Calcium carbonate:

$$\% \text{ Inhibition} = 100 \times (Ca_0 – Ca_{time})/Ca_0 \quad \text{(Eq 6)}$$

Where : Ca_0 is the analyzed calcium concentration at time = 0
Ca_{time} is the analyzed calcium concentration after a given time period.

Ideally, samples could be taken at regular intervals and analyzed. The logistics of the "analytical testing" method for end point, preclude its widespread use in laboratory studies. It is more appropriate for use in set time studies (e.g 15 hours, 24 hours).

pH Recording: As calcium carbonate precipitates, pH drops. pH can readily be monitored using the recording function of most pH meters, or through more sophisticated data logging schemes. Figure 1 depicts the graphical solution for the "end point." Statistical methods also provide a consistent means for determining the end point based upon pH versus time.

Turbidity: Turbidity monitoring is used for monitoring the initiation and formation of many mineral scales. Minature turbidity probes are available that have performed adequately in scale studies.[8] The end point is determined by graphical or statistical methods, similarly to the pH endpoint determination.

Quartz Crystal Microbalance: An accurate, but expensive approach to monitoring deposition and loss of control is the quartz crystal microbalance. [9] The quartz crystal transducer is a wafer coated with a metal such as gold. A high frequency current is applied. A frequency shift occurs as precipitation on the quartz crystal wafer occurs and growth occurs. The microbalance can measure precipitation with nanogram sensitivity. The quartz wafer can be used to model a clean system, or it can be prepared with a deposit of the scale under study to provide a measurement of growth on an existing substrate. The profile versus time can be evaluated using graphical or statistical techniques to determine the time where control loss occurred.

EXPERIMENTAL DESIGN

The exact experimental design will vary with the scale being studied. Steps for any scale include:

1) Determine the saturation ratio range of interest: This will typically be from slightly supersaturated to 20% above the common failure point. In the case of calcite, a 25 to 275x saturation range provides a workable range for the study. Use a software package to calculate the solutions needed to achieve the desired saturations. It is recommended that Cation to Anion ratios be varied within the experimental design to account for any impact, e.g. Ca to CO_3 ratio, Ca to SO_4 ratio, etc.
2) Determine the temperature range of interest: Typical ranges of study are from 25 ^oC to 80 ^oC for tests at atmospheric pressure.
3) It is also advisable to run the studies over a range of pH to account for inhibitor dissociation. [5, 6, 7]

4) Studies may be conducted at increasing ionic strength to assess the impact of inhibitor activity coefficients upon efficacy. NaCl is typically used to spike the test solutions in a range up to 250,000 TDS.

TEST SOLUTIONS GENERALIZED PROCEDURE

Tests are generally run using anion stock solutions, cation stock solutions, inhibitor stock solutions, and in some cases, a buffer. This procedure is written for the "classical" jar test procedures. Elements of the method apply to other test types such as constant composition tests.

1) Add DI water to the solution test container. The amount will be the test solution weight, less the calculated weights for the stock anion solution, cation solution, inhibitor solution, and buffer solution (if any). Begin stirring.
2) Add the anion stock solution to a test container (e.g. 500 ml beaker). Add any stock buffer solution.
3) Add the inhibitor solution.
4) Add the cation solution. Start the timer as t = 0.

Then monitor any end point parameters. Evaluate the data for the end point using any statistical software that calculates slope rate of change. Titration software can be used by entering pH and time rather than pH and mL titrant.

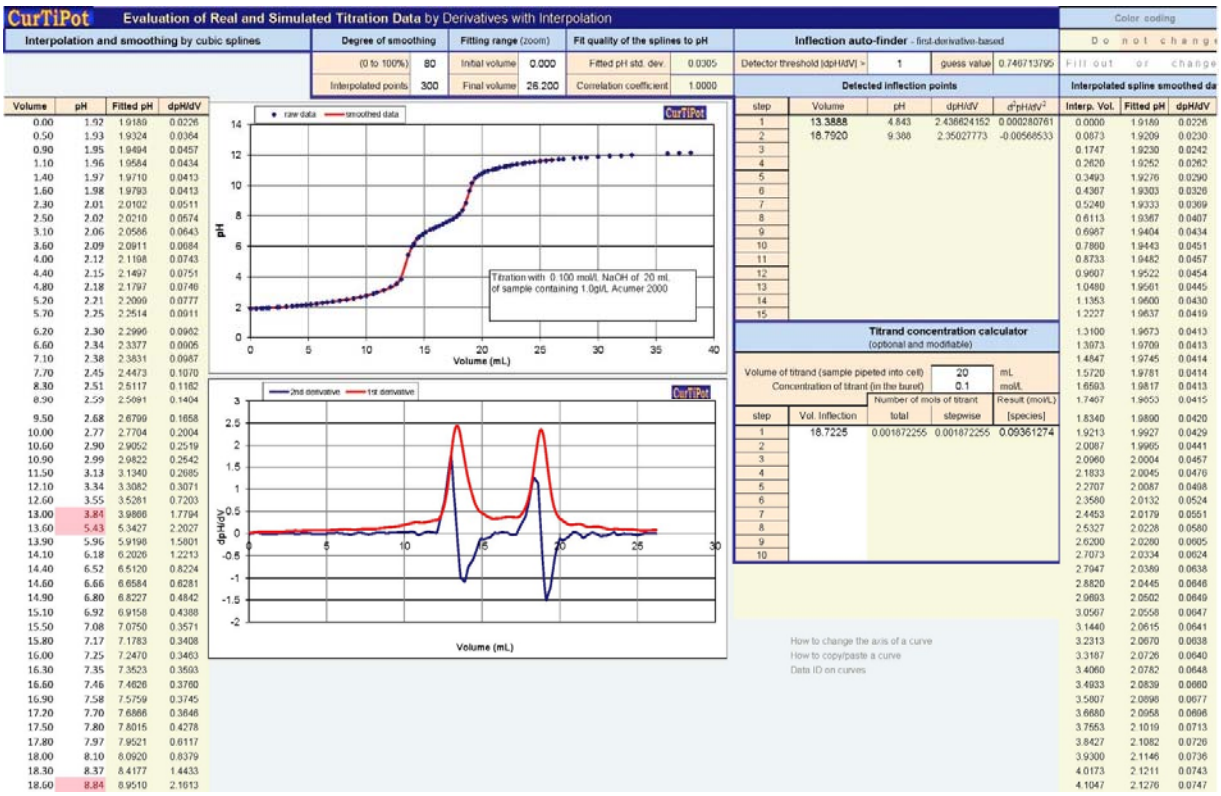
Test Solution Stability

The pH and HCO_3^- <-- > $CO_3^=$ distribution for strong $HCO_3^-/CO_3^=$ solutions has been observed to change significantly with aeration, as equilibrium is established with the atmosphere. The effect can be exaggerated as the solution is heated. Aeration of solutions prior to mixing can lead to a more stable and reproducible test.

TITRATE INHIBITOR FOR pKa DETERMINATION

Refer to Reference 10 for the titration procedure and evaluation software. Titrations should be performed at a minimum of two (2) temperatures, and in a TDS range from deionized water to 250,000 mg/L as NaCl. The pKa at infinite dilution, van't Hoff dH for temperature variation, and coefficients for a Helgeson B dot or similar activity correlation should be calculated. Figure 2 profiles a typical pKa plot, as evaluated by the Freeware Excel® addon, CurTiPlot. [11]

Figure 2: Example CuTiPlot For pKa Determination



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. A “Progressive Carbonate Test” was used to estimate and compare upper limits. Two solutions where prepared for the test:

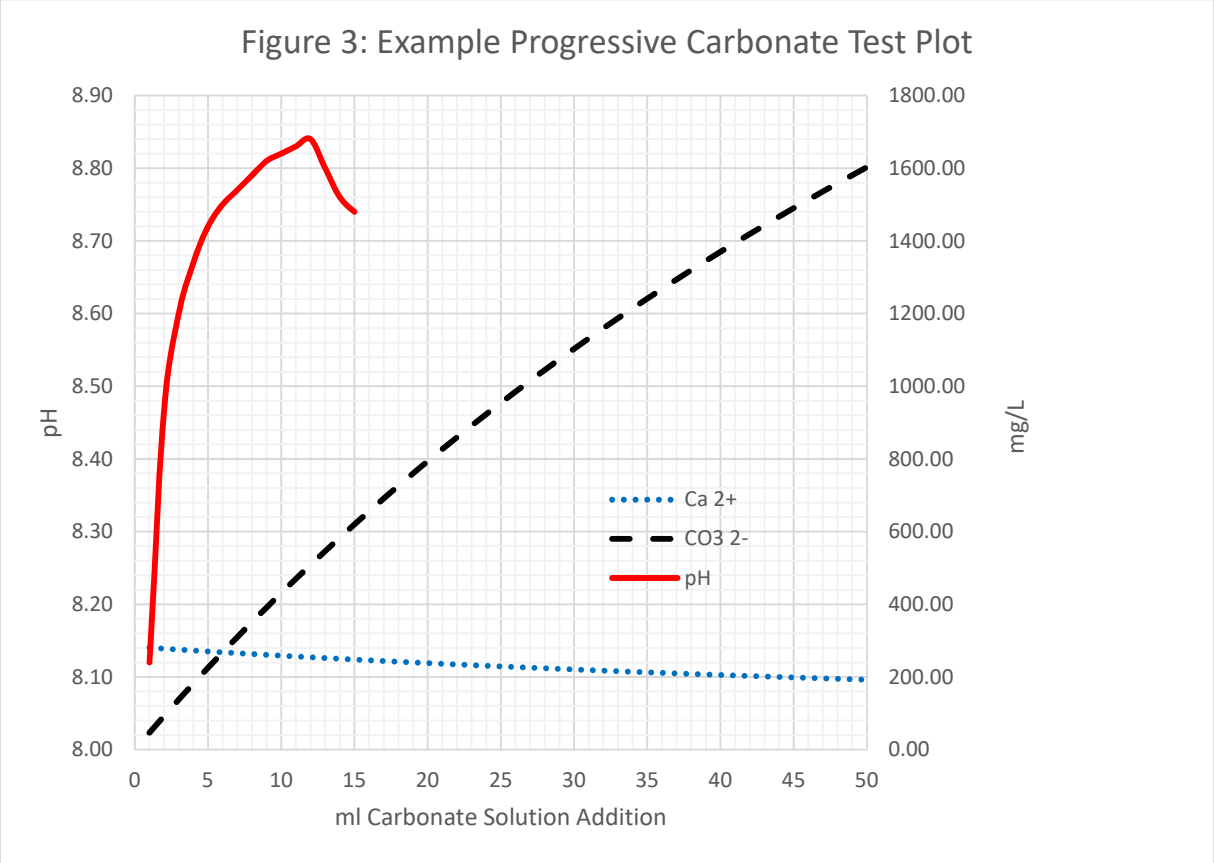
- An anion solution of bicarbonate and carbonate.
- A cation solution of calcium.

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.



MODEL DEVELOPMENT

Data reduction and model development can be done using a standard statistical multiple regression program from the data after calculating the appropriate indices. Proprietary software may also be available to ease data preparation, raw data entry, and database creation for the study, and test model parameters interactively. For best results, include the pKa' for the inhibitor being evaluated, as well as the activity coefficient data for the inhibitor pKa. Correlations should be made to the dissociated concentration of the inhibitor present, rather than the total inhibitor concentration.

Figure 4 specifies a model for Active Inhibitor Minimum Effective Dosage in the form

$$\text{Log(Dosage)} = \log(A) + Ea/(RT) + M \log(S\text{-}1) + N \log(t) \qquad \text{(Eq 7)}$$

Where A is a calculated coefficient that includes collision frequency from the Arrhenius Equation portion of the model (Ea/RT), and a normalization coefficient for the other factors.

Ea is a calculated Activation Energy for the Arrhenius relationship

R is the Gas Constant

T is absolute temperature

N is a coefficient for the time parameter.

Figure 5 outlines the correlation of the data to Equation 7.

Figure 4: Inhibitor Model Specification

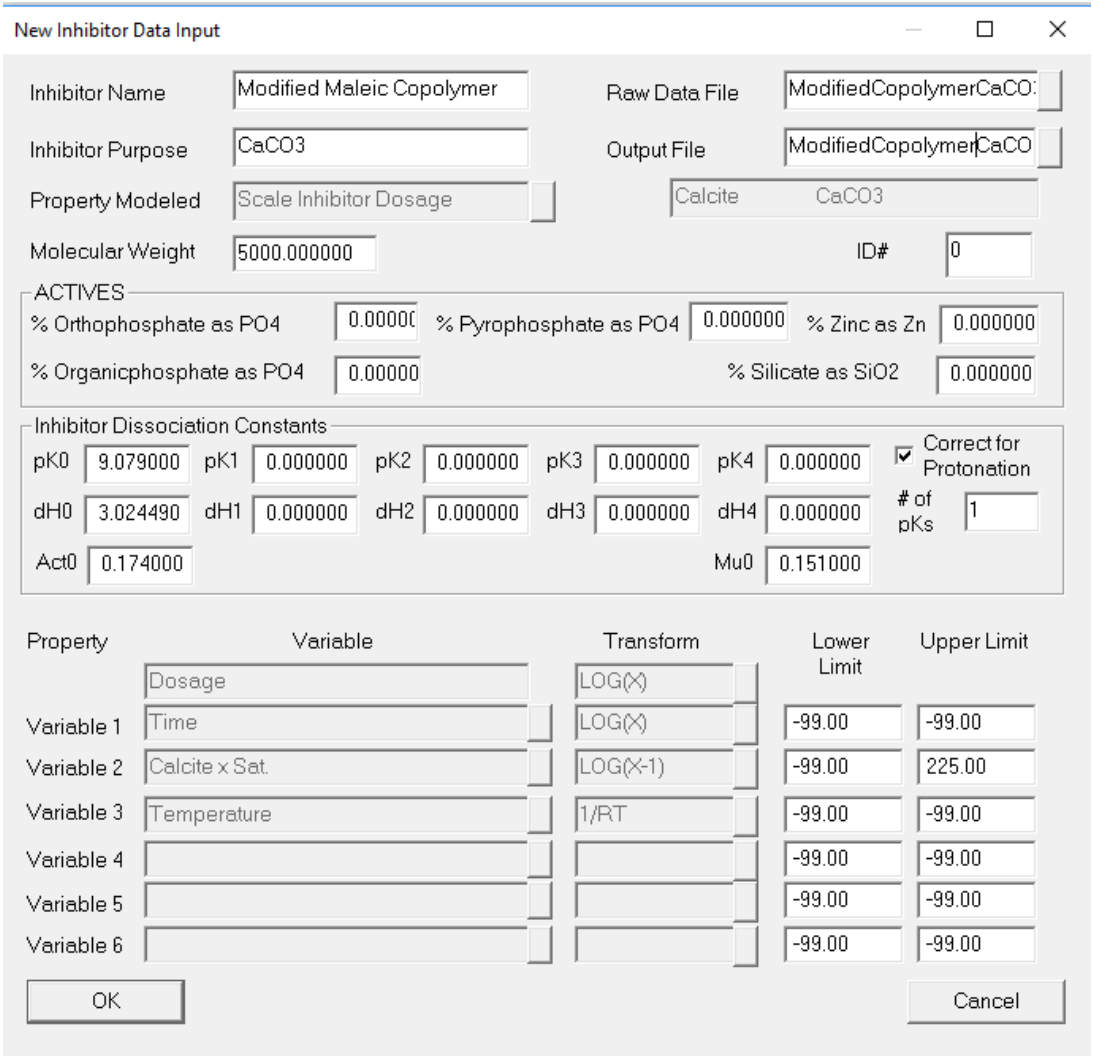


Figure 5: Inhibitor Model Developed Using Equation 7

	Intercept	Time LOG(X)	Calc. Sat LOG(X-1)	Temp. 1/RT
Coef.	-30.37	0.71	1.50	599.98
Std.Error	6.20	0.16	0.38	3516
Sig.Level	< 0.001	< 0.001	< 0.01	0.87

R-SQRD 0.923 Correlation Problems? NO

Anal.#	Observed	Predicted	Difference	% Error
0	0.06868	0.08861	0.0199	29.01240
1	0.16386	0.16407	0.0002	0.12941
2	0.49159	0.26256	-0.2290	-46.58934
3	1.06508	0.80231	-0.2627	-24.67139
4	5.87441	7.11192	1.2375	21.06609
5	0.09908	0.18006	0.0809	81.71989
6	0.19817	0.39710	0.1989	100.37956
7	0.59453	0.45234	-0.1421	-23.91582
8	0.99089	0.49263	-0.4982	-50.28426
9	6.88099	5.96471	-0.9162	-13.31613
10	5.19563	6.91596	1.7203	33.11106

SUMMARY

This "White Paper" outlines a basic approach to developing the data and a scale inhibitor model for dosage optimization. Such models should be correlated to field applications, and can also include pilot plant data (e.g. Pilot Cooling Towers, Pilot Scale RO Units), and field data if available. (13, 14, 15)

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