ANATOMY OF A MULTIFUNCTIONAL PRODUCT

Robert J. Ferguson
French Creek Software
Kimberton, PA 19442-0684

ABSTRACT

Multifunctional cooling water products address scale and corrosion control and include blends of inhibitors in "one drum". Less than optimum ratios of inhibitors can result in product overfeed, increased costs, and in some cases, inhibitor induced fouling. This paper describes the use of computer modeling to optimize ratios of scale and corrosion inhibitors for different waters.

INHIBITOR MODELS

Computerized modeling and optimization of cooling water inhibitors has been common practice since the late 1970's. [1,2,3] Models have been used for screening molecules as potential scale inhibitors,[4] for online real time control,[5] as a formulating aid, for troubleshooting failures and as sales tools. Models have been developed for most cooling water scale inhibitors and corrosion inhibitors and refined through in field usage. Typical models are as follows:

Scale Inhibitors The development of scale inhibitor models has been covered thoroughly in the literature. [2,5,6,7] Models typically predict the inhibitor dosage required to "delay" precipitation or growth until after the water has passed through the system.

Typical parameters for the models are:

a) **Driving Force:** Ion association saturation ratios are typically used driving force for seed crystal formation and growth including calcite saturation index (CSI) for calcium carbonate, gypsum and anhydrite saturation indices for calcium sulfate, tricalcium phosphate and hydroxylapatite saturation indices for calcium phosphate scale inhibition, silica saturation and magnesium silicate saturation level for silica control.
b) **Temperature:** Temperature affects the rate of reactions and has been found to directly influence dosages, all other factors being equal.
c) **Time:** Higher dosages are required to delay scale formation or growth. The longer the time during which an inhibitor must prevent scale, the higher the dosage.

Equation 1 **Dosage = function (Saturation, Temperature, Time)**

Models of this type are developed from data that includes water chemistry, temperature, inhibitor dosage and the time delay (induction time) before scale forms. The models in this paper use an ion association model system for calculation of the driving force.[9,10]

Corrosion Inhibitors Two types of corrosion models are typically used to characterize and optimize corrosion inhibitor dosages depending upon solubility. The maximum dosages for inhibitors such as zinc, orthophosphate and to a lesser extent polyphosphate, are under solubility control. Over feed of these inhibitors can result in fouling. The maximum dosage in a cooling water is typically a function of the solubility.

For example, it is common practice to run alkaline zinc programs at a pH where filtered (soluble) zinc is approximately half of the unfiltered (total) zinc. Orthophosphate treatments are controlled in many cases at a low (300 – 500) tricalcalcium phosphate saturation ratio.

Dosages and control limits for solubility limited inhibitors are based upon maximum soluble inhibitor levels. Figures 1, 2 and 3 profile the maximum solubility of zinc, pyrophosphate, and orthophosphate in a great lakes water at five (5) cycles of concentration.

Models have also been developed for inhibitors such as molybdate, and organic materials such as phosphino carboxylic acid.[12] These inhibitors are modeled in the same manner as corrosion rate models.[8] In fact, dosage optimization models developed for these materials may include a target corrosion rate as a parameter.

Data used to develop these models includes water chemistry, inhibitor level, temperature, and observed corrosion rate. Parameters such as buffer capacity may be calculated from the data and included as parameters in the models. Models can be developed for predicting corrosion rate and for optimizing inhibitor levels.

Figure 1
Maximum Zinc Solubility

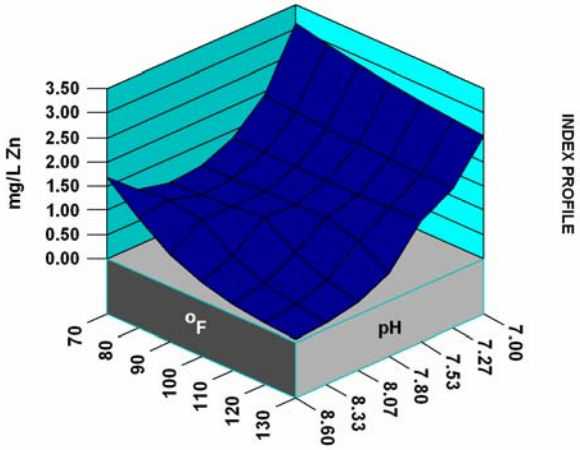


Figure 2
Maximum PPO4 Solubility

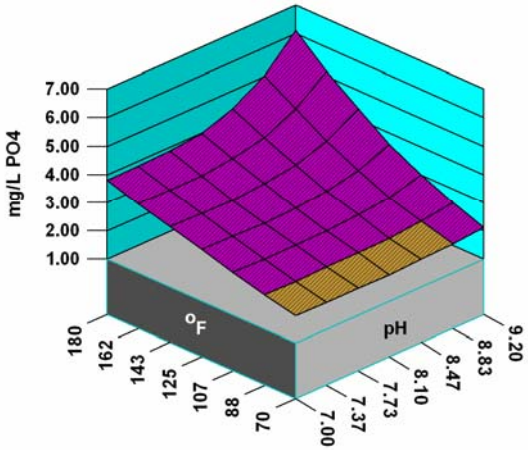
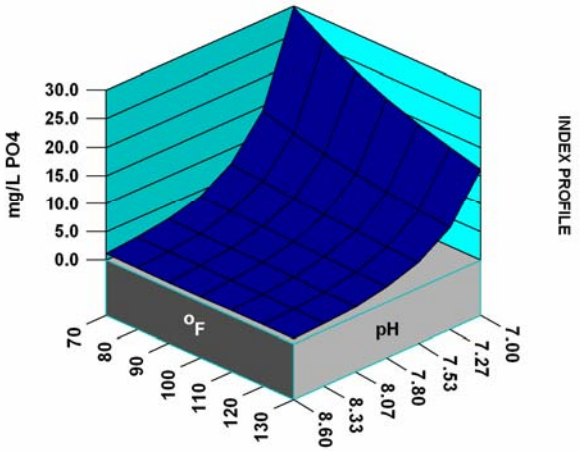


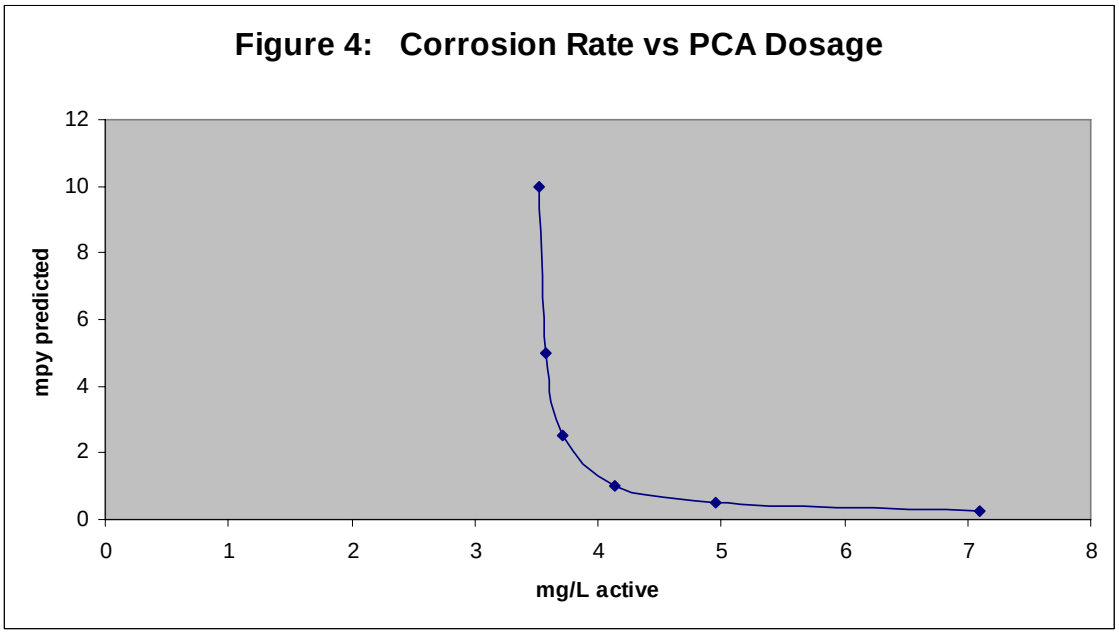
Figure 3
Maximum PO4 Solubility



Equation 2 Corrosion rate = function(water chemistry, inhibitor dosage, temperature)

Equation 3 Inhibitor dosage = function(target corrosion rate, water chemistry, temperature)

Figure 4 profiles the dosage requirement for PCA as a function of target corrosion rate for a great lakes water source at five (5) cycles. Models in this format can be used to offer customer relative cost options for increasing levels of corrosion control.



Corrosion Inhibitor Blends Blends of corrosion inhibitors are used to overcome the shortcomings for an inhibitor under given conditions. Polyphosphate, for example, functions most effectively in the present of higher levels of a divalent ion such as calcium. In lower calcium waters, zinc is used to supplement the native calcium.

Stabilization Agents Solubility mode corrosion control programs frequently include a stabilization agent. Models for zinc stabilizers can be developed from laboratory data or based upon stoichiometry, and included in product models.

OPTIMIZING INHIBITOR BLENDS

Water chemistry modeling software has been used effectively to optimize inhibitor ratios using a system similar to this stepwise procedure. In the first example, an alkaline phosphate program is being optimized for a great lakes water at five (5) cycles. Expected maximum water temperature is 130 ^{o}F. The product is being formulated for treatment at 100 ppm (as product) in the recirculating water.

Inhibitors used in the desired formulation include:

- PBTC for calcium carbonate scale control;
- AA-AMPS for calcium phosphate scale control;
- Orthophosphate as a corrosion inhibitor.

Step 1: Confirm Water Chemistry and Problems.
The first step in optimizing an inhibitor blend for a water is to model its properties at the target concentration ratio and operating range. Once the water is concentrated by the computer, predict the scales that must be controlled and the expected mild steel corrosion rate without treatment. These factors will usually be known based upon experience with the water under study. Figure 5 models a Lake Michigan water at Chicago, Il, at five (5.0) cycles of concentration. Predicted corrosion rates are for an untreated system. Table 1 summarizes the scales and predicted corrosion rate for the water as it cycles.

Step 2: Determine Corrosion Inhibitor Requirement (orthophosphate).
Select the corrosion inhibitor to be optimized. Many corrosion inhibitors are potential foulants, so the expected level in the recirculating water must be known so that adequate stabilization agents can be added to control potential deposits from the inhibitor. Figure 6 depicts the computer model orthophosphate dosage in the target operating range.

Step 3: Determine Calcium phosphate Inhibitor Requirement. (AA-AMPS)
Set background phosphate to desired orthophosphate level in the recirculating water. Use a model for the calcium phosphate inhibitor to determine the AA-AMPS requirements. Figure 7 depicts the AA-AMPS requirement as recommended by the computer model.

Figure 5
1010 Carbon Steel Corrosion Profile

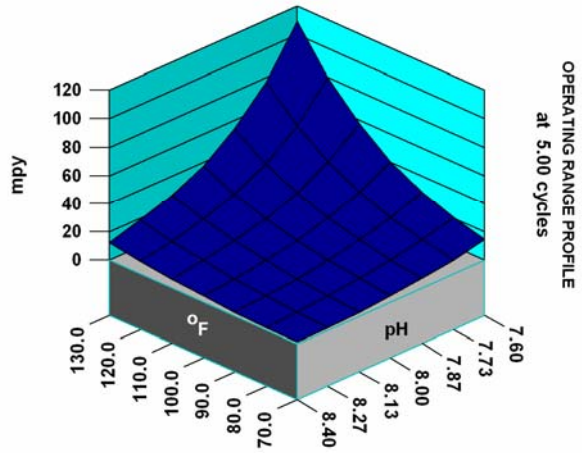


Figure 6
Orthophosphate Dosage Profile

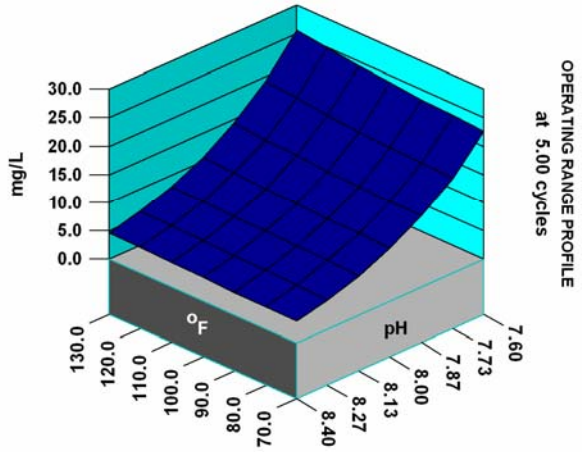


Figure 7
AA-AMPS Dosage Profile

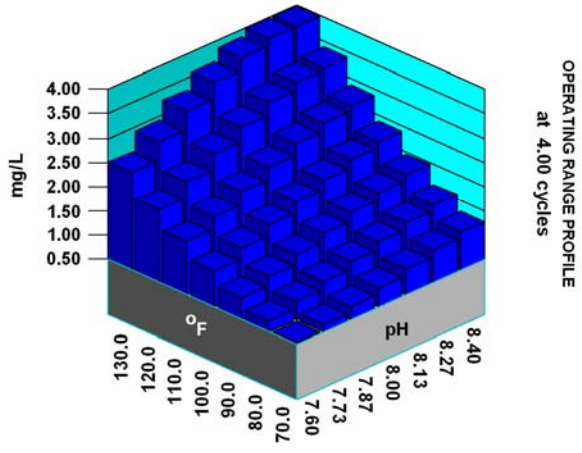


Table 1

WATER CHEMISTRY
VERSUS pH at 5.0 CYCLES

Lake Michigan
at 5 cycles

Chicago, IL
Sulfuric acid pH Control

Report Date: 07-24-2006
Sample #: 0

Sampled: 07-24-2006
at 1129

	pH						
CATIONS	**7.60**	**7.80**	**8.00**	**8.20**	**8.40**	**8.60**	**8.80**
Calcium (as CaCO3)	400.00	400.00	400.00	400.00	400.00	400.00	400.00
Magnesium (as CaCO3)	205.00	205.00	205.00	205.00	205.00	205.00	205.00
Sodium (as CaCO3)	95.00	95.00	95.00	95.00	95.00	95.00	95.00
ANIONS							
Chloride (as CaCO3)	45.00	45.00	45.00	45.00	45.00	45.00	45.00
Sulfate (as CaCO3)	538.44	506.31	464.40	409.60	337.96	244.30	121.85
Acidity	89.5	111.3	138.1	169.7	204.4	239.3	270.5
"M" Alkalinity	85.7	112.1	146.7	191.9	251.2	328.7	430.4
"P" Alkalinity	1.7	3.4	6.7	13.1	25.0	46.0	81.0
Silica(as SiO2)	11.50	11.50	11.50	11.50	11.50	11.50	11.50
Phosphate(as PO4)	27.29	17.43	11.17	7.21	4.70	3.10	2.07
PARAMETERS							
pH	7.60	7.80	8.00	8.20	8.40	8.60	8.80
Temperature(°F)	130.00	130.00	130.00	130.00	130.00	130.00	130.00
Calculated TDS	956.69	944.66	935.23	925.23	911.02	887.89	850.05
Calculated Cond.	986.92	980.70	971.13	955.51	929.34	885.46	813.43
SATURATION LEVEL							
Calcite	2.36	4.84	9.79	19.41	37.31	68.85	120.54
Aragonite	1.98	4.07	8.24	16.32	31.39	57.91	101.38
Calcium oxalate	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Anhydrite	0.278	0.264	0.245	0.217	0.179	0.129	0.0635
Gypsum	0.245	0.233	0.215	0.191	0.158	0.114	0.0558
Calcium phosphate	3546	3589	3362	2895	2272	1612	1022
Hydroxyapatite	754.39	1225	1768	2243	2468	2319	1820
Fluorite	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Silica	0.0492	0.0486	0.0478	0.0465	0.0446	0.0419	0.0381
Brucite	0.00100	0.00255	0.00647	0.0164	0.0415	0.104	0.256
Magnesium silicate	0.0225	0.0564	0.141	0.347	0.842	1.98	4.44
SIMPLE INDICES							
Langelier	0.584	0.903	1.22	1.54	1.86	2.19	2.51
Ryznar	6.43	5.99	5.56	5.12	4.67	4.23	3.77
Puckorius	6.66	6.25	5.84	5.43	5.02	4.60	4.17
Larson-Skold	6.82	4.93	3.48	2.38	1.53	0.89	0.39
DOSAGE (mg/L)							
98% Sulfuric Acid	448.44	416.31	374.40	319.60	247.96	154.30	31.85
Orthophosphate	27.58	17.55	11.22	7.23	4.71	3.10	2.07
AA-AMPS	25.5	16.8	10.5	6.20	3.44	1.77	0.84
PBTC	0.22	17.55	0.62	1.00	1.56	2.38	3.48

Step 4: Determine Calcium carbonate Inhibitor Requirement. (PBTC)
Select a model for the calcium carbonate inhibitor to determine the PBTC requirements. Figure 8 depicts the PBTC requirement as recommended by the computer model.

Step 5: Calculate the Product Formulation
The computer models used are based upon active inhibitor levels. The active levels and calculated formulation percentages are highlighted in tables 2.

Step 6: Verify blend
The modeling software used for this report checks to assure that sufficient polymer is present to control any calcium phosphate scale potential created by the treatment. First the program calculates the phosphate level required under the conditions evaluated. Then the program calculates the treated water calcium phosphate scale potential , and the polymer requirement to control it. If sufficient polymer is present, greater to or equal to that recommended for the orthophosphate present, the program proceeds without warning.

If the program finds insufficient polymer present, it warns that the polymer to phosphate ratio is too low, either by color coding graphs magenta, or by enclosing dosages in brackets.

Figure 8
100% PBTC Dosage Profile

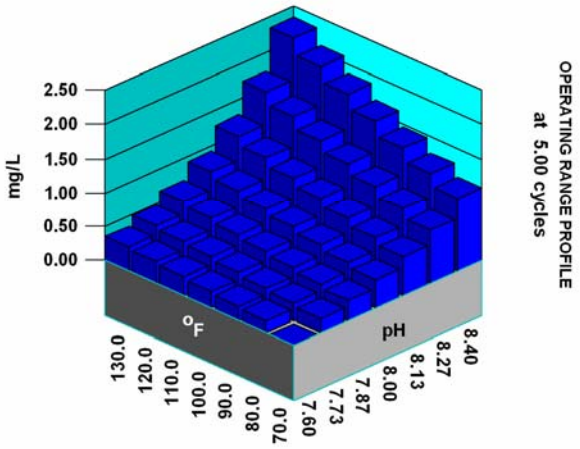


Figure 9
Alkaline Hi PO4 Dosage Profile

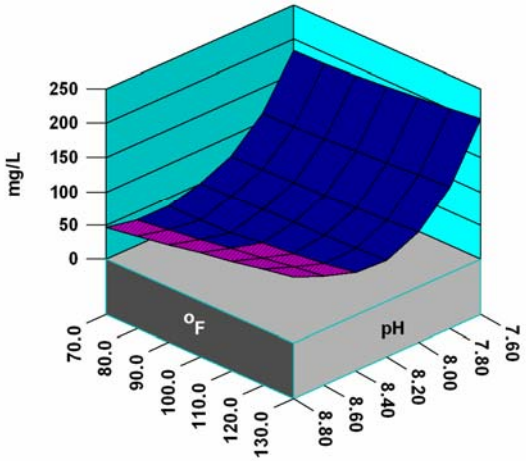


Figure 9 profiles the treatment requirement for the product formulated. Note that the product was formulated to handle a pH of 8.0 at 130°F. The shaded values in Table 2 were used for formulation.

Table 2 Recommended Inhibitor Dosages
High Phosphate Alkaline Treatment
at 5 cycles of concentration

INHIBITOR	pH 7.6	pH 8.0	pH 8.4	pH 8.8
Orthophosphate (PO4)	27.6	11.2	4.71	2.07
AA-AMPS	25.5	10.5	3.40	0.85
PBTC	0.24	0.62	1.56	3.48
$Ca_3(PO_4)_2$ Saturation	3,536.	3,282.	2,162.	946.
$CaCO_3$ Saturation	2.16	9.48	36.1	116.

OTHER ALKALINE PHOSPHATE TREATMENT SCHEMES

The scenario evaluated is for a high phosphate treatment approach, which is applicable to high flow velocity systems. Modeling software has been used successfully to optimize two other scenarios as well.

Low Phosphate Approach: Early alkaline phosphate treatment programs operated on the razor edge of calcium phosphate scale solubility. Phosphate levels were controlled near or slightly above the maximum soluble orthophosphate level. Low levels of polymer were introduced into the formulations with the goal of controlling scale at a level low enough so that the scale control agent present would not interfere with inhibitor film formation. Control levels for a low phosphate approach are outlined in Table 3. The phosphate levels recommended follow from Figure 3.

Table 3 Recommended Inhibitor Dosages
Alkaline Low Phosphate Treatment
at 5 cycles of concentration

INHIBITOR	pH 7.6	pH 8.0	pH 8.4	pH 8.8
Orthophosphate (PO_4)	3.98	1.97	1.21	0.90
AA-AMPS	3.43	0.97	0.56	0.27
HEDP	0.07	0.24	0.83	8.06
$Ca_3(PO_4)_2$ Saturation	198.	103.	157.	180.
$CaCO_3$ Saturation	2.33	9.48	36.1	116.

Moderate Tricalcium phosphate Approach: Alkaline phosphate treatment programs in large volume heavy industrial systems are operated in many cases at a moderate degree of calcium phosphate supersaturation. Phosphate levels are controlled so that the water has a tricalcium phosphate (TCP) saturation level on the close order of 500x saturation. Moderate levels of polymer are required in these formulations to prevent scale formation in low flow velocity exchangers. Control levels for a Moderate TCP approach are outlined in Table 4.

Table 4 Recommended Inhibitor Dosages
Moderate Tricalcium phosphate Approach
at 5 cycles of concentration

INHIBITOR	pH 7.6	pH 8.0	pH 8.4	pH 8.8
Orthophosphate (PO_4)	10.3	4.45	2.30	1.5
AA-AMPS	6.66	2.83	1.28	0.54
HEDP	0.07	0.25	0.83	8.04
$Ca_3(PO_4)_2$ Saturation	505	488	518	497
$CaCO_3$ Saturation	2.3	9.64	36.2	116.

Other Treatment Approaches: Computer modeling has been used successfully for modeling multifunctional treatment programs based upon other combinations of inhibitors such as organic phosphate (e.g. PCA), zinc, polyphosphate, and orthophosphate. In all cases, the models are used to balance corrosion inhibitor level and performance with scale control agent dosage.

SUMMARY

Computer modeling provides insight into the operation and formulation of multifunctional inhibitor blends. Models can be used to optimize formulations and assure that sufficient scale control agent levels are present to control any fouling potential created by the treatment (e.g. Zn, PO_4). Evaluations of a treatment scheme also provides insight into the limitations of treatments with respect to the pH and temperature limitations of a formulation due to the ratio of scale control agent to potential scale forming corrosion inhibitors.

Computer modeling is not a panacea. It requires reasonable models for scale and corrosion inhibitors as well as knowledge of the target cooling system operating range.

TABLES AND FIGURES

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