FORMULATING FOR COST PERFORMANCE

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ABSTRACT

Not all inhibitors perform equally under different conditions. Many have an application niche where they excel. Some inhibitors require lower dosages than others under typical operating conditions. Others extend the limits under which a system can operate without failure. This paper returns to the basics of formulating for cost performance through a procedure where: 1) the formulator targets the operating range for a treatment approach. 2) potential 'ingredients' are chosen for evaluation based upon typical properties and known failure points. 3) individual component dosages are optimized and compared. 4) improvements are considered such as the blending of polymaleic anhydride with phosphonates to extended the useful operating limits for cycles, pH and temperature. 5) cost performance is compared. This approach is especially useful in an economic environment where cost minimization is essential, and raw material costs can shift drastically in a short time period. The approach discussed allows a water treater to optimize treatment approach as cost performance varies due to rapidly changing cost of goods. Computer modeling and a visual chemistry approach for evaluation are used to illustrate the principals of formulating for cost performance.

There is a difference between ***treatment cost*** and ***treatment cost performance***. Many treatment program dosages (and therefore costs) are based upon general application guidelines and rules-of-thumb.

In this paper, cost performance is defined as treatment cost at the minimum effective dosage. Performance curves for scale inhibitors can be developed for scale inhibitors and blends for the minimum dosage as a function of critical parameters such as scale potential (saturation level), temperature as it affects rate, the time for which scale must prevent scale formation or growth, and in some cases, parameters such as pH which can affect the form, stereochemistry, and therefore efficacy of inhibitors.

The minimum effective dosage for a scale inhibitor treatment is usually much less than the actual dosage used based upon general application guidelines, and treatment economics suffer.

Unfortunately, the use of general guidelines sometimes leads to treatment at less than the minimum requirement, and scale can result.

The use of cost performance for optimizing formulations for a given water is of special import when raw material costs, and availability, are fluctuating quickly and disparately. Optimizing formulations for cost performance can assist the water treatment service company in minimizing the impact of raw material costs and availability on treatment program performance.

REQUIREMENTS FOR COST PERFORMANCE OPTIMIZATION

In order to optimize a treatment program formulation to cost performance, the following information and tools are essential:

1) A thorough evaluation of scale and corrosion problems, their severity, and difficulty of control;
2) Performance models for minimum effective dosage including a) performance models for individual inhibitors, and either b) mixing model for blended inhibitors, or c) performance model for inhibitor blends;
3) Treatment constraints including a) scales controlled and their saturation level limits, b) target corrosion rates, and c) environmental restrictions;
4) Baseline raw material costs/cost of goods; and
5) Current Raw material costs/cost of goods for comparison.

DOSAGE OPTIMIZATION

Models for calculating the minimum effective scale inhibitor dosage are well documented in the literature.[1,2,3] Scale inhibitor models use a scale potential to modulate the dosage. Ion association model saturation levels have been found to be the most effective driving forces for use as a parameter in modeling minimum effective dosage.[4,5,6]

Induction Time: The Key To The Models

Reactions do not occur instantaneously. A time delay occurs once all of the reactants have been added together. They must come together in the reaction media to allow the reaction to happen. The time required before a reaction begins is termed the induction time.

Thermodynamic evaluations of a water scale potential predict what will happen if a water is allowed to sit undisturbed under the same conditions for an infinite period of time. Even simplified indices of scale potential such as the ion association model saturation index can be interpreted in terms of the kinetics of scale formation. For example, calcium carbonate scale formation would not be expected in an operating system when the saturation index for the system

is only slightly above 1.0 x saturation. The driving force for scale formation is too low for scale formation to occur in finite, practical system residence times. Scale would be expected if the same system operated with a saturation index of 50. The driving force for scale formation in this case is high enough, and induction time short enough, to allow scale formation in even the longest residence time systems.

Scale inhibitors don't prevent precipitation, they delay the inevitable by extending induction time.[1, 2, 6, 7]

Formula 1:

$$\text{Induction Time} = \frac{1}{k\,[\text{Saturation Level} - 1]^{P-1}}$$

Where:

Induction Time is the time before crystal formation and growth occurs;
k is a temperature dependent constant**;**
Saturation Level is the degree of super-saturation;
P is the critical number of molecules in a cluster prior to phase change

Temperature is a second parameter affecting dosage and is represented by the temperature dependent constant k in Formula 1. A common concept in basic chemistry is that reaction rates increase with temperature. The rule-of-thumb frequently referenced is that rates approximately double for every ten degrees centigrade increase in temperature. The temperature constant above was found to correlate well with the Arrhenius relationship, as outlined in figure 2.

Formula 2:

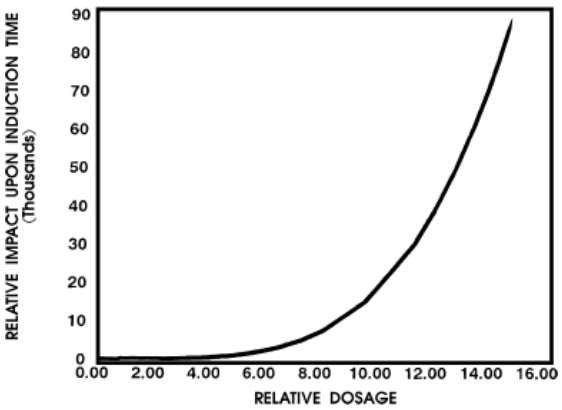
$$K = A\,e^{-Ea/RT}$$

Where:

k is a temperature dependent constant;
Ea is activation energy;
R is the Gas Constant;
T is absolute temperature.

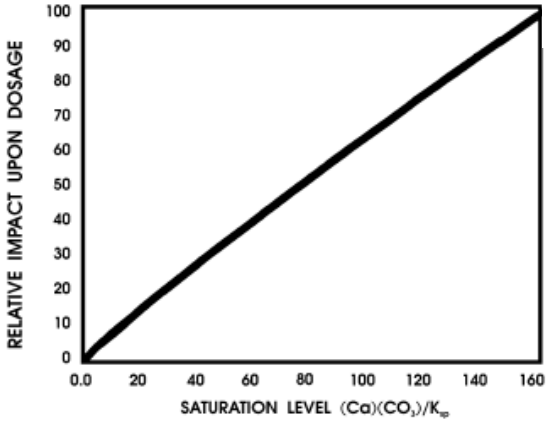
Models for optimizing dosage demonstrate the impact of dosage on increasing induction time. An example is profiled in Figure 1. Saturation level and temperature impacts upon the dosage requirement to extend induction time are depicted in figures 2 and 3. Factors impacting the anti-scalant dosage required to prevent precipitation are summarized as follows:

Figure 1 Dosage Impact Upon Induction Time



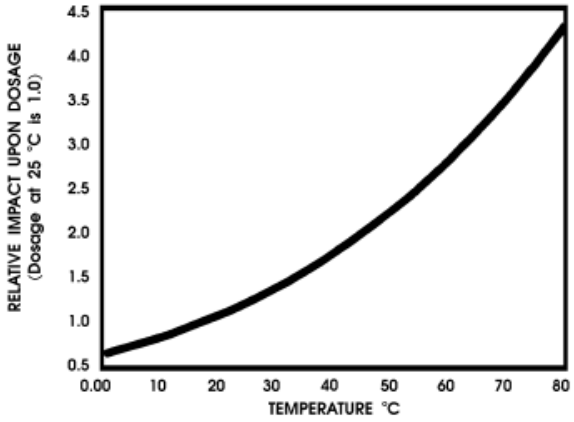
Time The time selected is the residence time the inhibited water will be in the cooling system. The inhibitor must prevent scale formation or growth until the water has passed through the system and been discharged. Figure 1 profiles the impact of dosage upon induction time with all other parameters held constant.

Figure 2 Saturation Level Impact On Dosage



Degree of Supersaturation An ion association model saturation level is the driving force for the model outlined in this paper, although other similar driving forces have been used. Calculation of driving force requires a complete water analysis, and the temperature at which the driving force should be calculated. Figure 2 profiles the impact of saturation level upon dosage, all other parameters being constant.

Figure 3 Temperature Impact Upon Dosage



Temperature Temperature affects the rate constant for the induction time relationship. As in any kinetic formula, the temperature has a great impact upon the collision frequency of the reactants. This temperature effect is independent of the effect of temperature upon saturation level calculations. Figure 3 profiles the impact of temperature upon dosage with other critical parameters held constant.

pH pH affects the saturation level calculations, but it also may affect the dissociation state and stereochemistry of the inhibitors[6,7]. Inhibitor effectiveness can be a function of pH due to its impact upon the charge and shape of an inhibitor molecule. This effect may not always be significant in the pH range of interest (e.g. 6.5 to 9.5 for cooling water).

Active sites It is easier to keep a clean system clean than it is to keep a dirty system from getting dirtier. This rule of thumb may well be related to the number of active sites for growth in a system. When active sites are available, scale forming species can skip the crystal formation stage and proceed directly to crystal growth.

Other factors can impact dosage such as suspended solids in the water. Suspended solids can act as sources of active sites, and can reduce the effective inhibitor concentration in a water by adsorption of the inhibitor.

Table 1 summarizes some of the inhibitor models available for scales of economic interest.

Table 1: 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	$CaCO_3$, $CaSO_4$, $BaSO_4$
PBTC	2-phosphonobutane-1,2,4-tricarboxylic acid	$CaCO_3$, $CaSO_4$, $BaSO_4$
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

SYNERGY AND INHIBITOR BLENDS

Although many water treatment chemists and field personnel promote their products on the basis of "synergy," most blends of inhibitors are not quite as effective as either inhibitor alone. Inhibitor performance models demonstrate that inhibitors compete with each other for "active sites." Data for blends correlates to models used for competitive inhibition.

Inhibitors may have a particular operating range where they are most effective. A blend of the common scale control agents ATMP and HEDP demonstrates this effect. In this case, a blend of complementary inhibitors might seem to be synergistic. In actuality, the dosage for one of the

inhibitors in a blend will have an optimum dosage lower than the dosage requirement for the blend. For example:

a) HEDP is typically most cost effective at lower temperatures and lower saturation levels.
b) ATMP is typically most cost effective at higher temperatures and higher saturation levels.
c) An HEDP/ATMP blend provides a smoothing effect over a broad application range of saturation level and temperature.

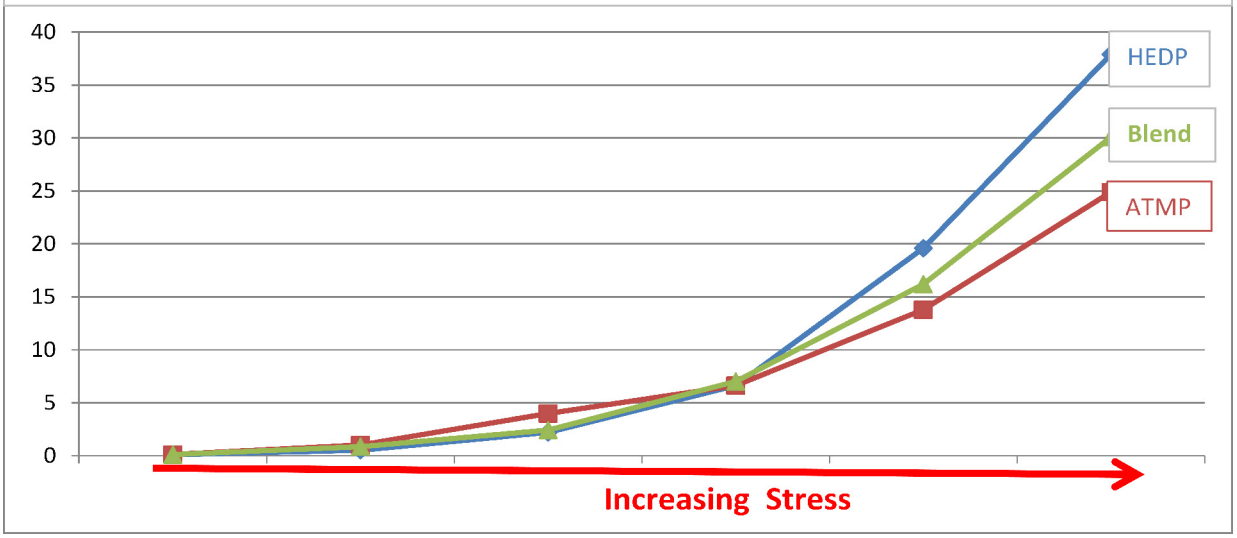
Table 2 summarizes dosage requirements for each phosphonate, and for a one-to-one blend, versus scale stress. Figure 4 presents the same data graphically.

Table 2: Dosage Requirements for ATMP, HEDP, and a 1:1 BLEND

	pH 7.9 70 °F	pH 8.1 123 °F	pH 8.5 123 °F	pH 8.7 137 °F	pH 8.9 150 °F	LEGEND
HEDP	0.10	0.52	2.21	8.70	19.6	HIGH DOSAGE
ATMP	0.13	1.02	3.99	10.6	13.8	MID DOSAGE
BLEND	0.11	0.86	2.42	10.2	16.2	LOW DOSAGE
AVERAGE	0.12	0.77	3.10	9.65	16.7	
X SAT	10.3	35.3	70.6	102	131	
	→ *increasing $CaCO_3$ stress* →					
	Treatments are 20% active, Dosages are at 24 hours					

HEDP dosages are lower at lower temperatures and saturation levels. ATMP dosages gain an advantage under conditions of increasing temperature and saturation level stress.

Figure 4: Minimum Effective Dosages versus Temperature and $CaCO_3$ Saturation Stress



APPLICATION NICHES

Inhibitors and their blends have specific application niches where they tend to be used. For purposes of this paper three treatment niches will be defined:

The "Comfort Zone"

The "Comfort Zone" is defined as a region where achieving scale and corrosion control is a relatively stress free operation. Calcium carbonate scale potential is well below the accepted limits for common phosphonates (Calcite x saturation 30 to 80, versus a limit of 135 to 150 x saturation).[11, 12] Temperatures are below 120 ^{o}F. HEDP tends to be used with polymers and copolymers in the "comfort zone." Other treatments may be used due to treatment program constraints such as all polymer treatments where phosphate discharge is restrictive.

The "Stressed $CaCO_3$ Zone"

The "Stressed $CaCO_3$ Zone" is defined as a region where achieving scale and corrosion control is difficult and requires excellent control. Calcium carbonate scale potential is approaching or above the accepted limits for common phosphonates (Calcite x saturation 120 to 200 versus a standard treatment limit of 135 to 150 x saturation). Stressed inhibitors such as PBTC, and blends of PBTC with PMA are required. Blends of HEDP and PMA are sometimes used. Skin temperatures are typically above 120 ^{o}F.

The "Stressed Phosphate Zone"

The "Stressed Phosphate Zone" is defined as a region where corrosion control is achieved by super-saturating the water with a solubility limited inhibitor such as orthophosphate, pyrophosphate, or zinc (in which case a purist would define the niche as a "Stressed Zinc Zone"). Calcium carbonate scale potential is typically controlled well below the accepted limits for common phosphonates. The solubility limited corrosion inhibitor is fed at a rate to assure the maximum presence of inhibitor without creating an inhibitor-based fouling problem.[13, 14]

Typical saturation level and solubility based control ranges for the inhibitors are outlined in Table 3. Maximum solubilities shown are calculated using a computerized ion association model as follows. The limiting factor for an ion's solubility is determined (e.g. $Ca_3(PO_4)_2$, $Zn_3(PO_4)_2$). The concentrations of other species for this ion are back calculated from the limiting factor. The maximum solubility is calculated as the sum as all bound forms of the ion under study, plus the free ion concentration. Analytically, the maximum soluble zinc equates to the maximum filtered zinc in a water having a difference between the measured "total" (unfiltered) and "soluble" (filtered) values. The impact of zinc, orthophosphate, and pyrophosphate on each other's solubility is iteratively determined in the actual simulation model used.

Table 3: Solubility Limited Inhibitor Saturation Level Control Range		
Inhibitor	**Low Level**	**Upper End**
Orthophosphate	$Ca_3(PO_4)_2$ 500 x Sat	$Ca_3(PO_4)_2$ 1,500 x Sat
Pyrophosphate	1.0 x Maximum Soluble Pyro	1.2 x Maximum Soluble Pyro
Zinc	1.0 x Maximum Soluble Zn	2.0 x Maximum Soluble Zn

TREATMENT COST PERFORMANCE EXAMPLES

During the past five years, raw material prices increased dramatically and disparately for cooling water inhibitors. Three time periods are covered in the examples. 2005 is used as a baseline case. Phosphate price increases are the first event used as an example trigger for the cost performance comparison. The recent increase in Glacial Acrylic acid and resultant increase in polymer costs provide the second event trigger for cost performance comparison.

A Great Lakes water (Lake Michigan at Chicago) was used for the comparison (Table 4).

Table 4: MAKE-UP WATER USED FOR SIMULATIONS

Lake Michigan at Chicago
Stressed $CaCO_3$ Zone

CATIONS		ANIONS	
Calcium (as $CaCO_3$)	80.00	Chloride (as $CaCO_3$)	5.00
Magnesium (as $CaCO_3$)	41.00	Sulfate (as $CaCO_3$)	1.00
Barium (as Ba)	0.02	"M" Alkalinity (as $CaCO_3$)	113.0
Sodium (as $CaCO_3$)	19.00	"P" Alkalinity (as $CaCO_3$)	0.00
Potassium (as $CaCO_3$)	0.00	Oxalic acid (as C_2O_4)	0.00
Ammonia (as $CaCO_3$)	0.00	Cyanide (as HCN)	0.00
Aluminum (as $CaCO_3$)	0.00	Phosphate (as PO_4)	0.00
Zinc (as Zn)	0.00	Pyrophosphate(as PO_4)	0.00
Fluoride (as $CaCO_3$)	0.00	Boron (as $CaCO_3$)	0.00
PARAMETERS		**COMMENTS**	
pH	8.20		
Temperature (°F)	77.00		
Calculated T.D.S.	222.19		
Calculated Cond.	263.92		

Raw material pricing used in the comparisons was provided by two major suppliers and a high volume distributor. The exact pricing is not included in the paper due to the Association of Water Technologies policy against price sharing. This paper limits cost performance evaluations to the "Comfort Zone" and "Stressed $CaCO_3$ Zone."

The "Comfort Zone"

The "comfort zone" treatment regime can be handled by most scale inhibitors or blends and is run in this projection without pH control. The HEDP:PMA treatment approach would provide an additional margin of safety for any system that might lose control. The HEDP:PMA treatment approach is superior to the HEDP:PAA approach and would be recommended based upon performance and cost in this scenario.

TABLE 5: "Comfort Zone" Treatment Cost Comparison			
TREATMENT 20% Active	**Baseline 2005**	**After Phosphate Crisis**	**After Glacial Acrylic Acid Shortage**
HEDP:PMA 3:1	1.89	3.67	2.72
HEDP:PMA1:3	4.23	6.59	6.07
HEDP:PMA 1:1	2.75	4.73	3.95
HEDP:PAA 3:1	2.21	4.47	3.31
HEDP:PAA1:3	4.77	9.66	7.16
HEDP:PAA 1:1	3.30	5.85	5.13
HEDP	0.87	1.10	1.45
PAA	5.73	7.26	9.55
PMA	2.96	4.24	4.24
PBTC	5.24	11.60	18.90

Comfort Zone treatments provide scale control up to the typical calcite saturation level limit of 135 to 150. Figure 5 profiles the maximum cycles where control would be expected in the comfort zone treatment range for this water.

Figure 5 "Comfort Zone" Treated Limits

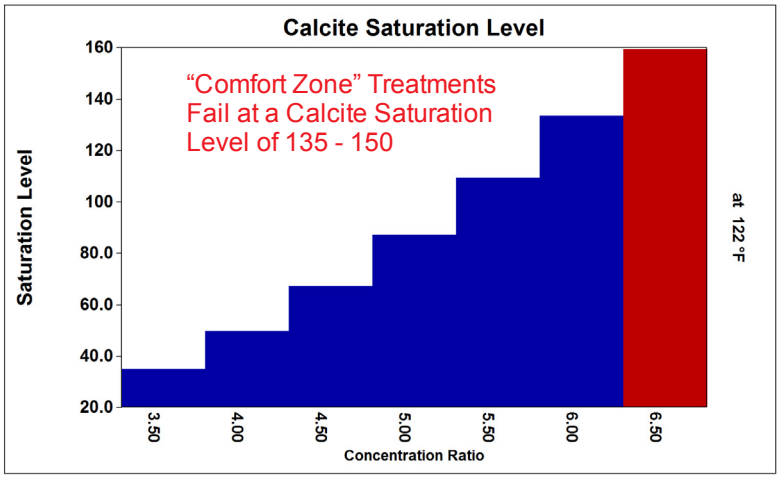


Figure 6 profiles the saturation level range at a concentration ratio of 4. Figure 7 depicts the minimum effective dosage profile for a typical Comfort Zone treatment, while its individual inhibitors are profiled in Figures 8 and 9. Comparable profiles for the higher stressed treatment are presented in Figures 10 and 11.

Operation at 4.0 cycles was chosen for the cost performance comparison, because it is near the Comfort Zone maximum Calcite saturation level of 135 to 150, which would be encountered should pH rise slightly higher than expected with a standard comfort zone treatment.

Fig. 6 **Calcite Saturation Level**

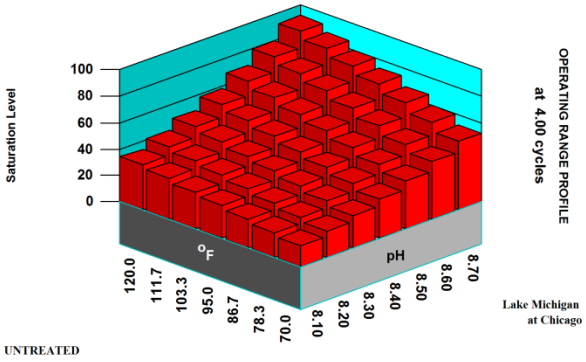


Fig. 7 **HEDP:PAA 3:1 Dosage Profile**

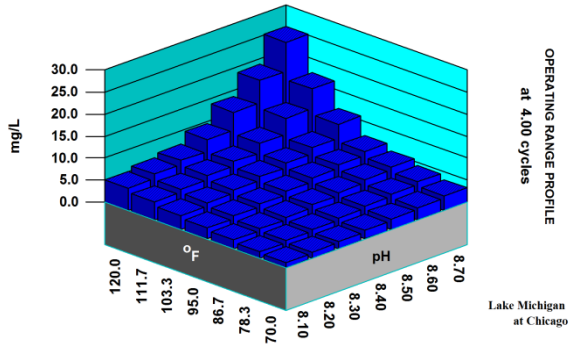


Fig. 8 **HEDP 20 Dosage Profile**

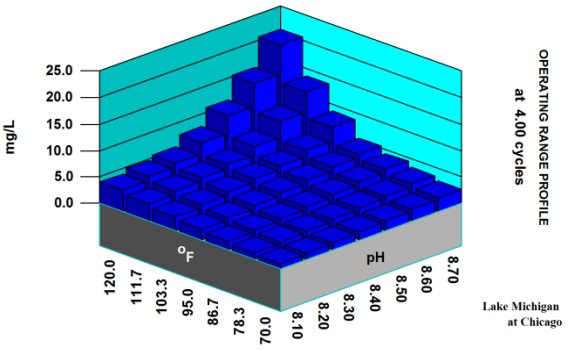


Fig. 9 **PAA 20 Dosage Profile**

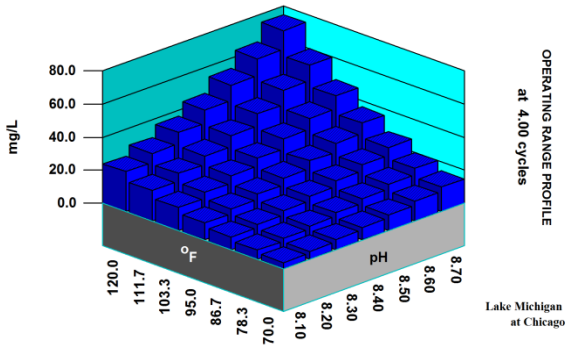


Fig. 10 **PMA 20 Dosage Profile**

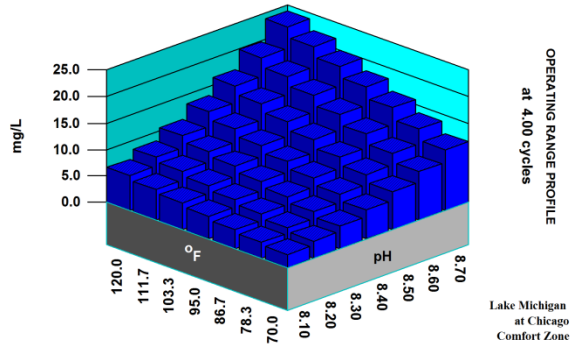
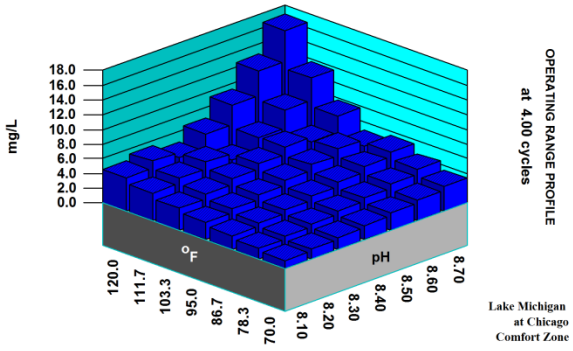


Fig. 11 **HEDP:PMA 3:1 Dosage Profile**



The "Stressed $CaCO_3$ Zone"

The "stressed $CaCO_3$ zone" treatment regime can be handled by stressed scale inhibitors or blends and is run in this projection without pH control. The PBTC:PMA treatment approach would be the treatment of choice.

TABLE 6: "Stressed $CaCO_3$ Zone" Treatment Cost Comparison			
TREATMENT 20% Active	**Baseline 2005**	**After Phosphate Crisis**	**After Glacial Acrylic Acid Shortage**
PBTC:PMA 3:1	14.15	27.57	20.17
PBTC:PMA1:3	17.60	27.69	25.20
PBTC:PMA 1:1	15.84	27.59	22.64
HEDP:PMA 3:1	26.75	29.97	22.17
HEDP:PMA1:3	32.39	28.38	26.14
HEDP:PMA 1:1	29.74	29.09	24.29
HEDP	**8.99**	**11.38**	**14.98**
PAA	**18.90**	**23.94**	**31.5**
PMA	24.13	34.61	34.61
PBTC	12.43	27.47	17.66
HEDP and PAA are nearing their upper saturation level limit of 150 x saturation for calcite and would not be recommended as sole treatments			

Stressed treatments based upon PBTC, PMA, or phosphonate copolymer combinations, extend the useful maximum calcite saturation limit, allowing scale control at higher cycles. Figure 12 profiles the maximum cycles where control would be expected in the stressed treatment range for this water.

Figure 12 "Stressed $CaCO_3$ Zone" Treated Limits

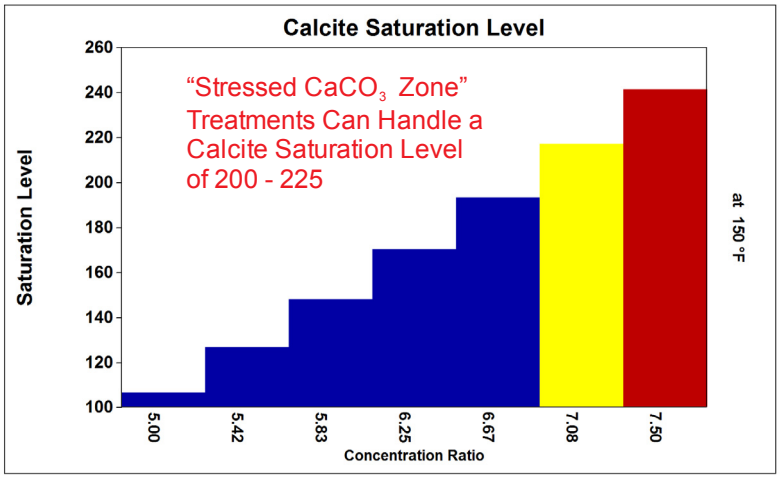


Figure 13 profiles the saturation level range at a concentration ratio of 5.5, while Figures 14 through 16 depict the minimum effective dosage for the PBTC:PMA blend and the individual inhibitors.

Operation at 5.5 cycles was chosen for the cost performance comparison, because it is near the maximum should pH rise slightly higher than expected.

Fig. 13 **Calcite Saturation Level**

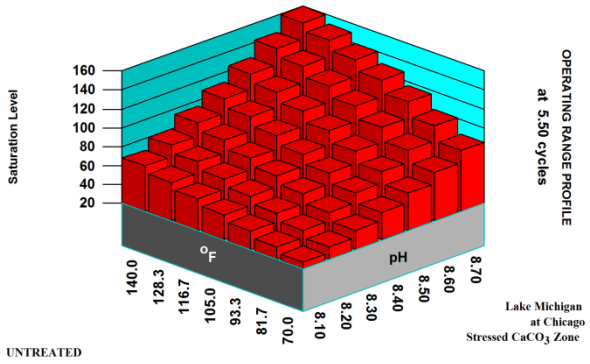


Fig. 14 **PBTC:PMA 3:1 Dosage Profile**

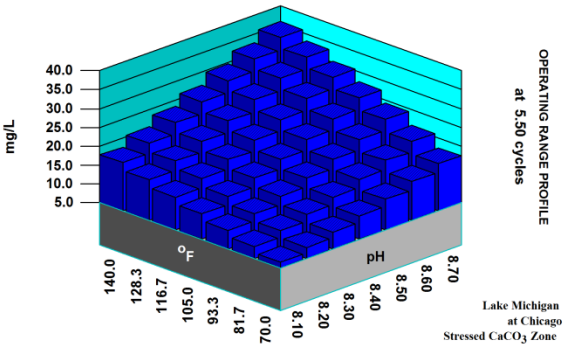


Fig. 15 **PBTC 20 Dosage Profile**

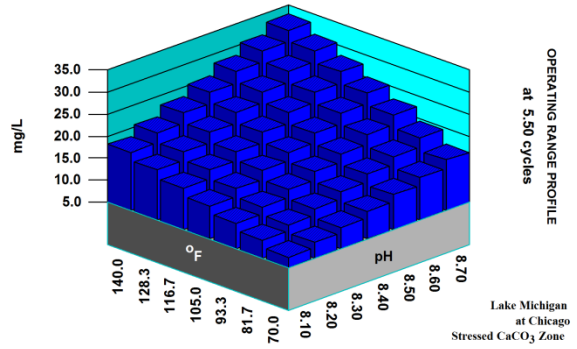
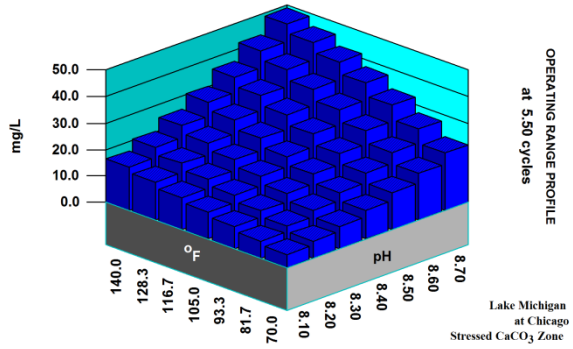


Fig. 16 **PMA 20 Dosage Profile**



SUMMARY

Cost performance comparisons provide a useful tool for minimizing treatment costs and dosage. Computerized models allow optimization of formulations for target waters and operating ranges. This approach also provides a means for formulating replacement treatment programs for a given water should raw material shortages or rapidly rising costs force a change in treatment approach. This treatment limits and optimum dosage approach also provides a product management tool for improving the consistency of treatment programs recommended and run by different field personnel.

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