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THIRTY YEARS OF ULTRA LOW DOSAGE SCALE CONTROL

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ABSTRACT

Utilities were confronted by a major cooling water treatment challenge in the 1970's. Central station power generation units were built with man made lakes for condenser cooling in the previous decades. These lakes concentrated with time creating a calcium carbonate scale problem in the once through cooled surface condensers and auxiliary cooling systems. In some cases, the problem was further aggravated and accelerated by the addition of multiple power generation units to the lakes, well beyond the original design specifications.

Condenser scale caused increased back pressure in the turbines, increased heat rate, and in many cases, deration. Traditional once through cooling water scale treatment approaches could not economically control the scale. Cost for treatment using the one(1) to nine(9) mg/L dosage rates for polyphosphate based scale control agents common at the time for once through scale control, were higher than the cost of increased fuel consumption and lost production capability. This paper describes the evolution and history of an economical treatment approach for high volume utility once through cooling systems based upon polymers and phosphonates. The theoretical and practical application of dosage optimization models used to modulate the inhibitor dosages is discussed in detail. The system described, or derivatives of it, are commonly used today for high volume utility once through scale control.

INTRODUCTION

Ultra low dosage approaches are based upon the concept that a scale control agent needs only to prevent scale for the time the cooling water is in the system in a perturbed state. Traditional dosages used for once through scale control were those found effective in long residence time municipal water supplies and industrial cooling systems. They typically would prevent scale for systems with twenty-four (24) hour residence times or greater. Utility once through cooling system inhibitors must only prevent scale for the five (5) to twelve (12) seconds that the cooling water is being heated in the one or two pass condenser.

Studies were conducted in the laboratory, on site at the impounded lakes, and in the operational systems to determine the minimum scale inhibitor dosages which would prevent scale formation on surface condenser heat transfer surfaces.[1]

Laboratory studies were based upon the constant composition method for evaluating scale inhibitor impact upon induction time.[2] On site studies utilized well instrumented heat exchangers operating under flow regime, heat transfer rate, and skin temperature conditions comparable to a surface condenser. The final step in evaluating treatment levels was to implement them on the operating condenser cooling system. Condenser performance tests were run up to several times a day during the in system evaluations to assure that scale was not forming. [3]

THEORETICAL BASIS FOR DOSAGE MODELS

The original models described in this paper were developed from a combination of field observations, common sense, and laboratory data. Evaluation of data from field and laboratory dosage optimization studies revealed that several parameters were critical to dosage: *time, temperature,* and the *degree of supersaturation*. The method outlined in this paper has been used to develop models of minimum effective inhibitor dosages from laboratory data, field data, and combinations of both. The inhibition of scales ranging from calcium carbonate to calcium phosphate have been modeled using the method outlined.[4] The models provide a natural path for bringing research data into the practical arena of the operating engineer or water chemist.

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 recognizable crystal formation and growth appear is termed the induction time.

Thermodynamic evaluations of a water's scale potential predict what will happen if it is allowed to sit undisturbed under the same conditions for an infinite period of time. Even simplified indices of scale potential such as the Langelier 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 Langelier saturation index for the system is 0.1 to 0.2 . The driving force for scale formation is too low for scale formation to occur in finite, practical residence times. Scale would be expected under the same conditions if the same system had a scale potential driving force as indicated by a Langelier saturation index of 2.8 .

Induction time has been modeled for economically important crystals such as sucrose. Models follow a formula similar to Equation (1):

EQUATION 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.

Gill and his associates demonstrated that commercially available scale inhibitors extend the induction time for calcium carbonate scale[(2)]. Their paper points out several critical parameters which impact the induction time prior to crystal growth:

- The degree of supersaturation.
- The temperature.
- The presence of active sites upon which growth can occur.
- The inhibitor level.

Gill's study used ion association model saturation level as the thermodynamic driving force for scale growth. Saturation level calculations performed using a computerized ion pairing (ion association) method eliminate most of the assumptions inherent in simplified indices[(5,6,7,8,9,10)]. They account for common ion effects which can increase the apparent solubility of a scale forming specie such as calcium carbonate. Driving forces for scale formation calculated using the ion pairing method are transportable between systems because they base their calculations upon free ion concentrations rather than the total analytical values.

Reconciling Laboratory Studies to Field Conditions: Prior to the use of induction time extension models for predicting the optimum scale inhibitor dosages, a great disparity was observed between dosages predicted in the laboratory, and those found successful in the field. Laboratory studies were typically run at the water chemistry and temperature conditions found in the operating systems. The laboratory studies differed from the operating systems with respect to the time for which the inhibitor must prevent precipitation. A twenty four (24) hour test was standard for laboratory studies while field systems may need only prevent scale for the five (5) to twelve (12) seconds required for the cooling water to pass through the condenser. Induction time was the variable that allowed normalizing longer residence time studies to shorter residence time systems. Figures 4 and 5 compare dosage requirements for the phosphonate HEDP in a 5 second residence time system to a system with a 24 hour residence time.

Critical Parameters

The parameters contributing to Equation (1) are included in the basic relationships used for inhibitor dosage modeling. Major data values required include the ***time period*** during which scale formation must be prevented, the ***degree of supersaturation*** which is the driving force which must be overcome, the ***temperature*** at which the inhibitor must function, and the ***pH*** of the cooling water. The surface area of ***active sites*** also impacts the dosage requirement.

These parameters have the following impacts upon dosage:

Time. The time selected is the residence time the inhibited water will be in a perturbed state. 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 induction time upon dosage with all other parameters held constant.

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.

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[9]. 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. 6.0 to 9.5).

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. These other factors are not taken into account in the models in this paper. Table 2 summarizes the factors critical to dosage modeling, and their impact upon dosage.

Data Base

The dosage models used as examples in this paper were developed from data collected in field studies,[1] laboratory studies, published data, or a combination of these sources.

Examples in this paper include data from side stream evaluation of the minimum effective dosages. In these studies, two parallel fouling probes were used to develop estimates of the minimum effective dosages for the phosphonates amino-tris-methylene phosphonic acid (AMP), 1,1-hydroxy ethylidene diphosphonic acid (HEDP), and polyacrylic acid (PAA). One probe was over-treated at a level where no calcium carbonate deposition would be anticipated. The parallel probe was not treated, and the time required for a measurable deposit to form determined. This was deemed the minimum period between dosage adjustments for the test. (Note: A minimum test duration of twice the time required for fouling was allowed to pass between dosage adjustments). Dosages were decreased until failure, as indicated by a measurable deposit formation.

Models should be derived from data over the range of water chemistry anticipated as well as over the range of saturation level anticipated. If a calcium carbonate scale inhibitor model will be used in waters ranging from a calcium level of 40 ppm to over 1000 ppm, this range should be covered from laboratory and/or field sources. The saturation level range anticipated should also be bracketed (e.g. 1.0 to 250 saturation level for calcite).

Although field data is the source of choice, field conditions can rarely be adjusted to cover the temperature, pH, time, and water chemistry ranges desired. The use of static laboratory tests designed to elucidate the variation of dosage with any of the parameters can be used to supplement field data. Field data, although desirable, is not always necessary for the development of a preliminary correlation. Each model developed should be compared to field results to assure that a correlation exists between the test data, the model, and actual field results.

DEVELOPMENT OF MODELS

A modified version of Equation (1) provided the basis for model correlation. Dosage was added as a factor to the equation on the right side to produce Equation (2).

EQUATION 2 $$\text{Induction Time} = \frac{\text{Dosage}^{M}}{k'[\text{Saturation level} - 1]^{P-1}}$$

Where

- Dosage is the molar inhibitor dosage
- M is a constant
- k' is a temperature dependent rate constant
- Saturation level is the ratio of Ion Activity Product $\{Ca\}\{CO_3\}$ to the solubility product, Ksp, for calcite
- P is the number of molecules in a critical cluster

The temperature dependent rate constant k' was found to correlate with the Arrhenius relationship shown by Equation (3).

EQUATION 3 $$k' = A\, e^{-Ea/RT}$$

Where

- A is a constant
- Ea is the activation energy for the reaction
- R is the gas constant
- T is absolute temperature

Saturation levels were calculated from water analysis input using a computerized ion association model. The time used for the correlation was the time to failure in laboratory tests, the residence time in a heated state for utility once through cooling systems, and the holding time index in open recirculating cooling systems.

Equation (2) was rearranged to solve for dosage in the first order. Regression analysis was used to estimate the coefficients.

TABLE 1: MAJOR FACTORS INFLUENCING DOSAGE

FACTOR	*IMPACT*
Time	**Dosage increases with residence time**
Degree of Supersaturation	**Dosage increases with saturation level**
Temperature	**Dosage increases with temperature due to its impact on reaction rate (in addition to any positive or negative effects temperature may have upon saturation level).**
Suspended solids	**Dosage requirements may increase as suspended solids increase due to adsorbtion of the inhibitor on the solids.**
Active sites	**Dosage requirements increase if active sites for scale growth are present.** **It is easier to keep a clean system clean than it is to keep a dirty system from getting dirtier.**

APPLICATION OF THE MODELS TO OPERATING SYSTEMS

Step Function: The first ultra low level treatments applied to operating condenser cooling systems were a simple step function. Typically, a dosage of 0.25 mg/L was fed to the once through during hotter months when calcium carbonate saturation indices are at their highest, and a lower dosage during cooler months when saturation indices were at their lowest. Onsite tests with deposition monitors were conducted to determine the minimum dosage needed. The step function dosages were established with a generous safety factor. Although the step function application resulted in over-dosing and higher chemical usage than optimum, it did bring the treatment costs for large volume utility condenser cooling systems to a practical level.

Modulation to Simple Indices: The simple step function quickly gave way to modulation to models using a simple saturation index such as the Langelier Saturation index as the driving force for calcium carbonate scale formation. These models were programmed into a spreadsheet such as Lotus 1-2-3, Excel, or Symphony. Plant chemists would input water analysis, residence time, and an evaluation temperature and adjust feed pumps manually as needed. These simple index models further brought down the treatment requirements. [(11)] Care was needed to prevent under-dosage of scale inhibitors in systems where water chemistry or temperature changed quickly. These models were usually applied based upon the "worst case" conditions anticipated between treatment adjustments, those being the highest pH, highest temperature, and longest residence time.

Real-time Control: Many cooling lakes exhibited a stable pH and water chemistry and were easily treated using manual water analysis and scale inhibitor feed pump adjustment. Other lakes demonstrated dramatic pH changes in a twenty four hour period due to algal respiration. In these lakes, pH was

observed to vary up to 1.2 units in a single day. The highest pH usually coincided with, or was near, the hottest temperatures and highest electrical demand. Manual adjustment to worst case conditions resulted in significant over feed and could easily result in inhibitor underfeed if actual conditions exceeded the predicted "worst case." By the 1980's, a combination of military spec PC's and programmable logic controllers were used for real time dosage modulation. Slowly changes variables such as calcium concentration, alkalinity, chloride and sulfate were input into the control system manually. Interlocking with the system provided online input of parameters which could change quickly such as temperature and pH. [12] Control systems of this type minimized the chemical usage while assuring that under treatment did not occur. Figures 6 through 8 depict the variation in driving force and dosage requirement for a typical day in the system for a 15% active phosphonate/polymer blend.

Modulation to More Sophisticated Ion Association Models: Ion association models were also used in the late 1970's to further refine the models and to improve their general applicability to cooling water conditions. Ion association model programs base indices such as the calcite saturation level on free ion concentrations rather than total analytical values. These indices account for ion pairing and common ion effects to provide a more accurate prediction of scale potential as a driving force for scale formation, and inhibitor models. Most dosage models in use today are based upon an ion association model for calculation of indices used in the dosage calculations. [4,6,13,14]

RESULTS USING THE MODELS

The calcium carbonate scale inhibitor dosage models described in this paper have been in use since the 1970's, and have been used in one form, or another by many water treatment companies.

The first recorded impounded lake cooling system treatment was implemented in a midwest central station power generation unit using a step feed method. The phosphonate AMP was fed directly to the lake initially under the hypothesis that phosphonate residuals would build up in the lake water. A continuous feed of AMP, and later, PAA, was eventually implemented and resolved the calcium carbonate scale problem.

Lake cooling systems throughout Texas and the Midwest have been treated using the various dosage modulation schemes outlined in this paper. Scale control has been acceptable when the models have been followed. One stations condensers scaled to the point where acid cleaning was required to restore capability when a different treatment scheme (from the lowest bidder) was implemented at levels significantly lower than those that had been fed using the dosage models described in this paper. Scale control was restored when a treatment scheme based upon the models was restored.

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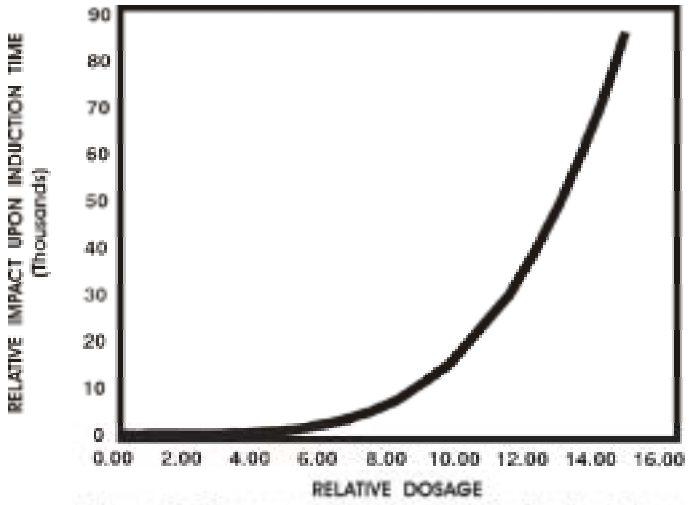

Figure 1: Dosage Impact Upon Induction Time

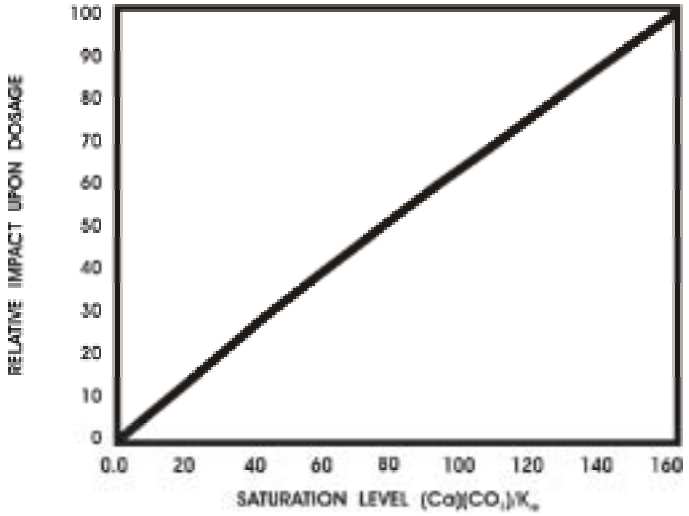

Figure 2: Saturation Level Impact On Dosage

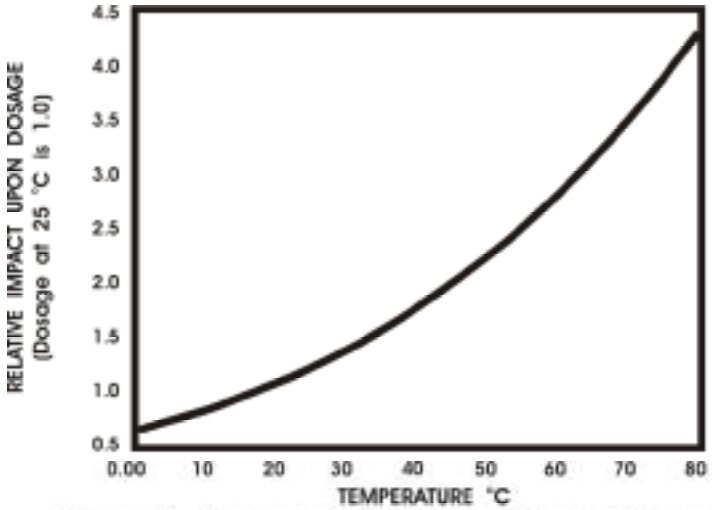

Figure 3: Temperature Impact Upon Dosage

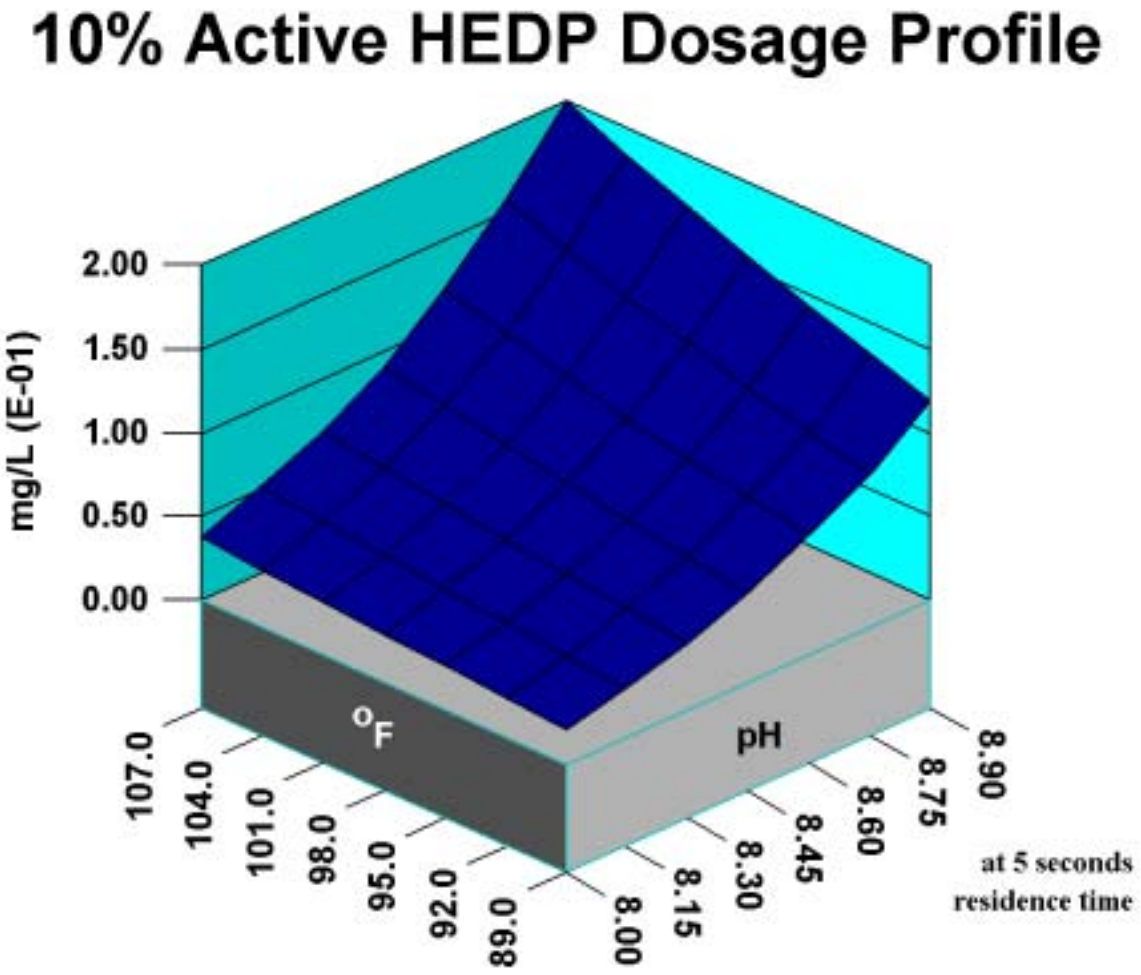

Figure 4: Daily Variation in HEDP Dosage Requirement for 5 Second Induction Time Extension

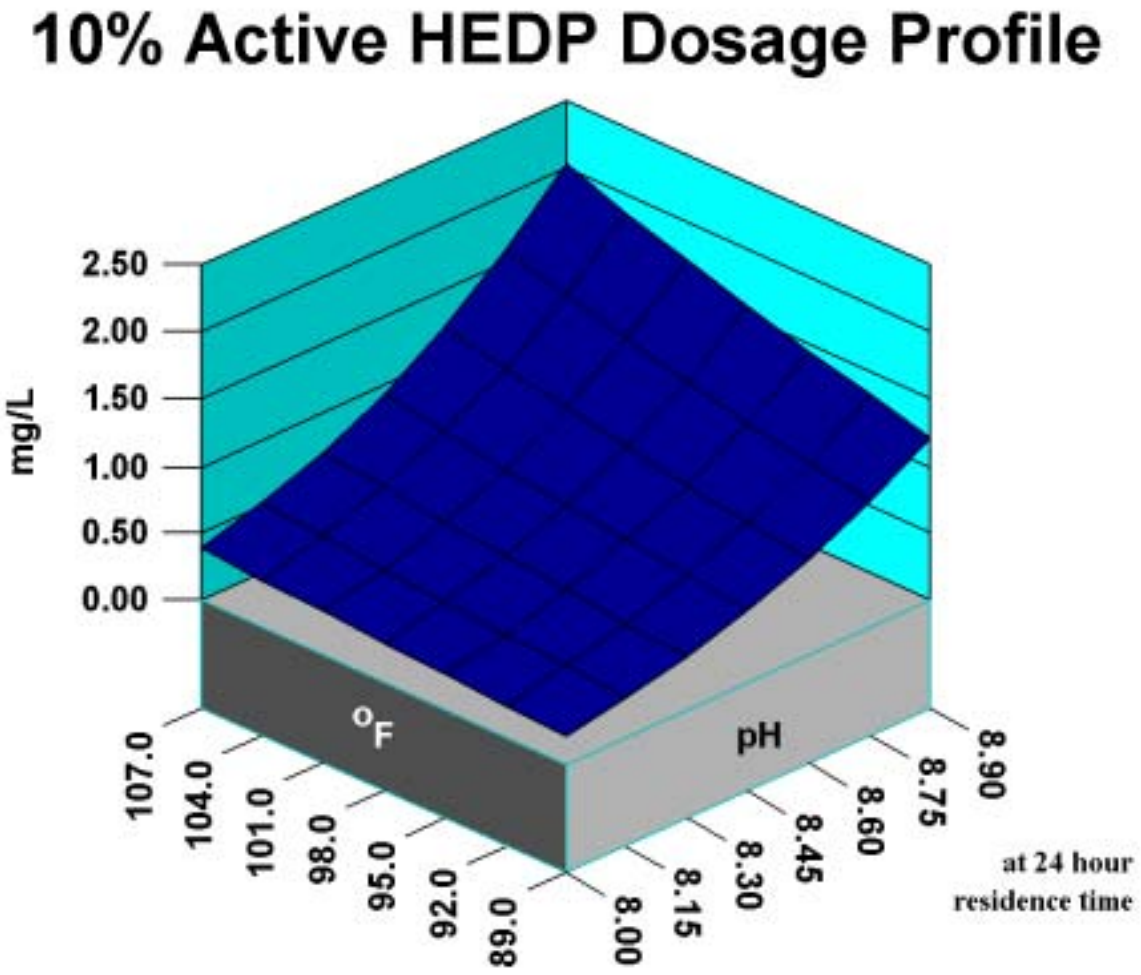

Figure 5: Daily Variation in HEDP Dosage Requirement for 24 Hour Induction Time Extension

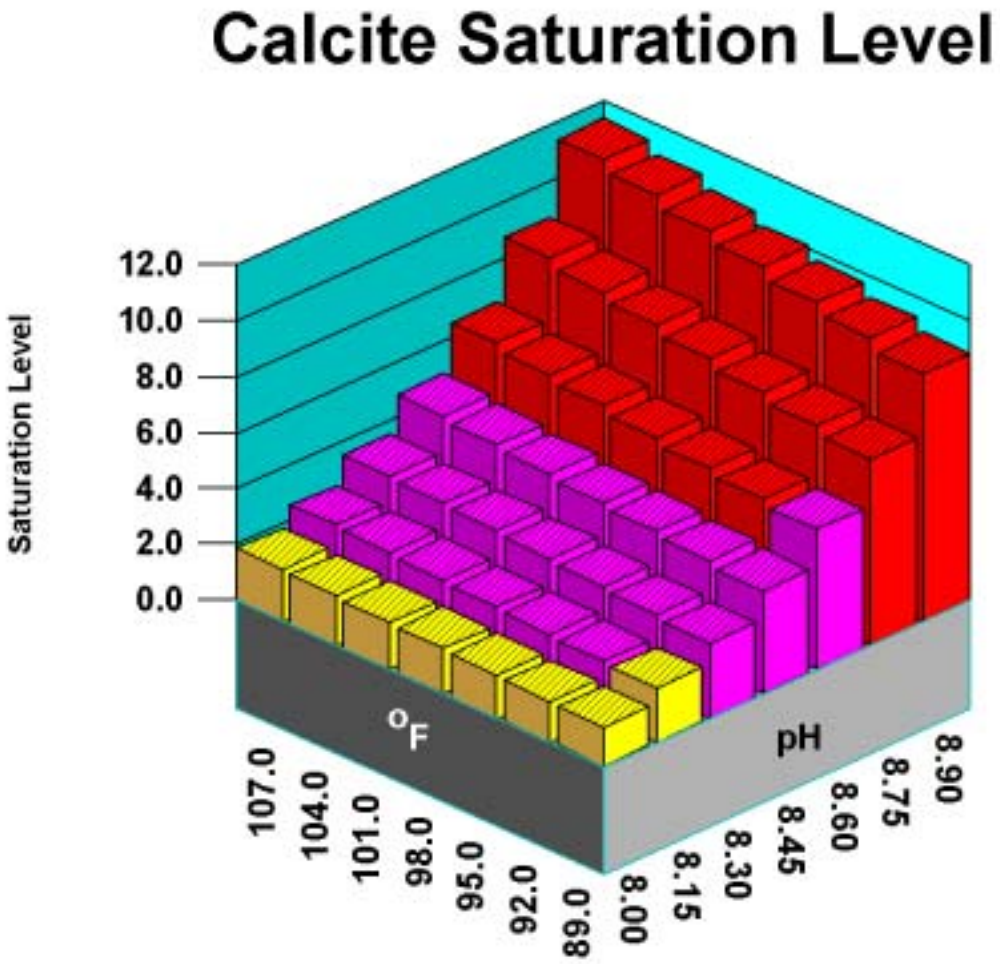

Figure 6: Daily Variation in $CaCO_3$ Saturation Level

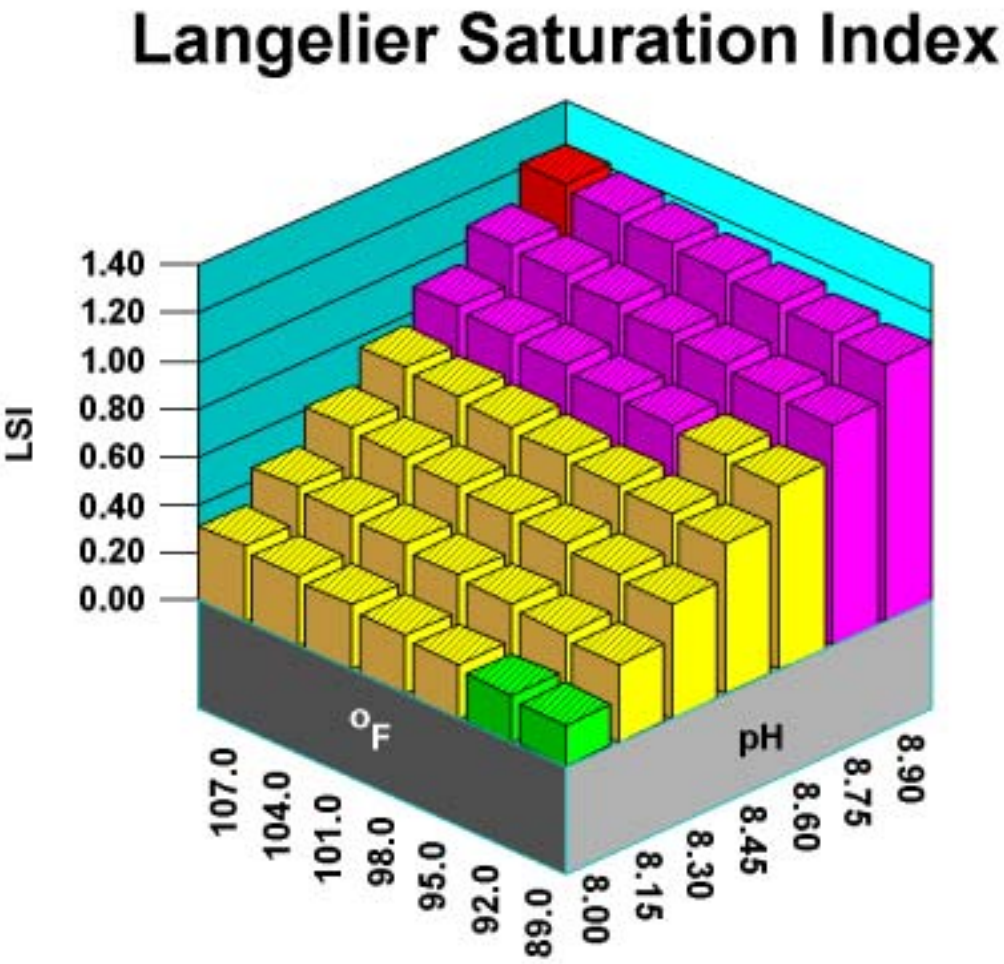

Figure 7: Daily Variation in Simple Saturation Index

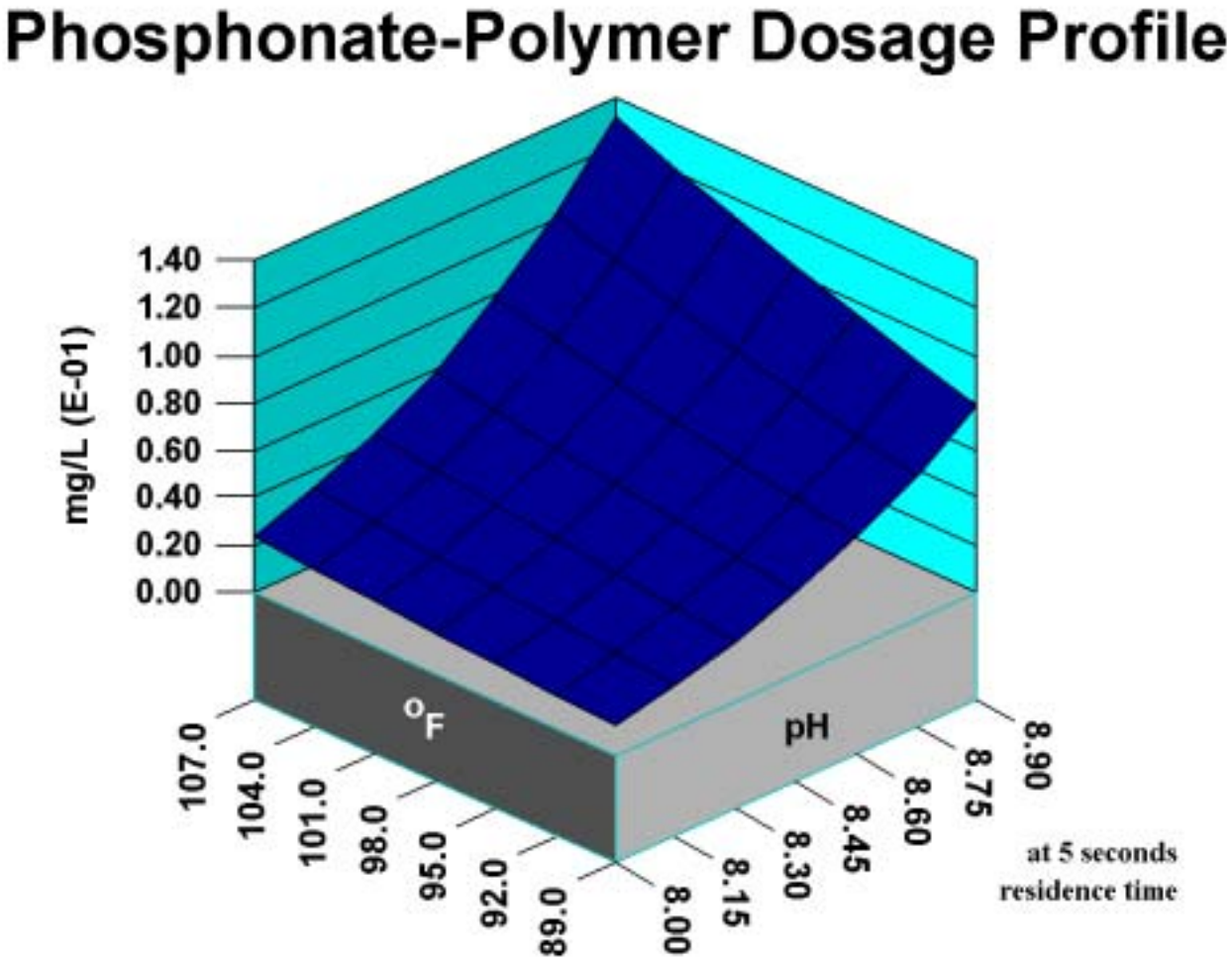

Figure 8: Daily Variation in Dosage Requirement For 5 Second Induction Time Extension

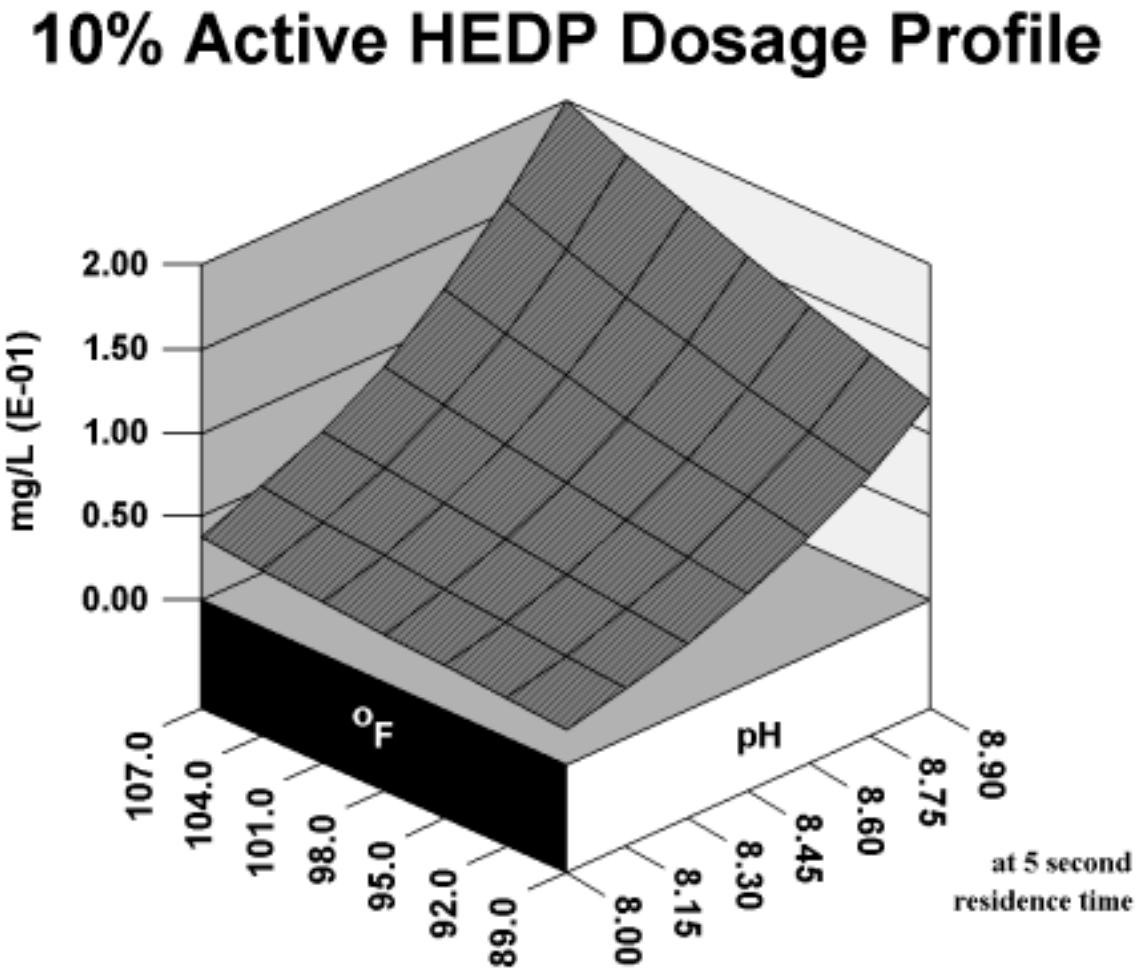

Figure 4: Daily Variation in HEDP Dosage Requirement for 5 Second Induction Time Extension

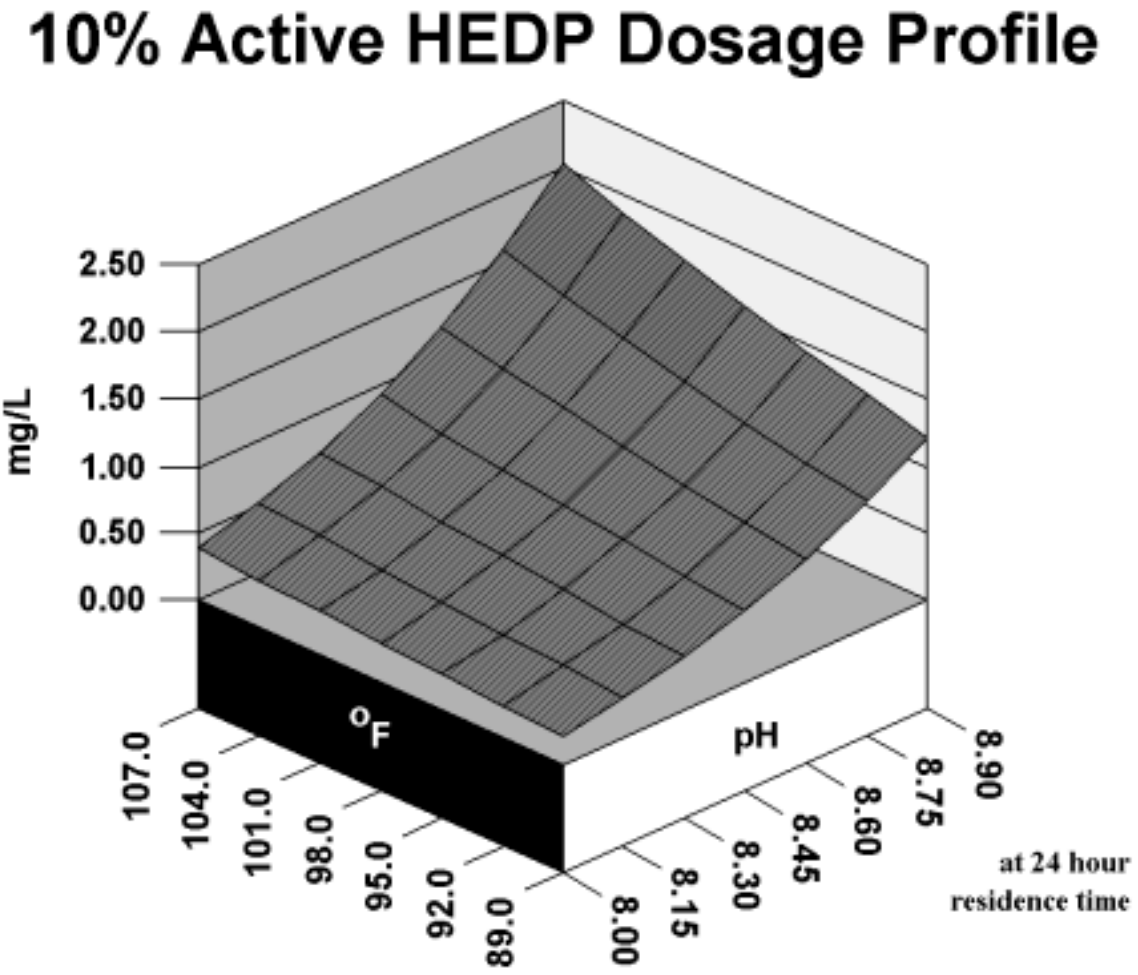

Figure 5: Daily Variation in HEDP Dosage Requirement for 24 Hour Induction Time Extension

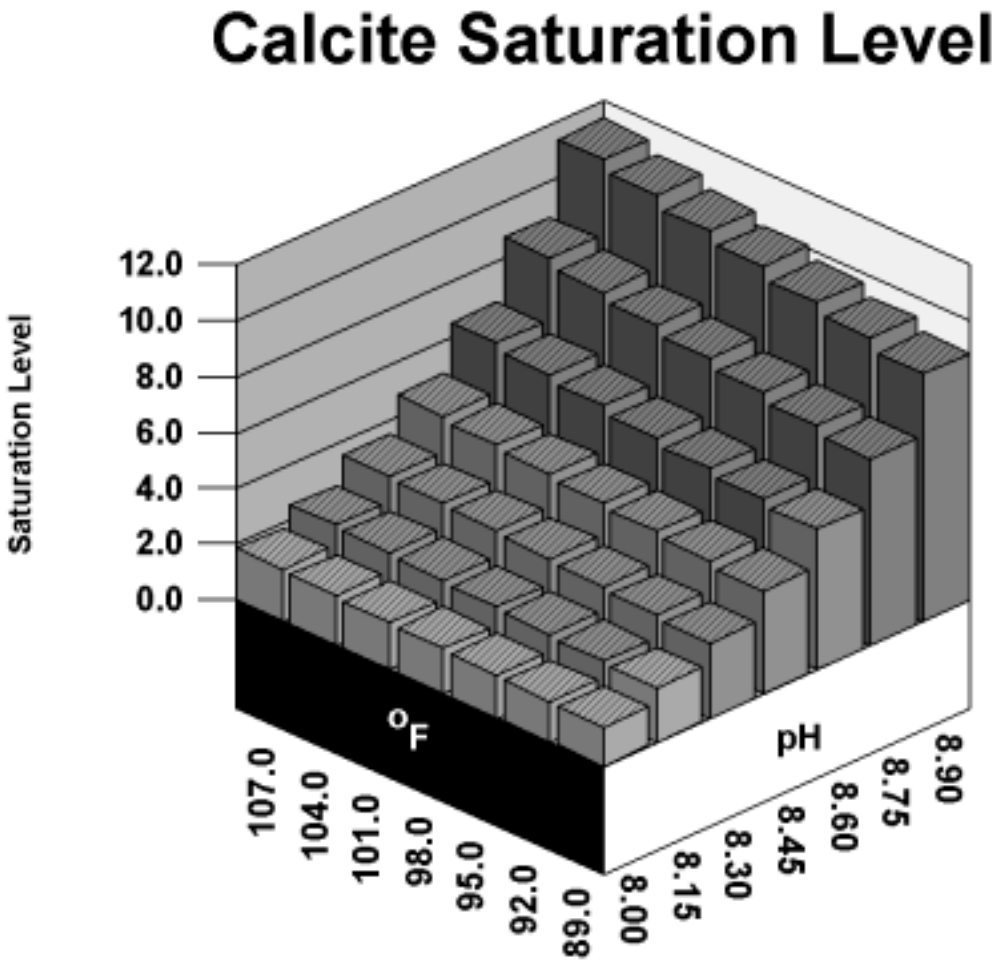

Figure 6: Daily Variation in $CaCO_3$ Saturation Level

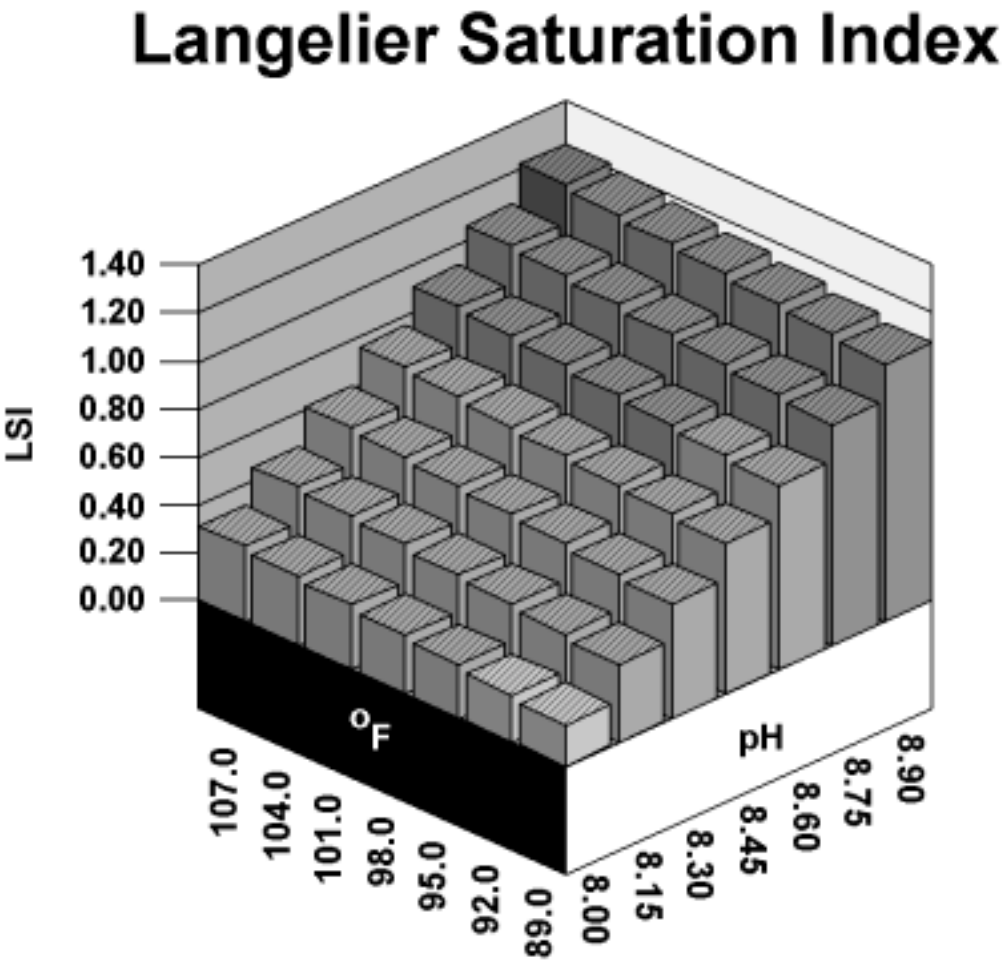

Figure 7: Daily Variation in Simple Saturation Index

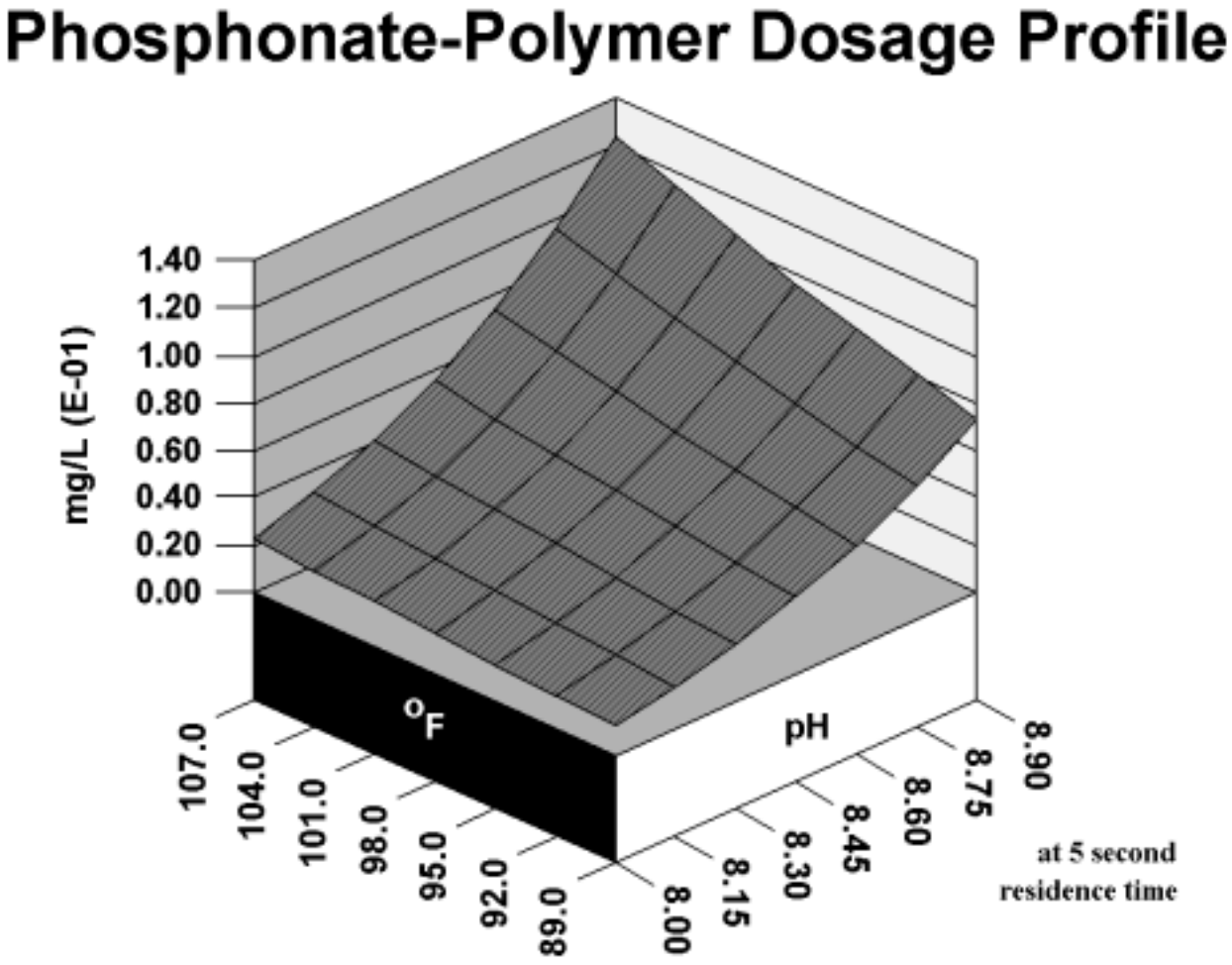

Figure 8: Daily Variation in Dosage Requirement For 5 Second Induction Time Extension