A condensation of four articles to be published in the AWT ***Analyst*** *during 2008.*

Formula Development -- Cooling Water Treatments

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Sufficient information is included in this paper for a water treatment engineer to design, manufacture, and apply scale and corrosion control remedies throughout a wide range of conditions. The proposed program is unique in that blending instructions for 55 gallon quantities end up with whole number quantities for each ingredient, making the production of such small batches easier. ***And it's just fine for larger batches too!***

Complete accuracy in production assures more precision in the percentages obtained for describing, prescribing, and testing concentrations!

First, we rush through some of the history and basic concepts of water treatment. Then we consider the generation and control of scaling and corrosion. We give particular attention to the merits of the phosphonates, both the scale preventative type and the corrosion control versions.

Next we describe some additional corrosion inhibiting materials. And move on to dispersants that control contaminants in the raw water and in the complexes formed from hardness and the inhibitors we might add. Combinations are then considered carefully as are the synergisms that result when appropriate additives are put together in optimal proportions.

At this point, we seek to better understand the challenges emanating from particular deposit forming agents, consider strategies to meet those problems, and discuss the chemicals required for the job. Concepts of concentration, cycling, and feeding are also examined at that time.

To conclude, we suggest five different water conditions and recommend treatment approaches. Detailed instructions will be supplied later for the creation, use, and modification of spreadsheets for a set of formulas designed to specifically meet the needs described.

Part One

Fundamentals of Scale and Corrosion Control

I - Introduction and History

Long ago, we learned that phosphates could add gentle persuasion to our existing arsenal of the big guns of alkalinity. Chelants were welcomed and provided resistance to deposition but no corrosion inhibition. Phosphonates were then considered for corrosion control but, at the beginning, sparingly employed -- later to become the ultimate weapon for scale inhibition. It was soon realized that several newer types of phosphonate had significantly greater corrosion reduction properties. Multi-functional copolymers, and highly versatile ones at that, then became available, and are now just about universally accepted. Slowly and reluctantly, we have come to accept that no single product can do it all!

As much as we have benefited from the many significant advances in recent years, we continue to respect the lore and legend of water treatment — the tried and true techniques which served us so well for so long. While we recall fondly our memories of these discoveries, we see that many experiences from "phosphate programs" are still applicable.

Advances have not been in new products alone but more importantly in the combining, feeding, and testing of traditional materials. Research by basic suppliers and reports in the publications of learned societies have contributed mightily to our knowledge. Resulting blends of phosphates, phosphonates, azoles, and dispersant polymers now allows us to provide:

An assortment of formulas for the protection of cooling water systems -- possibly supplemented with zinc at the corrosive end of the spectrum and high performance polymers at the scaling end.

II – Important Concepts

A. THRESHOLD TREATMENT

One of our most useful resources is the mechanism of "threshold treatment". It is a well established technique for inhibiting scale by introducing very small quantities of certain chemicals, i.e. amounts not even remotely approaching those required for sequestration.

The threshold approach allows us to provide effective, yet "affordable", results. Be warned, however, that: "If a little bit goes a long way, more may go too far!"

B. NATURAL INHIBITION

Fortunately, waters with a tendency to form scale possess a degree of "natural" corrosion inhibition. "... due, at least in part, to a protective film of calcium carbonate. Good corrosion rates ... are obtained at saturations as low as 50 times calcium carbonate, while excellent corrosion rates ... are obtained above 100 times saturation." (Cognetti and others)

"Natural factors" often need to be supplemented for the best action against scale and corrosion, and this can not always be done solely by calcium and alkalinity adjustment.

C. CALCIUM TOLERANCE

"Calcium tolerance" describes the ability of a chemical to resist complexation with calcium. Such rejection is highly desirable since whatever portions of the polymers and phosphonates are used up in sequestration are no longer available for dispersion.

Boffardi and Schweitzer supplied a list (later supplemented) of calcium tolerances. Calcium tolerance was shown at 9 for polyacrylate through 17 for HEDP, 42 for AMP, 75 for HPA, 100 for PBTC, 530 for PMA, and 1,640 for the SA/AA copolymer. It is likely that the calcium tolerance value for terpolymers is much greater, probably about 5,000.

They go on to say:

> "The poor calcium tolerance of the phosphonates can be suppressed by the addition of the AA/SA copolymer. ..... keeping the phosphonate totally active in solution."

AMPS based copolymers (AA/SA) and terpolymers have high calcium tolerances and their presence in a formula causes major improvement in the calcium tolerance of any phosphonates present, and also of homopolymers such as polyacrylate and polymaleate.

D. SYNERGISM

Dare we use the word "synergism" (related to the "new" math concept of 2+2 = 5)? Only if we can display results which confirm it! Synergism is roughly described as the ability of a combination of chemicals to perform better than we would anticipate from certain properties of the individual components.

It is not unusual to find that a product that sequesters stray metals also prevents the "poisoning" of other ingredients, nor is it surprising that enhancing "calcium tolerance" leads to better dispersion by polymers. Suppliers of combined prescription drugs usually stress the convenience of using one tablet rather than claiming a synergistic effect. Most often, their action is related to the financial concerns following the expiration of a patent.

E. DISPERSION

While phosphonates inhibit the formation of crystals, polymers distort them, prevent their further growth, and disperse them. The homopolymers are excellent control agents for calcium carbonate, silt, and iron under "normal" conditions, and their recommended dosage is less than that of copolymers or terpolymers. When raw material prices are factored in, this difference becomes even greater. There is, however, evidence that the dispersive advantage for homopolymers does not extend to calcium phosphate or to large quantities of iron.

Calcium phosphate, calcium phosphonate, and significant quantities of iron and silt are dispersed better by co/ter/quadpolymers than by homopolymers.

As another facet of their desirable properties, we expect polymers to carry inhibitors to heated surfaces to facilitate the formation of a protective film. As a part of this process, zinc and phosphate stabilization requires additional quantities of co- or ter-polymer.

Polymers, in their various configurations, perform many diverse functions including inhibition, stabilization, and the dispersion of organic and inorganic entities.

III - Deposit Formation and Control

A. FACTORS INFLUENCING SCALING

Calcium by itself does not define scaling potential. For this determination, we must turn to either the Calcite Saturation Index (CSI) or other less precise measures such as LSI, RSI, or PSI. If we have a complete raw water analysis, the CSI and associated cycled values can be determined from a WaterCycle® program. If not, any indications of scaling must be carefully noted, be they congestion, reduced heat transfer, or the clogging of filters.

B. SCALE CONTROL PHOSPHONATES

Usually scale control phosphonates are the preferred initial additive because of their superior metal and clay dispersing performance and excellent scale inhibiting properties. The most common versions of this class of products are AMP, HEDP, and PBTC.

The outstanding abilities of AMP and HEDP (alone and in combination) are well known as are their shortcomings, including the limited solubility of their salts, and poor resistance to oxidizers. This last problem is evidenced by reports of attack by chlorine on AMP and by bromine on HEDP. PBTC is the phosphonate most resistant to degradation.

1. Dosage of Scale Control Phosphonates

Much has been written about the phosphonates but, until recently, almost no specific techniques had been suggested for the establishment of treatment levels. Dan Vanderpool now describes the concepts necessary to evaluate these materials for scale inhibition, and in so doing, quantifies effective minimum dosages for them at varying levels of calcium, iron, and silt.

Specified dosages for phosphonates are listed by Vanderpool in mg/L of 100% material, with lower numbers indicating more economical performance. His findings are that:

a) Even for low hardness, phosphonate is necessary for iron and silt control.
b) " ... under typical cooling water conditions (say 5 cycles, 95° F, pH 8, 20-50 times saturation, half life of 24 hours or less), there is little difference in the threshold performance of HEDP, AMP, and PBTC.
c) If we encounter calcium carbonate alone (without iron or silt), HEDP > AMP > PBTC for CSI values between 50 and 125.

Too often, the impact of metals (either from the make-up or from corrosion by-products), is not adequately considered in the selection and dosage of phosphonates.

d) Under most circumstances, some iron is present and the use of AMP then becomes uneconomical. For $Fe(OH)_3$ up to and including 0.3 ppm, CSI 50, 104° F, the order remains HEDP > PBTC.

e) For iron content above the 0.3 ppm level (other factors the same), PBTC > HEDP. For iron [$Fe(OH)_3 \geq 1.0$], the relationship PBTC > HEDP continues.
f) As temperatures rise to above 122° F, HEDP recaptures the lead, HEDP > PBTC. We must be sure that the solubility of HEDP salts under stress is not exceeded.

These calculated dosages are minimums and some cushion must be allowed for degradation by oxidizers and for variations in temperature and alkalinity.

We calculated dosages for scale and particulate control for several water conditions, and in so doing, demonstrated that this process for phosphonate choice and dosage can be applied to a wide variety of water compositions and other circumstances.

IV - Phosphonates for Corrosion Prevention

As a result of mounting dissatisfaction with the performance of phosphates as corrosion inhibitors, the industry became receptive to more expensive products based on organic phosphorus compounds. This led to a different type of phosphonate, hydroxyl phosphonocarboxylic acid (HPA), whose 50% active commercial version is Belcor 575.

> "The unique feature of HPA in comparison to other phosphonates is that the corrosion inhibition is not activated by the formation of a calcium complex but rather by the corrosion process itself. Further, (this) also explains why its corrosion control properties are not compromised in soft water." (Sullivan and Hepburn)

> "The phosphonates 'extend' the solubility of $CaCO_3$ as well as forming (stable) calcium phosphonate salts. These two processes help to inhibit corrosion by permitting operation under highly buffered conditions." (Sullivan and Hepburn)

For many reasons, HPA has become the recognized standard for corrosion inhibitors, and an essential part of most modern formulations.

Part Two

Additional Contributions to Chemical Treatment

Having reviewed some basic theories and described the merits of phosphonates, we now investigate additional chemical resources and then move on to the benefits of combinations.

I - Other Corrosion Reducing Materials

A. PHOSPHATES

For many years, we depended upon inexpensive (and often inadequate) inorganic phosphates for the protection of water circulating systems. Included in this category were the orthophosphates as anionic inhibitors and the complex phosphates as cathodic ones.

Orthophosphates are supplied as phosphoric acid or its sodium or potassium salts. Complex phosphates are chosen because of their sequestering properties and their sustained solubility. Popular versions are sodium hexametaphosphate (SHMP) and tetrapotassium pyrophosphate (TKPP). TKPP has especially good stability and iron sequestering properties.

Addition of HPA to a formula often reduces the need for the high phosphate content formerly required. In addition, it allows the better use of alkaline phosphate technology, providing advanced polymers are adequately utilized for full dispersion.

B. TRIAZOLES

Triazoles protect non-ferrous metal or copper-based alloys and help disperse and/or sequester stray metals. By deactivating free copper, these products help to prevent galvanic corrosion and reduce particulate formation. Benzotriazole (BT, BZT) and tolyltriazole (TT, TTA) are the leading agents for these functions. The most convenient forms are sodium salt solutions, 50% active (actually 43%) TTA, and 40% active (actually closer to 32%) BZT.

C. ZINC AND MOLYBDATE

If calcium levels go below 20 ppm, we probably have a corrosive system and should introduce zinc. Zinc may also be used in the CSI 20-49 range but polyphosphates work equally well there. When introduced at levels of 1.0 to 3.0 mg/L into a phosphate-containing system, zinc facilitates excellent anodic/cathodic protection. Zinc phosphate underlies the traditional “metal” program with the best pH range for recirculating systems being between 6.5 and 8.0. Such products bring rapid initial protection from zinc, with phosphates subsequently supplying a more durable film.

Not only is zinc dispersed by sulfonic acid-containing copolymers, it is synergistic with them when they are used for calcium phosphate control, allowing a reduction of 3 mg/L in AA/SA and of 2 mg/L in AA/SA/SS from an original 5 mg/L dosages. (Amjad and others).

Molybdates can be helpful for corrosion control but require the presence of zinc, phosphate, or phosphonates for their greatest effectiveness. Molybdates can also serve as treatment level indicators and combine with other inhibitors to prevent pitting.

II - Polymers for Dispersion

Low molecular weight polymers, based on acrylates, acrylamides, etc., when used individually or in combination, are valuable dispersants in cooling water systems. Even when the water is soft, the need for general dispersion and for control of metals leads to the use of the advanced AMPS based terpolymers. It seems unlikely that high tolerance terpolymers, excellent stabilizers as they may be, would form irreversible bonds with calcium, zinc, or phosphate.

Might polymer redundancy from over dosage be costly but perhaps less troublesome and risky than excess phosphates or phosphonates?

In any event, we have chosen to keep polymer content proportional to the phosphonate and metal present plus orthophosphate that might evolve from degradation. Ratios of active terpolymer to PO_4 between 1:1 and 3:1 are often recommended, depending on the levels of particulate contaminants and the zinc stabilization requirements.

III – Combinations

The introduction of phosphonates was a significant contribution to water treatment. It soon became evident that their combination with phosphates produced better scale and corrosion protection than their separate contributions might have predicted.

Subsequent investigations confirmed that blending phosphonates with polymers also greatly improved treatment results. This approach is now accepted practice.

> " ... because there are two possible and distinct mechanisms (stabilization and dispersion), it is reasonable to suggest that the reason combination products are so successful is that they can take advantage of both of these mechanisms". (Thomas and Mullins)

Dividends from this discovery were, at times, diminished by poor calcium phosphate and calcium phosphonate solubility, a shortcoming compensated for later by tight dosage controls and highly effective AMPS copolymers and terpolymers. These copolymers disperse zinc, calcium phosphate, and calcium phosphonate, and thus allow the other components of a formula to fully execute their designated functions.

HPA's performance as a corrosion inhibitor, excellent on its own, is improved when used as part of an anodic/cathodic combination with phosphates, or with the strongly cathodic zinc.

Success in combining pairs of materials was a precursor to even better results. Since good things often come in threes, it was not at all difficult to anticipate the next development!

A patent granted to Gill in 1998 described an approach to calcium carbonate and calcium phosphate control in highly scaling waters. It recommended a mixture of PAPEMP (a scale preventing phosphonate)/Aquatreat AR-540 (a dispersant ter/quad polymer)/Belcor 575 (a corrosion inhibiting phosphonate), in ratios such as 1/2/1. It reported a sizable reduction in phosphonate demand for these systems.

Most cooling tower applications benefit from the presence of differing structures such as those described above, including two, three, and four part combinations.

The movement to ever more complex terpolymers has been rewarding. There is evidence that most multi-functional formulas are versatile and forgiving, with various ingredients able to cover for one another. ***But the piper must be paid*** *(rather than the plumber?)****.*** As we continue to design more complex remedies, we also increase the number of formulas in our line and the expense of stocking them.

Combinations are not always beneficial. We must not consider "synergism" to be a given and must also realize that some combinations are less than additive. We should carefully ponder the implications of such frightening words and concepts as <u>incompatible</u>, <u>antagonistic</u>, and <u>overkill</u>.

We strongly recommend using multiple function products (in restrained and informed ways), whether introduced as a single ingredient or as more than one distinct material!

Part Three

Controlling Deposits and Corrosion

We earlier promoted combinations as the preferred treatment mode, and now seek to choose among them and establish their proportions by relating their performance to the tasks we set before them. Important issues of concentration are then introduced to assure that each ingredient is present in the system at proper levels.

I. Specific Challenges

It is desirable that we examine the metals and hardness complexes which cause the most trouble and suggest ways to neutralize, complex, or remove them.

A. CALCIUM CARBONATE

Control of calcium carbonate is best provided by the phosphonates and homopolymers supplemented with copolymers as versatile reserves. Boffardi and Schweitzer suggest that:

> "One would not use the copolymer (AA/SA) exclusively for calcium carbonate control since the other building blocks are more efficacious."

B. CALCIUM PHOSPHONATE

It was found that a terpolymer inhibited the precipitation of calcium HEDP much more effectively than did a copolymer. This superiority extends to other copolymers and phosphonates and persists as temperature, pH and hardness increase. The homopolymers have no proven appreciable influence on phosphonate stability.

C. CALCIUM PHOSPHATE

AMPS copolymers were found to be excellent dispersants for calcium phosphate when no iron was present. We might then ask under what conditions the higher price for the terpolymers is justified. It took 10 mg/L of the copolymer AA/SA-25 to achieve 90% inhibition of phosphate precipitation when no contaminants were present, while only 7.5 mg/L of the terpolymer AA/SA/SS was required to reach the same level of inhibition. At these levels, the terpolymer resulted in almost no increase in total cost (Amjad and others).

Where iron content is low, the copolymers perform just about as well as the terpolymers for calcium phosphate. One report found terpolymers to be almost twice as effective as the copolymers in the presence of 1.0 mg/L of iron. These tests showed more significant change when iron was increased to 2.5 mg/L, the terpolymer then becoming three times as effective. Both copolymers were superior to the homopolymer (polyacrylate).

Another area of comparison might be between different versions of the AA/AMPS copolymer. It is thought by some that we can improve results by using the AA/AMPS-40 product rather than the less expensive 25% version. We have found that the two products (based on actives content) are, in fact, about equivalent in cost at current prices.

D. SOLUBLE IRON

Iron, in all its forms (and even at very low concentrations) can seriously interfere with the dispersive capabilities of polymers. From one source (Sherwood and Smith) we learn that:

> "Under the test conditions, calcium interferes with polyacrylic acid's performance as an iron oxide dispersant. ... AA/SA remains an effective dispersant even under high calcium ion concentration because it is relatively insensitive to the calcium ion".

E. PARTICULATE IRON

"Polymers are the most effective class of chemicals for dispersing particulate iron oxide. Polyphosphates and phosphonates exhibit poor dispersancy power". ..... In general, "terpolymer > copolymer > homopolymer". (Amjad)

II - Guidelines for Chemical Choice

A. We bring together the concepts previously considered:

1. A phosphonate such as HEDP or PBTC is essential for calcium carbonate control and to disperse iron and silt.
2. Phosphates are well established components for corrosion inhibition but have serious solubility limits at high pH levels.
3. Zinc, having strong cathodic functionality and synergism with other inhibitors, is a welcome addition in highly corrosive settings.
4. HPA, because of its excellent solubility, stability, and corrosion inhibition, should be present across the treating spectrum.
5. Terpolymers are highly effective for dispersing phosphate and phosphonate complexes as well as larger concentrations of iron, zinc, and silt.
6. Azoles protect non-ferrous metals and also prevent metallic contamination.
7. All formulas should contain PBTC, HPA, azole, and terpolymer because of their individual effectiveness, their versatility, and their synergism.

III. Concentration, Cycling and Feeding

A. CONCENTRATION

Initially we make the critical decision of how much of each chemical we want in a system. The rest is routine calculation to arrive at proper feed rates. Since concentrations are indicated by different people in different ways we must, at times, also reconcile:

1. Production formulas are stated as percent by weight of commercial chemical, e.g., percentage of 60% HEDP solution to be incorporated into the formula.

2. Specifications for chemical content in a system are usually stated as mg/L, based on 100% active materials. These values are obtained by adjusting commercial products for their degree of activity. For example, 1.0% of 60% HEDP solution results in 0.6% of active HEDP. If specified as PO_4, 1.0% of 60% HEDP gives us 0.56% of PO_4. The concentration in a system is related to the number of cycles we hope to achieve. For example, 0.6% of active HEDP cycled 5 times results in 3.0% active HEDP or 2.8% PO_4.

B. CYCLING

Clearly, estimates of cycling are necessary to establish correspondence between the targeted system concentration of a chemical and the amount being fed with the make-up. In general, cycles of concentration will run between 2 and 8. If a formula is based on 5 cycles, good results can still be obtained from 4 cycles, particularly if the dosage rate is increased by 25% (5/4 = 1.25). The cost savings obtained by increased cycling are recognized and sought, especially at the lower levels (e.g. from 2 to 5).

High cycling is not always desirable! Experience has shown that for systems operating above about eight cycles, treatment must often be increased to unacceptably high amounts.

C. FEEDING

Instructions for feeding water treatment chemicals are usually given as 100 mg/L of a formula made up from commercial materials. Since analytical balances for weighing milligrams and a generous stock of one liter flasks are not available at most powerhouse or production locations, the addition of one pint of treatment for each 1000 gallons of water added has been found to be a most convenient approach.

If we feed one pint of a product (9.1 #/gal and designed to be fed at 100 mg/L for every 2000 gallons of make up water), we obtain 68.25 ppm of treatment. Correspondence to the original guidelines (mg/L) can be obtained by feeding one pint for each 1365 gallons.

If a formula is found to be unacceptable in any respect, further action must be taken. When the basic formula is well balanced, and a change is intended to increase the amount of treatment in the system, a larger dosage should suffice. If operating conditions will not tolerate the targeted cycles, this may indicate that hardness is higher than anticipated or that there are other limiting factors. This may call for switching to a formula better suited to the water being treated.

Part Four

Formula Development

*This section will almost complete our program to develop cooling water formulas. We list below the characteristics for five waters and suggest approaches to their treatment. Unfortunately, listing the actual formulas would occupy too much space in this abbreviated version and is delayed until the final articles are published in the **Analyst**.*

I - Scaling Categories

A. Very Soft Water, No Scaling, High Corrosion, CSI < 2.0, 8 Cycles

In this category, special attention is given to protection against corrosion. A scale preventive phosphonate is not needed for calcium carbonate control but is included to handle silt and iron. PBTC is especially appropriate because of its ability to control iron at low dosages. HPA should be present here, as in all formulas, as a very effective cathodic inhibitor.

In corrosive water (low calcium, some chlorides and sulfates), a phosphate program is generally required, preferably one including cathodic inhibition. Polyphosphate will enhance whatever cathodic protection is already supplied by calcium and/or zinc.

B. Soft Water, Light Scaling, Some Corrosion, CSI 2-19, 6 Cycles

Progressing to a less corrosive water, we most likely will adapt to a lower phosphate content utilizing calcium and other sources for cathodic inhibition. For this soft water and for the very soft water in “A” above, some cushion beyond the calculated value should be provided.

For waters with less than 20 times calcite saturation, Vanderpool indicated that calcium carbonate itself was not the major challenge, but rather the iron and silt that would precipitate onto calcium carbonate and other surfaces. If an aqueous system has a CSI < 20, it is usually desirable to include zinc metal. The usual approach is 0.5 to 1.5 mg/L of cathodic zinc and an inorganic phosphate at or near the ratio for PO_4/Zn of between 1/1 and 3/1.

C. Slightly Hard Water, Moderate Scaling, CSI 20-84, 5 Cycles

Low phosphate programs also work well in moderately soft water, providing that there is adequate alkalinity present. Corrosion inhibitor content can usually be reduced as hardness goes up. In the moderate hardness range of CSI = 50 and above, the cushion can be dispensed with and dosage levels kept close to the amounts calculated by Vanderpool.

D. Moderately Hard Water, Heavy Scaling, CSI 85-149, 4 Cycles

Corrosion inhibitors can be reduced and scale inhibitors increased as hardness goes up. For hard waters (CSI > 100), the solubility limitations on HEDP must be carefully considered. Inorganic phosphates can not be used above these CSI values. PBTC has both the best overall solubility and the greatest stability of the scale control phosphonates

E. Hard Water, Very Heavy Scaling, CSI 150-199, 3 Cycles

One definition of “stress” in a water is the existence of high levels of hardness, alkalinity, or solids (those of greatest concern being calcium, iron, phosphate or silica). These adverse conditions result when there is poor quality make-up water, corrosion products are measurably high, or greater cycles of concentration are being sought.

PBTC exhibits better inhibitor activity than AMP and HEDP, especially in moderately stressed conditions (i.e 180x calcite saturation) (Amjad and others). For CSI over 150, even PBTC must be used with caution.

Attempts to deal with scale formation under stressed circumstances have moved in the direction of using more sophisticated phosphonates or even to abandoning phosphonate technology completely in favor of polymers. Versaflex ONE (VF-1) can be a good dispersant for stressed waters, especially when combined with PBTC and a terpolymer.

II - Explanation of Process

Production formulas generally list the weight percentages for the commercial versions of each ingredient. If the finished product is added to the system at the rate of 100 milligrams per liter, it thereby introduces the same parts per million of a particular chemical that the percentage constitutes in the formula. If we are to properly determine system concentrations, further adjustments must be made to convert to a fully active percentage.

Formulas are not so divinely mandated as to prevent us from specifying a range of chemical levels rather than an exact figure (even if carried out to four decimal places). We therefore feel comfortable and slightly virtuous in selecting whole number values for production batches. As a result, we end up with an even number of pounds for each material in a 55 gallon batch.

III - Spreadsheets

In the extended version of Part Four (due in late 2008), we will suggest seven complete formulas for scale and corrosion control. This will include spreadsheets to facilitate changes in the formulas without sacrificing any of the basic relationships. The spreadsheet will then automatically display values for:

A. Pounds of each raw material present in a 55 gallon batch
B. Percentage of each commercial product in a formula,
C. Parts per million of 100% active (for each chemical) material in the system,
D. Parts per million of phosphate (as PO_4) in the system.