



WaterCycle User Manual

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WHY USE WaterCycle®?

WaterCycle allows a water treatment chemist to evaluate the scale potential for common scalants over the range of water chemistry, temperature, and pH anticipated in an operational cooling system. Systems have been scaled with silica because the water treater in charge evaluated scale potential at the highest temperature in the system: the temperature most conducive to fouling for most compounds. Overlooking the solubility profile of silica versus temperature resulted in a scaled condenser inlet area, while the outlet area remained clean. Evaluating the scale potential for common scalants at both the lowest and highest temperatures anticipated, (and at the lowest and highest pH values expected), could have foretold the impending scale and kept the condenser clean

WaterCycle was developed to allow a water treater to readily evaluate the scale potential for common scalants over the broadest of operating ranges without the necessity for tedious manual calculations for the Langelier saturation index, Ryznar stability index, Puckorius equilibrium index, and tricalcium phosphate saturation level. Even when all of these common indices are available conflicting results can cloud interpretation of what they are foretelling. WaterCycle provides additional information in the form of indicators of scale and corrosion potential which are useful, and would be popular, if they weren't so difficult to calculate with a pencil, paper, tables, and a calculator. WaterCycle allows a water treater to review popular and some less known indicators relatively painlessly to develop a more complete picture of problems, and potential problems confronting a cooling system, and its water treater.

WaterCycle calculates theses indicators over the operating parameter ranges you specify, and presents them in graphical as well as tabular form. The indicators are applicable to both once through cooling waters and open recirculating cooling tower systems -*WHEN TEMPERED BY YOUR EXPERIENCE AND KNOWLEDGE OF WATER TREATMENT*. The program can be applied to long, as well as short, residence time systems.

WaterCycle can assist the cooling tower operator or water treater in establishing control limits based on concentration ratio (cycles of concentration), pH, and temperature profiles. The program can help estimate sulfuric or Hydrochloric acid requirements to maintain a prescribed pH control point.

In summary you should use WaterCycle:

- 1. To develop an overall profile of scale potential for common cooling system scalants over the entire range of critical operating parameters anticipated.
- 2. To evaluate the scale potential of an open recirculating cooling system versus concentration ratio as an aid in establishing control limits.
- 3. To evaluate the benefits of pH control with respect to scale potential and to estimate acid requirements.
- 4. To quickly review these indicators as water quality changes, or environmental constraints force operation with reduced water quality and increased scale potential.
- 5. To learn more about the interaction of water chemistry and operating conditions (pH, temperature) by using the program as a system simulator.
- 6. To save time. WaterCycle can calculate and save the indices you currently calculate by hand, and store the water analyses and calculated indices. In many cases, WaterCycle allows you to prepare presentation quality graphical profiles in about the same time it would take to manually calculate the Langelier and Ryznar indices. WaterCycle provides a complete profile for the manpower cost of calculating a few indices using a nomograph or cooling water slip-stick.
- 7. Additionally, the Rx series develops models of inhibitor performance and optimizes treatment program applications.

WHAT INDICATORS DOES WaterCycle® CALCULATE?

WaterCycle calculates indicators of scale potential for calcium carbonate, tricalcium phosphate, hydroxylapatite, silica, calcium sulfate, calcium fluoride, magnesium hydroxide, magnesium silicate, iron hydroxide, iron carbonate, and iron phosphate. It also calculates a corrosivity index based upon the work of Drs. Larson and Skold on the corrosivity of Great Lakes waters towards mild steel.

- Indices calculated over the range of operating conditions specified include:
- the most common (*Langelier* and *Ryznar*);
- an evolving and currently being promoted index (*Puckorius*);
- those that have been used by the major water treatment companies but have generally been unavailable to most water treaters (*Saturation levels* based upon an ion association model);
- and some that the program author has found useful and realistic (*Momentary excess* and the *Larson-Skold* index).

A detailed review of these indices is included in a later section of this manual, and in references in the bibliography.

WHAT WaterCycle® WON'T DO!

WaterCycle will not recommend a treatment program. It will not turn the computer screen red and scream - "Your scale inhibitor can not handle this high a calcite saturation level, at this temperature, and this residence time." You will have to provide the interpretation based upon your, and your water treatment company's, knowledge of inhibitor effective limits.

WaterCycle R_x programs will provide guidelines for treatment levels, and where inhibitor limitations are known, warn you of projected inhibitor failure through color coding. Dosages turn RED when out of range.

The Langelier Saturation Index

The Langelier Saturation index (LSI) is a purely equilibrium model derived from the theoretical concept of saturation. A water is said to be saturated with calcium carbonate when it will neither dissolve, or precipitate calcium carbonate "scale". This equilibrium condition is based upon an undisturbed water, at constant temperature, which is allowed to remain undisturbed for an infinite period of time. A water is said to be under-saturated if it will dissolve an existing calcium carbonate substrate if left at rest for the same infinity. A supersaturated water will precipitate calcium and carbonate from a water if allowed to rest. The Langelier saturation index provides an indicator of a water's degree of saturation with respect to calcium carbonate.

Saturation is referenced to the solubility product for a compound. By definition the ion activity product of reactants (e.g. Ca and CO_3) is equal to the solubility product (K_{sp}) when the water is in equilibrium.

$$[Ca]\alpha Ca[CO_3]\alpha CO_3 = Ksp$$

A saturation level is defined as the ratio of the ion activity product to the solubility product.

Saturation level =
$$\underline{\alpha Ca[Ca]\alpha CO_3[CO_3]}$$

 K_{sp}

If a water is under-saturated with respect to calcium carbonate, the saturation level will be less than 1.0. When a water is at equilibrium, the saturation level will be 1.0 by definition (although our estimation of the ion activity product or solubility product might be in error). A water which is supersaturated with calcium carbonate will have a saturation level greater than 1.0.

Saturation level is the driving force for crystal formation, and crystal growth. As the saturation level increases beyond 1.0, the driving force for calcium carbonate crystal formation or crystal growth increases.

It can be shown that the Langelier saturation index approximates the base 10 logarithm of calcite saturation level. The Langelier saturation level approaches the concept of saturation using pH as a master variable(1). The Langelier saturation index can be interpreted as the pH change required to bring a water to equilibrium. A water with a Langelier saturation index of 1.0 is one pH unit above saturation. Reducing the pH by 1 unit will bring the water into equilibrium. This occurs because the portion of total alkalinity present as CO₃ (the bad actor) decreases as the pH decreases. A pH decrease of 1 unit will decrease the CO₃ concentration of the water about ten fold. This impacts saturation level directly by also decreasing the ion activity product tenfold. So a 1 pH unit decrease will decrease the Langelier saturation index by 1 unit. A 1 pH unit decrease will also decrease the saturation level (IAP/K_{sp}) ten fold.

A negative Langelier saturation index indicates that a water is under-saturated with respect to calcium carbonate (calcite). If the LSI is -1.0, raising the pH of the water 1 unit will increase the calcium carbonate (calcite) saturation level to equilibrium. The 1 pH unit increase does this by increasing the CO₃ portion of the carbonate alkalinity present ten fold. The calcite saturation level increases accordingly (ten times).

The Langelier saturation index is probably the most widely used indicator of cooling water scale potential. It is purely an equilibrium index and deals only with the driving force for calcium carbonate scale formation and growth. It provides no indication of how much scale (CaCO₃) will precipitate to bring a water to equilibrium. It simply indicates the driving force for scale formation and growth in terms of pH as a master variable.

The Langelier saturation index is defined as:

Langelier saturation index = pH - pHs

- pH is the measured water pH
- pHs is the pH where the water will be saturated (at equilibrium) with respect to CaCO₃.

In the cooling water pH range of 6.5 to 9.5, the pH_s calculation simplifies to:

$$pH_s = (pK_2 - pK_s) + pCa + pAlk$$

- pK_2 is the negative log_{10} of the second dissociation
- constant for carbonic acid;
- pK_s is the negative log_{10} of the solubility product for calcite;
- pCa is the negative log₁₀ of calcium measured in the water;
- pAlk is the negative log 10 of the total alkalinity measured for the water being evaluated.

WaterCycle uses the full iterative method for estimating the pH of saturation for calcite for calculating the Langelier saturation index.

The LSI is analogous to voltage for those who are electrically minded. A voltage is the driving force for moving electrons across a resistance. As voltage potential difference increases, there is a higher driving force for current (electron) flow. Voltage, however, indicates nothing of the current being moved. The LSI, and other saturation level based indices, describe the driving force for scale formation and growth, but say little of the amount of scale which will form (or be dissolved) in order to bring a water to equilibrium. Although they are very useful, a second factor must be considered in interpreting saturation level based indices. Saturation level based indices indicate the potential for scale formation if a water is unperturbed for an infinite period of time. Most cooling water systems have a substantially shorter holding time index.

A final point on the Langelier index deals with the concept of "corrosivity." The LSI was not intended as an indicator of corrosivity towards mild steel or other metals of construction. The LSI describes only the corrosivity of a water towards an existing calcium carbonate scale, or other calcium carbonate bearing structure. The LSI does describe the tendency of a water to dissolve (corrode) calcite scale. It has also been used to control the "corrosion" of asbestosconcrete-board (ACB) fill which uses calcium carbonate as part of the binder. Water is adjusted to be non-corrosive to ACB fill by increasing the pH to a saturated, "non-corrosive" LSI. But the interpretation of corrosivity towards metals is not explicit in the LSI.

It has been postulated that a supersaturated water will form an eggshell like film of calcium carbonate scale which will act as an inhibitor film for corrosion of mild steel. This can occur in highly buffered waters. The LSI or other saturation based indices do not guarantee this inhibitory behavior. Calcium carbonate film formation is typically observed in highly buffered waters.

Researchers (Stumm(3), Lowenthal, and Marais(4)) have shown that waters supersaturated with calcium carbonate often develop tubercular deposit which do not inhibit corrosion on mild steel. This behavior is typically associated with waters of low buffer capacity. Puckorius(5) also warned against using saturation level derived indices as the basis for foretelling corrosion problems in cooling systems.

The Langelier saturation index is elegantly derived in the original published form(2). It is also thoroughly explained by Lowenthal and Marais(4).

RYZNAR STABILITY INDEX

The Ryznar stability index attempts to correlate an empirical data base of scale thickness observed in municipal water systems to the water chemistry. Like the Langelier saturation index, the Ryznar stability index has its basis in the concept of saturation level. Ryznar attempted to quantify the relationship between calcium carbonate saturation state and scale formation. The Ryznar index takes the form:

Ryznar stability index = $2(pH_s)$ - pH

The empirical correlation of the Ryznar stability index can be summarized as follows:

RSI << 6 scale tendency increases as the index decreases;

RSI >> 7 calcium carbonate formation will probably not lead to a protective corrosion inhibitor film;

RSI >> 8 mild steel corrosion becomes an increasing problem.

WaterCycle uses the pH_s calculated by the rigorous iterative method for RSI estimation.

PUCKORIUS SCALING INDEX

The Puckorius (or Practical) scaling index attempts to further quantify the relationship between saturation state and scale formation by incorporating an estimate of buffering capacity of the water into the index. The previously discussed saturation derived indices only account for the driving force for calcium carbonate scale formation. They do not account for two other critical

parameters: the buffering capacity of the water, and the maximum quantity of precipitate that can form in bringing a water to equilibrium.

A water high in calcium, but low in alkalinity and buffering capacity can have a high calcite saturation level. The high calcium level increases the ion activity product. A plot of ion activity product versus precipitate for the water would show a rapid decrease in pH as calcium precipitated due to the low buffering capacity. Even minuscule decreases in carbonate concentration in the water would drastically decrease the ion activity product of the water due to the small quantity present prior to the initiation of precipitation. The water might have a high tendency to form scale due to the driving force, but scale formed might be of such a small quantity as to be unobservable. The water has the driving force but no capacity and no ability to maintain pH as precipitate forms.

The Puckorius scaling index is calculated in a manner similar to the Ryznar stability index. Puckorius uses an equilibrium pH rather than the actual system pH to account for the buffering effects:

Puckorius scaling index =
$$2 (pH_{eq}) - pH_{s}$$

WaterCycle calculates the pH_s for this index using the rigorous iterative method. Puckorius' formula for $pH_{eq}(5)$ is used

$$pH_{eq} = 1.465 \text{ x } log_{10}(\text{"M" Alkalinity}) + 4.54$$

The Puckorius scaling index provides another tool for evaluating the calcium carbonate scale potential for a water and is included in the WaterCycle indices of calcium carbonate scale potential.

LARSON-SKOLD INDEX

The Larson-Skold index describes the corrosivity of water towards mild steel. The index is based upon evaluation of in-situ corrosion of mild steel transport lines in systems transporting Great Lakes waters. The index is the ratio of equivalents per million (epm) of sulfate (SO_4) and chloride (CI) to the equivalents per million of alkalinity in the form bicarbonate plus carbonate ($HCO_3 + CO_3$).

Larson-Skold index =
$$(epm Cl + epm SO_4)$$

(epm HCO₃ + epm CO₃)

As outlined in their paper (6), the index correlated closely to observed corrosion rates and to the type of attack in the Great Lakes water study.

It should be noted that the waters studied in the development of the relationship were not alkalinity or buffering capacity deficient. They were capable of forming an inhibitory calcium carbonate film, if no interferences were present.

The results of the study demonstrate that chlorides and sulfates increase the aggressiveness of a cooling water with adequate buffering capacity and alkalinity to otherwise not be overly aggressive. Perhaps the presence of chloride and sulfate interferes with the film formation which otherwise would be expected.

It must be noted that the Larson-Skold relationship is based upon Great Lakes waters. Extrapolation to other waters, such as those of low alkalinity or extreme alkalinity, goes beyond the range of the original data. Such extrapolations should be closely scrutinized or weighted lightly. Most water treaters will agree, however, that the aggressiveness of a water increases with increasing chloride and/or sulfate levels, and that corrosivity also increases with decreasing alkalinity.

The index has proven a useful tool in predicting the aggressiveness of once through cooling waters. It is included in WaterCycle due to the preponderance of waters of composition similar to the Great Lakes waters, and due to its potential usefulness as in indicator of aggressiveness in reviewing the applicability of corrosion inhibition treatment programs which rely heavily on the natural alkalinity and film forming capabilities of a cooling water.

The index might be interpreted by the following guidelines:

Larson-Skold	Indication
<< 0.2	chlorides and sulfate probably will not interfere with natural film formation.
>> 0.2 but << 0.6	chlorides and sulfates may interfere with natural film formation. Higher than desired corrosion rates might be anticipated.
>> 0.6	the tendency towards high corrosion rates of a local type should be expected as the index increases.

SATURATION LEVEL

Saturation level has been previously discussed as the basis for many of the common indices used by water treaters. The saturation level is defined as the ratio of the ion activity product of the reactants to the solubility product. Saturation level can be defined as follows for common cooling system scalants based upon their respective solubility products:

For CaCO₃ (calcite and aragonite)

$$Ca + CO_3 \Leftrightarrow CaCO_3$$

Saturation Level = $[Ca] \alpha Ca [CO_3] \alpha CO_3$

Ksp

where aCa is the activity coefficient for calcium aCO₃ is the activity coefficient for carbonate [Ca] is the molar concentration of calcium [CO₃] is the molar carbonate concentration

This relationship can be simplified if we incorporate the activity coefficients into the solubility product so that our examples can be expressed in a more readily viewed format. The conditional solubility product incorporates the activity coefficients into the solubility product:

$$Ksp_c CaCO_3 = Ksp x (1/\alpha Ca) x (1/\alpha CO_3)$$

This notation (Ksp_c) will be used for the remainder of the examples.

For Calcium sulfate (anhydrite):

$$Ca + SO_4 \Leftrightarrow CaSO_4$$

$$Saturation \ level_{(CaSO4)} = \underbrace{ \ [Ca][SO_4] }_{Ksp_{c \ (CaSO4)}}$$

For Silica

$$SiO_2 + 2 H_2O \Leftrightarrow H_4SiO_4^{\circ}$$

Saturation level (SiO₂) =
$$\underline{H_4SiO_4}$$

([H₂O][H₂O] Ksp_c)

Note that the activity of water is included in the calculation.

For tricalcium phosphate, a higher order of reaction is encountered:

$$3 [Ca] + 2 [PO_4] \Leftrightarrow Ca_3(PO_4)_2$$

Saturation level =
$$\frac{[Ca]^3[PO_4]^2}{Ksp_c}$$

A higher order of reaction is also encountered for calcium fluoride (Fluorite)

$$[Ca] + 2 [F] \Leftrightarrow CaF_2$$

Saturation level =
$$\frac{[Ca][F]^2}{Ksp_c}$$

and magnesium hydroxide (Brucite):

[Mg] + 2 [OH]
$$\Leftrightarrow$$
 Mg(OH)₂
Saturation level = $\frac{[Mg][OH]^2}{Ksp_c}$

The method used for estimating activity coefficients is a major target of criticism for most indices. WaterCycle uses the mean salt activities for estimating ion activity coefficients based upon temperature and ionic strength. The method is well covered in reference Truesdell and Jones(7). The use of ion pairing expands the usefulness of WaterCycle calculated saturation levels.

The simple indices previously described are based upon saturation levels calculated using the total ions present. For example, calcium carbonate indices, such as the Langelier saturation index, assume that all calcium is present as free calcium ions, and that all carbonate is present as the unbound ion. In actual waters, the reactive species are present in many forms. Not all of the ion measured analytically is available to react. For example, calcium can be bound with hydroxide, sulfate, carbonate, and bicarbonate and unavailable for other reactions. This binding, or reduced availability of the reactants, decreases the effective ion activity product for a saturation level calculation. WaterCycle uses an ion association model to estimate the available (or free) ions present in the water. The ion association method is well described in the literature. WaterCycle uses the free ion concentrations estimated by the ion association method in saturation level calculations. The resultant saturation levels calculated are significantly lower than those based upon total analytical values.

The ion association model saturation levels have been in use by the major water treatment companies since the early 70's. The indices tend to give a more accurate indication of the driving force for scale formation. They have not been in general use, however, due to the difficulty of calculating them. The iterative approach required for the calculations mandates the use of a computer. One of the purposes of WaterCycle is to make the ion association method for saturation levels available to all Water Treaters.

Saturation levels, no matter how refined, are still an equilibrium based index. They provide a measure of the driving force for a scalant to form, but do not incorporate the capacity of the water for continued scaling. A water can have a high saturation level with no visible scale formation. The driving force might be present but there is insufficient mass for gross precipitation.

Saturation levels should be viewed as another tool for developing an overall picture of a water's scale potential. They can point out what scales won't form under the conditions evaluated, but they can not predict that deposits of an economically significant quantity will form. The next index covered incorporated the properties of quantity as well as driving force to round out the WaterCycle indicators of scale potential.

MOMENTARY EXCESS (PRECIPITATION TO EQUILIBRIUM)

This index is adapted from a little used calculation of Momentary Excess. This index describes the quantity of scalant which would have to precipitate instantaneously to bring a water to equilibrium. In the case of calcium carbonate:

$$[Ca][CO_3] = Ksp_c$$
 at equilibrium.

If a water is supersaturated:

$$[Ca][CO_3] \gg Ksp_c$$

Precipitation to equilibrium assumes that one (1) mole of calcium will precipitate for every mole of carbonate that precipitates. On this basis, we can estimate a quantity X, the precipitation required to restore a water to equilibrium, as follows:

$$[Ca - X][CO_3 - X] = Ksp_c$$

X is a quantitative indicator of precipitation reserve for a water. X will be a small value when either calcium is high and carbonate low, or when carbonate is high and calcium low. It will increase to a maximum when equal parts of calcium and carbonate are present. As a result, this index (Precipitation to Equilibrium) will provide vastly different values for waters with the same saturation level. Although the original Momentary Excess index was applied only to calcium carbonate scale, WaterCycle extends the index to other scale forming species.

In the case of sulfate, momentary excess is calculated by solving for "X" in the relationship:

$$[Ca - X][SO_4 - X] = Ksp_c$$

The solution becomes more complex for tricalcium phosphate:

$$[Ca - 3X]^3 [PO_4 - 2X]^2 = Ksp_c$$

The index provides a quantitative indicator of scale potential and has been used to correlate scale formation in a kinetic model(12). The index does not account for two critical factors. The pH will change in some cases as precipitate forms by the precipitation of alkalinity contributors such as carbonate or phosphate. Secondly, the index does not account for changes in driving force as the reactant levels decrease due to precipitation.

WaterCycle includes Momentary Excess (precipitation to equilibrium) as a final indicator of scale potential for the scalants covered by the computer program. WaterCycle expresses the precipitation to equilibrium in parts per million.

Momentary Excess does not represent a quantitative assessment of the amount of a fouling which will precipitate. It is an indicator of the capacity of a water to scale, and can be compared

to the buffer capacity of a water. The calculation method is covered in more detail in the literature (12).

INTERPRETING WaterCycle INDICES

Scale Potential As Indicated By Saturation Level

All but one of the indices discussed in this section describe the tendency of a water to form, or dissolve, a particular scale. These indices are derived from the concept of saturation. For example, saturation level for any of the scalants discussed is described as the ratio of a compounds observed ion activity product (IAP) to the ion activity product expected if the water were at equilibrium (Ksp). In WaterCycle graphically profiles, the degree of supersaturation is labeled as this ratio (IAP/Ksp). This ratio has many names and is referred to as Saturation Level, Degree of supersaturation, and x Saturation. This ratio will be referred to as Saturation Level or Degree of supersaturation throughout the manual.

The following general guidelines can be applied to interpreting the degree of supersaturation:

- 1) If the saturation level is less than 1.0, a water is under saturated with respect to the scalant under study. The water will tend to dissolve, rather than form, scale of the type for which the index was calculated. As the saturation level decreases and approaches 0.0, the probability of forming this scale in a finite period of time also approaches 0.
- 2) A water in contact with a solid form of the scale will tend to dissolve or precipitate the compound until an IAP/Ksp ratio of 1.0 is achieved. This will occur if the water is left undisturbed for an infinite period of time under the same conditions. A water with a saturation level of 1.0 is at equilibrium with the solid phase. It will not tend to dissolve, or precipitate the scale.
- 3) As the saturation level (IAP/Ksp) increases above 1.0, the tendency to precipitate the compound increases. Most waters can carry a moderate level of supersaturation before precipitation occurs in a finite period of time such as the seconds to minutes a water is present in a once through cooling system, or the hours to days a water is present in a cooling tower system. Most cooling systems can carry a small degree of supersaturation. The degree of supersaturation acceptable for a system varies with parameters such as residence time, the order of the scale reaction, and the amount of solid phase (scale)present in the system. To be on the safe side, it is recommended that an appropriate inhibitor be fed to a cooling system if the saturation level is above 1.0.

The acceptable degree of saturation for a given system should be based upon your experience. The author has found the following guidelines useful.

Calcium carbonate: In once through cooling systems, treatment is necessary when the saturation level at the highest temperature and pH in the system is above 1.2 to 1.5.

A slightly higher degree of supersaturation can be carried in some cooling towers.

Calcium sulfate: Treatment is recommended when the saturation level for gypsum exceeds 1.0. In higher temperature systems (>> 130 °F), treatment is required normally when anhydrite saturation level exceeds 1.0.

Silica: Most cooling waters can carry a silica saturation level of 1.1 to 1.2. WaterCycle silica saturation levels are calculated using the solubility product for amorphous silica. A saturation level in this range equates to a cooling water silica level of around 150 ppm (as SiO₂) at an acid to neutral pH, and 180 ppm or above in waters with a pH above 8.0. This is comparable to the old guidelines for "acid chromate programs" (150 ppm as SiO₂) used by most water treatment companies when such treatments were acceptable, and for the guidelines for the new "All Organic" programs (180 to 200 ppm) operating in the pH range of 8.0 to 9.0+.

It is of particular importance to evaluate silica saturation level in systems with borderline solubility as cooling water temperature or pH decrease seasonally.

Magnesium silicate: Mag-silicate compounds do not necessarily form due to a stoichiometric reaction. The author believes that magnesium silicate forms through the adsorption of silica onto precipitated magnesium hydroxide. Brucite saturation level was added to WaterCycle calculated indices as a measure of the potential for magnesium silicate to form in a cooling system based upon this philosophy. If a water is supersaturated with magnesium hydroxide (Brucite) and even low levels of reactive silica are present in the cooling water, magnesium silicate formation is possible. Magnesium silicate formation is probable when the water is supersaturated with Brucite and silica levels are 40 ppm (as SiO₂) or above.

A recent NACE paper reported the formation of stoichiometric magnesium silicate scales in cooling systems. A stoichiometric form was added to the scales evaluated by WaterCycle as a result of this paper. Precipitation might be expected when the magnesium silicate saturation level exceeds 1.2.

Calcium fluoride: Treatment, or operating parameter changes, are recommended when the saturation level for Fluorite exceeds 1.0.

Tricalcium phosphate: Tricalcium phosphate saturation level calculations are a fifth order affair. As a consequence, small changes in free phosphate concentration, or even smaller changes in calcium concentration, have a dramatic impact on the calculated saturation level. For this reason, high saturation levels, on the order of 100,000 or above, can be observed in cooling waters treated for calcium phosphate scale control. The authors experience is as follows:

Beware when a system is supersaturated with tricalcium phosphate.

A tricalcium phosphate saturation level below 100 is easily treated. Most inhibitor treatments can prevent scale formation, even if not specifically directed towards tricalcium phosphate. pH decrease can decrease tricalcium phosphate saturation level to an acceptable level.

pH reduction and/or a tricalcium phosphate specific treatment program is recommended when tricalcium phosphate saturation level rises above the 100 to 1000 range.

hydroxylapatite: Hydroxylapatite saturation level calculations are a ninth order affair even higher than that of tricalcium phosphate. As a consequence, small changes in free phosphate concentration, or even smaller changes in calcium concentration, have a dramatic impact on the calculated saturation level. For this reason, high saturation levels, on the order of 100,000 or above, can be observed in cooling waters treated for calcium phosphate scale control. Saturation level guidelines are similar to those for tricalcium phosphate, although a significantly higher hydroxylapatite saturation level can be carried in the presence of a copolymer, terpolymer, or other calcium phosphate scale control agents.

Iron carbonate: Siderite, the mineral name for iron carbonate, is usually found in conjunction with calcium carbonate scale in cooling system. Iron carbonate scale can be expected when the saturation level exceeds 1.2.

Amorphous iron hydroxide: Iron hydroxide precipitation can be expected in cooling water when the saturation level exceeds 1.0, a very common situation when iron is present. Iron may precipitate in the bulk water as iron hydroxide, but not form scale in high flow rate systems. Remedial action, such as a dispersant, should be taken in systems with high iron hydroxide saturation levels. Note that iron hydroxide momentary excess values reported will almost always be negligible. This ids due to the high order of the reaction. Rely upon the saturation level for deposition prediction and ignore the momentary excess in most cases.

Iron phosphate: Strengite, the iron phosphate mineral modeled by WaterCycle, should be considered a problem when the saturation level exceeds 1.0. Momentary excess for this scale former will be negligible in most cases due to the low level of "free" phosphate typically available. Rely upon the saturation level for prediction of iron phosphate scale.

CaCO₃ Scale & Corrosion Potential As Inferred From Simple Indices

The Langelier Saturation Index, Ryznar Stability Index, and Puckorius (or Predictive) Scaling Index are well documented. Values calculated by WaterCycle for these indices should be very close to those calculated using normal methods. Guidelines for these indices are covered in their respective sections of this manual. It should be noted that these indices are limited to calcium carbonate scale potential. They are based upon total calcium and total alkalinity present and may be of limited usefulness in high TDS waters for this reason. The do not account for ion pairing. It is recommended that these indices be used as points of reference only and that the more rigorous saturation level for calcite be adopted, especially in high TDS waters.

WaterCycle COLOR CODING

Graphs produced by WaterCycle are color coded as an aid in interpreting them. This section discusses the meaning of the colors.

Saturation Level and Simple Scale Indices

RED - Red signifies a definite problem prediction. Corrective action such as treatment, pH adjustment, or concentration ratio decrease (blowdown) should be taken to eliminate, or alleviate, the problem. Red signifies loss of control in TREATED SATURATION LEVEL PROFILES.

MAGENTA - Magenta (purple) signifies that a problem is highly likely. Some systems might be able to carry the degree of supersaturation indicated by magenta without deposition occurring. Most system will scale if operated in the Magenta range without treatment.

YELLOW - Yellow signifies that a problem will occur with a minimum of change. Make sure of your measurements. A slight error in pH could mean that you are really operating in a RED zone. The system is borderline and should be watched.

GREEN - No problems are likely. Significant changes (e.g. a 0.1 pH increase, a 10 °C increase) could result in a problem.

BLUE - Blue signifies a safe operating range where deposition from the scale evaluated would not be expected. Blue is also used to signify a successful treatment in TREATED SYSTEM PROFILES.

Dosage Profiles

RED - Red signifies a definite problem prediction. The treatment will not work regardless of dosage level. The system is out of range (e.g. too high a saturation level) for the treatment selected.

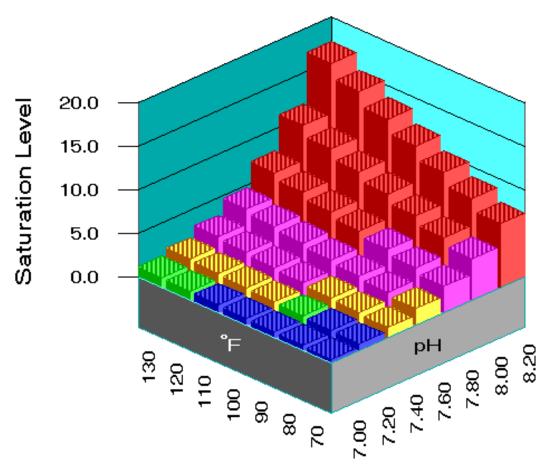
MAGENTA - Magenta (purple) signifies that a problem is approaching or highly likely. In the case of calcium carbonate inhibitors, MAGENTA signifies that the system is within ten (10%) percent of the limit for the inhibitor (e.g. 135 calcite saturation level to 149 calcite saturation level for an inhibitor that fails at 150 or above).

In the case of blended orthophosphate/copolymer products, MAGENTA signifies that insufficient polymer is present for calcium phosphate scale control when the product is dosed at the level required for adequate corrosion protection. The corrective action is to increase the ratio of copolymer to phosphate.

BLUE - Blue signifies a safe operating range where the treatment will prevent deposition of the scale evaluated.

WaterCycle's "Fuzzy Chemistry" Profiles Predict Problems Over A Broad Range of Operating Conditions

Calcite Saturation Level



Color coding identifies the severity of the problem.

Blue signifies a safe range.

Green indicates a mild problem potential if conditions change slightly.

Yellow warns you to check measurements, trouble is near.

Magenta indicates a problem is likely. Take corrective action.

Red warns of a problem. Treatment or other remedial action is required.

OPERATING RANGE PROFILE

at 1.30 cycles

WaterCycle Rx Series

Most of us use our own system for varying inhibitor treatment levels with water chemistry. Over the years we've developed our own rules of thumb. For example,

- Most of use apply higher levels of inhibitors as temperature increases.
- Most of us increase dosage as the driving force for scale formation increases. Higher levels of CaCO3 inhibitors are applied as the Langelier Saturation index or calcite saturation level increase.
- Many of us will feed higher inhibitor levels to a 72 hour holding time index system than to a 3 hour residence time system. We will definitely feed higher levels to a long holding time cooling tower than to a once through cooling system.
- And finally, most of us will feed a slightly higher dosage in high pH systems. All other things being equal, dosages for scale inhibitors are applied as a function of a driving force for scale formation and growth (e.g. Calcite saturation level), temperature as it affects reaction rates, pH as it affects the dissociation state of the inhibitor, and time. WaterCycle Rx allows you to develop mathematical models for the minimum effective scale inhibitor dosage as a function of these parameters: driving force, temperature, pH and time. Mathematical models for inhibitors can be developed using the Laboratory version of WaterCycle by editing water chemistry, temperature, and time data developed in the laboratory, through field experience, or both.

The WaterCycle Rx series is composed of the following programs:

- WaterCycle Rx Salesman's Edition This version of the program allows a user to select a product and obtain a dosage or dosage profile. Product (.PRD) files must be supplied for each product the salesman's version can model. The program can also perform all functions of the basic WaterCycle program. Dosage recommendations are incorporated into the basic WaterCycle system as an additional line of output on the tables output, and as an additional graph selection in the "What-if" modules.
- WaterCycle Rx Product Manager's Edition This version allows a user to input a product formulation and create a Product (.PRD) file. The program must have access to Inhibitor(.INH) files for an inhibitor to be incorporated into a formulation. The Product Manager's version incorporates all functions and printouts available in the basic WaterCycle program, and in the Salesman's Edition of the WaterCycle Rx series.
- WaterCycle Rx Laboratory Edition This version allows a user to develop mathematical
 models for scale and corrosion inhibitors, in addition to the functions of the other programs
 in the series. Mathematical model templates are available for common inhibitors types.
 Laboratory and/or field data can be entered in forms almost identical to the regular
 WaterCycle chemistry input forms.

Additional fields in the Laboratory version are time and dosage. Mathematical models for an inhibitor are developed by the program using multiple regression. The correlations (models) developed are output in the form of inhibitor (.INH) files. The goodness of fit for the data can be presented in table and graphical format.

The WaterCycle Rx Laboratory and Product Manager's Editions are shipped with inhibitor files for common materials such as AMP, HEDP, PBTC, and PAA to name a basic few. Inhibitor files are also available for calcium sulfate control agents, calcium phosphate control, corrosion inhibitors, and modeling corrosion rates on mild steel. Additional files are available from inhibitor's manufacturers.

The WaterCycle Rx Laboratory Edition includes the raw data for AA-AMPS as published by Calgon in a NACE paper.

Correlations can be developed for dosages versus any of the WaterCycle indices, any of the data input, and some internal calculated values such as buffer capacity..

DIFFERENCE BETWEEN WaterCycle and the WaterCycle Rx Series

The WaterCycle Rx series adds one or two pull down menus to the main WaterCycle menu. The Salesman's Edition has one selection on the additional menu (FORMULARY) and one additional selection - SELECT PRODUCT. This module displays a list of the products on file, and their description. The Product Names and Descriptions listed are derived from the Product(.PRD) files. Printouts contain one additional line for the recommended dosage for the current product selected. An additional graph selection is available for Product dosage profiles. Although the Salesman's Edition of the program allows the use of the mathematical models and formulation data in the product file, the original data cannot be accessed. Someone with a product file cannot determine the active ingredients or their percentage in the formulated product.

The Product Manager's Edition adds a second additional selection to the FORMULARY menu-INPUT PRODUCT. The product's name, description, and formulation are entered in this menu to create a Product (.PRD) file. Only inhibitors for which you have Inhibitor (.INH) files can be included in the formulations.

The Laboratory Edition adds a second additional pull down menu, which is appropriately labeled - LABORATORY. Water chemistry data, dosage, temperature, and the time period during which the water was "stable" are entered into the RAW DATA INPUT module. Once data is entered, multiple regression is used to develop a model and determine the goodness of fit between your data, and the model. This module generates Inhibitor files for use by the Product Manager version of the program, or the related modules in the Laboratory version. Note: the Laboratory version can perform any function done by the Salesman's or Product Manager Versions.

WaterCycle Rx Files

The WaterCycle Rx series uses three (3) file types in addition to those generated by the original WaterCycle program. The original files included the .WAT work files and the .PCX graphic output files. The Rx series adds the .PRD product information file, the .INH inhibitor correlation file, and the .COR, laboratory data for correlation file.

Original WaterCycle Files -

- **.WAT** (workspace) files store water analysis entered into WaterCycle, units information, ""What-if" parameters, and any indices which were calculated prior to being stored in .WAT file format. .WAT files are WaterCycle work files which allow you to stop work, save what you have completed, and return at another time. A .WAT file returns the WaterCycle program, analysis, and values to the same condition they were when the file was saved.
- **.CHM** (chemistry) files store water analysis entered into WaterCycle. Only water chemistry parameters are overwritten when a .CHM chemistry file is loaded. This allows you to load the same makeup or source water analysis into a variety of systems, without re-entering the water chemistry manually.
- **.SPC** (system specification) files store system specifications entered into either the once through or cooling water specifications input form. System specification files only overwrite parameters such as cooling water flow rate, residence time, holding capacity, etc. when loaded. This allows a chemistry file and a specification file to be retreived to complete a work space.
- **.PCX** files are a standard graphic format used to store pictures on the screen for transfer to other programs. WaterCycle creates a type 5 .PCX file with all color (palette) information stored as well as the graphic information.
- **.BMP** files are a standard windows graphic format. BMP bitmap files store the same einformation as .PCX files, but tend to be significantly larger.
- .TIF files are a third graphic format used to store pictures on the screen for transfer to other programs.

WaterCycle Rx Salesman Edition Files -

The Salesman Edition creates the same files (.WAT, .SPC, .CHM and graphic files) that are created by the original WaterCycle program. The Salesman Edition .WAT file includes any dosage recommendations calculated prior to the file being saved as well as information on the current product.

The Salesman Edition uses (but cannot create, modify, or display) product information files (.PRD). .PRD files contain product formulation information such as active ingredients and their percentages. This information is used in conjunction with mathematical inhibitor model coefficients to calculate dosage recommendations. The Salesman Edition can use the information in the files, but is not capable of displaying this sometimes proprietary information. The active

ingredient list, and their percentages, cannot be obtained by loading a product (.PRD) file into the Salesman Edition program.

WaterCycle Rx Product Manager Edition Files -

The Product Manager Edition creates the same files that are created by the original WaterCycle program. Additionally, the Product Manager Edition can create product (.PRD) files. It can also access inhibitor (.INH) files.

The Product Manager Edition can create, modify, and display product information files (.PRD). The INPUT FORMULATION module is used to access or create a .PRD file. Active ingredients information is added to the .PRD files through the loading of the inhibitor file for the active ingredient being added. The appropriate percentage(s) for active ingredients thus loaded are entered into the form. The inhibitor (.INH) files contain the mathematical inhibitor model coefficients to calculate dosage recommendations. The Product Manager Edition can use the information in the .INH files, but is not capable of displaying this sometimes proprietary information, or the laboratory data which was used to generate the inhibitor correlations.

The Product Manager Edition has full access to the formulation information such as active ingredients, and their percentages.

WaterCycle Rx Laboratory Edition Files -

The Laboratory Edition creates the same files that are created by the original WaterCycle program. The Laboratory Edition has all of the capabilities of the Product Manager Edition. It can create product (.PRD) files.

Additionally, the Laboratory Edition can be used to directly edit inhibitor (.INH) files. The Laboratory Edition has the unique capability of processing .COR file data to generate inhibitor (.INH) files.

The Laboratory Edition can create, modify, and display product information files (.PRD). The Laboratory Edition has full access to .INH files, including the capability of displaying the sometimes proprietary information stored in them.

The Laboratory Edition has full access to laboratory and field data stored in .COR files. .COR files contain water chemistry information, dosage required for 100% inhibition, and temperature data for laboratory and/or field data. A series of analysis can be used to statistically model the inhibitor performance and develop a .INH file mathematical model. A minimum of five (5) analysis are required for a .COR file to be used.

GETTING STARTED

System Requirements

Installation

Selecting Analytical Units

Carbonate Calculations

System Requirements

As a general rule, French Creek Software programs will run on the minimum system configuration for a given Windows operating system. Performance increases with memory and processor speed. Suggested minimums are as follows.

	Windows 3.1	Windows 95	Windows NT
Processor	80386 Minimum	80486 DX2-66	Pentium 75
RAM Memory	8 Megabytes	8 Megabytes (12 Preferred)	12 Megabytes (16 Preferred)
Hard Drive	4 Megabytes	4 Megabytes	4 Megabytes
Space			
	VGA (640 x 480)	VGA (640 x 480)	VGA (640 x 480)
Video	SVGA (800 x 16) preferred	SVGA (800 x 16) preferred	SVGA (800 x 16) preferred
Notes	Math Coprocessor required	Math Coprocessor required	Math Coprocessor required

Please note that each workspace file will consume up to 50K of hard drive space. Each graph stored as a PCX file will use around 50K. Each graph stored as a .BMP file can take up to 600K of hard drive space.

If you choose to install the program on a 386 or 486 system insure that a math coprocessor (80386/80387 or 486SX/487SX or 486DX). Pentium processors (and equivalents) include a math coprocessor.

INSTALLATION

BEFORE YOU DO ANYTHING ELSE, WHY NOT MAKE A BACKUP COPY OF THE PROGRAM DISK(S). PUT THE ORIGINAL DISKETTE(S) IN A SAFE PLACE AND USE THE BACKUP AS YOUR WORKING INSTALLATION DISK. WRITE PROTECT THE BACKUP DISKETTE(S) ONCE THE COPY IS MADE.

The program is installed like most Windows software: by running the SETUP.EXE file on the installation diskette.

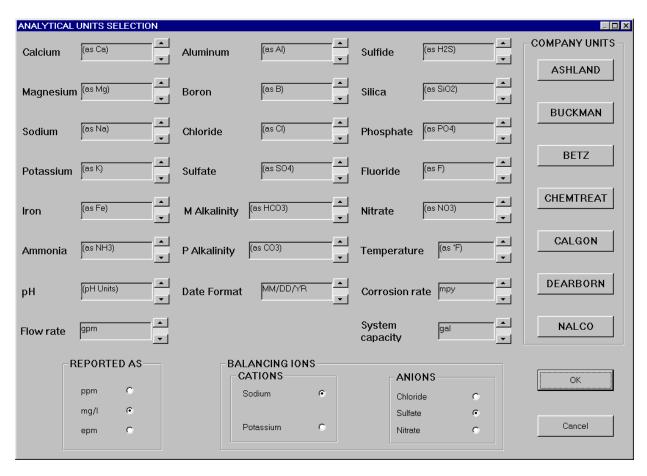
- 1) Insert the program diskette in the floppy drive.

You can also execute by double clicking on the SETUP.EXE program icon from FILE MANAGER, FILE EXPLORER, or MY COMPUTER, depending on your version of Windows. replace A: with B: to install from the B drive.

- **3) The install program will search for an existing installation.** You must install to the WATER directory, e.g. C:\WATER or D:\WATER ...
- 4) Execute the program by clicking on the French Creek Software Icon, by using the Windows RUN command, or from the Windows START menu.

Selecting Analytical Units

The first time WaterCycle is run, it will display a warning that default analytical input units are in affect. This is a reminder to run the **Input Units** module (which can be selected from the **Preferences** menu) and choose the analytical reporting units used by your company.

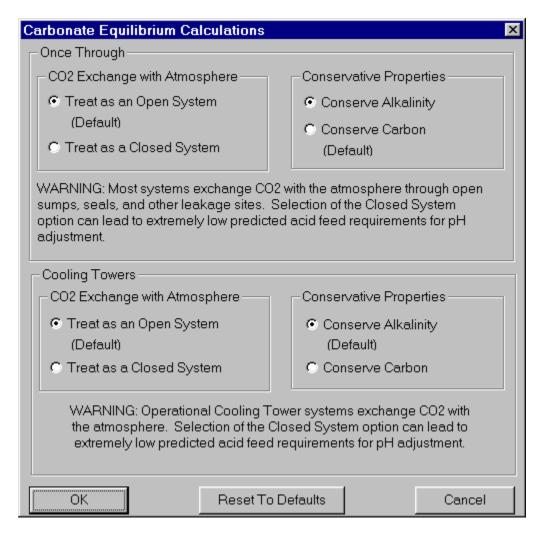


Analytical units are available for almost any reporting method in use. Date format can also be changed in this module. You might also wish to select the ions which will be used to balance incomplete water analyses.

Carbonate Calculations

WaterCycle deals with the carbonate equilibrium in two basic ways as it cycles a water: *Conservation of Alkalinity* or *Conservation of Total Molar Carbon*.

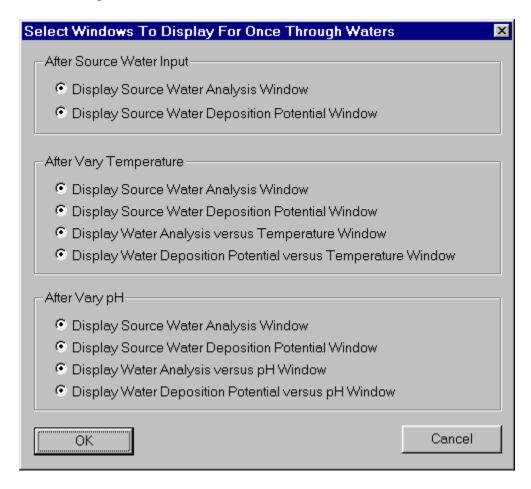
Carbonate based Alkalinity is conserved in systems open to the atmosphere such as cooling towers, due to the free exchange of carbon dioxide (CO_2) with the atmosphere. Molar carbon is conserved in totally closed, air tight systems. For most systems, carbonate calculations should be based upon the conservation of alkalinity.



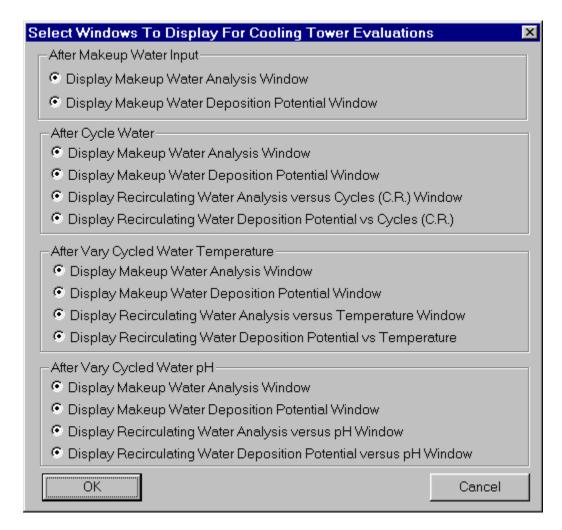
You can select the appropriate method for carbonate calculations in the CO₃ Calculations module which can be selected from the Preferences menu. When in doubt, conserve alkalinity!

Selecting Windows To Display

WaterCycle displays an enormous amount of information. At times a total display is useful. At other times two much information is confusing or a nuisance. You can determine which informational output windows will be displayed in **the Cooling Tower Windows To Display** and **Once Through Windows To Display** modules which can be accessed from the preferences menu.



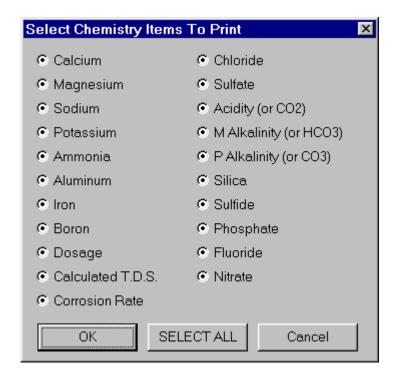
These forms allow you to customize the display of these output windows.

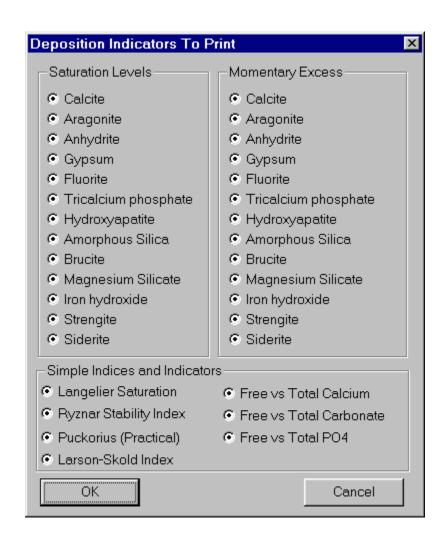


It is recommended that new users set all windows to display. They can be deactivated and reactivated as desired using these forms.

CHOOSING DATA TO PRINT

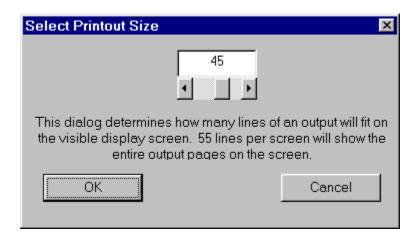
You can also determine what analytical values and indices will be included in printouts by activating or deactivating individual items in the **Choose Ions To Print** and **Choose Scales To Print** forms, which can be accessed from the **Preferences** menu.





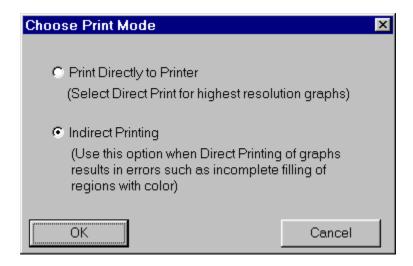
CHOOSING DISPLAY SIZE

The **Output Size On Screen** form allows you to select the number of lines form a printout that will be display on the screen. This allows you to size the output window so that an entire printout can be displayed on the screen. This form is also accessed through the **Preferences** menu.



PRINT MODE

The final setup form is rarely needed. It allows the selection of either directly printing to a printer or printing indirectly by preparing the printout in the computer's memory prior to transmitting to the printer. Choose Direct Print initially. Change your selection to Indirect Print if problems are encountered printing graphs.



What-if Scenario Modeling

Introduction

Once Through "What-if"

Cooling Tower "What-if"

Setting Constant Phosphate or Silica Levels

Predicting pH

Report Options

Copy to the Clipboard

Print

Choosing lons/Scales to Print and Copy/Paste

Change Range/Change Treatment

Tables Graphs

Suggested Work Flow Diagrams

Once Through
Open Recirculating Cooling Tower

"WHAT-IF" SCENARIO MODELING

What-IF SCENARIO modules allow you to visualize what will happen to the scale potential and corrosivity of a cooling water as operating parameters and water chemistry change. The What-If scenarios allow you to evaluate the current cooling water over the entire range of operating parameters. The What-If's also provide a predictor for use in evaluating new cooling systems, and as an aid in establishing control ranges and operating parameters.

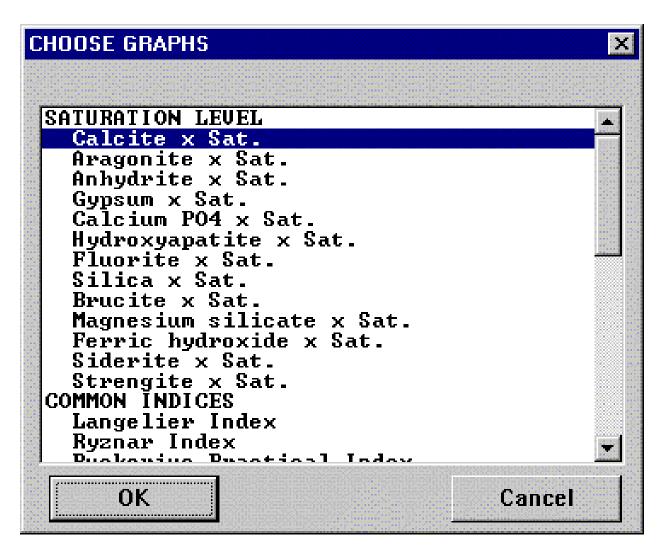
For once through cooling systems, the What-If scenarios allow you to evaluate the scale potential of a cooling water over the temperature range expected, and the pH range encountered. Input parameters for selecting the What-If scenario ranges include minimum and maximum temperature, and minimum and maximum pH values. Use of this modeling capability allows a painless evaluation of scale potential and corrosivity indicators from the minimum inlet water temperature anticipated to the highest discharge temperature predicted, and from the lowest pH encountered to the highest.

For open recirculating cooling tower systems, the What-If scenarios allow you to evaluate these indicators over a broad concentration ratio range. The modules provide a means to evaluate the impact of pH control range choice on scale potential. An overall evaluation with the What-If Scenario family of modules allows you to review the water from the perspective of many complementary indices and reach conclusions tempered by your water treatment expertise. The next section discusses the What-If Scenario family from the perspective of functions both the ONCE THROUGH and COOLING TOWER modules have in common, and based upon their own unique properties.

COMMON FUNCTIONS

Both the **ONCE THROUGH** and **COOLING TOWER** modules require the input of a Source or Make-up water analysis I*n the respective modules. Cooling tower scenarios also require that the water be "concentrated" using the Cycle module.

The final common thread between the scenarios is the selection of graphs for modeling. Graphs can be selected using the Choose Graphs module or from the OPTIONS menu bar when a graph is displayed.



CONVENIENCE GROUPS

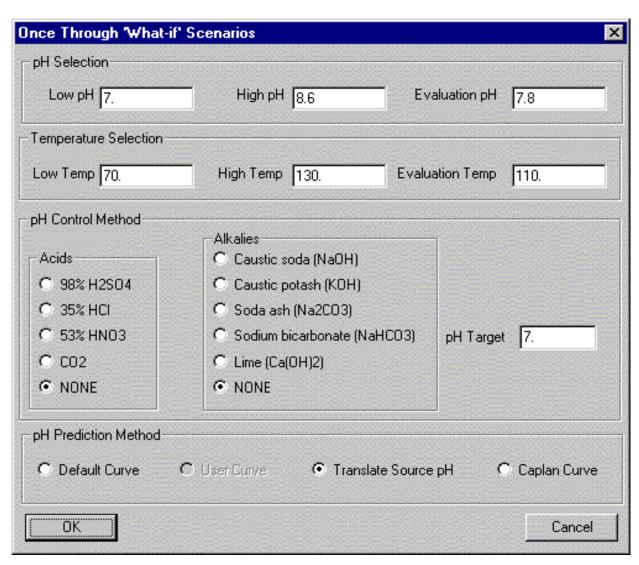
Three **CONVENIENCE GROUPS** have been programmed into WaterCycle® to allow multiple graph selection of common groups.

- The *Common Foulants* convenience group includes *Calcite, Silica, Tricalcium phosphate*, and *Anhydrite* saturation levels.
- The *Common Indices* convenience group includes the *Langelier*, *Ryznar*, *Puckorius* and *Larson-Skold Ratio* indices.
- The *Calcium Carbonate* convenience group includes *Calcite saturation level, Langelier Saturation Index, Ryznar Stability Index*, and *Puckorius (practical) Scaling Index*.

The graphs are prepared using the profile modules which are unique to the system type and are discussed separately in the following sections.

ONCE THROUGH "WHAT-IF"

Three scenario types can be run for once through systems. The scenarios calculate the indicators of scale potential and corrosivity versus pH, temperature, or both. The modules are called *VARY TEMPERATURE*, *VARY pH*, and *3D PROFILE* for these scenarios.

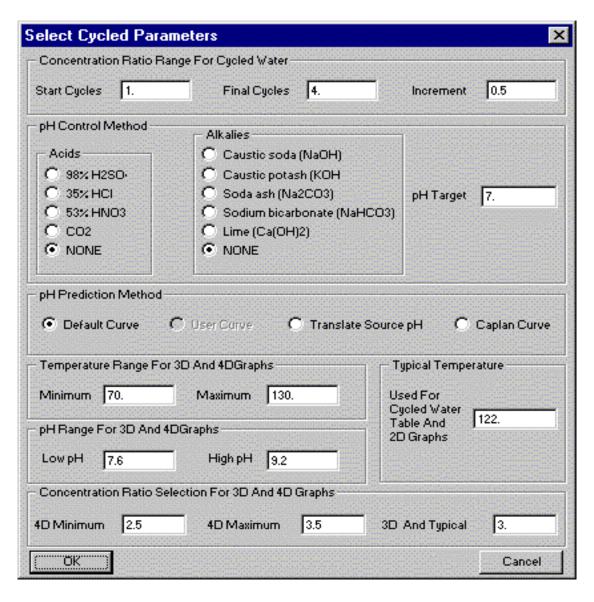


When you enter any of these modules, a menu pops-up requesting information on the minimum and maximum pH for the scenario calculations, and on the minimum and maximum temperature for the calculations. The typical pH is the pH which will be used for 2D plots which **VARY TEMPERATURE**. The typical temp is the temperature which will be used for 2D plots which **VARY pH**. When **the 3D PROFILE** is run, both the pH and temperature ranges selected for the scenario are used for calculations.

Once a graph is displayed, it can be printed from the **options menu** bar, copied to the Windows clipboard and pasted into another application, or saved as a PCX, TIF, or BMP file.

COOLING TOWER "WHAT-IF"

All of the graphs can be generated using the Cooling Tower "What-If" scenario modules. The first step in generating any of the cooling tower graphs is to **SELECT PARAMETERS** for the scenario. Parameters can be selected from the **SELECT PARAMETERS** module (see form below). The parameters you can vary include concentration ratio, and increment, whether or not to use acid for pH control, and the pH-Alkalinity relationship to use for predicting pH as the water cycles. Run the **SELECT PARAMETERS** module prior to **CYCLE** or any of the **OPERATING RANGE PROFILES**.



CYCLING COOLING WATER AND CALCULATING INDICES VERSUS CONCENTRATION RATIO

The Cycle module concentrates the cooling tower make-up water. Water is cycled according to the Start, Maximum and Increment entered in the WaterCycle **PARAMETERS** menu under the Concentration Ratio heading. The water is cycled at the Typical Temperature entered. If pH control is selected, the appropriate acid is used to maintain a maximum of the Control pH selected. Tables summarizing the recirculating water chemistry and calculated indices are displayed upon completion of the **CYCLE** module.

The indices can be graphed in 2D format versus concentration ratio using the **GRAPH** module. The tables can be printed from the Options Menu Bar when they are displayed on the screen, or by selecting the **Cycled Water** module in the **REPORTS** menu. The Options Menu Bar also contains options to Copy the report to the Windows clipboard for pasting into another application such as a word processor.

3D OPERATING RANGE PROFILES

This module uses the Operating Range Specification to model the operating range at the Typical Concentration Ratio over the Low to High Temperature range, and the Low to High pH range. IF an acid pH control option was selected, pH control is used.

Graphs can be displayed as 3D bar graphs or as 3D contour plots. The Options Menu Bar has selections to toggle the graph type from 3D Bar to 3D contour when a bar graph is displayed, and to toggle the graph type between 3D Contour and 3D Bar plots.

4D OPERATING RANGE PROFILES

The 4D profiles calculate and plot the indices over the Low to High pH and Temperature operating range entered in the PARAMETERS menu. The indices are calculated at both the Low and the High Concentration Ratio entered. 4D bar graphs are Minimum-Maximum bar plots. 4D contour plots stack the Low and High concentration ratio profiles.

FEATURES COMMON TO ONCE THROUGH AND COOLING TOWER GRAPHS

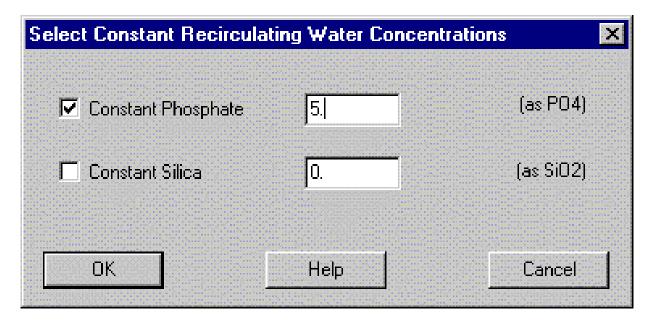
The **CHOOSE GRAPHS** module can be used to select the graphs desired. It presents an identical menu of graphs as the CHOOSE GRAPHS options on the menu bar at the top of a displayed graph. Once a graph is displayed on the screen, it can be saved as a PCX, BMP, or TIF file for use in other programs such as word processing programs, or printed.

Calculated values used to plot the 3D and 4D graphs can be exported as quotation mark-comma delimited ASCII files. These .DAT files can be imported into most spreadsheet and graphics programs and used to recreate graphs, or further manipulate the data.

SETTING CONSTANT PHOSPHATE OR SILICA LEVELS_

The "What-if Scenario" and "Cycle" modules will concentrate the phosphate in the make-up water to the concentration ratio being evaluated unless you force it to maintain a constant recirculating concentration. For example, if there is 5 ppm of PO4 in a make-up water, the cycle module will use 25 ppm (5 ppm make-up x 5 cycles) for its calculations at a concentration ratio of 5.

The "Set Constant Values" module allows you to override the default concentration of make-up levels and substitute a constant value for calculations. For example, if you wish to evaluate a treatment program in the concentration ratio range of 3 to 5, at a constant phosphate level of 15 ppm, use the "Set Constant Values" module to easily accomplish this modeling.



The "Set Constant Values" module can be used to set either constant phosphate levels, constant silica levels, or to maintain both at a constant level in the recirculating cooling water.

The "Set Constant Value" module can be accessed from the "Make-up Analysis" input form Constant Values button, or from the PREFERENCES pull down menu.

pH PREDICTION

Predicting pH as the water cycles is one of the more difficult aspects of computer modeling. WaterCycle provides three options, chosen from the **SELECT PARAMETERS** menu form.

- The **DEFAULT** curve is a pH:Alkalinity curve which is used by several of the major water treatment companies for predicting pH from alkalinity.
- The **USER DEFINED** curve uses data input in the **INPUT pH-ALKALINITY** module to predict pH from alkalinity.
- The **Caplan curve** is similar to the default curve. It is derived from a paper published by Gary Caplan at Corrosion '90 (NACE).
- The **Translate Source Water** option is based upon a modified Lawrence Caldwell method, more commonly applied to pH prediction of softened or mixed waters.

Report Options

Choosing What Output Windows To Display and When

Several options are available for displaying and printing table and graphs from WaterCycle. The output windows which will display can be selected from the **Choose Once Through Windows To Display** and **Choose Cooling Tower Windows To Display** modules in the Preferences menu. (See the **Getting Started** section of the manual for an example).

Choosing What Scale Indices and Ions To Display

A report can become cluttered and information sometimes overlooked in an extremely detailed report. WaterCycle options allow you to choose the ions to include in reports copied to the Windows Clipboard or printed. WaterCycle options also allow you to choose the indicators of scale to include in reports copied to the Windows Clipboard or printed. Reports can be customized, for example, to exclude all Momentary Excess indices. Refer to the Getting Started section for examples of the forms **Choose Ions To Print** and **Choose Scales To Print**. These may be accessed from the **Preferences Menu**.

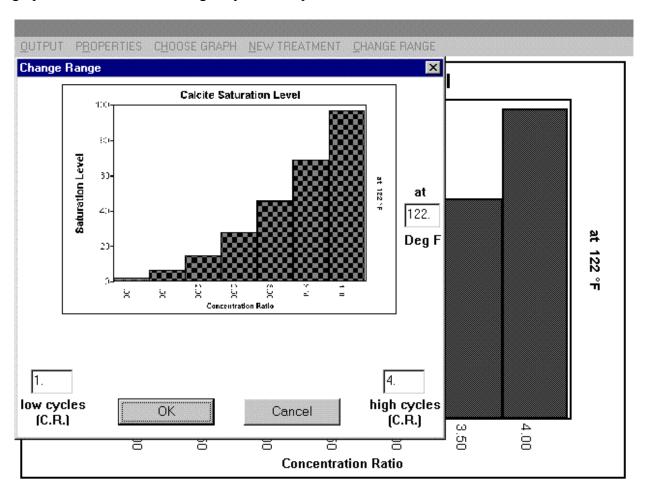
Change Range -- New Product Options

In early versions of WaterCycle changing products and displaying the new results could be a cumbersome, and sometimes inefficient process. You had to leave a graph or table, access the Select Parameters form, and then go back to the output form or graph to see the results of the change. Version 3.0 adds the ability to change the range for a report and see the results updated on the screen without leaving the graph or report. For pH profiles, you can press the Change Range button on the output form, and input a new pH range. For Temperature profiles, you can press the Change Range button on the output form, and input a new Temperature range. The New Product and Change Product buttons allow you to select a new treatment, and view the new dosages and color coded ranges on the screen.

The NEW TREATMENT and CHANGE RANGE selections on output windows allows you to quickly see the impact of parameter or treatment changes.

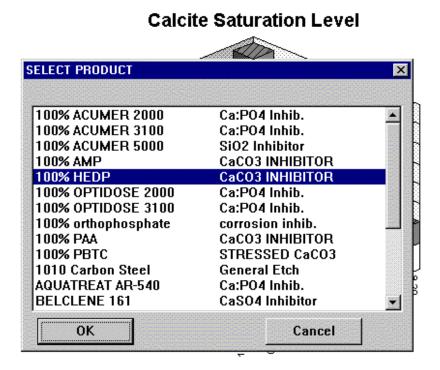
RECIRCULATING WATER CHEMISTRY OPTIONS NEW TREATMENT CHANGE RANGE									
Sample ID: 0	Report 1	aljalionauptinon	-16-1999	Samp l	led: 12-1	16-1999 :	ıt 1312		
	CONCENTRATION RATIO								
CATIONS	1.00	1.50		2.50	3.00	3.50	4.00		
Calcium(as Ca)	111.00	166.50	222.00	277.50	333.00	388.50	444.00		
Magnesium(as Mg)	0.00	0.00	0.00	0.00	0.00	0.00	0.00		
Sodium(as Na)	0.00	0.00	0.00	0.00	0.00	0.00	0.00		
Potassium(as K)	0.00	0.00	0.00	0.00	0.00	0.00	0.00		
Iron(as Fe)	0.00	0.00	0.00	0.00	0.00	0.00	0.00		
Ammonia(as NH3)	0.00	0.00	0.00	0.00	0.00	0.00	0.00		
Aluminum(as Al)	0.00	0.00	0.00	0.00	0.00	0.00	0.00		
Boron(as B)	0.00	0.00	0.00	0.00	0.00	0.00	0.00		
ANIONS									
Chloride(as Cl)	0.0	0.0	0.0	0.0	0.0	0.0	0.0		
Sulfate(as 304)	159.6	239.4	319.2	399.0	478.8	558.5	538.3		
Acidity	124.1	172.9	219.5	252.9	302.5	338.3	370.3		
"M" Alkalinity	111.0	155.4	221.8	277.1	332.2	387.3	442.3		
"P" Alkalinity	1.0	3.0	6.5	11.9	19.2	28.5	39.0		
Silica(as SiO2)	0.0	0.0	0.0	0.0	0.0	0.0	0.0		
Phosphate(as P04)	0.0	0.0	0.0	0.0	0.0	0.0	0.0		
H23 (as H23)	0.0	0.0	0.0	0.0	0.0	0.0	0.0		
Fluoride(as F)	0.00	0.00	0.00	0.00	0.00	0.00	0.00		
Nitrate(as NO3)	0.00	0.00	0.00	0.00	0.00	0.00	0.00		
PARAMETERS									
PH	7.42	7.68	7.85	7.99	8.10	8.20	8.28		
Temperature(Deg F)	122.00	122.00	122.00	122.00	122.00	122.00	122.00		
Calculated T.D.S.	414.15	612.93	810.40	1005.87	1198.77	1389.40	1577.59		
DOSAGE									
100% HEDP	0.04	0.11	0.27	0.53	0.90	2.08	4.59		

The CHANGE RANGE and NEW TREATMENT selections on the menu bar when a graph is displayed work in a similar manner. The Change Range option displays a smaller version of the graph with edit fields to change any relevant parameters.



The NEW TREATMENT option displays the CHOOSE PRODUCT menu over the current graph or table.





These new features are common throughout the French Creek Software product line. Other menu bar selections, such as PROPERTIES and OUTPUT allow you to further customize a graph or table. Use PROPERTIES to switch a graph from treated to untreated color coding, or from bar graph format to contour. PROPERTIES also can switch between grey scale and color display and printing. PROPERTIES also allows the reversal of axis, when appropriate.

The OUTPUT selections include Copy to the clipboard, which will copy a table or graph to the clipboard for pasting into another application.

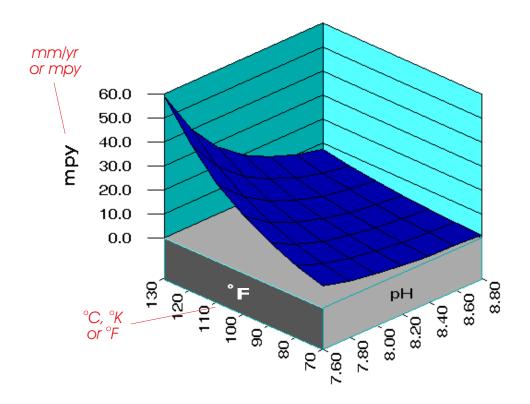
NOTE: WHEN COPYING A TABLE TO A WORD PROCESSING PROGRAM, MAKE SURE A *FIXED WIDTH* FONT SUCH AS COURIER IS SELECTED. The table may lose all alignment when pasted into a word processing window with a variable width font (e.g. Times New Roman) selected as the current font. If you encounter this don't despair:

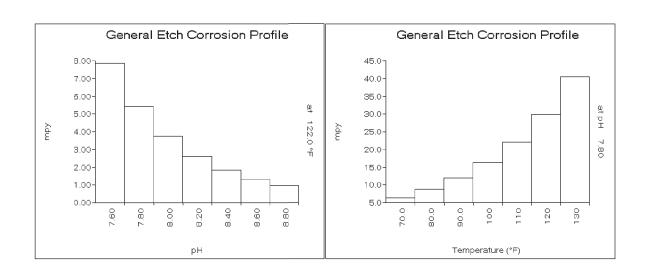
- 1) Go to the Word Processors SELECT ALL command. The entire table should be highlighted.
- 2) Go to the FONT selection menu for the word processor and select a fixed width font like Courier or Courier New.
- 3) You may have to adjust the margins to the minimum, or select a smaller sized font.

WaterCycle R

Models & Predicts Corrosion Rate Load the product "General Etch" using the SELECT PRODUCT module to predict corrosion rates.

General Etch Corrosion Profile

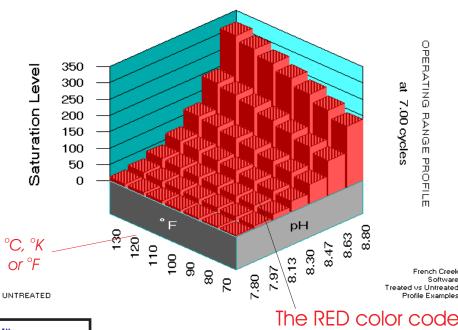




WaterCycle R

Compares The Safe Operating Range For a Treated versus Untreated System

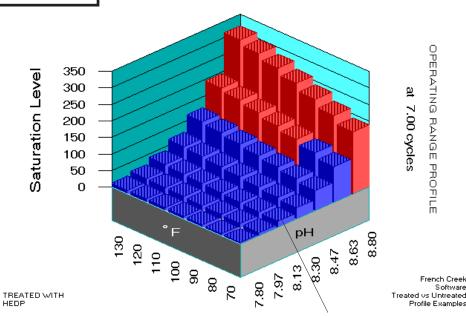
Calcite Saturation Level



Chooset he "Treated" or "Untreated" color coding optionf rom the Options Pop-upM enu.

The RED color code indicates potential trouble.

Calcite Saturation Level

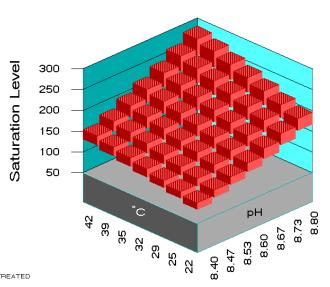


The BLUE color code indicates a safe zone for operation.

WaterCycle R

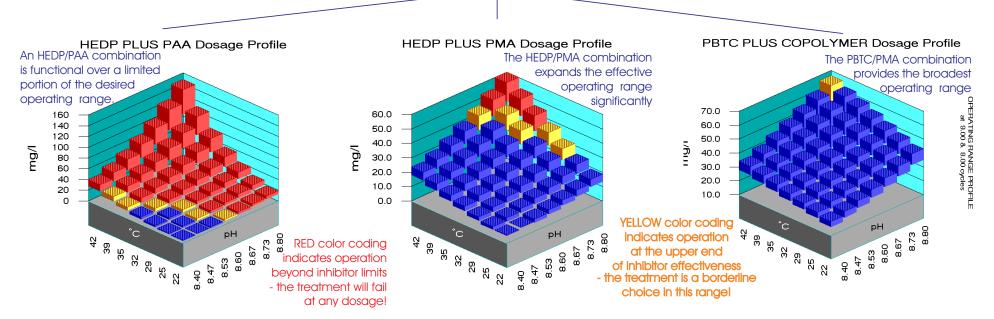
helps you choose the optimum treatment & identifies inhibitor upper limits



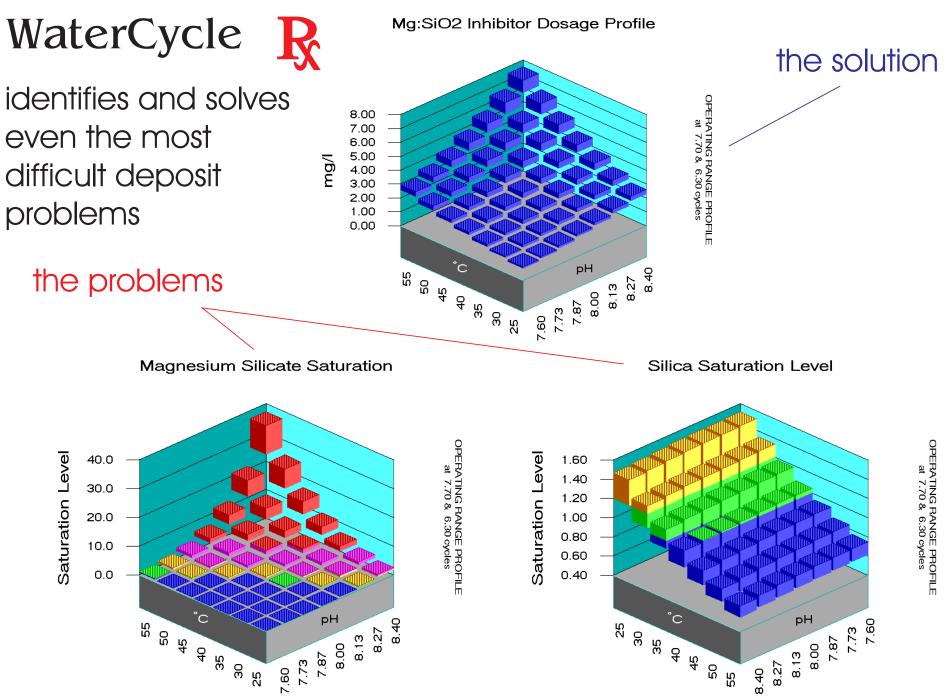


the problem extreme CaCO₃ scale potential

solution options



French Creek Software, Inc. Kimberton & Hares Hill Roads, Box 684 Kimberton, PA 19442 U.S.A. telephone (610) 935-8337 http://www.frenchcreeksoftware.com/ facsimile (610) 935-1008



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DEVELOPING AND USING INHIBITOR MODELS

SELECTING A PRODUCT

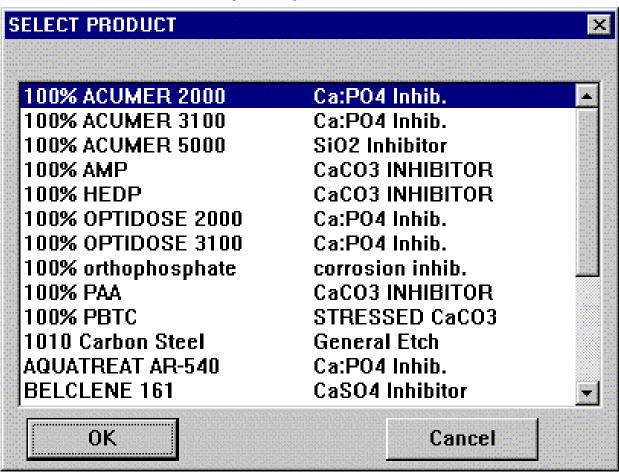
INPUTTING A FORMULATION

DOSAGE MODULATION

DEVELOPING INHIBITOR MODELS

SELECTING A PRODUCT

WaterCycle® products can be accessed from the FORMULARY menu, by clicking on SELECT PRODUCT, or from the Options Menu Bar on Table displays and graphs. Clicking on the SELECT PRODUCT or NEW TREATMENT buttons elicits the following menu for product selection:



A product file (.PRD) is associated with every menu selection. Each product file contains the models for the components and the product formulation "recipe". Loading the product file loads the mathematical models for the inhibitors in the product into WaterCycle. Once loaded, they are used by the program for calculating optimum treatment rates (dosages).

Starting with Version 6, users can select up to two products for sequential evaluation. For example, you can select a phosphate packabe as product 1, and a scale inhibitor - phopshate control package for product 2. WaterCycle will evaluate product 1 and add the appropriate phosphate levels to the water and reclaulate all indices. Then it will evaluate the dosage requirements for product 2, using the phosphate treated water.

Select a zinc inhibitor package for product 1, and a scale control - zinc stabilization package for product 2. You could also select a scale control product for product 1, and a silica dispersant/inhibitor for product 2.

Version 6 provides the additional sequential product evaluation capability especially to optimize phosphate treatments. It is recommended that single products be selected as product 1.

INPUTTING A PRODUCT FORMULATION

The Input Product module, in the FORMULARY pull down menu is used to create a product (.PRD) file. The Input Product module is available only in the WaterCycle Rx Product Manager and Laboratory Editions.

Inhibitor Formulation Input Form									
Formulation Name	100% PAA Description CaCO3 INHIBITOR								
Product File Name PAA.PRD									
Inhibitor 1	PAA			100.000	- %				
Inhibitor 2				0.000	7.				
Inhibitor 3				0.000	7 %				
Inhibitor 4				0.000	_ %				
Inhibitor 5				0.000	- %				
Inhibitor 6				0.000	7 %				
Inhibitor 7				0.000	_ /				
Password			% Actives	100.000	7 %				
	ENCRYPT	ON	% Water	0.000	7.				
ОК	Cale %	Delete File	Help	Can	cel				

Use the Input Product module to create a new product file or modify an existing product file's Product Name, Description, or Formulation. All entries are made in the form reproduced on the next page. The Product Name and Description information entered are stored in the product file and used as the Product Name and Description list in the Select Product module pop up menu.

Inhibitors MUST be selected from the pop-up menu list of available inhibitors on file. Move the cursor to the Inhibitor Field. Click on the button next to the ingredient field to pop-up the list of available inhibitors. Select the inhibitor of interest. The inhibitor file will be loaded for the ingredient selected.

ENTER THE % IN THE FORMULATION BASED UPON 100% ACTIVE INGREDIENTS!! e.g. if you are using a material which is 50% active AMP, and you wish to have the product be 10% active, you would enter 20% on a manufacturing batch sheet for the material on an "as-is" basis. Enter 10% on the WaterCycle Rx formulation sheet for the material on an active basis.

WaterCycle will I total the active ingredients and balance the formula with water.

Pressing the OK button saves the formulation and inhibitor information in the product (.PRD) file named in the File Name field. Copies of this file can be distributed to users of the WaterCycle Rx Salesman Edition program.

NOTE: Inhibitors should be re-loaded into a formulation sheet when an inhibitor file is updated. Product files load a copy of the inhibitor file when they are created. They DO NOT automatically re-load a new file when the inhibitor data is updated.

The module accepts input data for a product file, loads the mathematical correlations for the individual inhibitors in the formulation, and outputs the new or updated product file.

An inhibitor file (*.INH) must be in the \WATER\INHIB\ sub directory for each inhibitor which is an active ingredient.

Inhibitor files are created in the Input Lab Data module of the LABORATORY pull down menu in the WaterCycle Rx Laboratory Editions. They can be created from in-house laboratory and/or field data, or obtained from raw material suppliers who use the WaterCycle Rx series as a technical support tool.

The ENCRYPTION option allows product files to be encrypted as a precaution against prying.

DOSAGE MODULATION

The section describes the basis for the models used by and developed using WaterCycle Rx. Models are discussed by parameter.

DRIVING FORCE - The basic parameter to which scale inhibitor dosages have been correlated historically is the driving force for crystal formation, and crystal growth. Early models attempted to develop models based upon the Langelier Saturation Index or the Ryznar Stability Index. More recently, correlations have been published to the Practical Stability Index on the back of the Puckorius and Associates slide rule. Most water treaters are in agreement that dosage requirements increase with the driving force for scale formation. They differ in which driving force is used. Calcite saturation level provides an excellent driving force for calcium carbonate scale inhibitor models, gypsum saturation level for calcium sulfate in the cooling water temperature range, and tricalcium phosphate saturation level for calcium phosphate scale prevention. The Momentary Excess indices can also be used effectively to model dosage requirements. WaterCycle Rx allows the water treatment chemist to develop models using any of the indices calculated by WaterCycle.

TIME - A second critical factor in determining an effective dosage, or developing a model for an inhibitor is time. Time is the residence time of scale forming species in the cooling system you wish to treat. The time where scale inhibition can be as short as 4 to 10 seconds in a utility condenser cooling system, or extend into days for cooling towers. Induction time is a term applied to the period before a water will begin to form scale. In high saturation level systems, the induction period can be very short. In systems where a water is barely supersaturated, the induction time can approach infinity. Scale inhibitors have been observed to extend the induction time before scale formation, or growth on existing scale substrate, occurs.

Gill et al. presented a paper at the 1984 International Water Conference which provides excellent examples of the variation of dosage requirements as critical parameters change.

IMPACT OF HEDP CONCENTRATION ON INDUCTION TIME

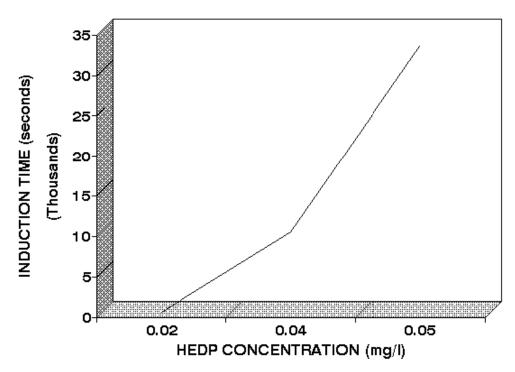
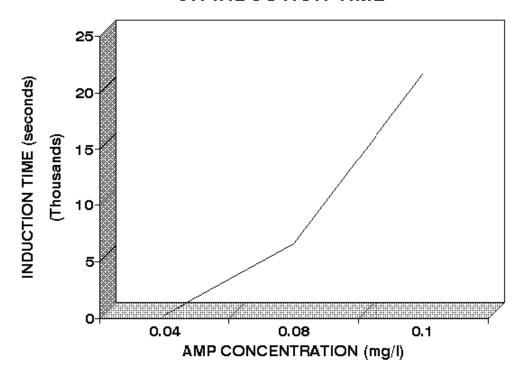


Figure 1 portrays the impact of HEDP dosage on induction time at constant driving force. Figure 2 presents similar data for AMP.

IMPACT OF AMP CONCENTRATION ON INDUCTION TIME



It can be seen from figures 1 and 2 that induction time increases as inhibitor dosages increases. In cooling water systems, scale inhibitors may function by increasing the induction time until the water has passed through the system.

IMPACT OF CALCITE SATURATION LEVEL ON INDUCTION TIME

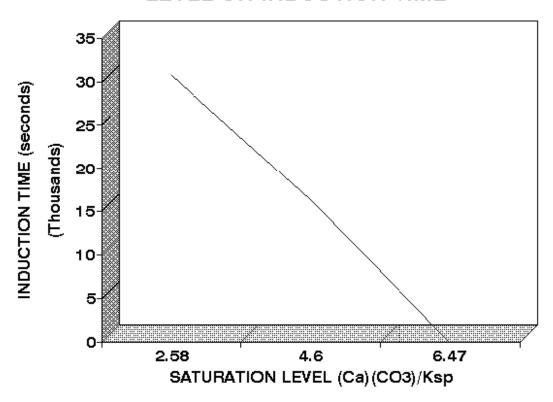


Figure 3 demonstrates that induction time decreases with saturation level, even in the presence of an inhibitor.

A simple mathematical description of these relationships might be modeled as:

Induction Time = function(1./Saturation Level)

This models the decrease in induction time as saturation level increases. The degree of supersaturation is the driving force which increases the rate at which scale will form.

Induction Time = function(Inhibitor Dosage)

Inhibitors extend the time before scale will form in a system by interfering with the kinetics of crystal formation and growth. Rate decreases as inhibitor dosages increase.

Induction Time = function(Inhibitor Dosage, 1./Saturation Level)

In cooling systems, the inhibitors fight the driving force for scale formation and growth. Inhibitors increase the induction time, and interfere with reaction rates, so that scale formation will not occur until the treated water has passed through the system.

WaterCycle Rx uses more sophisticated relationships than these to model the dosage requirements for scale inhibition. Additional parameters include temperature, as it affects the rate of crystal formation and/or growth.

Dosage changes with temperature can be modeled by the Arrhenius relationship:

where

- A is a constant
- Ea is the activation energy
- **R** is the gas constant
- T is absolute temperature.

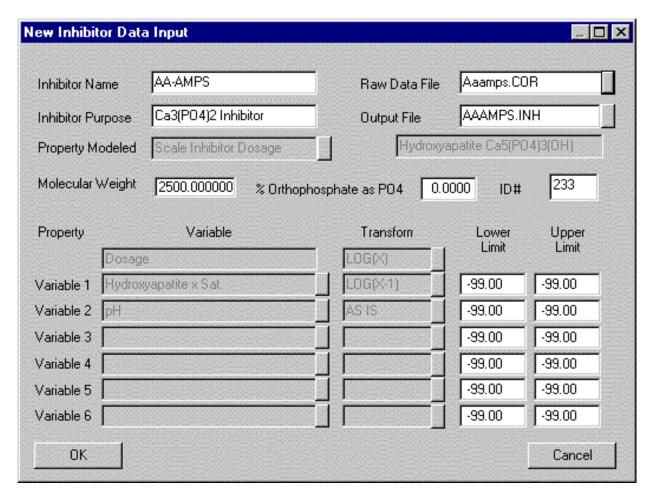
pH can also be included in the models. pH is an important parameter to include when an inhibitor can exist in two or more forms within the pH range of use, and where one of the forms is much more active as a scale inhibitor than the other(s). pH can also affect the type of scale that forms (e.g. Tricalcium phosphate versus hydroxylapatite).

DEVELOPING INHIBITOR MODELS

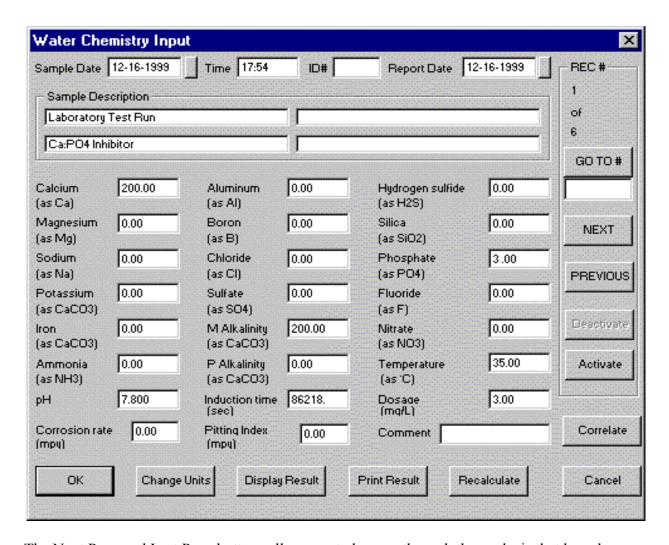
This section describes the use of the Laboratory Edition Modules for:

- Inputting laboratory and field data to develop an inhibitor model.
- Editing inhibitor files to add special rules for handling iron.
- Editing inhibitor files to include a safety factor.

The Input Lab Data module, in the **LABORATORY** pull down menu is used to create inhibitor (.INH) file. The module accepts initial specifications for the inhibitor (e.g. Name, Description, Molecular weight) and instructions for developing a model (e.g. the Driving Force to use, the modeling method).



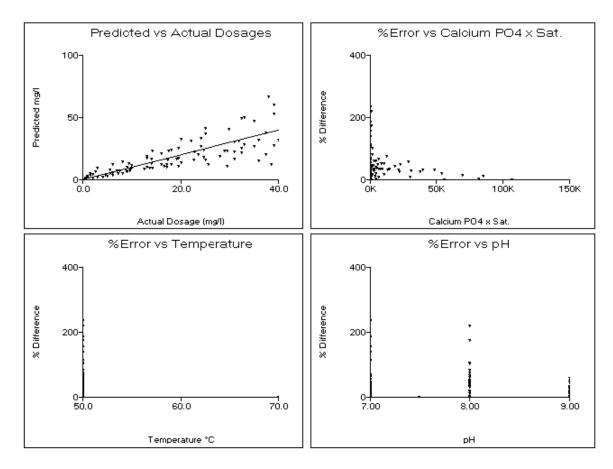
After this preliminary data is entered, and the Correlate button is pressed to signify completion, the module accepts input of water analysis data through almost the same analytical input form that is used in the Once Through Source Analysis module and Cooling Tower Make-up Analysis modules. The Input Lab Data form adds two (2) significant fields to the water analysis forms - dosage and time. The input form differs in another way - operation. The Lab Data Input Form replaces itself with a fresh form every time OK is pressed.



The Next Page and Last Page buttons allow you to browse through the analysis that have been input and make changes. The program will sound a warning when the first analysis on file is reached. The program will ask if you wish to add another analysis when the last analysis is reached.

Once all data has been entered, press **Correlate** to invoke the statistical analysis of the data and generation of an inhibitor file. A table of predicted versus input dosages will be displayed. Use this table to determine crudely how well the data was modeled. A correlation coefficient is also output. Typical coefficients for usable models will range from 0.9 to 1.00.

Pressing the Graph button will present further information on the correlation in graphical format.



The Input Lab Data module is available only in the WaterCycle Rx Laboratory Edition. The Edit Coefficients module is used to add special rules and safety factors to the inhibitor files.

The raw laboratory analysis and calculated values are stored in a .COR file. The data is used to create an inhibitor (.INH) file.

OPERATION HINTS:

- 1. Enter inhibitor dosages on a 100% ACTIVE BASIS.
- 2. Make backup copies of .COR files under another name. This will prevent anguish and stressed tempers when a .COR file with a thousand or so analysis is over-written unintentionally.
- 3. Always press Graph after completing the correlation to see the graphs of predicted versus observed dosages, and graphs of error % versus versus the independent parameters.
- 4. The Options Menu Bar allows correlation graphs to be saved as a .PCX, TIF or BMP file.
- 5. Always enter at least 5 valid analysis.

DEVELOPING LABORATORY DATA

A common question from WaterCycle Rx users is What should I use for an experimental design? French Creek Software recommends that the experimental designs for developing mathematical models for inhibitors include:

FIVE TEMPERATURES PREFERRED: Data should be run at a minimum of three temperatures to account for variation in dosage due to the effect of temperature on reaction rate. When possible, an experimental design should include five temperatures. The temperature range studied should include the lowest and highest temperatures expected in the field, or where the models generated by WaterCycle Rx.

THREE TO FIVE pH POINTS PREFERRED: Data should be run at a minimum of three different pH to account for variation in dosage due to the effect of pH on the form in which the inhibitor exists (see Hann and Bardsley). When possible, an experimental design should include five pH points. The pH range studied should include the lowest and highest expected in the field.

THREE TO FIVE INDUCTION PERIODS PREFERRED: Data should be run at a minimum of three different times to allow for the correlation of induction time versus inhibitor dosage. In some test methods, the times for each replicate will vary naturally. In other methods, dosages are evaluated at constant time extensions, and the last dosage to provide 100% inhibition is selected as the minimum effective dosage. Assure that the time spans covered by the data cover the full range over which you expect to use the model.

INCLUDE THE MINIMUM AND MAXIMUM FOR CRITICAL PARAMETERS:

Tests should ideally be run over the range of parameters under which the model will be used for inhibitor dosage recommendations. For example, the experimental design should include the minimum and maximum driving force where the model will be used. If a calcium carbonate inhibitor is being evaluated, the range of calcium and hardness levels anticipated should be bracketed as well as the range of calcite saturation levels.

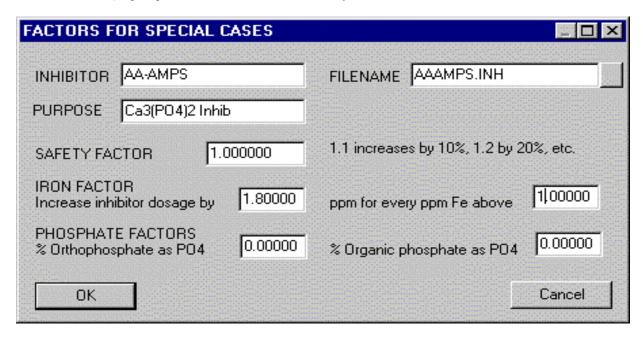
RUN SUPPLEMENTAL TESTS WHERE APPROPRIATE: Some inhibitors are known to lose activity in the presence of iron. Tests run in the presence and absence of iron can help to expand the accuracy of models by allowing an Iron Factor to be input using the Edit Coefficients module.

Several papers are referenced in the Appendix of this manual which outline test methods which have been used effectively to characterize the performance of inhibitors. Successful correlations can also be developed based upon the field experience of water treatment personnel have worked with an inhibitor over a broad range of conditions.

EDITING INHIBITOR FILES TO ADD SAFETY FACTORS

The EDIT COEFFICIENTS module in the Laboratory menu allows

- 1) adding a safety factor to a model;
- 2) adding a safety factor to account for iron; and
- 3) phosphate content of the inhibitor, if any



A 20% to 100% general safety factor (1.20 - 2.00) typically is added to account for scatter in the data.

The Iron Factor accounts for demand for polymer by iron in the cooling water.

Contact French Creek Software for custom editing of models, such as the combination of several discrete models into one correlation.

CURRENT & PAST WaterCycle Rx Models

Early versions of WaterCycle Rx provides four (4) fixed basic models as well as the current custom option for developing inhibitor correlations. The fixed options are included for historic perspective. The same models can be setup using the current custom option forms. Older models are updated to the custom format when imported into newer version of WaterCycle Rx. Older models are as follows:

- 1. **Model 0 Dosage = f(DF-1, time)** The first model develops a correlation of dosage as a function of driving force, temperature, and time, The driving force selected for this, or other models, should be appropriate for the scale forming species under study. For example, calcite saturation level is a common driving force used to model calcium carbonate scale inhibitors. Tricalcium phosphate saturation level is a recommended driving force for use in modeling the effectiveness of calcium phosphate control agents. Gypsum saturation level is recommended for modeling calcium sulfate control at low (< 130 °F) temperature, while anhydrite saturation level might be more appropriate at higher temperatures. This model subtracts 1.0 from the saturation levels. This accounts for the driving force for scale formation not being present until the test water becomes supersaturated at a saturation level above 1.0.
- 2. **Model 1 Dosage = f(DF, time)** The second model differs from the first in that the correlation is developed to the raw driving force rather than to the driving force 1.
- 3. **Model 2 Dosage = f(DF-1, time, pH)** The third model is identical to model 0 with one exception. pH is included as a variable to account for the impact of pH upon the form in which an inhibitor exists. This is typically the model of choice for developing a correlation for a scale inhibitor.
- 4. **Model 3 Corrosion Model** This method should be used to model the performance of a corrosion inhibitor versus water chemistry, temperature, and time. Data should be selected to be at a milestone for desired results. For example, all data might be collected at < 1.0 mpy, < 2 mpy, < 5 mpy, or another performance target. This will allow for the development of a model of dosage required to achieve the target mpy or less.

DEACTIVATING ANALYSIS FILES

There will be times when it is desired to perform a statistical modeling of the data with the results of one or more analysis excluded from the evaluation. This can be valuable in eliminating outliers to see their impact. Pressing the ACTIVATE or DE-ACTIVATE buttons when an analysis is on the screen ACTIVATES or DE-ACTIVATES an analysis. De-activating does not eliminate the data from the .COR file, it merely excludes it from statistical evaluation.

LEARNING THE LABORATORY MODULES

The best way to learn these modules is by using them. A .COR file is included for practice on modeling inhibitor performance and requirements.

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WaterCycle ® Rx LICENSE AGREEMENT

FRENCH CREEK SOFTWARE, INC. ("FRENCH CREEK") Kimberton & Hares Hill Road, Box 684 Kimberton, PA 19442

French Creek has developed the automated capability to predict certain chemical properties of water samples. French Creek refers to this computer software as WaterCycle Rx, sometimes referred to as WaterCycle Rx or System in this Agreement.

WaterCycle Rx is a predictive tool which will enable Customer to obtain a more complete understanding of the chemistry of the water being analyzed. WaterCycle Rx should be used as a supplement to Customer's historical experience and other testing procedures which Customer may utilize. WaterCycle Rx is not intended as a substitute for the exercise of judgment by Customer's employees or consultants.

These terms and conditions state the legally binding understandings between French Creek and Customer relating to the licensing of the System and the performance of services indicated in the French Creek Software Order Form ("Order Form"). The terms of this Agreement are incorporated by reference into the Order Form.

1. WaterCycle Rx

Customer desires to license WaterCycle Rx as indicated by Customer on the Order Form and more fully described in its accompanying documentation. The System documentation indicates the equipment configurations which may be used to operate WaterCycle Rx, and is hereby incorporated by reference. Customer should specify on the Order Form the number of copies of the System to be licensed under this Agreement.

2. DELIVERY AND SUPPORT

French Creek will ship the number of copies of WaterCycle Rx as indicated on the Order Form as well as System documentation upon French Creek's receipt and acceptance of an executed Order Form and accompanying fees. Delivery will be made at a mutually agreeable time, but no later than thirty (30) days after French Creek has accepted the Order Form. Payment of applicable fees is due upon execution of the Order Form.

WaterCycle Rx is capable of being installed by Customer by following the installation instructions in the documentation. As part of the license fee, French Creek provides 30 days of technical support. Technical support refers to assisting Customer to learn how to operate WaterCycle Rx, but does not include technical assistance in the interpretation of the various indices calculated by WaterCycle Rx. If additional assistance is required, French Creek will use its best efforts to assist Customer and will charge Customer for such services at its then current consulting charges.

3. PAYMENT

The fees and payment terms for the System and services are set forth in the Order Form.

Customer shall be responsible for the payment of any and all taxes or amounts paid in lieu thereof, however designated, levied or based on the System license granted hereunder or upon the services to be rendered or otherwise on account of this Agreement, exclusive only of taxes based on French Creek's net income.

French Creek reserves the right to terminate the System license for failure to pay related license fees or taxes, and/or to terminate any service for failure to pay related service fees or taxes, as stated in the Order Form.

4. CONDITIONS TO SYSTEM LICENSE

French Creek hereby grants Customer a license to operate the System, subject to the terms and conditions of this Agreement. The WaterCycle Rx license is a non-exclusive, non-transferable right to use the System. Failure to abide by any of the conditions stated in this Agreement may result in termination of the license granted in this Agreement.

The WaterCycle Rx license is subject to the following conditions:

(a) Customer acknowledges that the software and other technical data licensed hereunder are subject to export

controls imposed on Customer and French Creek by the provisions of the United States Export Administration Act of 1979, as amended, and that the software is exported under a General Export License, designation GTDR, and that the documentation is exported under a General License, designation GTDA. Customer certifies to French Creek that neither the technical data, (in the form of software or manuals), nor the direct product thereof is intended to be shipped, either directly, or indirectly, to Country Groups Q,S,W,Y, or Z, nor Afghanistan or the Peoples' Republic of China, without further compliance with the Validated License requirements of the Office of Export Administration, United States Department of Commerce. Customer agrees to use this technical data only at authorized destinations, and Customer will not knowingly permit exportation or transshipment in violation of the above law and regulations thereunder.

Customer agrees to indemnify and hold French Creek harmless from any and all costs, damages, fines, or other expenses incurred by French Creek by reason of Customer's violation of these representations of Customer.

- (b) Each copy of the System may only be used by Customer on one equipment work station as defined in the System documentation at any one time. Customer may not use or allow use of the System in any time-sharing or service bureau arrangement, or with any interactive cable system or local area network. Customer may only use the System for its own internal business or in servicing the business requirements of its clients for whom Customer performs services.
- (c) Customer shall not release, or allow the release of, the System or its related documentation, in any form to any third party, except to Customer's employees who are directly concerned with the licensed use of the System, except as otherwise specifically stated herein.
- (d) Customer shall not copy the System, except for purposes of normal backup and testing, without the prior written consent of French Creek. In the event that Customer copies the System or its accompanying documentation as stated herein, Customer agrees to also copy French Creek's copyright notices and/or other proprietary notices in the same manner, location and method of presentation as existed in the materials supplied by French Creek to Customer.
- (e)Other than as stated in this Agreement, Customer understands and agrees that it has no right, title or interest in the System, and agrees that it shall not attempt at any time to transfer its rights to use the System without the prior written consent of French Creek. Customer agrees that it will not use System, except as stated herein. Customer further agrees that it will not modify, decompile or disassemble the System, nor shall Customer incorporate the System into any updated or derivative work without the prior written consent of French Creek. For purposes of this Agreement, the term, "updated or derivative work", is intended to refer to the use of the System, either in whole or in part, in the development of some other system of work, whether or not such other system or work is operated by computer or otherwise. The term, "updated or derivative work", is not intended to refer to any interfaces or other methods of access to the System.

5. WARRANTY

For a period of thirty days following Customer's receipt of the System, French Creek warrants that Customer shall have the right to return the System and to receive a full refund of related license and initial maintenance fees (exclusive of travel, living and out-of-pocket expenses), if the System fails to operate substantially in accordance with the System documentation.

EXCEPT AS OTHERWISE STATED HEREIN, FRENCH CREEK MAKES NO REPRESENTATION OR WARRANTY (EXPRESS, IMPLIED OR STATUTORY) CONCERNING THE SYSTEM OR SERVICES PROVIDED HEREUNDER. FRENCH CREEK SPECIFICALLY DISCLAIMS ANY EXPRESS OR IMPLIED WARRANTY OF MERCHANTABILITY OR FITNESS FOR A PARTICULAR PURPOSE FOR SUCH SYSTEM OR SERVICE. CUSTOMER UNDERSTANDS AND AGREES THAT THE SYSTEM IS LICENSED STRICTLY ON AN "AS IS" BASIS.

The terms and conditions of this section shall survive any termination of this Agreement.

6. INDEMNITY

French Creek warrants that it has all necessary rights to license the System to Customer. French Creek agrees to indemnify, defend and hold Customer harmless for breach of such warranty, provided that, Customer gives French Creek prompt notice of a claim alleging such breach and, provided further, that French Creek shall have full

authority to defend, settle or compromise such claim. If the use of the System provided hereunder is prohibited based on a claim of infringement of another party's rights, then French Creek shall either:

- (a) procure the right for Customer to use such licensed System;
- (b) modify such portion of the System to become non-infringing, provided that such modification does not adversely affect Customer's intended use of the System as contemplated hereunder;
- (c) replace the infringing portions of the System with equally suitable, compatible and functionally equivalent non-infringing programs and/or other materials at no additional charge to Customer;
- (d) if none of the above are commercially practicable, then Customer shall terminate its use of the licensed System and accept from French Creek as compensation therefor all license fees paid

hereunder less an amount equal to such license fees, divided by 60, multiplied by the number of months of Customer's use of the System, commencing with the date of System delivery.

This warranty and indemnity shall not apply if Customer is in material breach of this Agreement and such breach gave rise to French Creek's liability hereunder. Similarly, this warranty and indemnity shall not apply if the basis for the infringement claim is due to the System being used in conjunction with software not supplied by French Creek hereunder, or which differs in any way from the software or equipment configuration specified in the documentation for use with the System.

This section states French Creek's entire liability concerning allegations that French Creek lacked the right to license the System hereunder. The terms and conditions of this section shall survive any termination of this Agreement.

7. CONFIDENTIAL INFORMATION

Customer acknowledges that the System and accompanying documentation constitute valuable and proprietary property of French Creek. Customer understands and agrees that French Creek may suffer irreparable harm in the event of any unauthorized disclosure of any portion of the System and/or its accompanying documentation which may substantially diminish the value of such System and documentation to French Creek. Therefore, Customer agrees not to disclose any portion of the System or accompanying documentation without the prior written consent of French Creek, except that Customer may disclose such materials (a) to employees of Customer who have a need to be familiar with the operation of the System or its accompanying documentation; (b) to any governmental agency with supervisory authority over Customer, or pursuant to compulsory legal process; or (c) to others in a strict confidential relationship with Customer. In this regard, Customer shall take all steps as are necessary or appropriate to fulfill this obligation.

In the event that Customer materially breaches its obligations under this section, Customer understands and agrees that French Creek has the right to terminate this Agreement upon written notification to Customer. Customer further agrees upon such termination to return to French Creek the original and all copies of the licensed System and related documentation. Furthermore, Customer acknowledges that French Creek shall be entitled to an injunction prohibiting the use and further disclosure of such licensed System and materials, and further entitled to money damages resulting from such unauthorized disclosure. The rights and remedies set forth herein are not exclusive and are in addition to any other rights and remedies provided by law, and the exercise of one right shall not preclude the exercise of any other right stated herein.

The terms and conditions of this section shall survive any termination of this Agreement.

8. MAINTENANCE

Customer may elect to have French Creek perform maintenance services for the System by so indicating on the Order Form. Maintenance services will commence upon Customer's execution of the Order Form and French Creek's receipt of the appropriate maintenance fee. Maintenance services will be provided for an initial term of one year, and will renew for additional one year terms unless either party gives 60 days prior written notice of its intention to terminate such services. Fees for renewal terms of maintenance services will be calculated as a percentage of the then current license fee for the System at time of renewal.

Under maintenance, French Creek will provide Customer with periodic releases of the System that will include minor enhancements as well as modifications to keep the System operating in accordance with its accompanying documentation. Prior releases of the System will be supported for three (3) months after a new release becomes available to Customer.

Support services under maintenance include telephone consultation and other reasonable services necessary to keep the System (as supplied by French Creek) performing in accordance with its documentation. These services will be performed during French Creek's normal East Coast (US) business hours. Ordinarily, French Creek will be able to correct the problem over the telephone. However, if requested by French Creek, Customer will document the circumstances giving rise to such problem and provide such explanation to French Creek in writing. If French Creek is unable to correct the problem within 48 business hours of receipt of such written explanation and such problem prevents normal operation of the System consistent with its documentation, French Creek will provide Customer with another copy of the System to help resolve the problem. If it is determined that the problem was caused by Customer or that Customer failed to properly follow French Creek's directions, French Creek shall be entitled to be reimbursed for all out-of-pocket expenses, plus consulting time at French Creek's then current billing rates.

If Customer declines maintenance at time of licensing or fails to continue maintenance services, and then elects to begin or resume maintenance coverage, Customer shall pay to French Creek all maintenance fees that would have been payable to French Creek if Customer had been or remained on maintenance plus an additional 10% reinstatement fee.

Customer may also request that French Creek provide other future modifications and enhancements under a separate agreement for such services.

The terms and conditions of this section state French Creek's entire responsibility to provide maintenance services hereunder.

9. UNINTENDED USE

Customer agrees that it will use the System as supplied by French Creek only for the purposes and in the manner set forth in this Agreement and accompanying documentation. In the event that Customer breaches its responsibility under this section or if Customer is not using the System in accordance with its documentation, then French Creek will have no further obligation to provide technical support or maintenance services hereunder and Customer shall not be entitled to a refund of any amount paid to French Creek. In certain circumstances, French Creek may also have the right to terminate this Agreement.

10. LIMITATION OF LIABILITY

French Creek's liability during the 30 day period following delivery of the System shall be limited to attempting to repair any System error condition, or to accept return of the System and refund to Customer all related license and initial maintenance fees, exclusive of travel, living and out-of-pocket expenses, paid to French Creek on account of this Agreement. Thereafter, French Creek's liability to Customer shall not exceed the amount of license fees paid to French Creek on account of the System. French Creek shall have no liability to Customer for damages resulting from causes beyond French Creek's reasonable control.

IN NO EVENT WILL FRENCH CREEK BE LIABLE FOR ANY SPECIAL, INDIRECT OR CONSEQUENTIAL DAMAGES (INCLUDING LOSS OF PROFITS OR GOODWILL) ARISING FROM OR IN CONNECTION WITH THE SYSTEM OR SERVICES PROVIDED UNDER THIS AGREEMENT, EVEN IF FRENCH CREEK IS ADVISED OF THE POSSIBILITY OF SUCH DAMAGES.

THIS SECTION STATES CUSTOMER'S EXCLUSIVE REMEDIES UNDER THIS AGREEMENT. THIS SECTION SHALL SURVIVE ANY TERMINATION OF THIS AGREEMENT.

11. TERM AND TERMINATION

The license granted in this Agreement is for a term of twenty (20) years, or until sooner terminated as stated herein. Upon termination, Customer shall return to French Creek the original and all copies of the licensed System and related documentation, or certify in writing to French Creek the destruction of such materials. French Creek reserves the right to terminate any service provided hereunder as stated herein or in the Order Form.

12. GENERAL

- (a) AMENDMENT: No amendment or supplement to this Agreement shall be binding unless consented to in writing and signed by both parties, provided that such consent shall not be unreasonably withheld. The party requesting any consent under this Agreement shall reimburse the other party for any expenses, including attorneys' fees, which result from the request for consent.
- (b) ASSIGNMENT: Neither party may assign, sub-license, sub-lease, lend, rent or otherwise transfer this Agreement or the rights granted hereunder to any person, whether by operation of law or otherwise, without the other party's prior written consent, which consent shall not be unreasonably denied, PROVIDED HOWEVER, that no consent shall be required for any assignment or transfer Pursuant to any merger, consolidation or reorganization to which either Customer or French Creek is a party. This Agreement shall bind and inure to the benefit of any such successor or assign. The license granted hereunder shall not be assigned or assignable in any proceeding involving the liquidation of Customer.
- (c) RELATIONSHIP OF THE PARTIES: It is clearly understood between the parties that at all times during this Agreement that the relationship between French Creek and Customer is solely as independent contractors and in no other capacity. The parties agree that there are no intended or incidental third party beneficiaries of this Agreement.
- (d) COST OF ENFORCEMENT: If either party is required to engage in legal proceedings to enforce the obligations of the other, in law or in equity, the prevailing party shall be entitled to reasonable attorneys' fees and all related necessary and reasonable costs and expenses.
- (e) SEVERABILITY: In the event that any one or more of the provisions of this Agreement shall for any reason be held to be invalid, illegal or unenforceable, the remaining provisions of this Agreement shall be unimpaired, and the invalid, illegal or unenforceable provisions shall be replaced by a mutually acceptable provisions, which being valid and legally enforceable, comes closest to the intention of the parties underlying the invalid, illegal or unenforceable provision. If this Agreement or any provisions hereof are held to be invalid, illegal or unenforceable under the laws of a particular jurisdiction, it is the intention of the parties that all of the provisions of this Agreement shall remain in full force and effect in all other states and jurisdictions.
- (f) ATTACHMENTS: The terms and conditions of the attachments and Exhibits to this Agreement are incorporated herein by this reference and shall constitute a part of this Agreement as if fully set forth herein.
- (g) HEADINGS: The section headings in this Agreement are for the purposes of reference only

and shall not limit or otherwise affect any of the terms hereof.

- (h) AUTHORITY: Both parties warrant that all approvals necessary for the execution of this Agreement have been obtained, and that the individuals signing the Order Form on behalf of their respective parties have full authority to do so.
- (i) NOTICES:Unless otherwise provided herein, all notices or other communications under this Agreement must be in writing and signed by a duly authorized representative of the party giving such notice, or such other persons as either party shall specify in a written notice to the other. All such notices shall be deemed given and received when delivered by hand, or placed in the mails addressed to the other party, first class registered mail, postage prepaid, at the addresses indicated following the signatures of the parties on the Order Form or such other addresses as may be specified in writing.
- (j) ENTIRE AGREEMENT: The terms and conditions stated herein constitute the entire and exclusive agreement between the parties for the System, and no other statements, unless agreed to in writing, shall be binding upon the parties. No statement of any marketing representative shall be binding on French Creek, unless set forth in writing and agreed to by French Creek. This Agreement shall be effective only after its acceptance by French Creek at its offices in Pennsylvania.
- (k) GOVERNING LAW: This Agreement shall be governed and construed in accordance with the laws of the Commonwealth of Pennsylvania.

TECHNICAL SUPPORT

Via e-mail

frenchcreek@worldnet.att.net

At Our Web Site

http://www.frenchcreeksoftware.com

By Telephone

Voice (610) 935-8337 FAX (610) 935-1008

SOFTWARE UPDATES

At Our Web Site

Registered users with active Annual Maintenance Agreements can download updates from our web site. A USER ID and PASSWORD is required.

To register for a USER ID and PASSWORD Visit our web site and REGISTER FOR UPDATES

To download updates, visit the LICENSED USER DOWNLOAD AREA http://www.frenchcreeksoftware.com

FAST TRACK INSTALLATION

Insert the diskette in floppy drive A: or B:

Execute the program **SETUP.EXE** from FILE MANAGER

or

Use the Windows RUN command to SETUP.EXE launch

Be sure to install to the **WATER** directory, e.g. C:\WATER or D:\WATER ... Z:\WATER

To Execute WaterCycle R

Click on the Cooling Tower icon (or use the run command for **WATERWATWIN.EXE**)

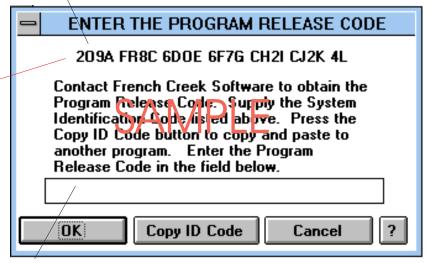
Click on the START Button in Win95/98/2000/Me/XP or NT and select the WaterCycle icon in the French Creek program group

The Security System

The software is protected against unauthorized access. To activiate the software, you must obtain a **Program Release Code** from French Creek Software. The following dialog box will appear when the software is run prior to activating with a **Program Release Code**.

System Identification Code (submit the actual System ID displayed on your computer to French Creek to receive your computer/installation specific Program Release Code)

Example - A System ID specific to your computer and installation will be displayed. Submit the actual ID displayed on YOUR computer.



Enter Program Release Code Here (Calculated from System ID by French Creek)

TO OBTAIN A COMPUTER SPECIFIC PROGRAM RELEASE CODE:

1) Copy the 26 character System Identification Code. This System Identification will be displayed when you run the software, until a Program Release Code is entered. Each system will have a unique System Identification Code. YOU MUST SUBMIT THE SYSTEM ID DISPLAYED ON YOUR COMPUTER – NOT THE ID IN THIS MANUAL

2) Send this code to French Creek Software

BY FAX TO (610) 935-1008 BY E-MAIL TO frenchcreek@worldnet.att.net (preferred method) BY VOICE TO (610) 935-8337

3) French Creek will respond with a System Release Code

HELPFUL HINTS

Press the COPY ID CODE button to copy the System Identification Number to the Windows clipboard.

Start an application such as a Word Processor or E-Mail program.

Paste the System Identification Number into the application.

You might wish to Paste the number into the Subject field of an E-Mail. Or you might wish to paste it into the subject field of a FAX.