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COMPUTER MODELING OF BLENDED STREAMS FOR WATER REUSE AND DISCHARGE

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Computer Modeling Of Blended Streams For Water Reuse And Discharge

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Optimizing water usage within a facility is a formidable task. Mixing of available water sources within a plant can help to minimize discharge and maximize water reuse. Computer modeling of blended streams and their impact upon maximum cycles and treatment options is discussed. Operating cooling systems at higher cycles can also lead to the formation of scales previously not common in cooling systems. A visual chemistry approach is used for data presentation to clearly define options and safe ranges.

Mixing

Predicting the properties of blended waters combines straightforward chemistry, common sense, and linear algebra with sophisticated physical chemistry. Mixing calculations include:

- Simple mixing
- Mixing with pH controlled by a weak acid
- Mixing with pH controlled by weak acids
- Mixing several waters

Mixing calculations differ for “closed” and “open” systems. Calculations for mixing must account for CO₂ exchange with the atmosphere if mixed in a system open to the atmosphere, or in a closed environment where CO₂ builds up in the system and does not flash to the atmosphere. The prediction of scale in cooling systems must also be done at different cycles of concentration, so that the impact of different blends can be modeled. As systems are cycled to new heights and lower quality water sources are used for make-up, scales such as Barite (BaSO₄) and celestite (SrSO₄) should be included in evaluations.

Simple Mixing

In the simplest case, mixing of two NaCl solutions provides a straightforward example. Solutions will be described on a weight basis.

$$\text{Eq 1)} \quad [\text{NaCl}]_{\text{mix}} = (\% \text{ one}/100) [\text{NaCl}]_{\text{one}} + (\% \text{ two}/100) [\text{NaCl}]_{\text{two}}$$

or including volumes and specific gravity

$$\text{Eq 2)} \quad [\text{NaCl}]_{\text{mix}} = \frac{V_{\text{one}} \times \text{Specific Gravity}_{\text{one}} [\text{NaCl}]_{\text{one}} + V_{\text{two}} \times \text{Specific Gravity}_{\text{two}} [\text{NaCl}]_{\text{two}}}{V_{\text{one}} \times \text{Specific Gravity}_{\text{one}} + V_{\text{two}} \times \text{Specific Gravity}_{\text{two}}}$$

or using flows and specific gravity

$$\text{Eq 3)} \quad [\text{NaCl}]_{\text{mix}} = \frac{\text{Flow}_{\text{one}} \times \text{Specific Gravity}_{\text{one}} [\text{NaCl}]_{\text{one}} + \text{Flow}_{\text{two}} \times \text{Specific Gravity}_{\text{two}} [\text{NaCl}]_{\text{two}}}{\text{Flow}_{\text{one}} \times \text{Specific Gravity}_{\text{one}} + \text{Flow}_{\text{two}} \times \text{Specific Gravity}_{\text{two}}}$$

These calculations are as straightforward as a junior high math problem in percentages. It is of note that the calculations can be done for mixing based upon percent, volume, or flows. In many cases, a specific gravity of 1.0 can be used for practical water treatment problems. The simple case is limited to waters where no reaction occurs, where precipitation does not occur, and where a buffer system is not present.

Mixture calculations become more interesting when a weak acid, such as carbonic acid is present.

Mixing with a weak acid present

Most waters treatment chemists work with will be under pH control of a carbonic acid buffering system. The easiest way to predict the pH of a final mixture is by using a pH-alkalinity-acidity diagram.^(1,2) Iterative solutions to the equations involved can also be setup using the computer power available today. The pH of the mixture can be derived in the following manner for as many waters as are mixed.

$$\text{Eq 4)} \quad \text{Alkalinity}_{\text{mix}} = R_{\text{one}} \times \text{Alkalinity}_{\text{one}} + R_{\text{two}} \times \text{Alkalinity}_{\text{two}} + \dots R_n \times \text{Alkalinity}_n$$

$$\text{Eq 5)} \quad \text{Acidiity}_{\text{mix}} = R_{\text{one}} \times \text{Acidity}_{\text{one}} + R_{\text{two}} \times \text{Acidity}_{\text{two}} + \dots R_n \times \text{Acidity}_n$$

$$\text{Eq 6)} \quad \text{Ct}_{\text{mix}} = R_{\text{one}} \times \text{Ct}_{\text{one}} + R_{\text{two}} \times \text{Ct}_{\text{two}} + \dots R_n \times \text{Ct}_n$$

Alkalinity and acidity are the analytical values for the titrations

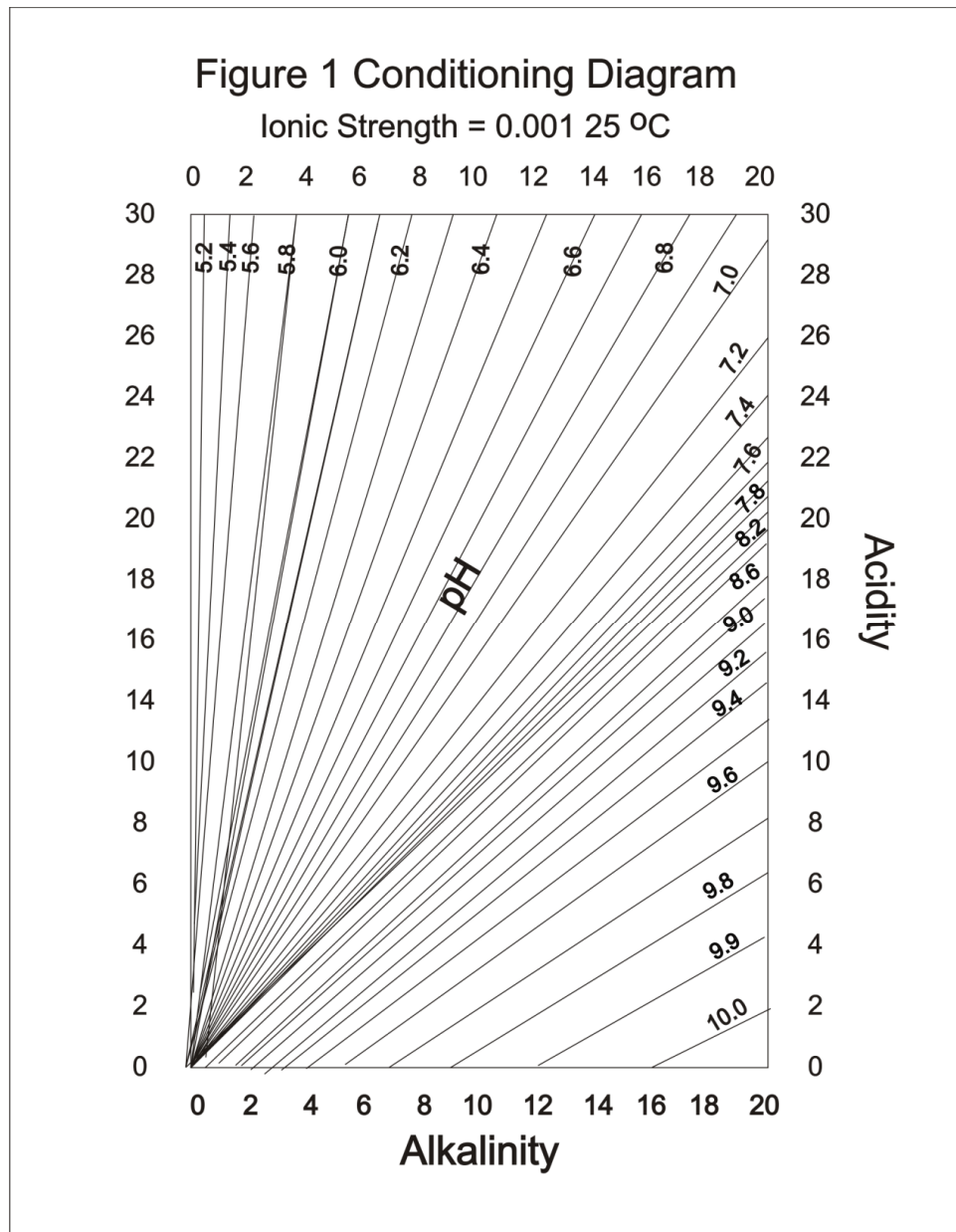
- to the H_2CO_3 equivalence point with a standardized strong acid for alkalinity
- to the Na_2CO_3 equivalence point with a standardized strong base for acidity.

Ct is total carbonic acid species..

$$\text{Eq 7)} \quad \text{Ct} = [\text{H}_2\text{CO}_3] + [\text{HCO}_3^-] + [\text{CO}_3^{2-}]$$

The pH can be read directly from an alkalinity / acidity / pH conditioning diagram (Figure 1) or from an alkalinity, Ct, pH diagram. If two of the parameters are known, the third can be readily calculated.^(1,2,3)

A detailed discussion on the derivation of the conditioning diagrams is available in reference 1, (Loewenthal and Marais). Calculation of the distribution of H_2CO_3 , HCO_3^- , and CO_3^{2-} from alkalinity or Ct is covered elegantly in reference 3, Stumm and Morgan.



Closed versus Open Systems

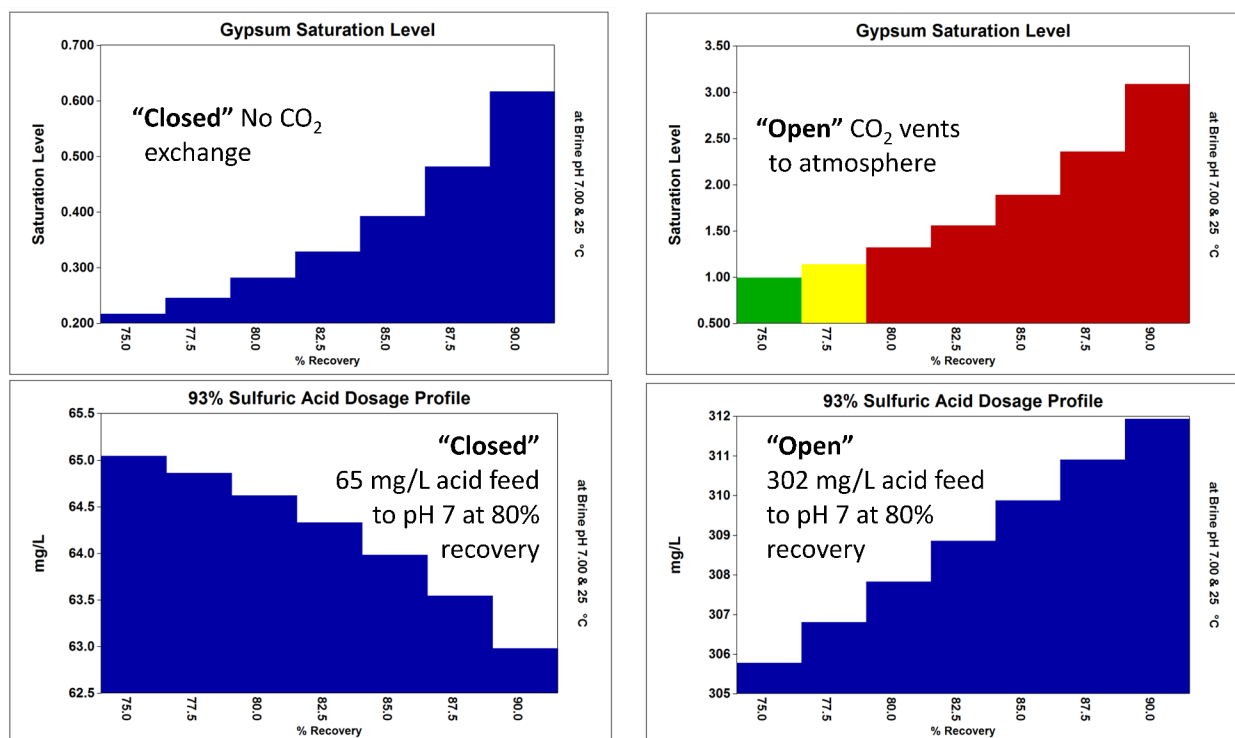
When a water is mixed in an open aerated environment, and CO_2 gas is exchanged freely between the water and the atmosphere, the system is termed an “Open” system. An open recirculating cooling system (cooling tower) provides a frequent example for an “Open” system. When a water is in a closed environment where CO_2 gas cannot exchange freely between the water and the atmosphere, the system is called a “Closed” system. A gas tight reverse osmosis system is such a closed system.

In an “Open” system, alkalinity and acidity are conserved as CO_2 is exchanged with the atmosphere to maintain charge balance. Total molar carbon (Ct) is not necessarily conserved. A classic case would be the re-carbonation of cold lime softened water. Hydroxide alkalinity is replaced by carbonate alkalinity as CO_2 is introduced into the water. Ct increases. Alkalinity, and acidity, remain constant. This assumes that alkalinity is not precipitated.

In a closed system, Ct is conserved. Alkalinity and acidity float to maintain balance. It is, again, assumed that no precipitation occurs.

The calculations involved in pH prediction, and acid feed, are different for closed versus open systems. Calculations performed for "closed" systems assume that CO_2 produced by acid addition builds up in the system. Calculations performed for "open" systems assume that CO_2 produced by acid addition is removed from the system. Figure 2 compares acid requirements, and the resultant sulfate contributions, for pH control in a "closed" versus "open" system.

Figure 2: pH Control in Closed versus Open Systems



In this case it can be seen that approximately five times as much acid is required for an "open" system than for a "closed" system. The difference is sufficient to create a calcium sulfate scale problem. Modeling software should be capable of treating a system as "closed" or "open" to assure that sulfate scale potential is evaluated accurately.

Scale Prediction and the Concept of Saturation

A majority of the indices used routinely by water treatment chemists are derived from the basic concept of saturation. A water is said to be saturated with a compound (e.g. calcium carbonate) if it will not precipitate the compound and it will not dissolve any of the solid phase of the compound when left undisturbed, under the same conditions, for an infinite period of time. A water which will not precipitate or dissolve a compound is at equilibrium for the particular compound.

By definition, the amount of a chemical compound which can be dissolved in a water and remain in solution for this infinite period of time is described by the solubility product (K_{sp}). In the case of calcium carbonate, solubility is defined by the relationship:

$$(Ca)(CO_3) = K_{sp}$$

where

- (Ca) is the activity of calcium
- (CO_3) is the carbonate activity
- K_{sp} is the solubility product for calcium carbonate at the temperature under study.

In a more generalized sense, the term $(Ca)(CO_3)$ can be called the Ion Activity Product (IAP) and the equilibrium condition described by the relationship:

$$IAP = K_{sp}$$

It can be shown that the Langelier Saturation Index is the base ten logarithm of calcite saturation level based upon total calcium in the water, an estimate of carbonate calculated from total alkalinity, and the solubility product for the calcite polymorph of calcium carbonate. ^(3,4)

The degree of saturation of a water is described by the relationship of the ion activity product (IAP) to the solubility product (K_{sp}) for the compound as follows:

- If a water is undersaturated with a compound: **$IAP < K_{sp}$**
(It will tend to dissolve the compound).
- If a water is at equilibrium with a compound: **$IAP = K_{sp}$**
(It will not tend to dissolve or precipitate the compound).
- If a water is supersaturated with a compound: **$IAP > K_{sp}$**
(It will tend to precipitate the compound).

The index called Saturation Level, Degree of Supersaturation, or Saturation Index, describes the relative degree of saturation as a ratio of the ion activity product (IAP) to the solubility product (Ksp):

$$\text{Saturation Level} = \frac{\text{IAP}}{\text{Ksp}}$$

In actual practice, the saturation levels calculated by the various computer programs available differ in the method they use for estimating the activity coefficients used in the IAP; they differ in the choice of solubility products and their variation with temperature; and they differ in the dissociation constants used to estimate the concentration of reactants (e.g. CO₃ from analytical values for alkalinity, PO₄ from analytical orthophosphate).^(6,7,8,9,10,11,12,13)

Table 1 defines the saturation level for common scale forming species and provides the basis for their discussion in this paper. Simple indices use analytical values for the ions, e.g. Ca.^(4,5,6,7) For example, by definition, the Langelier Saturation Index is the base ten logarithm of saturation level if calculated a) using analytical values rather than free ion concentrations, b) using an alkalinity which is not corrected for non-carbonate alkalinity, and c) using simple activity coefficients.⁽⁴⁾

Ion Association Reduces Available Ion Concentration

Ions in solution are not all present as the free species. For example, calcium in water is not all present as free Ca.⁺² Other species form which are not available as driving forces for scale formation. Examples include the soluble calcium sulfate species, hydroxide species, and bicarbonate - carbonates. Table 2 outlines example species that can be present in a typical water.

Speciation of a water is time prohibitive without the use of a computer for the iterative number crunching required. The process is iterative and involves:

1. Checking the water for a electroneutrality via a cation-anion balance, and balancing with an appropriate ion (e.g sodium or potassium for cation deficient waters, sulfate, chloride, or nitrate for anion deficient waters).
2. Estimating ionic strength, calculating and correcting activity coefficients and dissociation constants for temperature, correcting alkalinity for non-carbonate alkalinity.
3. Iteratively calculating the distribution of species in the water from dissociation constants (a partial listing is outlined in Table 1).
4. Checking the water for balance and adjusting ion concentrations to agree with analytical values.
5. Repeating the process until corrections are insignificant.
6. Calculating saturation levels based upon the free concentrations of ions estimated using the ion association model (ion pairing).

TABLE 1 - SATURATION LEVEL FORMULAS

Calcium carbonate	$S.L. = \frac{(Ca)(CO_3)}{K_{sp} CaCO_3}$
Barium carbonate	$S.L. = \frac{(Ba)(CO_3)}{K_{sp} BaCO_3}$
Strontium carbonate	$S.L. = \frac{(Sr)(CO_3)}{K_{sp} SrCO_3}$
Calcium sulfate	$S.L. = \frac{(Ca)(SO_4)}{K_{sp} CaSO_4}$
Barium sulfate	$S.L. = \frac{(Ba)(SO_4)}{K_{sp} BaSO_4}$
Strontium sulfate	$S.L. = \frac{(Sr)(SO_4)}{K_{sp} SrSO_4}$
Tricalcium phosphate	$S.L. = \frac{(Ca)^3(PO_4)^2}{K_{sp} Ca_3(PO_4)_2}$
Amorphous silica	$S.L. = \frac{H_4SiO_4}{(H_2O)^2 * K_{sp} SiO_2}$
Calcium fluoride	$S.L. = \frac{(Ca)(F)^2}{K_{sp} CaF_2}$
Magnesium hydroxide	$S.L. = \frac{(Mg)(OH)^2}{K_{sp} Mg(OH)_2}$

The use of ion pairing to estimate the free concentrations of reactants overcomes several of the major shortcomings of traditional indices. Indices such as the LSI correct activity coefficients for ionic strength based upon the total dissolved solids. They do not account for "common ion" effects.⁽⁸⁾ Common ion effects increase the apparent solubility of a compound by reducing the concentration of reactants available. A common example is sulfate reducing the available calcium in a water and increasing the apparent solubility of calcium carbonate. The use of indices which do not account for ion pairing can be misleading when comparing waters where the TDS is composed of ions which pair with the reactants versus ions which have less interaction with them.

When indices are used to establish operating limits such as maximum cycles or maximum pH, the differences between the use of indices calculated using ion pairing can be of extreme economic significance. In the best case, a system is not operated at as high a concentration ratio as possible, because the use of indices based upon total analytical values resulted in high estimates of the driving force for a scalant. In the worst case, the use of indices based upon total ions present can result in the establishment of operating limits too high. This can occur when experience on a system with high TDS water is translated to a system operating with a lower TDS water. The high indices which were found acceptable in the high TDS water may be unrealistic when translated to a water where ion pairing is less significant in reducing the apparent driving force for scale formation.

**Figure 3: ION PAIRING REDUCES LSI
(Sulfate Effect Greater Than Chloride)**

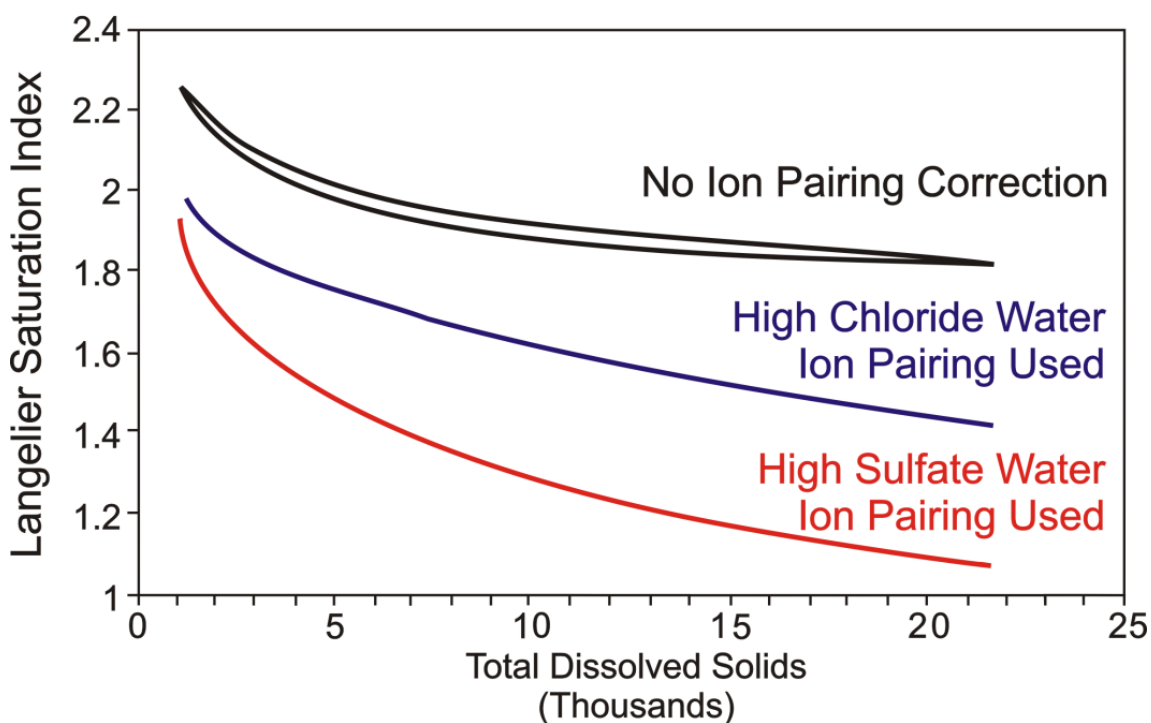


Figure 3 compares the impact of sulfate and chloride on scale potential. The curves profile the calculation of the Langelier Saturation Index in the presence of high TDS. In one case the TDS is predominantly from a high chloride water. In the other case, a high sulfate water is profiled. Profiles for the index calculated based upon total analytical values are compared with those calculated with ion association model free ion activities.

This paper uses ion association model saturation levels to represent scale potential so that the limits described can be translated directly to both high and lower TDS waters, low and high

sulfate waters. Each chemistry evaluation accounts for over 120 ion pairs. Table 2 outlines some of the ion pairs used in the model.

Table 2: Example Ion Pairs Used To Estimate Free Ion Concentrations

CALCIUM

$$[\text{Calcium}] = [\text{Ca}^{+II}] + [\text{CaSO}_4] + [\text{CaHCO}_3^{+I}] + [\text{CaCO}_3] + [\text{Ca(OH)}^{+I}] + [\text{CaHPO}_4] + [\text{CaPO}_4^{-I}] + [\text{CaH}_2\text{PO}_4^{+I}]$$

MAGNESIUM

$$[\text{Magnesium}] = [\text{Mg}^{+II}] + [\text{MgSO}_4] + [\text{MgHCO}_3^{+I}] + [\text{MgCO}_3] + [\text{Mg(OH)}^{+I}] + [\text{MgHPO}_4] + [\text{MgPO}_4^{-I}] + [\text{MgH}_2\text{PO}_4^{+I}] + [\text{MgF}^{+I}]$$

BARIUM

$$[\text{Barium}] = [\text{Ba}^{+II}] + [\text{BaSO}_4] + [\text{BaHCO}_3^{+I}] + [\text{BaCO}_3] + [\text{Ba(OH)}^{+I}]$$

STRONTIUM

$$[\text{Strontium}] = [\text{Sr}^{+II}] + [\text{SrSO}_4] + [\text{SrHCO}_3^{+I}] + [\text{SrCO}_3] + [\text{Sr(OH)}^{+I}]$$

SODIUM

$$[\text{Sodium}] = [\text{Na}^{+I}] + [\text{NaSO}_4^{-I}] + [\text{Na}_2\text{SO}_4] + [\text{NaHCO}_3] + [\text{NaCO}_3^{-I}] + [\text{Na}_2\text{CO}_3] + [\text{NaCl}] + [\text{NaHPO}_4^{-I}]$$

POTASSIUM

$$[\text{Potassium}] = [\text{K}^{+I}] + [\text{KSO}_4^{-I}] + [\text{KHPO}_4^{-I}] + [\text{KCl}]$$

IRON

$$[\text{Iron}] = [\text{Fe}^{+II}] + [\text{Fe}^{+III}] + [\text{Fe(OH)}^{+I}] + [\text{Fe(OH)}^{+II}] + [\text{Fe(OH)}_3^{-I}] + [\text{FeHPO}_4^{+I}] + [\text{FeHPO}_4] + [\text{FeCl}^{+II}] + [\text{FeCl}_2^{+I}] + [\text{FeCl}_3] + [\text{FeSO}_4] + [\text{FeSO}_4^{+I}] + [\text{FeH}_2\text{PO}_4^{+I}] + [\text{Fe(OH)}_2^{+I}] + [\text{Fe(OH)}_3] + [\text{Fe(OH)}_4^{-I}] + [\text{Fe(OH)}_2] + [\text{FeH}_2\text{PO}_4^{+II}]$$

ALUMINUM

$$[\text{Aluminum}] = [\text{Al}^{+III}] + [\text{Al(OH)}^{+II}] + [\text{Al(OH)}_2^{+I}] + [\text{Al(OH)}_4^{-I}] + [\text{AlF}^{+II}] + [\text{AlF}_2^{+I}] + [\text{AlF}_3] + [\text{AlF}_4^{-I}] + [\text{AlSO}_4^{+I}] + [\text{Al(SO}_4)_2^{-I}]$$

Total Analytical Value

Free Ion Concentration

MYSTERY SCALES

Mystery scales are not so mysterious in other areas of water treatment. Both BaSO₄ and SrSO₄ are commonly evaluated in oil field and reverse osmosis applications. But Barium sulfate and strontium sulfate are not scales typically found in, or analyzed for, in cooling water systems. Their formation would not be expected in cooling systems operated in traditional concentration ratio ranges, using fresh water makeup. As concentration ratio increases, and/or less desirable waters are used for make-up, barium and strontium based scales can become troublesome.

The chemistry of barite (BaSO_4) compares to calcite (CaCO_3) as follows:

- Barite solubility increases with temperature, as opposed to the inverse temperature solubility of calcium carbonate.
- Barite solubility is for the most part pH independent as opposed to the high pH dependence of calcium carbonate.
- Barite solubility is lower than calcium carbonate.

Celestite (SrSO_4) chemistry compares to calcite (CaCO_3):

- Celestite solubility decreases with temperature, like calcium carbonate.
- Celestite solubility, like that of barite, is for the most part pH independent as opposed to the high pH dependence of calcium carbonate.
- Celestite solubility is higher than calcium carbonate.

Pure barite or celestite scale is not typically encountered in operating systems. Most barite scales will contain strontium within the crystal lattice.¹⁸

Figures 4 and 5 show the impact of low levels of barium and strontium in a make-up water upon BaSO_4 and SrSO_4 scale potential. It is of interest that 0.007 mg/L of barium in a make-up water will not cause a problem in the a typical surface water analysis in the concentration ratio range of 1 to 5 cycles. Pushing the concentration ratio above ten times can create a previously unencountered scale. It is recommended that barium and strontium be included in the analysis of make-up waters for use in systems to be operated at high cycles, or when new water sources from reuse are to be concentrated.

Table 2 compares the solubility of common scales at 25°C and 50 °C, and provides a note on the general solubility trends as temperature increases. Please note that the solubilities are shown as solubility product and as the compound. The compound values are for reference only. Please note that solubility trends are more complicated than two points can demonstrate. Gypsum solubility, for example, increases with temperature to the 20°C to 30°C range and then decreases with further increase in temperature.

Different forms may also be expected in different temperature ranges. For example, gypsum is expected at lower temperatures, while anhydrite would form preferentially at higher temperatures.

FIGURE 4: THE IMPACT OF EXTREMELY LOW BARIUM IN MAKE-UP

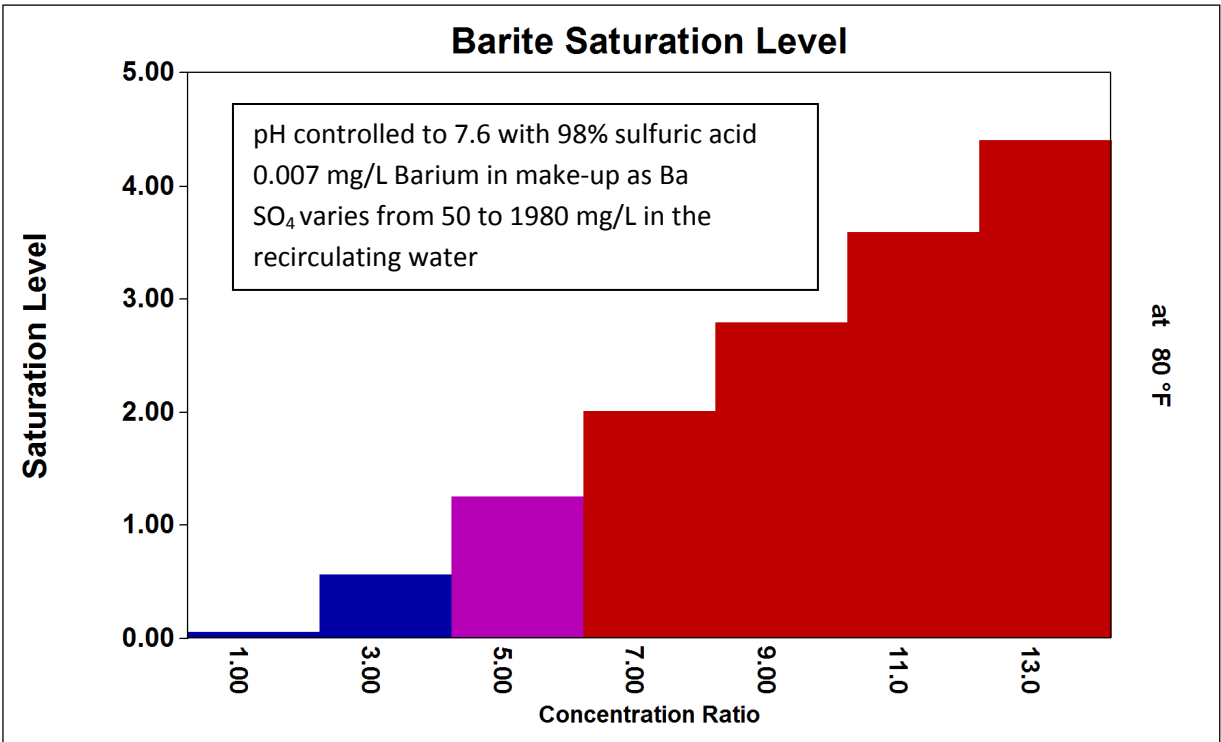


FIGURE 5: THE IMPACT OF STRONTIUM IN MAKE-UP

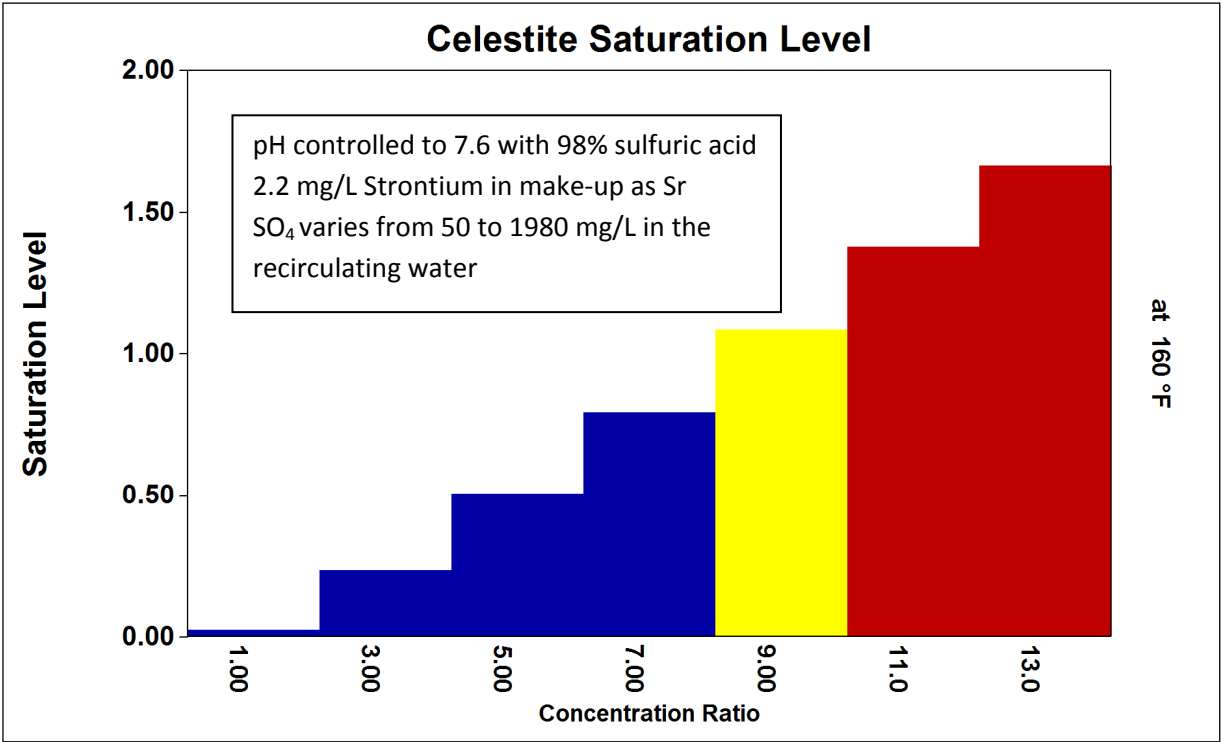


TABLE 3: SOLUBILITY PRODUCT COMPARISON					
SCALE FORMING SPECIE	FORMULA	MINERAL	Ksp 25°C (mg/L)	Ksp 50°C (mg/L)	Solubility Change As Temperature Increases
Calcium carbonate	CaCO ₃	Calcite	4.27e-9 (6.84)	2.81e-9 (3.81)	Decreases
Calcium sulfate	CaSO ₄ *2H ₂ O	Gypsum	2.62e-5 (881)	2.42e-5 (778)	Increases then Decreases
Barium sulfate	BaSO ₄	Barite	1.07e-10 (2.20)	2.16e-10 (5.75)	Increases
Strontium sulfate	SrSO ₄	Celestite	2.23e-7 (89.6)	1.85e-7 (63.6)	Increases then Decreases
Silica	SiO ₂	Amorphous silica	1.95e-3 (103)	3.48e-3 (209)	Increases
Tricalcium phosphate	Ca ₃ (PO ₄) ₂		2.00e-29 (0.56)	4.68e-30 (0.42)	Decreases

The same scale inhibitors that are effective against calcium carbonate and calcium sulfate are usually also effective in controlling strontium and barium derived scales. Limits are compared in Table 4. Scale inhibitors have not been observed to be effective above the upper limit, regardless of dosage.

TABLE 4: TREATED LIMITS COMPARISON				
SCALE FORMING SPECIE	FORMULA	MINERAL NAME	TYPICAL SATURATION RATIO LIMIT	STRESSED TREATMENT LIMIT
Calcium carbonate	CaCO ₃	Calcite	135 - 150	200 - 225
Calcium sulfate	CaSO ₄ *2H ₂ O	Gypsum	2.5 - 4.0	4.0 +
Barium sulfate	BaSO ₄	Barite	80	80
Strontium sulfate	SrSO ₄	Celestite	12	12
Silica	SiO ₂	Amorphous silica	1.2	2.5
Tricalcium phosphate	Ca ₃ (PO ₄) ₂		1500 - 2500	125,000

BLENDING MAKE-UP

The use of blended water sources is increasing as facilities work towards maximizing water reuse and minimizing discharge . This example describes blending a municipal water to maximize cycles in an open recirculating cooling system. An ion association model system was used to project scale potential of cycled water and to determine the limiting factors maximum cycles. so the water source used, or the mix ratio, also has an economic impact upon non-regulated uses.

A further constraint was placed upon this system: the blended water is also used as a potable water source. Federal and state governments mandate that municipal water providers treat their water to

provide lead and copper levels below certain limits. The current EPA action levels for Pb and Cu are 15 ppb and 1.3 mg/L respectively. Calculating the maximum lead and copper solubility has been used as a method for optimizing treatment and blending to minimize lead and copper levels. In some cases computer simulation of the maximum soluble levels has been accepted by authorities in lieu of rigorous field testing.⁽¹⁹⁾

A municipality switches between surface water and well water source and mixes in various ratios. This water is also used as cooling tower make-up. The blended water is summarized in Table 5. As depicted in Table 6. The well water source has a high solubility for lead and copper, above the current EPA action limits. Blending the waters, and avoiding high ratios of well water to surface water, can reduce the maximum solubility of lead and copper below the action limits.

TABLE 5: MIXED WATER CHEMISTRY AT VARIOUS RATIOS

	Water One – Surface Source Water Two – Well Source						
	% SURFACE WATER						
CATIONS	0.00	16.67	33.33	50.00	66.67	83.33	100.00
Calcium (as CaCO ₃)	140.00	119.00	98.00	77.00	56.00	35.00	14.00
Magnesium (as CaCO ₃)	30.00	26.67	23.33	20.00	16.67	13.33	10.00
Sodium (as Na)	0.00	1.67	3.33	5.00	6.67	8.33	10.00
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
Manganese (as Mn)	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Ammonia (as N)	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
Zinc (as Zn)	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)	12.00	10.50	9.00	7.50	6.00	4.50	3.00
Sulfate (as SO ₄)	36.00	31.17	26.33	21.50	16.67	11.83	7.00
Dissolved CO ₂	4.7	5.0	5.4	5.8	6.3	6.7	6.7
Bicarbonate	212.3	183.6	154.5	125.2	95.7	66.0	36.3
Carbonate	3.0	1.9	1.2	0.6	0.3	0.1	0.0
Oxalate(as C ₂ O ₄)	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Silica(as SiO ₂)	55.00	50.83	46.67	42.50	38.33	34.17	30.00
Phosphate(as PO ₄)	0.700	0.700	0.700	0.700	0.700	0.700	0.700
Pyrophosphate(PO ₄)	0.00	0.00	0.00	0.00	0.00	0.00	0.00
H ₂ S(as H ₂ S)	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Fluoride(as F)	1.00	0.950	0.900	0.850	0.800	0.750	0.700
Nitrate(as NO ₃)	0.00	0.00	0.00	0.00	0.00	0.00	0.00
PARAMETERS							
pH	8.00	7.91	7.80	7.67	7.51	7.31	7.02
Temperature(°F)	77.00	77.00	77.00	77.00	77.00	77.00	77.00
Calculated TDS	421.09	370.98	320.93	270.93	220.94	170.87	120.45
CORROSION RATE (mpy)							
1010 Carbon Steel	1.77	2.20	2.85	3.89	5.75	9.73	23.21

TABLE 6: MIXED WATER CHEMISTRY AT VARIOUS RATIOS

		Water One – Surface Source		Water Two – Well Source				
		% SURFACE WATER						
SATURATION LEVEL		0.00	16.67	33.33	50.00	66.67	83.33	100.00
Calcite		3.24	2.00	1.12	0.553	0.226	0.0649	0.00767
Aragonite		2.82	1.74	0.975	0.482	0.196	0.0565	0.00668
Calcium oxalate		0.00	0.00	0.00	0.00	0.00	0.00	0.00
Anhydrite		0.00952	0.00746	0.00556	0.00385	0.00236	0.00116	< 0.001
Gypsum		0.0154	0.0121	0.00902	0.00624	0.00383	0.00188	< 0.001
Calcium phosphate		0.773	0.372	0.150	0.0468	0.00981	< 0.001	< 0.001
Hydroxyapatite		0.00119	< 0.001	< 0.001	< 0.001	< 0.001	< 0.001	< 0.001
Ca pyrophosphate		0.00	0.00	0.00	0.00	0.00	0.00	0.00
Zinc phosphate		0.00	0.00	0.00	0.00	0.00	0.00	0.00
Fluorite		0.00239	0.00191	0.00148	0.00109	< 0.001	< 0.001	< 0.001
Silica		0.464	0.430	0.395	0.361	0.326	0.291	0.256
Brucite		< 0.001	< 0.001	< 0.001	< 0.001	< 0.001	< 0.001	< 0.001
Magnesium silicate		0.00840	0.00465	0.00233	0.00104	< 0.001	< 0.001	< 0.001
Ferric hydroxide		0.00	0.00	0.00	0.00	0.00	0.00	0.00
Siderite		0.00	0.00	0.00	0.00	0.00	0.00	0.00
Strengite		0.00	0.00	0.00	0.00	0.00	0.00	0.00
SIMPLE INDICES								
Langelier		0.570	0.351	0.0915	-0.224	-0.625	-1.19	-2.20
Ryznar		6.86	7.20	7.61	8.12	8.76	9.69	11.42
Puckorius		7.02	7.37	7.78	8.29	8.96	9.92	11.74
Larson-Skold		0.304	0.308	0.312	0.318	0.327	0.344	0.387
C.C.P.P.		4.40	2.58	1.19	0.150	-0.675	-1.53	-3.31
TOTAL VERSUS FREE IONS								
Ca	Total	56.07	47.66	39.25	30.84	22.43	14.02	5.61
Free		51.01	43.89	36.58	29.09	21.41	13.54	5.49
CO3	Total	2.99	1.95	1.17	0.643	0.306	0.115	0.0263
Free		1.22	0.843	0.545	0.323	0.170	0.0725	0.0195
PO4	Total	0.700	0.700	0.700	0.700	0.700	0.700	0.700
Free		< 0.001	< 0.001	< 0.001	< 0.001	< 0.001	< 0.001	< 0.001
CHEMICAL PROPERTIES								
Pb Solubility(ug/L)		0.873	1.27	1.99	3.38	6.47	15.19	55.15
Cu Solubility(mg/L)		0.741	0.770	0.815	0.878	0.967	1.12	1.63
Zn Solubility(mg/L)		1.18	0.927	0.757	0.654	0.616	0.670	0.996
PPO4 Solubility(mg/L)		2.86	3.25	3.81	4.72	6.42	10.66	34.90
PO4 Solubility(mg/L)		1.80	2.41	3.52	5.81	11.63	33.85	279.78
D.I.C.		43.27	37.46	31.66	25.88	20.10	14.30	8.44

An evaluation of the projected recirculating water chemistry using the blended make-up water revealed that:

- silica solubility would be the limiting factor for maximum cycles
- higher cycles were obtainable at the highest percentage of well water in the blend

- The maximum well water percentage recommended for potable water would be 67% well water based upon the limits for lead and copper.

A silica saturation level limit was used to determine the maximum cycle for the system. Table 7 depicts the cycles of concentration where silica saturation level hits 1.2 x. A target concentration ratio of 2.8 was established based upon this limit.

TABLE 7: CONCENTRATION RATIO LIMITS FOR BLENDED WATER

	100% Well	67% Well	33% Well	0 % Well
Cycles @ 1.2 X Sat	2.3	2.8	3.3	4.3
SiO ₂ mg/L	130	128	128	128
pH	8.2	8.2	8.0	7.5

It was determined that standard treatments for calcium carbonate scale control and the low phosphate scale potential would suffice at the target cycles of concentration.

pH PREDICTION OF RECIRCULATING WATER

It should be noted that the pH of the recirculating cooling water at one (1.0) cycle is rarely the same as that of the make-up, particularly in blended waters. Examples of this phenomena include the use of non-recarbonated cold lime softened water as make-up, and the use of deep well water under a high pCO₂ (partial pressure of CO₂).

In the case of the cold lime softened make-up, CO₂ is adsorbed from the atmosphere and the pH drops. Alkalinity is maintained as hydroxide alkalinity is replaced by carbonate alkalinity. Total molar carbon (Ct) will change. The recirculating water should be treated as an open system with respect to CO₂ exchange with the atmosphere.

In the case of deep well water, it is not unusual for carbon dioxide to flash to the atmosphere, causing the pH to rise. Alkalinity is again conserved in the open system. Total molar carbon will decrease.

pH calculations for models should account for the "equilibration" (or almost equilibration) of carbonic acid species and other volatile acids with the atmosphere.

INJECTION WELL FOR DISPOSAL

Saturation level profiles of waters mixed in varying proportions can predict precipitation from the blend and assist in optimizing mix ratios. The mixing models have found wide usage in predicting the impact of waters injected into aquifers (or oil fields) upon the formation. Ratios of injection and formation waters are sought where precipitation of scale will not be expected. Precipitation of scale in the formation can restrict water flow by clogging or restricting pore size.

Injection wells are used to dispose of water from a process, and in oil production. For every barrel of oil produced up to 100 barrels of brine accompany it to the surface. The oil is separated from the brine and returned to the formation using injection wells. Problems can arise due to changes in the properties of the brines as they come to the surface.

Pressure and $p\text{CO}_2$ decrease, resulting in a rise in pH. Returning the brine to the formation can create a deposition problem, adversely affect porosity and production. Mixing models are used to predict the impact of mixing the produced water and the formation water in different ratios. Ion association model saturation levels are used to model the mixing of the waters in the formation and their impact of the mix upon scale formation.

The same mixing models can be used to predict the safe range for injection water versus formation water when an injection well is used for disposal.

SUMMARY

Mixing waters for reuse and discharge is not as simple a matter as calculating a weighted average. Alkalinity must be mixed with consideration for CO_2 exchange with the atmosphere. "Closed" systems will mix differently than "open" systems. The resultant blend will also change as it cycles in a cooling tower. As new, less desirable water sources are employed as make-up water, previously rare scales such as barite and celestite can become a problem. They can also become significant as towers are run at higher concentration ratios. Injection wells are also being used for water disposal. The impact of injection waters on any aquifers into which they are discharged should be studied to minimize adverse impacts from scale formation. Computer modeling with ion association model predictions of scale formation can assist in optimizing flows, maximizing cycles, and minimizing the impact upon the environment.

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TABLE 8: RECIRCULATING WATER CHEMISTRY AT CONCENTRATION RATIO

Make-up Water: Well Water 67%, Surface Water 33%

CATIONS	Concentration Ratio					
	2.00	2.20	2.40	2.60	2.80	3.00
Calcium (as CaCO ₃)	196.00	215.60	235.20	254.80	274.40	294.00
Magnesium (as CaCO ₃)	60.00	66.00	72.00	78.00	84.00	90.00
Sodium (as Na)	40.88	44.97	49.06	53.15	57.24	61.32
Iron (as Fe)	0.00	0.00	0.00	0.00	0.00	0.00
Ammonia (as NH ₃)	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
Zinc (as Zn)	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
ANIONS						
Chloride (as Cl)	18.00	19.80	21.60	23.40	25.20	27.00
"M" Alkalinity	260.8	286.7	312.7	338.6	364.5	390.3
Oxalate(as C ₂ O ₄)	0.00	0.00	0.00	0.00	0.00	0.00
Silica(as SiO ₂)	93.34	102.67	112.01	121.34	130.68	140.01
Phosphate(as PO ₄)	1.40	1.54	1.68	1.82	1.96	2.10
H ₂ S(as H ₂ S)	0.00	0.00	0.00	0.00	0.00	0.00
Fluoride(as F)	2.00	2.20	2.40	2.60	2.80	3.00
Nitrate(as NO ₃)	0.00	0.00	0.00	0.00	0.00	0.00
PARAMETERS						
pH	7.96	8.01	8.07	8.12	8.16	8.21
Temperature (°F)	70.00	70.00	70.00	70.00	70.00	70.00
Calculated TDS	678.77	744.35	809.71	874.81	939.63	1004
Calculated Cond.	611.77	664.33	715.63	765.72	814.60	862.33

TABLE 9: DEPOSITION POTENTIAL INDICATORS AT CONCENTRATION RATIO

Make-up Water: Well Water 67%, Surface Water 33%

SATURATION LEVEL	Concentration Ratio					
	2.00	2.20	2.40	2.60	2.80	3.00
Calcite	4.60	6.15	8.00	10.16	12.67	15.52
Aragonite	4.02	5.38	7.00	8.90	11.09	13.59
Calcium oxalate	0.00	0.00	0.00	0.00	0.00	0.00
Anhydrite	0.0148	0.0171	0.0194	0.0218	0.0242	0.0267
Gypsum	0.0263	0.0303	0.0344	0.0387	0.0430	0.0474
Calcium phosphate	2.63	4.79	8.18	13.26	20.56	30.71
Hydroxyapatite	0.00629	0.0183	0.0477	0.114	0.250	0.516
Ca pyrophosphate	0.00	0.00	0.00	0.00	0.00	0.00
Fluorite	0.0120	0.0154	0.0194	0.0238	0.0289	0.0345
Silica	0.872	0.958	1.04	1.13	1.21	1.30
Brucite	< 0.001	< 0.001	< 0.001	< 0.001	< 0.001	< 0.001
Magnesium silicate	0.0138	0.0213	0.0317	0.0456	0.0637	0.0868
Ferric hydroxide	0.00	0.00	0.00	0.00	0.00	0.00
Siderite	0.00	0.00	0.00	0.00	0.00	0.00
Strengite	0.00	0.00	0.00	0.00	0.00	0.00
Zinc hydroxide	0.00	0.00	0.00	0.00	0.00	0.00
Zinc carbonate	0.00	0.00	0.00	0.00	0.00	0.00
Zinc phosphate	0.00	0.00	0.00	0.00	0.00	0.00
Zinc pyrophosphate	0.00	0.00	0.00	0.00	0.00	0.00
SIMPLE INDICES						
Langelier	0.730	0.864	0.986	1.10	1.20	1.30
Ryznar	6.49	6.29	6.10	5.92	5.76	5.61
Practical	6.37	6.16	5.97	5.79	5.63	5.48
Larson-Skold	0.308	0.308	0.308	0.308	0.308	0.309
Max. Sol. Zn	1.2	1.4	1.6	1.9	2.3	2.7
Max. Sol. Pyro	2.7	2.6	2.5	2.4	2.3	2.2
Max. Sol. Ortho	2.2	1.9	1.7	1.6	1.4	1.3
mg/L above Equilibrium						
Calcite	2.02	2.73	3.54	4.43	5.42	6.51
Aragonite	1.94	2.66	3.46	4.36	5.35	6.44
Calcium oxalate	-0.267	-0.253	-0.241	-0.230	-0.221	-0.213
Anhydrite	-854.80	-857.11	-858.89	-860.21	-861.15	-861.74
Gypsum	-686.85	-685.45	-683.68	-681.62	-679.29	-676.75
Calcium phosphate	< 0.001	< 0.001	< 0.001	< 0.001	< 0.001	< 0.001
Hydroxyapatite	-399.47	-404.02	-408.31	-412.37	-416.23	-419.91
Ca pyrophosphate	-0.0021	-0.0020	-0.0019	-0.0018	-0.0017	-0.0017
Fluorite	-29.27	-28.18	-27.15	-26.20	-25.29	-24.43
Silica	-13.94	-4.57	4.77	14.08	23.35	32.59
Brucite	-3.89	-3.79	-3.70	-3.62	-3.54	-3.48
Magnesium silicate	-189.45	-190.52	-191.52	-192.46	-193.35	-194.20
Ferric hydroxide	>-0.001	>-0.001	>-0.001	>-0.001	>-0.001	>-0.001
Siderite	-0.0196	-0.0160	-0.0133	-0.0112	-0.0096	-0.0083
Strengite	>-0.001	>-0.001	>-0.001	>-0.001	>-0.001	>-0.001
Zinc hydroxide	>-0.001	>-0.001	>-0.001	>-0.001	>-0.001	>-0.001
Zinc carbonate	-0.898	-0.784	-0.683	-0.596	-0.522	-0.460
Zinc phosphate	-0.0155	-0.0158	-0.0161	-0.0164	-0.0167	-0.0170
Zinc pyrophosphate	-2.01	-2.11	-2.21	-2.31	-2.40	-2.50
