

Predicting Properties of Blended Waters

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Abstract

The use of blended waters for industrial water treatment systems is increasing as a method for water conservation and environmental compliance. This paper discusses methods for predicting and optimizing blended waters for pretreatment applications such as reverse osmosis, cooling water make-up, and for adjusting properties prior to discharge. Evaluations of mixed waters for cooling water make-up, lead and copper solubility minimization in a municipal system, and for an injection well provide examples. Computer modeling of the mix ratios allows the water treatment chemist to determine if treatment is needed to prevent scale or corrosion, and to determine at what ratios the water quality will be acceptable for use or discharge.

Introduction

Predicting the properties of blended waters combines straightforward chemistry, common sense, and linear algebra with sophisticated physical chemistry. This paper describes:

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

Mixing in “closed” and “open” systems are discussed.

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 density

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

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, or density of 8.34 pounds/gallon 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 water 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 is derived in the following manner for as many waters as are mixed.

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

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

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

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.

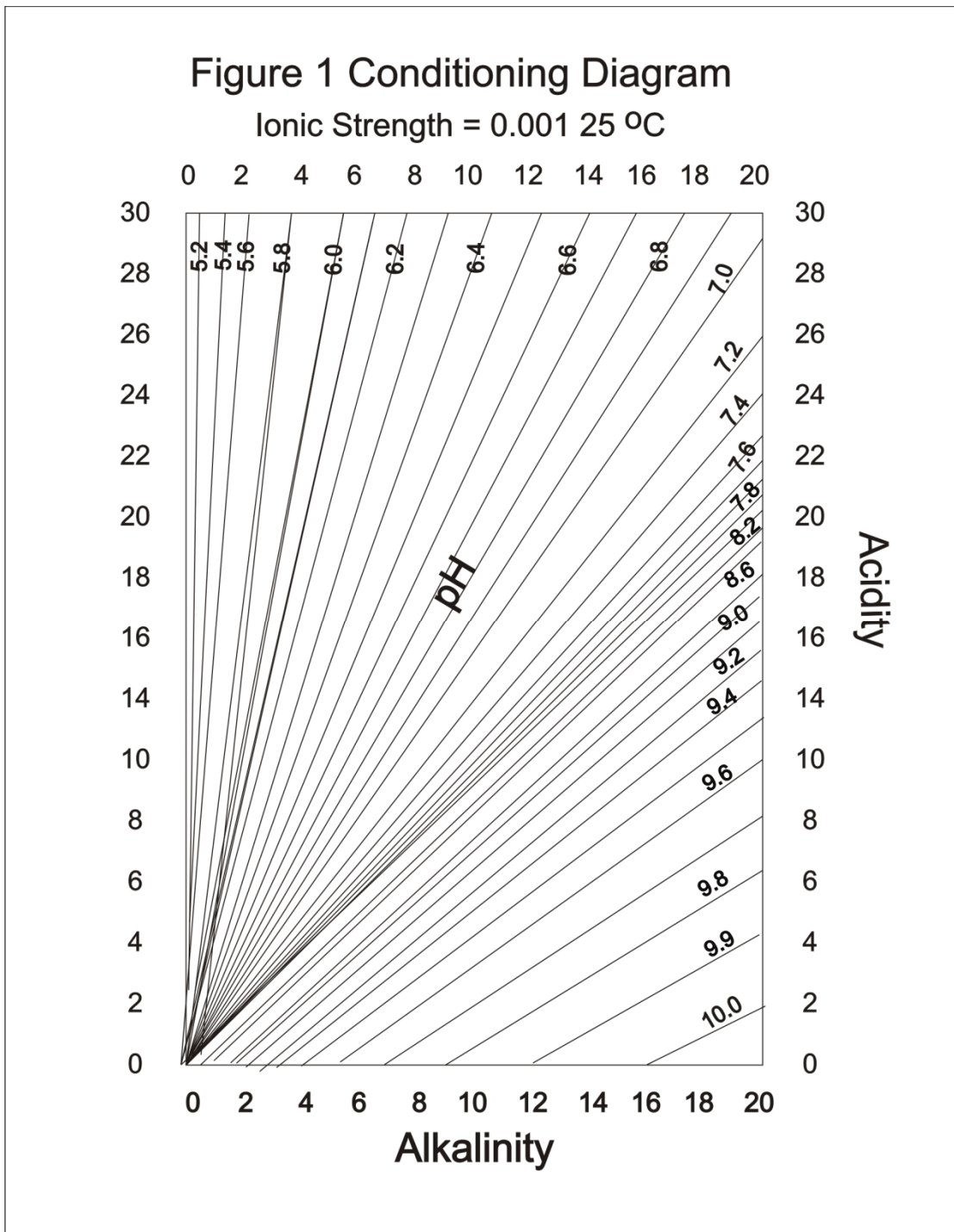
Ct is total carbonic acid species.

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

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.



Predicting pH – Closed Versus Open Systems

Carbonic acid calculations and pH prediction are handled differently for “Open” and “Closed” systems.

“Open” System: An “Open” system occurs when a water can freely exchange CO_2 with the atmosphere. Alkalinity is conserved as water concentrates and is heated. CO_2 “flashes” or is adsorbed during pH adjustments. The open system phenomena can be described by looking at the question: “Why isn’t the pH of water at one (1.0) cycle in a cooling tower the same as the make-up water pH?”

Two examples describe the condition.

Example 1: A non-recarbonated cold lime softened make-up water might have a pH above 10.0. When the water circulates and equilibrates with the atmosphere, CO_2 is absorbed into the aerosol as the water goes over the tower. Hydroxide alkalinity recarbonates to carbonate and bicarbonate. The pH of the water drops, probably into the mid pH 8 range. Alkalinity is conserved. The recirculating water pH at one (1.0) cycle is much lower than the make-up water pH for this reason.

Example 2: Well waters can have a high partial pressure of CO_2 . The High pCO_2 depressed the pH in the water. Well water make-up water might have a pH in the 6.0 to 7.0 range. When the water circulates and equilibrates with the atmosphere, CO_2 is released from the aerosol as the water goes over the tower. The carbonic acid equilibrium moves to the right from H_2CO_3 to HCO_3^- and CO_3^{2-} as a result. The pH rises into the pH 7 to pH 8 range as a result. Alkalinity is conserved.

A corollary of the open system is that CO_2 is lost from the water as acid is added for pH control.

“Closed” System: An “Closed” system occurs when a water cannot exchange CO_2 with the atmosphere. Molar carbon is conserved as water concentrates, and as acid is added for pH control. CO_2 produced remains in the system during pH adjustments.

An air tight reverse osmosis system can be a closed system. As acid is added, or the system concentrates, molar carbon is conserved. As acid is added, carbonic acid builds up in the system.

pH is described by directly varying the ratio of HCO_3^- to CO_3^{2-} and H_2CO_3 to HCO_3^- .

Table 1 compares pH, carbonic acid equilibria, and acid requirements for pH control in a “closed” versus “open” reverse osmosis system. It is of interest to note that the pH increase with concentration is much less in the case of the closed system than when treated as an open system. Acid feed requirements to achieve the same pH are also significantly lower.

It is important to use the appropriate carbonic acid equilibria calculations when modeling a closed or open system.

MIXING EXAMPLES

Two examples follow for modeling the impact of blended waters on a system. The first is an injection well used for disposal of brines from oil or gas production. The properties of the mixed waters are used to determine the impact mixing an injection water with a formation water will have on the formation. Scale formation can lead to decreased production require acidification or restore production.

The second example describes blending a municipal water to minimize lead and copper solubility, and to maximize cycles in a silica limited cooling tower.

CASE ONE: INJECTION WELL

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.

It can be seen that mixing the two brines in this case (North Sea Water and Formation Water) will result in Barium sulfate scale when mixed. Scale potential is highest when mixed in approximately equal proportions. Tables 2 and 3 summarize the chemistry involved. Figures 2, 3 and 4 depict the barium sulfate and calcium carbonate scale potential.

CASE TWO: MINIMIZING LEAD AND COPPER SOLUBILITY

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. 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. Silica is the limiting factor in the make-up water as far as maximum concentration ratio, so the water source used, or the mix ratio also has an economic impact upon non-regulated uses.

As depicted in Table 5 and Figures 5, 6 and 7, 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.

pH adjustment can also be beneficial to limiting lead and copper solubility.

Table 6 summarizes the maximum recommended concentration ratio for a cooling system based upon the limiting factor of silica from the blended well and surface water.

SUMMARY

Predicting properties of blended waters can provide insight into water reuse in a system, and provide solutions for minimizing problems by blending streams. Care should be taken in mixing calculations to assure that the system is treated accordingly as “Closed” or “Open” to the atmosphere. Subsequent evaluation of the blends as they will be used in their intended application, can provide further insight into the probability of success for using the blends.

References

- 1) R.E. Loewenthal and G.v.R. Marais, Carbonate Chemistry of Aquatic System, Theory and Application, 1982, Ann Arbor Science, pp 138 – 165.
- 2) James N. Jensen, A Problem Solving Approach to Aquatic Chemistry, 2003, John Wiley and Sons, pp 283 – 289.
- 3) Werner Stumm and James J. Morgan, Aquatic Chemistry Chemical Equilibria and Rates in Natural Waters, 1996, John Wiley and Sons.

TABLE 1

TABLE 2: WATER CHEMISTRY AT VARIOUS RATIOS OF INJECTION AND FORMATION WATER

	North Sea Water	Forties Water					
	% INJECTION						
CATIONS	0.00	16.67	33.33	50.00	66.67	83.33	100.00
Calcium (as Ca)	3110	2659	2208	1757	1305	854.17	403.00
Magnesium (as Mg)	480.00	620.00	760.00	900.00	1040	1180	1320
Barium(as Ba)	250.00	208.33	166.67	125.00	83.33	41.67	0.00
Strontium(as Sr)	660.00	550.00	440.00	330.00	220.00	110.00	0.00
Sodium (as Na)	30200	27000	23800	20600	17400	14200	11000
Potassium (as K)	430.00	415.00	400.00	385.00	370.00	355.00	340.00
Lithium(as Li)	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
Manganese(as Mn)	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
Lead(as Pb)	0.00	0.00	0.00	0.00	0.00	0.00	0.00
ANIONS							
Chloride (as Cl)	53000	47467	41933	36400	30867	25333	19800
Sulfate (as SO4)	0.00	413.33	826.67	1240	1653	2067	2480
Bromine (as Br)	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Dissolved CO2	0.1	0.5	0.8	1.2	1.6	2.1	2.6
Bicarbonate	219.2	226.8	225.4	213.2	191.7	163.7	131.4
Carbonate	138.9	94.5	58.9	34.0	18.2	8.8	3.7
Silica(as SiO2)	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Phosphate(as PO4)	0.00	0.00	0.00	0.00	0.00	0.00	0.00
H2S(as H2S)	0.00	0.00	0.00	0.00	0.00	0.00	0.00
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	7.79	7.65	7.49	7.33	7.16	6.99	6.80
Temperature(°C)	100.00	100.00	100.00	100.00	100.00	100.00	100.00
Pressure(bars)	300.00	300.00	300.00	300.00	300.00	300.00	300.00
Density(g/mL)	1.00	1.00	1.00	1.00	1.00	1.00	1.00
Calculated TDS	88496	79660	70824	61989	53153	44318	35483

Table 3: DEPOSITION POTENTIAL INDICATORS AT VARIOUS INJECTION AND FORMATION RATIOS

	North Sea Water		Forties Water					
	% INJECTION							
SATURATION LEVEL	0.00	16.67	33.33	50.00	66.67	83.33	100.00	
Calcite	20.49	12.88	7.33	3.78	1.74	0.665	0.167	
Aragonite	16.32	10.26	5.84	3.01	1.38	0.529	0.133	
Witherite	0.233	0.156	0.0937	0.0500	0.0226	0.00729	0.00	
Strontiante	1.61	1.08	0.649	0.346	0.157	0.0505	0.00	
Magnesite	12.21	11.30	9.24	6.91	4.80	3.09	1.78	
Anhydrite	0.00	0.254	0.433	0.535	0.556	0.484	0.298	
Gypsum	0.00	0.134	0.231	0.289	0.303	0.267	0.166	
Barite (BaSO4)	0.00	12.31	22.12	28.25	28.91	21.20	0.00	
Celestite (SrSO4)	0.00	0.213	0.383	0.489	0.501	0.367	0.00	
Tricalcium phosphate	0.00	0.00	0.00	0.00	0.00	0.00	0.00	
Hydroxylapatite	0.00	0.00	0.00	0.00	0.00	0.00	0.00	
Fluorite (CaF2)	0.00	0.00	0.00	0.00	0.00	0.00	0.00	
Silica (SiO2)	0.00	0.00	0.00	0.00	0.00	0.00	0.00	
Brucite (Mg(OH)2)	1.89	1.19	0.664	0.350	0.179	0.0874	0.0387	
Magnesium silicate	0.00	0.00	0.00	0.00	0.00	0.00	0.00	
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	
Halite (NaCl)	0.0125	0.00975	0.00742	0.00548	0.00389	0.00260	0.00159	
Thenardite (Na2SO4)	0.00	< 0.001	< 0.001	< 0.001	< 0.001	< 0.001	< 0.001	
Iron sulfide (FeS)	0.00	0.00	0.00	0.00	0.00	0.00	0.00	
SIMPLE INDICES								
Langelier	2.34	2.07	1.76	1.42	1.04	0.589	-0.0429	
Ryznar	3.10	3.51	3.98	4.49	5.09	5.81	6.89	
Oddo-Tomson	2.19	1.95	1.68	1.39	1.08	0.699	0.155	
Stiff-Davis	3.59	3.29	2.98	2.63	2.26	1.81	1.19	
Puckorius	2.51	2.90	3.33	3.81	4.37	5.08	6.13	
Larson-Skold	181.84	196.26	212.13	227.50	241.47	254.46	268.01	
Ca Total	3110	2659	2208	1757	1305	854.17	403.00	
Free	3033	2545	2072	1613	1169	742.09	336.63	
Ba Total	250.00	208.33	166.67	125.00	83.33	41.67	0.00	
Free	249.98	208.32	166.66	125.00	83.33	41.67	0.00	
CO3 Total	138.90	94.50	58.89	33.98	18.18	8.84	3.71	
Free	1.55	1.18	0.827	0.543	0.335	0.191	0.0969	
PO4 Total	0.00	0.00	0.00	0.00	0.00	0.00	0.00	
Free	0.00	0.00	0.00	0.00	0.00	0.00	0.00	
SO4 Total	0.00	413.33	826.67	1240	1653	2067	2480	
Free	0.00	144.69	297.68	458.05	624.15	793.16	959.90	

TABLE 4: MIXED WATER CHEMISTRY AT VARIOUS RATIOS

Water One – Surface Source	Water Two – Well Source
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	% WATER ONE						
	0.00	16.67	33.33	50.00	66.67	83.33	100.00
CATIONS							
Calcium (as CaCO3)	140.00	119.00	98.00	77.00	56.00	35.00	14.00
Magnesium (as CaCO3)	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 SO4)	36.00	31.17	26.33	21.50	16.67	11.83	7.00
Dissolved CO2	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 C2O4)	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Silica(as SiO2)	55.00	50.83	46.67	42.50	38.33	34.17	30.00
Phosphate(as PO4)	0.700	0.700	0.700	0.700	0.700	0.700	0.700
Pyrophosphate(PO4)	0.00	0.00	0.00	0.00	0.00	0.00	0.00
H2S(as H2S)	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 NO3)	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 5: MIXED WATER CHEMISTRY AT VARIOUS RATIOS

Water One – Surface Source	Water Two – Well Source
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	% WATER ONE							
	0.00	16.67	33.33	50.00	66.67	83.33	100.00	
SATURATION LEVEL								
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

TABLE 6: 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

FIGURE 3 : INJECTION WELL BARITE TEMPERATURE vs % PROFILE

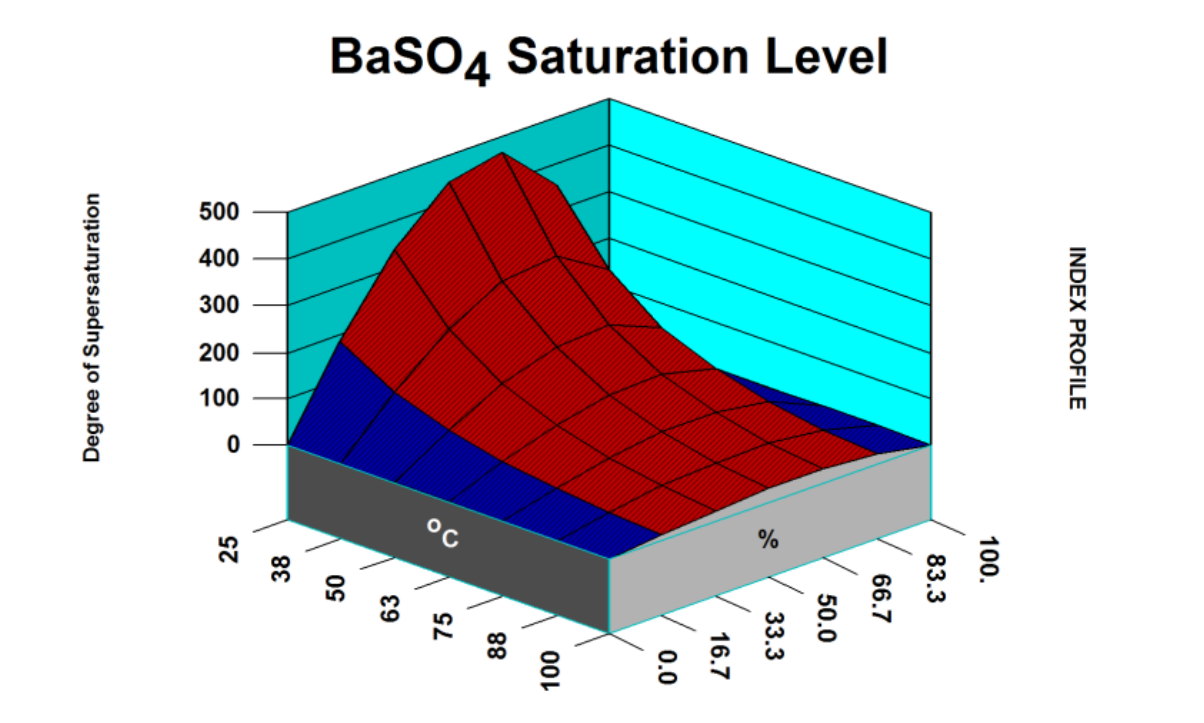


FIGURE 5: MUNICIPAL MIXING LEAD SOLUBILITY PROFILE

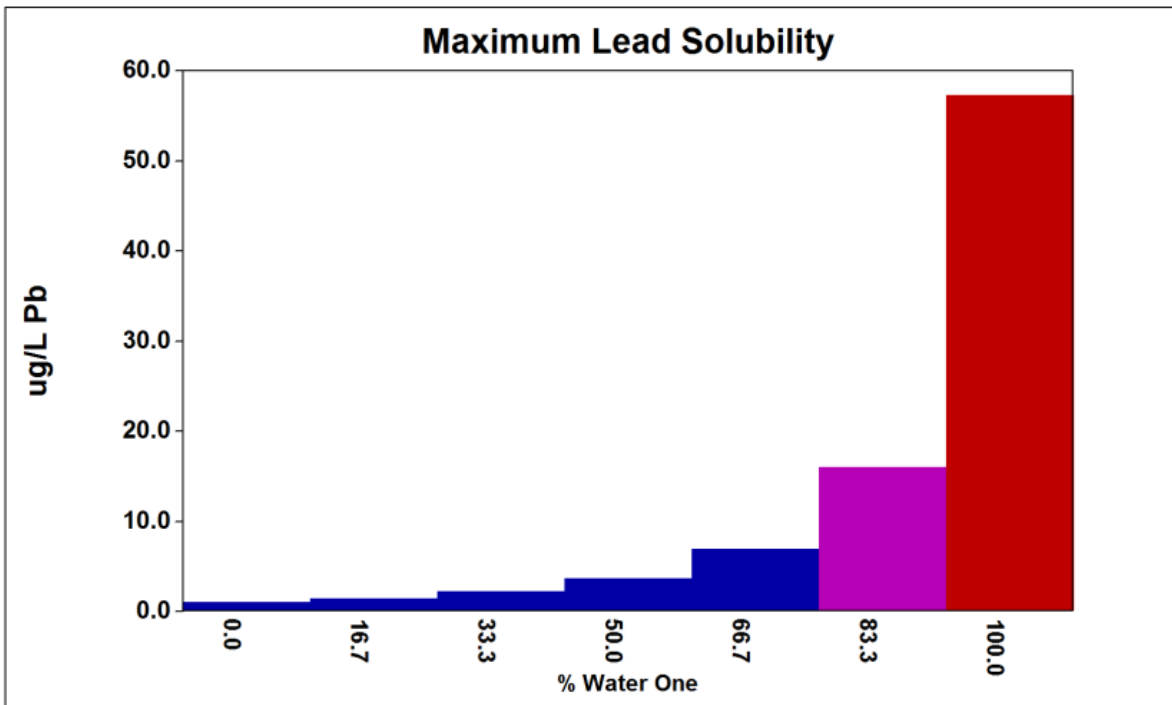


FIGURE 6: MUNICIPAL MIXING COPPER SOLUBILITY PROFILE

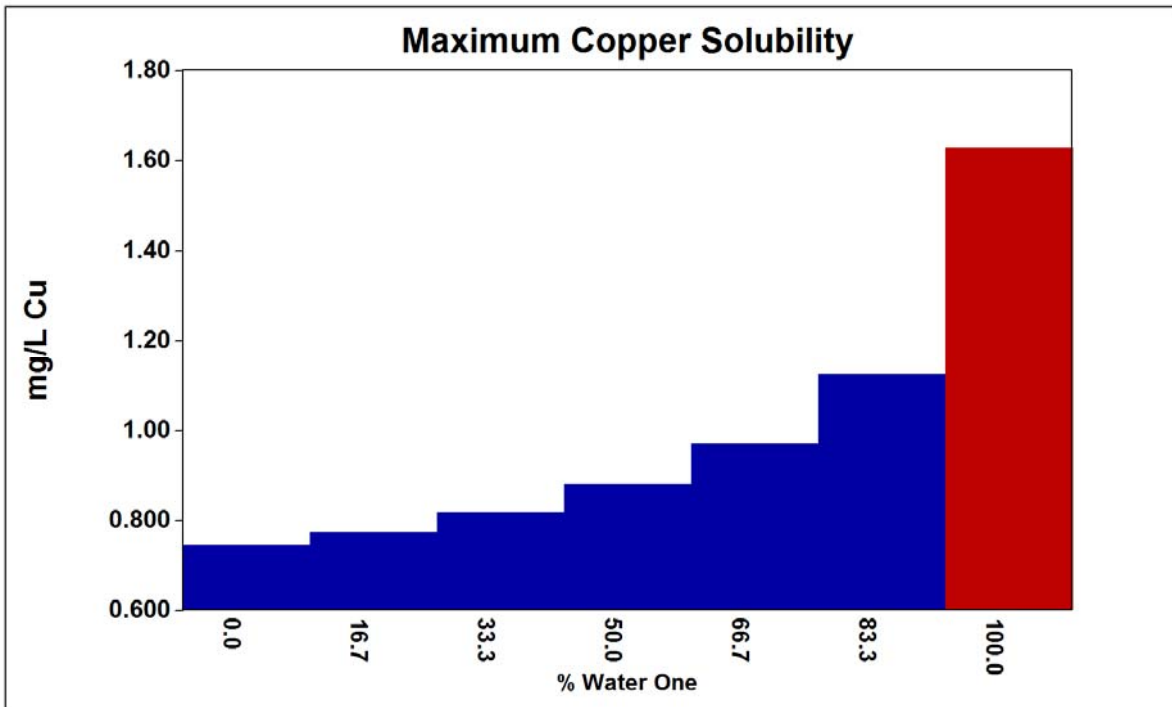


FIGURE 7: MUNICIPAL MIXING LEAD SOLUBILITY PROFILE

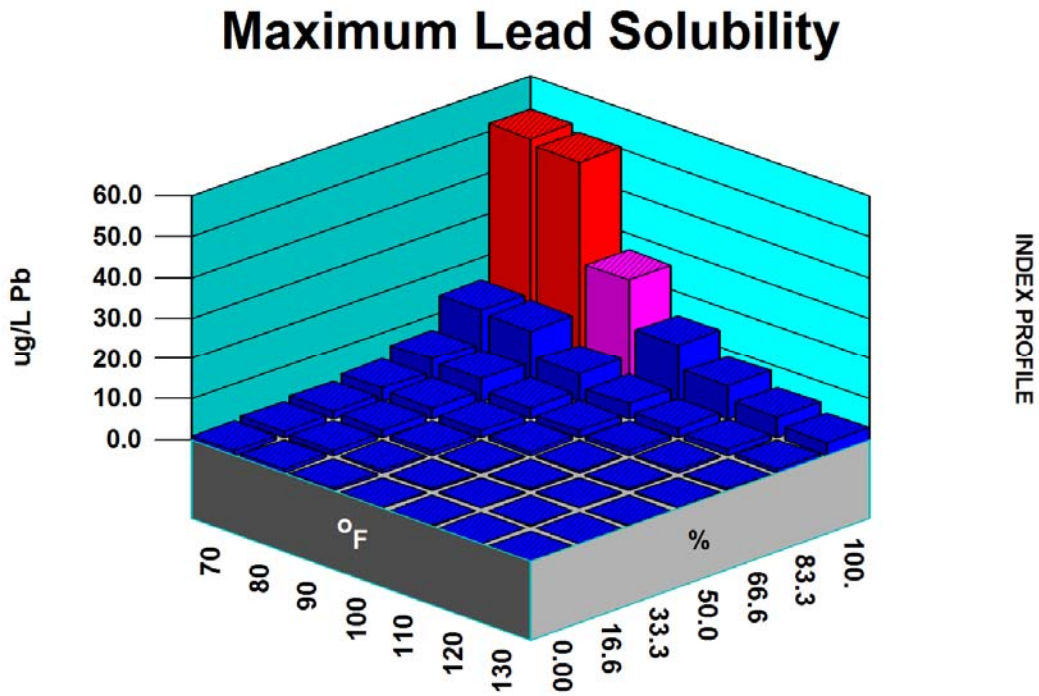


FIGURE 8: MUNICIPAL MIXING COPPER SOLUBILITY PROFILE

