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Literature Review of Boric Acid Solubility Data

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EXECUTIVE SUMMARY

A new solvent system is being evaluated for use in the Modular Caustic-Side Solvent Extraction Unit (MCU) and in the Salt Waste Processing Facility (SWPF). The new system replaces the current dilute nitric acid strip solution with 0.01 M boric acid. This literature study is performed to determine if there is a potential for boric acid to crystallize in the lines with emphasis on the transfer lines to the Defense Waste Processing Facility. This report focuses on the aqueous phase chemistry of boric acid under conditions relevant to MCU and SWPF. Operating and transfer conditions examined for the purpose of this review include temperatures between 13 °C (McLeskey, 2008) and 45 °C (Fondeur, 2007) and concentrations from 0 to 3M in nitric acid as well as exposure of small amounts of entrained boric acid in the organic phase to the sodium hydroxide caustic wash stream. Experiments were also conducted to observe any chemical reactions and off-gas generation that could occur when 0.01 M boric acid solution mixes with 3 M nitric acid solution and vice versa.

Based on the low concentration (0.01M) of boric acid in the MCU/SWPF strip acid and the moderate operating temperatures (13 °C to 45 °C), it is unlikely that crystallization of boric acid will occur in the acid strip solution under process or transfer conditions. Mixing experiments of boric and nitric acid show no measurable gas generation (< 1 cc of gas per liter of solution) under similar process conditions.

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LIST OF ABBREVIATIONS

cc	cubic centimeter
MCU	Modular Caustic-Side Solvent Extraction Unit
SWPF	Salt Waste Processing Facility

1.0 Introduction

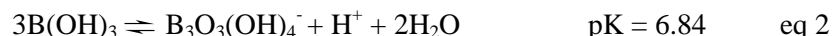
A new solvent system is being evaluated for use in the Modular Caustic-Side Solvent Extraction Unit (MCU) and in the Salt Waste Processing Facility (SWPF). The new system replaces the current dilute nitric acid strip solution with 0.01 M boric acid. This study is being performed to determine if there is a potential for boric acid to crystallize in the transfer lines to the Defense Waste Processing Facility (Deshpande, 2011; Newell, 2011). This report focuses on the aqueous phase chemistry of boric acid under conditions relevant to MCU and SWPF. Operating and transfer conditions are defined for the purpose of this review as temperatures between 13 °C (McLeskey, 2008) and 45 °C (Fondeur, 2007) and concentrations from 0 to 3M in nitric acid. Additionally, operating conditions involving the exposure of boric acid strip solution to sodium hydroxide are considered such as exposure of the boric acid strip solution to small amounts of entrained 0.025 M NaOH scrub feed in the organic phase or small amounts of entrained boric acid in the organic phase to the 0.01 M sodium hydroxide caustic wash stream. Also, experiments to evaluate mixing of boric acid and nitric acid were conducted to determine if any gas is generated upon mixing the boric and nitric acids.

1.1 Boric Acid Acidity

Boric acid is a very weak acid that acts as a Lewis acid accepting OH^- rather than as a proton donor (eq 1, Cotton and Wilkinson, 1972). At concentrations less than or equal to 0.025M, only



monomeric species B(OH)_3 and B(OH)_4^- exist.. At higher concentrations (greater than 0.025 M) the formation of polyborates are indicated by an increase in acidity (eq 2). These polyborates are typically ring structures or chains.



Hydrated borates can crystallize from aqueous solutions. Borax, $\text{Na}_2[\text{B}_4\text{O}_5(\text{OH})_4] \cdot 8\text{H}_2\text{O}$, the tetraborate anion, is an example of a polyborate anion. Addition of acid, such as HCl, readily converts borax to boric acid. Rapid exchange between boric acid labeled with ^{18}O and borates indicates that equilibrium in solution is rapidly reached (Cotton and Wilkinson, 1972).

Although polyborates can be formed at higher concentrations, only mononuclear B(OH)_3 and B(OH)_4^- should be present under expected process operating conditions (i.e., boron concentrations should be 0.01M which is less than 0.025 M). The potential solubility effects of borates on MCU/SWPF process conditions are discussed in Section 2.4 below.

2.0 Boric Acid Solubility

2.1 Water

Boric acid, H_3BO_3 , is moderately soluble in water (roughly 0.4 M at 0 °C, 0.9 M at 25 °C and 3 M at 80 °C). Due to its negative heat of solution, the solubility of boric acid in water increases with temperature. Solubility data reported from several sources (Linke, 1958, Perry, 1997, Lange, 1992) is plotted in Figure 1. Appendix A includes boric acid solubility in water data. The primary reference (either directly or indirectly) for these compilations of solubility data is Blasdale and Slansky, 1939. There is some variability in these compilations even in different editions for the same source including both the data itself and the temperatures at which the data is reported. For comparison since the available data is reported in a variety of units, Figure 1 plots solubility data converted to molarity (assuming a solution density of 1 g/mL for either water or boric acid for simplicity). Limited density data has been reported for boric acid solutions in water at 25 °C and was found to range from 0.9992 for 0.08 M boric acid solutions to 1.0110 g/mL for 0.6 M boric acid (Holcomb, 1983a).

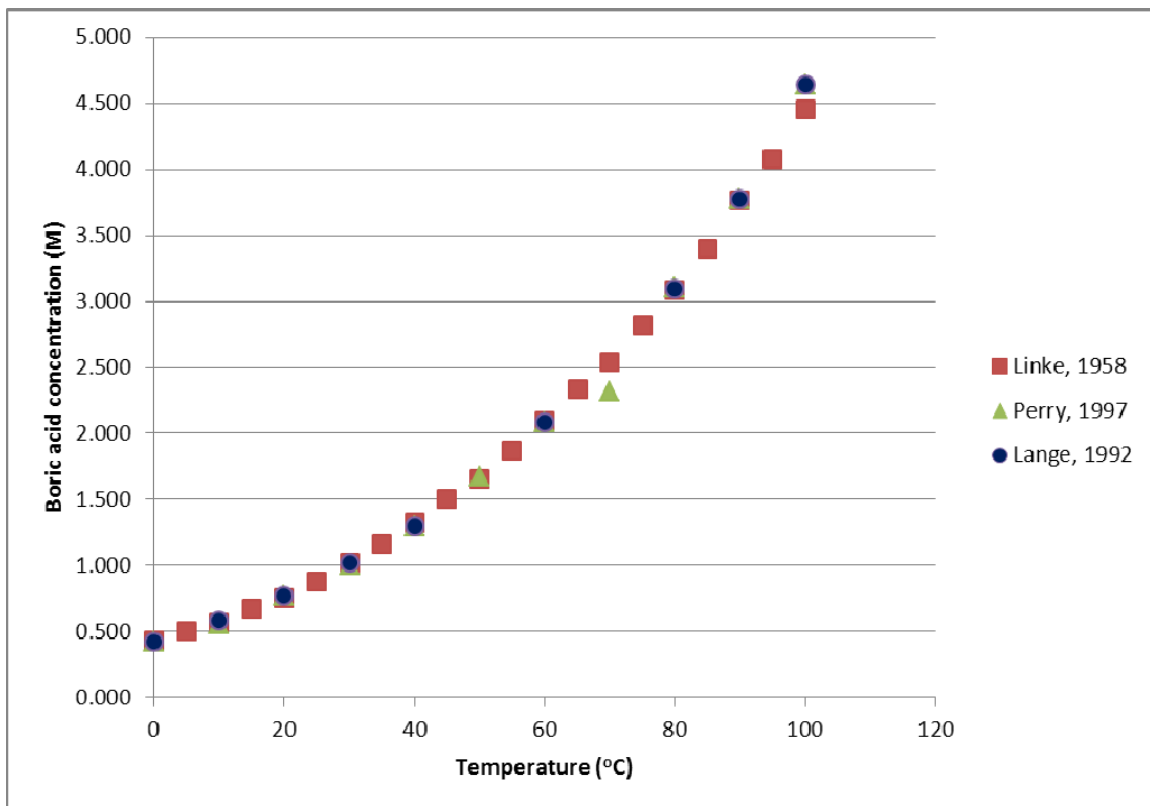


Figure 1. Boric Acid Solubility in Water.

Thermodynamic models for aqueous solutions of boric acid (Di Giacomo, 1988) have also been reported that predict boric acid activity coefficients using experimental solubility and vapor pressure data.

Boric acid is soluble in water to greater than 0.4 M at 0 °C (Figure 1) which is a lower temperature than process conditions expected in underground transfer lines. Therefore, no precipitation potential of 0.01 M boric acid process solution is expected.

2.2 Nitric Acid and Other Mineral Acids

Nitric acid and other mineral acids (hydrochloric, sulfuric) are reported to decrease the solubility of boric acid (Linke, 1958). Figure 2 compares data for nitric acid (Holcomb, 1983) with a fit of the boric acid solubility in water. Nitric acid solubility data is included in Appendix A. At dilute concentrations of nitric acid (< 1 M), there is little effect on the solubility at 25 °C. At 25 °C and less than 3 M nitric acid, the solubility of boric acid is still greater than 0.5 M which is more than an order of magnitude higher than the expected MCU/SWPF operating boric acid concentration (0.01 M). Although literature data below 25 °C was not found, data from 25 °C to 75 °C indicate that the effect of nitric acid on the solubility is greater with increasing temperature. Making the assumption that this observed trend is valid for temperatures between 10 °C and 25 °C, the solubility of boric acid in 3 M nitric at 13 °C can be estimated to be greater than 0.235 M.¹ Based

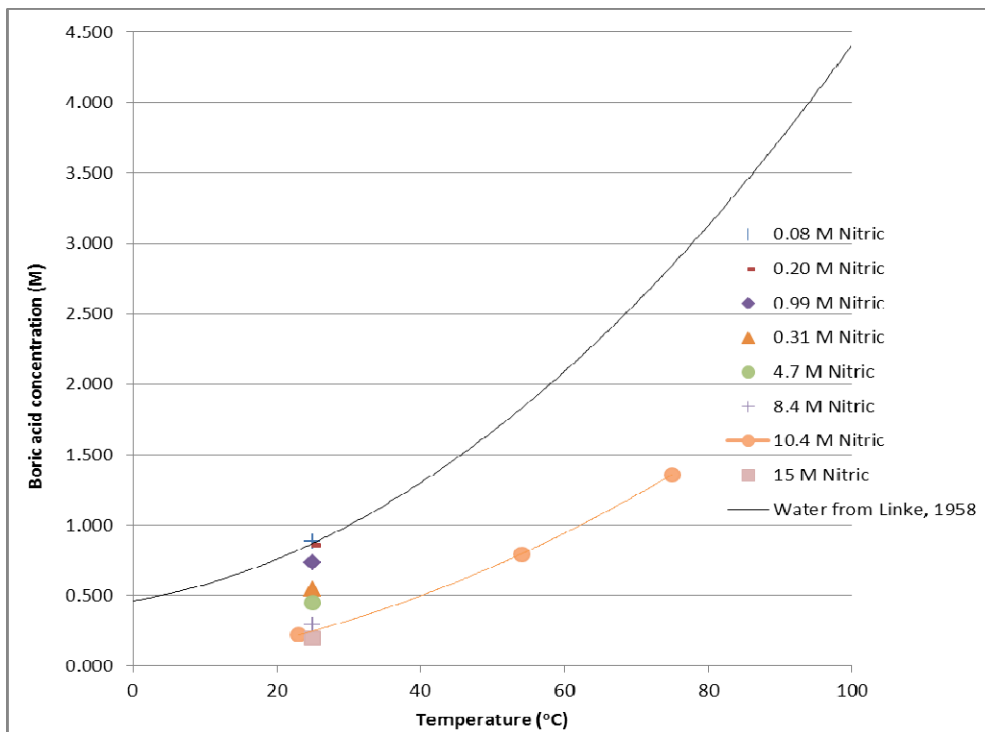


Figure 2. Boric Acid Solubility in Water versus Nitric Acid.

¹ At 25 °C boric acid solubility decreases from 0.878 M in water to 0.544 M in 3.1 M nitric acid. Using available data for the solubility of boric acid in water at 10 °C (0.569 M; a conservative assumption because the solubility of boric acid in water is greater at 13 °C) and assuming the same magnitude of decrease in solubility reported at 25 °C (a conservative assumption because the magnitude of the decrease in solubility at 13 °C should be smaller), the solubility of boric acid is estimated to decrease to no lower than 0.235 M in 3.1 M nitric acid at 13 °C.

on this estimate, no precipitation of 0.01 M boric acid in nitric acid would be expected under MCU/SWPF processing conditions (0 to 3 M nitric acid, and 13 °C to 45 °C)

2.3 Effect of Other Ions

The solubility of boric acid in LiCl, NaCl, KCl, RbCl, and CsCl salt solutions has been determined as a function of ionic strength (0-6 mol/kg) at 25 °C (Figure 3) (Chanson, 2006).

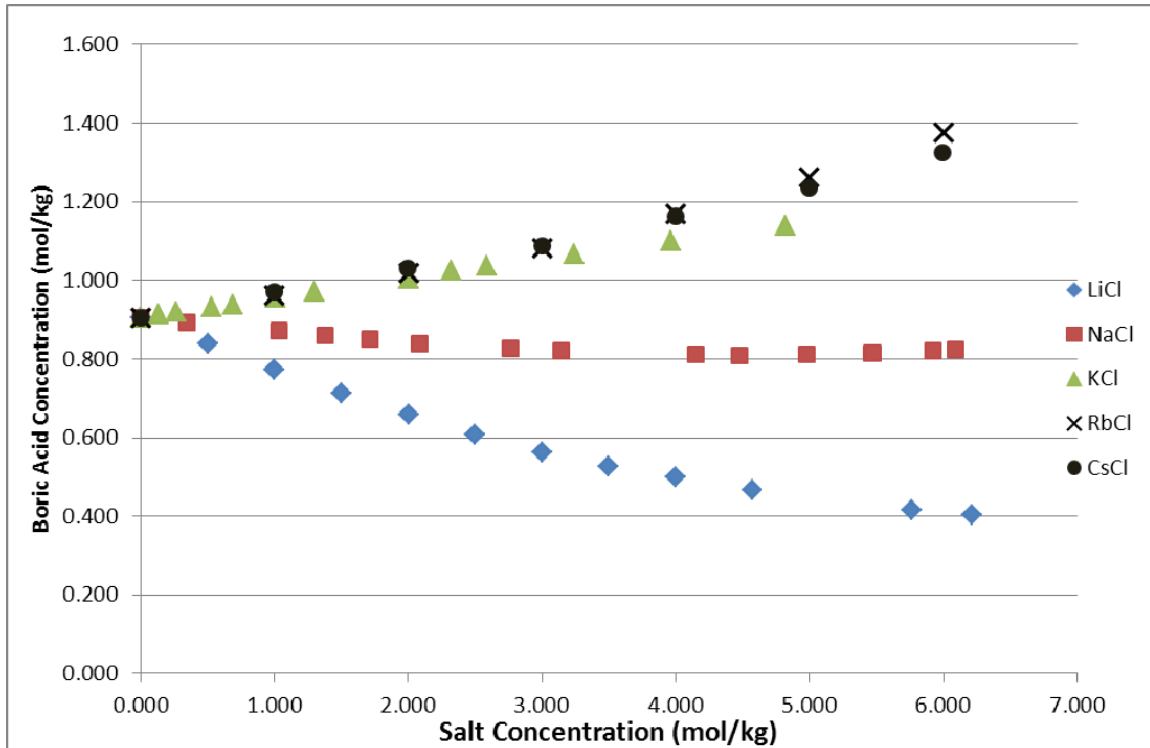


Figure 3. Boric Acid Solubility at 25 °C in LiCl, NaCl, RbCl, and CsCl Solutions as a Function of Molality.

These results along with literature data in terms of molal solubilities were fit to the second degree equation (eq 3)

$$\ln\{[B]^0/[B]\} = \ln\gamma_B = am + bm^2 \quad \text{eq 3}$$

where $[B]^0$ is the concentration of boric acid in water and $[B]$ in solution, γ_B is the activity coefficient, and m is the salt molality. This equation is in the form of the Pitzer equation. The coefficients are related to Pitzer parameters by: $a = k_s = 2v_c\lambda_{Bc} + 2v_a\lambda_{Ba}$ where k_s is the salting coefficient and v_i is the number of ions (i), and λ_{Ba} and λ_{Bc} are parameters related to the interaction of boric acid with cation (c) and anion (a), and $b = v_c v_a \zeta_{B-a-c}$ where ζ_{B-a-c} is related to the interaction of boric acid with both cation and anion. For 1-1 electrolytes ζ_{B-a-c} is equal to b . For 1-2 electrolytes ζ_{B-a-c} is $b/2$. Appendix B gives detailed tables of experimental data for boric acid solubility in LiCl, NaCl, KCl, RbCl, CsCl, and NaCl-MgCl₂ solutions at 25 °C, fitting parameters a and b (eq 3), k_s as a function of temperature and associated adjustable parameters, and Pitzer Parameters λ_{B-i} and ζ_{B-a-c} . Although the Chanson modeling was directed at chloride systems, parameters are also provided for the effects of common nitrate salts. (The original papers should be consulted for additional detail prior to use of this model.)

The solubility of boric acid in lithium, sodium, and potassium chloride solutions is not a strong function of temperature. Chanson (2006) recommends that salting coefficients and other parameters derived in their study can be used over the temperature range 5-35 °C because temperature appears to have little effect on LiCl, NaCl, and KCl solutions. Figure 5 in Appendix B shows literature data from Linke (1958) used to plot salting coefficients as a function of temperature (Chanson, 2006). Boric acid is soluble in the order: cesium > rubidium > potassium > sodium > lithium > hydrogen and barium > strontium > calcium > magnesium in common anion salt solutions (Chanson, 2006). Boric acid is soluble in the order: sulfate > nitrate > and fluoride > chloride > bromide > iodide in common cation solutions (Chanson, 2006).

Thermodynamic modeling has been reported for sodium and potassium chloride solutions with boric acid in the temperature range 30-100 °C (Di Giacomo, 1993) as well as sodium and potassium sulfate (Di Giacomo, 1992). Sodium chloride appears to have little effect on the solubility of boric acid in the 30-100 °C range while potassium chloride and sodium and potassium sulfate increase solubility of boric acid and the effect increases with increasing temperature in the same range (30-100 °C).

2.4 Relevance of Borates

The formation of borates may occur on exposure of the boric acid strip solution to dilute basic solutions such as exposure of small amounts of entrained boric acid solution in the organic phase to 0.01 M sodium hydroxide caustic wash or exposure of the boric acid strip solution to small amounts of entrained 0.025 M NaOH scrub in the organic phase. Borates, such as borax, are typically more soluble in water than boric acid (Holcomb, 1983). The system $\text{Na}_2\text{O}/\text{B}_2\text{O}_3/\text{H}_2\text{O}$ has been well studied (Blasdale and Slansky, 1939; Nies and Hulbert, 1967, Rothbaum et al. 1956). Appendix C includes solubility data for sodium borates (Blasdale and Slansky, 1939; Nies and Hulbert, 1967). The presence of borax has been reported to increase the solubility of more concentrated boric acid solutions presumably by the formation of polyborates (Tuunanen, 1994) even under conditions known to favor boric acid crystallization, such as high temperature sufficient to vaporize boric acid (100 °C), heating/cooling cycles, and evaporative loss of aqueous phase.

The presence of borates would be expected to increase the overall solubility of boron-containing species in the acid strip solution. At these dilute boric acid concentrations this increased solubility effect would only be appreciable if the MCU/SWPF process strip acid solution was concentrated to greater than or equal to 0.025M in boron. At the planned low initial boric acid concentrations (0.01 M in the acid strip solution), only monomeric species are expected and little effect would be observed on the overall solubility of all boron containing species in an acid strip solution that has been partially neutralized by mixing with caustic solution.

3.0 Reactivity of Boric Acid with Nitric Acid

Transfer lines containing 0.01 M boric acid solution may alternatively contain 3 M nitric acid solution. Without flushing, boric acid solution may mix in the transfer line with nitric acid and vice versa. Several experiments were performed to observe any chemical reactions and off-gas generation that could occur when these solutions are mixed.

3.1 Experimental

The experimental setup consisted of a 100 mL 3-port boiling flask fitted with a small condenser (shown in Figure 4). A 12 mL graduated addition funnel with gas by-pass allowed addition of boric acid to nitric acid without venting the system. Stirring was provided by a Teflon® stirring bar and hotplate with measurement of both the pressure and the solution temperature. Nitric acid was also added to boric acid. A digital manometer (with 0.01 psig resolution) was used to measure the pressure in the system. A K-type Teflon® coated thermocouple and hotplate display was used to monitor the solution temperature (with 0.1 °C resolution).

3.2 Results

The addition of 12 mL of 0.01 M boric acid to 50 mL of 3.16 M nitric acid did not result in any detectable pressure or temperature rise. Some light refraction was noted as the solutions mixed

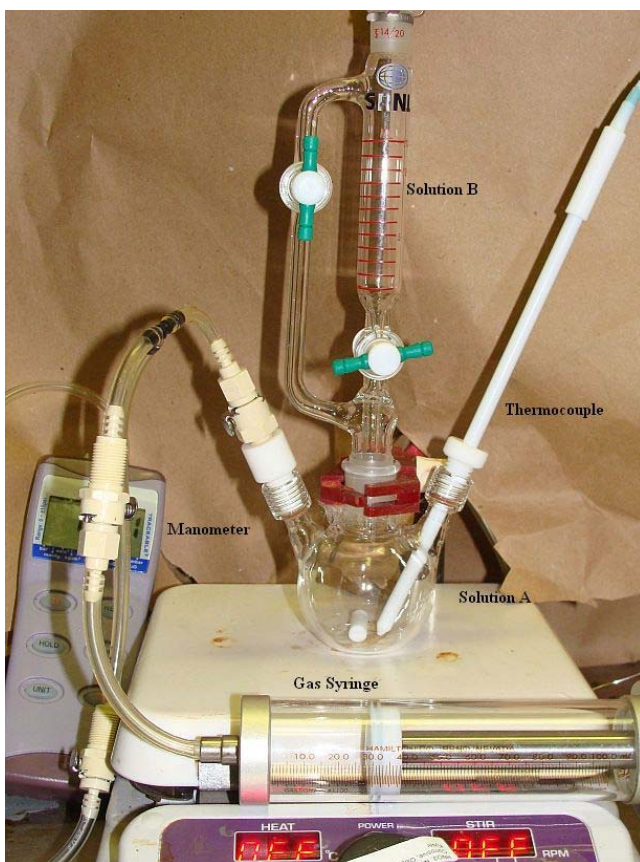


Figure 4. Apparatus for Measurement of Mixing Effects.

but this quickly dissipated. There was no visible evidence of any NO_x evolution. The addition of 12 mL of nitric acid to 50 mL of boric acid (same concentrations as before) gave identical result. For a test of the sensitivity, 1 cc of air at ambient temperature and pressure was injected into the system via a gas syringe connected to the manometer line which resulted in a pressure increase of 0.14 psig. Consequently, for this experimental setup, a detectable pressure rise of 0.01 psig (digital manometer has 0.01 psig resolution) corresponds to 0.07 cc of gas generated. Based on this result, the sensitivity of this test for gas generation is estimated to be < 0.07 cc (@18 °C) or < 0.1 vol %, for the volumes of solution that were mixed.

The mixing of solutions of 3.16 M nitric acid and 0.01 M boric acid did not show any evidence of significant gas generation (< 1 cc of gas per liter of solution).

4.0 Conclusions

Based on the expected low concentration (0.01 M) of boric acid in in the MCU/SWPF process strip acid and the moderate operating temperatures (13 °C - 45 °C), it is unlikely that crystallization of boric acid will occur in the acid strip solution under process conditions. If the boric acid in the strip acid is exposed to neutralizing conditions, it is unlikely that these conditions will cause the boric acid to crystallize. Rather, the formation of borates would be expected to increase the overall solubility of boron containing species in the solution. Contact of the boric acid strip solution with nitric acid solutions would be expected to reduce the solubility of boric acid. At concentrations of nitric acid less than 3 M after mixing, the solubility of boric acid remains greater than an order of magnitude higher than the expected boric acid concentration in the acid strip solution at 25 °C. The greatest uncertainty for results of mixing nitric acid solutions and boric acid would be in the temperature range less than 25 °C where literature data was not available. Based on estimates from available data, the solubility of boric acid between 13 °C and 25 °C is estimated as more than an order of magnitude higher than 0.01 M. Furthermore, conditions known to favor the formation of solids from aqueous solutions of boric acid such as elevated temperatures (100 °C), evaporative concentration due to breach of containment in the process lines, and heating cooling cycles are unlikely to be encountered under normal MCU/SWPF process conditions. Additionally, the mixing of 3.16 M nitric acid and 0.01 M boric acid do not show any evidence of significant gas generation (< 1 cc of gas per liter of solution).

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Appendix A

Table 1. Solubility of Boric Acid in Water.

Temperature (°C)	g H ₃ BO ₃ / 100g sat sol w/ H ₂ O (Linke, 1958)	g H ₃ BO ₃ / 100g H ₂ O (Perry, 1997)	g H ₃ BO ₃ / 100g H ₂ O (Lange, 1992)
0	2.70	2.66	2.67
5	3.14	-	-
10	3.52	3.57	3.73
15	4.17	-	-
20	4.65	5.04	5.04
25	5.43	-	-
30	6.34	6.60	6.72
35	7.19	-	-
40	8.17	8.72	8.72
45	9.32	-	-
50	10.23	11.54	-
55	11.54	-	-
60	12.96	14.81	14.81
65	14.42	-	-
70	15.75	16.73	-
75	17.40	-	-
80	19.06	23.75	23.62
85	21.01	-	-
90	23.27	30.38	30.38
95	25.22	-	-
100	27.53	40.25	40.25

- Indicates no data available at this temperature.

Table 2. Solubility of Boric Acid as a Function of Nitric Acid Concentration at 25 °C (Holcomb, 1983)

HNO ₃ (moles/Liter)	moles H ₃ BO ₃ / Liter saturated solution
0.0779	0.8820
0.1951	0.8610
0.5337	0.8028
0.9890	0.7361
1.580	0.6685
2.372	0.5493
3.118	0.5444
3.806	0.4977
4.698	0.4471
8.410	0.2963

Table 3. Solubility of Boric Acid in 50 % Nitric Acid as a Function of Temperature (Holcomb, 1983)

Temperature °C	moles H ₃ BO ₃ / Liter saturated solution
23	0.22
54	0.80
75	1.36

Appendix B

Table 4. Boric Acid Solubility in LiCl, NaCl, KCl, RbCl, CsCl, and NaCl-MgCl₂ Solutions at 25 °C (Chanson, 2006).

[B] ^a	<i>m</i> ^a	ln(γ_B)
LiCl		
0.905	0.000	0.000
0.840	0.501	0.079
0.774	1.000	0.161
0.712	1.501	0.245
0.658	2.001	0.323
0.608	2.500	0.402
0.564	3.001	0.477
0.528	3.500	0.542
0.500	4.002	0.599
0.467	4.572	0.666
0.415	5.765	0.785
0.405	6.220	0.808
NaCl		
0.905	0.000	0.000
0.894	0.343	0.017
0.871	1.031	0.044
0.861	1.376	0.055
0.850	1.717	0.068
0.839	2.082	0.081
0.826	2.764	0.096
0.820	3.140	0.104
0.811	4.146	0.114
0.810	4.480	0.116
0.811	4.982	0.115
0.816	5.467	0.109
0.815	5.472	0.110
0.822	5.927	0.101
0.825	6.092	0.097
NaCl-MgCl₂^b		
0.864 ^c	0.482	0.046
0.866 ^d	0.482	0.045
KCl		
0.905	0.000	0.000
0.915	0.134	-0.006
0.921	0.267	-0.013
0.932	0.534	-0.025
0.939	0.693	-0.032
0.955	1.007	-0.050
0.970	1.303	-0.065
1.005	2.001	-0.100
1.024	2.321	-0.119
1.037	2.590	-0.131
1.066	3.241	-0.160
1.101	3.963	-0.191
1.139	4.822	-0.226

Table 4. (Continued).

[B] ^a	<i>m</i> ^d	ln(γ_B)
RbCl		
0.905	0.000	0.000
0.963	1.001	-0.058
1.019	2.001	-0.114
1.082	2.999	-0.174
1.169	3.999	-0.252
1.261	4.997	-0.327
1.376	6.001	-0.414
CsCl		
0.905	0.000	0.000
0.971	0.997	-0.066
1.031	2.000	-0.125
1.087	3.002	-0.179
1.164	3.996	-0.247
1.234	4.995	-0.306
1.326	5.996	-0.377

^aUnits in mol · kg⁻¹.

^b0.427 mol · kg⁻¹ NaCl and 0.055 mol · kg⁻¹ MgCl₂.

^cMeasured.

^dCalculated from Eq. (27).

Eq 27 available in the original paper by Chanson (2006).

Table 5. Fitting Parameters a and b for Equation 3 (Chanson, 2006).

Salt	Maximum <i>m</i>	<i>a</i>	<i>b</i>	SD	Reference
HCl	1.546 ^a	0.240 ^a	-0.032 ^a	0.003	(3)
	16.031	0.193	-0.009	0.045	(3)
LiCl	6.22	0.178	-0.008	0.009	This study
	4.124	0.167 ^b	0.000	0.005	(3)
NaCl	6.092	0.047	-0.005	0.002	This study
	3.493	0.062 ^c	-0.010	0.000	(3)
KCl	4.822	-0.050	0.000	0.002	This study
	3.133	-0.051 ^d	0.001	0.001	(3)
RbCl	6.001	-0.053	-0.003	0.003	This study
	2.613 ^a	-0.085 ^a	0.004 ^a	0.000	(3)
CsCl	1.299	-0.018	-0.018	0.002	(3)
	5.996	-0.063	0.000	0.004	This study
KI	2.400 ^a	-0.074 ^a	0.000 ^a	0.001	(3)
	2.708 ^a	-0.008 ^a	0.004 ^a	0.000	(3)
MgCl ₂	2.073 ^a	0.382 ^a	-0.016 ^a	0.002	(3)
CaCl ₂	2.450 ^a	0.329 ^a	-0.010 ^a	0.001	(3)
BaCl ₂	0.815 ^a	0.180 ^a	-0.052 ^a	0.000	(3)
HNO ₃	27.198	0.136	-0.003	0.049	(3)
NaNO ₃	0.941	-0.042	-0.008	0.001	(3)
KNO ₃	0.791	-0.120	-0.012	0.002	(3)
Na ₂ SO ₄	0.563	-0.303	-0.065	0.002	(3)
K ₂ SO ₄	0.459	-0.510	-0.043	0.001	(3)
KF	0.330 ^e	-0.980 ^e	-0.989 ^e	0.081	(3)

^aValues at 18 °C; units mol · kg⁻¹ for this column.

^b*a*₀ = 0.167, *a*₁ = 0.002.

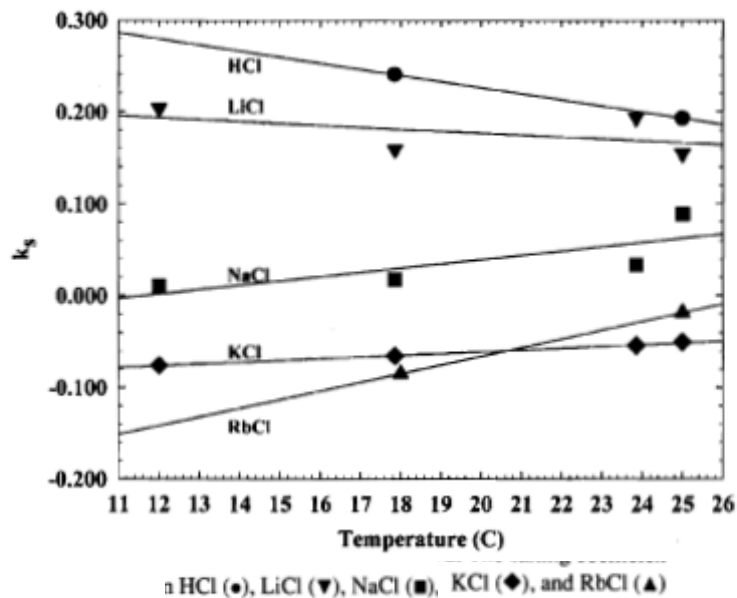
^c*a*₀ = 0.062, *a*₁ = -0.005.

^d*a*₀ = -0.051, *a*₁ = -0.002.

^eValues at 30 °C.

(3) (Linke, 1958)

Note 1. See Figure 5 of this report for an explanation of the fitting parameters *a*₀ and *a*₁.



fitted by

$$a = a_0 + a_1(25 - t)$$

Note 1. See Table 5 for actual values of associated adjustable parameters a_0 and a_1 used.

Figure 5. The Salting Coefficients, k_s , of Boric Acid in HCl, LiCl, NaCl, KCl, and RbCl as a Function of Temperature (t in °C) (Chanson, 2006).

Table 6. Pitzer Parameters λ_{B-i} and ζ_{B-a-c} for the Solubility of Boric Acid (Chanson, 2006).

Ion	$\lambda_{(B-i)}$	c-a	ζ_{B-c-a}
H ⁺	0.109	H-Cl	-0.021
Li ⁺	0.087	Li-Cl	-0.004
Na ⁺	0.028	Na-Cl	-0.008
K ⁺	-0.026	K-Cl	0.001
Rb ⁺	-0.026	Rb-Cl	-0.006
Cs ⁺	-0.035	Cs-Cl	0.000
Mg ²⁺	0.191 ^a	Mg-Cl	-0.016 ^a
Ca ²⁺	0.165 ^a	Ca-Cl	-0.010 ^a
Sr ²⁺	0.141 ^b		
Ba ²⁺	0.090 ^a	Ba-Cl	-0.052 ^a
F ⁻	-0.465 ^c	K-F	-0.989 ^c
Cl ⁻	0.000		
Br ⁻	0.007 ^d		
I ⁻	0.022 ^a	K-I	0.004 ^a
NO ₃ ⁻	-0.041 ^e	H-NO ₃	-0.003
		Na-NO ₃	-0.008
		K-NO ₃	-0.012
SO ₄ ²⁻	-0.205 ^f	Na-SO ₄	-0.065
		K-SO ₄	-0.043

^aValues at 18 °C.

^bCalculated from $K_s(\text{SrCl}_2)$ in Table 7.

^cValues at 30 °C.

^dCalculated from $K_s(\text{KBr})$ in Table 7.

^e-0.029 from H⁺, -0.045 from Na⁺, and -0.035 from K⁺.

^f-0.199 from Na⁺ and -0.205 from K⁺.

Table 7. Partial Molal Volume of the Salts and the Best Current Estimated Salting Coefficients and Pitzer Parameter ζ_{B-a-c} (Chanson, 2006).

Salt	$(V_{\text{salt}}^\circ)^a$	$(k_S)^b$	$(k_S)^c$	Cation	Anion	$(\zeta_{B-c-a})^d$
HCl	14.9	0.217	0.217	H	Cl	-0.021
LiCl	15.4	0.173	0.173	Li	Cl	-0.004
NaCl	17.0	0.055	0.055	Na	Cl	-0.008
KCl	20.8	-0.051	-0.051	K	Cl	0.001
RbCl	23.1	-0.051	-0.052	Rb	Cl	-0.006
CsCl	27.1	-0.069	-0.069	Cs	Cl	0.000
MgCl ₂	30.5	0.382	0.382	Mg	Cl	-0.016
CaCl ₂	32.2	0.329	0.329	Ca	Cl	0.010
SrCl ₂	33.4	0.283 ^e	0.283			
BaCl ₂	36.0	0.180	0.180	Ba	Cl	-0.052
HBr	18.7	0.230	0.230			
LiBr	19.2	0.186	0.186			
NaBr	20.8	0.068	0.068			
KBr	24.6	-0.038 ^f	-0.038			
RbBr	26.9	-0.039	-0.039			
CsBr	30.9	-0.056	-0.056			
MgBr ₂	38.1	0.409	0.409			
CaBr ₂	39.8	0.356	0.356			
SrBr ₂	41.0	0.310	0.310			
BaBr ₂	43.6	0.207	0.207			
HI	25.4	0.260	0.260	H	I	-0.018
LiI	25.9	0.216	0.216	Li	I	-0.001
NaI	27.5	0.098	0.098	Na	I	-0.005
KI	31.3	-0.008	-0.008	K	I	0.004
RbI	33.6	-0.009	-0.009	Rb	I	-0.003
CsI	37.6	-0.026	-0.026	Cs	I	0.003
MgI ₂	51.5	0.468	0.468	Mg	I	-0.010
CaI ₂	53.2	0.41	0.415	Ca	I	-0.004
SrI ₂	54.4	0.372 ^g	0.369			
BaI ₂	57.0	0.266	0.266	Ba	I	-0.046
HNO ₃	21.1	0.136	0.135	H	NO ₃	-0.003
LiNO ₃	21.6	0.094	0.091	Li	NO ₃	-0.002
NaNO ₃	23.2	-0.042	-0.027	Na	NO ₃	-0.008
KNO ₃	27.0	-0.120	-0.133	K	NO ₃	-0.012
RbNO ₃	29.3	-0.134	-0.134	Rb	NO ₃	-0.004
CsNO ₃	33.3	-0.151	-0.151	Cs	NO ₃	0.002
Mg(NO ₃) ₂	42.9	0.217	0.217	Mg	NO ₃	-0.013
Ca(NO ₃) ₂	44.6	0.164	0.164	Ca	NO ₃	-0.007
Sr(NO ₃) ₂	45.8	0.120 ^h	0.118			
Ba(NO ₃) ₂	48.4	0.015	0.015	Ba	NO ₃	-0.049
H ₂ SO ₄	21.7	0.024	0.024	H	SO ₄	-0.089
Li ₂ SO ₄	22.7	-0.065	-0.065	Li	SO ₄	-0.055
Na ₂ SO ₄	25.9	-0.303	-0.301	Na	SO ₄	-0.065
K ₂ SO ₄	33.5	-0.510	-0.513	K	SO ₄	-0.043

Table 7. (Continued).

Rb ₂ SO ₄	38.1	<i>-0.515</i>	<i>-0.515</i>	Rb	SO ₄	<i>-0.059</i>
Cs ₂ SO ₄	46.1	<i>-0.549</i>	<i>-0.549</i>	Cs	SO ₄	<i>-0.047</i>
MgSO ₄	22.4	<i>-0.029</i>	<i>-0.029</i>	Mg	SO ₄	<i>-0.117</i>
CaSO ₄	24.1	<i>-0.082</i>	<i>-0.082</i>	Ca	SO ₄	<i>-0.111</i>
SrSO ₄	25.3	<i>-0.128^d</i>	<i>-0.128</i>			
BaSO ₄	27.9	<i>-0.230</i>	<i>-0.231</i>	Ba	SO ₄	<i>-0.153</i>

^aCalculated from V_{cryst}° (15,17)

^bThe italic values of this column are calculated from Eq. (18).

^cThe italic values of this column are calculated from Eq. (2).

^dThe italic values of this column are calculated from Eq. (20).

^e $k_S = -0.037V_{\text{salt}}^{\circ} - 1.519$ using k_S values of MgCl₂, CaCl₂, and BaCl₂.

^f $k_S = 0.004V_{\text{salt}}^{\circ} - 0.106$ using k_S values of KCl and KI.

^g $k_S = -0.037V_{\text{salt}}^{\circ} - 2.385$ using k_S values of MgI₂, CaI₂, and BaI₂.

^h $k_S = -0.037V_{\text{salt}}^{\circ} - 1.815$ using k_S values of Mg(NO₃)₂, Ca(NO₃)₂, and Ba(NO₃)₂.

ⁱ $k_S = -0.037V_{\text{salt}}^{\circ} - 0.808$ using k_S values of MgSO₄, CaSO₄, and BaSO₄.

Note: The equation numbers in notes b, c, and d refer to equations in the original reference by Chanson (2006).

Appendix C

Table 8. Solubility Data in the System Na₂O-B₂O₃-H₂O (Nies and Hulbert, 1967).

0:1:3	= H ₃ BO ₃
1:1:1	= Na ₂ O·B ₂ O ₃ ·H ₂ O or NaBO ₂ ·0.5H ₂ O
1:1:4	= Na ₂ O·B ₂ O ₃ ·4H ₂ O or NaBO ₂ ·2H ₂ O
1:1:8	= Na ₂ O·B ₂ O ₃ ·8H ₂ O or NaBO ₂ ·4H ₂ O
1:2:4	= Na ₂ O·2B ₂ O ₃ ·4H ₂ O
1:2:5	= Na ₂ O·2B ₂ O ₃ ·5H ₂ O
1:2:10	= Na ₂ O·2B ₂ O ₃ ·10H ₂ O
1:5:10	= Na ₂ O·5B ₂ O ₃ ·10H ₂ O or NaB ₅ O ₈ ·5H ₂ O
2:5:5	= 2Na ₂ O·5B ₂ O ₃ ·5H ₂ O
2:5.1:7	= 2Na ₂ O·5.1B ₂ O ₃ ·7H ₂ O
2:9:11	= 2Na ₂ O·9B ₂ O ₃ ·11H ₂ O
(m)	= Metastable

Na ₂ O, Wt. %	B ₂ O ₃ , Wt. %	Na ₂ O/B ₂ O ₃ , Mole Ratio	Solid Phases
Temperature, 0° C.			
0	1.42	0	0:1:3
0.18	2.18	0.095	0:1:3
0.70	4.23	0.186	0:1:3
0.82	4.79	0.192	1:5:10(m)
0.81	4.66	0.196	0:1:3 & 1:2:10
0.88	4.93	0.201	1:5:10(m)
0.90	4.94	0.205	1:5:10(m)
0.53	2.85	0.208	1:2:10
0.31	1.14	0.306	1:2:10
0.324	0.727	0.500	1:2:10
1.401	1.607	0.980	1:2:10
4.67	5.27	0.997	1:2:10
6.80	7.63	1.002	1:2:10 & 1:1:8
7.14	6.67	1.203	1:1:8
Temperature, 5° C.			
0	1.677	0	0:1:3
0.195	2.47	0.089	0:1:3
0.763	4.81	0.179	0:1:3
0.99	5.68	0.197	0:1:3 & 1:5:10
1.02	5.73	0.200	1:5:10
1.15	6.28	0.206	0:1:3 & 1:2:10(m)
1.09	5.90	0.207	1:2:10 & 1:5:10;
0.88	4.70	0.210	1:2:10
0.715	3.71	0.217	1:2:10
0.48	2.14	0.251	1:2:10
0.382	1.137	0.380	1:2:10
0.402	0.902	0.501	1:2:10
0.556	0.821	0.762	1:2:10
5.43	6.13	0.996	1:2:10
7.35	8.29	1.00	1:2:10 & 1:1:8
7.69	7.24	1.19	1:1:8
Temperature, 10° C.			
0	1.967	0	0:1:3
0.27	3.11	0.096	0:1:3
0.73	4.97	0.164	0:1:3
1.13	6.57	0.193	0:1:3 & 1:5:10
1.21	6.74	0.201	1:5:10
1.65	8.62	0.215	0:1:3 & 1:2:10(m)
1.36	7.04	0.217	1:5:10 & 1:2:10
1.21	6.2	0.220	1:2:10
0.90	4.4	0.229	1:2:10
0.70	3.2	0.246	1:2:10
0.56	2.25	0.279	1:2:10
0.502	1.78	0.317	1:2:10
0.499	1.125	0.500	1:2:10
0.555	1.02	0.612	1:2:10
0.632	1.00	0.710	1:2:10
0.997	1.26	0.888	1:2:10
2.23	2.595	0.975	1:2:10
5.38	6.10	0.991	1:2:10
8.03	9.05	0.996	1:2:10 & 1:1:8
8.13	8.24	1.110	1:1:8
8.36	7.72	1.218	1:1:8
Temperature, 20° C.			
0	2.66	0	0:1:3
0.373	4.29	0.098	0:1:3
0.97	6.80	0.160	0:1:3
1.43	8.68	0.1855	0:1:3 & 1:5:10
1.59	8.96	0.200	1:5:10
1.87	9.56	0.220	1:5:10
3.45	16.41	0.236	0:1:3 & 1:2:10(m) ^a
2.19	10.35	0.238	1:5:10 & 1:2:10

Table 8. (Continued).

Na ₂ O Wt. %	B ₂ O ₃ , Wt. %	Na ₂ O/B ₂ O ₃ , Mole Ratio	Solid Phases
Temperature, 20° C.			
1.40	6.3	0.25	1:2:10
1.05	4.4	0.268	1:2:10
0.783	2.5	0.352	1:2:10
0.765	1.72	0.500	1:2:10
0.994	1.53	0.279	1:2:10
1.77	2.18	0.911	1:2:10
6.27	7.18	0.981	1:2:10
9.53	10.88	0.984	1:2:10 & 1:1:8
9.54	9.63	1.114	1:1:8
9.74	9.14	1.198	1:1:8
Temperature, 30° C.			
0.517	5.83	0.100	0:1:3
1.237	8.8	0.158	0:1:3
1.83	11.22	0.183	0:1:3 & 1:5:10
2.12	11.75	0.203	1:5:10
2.91	13.6	0.240	1:5:10
5.14	23.16	0.249	0:1:3 & 1:2:10(m) ^a
3.46	15.08	0.258	1:5:10 & 1:2:10
2.33	9.7	0.270	1:2:10
1.59	6.04	0.296	1:2:10
1.27	3.94	0.362	1:2:10
1.17	2.63	0.499	1:2:10
1.36	2.32	0.661	1:2:10
1.97	2.66	0.831	1:2:10
3.24	3.95	0.921	1:2:10
4.63	5.49	0.949	1:2:10
11.48	13.46	0.959	1:2:10 & 1:1:8
8.20	9.59	0.961	1:2:10
11.07	12.37	1.006	1:1:8
11.18	11.42	1.100	1:1:8
11.47	10.70	1.205	1:1:8
Temperature, 40° C.			
0.68	7.6	0.101	0:1:3
1.48	11.1	0.150	0:1:3
2.26	14.25	0.178	0:1:3 & 1:5:10
2.76	15.1	0.205	1:5:10
3.57	17.0	0.236	1:5:10
4.29	18.86	0.255	1:5:10 & 2:5.1:7
5.51	22.17	0.280	1:5:10 & 1:2:10(m)
3.78	15.77	0.270	2:5.1:7
4.70	18.6	0.284	1:2:10(m)
3.39	12.92	0.295	1:2:10 & 2:5.1:7
2.74	9.9	0.311	1:2:10
2.31	7.7	0.337	1:2:10
1.893	5.32	0.399	1:2:10
1.82	4.10	0.499	1:2:10
2.00	3.67	0.613	1:2:10
2.71	3.95	0.772	1:2:10
4.68	5.93	0.884	1:2:10
14.48	18.33	0.888	1:2:10 & 1:1:8
12.72	15.88	0.900	1:2:10
9.83	12.03	0.917	1:2:10
13.14	14.78	1.000	1:1:8
13.27	13.71	1.088	1:1:8
13.60	12.72	1.202	1:1:8
42.17	4.46	10.63	1:1:1 ^b
Temperature, 50° C.			
0	5.78	0	0:1:3
0.912	9.93	0.103	0:1:3
2.76	17.74	0.175	0:1:3 & 1:5:10
3.44	20.49	0.189	0:1:3 & 2:9:11(m) ^a
3.33	18.53	0.202	1:5:10
4.20	21.48	0.220	2:9:11(m) ^a
4.34	20.9	0.233	1:5:10
4.98	22.73	0.246	2:5.1:7 & 2:9:11(m)
4.88	22.13	0.247	1:5:10 & 2:5.1:7
5.63	24.27	0.260	2:9:11 & 1:5:10(m)
3.77	14.84	0.286	2:5.1:7
8.64	32.09	0.303	1:5:10 & 1:2:10(m)
8.23	30.52	0.303	2:9:11 & 1:2:10(m)
6.89	25.3	0.306	1:2:10(m)
4.63	15.9	0.327	1:2:10(m)
3.48	10.75	0.364	1:2:10 & 2:5.1:7
3.19	9.06	0.396	1:2:10
2.91	6.56	0.499	1:2:10
3.16	5.88	0.605	1:2:10
3.99	6.24	0.719	1:2:10
17.13	23.99	0.803	1:2:10(m) ^a
19.34	26.50	0.820	1:2:5 & 1:1:8

Table 8. (Continued).

Na ₂ O, Wt. %	B ₂ O ₃ , Wt. %	Na ₂ O/B ₂ O ₃ , Mole Ratio	Solid Phases
Temperature, 50° C.			
19.62	26.90	0.820	1:2:5 & 1:1:4(m)
6.36	8.70	0.821	1:2:10
16.94	22.81	0.835	1:2:5
13.27	17.83	0.837	1:2:5
8.51	11.35	0.842	1:2:10
17.67	22.25	0.893	1:1:8
16.17	18.25	0.996	1:1:8
16.02	17.90	1.006	1:1:8
16.12	16.74	1.082	1:1:8
16.56	15.95	1.167	1:1:8
Temperature, 60° C.			
0	7.22	0.000	0:1:3
1.04	11.9	0.098	0:1:3
2.08	16.5	0.142	0:1:3;
3.36	21.77	0.174	0:1:3 & 1:5:10
3.58	22.60	0.178	0:1:3 & 2:9:11(m)
3.97	22.62	0.198	1:5:10 & 2:9:11
4.30	23.68	0.204	1:5:4(m) ^a
4.13	22.74	0.204	2:9:11
4.21	23.10	0.205	1:5:10(m)
5.61	26.13	0.241	1:5:10 & 2:5.1:7(m)
5.40	24.83	0.245	2:9:11 & 2:5.1:7
7.09	29.90	0.266	1:5:10(m)
4.36	17.80	0.275	2:5.1:7
10.25	37.92	0.304	1:5:10 & 1:2:4(m)
9.18	33.29	0.310	1:2:4 & 2:9:11(m)
10.98	39.57	0.312	1:5:10 & 1:2:5(m)
11.85	41.84	0.318	1:5:10 & 1:2:10(m)
9.52	33.51	0.319	1:2:5(m)
7.55	26.00	0.326	1:2:4(m)
7.88	26.31	0.337	1:2:5(m)
7.56	24.68	0.344	1:2:5(m)
8.11	26.48	0.344	1:2:10(m) ^a
6.71	21.01	0.359	1:2:5(m) ^a
6.96	21.63	0.361	1:2:10(m) ^a
3.94	11.83	0.375	2:5.1:7
5.40	16.07	0.378	1:2:4(m)
5.52	15.72	0.395	1:2:10
6.14	18.25	0.378	1:2:10(m) ^c
6.09	18.02	0.380	1:2:5(m) ^a
5.59	15.83	0.397	1:2:5(m)
4.63	11.58	0.450	1:2:4 & 2:5.1:7
5.01	12.45	0.452	1:2:10(m)
5.11	12.71	0.452	1:2:5(m)
4.95	11.89	0.468	1:2:10 & 2:5.1:7(m)
5.03	11.32	0.499	1:2:5(m)
4.52	10.23	0.497	1:2:4
4.94	11.14	0.498	1:2:10(m)
5.28	10.02	0.592	1:2:10(m)
5.40	10.22	0.594	1:2:5(m)
4.96	9.29	0.601	1:2:4
5.70	10.30	0.621	1:2:5(m) ^b
5.72	10.23	0.629	1:2:10(m) ^a
5.89	10.36	0.639	1:2:5(m) ^c
6.05	10.57	0.643	1:2:10(m) ^a
6.69	10.94	0.688	1:2:5(m) ^d
6.27	9.98	0.706	1:2:4
7.77	12.27	0.712	1:2:10(m) ^e
8.47	12.73	0.748	1:2:5(m)
8.22	11.94	0.773	1:2:4
21.56	31.42	0.771	1:2:5 & 1:1:4(m)
12.00	16.92	0.797	1:2:5(m)
18.83	26.45	0.800	1:2:5(m)
15.65	21.83	0.806	1:2:5(m)
20.66	28.58	0.813	1:2:4 & 1:1:4
13.43	18.20	0.829	1:2:4
16.66	22.52	0.831	1:2:4
19.46	24.64	0.888	1:1:4
18.14	20.55	0.992	1:1:4
18.03	18.48	1.096	1:1:4
18.39	16.53	1.250	1:1:4
19.45	13.14	1.664	1:1:4
21.77	9.52	2.57	1:1:4
28.49	6.31	5.07	1:1:4

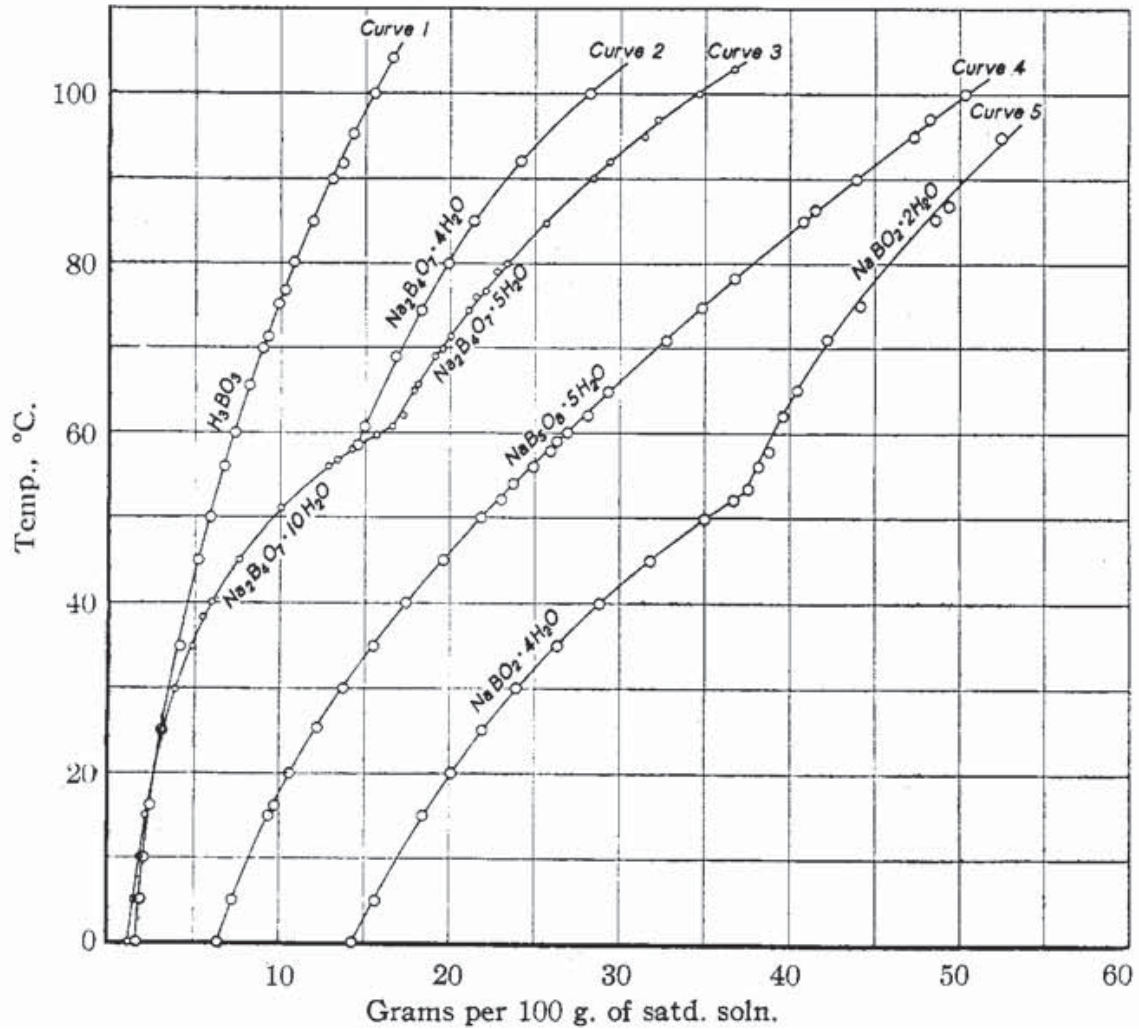


Figure 6. Solubility of Sodium Borates as Compared to Boric Acid ((Blasdale and Slansky, 1939).

Distribution:

A.B. Barnes, 999-W J.M. Bricker, 704-27S H.H. Burns, 773-41A K.P. Crapse, 773-A R.E. Edwards, 773-67A T.L. Fellingner, 704-26S S.D. Fink, 773-A F.F. Fondeur, 773-A M. Geeting 241-152H B. Giddings, 786-5A B.A. Gifford, 704-56H C.C. Herman, 999-W E.W. Holtzscheiter, 704-15S J.F. Iaukea, 704-30S E. A. Kyser, 773-A	D.H. McKenzie, 241-197H S.L. Marra, 773-A B.A. Oard, 241-197H J.E. Occhipinti, 704-S F.M. Pennebaker, 773-42A T.B. Peters, 773-42A R.A. Pierce, 773-A H.P. Boyd, 704-27S J.W. Ray, 704-S A. Samadi-Dezfouli, 241-197H D.C. Sherburne, 704-S A.V. Staub, 704-27S M.E. Stone, 999-W K.H. Subramanian, 766-H J.P. Vaughan, 773-41A
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