

SOLUBILITY OF BAYER LIQUOR IMPURITIES

IN EVAPORATIVE CRYSTALLIZATION

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Equations have been developed to calculate the solubility of Na_2CO_3 and Na_2SO_4 in Bayer liquor during evaporative crystallization. The equations predict impurity equilibrium concentrations from the free Na^+ ion concentration. The correlations are based on the liquor molality and assume the presence of uni-univalent ions in caustic solutions as proposed by Dewey.

Introduction

This laboratory is engaged in the development of rigorous energy and mass balance mathematical models for operating Bayer plants. In addition to the usual unit operation descriptions, these models require mathematical descriptions of the properties of the Bayer plant liquors and of the chemical reactions and equilibria important to various sections of the plant. This paper presents results of a study of the equilibria involved in the removal by crystallization of a portion of the oxalate, sulfate, and carbonate impurities from the recirculating caustic liquor.

Evaporative crystallization is commonly used in Bayer plants to remove a portion of the carbonate, sulfate and oxalate impurities from the liquor. The process typically involves evaporation of a fraction of the liquor stream from which the bulk of alumina has been crystallized. The liquor is evaporated to concentrations exceeding the solubility level of the impurities, which precipitate and are removed by filtration, centrifugation, etc. The residual liquor with its reduced impurity level is then returned to the plant stream.

The purpose of this work is to provide mathematical relationships which enable calculation of the amount of impurity removed by evaporative crystallization. Since the precipitated salts comprise a mixture of crystals of several carbonate-sulfate compounds, equilibrium constants could not be determined for the individual salts. However, empirical expressions relating the equilibrium solubility of carbonate and of sulfate in solution to the free Na^+ concentration were obtained. These expressions enable calculation of the carbonate and sulfate concentration in the liquor after crystallization, from which the amount of carbonate and sulfate removed from a specified feed liquor can be calculated for various amounts of evaporation. No expression for oxalate was obtained due to analytical problems which will be resolved later.

Experimental Expressions for Carbonate and Sulfate

Empirical expressions for the equilibrium concentration of carbonate and sulfate in Bayer liquor were derived as functions of the free Na^+ concentration. The equations are:

$$(1) \ln[\text{NaCO}_3^-] = -2.6642(\pm 0.053) \times \ln[\text{free Na}^+] + 5.3677 (\pm 0.17)$$

$$(2) \ln[\text{NaSO}_4^-] = -2.6069(\pm 0.107) \times \ln[\text{free Na}^+] + 4.2731 (\pm 0.23)$$

The crystalline phases of the salts precipitated from Bayer liquor or from comparable synthetic liquor by evaporative crystallization are Na_2CO_3 , $\text{Na}_2\text{C}_2\text{O}_4$, $\text{Na}_6\text{CO}_3(\text{SO}_4)_2$, $\text{Na}_4\text{CO}_3\text{SO}_4$, $\text{Na}_6(\text{CO}_3)_2\text{SO}_4$. The solids from each evaporative crystallization test comprised all of the above phases.

The fit of the regression lines is shown in Figures 1 and 2. The logarithm of the carbonate or sulfate concentration was regressed against $\ln[\text{free Na}^+]$ and temperature. In both cases, the temperature coefficient was statistically insignificant.

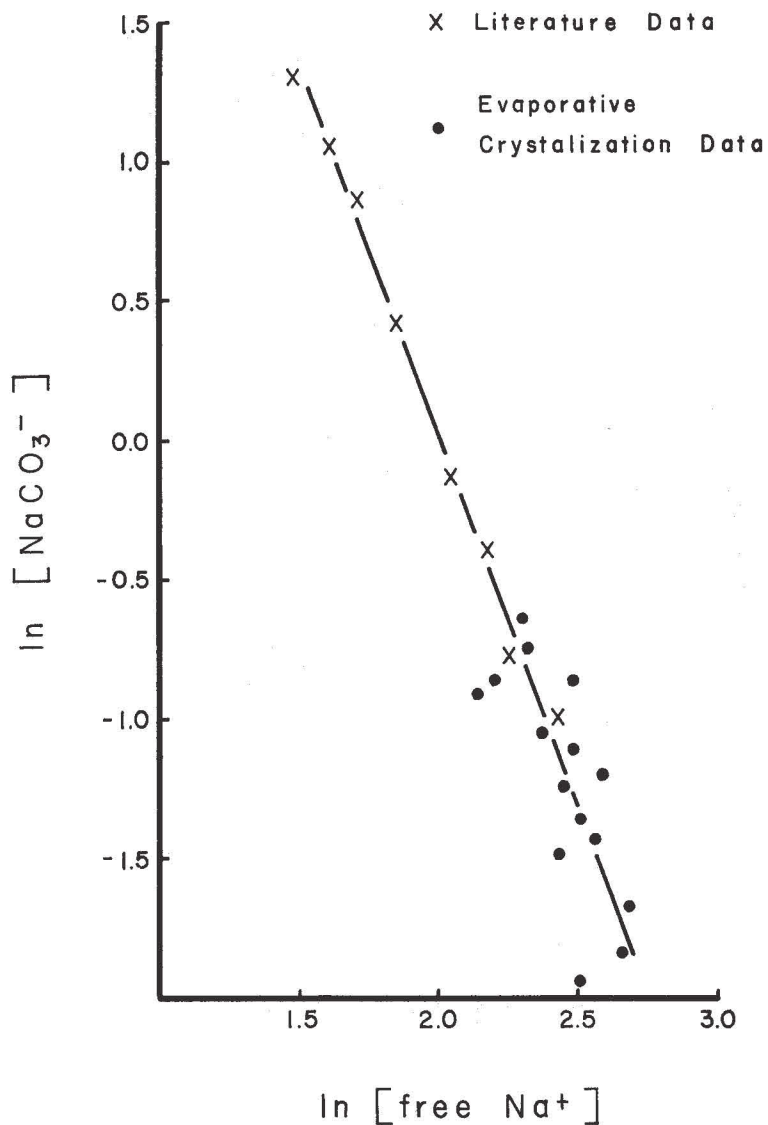


Figure 1. Solubility of Na₂CO₃

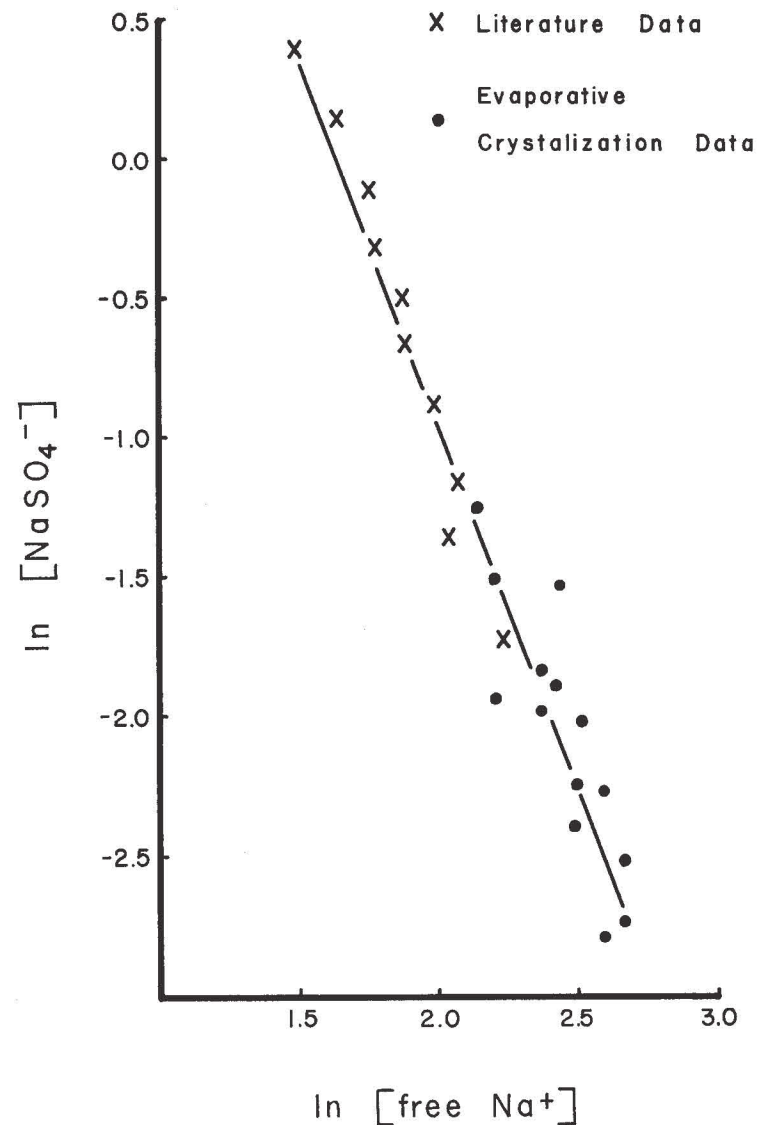


Figure 2. Solubility of Na₂SO₄

DISCUSSION

Calculation of the free Na^+ concentration is based on the theory of uni-univalent ion populations in concentrated caustic solutions as proposed by Dewey(1). This assumes the presence of only mono-valent ions in solution (e.g., AlO_2^- , NaCO_3^- , NaSO_4^- , etc.). Thus, Na_2CO_3 and Na_2SO_4 each contribute only one sodium ion to the total "free" Na^+ concentration.

The solubility expressions were obtained by regression analysis of data from 29 laboratory evaporative crystallization tests along with literature solubility data.

The literature carbonate solubility tests used in the analysis were conducted with the following types of solutions: (1) NaOH (2.2-30%) and Na_2CO_3 ; (2) NaOH (2.2-30%), Na_2SO_4 (0.5-3.1%), and Na_2CO_3 ; (3) NaOH (8.7-18.6%), NaCl (1.7-15%), and Na_2CO_3 ; and (4) NaOH (8.8-18.6%), NaCl (1.7-14.8%), Na_2SO_4 (0.4-2.3%) and Na_2CO_3 .

The sulfate solubility tests used from the literature were conducted in these solutions: (1) NaOH (8.7-18.6%) and Na_2SO_4 ; (2) NaOH (8.7-18.6%), NaCl (3-17.3%), and Na_2SO_4 ; (3) NaOH (8.6-19.5%), Na_2CO_3 (1.1-4.0%), and Na_2SO_4 ; and (4) NaOH (8.9-18.3%), NaCl (1.9-17.3%), Na_2CO_3 (0.2-4.0%), and Na_2SO_4 . Temperatures ranged from about 50 to 120°C.

Both synthetic and Bayer plant liquors were used in the evaporative crystallization tests, with resulting NaOH and NaAlO_2 concentrations ranging from about 11.9-16.3% and 7.9-20.7%, respectively. The ranges of impurities in the evaporation test liquors are: (1) Na_2CO_3 , 0.9-3.6%. (2) Na_2SO_4 , 0.3-2.7%; (3) NaCl , 0-10%; and (4) $\text{Na}_2\text{C}_2\text{O}_4$, 0-0.38%. Temperatures of the tests ranged from about 111 to 124°C.

The regression of the carbonate data contained 68 literature points from three experimenters (Hostalek (2), Green and Frattali (2), and Itkina (3)). Good agreement was found among the three sets of data and with the evaporative crystallization data, except for a few cases where NaCl was present as a solid phase as well as Na_2CO_3 (3). Carbonate solubility was substantially lower under these conditions. These data were not included in the regression, since the NaCl concentration was far outside the range typical of Bayer liquor.

The regression of the sulfate data contained 18 literature solubility points by Itkina. Data by Green and Frattali diverged at the higher concentrations and was not consistent with the results of Itkina or the evaporative crystallization tests.

The total molality (which is numerically equivalent to the free Na^+ concentration) of the liquors used in the correlations range from about 4.5 to 15. Liquors from the evaporative crystallization tests comprise the upper range of molalities (~8.5 to 15) and extend the range of the literature carbonate and sulfate data as seen in Figures 1 and 2.

An apparatus consisting of a 600 ml teflon beaker, rubber stopper, reflux condenser, and condensate draw-off tube was used in the laboratory tests. Heat and agitation were supplied by a hotplate with magnetic stirrer. The liquor was boiled at atmospheric pressure and allowed to evaporate by removing condensate from the system. Each test then was allowed to reflux overnight to equilibrate. The resulting slurries were vacuum filtered and the liquor diluted to ensure its stability for subsequent analysis. Solids were washed with "Reagent Alcohol", dried at 110°C, ground and analyzed by wet assay and x-ray diffraction.

Feed liquors consisted of synthetic and actual Bayer plant liquors having about 6% NaOH , 2% Na_2CO_3 and 6% NaAlO_2 , concentrations typical of feed to a plant evaporative crystallizer. The synthetic liquors were spiked with Na_2SO_4 , NaCl , and $\text{Na}_2\text{C}_2\text{O}_4$ to obtain a range of concentrations; some of the Bayer liquors were also spiked to obtain higher than typical amounts of these salts. The overall range of starting concentrations for these impurities are: (1) Na_2SO_4 , 0.87-2.05%; (2) NaCl , 0-2.8%; (3) $\text{Na}_2\text{C}_2\text{O}_4$, 0-0.4%.

Several evaporation tests were run with each feed liquor in order to span the range of soda concentrations normally encountered in the discharge liquor in plant operations. Analyses of the 29 test liquors are presented in the Appendix.

References

- (1) J. L. Dewey, "Boiling Point Rise of Bayer Plant Liquors," *LIGHT METALS 1981*, pp. 185-201, Gordon M. Bell, editor, The Metallurgical Society of AIME, New York.
- (2) W. F. Linke, *SOLUBILITIES OF INORGANIC AND METAL-ORGANIC COMPOUNDS*, Volume II, Fourth Edition, 1965, pp. 918-920, 923, and 1131.
- (3) L. S. Itkina, "The Solubility Isotherm of the System $\text{Na}_2\text{SO}_4 - \text{Na}_2\text{CO}_3 - \text{NaCl} - \text{NaOH} - \text{H}_2\text{O}$ at 50°," *Zhur. Priklad. Khim.*, (*J. Applied Chem.*), Vol. 22, pp. 278-89 (1949).

Appendix

Composition of Liquors from Evaporative Crystallization Tests (Molal Basis)
(Moles/kg H₂O)

Deg C	OH ⁻	AlO ₂ ⁻	Cl ⁻	F ⁻	NaCO ₃ ⁻	NaSO ₄ ⁻	NaC ₂ O ₄ ⁻	ORG ⁻	K ⁺	FREE NA ⁺
123.2	8.387	2.547	1.234	0.018	0.194	0.092	0.016	0.935	0.214	13.407
116.8	6.416	1.928	1.027	0.018	0.338	0.136	0.018	0.719	0.162	10.583
119.9	7.566	2.290	1.282	0.020	0.146	0.125	0.024	0.872	0.190	12.299
116.9	7.349	3.548	0.001	0.002	0.228	0.216	0.000	0.000	0.002	11.344
111.8	5.299	2.546	0.000	0.004	0.400	0.287	0.000	0.000	0.000	8.536
116.2	5.763	3.564	2.296	0.007	0.362	0.105	0.000	0.000	0.000	12.099
118.9	6.600	4.065	2.255	0.002	0.305	0.062	0.000	0.000	0.001	13.288
117.5	6.154	3.975	0.779	0.000	0.377	0.086	0.005	0.000	0.000	11.377
112.3	4.798	3.096	0.575	0.002	0.536	0.175	0.026	0.000	0.000	9.208
114.5	5.381	3.480	0.689	0.003	0.475	0.140	0.017	0.000	0.000	10.184
118.0	6.177	3.941	2.422	0.003	0.237	0.140	0.024	0.000	0.000	12.943
122.4	7.219	4.687	2.124	0.005	0.158	0.081	0.007	0.000	0.000	14.281
115.3	5.368	3.452	0.874	0.002	0.318	0.147	0.011	0.000	0.000	11.437
117.8	6.676	4.294	0.874	0.006	0.255	0.133	0.014	0.000	0.000	12.250
114.8	5.768	3.701	0.722	0.006	0.348	0.159	0.014	0.000	0.000	10.719
118.0	6.559	4.218	0.822	0.003	0.237	0.120	0.012	0.000	0.000	11.971
117.3	6.457	4.282	3.140	0.006	0.307	0.065	0.014	0.000	0.000	14.271
121.4	6.999	4.691	2.663	0.006	0.184	0.042	0.010	0.000	0.000	14.595
113.8	5.365	3.548	2.551	0.004	0.420	0.102	0.011	0.000	0.000	12.001
114.3	5.450	3.593	2.371	0.002	0.384	0.093	0.011	0.000	0.000	11.902
112.9	5.305	1.473	0.914	0.014	0.417	0.222	0.020	0.663	0.131	9.008
117.4	6.854	1.908	1.196	0.014	0.255	0.150	0.028	0.852	0.170	11.231
118.2	5.294	3.141	2.336	0.018	0.326	0.126	0.020	0.732	0.164	11.974
122.1	6.374	3.783	2.394	0.014	0.222	0.111	0.043	0.945	0.199	13.843
113.0	4.023	2.384	2.089	0.015	0.529	0.250	0.046	0.577	0.121	9.866
115.2	4.974	2.962	1.059	0.015	0.380	0.136	0.045	0.699	0.083	10.225
112.9	4.319	2.582	0.933	0.014	0.386	0.144	0.040	0.646	0.073	9.024
117.8	5.684	3.374	1.273	0.017	0.289	0.108	0.025	0.804	0.090	11.548
120.3	6.460	3.855	1.628	0.017	0.282	0.104	0.025	0.946	0.107	13.292