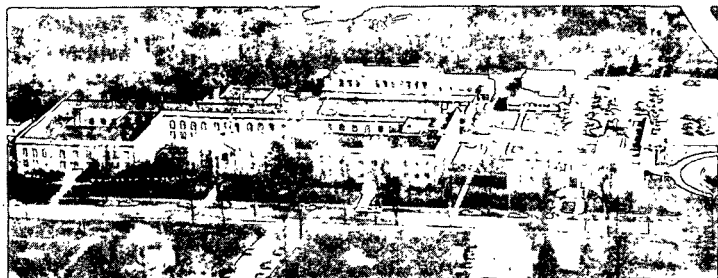


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SOLUBILITY LIMITS IN BLACK LIQUORS

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INTRODUCTION

The solubility limits of certain components in black liquor have an effect on recovery operations. Scaling in multiple-effect evaporators and in concentrators is directly related to solubility limits of the scaling materials. In addition, sludge formation in storage tanks, black liquor oxidation systems and direct-contact evaporators is a manifestation of solubility problems. Problems such as these have often been blamed on the organics in the liquor and especially on lignin precipitation. However, there are indications that they may actually be due to crystallization of inorganics from the liquor.

Since there is very little information available on the solubility of black liquor components, this study was designed to obtain data on the solubility limits of sodium sulfate and sodium carbonate in industrial black liquors and to determine the effects of liquor composition and temperature on the solubilities.

The attached paper is being presented at the International Symposium on Recovery of Chemicals and Energy, Boston, Massachusetts, September 7-10, 1975.

ABSTRACT

Solubility limits for various components in black liquor were determined at temperatures from 100°C to 140°C. The most important components are Na_2CO_3 and Na_2SO_4 . The solubility of carbonate and sulfate in black liquor is very similar to their solubility in caustic solutions. They precipitate together, and form a solid phase having a composition approximating that of Burkeite ($2 \text{Na}_2\text{SO}_4\text{-Na}_2\text{CO}_3$). The major variables affecting the solubility limit are the total sodium content of the liquor and the liquor solids content. A general correlation for Na_2CO_3 and Na_2SO_4 solubility in black liquor is presented. Temperature has a very minor effect on solubility over the range examined.

There was little evidence for organic precipitation in concentrating liquors up to 65% solids. Most organic which did precipitate was residual soap. Lignin appears to be resistant to precipitation during concentration of the liquor. Lowering of pH will lead to lignin precipitation. The latter effect is reversible.

INTRODUCTION

In alkaline pulping, the aqueous wastes (called black liquor) are collected and processed to recover the pulping chemicals. The nature and behavior of black liquor is important to these recovery operations. Black liquor contains the organic material dissolved from the wood during pulping (lignin, carbohydrates and extractives) and the residual inorganic pulping chemicals. The lignin is reported to be present in black liquor as a macro-molecular colloid stabilized by ionized phenolic and carboxylic acid groups. The carbohydrate material in the liquor originates mainly from hemicelluloses and is present as the sodium salts of various saccharinic acids. The extractives are mainly present as sodium salts of resin acids and fatty acids (soaps), and can form an association colloid.

The inorganics in the liquor stem from the pulping chemicals (white liquor). The main chemicals in the white liquor are usually NaOH, Na₂S, Na₂CO₃ and Na₂SO₄, with minor amounts of other compounds such as NaCl, Na₂S₂O₃. These minor components and Na₂CO₃ and Na₂SO₄ are essentially inert in the pulping process and are thus present in the black liquor. Some of the sulfide reacts with organic during the cook, but most will remain in the black liquor as NaHS. It may be oxidized to thiosulfate during the recovery process. Most of the NaOH will react during the cook and be present in the liquor as organically bound sodium (acetates, formates, saccharinic acid salts and with lignin). There can also be significant amounts of potassium in the liquor (1-3% on the solids) since some potassium enters with the wood and the system is fairly tightly closed.

Solubility limits of certain components in the liquor have an effect on recovery operations. Scaling in multiple-effect evaporators and in concentrators is directly related to solubility limits of the scaling materials. In addition,

sludge formation in storage tanks, black liquor oxidation systems and direct-contact evaporators is a manifestation of solubility problems. Problems such as these have often been blamed on the organics in the liquor and especially on lignin precipitation (which can occur on lowering the pH of the liquor). However, there are indications that they may actually be due to crystallization of inorganics (especially Na_2CO_3 and Na_2SO_4) from the liquor.

There is very little information available on the solubility of black liquor components. Berry (1) discussed scaling in multiple-effect evaporators. He listed sodium sulfate scale, calcium carbonate scale, silicate scale, soap scale, char scale, and combinations with fiber. No quantitative limits with regard to liquor composition were given. Backtemann and Marr (2) mentioned deposits caused by soap, inorganic salts such as Na_2CO_3 and Na_2SO_4 , and lignin precipitation, but offered no quantitative guidelines. Letonmyaki, et al. (3) examined the change in composition of black liquors during evaporation and the composition of the deposits formed. Their data are too limited to define saturation levels. They found the deposits to be enriched in Na_2SO_4 and Na_2CO_3 and resinous material and to contain considerably less organic than the liquor. Diedrichs and Hedstrom (4) considered the question of solubility limits for Na_2CO_3 and Na_2SO_4 in black liquor. They used the data of Green and Frattali (5) for the system $\text{NaOH}-\text{Na}_2\text{CO}_3-\text{Na}_2\text{SO}_4-\text{H}_2\text{O}$ to calculate limits for black liquor. They did not test this experimentally.

The main objectives of the present study were to obtain data on the solubility limits of Na_2SO_4 and Na_2CO_3 in industrial black liquors, determine the effects of liquor composition and temperature on the solubilities, evaluate the ability to use the data of Green and Frattali in interpreting solubilities in liquors, and to develop a general correlation for sulfate-carbonate solubility

in black liquor. In addition, attention was paid to the behavior of liquor organics and to the extent that organics would precipitate.

EXPERIMENTAL

Solubility data were obtained by equilibrating solution and solid phases in closed, stirred vessels immersed in a controlled temperature oil bath. The vessels had a capacity of about 3.5 liters of liquor. The stirrer blades wiped the walls so that precipitation and crystal growth occurred in the bulk of the liquor rather than on the walls. The vessels were designed so that they could be pressurized to permit measurements of solubilities above the normal boiling point of the liquors. An inert nitrogen atmosphere was maintained over the liquors during equilibration periods.

Samples of the solution phase were obtained by using fritted glass filters to exclude precipitated solids. This is similar to the method employed by Green and Frattali in their work on the $\text{Na}_2\text{CO}_3\text{-Na}_2\text{SO}_4\text{-NaOH-H}_2\text{O}$ system. Tubular filters, 5/8-inch diameter - 4-inches fritted length - coarse porosity (40-60 μm), were connected to ordinary Pyrex capillary tubes. At the end of the equilibration period, the filter assemblies were placed in the liquor and the vessels pressurized with nitrogen to force the solution samples through the filters. Initial attempts were made to use fritted filters of medium or fine porosity (pore sizes of 10-15 μm and 5 μm , respectively) to minimize the risk of small crystallites passing through with the solution phase. However, these were too impermeable to high solids black liquor. The validity of using coarse filters was established through the ability to duplicate Green and Frattali's results on the $\text{Na}_2\text{CO}_3\text{-Na}_2\text{SO}_4\text{-H}_2\text{O}$ system. Solution samples were caught in small glass weighing bottles. These were covered, cooled and weighed and then diluted up to a known volume. Measurement of the density and dissolved solids content of the diluted sample allowed a direct

calculation of the solids content of the original sample. All chemical analyses were carried out on the diluted samples.

Samples of solid phase were obtained from the sludge at the bottom of the vessels after decanting off the liquor. In order to do this, the vessels were removed from oil bath, cooled, opened and then the liquor decanted off. There are potential problems with this procedure because it is a nonequilibrium procedure and the liquor has an opportunity to cool. However, it was the only workable method found. Attempts to remove bulk liquor and collect solid phase by filtering off the solution were unsuccessful because of the high viscosity of the liquor.

The determination of the composition of the solid phase was complicated by the entrained liquor present in the sludge samples. This could not be washed away without dissolving most or all of the solid phase. Sludge samples were quantitatively diluted and analyzed in a manner identical to the solution samples. The composition of the solid phase was calculated by material balance assuming that all of the water present in the sludge sample was associated with entrained solution phase.

Equilibrium was approached slowly, and care was taken to minimize temperature and concentration gradients. If it was necessary to concentrate a liquor to reach a desired solids content, the concentration was done by free surface evaporation at 100°C, with a nitrogen sweep to carry off the water vapor. Three different methods of approaching equilibrium were used: addition of excess solid phase and approach by dissolution, concentration of liquor and approach by precipitation, and addition of a third component which would force precipitation. All three methods gave reasonable results.

Analysis of black liquors is not as precise as for purely inorganic systems. All analyses were performed on diluted samples and reported as wt.% on the dissolved solids. Procedures used were as follows:

Solids content: Liquor solids were determined by oven drying with an inert surface extender according to TAPPI procedure T 650 su-71.

Na₂SO₄: Precipitation as BaSO₄ according to TAPPI procedure T 625 ts-63.

Na₂CO₃: CO₂ evolution method as described in TAPPI procedure T 624 os-68.

Active alkali: (NaOH, Na₂S and other strongly alkaline salts) by titration with HCl to pH 8.3 corrected for Na₂CO₃ as determined separately.

Total sodium: Flame ionization spectrophotometry on digested samples as described in TAPPI procedure T 625 ts-63.

NaCl: Determined by Volhard procedure on an ashed sample.

Na₂S₂O₃: Determined with a mercury pool electrode as described in TAPPI procedure T 625 ts-63.

Organic was determined by difference between total solids and known inorganics plus organically bound sodium.

Material balances over the experiments were used as a method for testing the accuracy of the data and to verify that solid phase was truly present in the system.

Na₂CO₃-Na₂SO₄ SOLUBILITY

Understanding of the solubility behavior of Na₂CO₃ and Na₂SO₄ in black liquor is based upon the data of Green and Frattali (5) on the systems Na₂CO₃-Na₂SO₄-H₂O and Na₂CO₃-Na₂SO₄-NaOH-H₂O at 100°C. A phase diagram of the three-component system taken from their paper is shown in Fig. 1. The major solid phase is a solid solution of varying composition, approximating that of Burkeite (2 Na₂SO₄-Na₂CO₃) and having a range in composition from 1.4 Na₂SO₄•Na₂CO₃ to 2.2 Na₂SO₄•Na₂CO₃.

A phase diagram for the four-component system is shown in Fig. 2. The solid phases involved are the same as those in the 3-component system. The area between the two univariant lines represents saturated solutions in equilibrium with a solid solution ranging in composition from 1.4-2.2 $\text{Na}_2\text{SO}_4 \cdot \text{Na}_2\text{CO}_3$. Lines of constant total dissolved solids content are also shown on the diagram. There is a wide region where the total dissolved solids content changes only slightly with changes in composition. In this region, NaOH displaces Na_2SO_4 and Na_2CO_3 from solution on nearly a constant weight basis.

A comprehensive set of Na_2CO_3 - Na_2SO_4 solubility data was obtained on eight different black liquors at 45% solids and 100°C. The liquors used in the study were chosen to encompass a wide range of species and processing variables. Solid Na_2CO_3 and Na_2SO_4 in three different proportions were added to each liquor and equilibrium approached by dissolution. Compositions of the solution and solid phases are summarized in Appendix I. Except for the liquor solids content, all data are expressed as weight % on the solids.

These black liquor solubility data can be interpreted in terms of the data on the Na_2CO_3 - Na_2SO_4 -NaOH- H_2O system by following the suggestion of Diedrichs and Hedstrom (4) that all of the sodium salts in black liquor act on Na_2CO_3 and Na_2SO_4 as if they were NaOH. A comparison of the measured solubilities with those predicted by such a procedure is given in Table I. The average deviation is -1.3%, and the standard deviation is 6.5%. Phase distribution data (relative proportion of carbonate and sulfate in solution and solid phases) are shown in Fig. 3. The solid line is the expected phase distribution behavior based on Green and Frattali's data on the Na_2CO_3 - Na_2SO_4 -NaOH- H_2O system.

The remarkably good agreement between the solubility behavior in black liquor and the Na_2CO_3 - Na_2SO_4 -NaOH- H_2O system is somewhat surprising. It suggests

that 45% solids black liquor is an aqueous solution of inorganics and organics with little interference or competition for the available water between organic and inorganics. The main factor affecting Na_2CO_3 and Na_2SO_4 solubility is additional soluble sodium (by common ion effect) and this appears to be independent of the source of the sodium.

Additional data on Na_2CO_3 - Na_2SO_4 solubility in black liquor were obtained to determine the effects of total solids content, temperature and the addition of other sodium salts. These data are summarized in Appendix II. The amount of Na_2CO_3 and Na_2SO_4 expected to be present based on the Na_2CO_3 - Na_2SO_4 - NaOH - H_2O analogy is also given. A comparison between the amount of soluble carbonate and sulfate actually found and that predicted is given in Fig. 4. In general, the solubility is greater than expected and the deviation becomes greater as the solids content increases.

If allowance is made for the higher solids contents at which the tests were carried out, NaOH , NaCl and $\text{Na}_2\text{S}_2\text{O}_3$ appear to affect the solubility of Na_2CO_3 and Na_2SO_4 in the same manner as other sodium salts in the liquor. All three are very soluble in black liquor and would not normally be expected to precipitate. The main effect of adding NaCl , $\text{Na}_2\text{S}_2\text{O}_3$ or NaOH to the liquor is to decrease the solubility of Na_2CO_3 and Na_2SO_4 .

Temperature does not appear to have a strong effect on carbonate-sulfate solubility. The data at 120°C appears to line up quite well with the 100°C data. The data at 140°C is slightly less than predicted, even though the solids level is less than 45%. This seems to indicate that the solubility of Na_2CO_3 and Na_2SO_4 at 140°C is about 5% lower than it is at 100°C .

It is possible to develop a general correlation for $\text{Na}_2\text{CO}_3\text{-Na}_2\text{SO}_4$ solubility in black liquor by using the data of Green and Frattali and correcting it for the effect of liquor solids content. The major variables involved are the effective sodium content of the liquor defined as,

$$\text{Effective Sodium} = \text{Total Sodium} - 23 \left(\frac{\text{Na}_2\text{CO}_3}{53} + \frac{\text{Na}_2\text{SO}_4}{71} \right)$$

and total solids content. There is also a slight dependency on the $\text{Na}_2\text{CO}_3/\text{Na}_2\text{SO}_4$ ratio. A general correlation for a $\text{Na}_2\text{CO}_3/\text{Na}_2\text{SO}_4$ ratio of 80/20 is presented in Fig. 5. Correction factors to permit extending the curves to other $\text{Na}_2\text{CO}_3/\text{Na}_2\text{SO}_4$ ratios are given in Fig. 6. The value of soluble $\text{Na}_2\text{CO}_3 + \text{Na}_2\text{SO}_4$ read from Fig. 5 should be multiplied by the correction factor.

The relations summarized in Fig. 5 and 6 were able to correlate the data obtained in this study with a mean deviation of -0.6% and a standard deviation of 7.4%. These are only approximate relations. There are deviations from one liquor to another which are not accounted for by these curves. There are some indications that solubilities are higher in liquors with higher lignin contents, but the data are not conclusive. Reasons for deviations between different liquors remain obscure.

ORGANIC SOLUBILITY

The organic constituents considered most likely to precipitate were lignin and soap. Alkali lignin is present in the liquor as a macromolecular colloid whose stability is known to be pH dependent. In addition, Passinen (6) indicates that the colloidal stability is influenced by electrolyte concentration, so that it could tend to precipitate at high solids levels. Soaps form an association colloid and will precipitate as the liquor is concentrated. This

is the basis for their removal from the system in the evaporation sequence. All liquors used in this study were concentrated liquors taken after multiple-effect evaporation and thus generally low in soap content. Carbohydrate material was considered unlikely to precipitate because the saccharinic acid salts are quite soluble.

Organic solubility was studied indirectly by determining the amounts of organic in the solid phase during the solubility experiments. Organic was determined by difference between the total solids and the sum of known inorganics plus organically bound sodium. Organics in sludge samples were not characterized further. Characterizations of the liquors used are given in Appendix III.

In general, only small amounts of organic were found in the solid phase. In tests at lower solids contents, the greatest amounts of precipitated organic were found with those liquors having the greatest amounts of residual soap. They are considered to be mainly soap and entrained fiber. The sets in which organic precipitation was considered most likely to occur were those at the highest liquor solids contents. These data are summarized in Table II. Even under these severe conditions organic precipitation remains small and generally much less than carbonate and sulfate. Much of the organic which does precipitate is undoubtedly soap.

It would appear from these data that lignin is not precipitated by concentration of liquors to high solids contents. This is not an artifact of the procedures used. Experiments done using the same techniques on liquors which were acidified showed that as much as 15-25% of the total solids were precipitated and the precipitate was almost entirely organic. Lignin precipitation caused by lowering the pH was found to be completely reversible upon raising the pH by addition of caustic.

CaCO_3 SOLUBILITY

Attempts to apply these same techniques to the measurement of the solubility of CaCO_3 in black liquor were not successful. Part of the problem is analytical in nature. Accurate determinations of calcium in black liquors are very difficult. It also appears that a part of the calcium is present in the liquor as very small entrained particles able to pass through the filters. When successive samples of solution phase were taken through the same filter without cleaning it, the second sample was always found to be lower in calcium. This problem did not occur with the sodium carbonate-sulfate determination.

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TABLE I

COMPARISON OF MEASURED SOLUBILITIES WITH PREDICTIONS BASED
ON THE Na_2CO_3 - Na_2SO_4 - NaOH - H_2O SYSTEM

Sample	Measured $\text{Na}_2\text{CO}_3 + \text{Na}_2\text{SO}_4$	Predicted $\text{Na}_2\text{CO}_3 + \text{Na}_2\text{SO}_4$	Deviation, %
A-1	20.2	18.9	+6.9
A-2	19.1	19.6	-2.6
A-3	18.3	18.4	-0.5
B-1	18.9	19.2	-1.6
B-2	16.1	17.3	-6.9
B-3	13.6	15.8	-13.9
C-1	18.5	18.9	-2.1
C-2	15.6	17.3	-9.8
C-3	15.6	16.9	-7.7
D-1	22.5	21.8	+3.2
D-2	21.4	20.6	+3.9
D-3	18.8	19.2	-2.1
E-1	19.7	19.1	+3.1
E-2	16.8	17.6	-4.5
E-3	14.9	17.0	-12.4
F-1	20.2	18.9	+6.9
F-2	16.3	17.2	-5.2
F-3	15.8	17.2	-8.1
G-1	21.9	19.9	+10.0
G-2	19.4	18.9	+2.6
G-3	17.2	17.7	-2.8
H-1	22.3	20.0	+11.5
H-2	20.3	20.0	+1.5
H-3	18.0	18.3	-1.6

TABLE II

SUMMARY OF ORGANIC PRECIPITATION DATA

Run	Liquor Solids, %	Organic, % of solid phase	Na ₂ CO ₃ +Na ₂ SO ₄ , % of solid phase	Precipitated Organic, % of total solids ^a
1A	63.6	47.5	43.0	3.9
1B	69.7	23.0	59.7	1.5
1C	57.9	6.4	89.2	0.2
1D	62.6	23.6	73.4	2.8
1E	64.7	22.5	72.1	1.8
1F	58.1	10.9	82.8	0.2
1G	64.8	6.8	94.3	0.6
1H	58.7	13.2	75.1	0.0
6B	64.9	23.5	79.4	2.1
6D	65.5	24.8	68.3	2.6
6F	65.6	22.5	71.3	1.8
6G	63.9	16.1	82.2	1.3
6I	64.7	6.9	87.5	0.6
5A	59.1	34.4	61.6	0.0
5C	54.8	14.1	80.7	1.6
5D	57.7	14.4	82.8	1.1
5G	57.6	15.0	79.5	1.4
5H	58.4	31.6	58.8	1.7

^aBy material balance.

APPENDIX I

DATA ON SOLUBILITY OF Na_2CO_3 AND Na_2SO_4 IN BLACK LIQUORS
AT 45% SOLIDS

(Composition as wt.% of liquor solids)

Sample	Total Solids, %	Na_2CO_3	Na_2SO_4	Active Alkali as Na_2O	Total Na	Organic
A-1 Solid	47.9	11.8 17.3	8.4 42.9	4.8 1.1	20.0 23.3	37.3
A-2 Solid	47.0	9.2 12.1	9.9 58.6	5.05 0.1	18.5 23.2	30.1
A-3 Solid	46.6	8.3 8.8	10.0 68.6	5.05 0.0	19.1 25.8	22.7
B-1 Solid	46.1	12.9 35.4	6.0 58.1	7.95 0.2	20.8 35.6	4.9
B-2 Solid	46.0	10.4 27.8	5.7 70.9	8.4 -0.2	19.7 33.9	2.4
B-3 Solid	45.7	6.9 23.1	6.7 74.5	8.25 0.3	18.6 34.6	1.7
C-1 Solid	46.3	10.3 32.9	8.2 65.9	5.4 -0.3	19.6 36.2	0.5
C-2 Solid	45.7	7.3 28.9	8.3 70.6	5.55 -0.45	18.3 34.1	1.7
C-3 Solid	45.2	5.7 26.5	9.9 72.8	5.5 -0.3	18.5 31.8	3.9
D-1 Solid	47.3	14.9 31.5	7.6 67.8	4.8 0.5	19.7 32.3	3.6
D-2 Solid	47.3	12.5 32.2	8.9 64.6	4.6 -0.3	19.7 31.9	6.1
D-3 Solid	46.5	9.3 27.0	9.5 65.5	5.1 0.3	19.1 32.4	7.8
E-1 Solid	47.1	12.7 33.0	7.0 62.8	5.5 -0.2	20.2 36.3	2.5
E-2 Solid	46.2	10.1 26.4	6.7 71.6	5.65 -0.1	19.7 33.0	3.6
E-3 Solid	45.2	7.4 24.8	7.5 72.6	5.75 0.1	19.0 34.4	2.5

APPENDIX I (Continued)

DATA ON SOLUBILITY OF Na_2CO_3 AND Na_2SO_4 IN BLACK LIQUORS
AT 45% SOLIDS

(Composition as wt.% of liquor solids)

Sample	Total Solids, %	Na_2CO_3	Na_2SO_4	Active Alkali as Na_2O	Total Na	Organic
F-1	48.1	13.0	7.2	4.7	20.1	
Solid		31.6	61.3	0.0	33.0	7.6
F-2	46.5	8.5	7.8	6.1	19.3	
Solid		29.4	65.5	-0.3	33.4	5.6
F-3	46.1	7.1	8.7	6.0	18.5	
Solid		26.8	68.9	-0.1	33.5	4.7
G-1	47.5	13.3	8.6	3.7	20.9	
Solid		21.9	72.3	-0.2	33.4	5.3
G-2	47.3	10.5	8.9	3.8	19.7	
Solid		20.2	76.3	-0.3	32.9	4.1
G-3	46.7	8.0	9.2	3.75	18.8	
Solid		24.4	74.4	-0.3	33.3	2.6
H-1	47.7	14.4	7.9	4.7	21.2	
Solid		30.4	49.6	-0.2	32.8	16.3
H-2	46.4	11.6	8.7	4.7	20.1	
Solid		27.4	60.2	0.5	31.9	11.6
H-3	45.8	8.9	9.1	5.1	19.9	
Solid		27.6	64.0	-0.2	32.2	8.9

APPENDIX II

SUMMARY OF ADDITIONAL BLACK LIQUOR SOLUBILITY DATA

Set 1: 100°C - No materials added

Sample	Total Solids, %	Na ₂ CO ₃	Na ₂ SO ₄	Active Alkali as Na ₂ O	Total Na	Organic	Predicted Na ₂ CO ₃ +Na ₂ SO ₄
1A Solid	63.6	3.8 39.9	2.4 3.1	5.1 2.9	17.0 22.0	51.7	4.75
1B Solid	69.7	5.8 50.6	1.4 9.1	6.4 2.1	17.5 38.8	25.1	3.9
1C Solid	57.9	4.6 34.1	2.6 55.1	4.8 0.8	15.8 36.1	6.9	6.95
1D Solid	62.6	4.3 56.1	1.7 17.3	5.0 0.8	16.1 32.1	24.0	4.95
1E Solid	64.7	3.9 54.8	1.5 17.3	5.5 1.3	16.5 33.5	23.1	4.1
1F Solid	58.1	7.8 40.5	2.7 42.3	4.6 0.8	16.4 36.3	11.7	9.1
1G Solid	64.8	2.2 59.9	1.5 34.4	4.1 -0.5	16.8 37.0	5.8	3.0
1H Solid	58.7	11.1 57.8	1.7 17.3	1.8 1.9	14.4 40.0	14.6	11.7

Set 2: 100°C - Na₂CO₃ and Na₂SO₄ added

2A-1 Solid	47.1	13.4 33.6	7.5 61.9	4.5 -1.0	21.1 31.7	7.4	19.4
2A-2 Solid	50.2	12.0 30.9	5.3 60.0	4.9 -0.8	20.1 30.9	11.0	15.6
2A-3 Solid	55.2	10.1 31.2	3.6 56.3	5.2 -0.6	18.9 31.9	12.3	11.3
2A-4 Solid	59.2	8.0 33.9	2.6 50.3	5.35 0.6	18.7 32.4	14.0	7.8
2C-1 Solid	42.8	14.1 28.8	11.6 64.6	4.6 0.1	21.3 32.8	7.1	26.9
2C-2 Solid	45.5	12.3 32.5	8.1 62.5	4.8 -0.1	21.2 33.7	5.5	20.5
2C-3 Solid	49.6	10.0 37.1	5.6 57.8	5.2 -0.25	19.6 36.1	3.7	15.1
2C-4 Solid	53.4	8.2 40.6	4.6 52.9	5.4 -0.2	18.9 35.7	5.5	11.4

APPENDIX II (Continued)

SUMMARY OF ADDITIONAL BLACK LIQUOR SOLUBILITY DATA

Set 3: 100°C - NaCl added

Sample	Total Solids, %	Na ₂ CO ₃	Na ₂ SO ₄	Active Alkali as Na ₂ O	NaCl	Total Na	Organic	Predicted Na ₂ CO ₃ +Na ₂ SO ₄
3C-1	55.5	8.9	3.0	5.05	6.4	20.4		9.4
3C-2	56.4	6.8	2.0	4.8	12.4	22.3		6.65
C-2 Solid		40.3	31.8	0.3	16.3	36.3	9.2	
3D-1	56.7	8.4	2.4	4.95	7.2	19.8		8.5
3D-2	56.8	6.8	1.9	4.6	12.5	20.4		7.0
D-2 Solid		60.5	22.8	0.4	4.7	37.2	9.9	
3E-1	58.2	7.9	2.6	5.55	6.8	20.6		7.6
3E-2	57.5	4.7	1.4	5.3	12.6	20.8		5.05
E-2 Solid		45.0	20.3	0.2	29.9	38.4	4.1	
3F-1	56.7	7.4	2.8	5.4	6.6	20.5		7.95
3F-2	57.0	6.4	3.4	5.0	12.1	21.1		7.4
F-2 Solid		14.9	15.5	-0.2	56.7	38.2	8.4	
3G-1	57.7	7.1	3.6	3.8	6.5	20.2		7.95
3G-2	57.9	5.7	2.6	3.6	12.2	21.6		6.2
G-2 Solid		48.1	28.6	-0.3	5.9	36.6	13.2	

Set 4: 100°C - Na₂S₂O₃ added

Sample	Total Solids, %	Na ₂ CO ₃	Na ₂ SO ₄	Active Alkali as Na ₂ O	Na ₂ S ₂ O ₃	Total Na	Organic	Predicted Na ₂ CO ₃ +Na ₂ SO ₄
4E Solid	58.8	7.6	2.4	5.2	12.8	19.0		7.6
		31.0	23.2	0.1	20.4	44.3	7.8	
4G Solid	59.1	6.8	3.1	3.45	16.5	19.0		7.4
		26.4	12.2	-1.3	12.2	30.1	38.0	
4H Solid	58.8	9.2	2.5	2.7	13.8	18.6		8.8
		38.9	17.2	0.8	0.1	38.7	27.2	
4C-1 Solid	56.9	9.2	3.7	4.5	16.4	20.0		9.6
		36.9	40.5	0.7	2.1	33.4	16.4	
4C-2 Solid	57.2	9.3	3.6	4.3	17.1	20.2		9.35
		36.3	42.3	0.9	1.9	33.9	15.1	

APPENDIX II (Continued)

SUMMARY OF ADDITIONAL BLACK LIQUOR SOLUBILITY DATA

Set 5: 100°C - NaOH added

Sample	Total Solids, %	Na ₂ CO ₃	Na ₂ SO ₄	Active Alkali as Na ₂ O	Total Na	Organic	Predicted Na ₂ CO ₃ +Na ₂ SO ₄
5A	59.1	7.3	2.1	8.6	19.9		6.95
Solid		46.2	15.4	0.2	28.8	34.5	
5C	54.8	7.9	2.7	8.7	20.3		8.85
Solid		48.6	32.1	1.1	35.6	14.6	
5D	57.7	7.2	1.7	8.9	18.9		7.4
Solid		60.9	21.9	1.0	35.3	14.8	
5G	57.6	5.6	2.7	7.9	19.5		6.8
Solid		52.7	26.8	1.1	35.6	15.8	
5H	58.4	7.1	1.7	10.1	20.0		6.8
Solid		43.4	15.4	3.2	31.8	31.4	

Set 6: 120°C - Nothing added

6B	64.9	3.6	2.0	8.2	17.7		3.95
Solid		38.2	41.2	-2.6	27.5	22.9	
6D	65.5	6.3	2.1	3.7	16.3		5.6
Solid		54.2	14.1	5.0	30.4	26.6	
6F	65.6	4.6	2.8	5.8	16.7		4.95
Solid		48.1	23.2	0.3	32.2	24.6	
6G	63.9	3.1	2.5	4.5	18.8		4.95
Solid		60.3	21.9	1.0	33.4	17.0	
6I	64.7	3.6	2.3	5.2	16.2		4.4
Solid		75.3	12.2	3.9	39.3	7.6	

Set 7: 120°C - Na₂CO₃ and Na₂SO₄ added

7A	48.5	10.9	6.6	4.75	19.3		17.2
Solid		26.3	47.3	0.1	26.4	26.7	
7C	47.8	11.9	6.0	4.7	20.3		17.6
Solid		34.5	63.4	0.0	34.2	3.3	
7D	47.5	13.0	8.1	4.5	20.3		19.9
Solid		37.8	58.1	-0.2	34.5	4.8	
7E	47.1	10.5	4.9	5.3	19.7		16.8
Solid		34.7	64.7	0.0	34.8	1.8	
7H	48.4	12.2	7.7	4.7	20.7		17.8
Solid		33.4	52.6	-0.6	32.4	13.0	

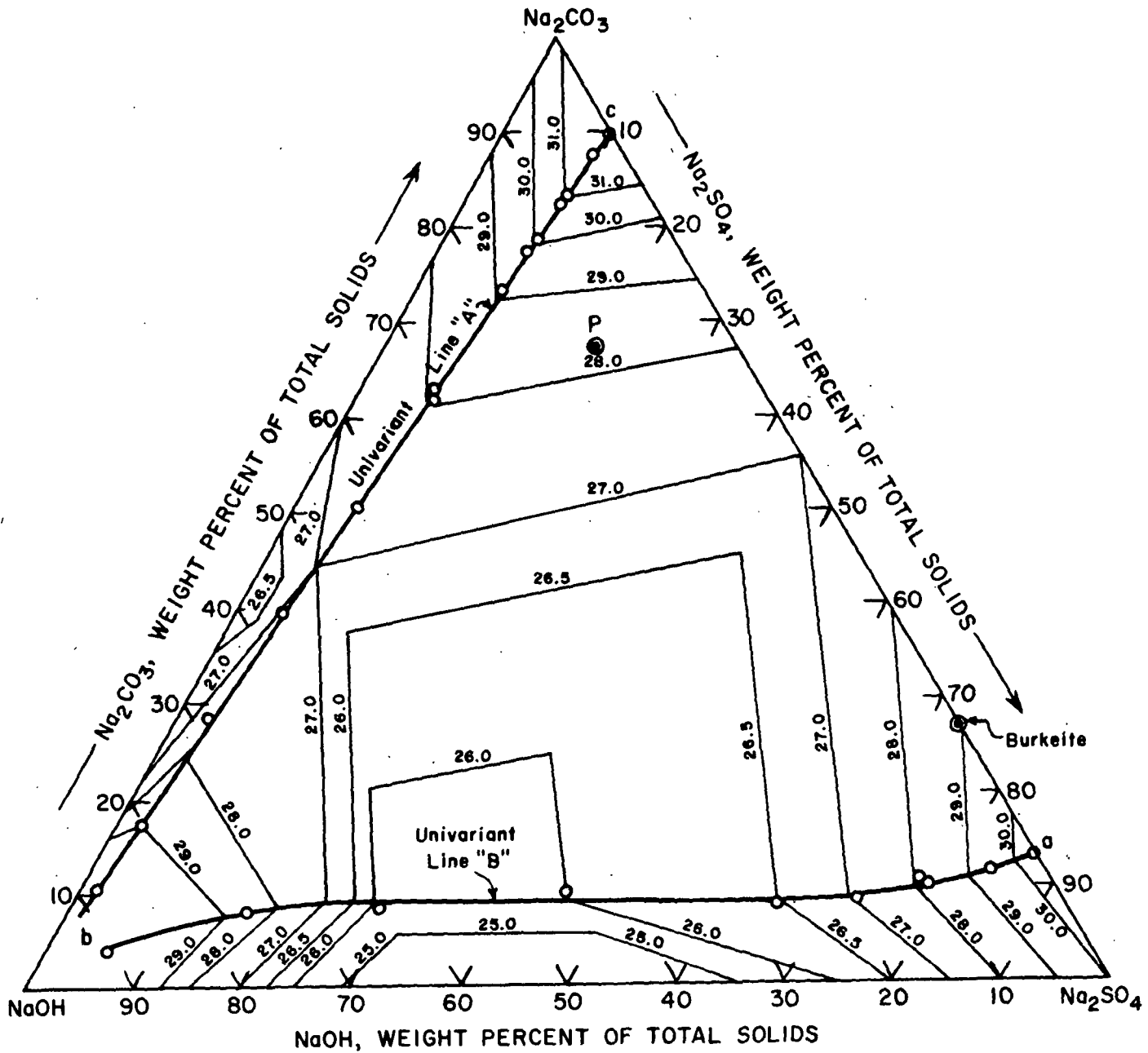


Fig. 2. Solubility curves for the system Na_2CO_3 - Na_2SO_4 - NaOH - H_2O at 100° :
 area below ab = Na_2SO_4 field; area abc = solid solution of Na_2SO_4
 and Na_2CO_3 ; area above bc = $\text{Na}_2\text{CO}_3 \cdot \text{H}_2\text{O}$ field; O , points fixing
 equilibria

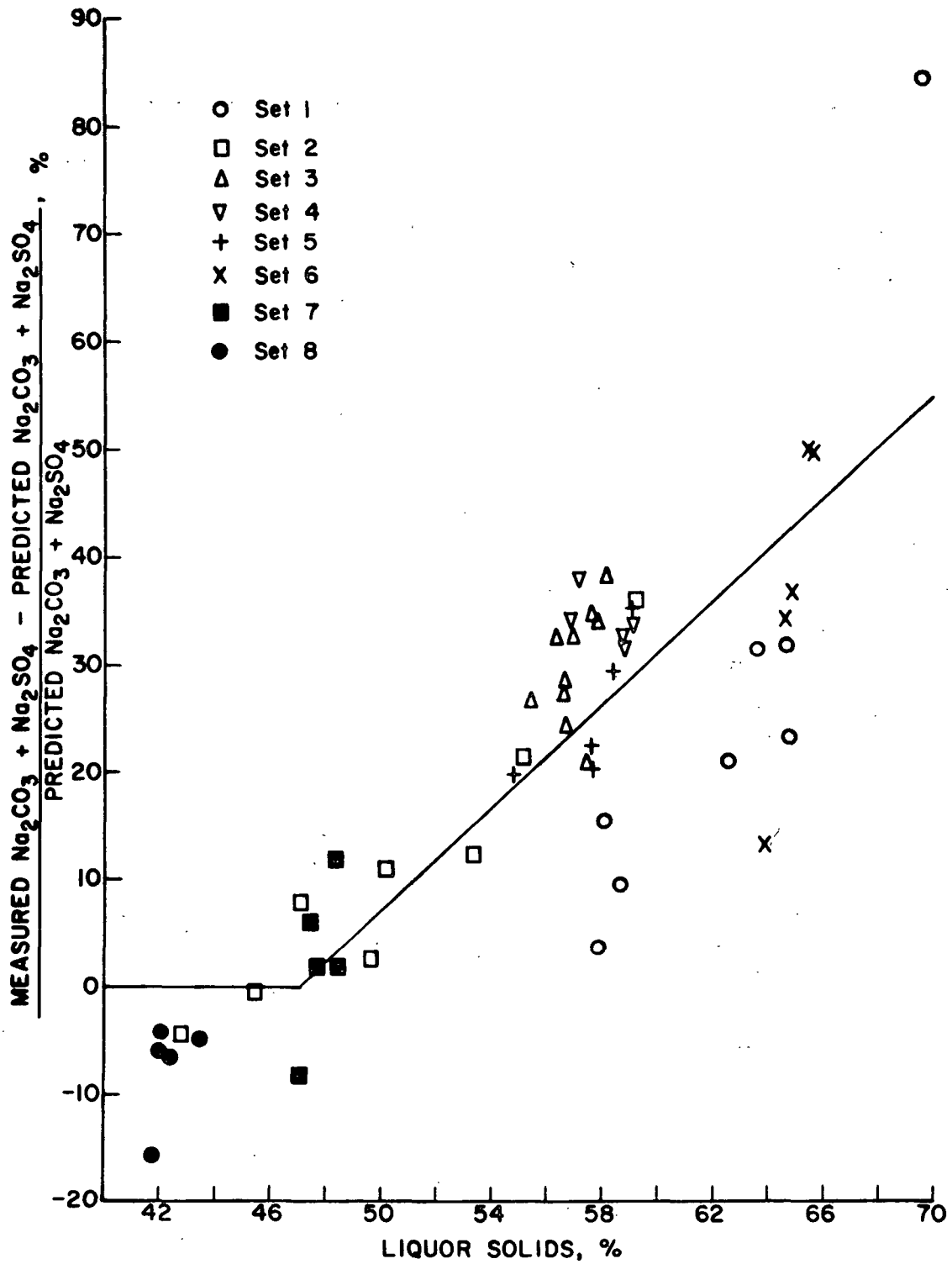


Fig. 3. Phase distribution behavior in 45% solids black liquor

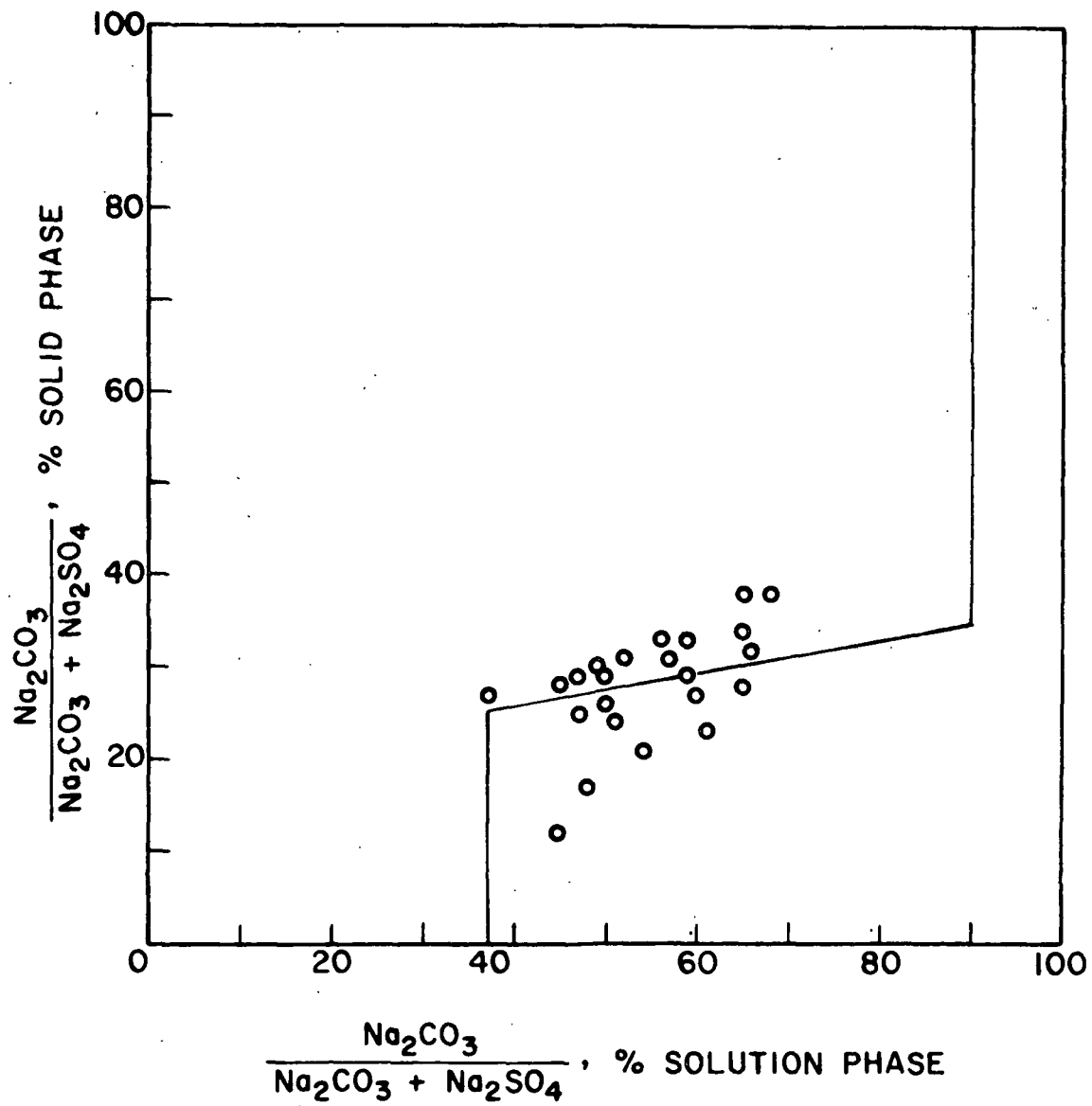


Fig. 4. Solubility behavior at high solids contents

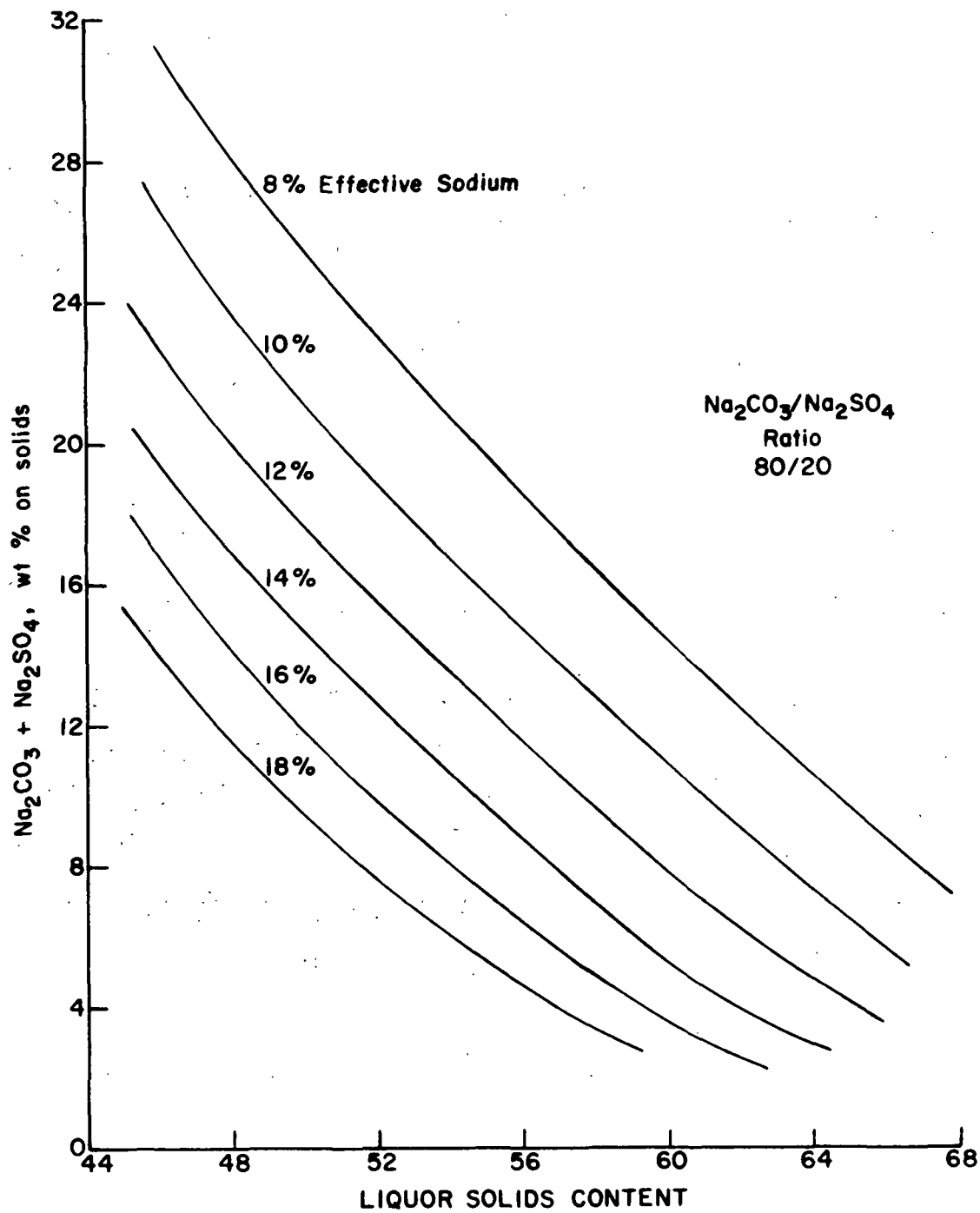


Fig. 5. Correlation of Na_2CO_3 - Na_2SO_4 solubility in black liquor

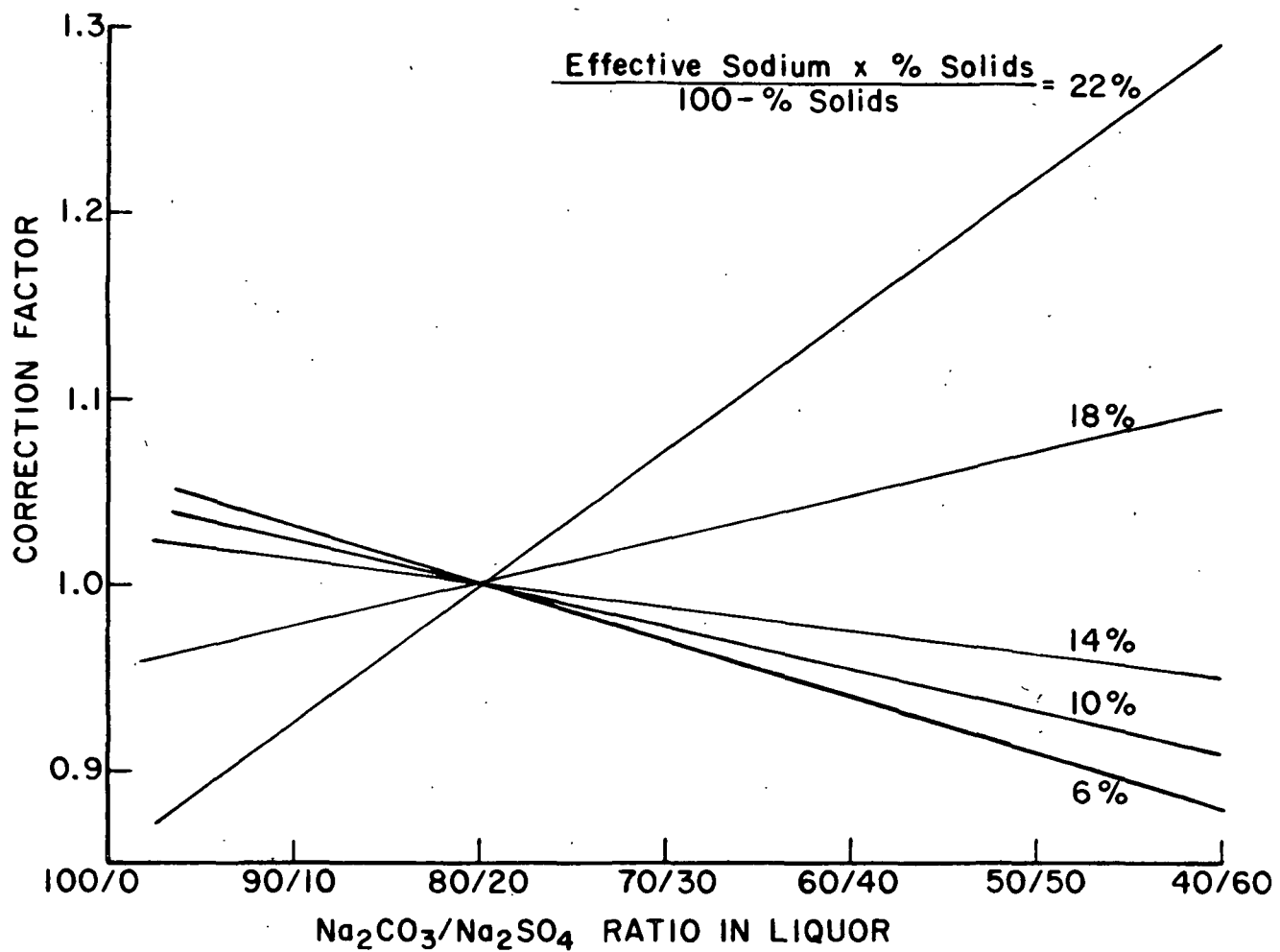


Fig. 6. Correction factor for different carbonate/sulfate ratios