

Crystallizing sodium salts from black liquor

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ABSTRACT: *A model has been developed for predicting the performance of concentrators that crystallize sodium salts from black liquor. When a black liquor solution becomes supersaturated, three different solid phases can precipitate: sodium sulfate, sodium carbonate, and solid solution of Burkeite with sodium sulfate or sodium carbonate. The model predicts the developed and residual supersaturations of the bulk liquor based on the solubility of the sodium salts and the physical parameters of the concentrator design. A properly designed black liquor concentrator will crystallize the sodium salts without scaling the heating surfaces.*

KEYWORDS: *Black liquors, concentrators, crystallization, models, sodium carbonate, sodium sulfate, solubility, supersaturation.*

Modern black liquor concentrators can produce liquors with solids as high as 80%. These liquors are slurries containing slightly supersaturated black liquor solutions and solid phases of sodium sulfate, sodium carbonate, or solid solution of Burkeite and sodium sulfate or sodium carbonate.

Supersaturation is the concentration difference between that of the supersaturated solution in which the crystal is growing and that of a solution in equilibrium with the crystal. A solution is supersaturated if its concentration is greater than the concentration at which the solution is in equilibrium with the crystal. In a properly designed crystallizer, the supersaturated black liquor solution adjusts

toward equilibrium by advancing the growth of crystals in the bulk liquor slurry rather than on the heating surfaces.

In an ideal financial situation with unlimited capital, the crystallizer purchased would have an infinite circulation rate and infinite active volume. Supersaturations in such a system would approach zero. In reality, one attempts to optimize crystallizer performance by providing enough circulation and active volume to keep the total supersaturation at an acceptably low level while keeping capital and operating expenditures at a minimum. Excessively high total supersaturation will cause nucleation on the heat exchanger tube wall, resulting in scaling and in reduced capacity.

An empirical method known as the "Hedrick Model" has been proposed to determine a crystallizer's performance (1). The key performance parameters are crystal size and supersaturation. The model may be applied to any type of crystallizer, such as a forced circulation unit or a falling film unit. For a given crystal production rate, performance is controlled by selecting the proper slurry circulation rate and the active volume of the crystallizer. These two design parameters may be varied to control the total supersaturation of the bulk liquor.

Developed and residual supersaturation

The total supersaturation of the bulk liquor system is the sum of the developed supersaturation and the residual supersaturation. Developed supersaturation is the amount of solute above the normal solubility in the solution resulting from a reaction or from the evaporation of solvent, the cooling of a normal solution, or the heating of an inverted solubility solution. Residual supersaturation is the amount of solute left in the solution above the normal solubility at that temperature as it leaves the crystallizer.

The developed supersaturation is a function of the circulation rate through the crystallizer. Increasing the circulation rate decreases the developed supersaturation. The performance of a unit suffering from a high developed supersaturation can be improved by installing a larger pump and greater circulation piping to increase the flow of the circulating liquor.

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The residual supersaturation is a function of the active liquor volume in the crystallizer. Increasing the active volume decreases the residual supersaturation. This volume includes the vapor head liquor volume, the circulation pump and piping, and the liquor volume in the heating element. In forced circulation units, the liquor volume of the heating element can contribute substantially more liquor volume than can that of falling film units.

Hedrick model

The Hedrick Model is presented in the following equations. The total supersaturation in the bulk liquor is given by:

$$S_{\text{total}} = 5P(kW + 60F\rho N)/(3kWF\rho N) \quad (1)$$

where

S_{total} = total supersaturation, %

P = production of crystals, lb/hr per ft³

k = growth factor, lb produced per hour per pound of crystal in the slurry

W = weight of crystals in slurry, lb/ft³

F = circulation, gal/min per ft³

ρ = density of circulating slurry, lb/gal

N = solute in circulating slurry, weight fraction.

The developed supersaturation, S_{dev} , is given by:

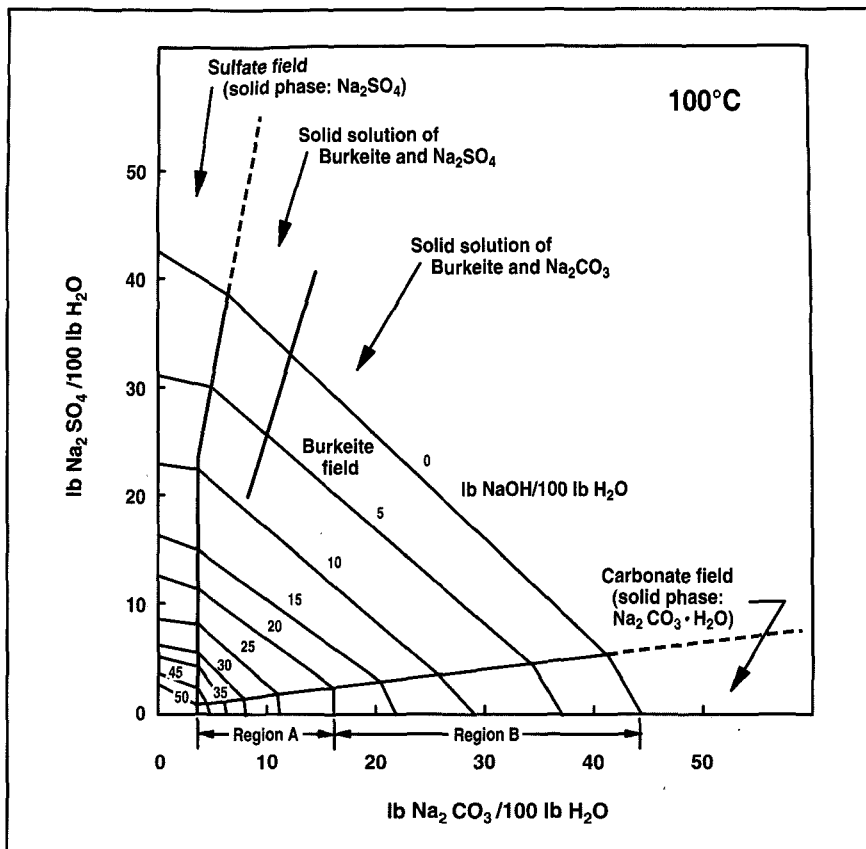
$$S_{\text{dev}} = 5P/(3F\rho N) \quad (2)$$

The residual supersaturation, S_{res} , is given by:

$$S_{\text{res}} = S_{\text{total}} - S_{\text{dev}} \quad (3)$$

The following empirical equations, Eqs. 4 and 5, are used to calculate the value of k , the growth factor, which is required to solve Eq. 1 (I):

1. Equilibrium in the system sodium carbonate, sodium sulfate, sodium hydroxide, and water at 100°C. In Region A, the carbonate field produces anhydrous sodium carbonate. In Region B, the carbonate field produces sodium carbonate monohydrate.



$$k = (33.9 - 5C + 0.5C^2)/(Id^{0.31} \mu^{1/6}) \quad (4)$$

where

C = solute in solution, wt. %

I = impurity factor

d = mean crystal diameter, μm

μ = liquid viscosity, cp.

Note that in Eq. 4 the value of I is 1.0 for common black liquors.

$$d = 805(C/M)^{0.23}/(S_{\text{total}} - 0.025)^{1.3} \quad (5)$$

where

d = mean crystal diameter, μm

M = molecular weight.

Equations 1, 4, and 5 must be solved via trial and error.

Solubility data

The solubility of sodium sulfate and sodium carbonate in black liquor has been studied previously (2). The solubility of the sodium salts is not greatly influenced by the liquor organic chemicals. In black liquor, the solubility is generally the same as for aqueous solutions of these inorganic sodium salts. The solubility of the sodium salts in aqueous solutions is shown in Fig. 1. Solubility data (3) were used to derive this phase diagram, which shows the following three distinct solid phases, referred to as "fields":

1. Sulfate field (Na_2SO_4)
2. Burkeite field: solid solution of Burkeite and Na_2SO_4 or Na_2CO_3 . (Burkeite is a double salt of Na_2SO_4 and Na_2CO_3 .)
3. Carbonate field (Na_2CO_3).

I. Operating data for the double-effect concentrator

	Feed	Vapor out	Crystal produc- tion	Liquor out	Slurry out
2nd Effect					
Temp., °F	210	216	...	234	234
Analysis, lb/h					
NaOH	27,484	...	...	27,484	27,484
Na ₂ CO ₃	9,994	...	3125	6,869	9,994
Na ₂ SO ₄	1,228	...	438	790	1,228
H ₂ O	106,762	25,153	...	81,609	81,609
Organic	73,532	...	...	73,532	73,532
Total	219,000	25,153	3563	190,284	193,847
Solids, wt. %	51.25	...	...	...	57.90
Slurry, wt. %	...	...	...	...	1.84
1st Effect					
Temp., °F	234	242	...	269	269
Analysis, lb/h					
NaOH	27,484	...	...	27,484	27,484
Na ₂ CO ₃	9,994	...	3937	2,932	9,994
Na ₂ SO ₄	1,228	...	495	295	1,228
H ₂ O	81,609	23,276	...	58,333	58,333
Organic	73,532	...	...	73,532	73,532
Total	193,847	23,276	4432	162,576	170,571
Solids, wt. %	57.90	...	...	...	65.80
Slurry, wt. %	1.84	...	...	...	4.69

The phase diagram in Fig. 1 was derived at 100°C. The diagram is accurate for black liquor up to 50% total solids and 120°C. Above 50% total solids, the solubility of Na₂SO₄ and Na₂CO₃ must be multiplied by a total solids correction factor, determined as follows:

$$CC = 1 + (2.936 TS - 146.8)/100 \quad (6)$$

where

CC = correction factor for total solids, dimensionless

TS = total solids, %.

Factor CC will correct for the increase in solubility caused by the higher solids.

Many materials exhibit an increasing solubility with increasing temperature. This type of solubility is defined

as normal solubility. A material has what is called an "inverted" solubility if its solubility decreases as the temperature is increased. In the Burkeite field and carbonate field, the solubility is inverted. A correction factor for temperature must be applied at temperatures above 120°C. In the Burkeite field and the carbonate field, the following temperature correction factor applies:

$$CF = 1 - [(T - 120)]/200 \quad (7)$$

where

CF = temperature correction factor, dimensionless

T = fluid temperature, °C.

In a sodium hydroxide solution, the solubility of sodium sulfate switches from inverted to normal. The following equation corrects for this change

and is used for the sulfate field:

$$CF = 1 + [(T - 100)]/73 \quad (8)$$

Application

The following percentages must be known in order to analyze a crystallizer system:

1. Percent total solids
2. Percent sodium
3. Percent sulfate
4. Percent carbonate.

All of the CO₃ and SO₄ is assumed to be associated with Na. All of the remaining Na is assumed to be associated with OH. The total sodium ion is effective regardless of the ions associated with it.

A material balance is calculated, as shown in Table I. The phase diagram shown in Fig. 1 and the solubility correction factors are used to determine the composition of the crystallizer feed, the product, and the crystals produced. Once a material balance is completed, the Hedrick Model is applied to calculate the supersaturations in the bulk liquor.

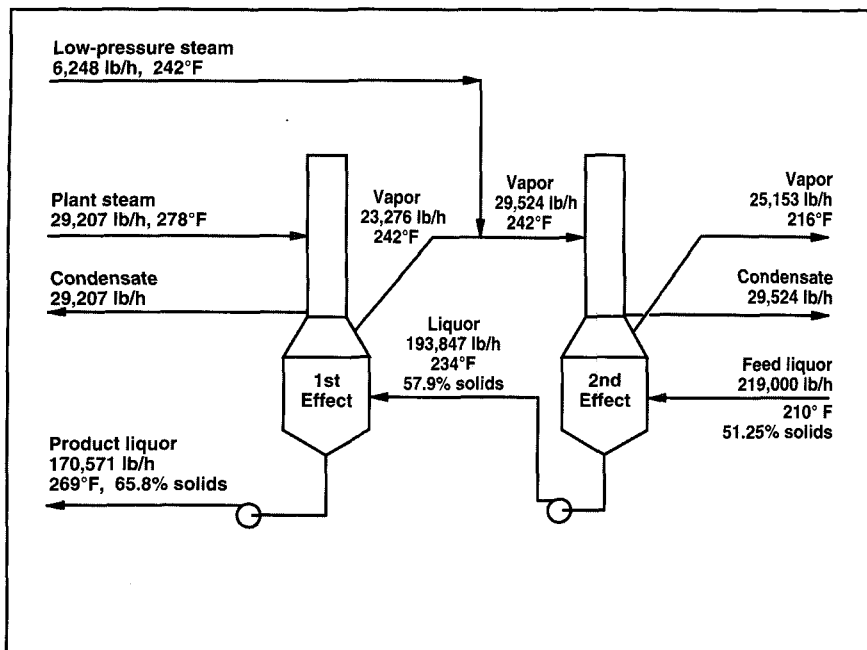
The effective weight of the material in solution being crystallized must be calculated. The common ion effect increases the effective solubility of the compound being crystallized. In the Burkeite field, the effective solubility of Burkeite is increased by the sodium from the NaOH. Similarly, the sodium from NaOH and Na₂SO₄ increases the effective amount of Na₂CO₃ in the carbonate field. The sodium from the NaOH and Na₂CO₃ increases the effective amount of Na₂SO₄ in the sulfate field. The effective weight calculations for the three fields are listed in the "Calculations" box.

Tube wall effects

The Hedrick Model is used to calculate the total supersaturation in the bulk liquor only. The liquor in the thermal boundary layer will be hotter than

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2. Flow diagram for the concentrator



II. Summary of supersaturation data

	Effect	
	1st	2nd
Feed, wt. fraction		
Sodium	0.10595	0.09378
Carbonate	0.02918	0.02583
Sulfate	0.00429	0.00379
Bulk phase liquor supersaturation		
Developed	0.03	0.02
Residual	2.87	2.85
Total	2.90	2.87
Tube wall temp. rise supersaturation		
Total	4.50	4.27
Average supersaturation at the tube walls		
Average crystal size	124	124

the bulk liquor. A maximum liquor temperature will be reached at the tube wall. Above 235°F, each 1 F° of tube wall temperature above the bulk liquor temperature will add approximately 0.2% supersaturation.

This additional supersaturation must be added to the bulk liquor supersaturation in the carbonate and Burkeite fields, since both of these fields exhibit an inverse solubility. The total supersaturation at the tube wall determines the rate of scaling in the tubes. The tube wall temperature is calculated using Eq. 12.

Actual operation

The Hedrick Model was used to analyze a concentrator system. Once a heat and material balance had been completed, the model was used to analyze the design. This case study pertains to a southern mill using pine liquor and falling film crystallizers.

These crystallizers operate for an indefinite time without scaling. They are washed out when other equipment requires washing.

The Hedrick model was applied to the design of this system before the equipment was fabricated. A heat and

Calculations

Burkeite Field:

$$2\text{Na}_2\text{SO}_4 \cdot \text{Na}_2\text{CO}_3, \text{ lb} =$$

$$\{[(\text{Na}, \text{ lb-moles})^6 \times (\text{CO}_3, \text{ lb-moles}) \times (\text{SO}_4, \text{ lb-moles})^2]^{1/9}\} \times 390 \quad (9)$$

Carbonate Field:

$$\text{Na}_2\text{CO}_3, \text{ lb} = [(\text{Na}, \text{ lb-moles})^2 \times (\text{CO}_3, \text{ lb-moles})]^{1/3} \times 106 \quad (10)$$

Sulfate Field:

$$\text{Na}_2\text{SO}_4, \text{ lb} = [(\text{Na}, \text{ lb-moles})^2 \times (\text{SO}_4, \text{ lb-moles})]^{1/3} \times 142 \quad (11)$$

Tube Wall Temperature:

$$T_{\text{wall}} = (H_{\text{liquor}} T_{\text{liquor}} + T_{\text{steam}} H_{\text{steam}}) / (H_{\text{liquor}} + H_{\text{steam}}) \quad (12)$$

where

T_{wall} = tube wall temperature

T_{liquor} = liquor bulk temperature

T_{steam} = steam temperature

H_{liquor} = liquor film coefficient

H_{steam} = steam film coefficient.

material balance for a double-effect falling film crystallizer is shown in Table I. **Figure 2** is a flow diagram of the concentrator system.

The solubility data shown in Fig. 1 have been used to determine the composition of the feed liquor as well as the liquor composition in each effect. Once the solubility of each liquor stream is determined, the crystal production can be calculated for any given effect. In the case presented, each effect has a total active liquor volume of 807 ft³. This volume represents the volume of liquor normally maintained in the vapor head and the liquor circulation pipe. Each effect is also provided with 8200 gal/min of liquor circulation.

The Hedrick Model is applied by first taking a value (typically 100 μ m) assumed to be an average for the crystal diameters. The growth factor is calculated using Eq. 4, and the total supersaturation is calculated using Eq. 1. Equation 5 is used to back-calculate a new value for the average crystal diameter. The values for the assumed diameter and the diameter calculated from Eq. 5 are compared. Based on the difference between the assumed diameter and the diameter calculated from Eq. 5, a new revised value for the assumed diameter is taken. Solutions are calculated by trial and error until the assumed diameter and the calculated diameter differ by less than 1%.

The results of the Hedrick Model for this case are shown in **Table II**. The feed to the double-effect crystallizer enters the second effect. The supersaturation calculations are first performed on the second effect, yielding an average crystal size of 124 μ m. Since the product from the second effect is the feed to the first effect, the first effect operates with seed crystals of 124 μ m. For the first effect, Eqs. 4 and 1 are solved for the growth factor and total supersaturation, respectively, without any trial-and-error solution for the crystal diameter.

The first effect is operated with 278°F steam. The tube wall temperature is 277°F, or 8°F above the bulk

liquor temperature. The tube wall effect adds an additional 1.6% supersaturation to that calculated for the bulk liquor.

The second effect is driven with 242°F steam. The tube wall temperature is 241°F, or 7°F above the bulk liquor. Here, the tube wall effect adds an additional 1.4% supersaturation.

A summary of all the supersaturations is presented in Table II. This equipment was designed with a bulk-phase liquor total supersaturation of less than 3% in each effect. The total supersaturation at the tube wall is no more than 4.5%. The equipment runs without scaling on a continuous basis and is washed periodically when other equipment is washed.

Summary

The Hedrick Model can be used to predict the scaling tendencies of sodium salts in black liquor. The model may be applied to any type of crystallizer, including tubular falling film units, plate-type falling film units, and forced circulation units. In a properly designed crystallizer, the total supersaturation in any effect should not exceed approximately 5%. This amount should include the tube wall effect. The following rules should be used to assure good crystallizer design:

1. Avoid excessive temperature differentials on crystallizers. The higher the temperature differential, the higher the tube wall effect.
2. If a unit exhibits a high developed supersaturation, increase the liquor circulation rate. In an existing unit, this may require making changes to the circulation piping and pump.
3. If a unit exhibits a high residual supersaturation, increase the liquor volume. In an existing unit, run with the vapor head liquor level as high as possible. If this is insufficient, additional tank capacity may be required to adequately increase the liquor volume.

Properly designed crystallizers are

able to precipitate sodium salts without scaling the tubes. The crystallizers used in the case study presented here operate for an indefinite period of time without scaling. □

Literature cited

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