A falling-film crystallizing concentrator for producing 80% black-liquor solids

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The concentrator delivers ultra-high black-liquor solids with little or no downtime for boilouts by controlling the growth of crystals on tube surfaces.

Mills that concentrate black liquor to a high solids level typically must cope with fouling and plugging when the dissolved inorganics in the supersaturated liquor crystallize on heat-transfer surfaces. However, black liquor can be concentrated to 80% or more without fouling the concentrator unit by applying the principles that control the growth of crystallization.

Several years ago, we initiated a research-and-development program to develop a high-solids concentrator that would resist fouling. Pilot trials in the laboratory and in the field led to the development of a falling-film crystallizing concentrator. The concentrator has been installed in several mills, and the results demonstrate that fouling can be prevented by controlling the parameters that govern crystal growth.

The falling-film crystallizing concentrator has been operating for over 18 months in one mill and has yet to undergo a forced boilout or cleaning to eliminate fouling on the heat-transfer surfaces in the concentrator or the flash tank. Results from this mill are illustrated in **Fig. 1**, which shows the calculated heat-transfer coefficients for the concentrator tubes during a six-month period when the unit was producing 80% black-liquor solids on a consistent basis. **Figure 2** shows heat-transfer coefficients collected when precipitator problems prevented the unit from consistently producing 80% black-liquor solids. Black-liquor solids during these time periods fluctuated between 75% and 80%, depending on the stack emissions from the recovery-boiler precipitator. Both figures show comparable performance, with little change in heat-transfer coefficient.

Black-liquor fouling

Older evaporator units with indirect-contact heat exchangers used long-tube vertical (LTV) evaporator bodies designed with extra capacity to permit frequent boilouts. These units typically required boilout every 3-10 days. The time between boilouts can be extended by modifying the unit with forced circulation. In recent years, the industry has been moving away from the LTV design in favor of two other design strategies, falling-film and forced-circulation. The primary reason for this movement is the LTV's inability to support the additional scale-preventive measures that are required for high-solids concentrations in particularly difficult liquors. While the falling-film and forced-circulation designs are inherently more resistant to fouling than the LTV, they also require a cleaning cycle at very high product concentrations (*1*).

The most common form of fouling on concentrator heat-transfer surfaces is the formation of sodium salt scale on the tube walls. There is a point in every black-liquor composition, usually between 52% and 58% black-liquor solids, at which the liquor becomes saturated with sodium salts, causing them to begin crystallizing out of solution. This point of crystallization is illustrated in **Fig. 3**.

If crystallization is not controlled, the heat-transfer surfaces become fouled by the growth of crystals on the tube. Because the LTV evaporator is not designed to prevent fouling at high solids concentrations, its tubes must be cleaned on a regular basis. Forced-circulation concentrators pump liquor through the tubes at a high flow rate, and the mechanical action helps retard crystalline growth on the tube walls. Forced circulation along with suppressed boiling is another tactic to reduce fouling by transferring the point at which boiling occurs. These two methods, along with flow reversing and frequent mini-boilouts, facilitate production of higher liquor solids.

The falling-film design is another way to achieve high solids without the high horsepower requirements of the forced-circulation/suppressed-boiling units. The typical horsepower requirement for a forced-circulation unit is 800-900 hp, compared with 300-500 hp for a falling-film unit. Recent Scandinavian studies demonstrate that the falling-film design is the best means of achieving high-solids black-liquor concentrations (*2*). However, falling-film units are still prone to fouling caused by uncontrolled crystallization of sodium salts.

Development of crystallizing concentrator

In the early 1980s, we undertook an R&D program to document the behavior of black liquor in tubular falling-film evaporators. Initial studies were conducted on laboratory-scale pilot-plant equipment and were later concluded on larger test equipment in a kraft pulp mill located in the southeastern United States.

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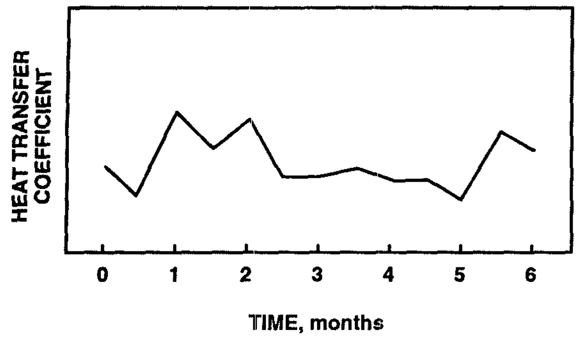
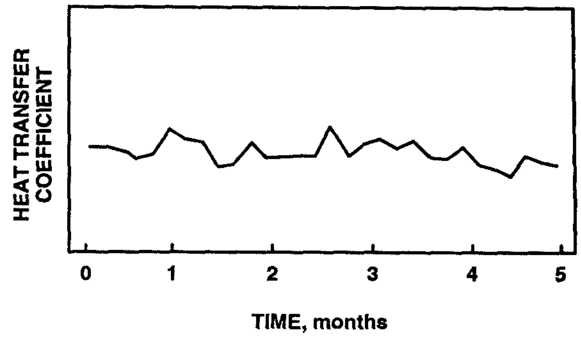
1. Change in heat-transfer coefficient for concentrator producing 80% liquor solids



2. Change in heat-transfer coefficient for concentrator producing 75–80% liquor solids



4. Computer-generated material balance for black liquor in a falling-film crystallizing concentrator

MATERIAL BALANCE FOR PERCENT SUPERSATURATION OF THE BLACK LIQUOR SYSTEM

	Temp. °F	lb NaOH	lb Na_2CO_3	lb NA_2SO_4	Total lb solids	lb H_20	lb total	Percent solids
Feed	237	47.833	17.944	6.289	185.7	100.0	285.7	65.0
Crystals in feed		13.005	4.558					
Soluble in feed	47.833	4.939	1.731	185.7	100.0	285.7	65.0	
Water evaporated					53.0			
Crystal production		2.408	1.494					
Soluble in product	285	47.833	2.531	0.237	185.7	47.0	232.7	79.8

Feed rate, lb/h = 215244
Feed solids, % = 65
Feed temperature, °F = 237
Liquor volume, Ft^3 = 600

Product temp., °F = 285

Product flow rate, lb/h = 175324

Wt. fraction Na = 0.1306
Wt. fraction CO_3 = 0.0355
Wt. fraction SO_4 = 0.0149
Recirculation Rate = 9000.0

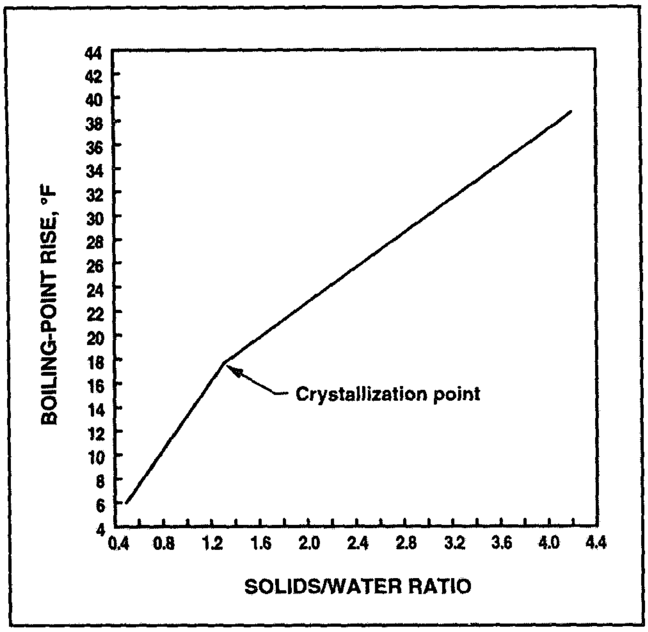
Product density, lb/gal = 11.96

Prod wt. fraction Na = 0.1604
Prod wt. fraction CO_3 = 0.0436
Prod wt. fraction SO_4 = 0.0183

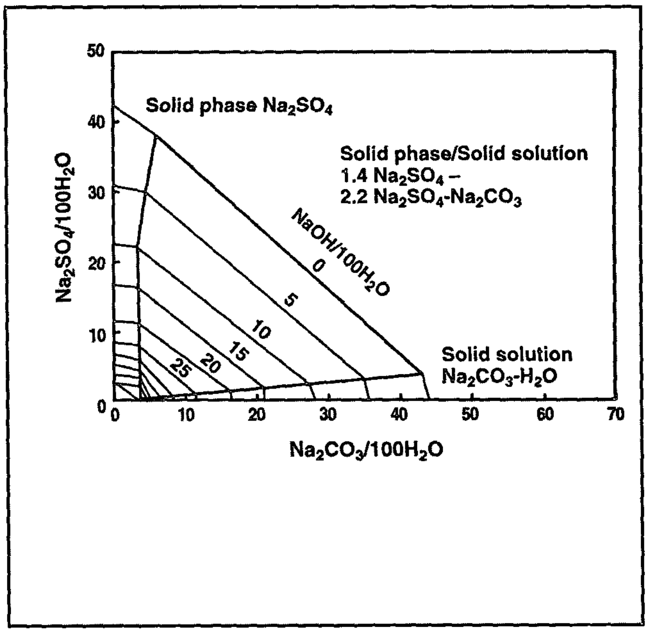
Burkeite field
Burkeite crystals

Crystal diameter = 145.8 Microns
% Supersaturation = 2.44

Developed supersaturation = 0.06
Residual supersaturation = 2.39



3. Boiling-point-rise curve with point of crystallization occurring at a solids/water ratio of 1.27 (55.9% solids)



5. Phase diagram for mixtures of sodium sulfate (Na_2SO_4) and sodium carbonate (Na_2CO_3) in a solution of sodium hydroxide and water at 100°C

A primary objective of the study was to identify the process parameters that influence crystallization in black liquor, particularly at higher-than-normal solids levels. The design engineers looked to the chemical-processing industry, where crystallization of inorganic salts from a saturated mother solution is a common manufacturing technique. Manufacturers typically manipulate process variables to control crystal size and minimize fouling of heat-transfer surfaces. To accomplish these objectives, analytical models of crystallization behavior must be developed. These models consist of complex sets of equations and are based on published theoretical relationships and experimentally determined empirical relationships. The algorithms are usually considered proprietary and generally are not published (*1*).

The crystallization behavior of a liquid chemical compound is analyzed by running the liquid through a crystallizer, and this technique was applied to black liquor. Crystal formation is affected by many interrelated factors, and the system parameters and chemical compositions must be known to solve the set of equations used in the modeling process. When the equations are solved, the model predicts crystal production rate, crystal size, and supersaturation.

Because supersaturation must exist if crystals are to be formed, the objective of the initial research was to produce a controlled supersaturation. This ensures that the crystal size needed to minimize fouling will be obtained. Output data from a computer program showing a material balance for percent supersaturation of black liquor is shown in **Fig. 4**.

All of this background information was used in pilot-plant studies in both the laboratory and the field. During initial evaluations at high black-liquor concentrations, there was a problem with excessive fouling in the tubes. Analysis of the fouling scale indicated that the pilot unit was crystallizing a combination of sodium carbonate and sodium sulfate. Sodium carbonate is inversely soluble, i.e., its solubility decreases with increasing temperature. Because of this characteristic, supersaturation is developed in the liquor film on the tube wall (*3*).

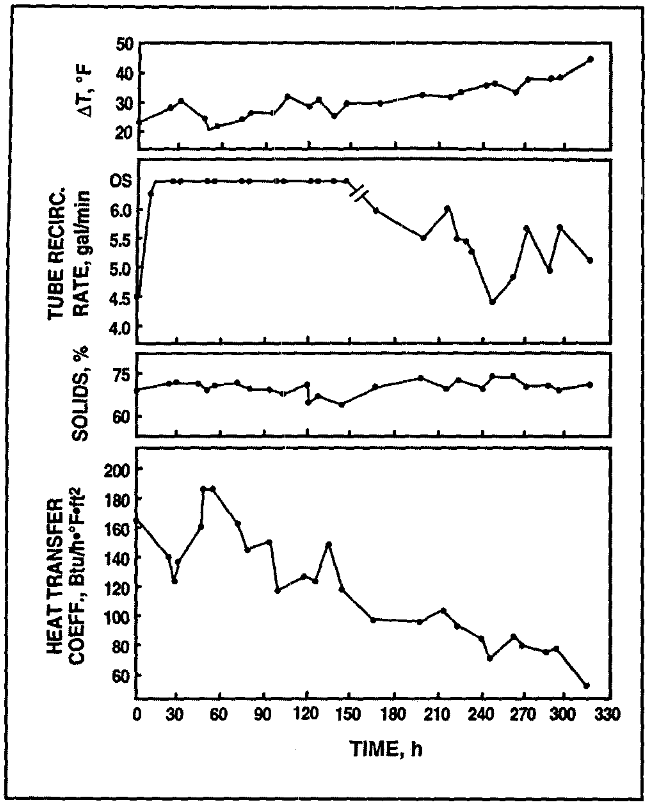
Using this information along with published data (*4*), design engineers developed solubility curves for sodium sulfate/sodium carbonate mixtures in sodium hydroxide/water solutions. This phase diagram is shown in **Fig. 5**.

The new data were incorporated in the crystallization algorithms, and the field pilot-plant tests were repeated. This time there was a reduction in the fouling rate at the higher black-liquor solids. Some of the data indicated the possibility of indefinite operation with a minimal decrease in the heat-transfer coefficient (*1*). Results for the first test run are given in **Fig. 6**. Corresponding results for the second test run are given in **Fig. 7**.

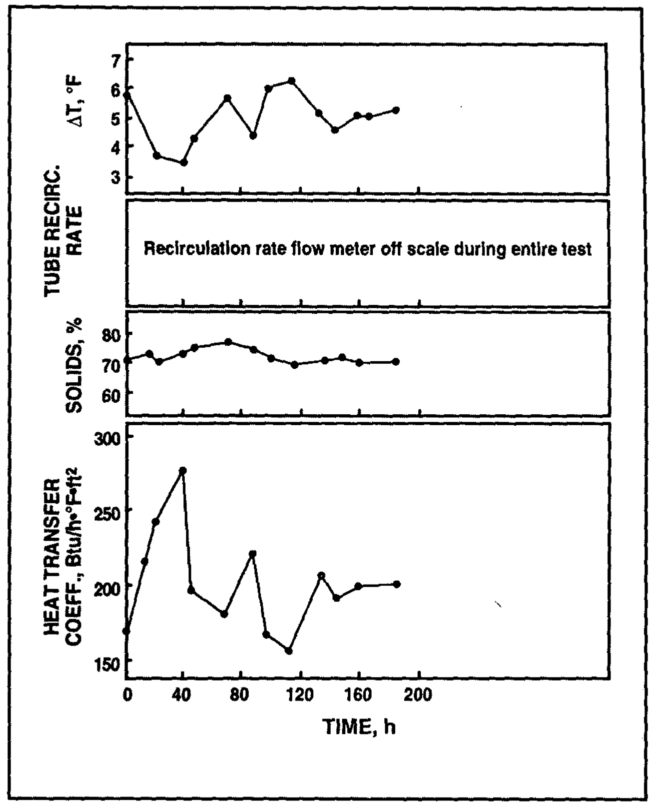
Subsequent tests showed that it was possible to design a falling-film crystallizing concentrator to produce black-liquor solids above 80%. Further, results showed that the fouling rate could be controlled by holding the supersaturation to low levels. The film had to flow at a particular rate through the concentrator's tubes to prevent the pilot unit from fouling. Because the film flow rates are dependent on the viscosity of the black liquor, it was necessary to determine the relationship between black-liquor solids and viscosity.

Liquor samples from various mills throughout the pulp and paper industry were collected for viscosity tests. Liquors were tested using a viscometer designed to measure viscosity over a range of pressures, temperatures, and black-liquor solids. The results were used to develop a nomograph delineating the relationship among the three parameters. Previously published nomographs did not provide information about viscosity at the higher black-liquor solids (*5*).

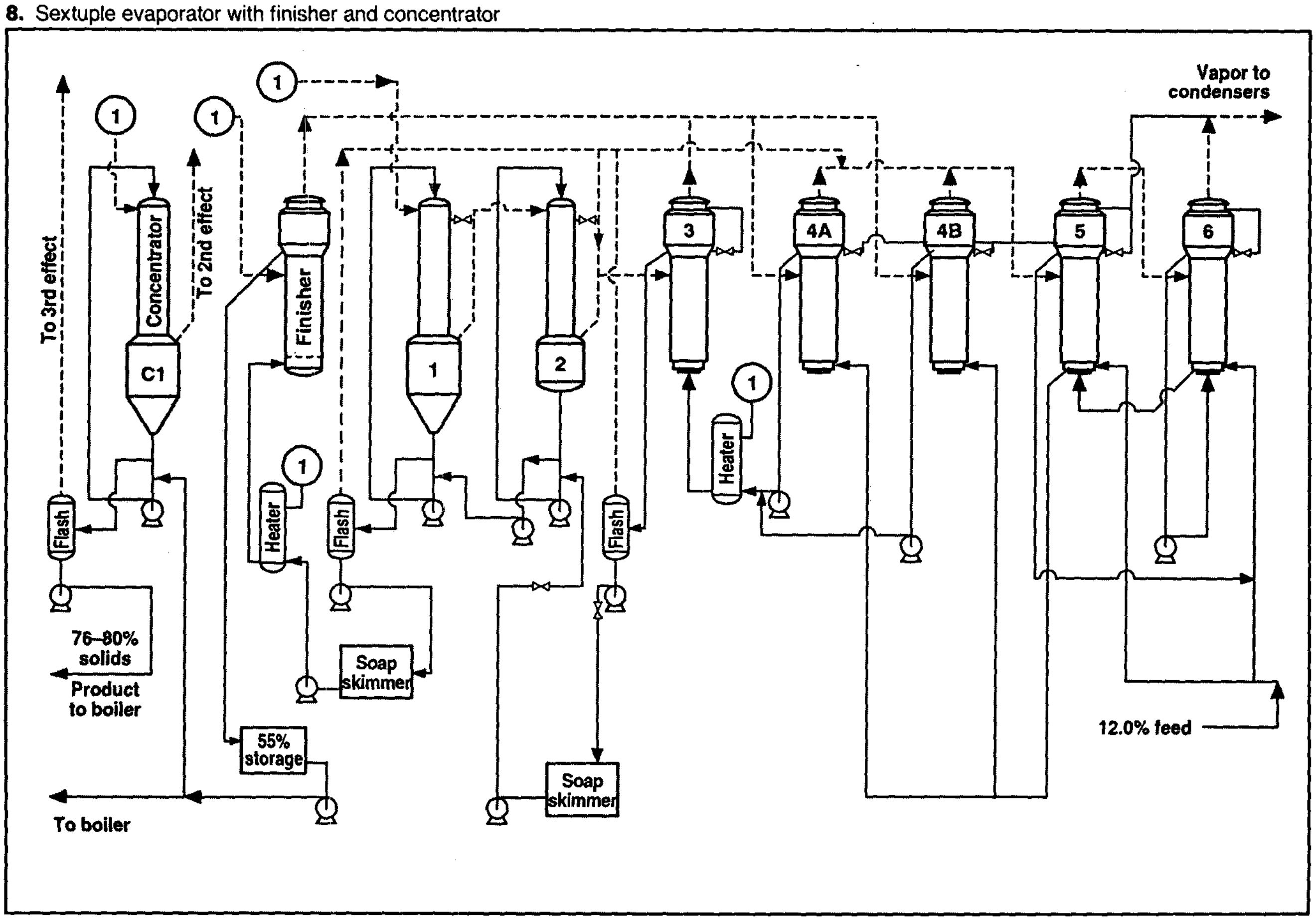
6. Field test results—Run 1



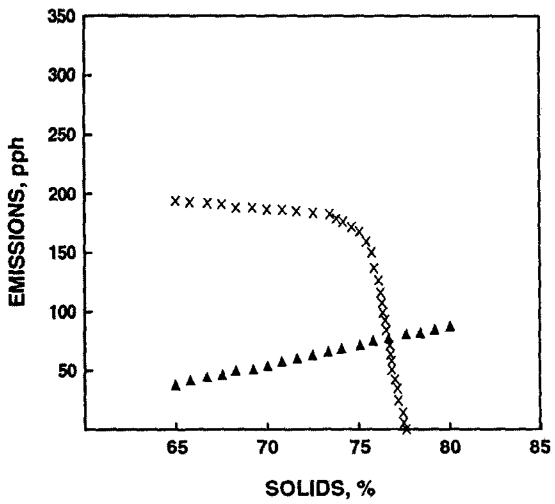
7. Field test results—Run 2



8. Sextuple evaporator with finisher and concentrator



9. Recovery-boiler emissions of SO_2 and NO_x as a function of black-liquor solids



Application of crystallizing concentrator

In early 1984, a full-scale application was installed in a mill in New England. The installation has been in service producing between 70% and 72% black-liquor solids since startup and has yet to undergo a boilout for scale removal. Reports from mill personnel indicate that the unit achieves virtually 100% uptime, with shutdowns only for inspection. The forced-circulation unit feeding this falling-film crystallizing concentrator undergoes yearly hydroblasting to clean scale from its heating surface.

In 1987, a falling-film crystallizing concentrator was installed in a kraft mill located in the southwest. Two falling-film bodies—one a falling-film crystallizing concentrator unit and the other a standard falling-film unit—were added to a modified evaporator as the first and second effects, respectively. These units have run up to three months between boilouts.

In February 1990, a high-solids falling-film crystallizing concentrator was tied in to the evaporator system of the same mill. **Figure 8** is a schematic of the complete system. The concentrator unit was designed to produce up to 82% black-liquor solids, although it produced solids between 86% and 88% during the initial startup phase.

High-solids firing

The falling-film crystallizing concentrator was designed to produce 80% solids, thus allowing the mill to fire high-solids liquor in its existing recovery boiler. The boiler had to be modified to accommodate the high-solids liquor from the concentrator. Emissions data were collected from the recovery boiler firing at black-liquor solids ranging from 65% to 80%. **Figure 9** shows some of the results from these tests. As seen in Fig. 9, there was a significant drop in the SO_2 levels when firing the higher-solids liquor. The NO_x levels increased as the black-liquor solids increased. These data verify other published data, which state that SO_2 levels are virtually zero at solids near 80% (*2*, *6*).

The higher-solids firing also has provided other benefits, including improved stability of the furnace bed and less carry-over. After a recent boiler outage and inspection, mill personnel reported the boiler to be exceptionally clean.

Further research

One area of research under consideration is the control of calcium scale with a falling-film crystallizing concentrator. Current research is focusing on the carbonate-to-sulfate ratio in black liquor and its effect on scaling or fouling rates. Early results indicate that there is a carbonate-to-sulfate ratio at which fouling is almost nonexistent (*3*).

Conclusion

Based on data from pilot-plant studies and full-scale operating units, the falling-film crystallizing concentrator is a reliable method of obtaining black-liquor solids rates of 80% or higher with minimal or no fouling. With mills facing increasingly stringent environmental regulation, the prospect of reducing sulfurous emissions by firing black liquor at ultra-high solids is attractive. The inherent energy efficiency of the falling-film design and the higher equipment uptime of a crystallizing concentrator are further benefits of this evolving technology.□

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