A new process for pulping with high initial hydrosulfide concentration

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ABSTRACT

A novel process improves conventional and modified kraft cooking by producing two or more white liquors of chemical concentrations optimized for the different phases of the cook. The process involves feeding the chips and hydrosulfide-rich liquor early in the cook followed by an alkali-rich liquor or liquors later in the cook. The author presents results of previous analytical and experimental work aimed at verifying process benefits and describes the proposed liquor-making process in conceptual terms and practical process options.

Application:

Integrating this new process with both conventional and modified pulping and liquor recovery processes and with possible future closed-cycle mill concepts improves kraft cooking.

In the last two decades, the driving forces for change in both kraft pulping and bleaching have come from a combination of technical efficiency, quality, and environmental concerns. Some might argue with strong justification that environmental concerns have predominated. Now the industry must address deficiencies in the two other areas.

There is little doubt, however, that there has been dramatic progress in meeting environmental concerns. By extending delignification before bleaching, it is possible to reduce the total load of dissolved contaminants—both chlorinated and nonchlorinated—discharged from the bleach plant. This minimizes any potential environmental impact. A greater delignification load taken early in pulping and in oxygen delignification decreases the load on the bleachery. Then a wider choice of bleach agents is economically and technically feasible. This situation has allowed the modern and efficient elemental chlorine-free and totally chlorine-free bleach sequences.

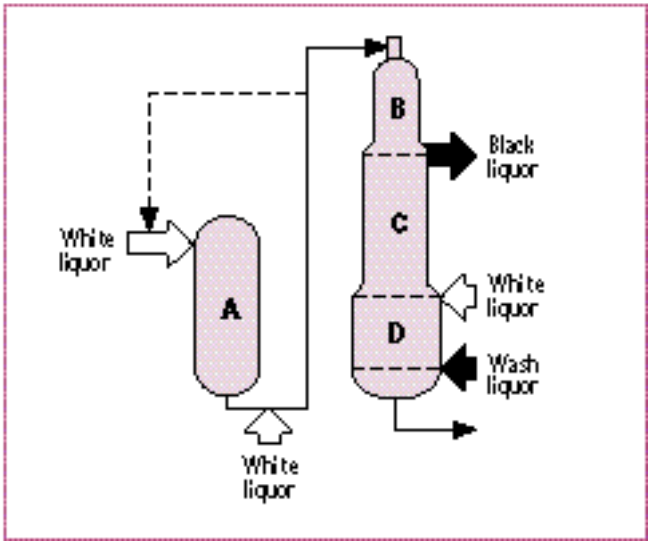
Extended delignification in the cooking process is possible because of many process modifications aimed at improving delignification selectivity. Workers attribute the original development of the growing body of knowledge about the kinetics of kraft pulping reactions to a set of modified cooking principles or "rules" from researchers associated with the Swedish Forest Products Research Laboratory (STFI) *(1-6)* and the Royal Institute of Technology, Department of Cellulose Technology, in Stockholm *(7-11)*. Many others in the global chemical pulp industry have also made significant contributions *(12-14)*. This was especially true in the early 1970s for hydrogen sulfide and polysulfide pulping.

To increase the selectivity of a kraft cook, conditions must increase the ratio between the rate of delignification and the rate of carbohydrate degradation. A review of the original set of modified cooking principles is instructive:

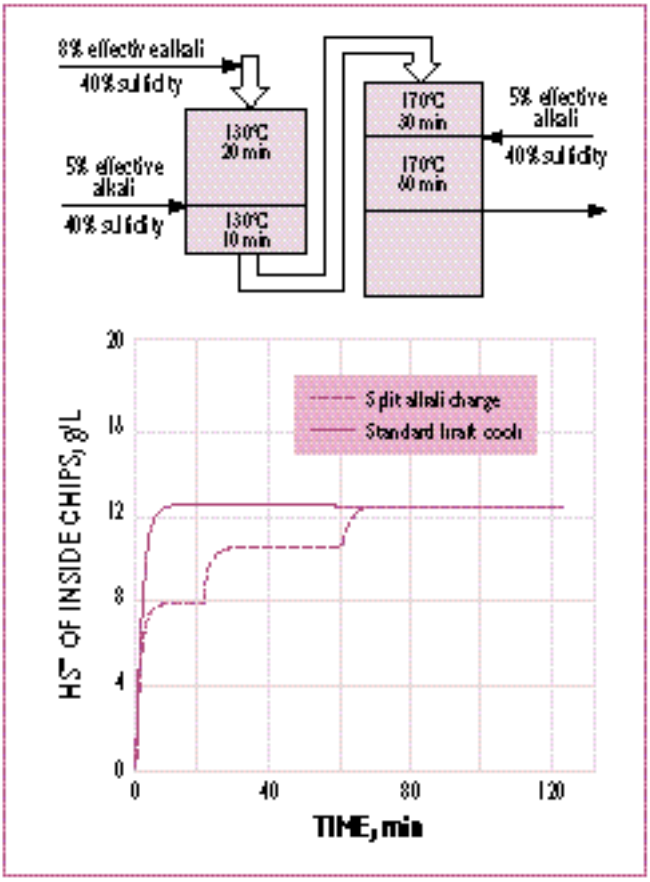
- The alkali profile throughout the cook should be level relative to conventional practice. In particular, one should avoid a high alkali concentration at the beginning of the cook and maintain an increased alkali concentration toward the end of the cook.
- The hydrosulfide ion concentration should be as high as possible in the initial phase and at the beginning of the bulk delignification phase. The concentration of "free hydrosulfide ions" is especially important. At the beginning of a conventional kraft cook, there is typically a depletion of "free hydrosulfide ions." This is probably the reason lignin can sometimes undergo soda-type cooking reactions in the initial phase of the cook that result in a residual lignin that is difficult to dissolve. *(15)*.
- The concentration of dissolved lignin and sodium ions in the cooking liquor should be as low as possible, especially in the final phase of pulping.
- Temperature should be as low as possible with an adjustment of the temperature profile—lower temperatures in the beginning and at the very end of pulping.

In actual industrial practice, it is very difficult to apply all these principles simultaneously, since some of them would appear to counteract each other. This is particularly true if one must use conventional pulping techniques and existing equipment. It has been possible to apply the "rules" in varying degrees to the various forms of modified continuous cooking and modified batch cooking.

The subject of this paper is a new technology that seeks to accomplish better the second "rule" to achieve an appropriately high level of hydrosulfide concentration early in the cook. In more general terms, the purpose of this technology is to enable hydrosulfide profiling in pulping.



1. Principle of modified continuous cooking where A is impregnation zone, B is the concurrent cooking zone, C is the countercurrent cooking zone, and D is the wash zone



2. Concentration profile for hydrosulfide ion in the liquor inside the chips when adding white liquor at three positions **(16)** *during conventional and split-alkali continuous cooking*

CURRENT STATUS OF MODIFIED PULPING PRACTICE

A brief review of current industrial practice toward using the modified cooking principles is pertinent to the discussion that follows. There is particular attention to the issue of hydrosulfide ion concentration to introduce the justification for the technology presented later.

Continuous systems

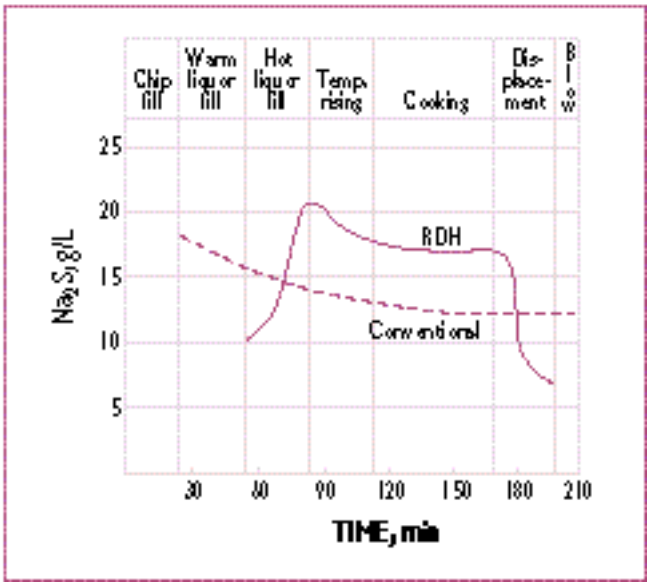
In commercially available digesters provided by Ahlstrom Machinery or Kvaerner Pulping, the total white liquor charge is usually split into three sequential applications, with the final zone of cooking operated in a countercurrent mode as **Fig. 1** shows. This practice results in a more uniform alkali concentration profile during the cook and lower lignin and sodium ion levels at the end of the cook. The hydrosulfide ion concentration is not higher during the initial phase of the cook but is lower.

Figure 2 shows the hydrosulfide ion concentration profile within chips while adding white liquor at three positions. Mathematical models formulated at STFI *(16)* developed this profile. A depleted rather than an enhanced hydrosulfide concentration during the early part of the cook is therefore a consequence of most forms of modified continuous cooking.

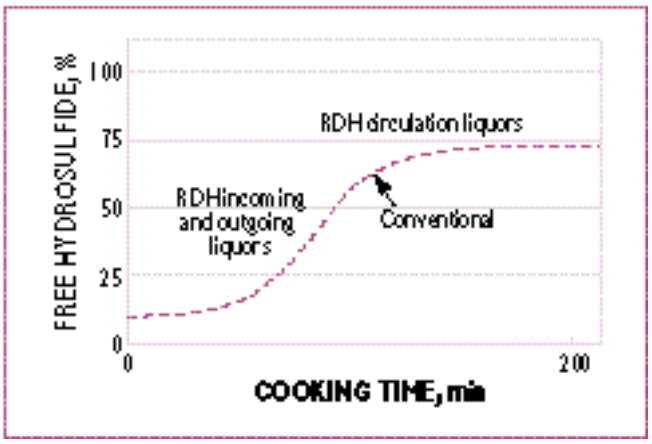
In the two modes of extended modified continuous cooking *(17, 18)*, the white liquor is split about 75% to the main cooking zones—in two or three separate charges as Fig. 1 shows—with the remaining 25% to the wash liquor circulation to achieve countercurrent cooking in the wash zone. The wash zone temperature is typically within a few degrees of the lower cooking zone temperature. Ideally, this lowers the average cooking temperature by a few degrees, resulting in a much longer and milder cook. In isothermal cooking, improvements to liquor extraction reportedly *(18)* enable a higher liquor circulation and help the operator achieve an even lower and virtually even temperature profile.

Other improvements to these basic modified continuous cooking schemes include low-solids cooking *(19)* and black liquor pretreatment *(20)*. In the former, there is liquor withdrawal from more than one digester recirculation loop and addition of wash filtrate, allowing more favorable lignin and sodium profiles. In the latter, recent steps to add black liquor pretreatment to the impregnation zone have reportedly *(20)* resulted in some additional improvements in pulp properties.

The benefits gained by addressing three of the four cooking "rules" have provided a stronger pulp at a lower kappa number with a better digester operation in terms of column movement. The issue of depleted hydrosulfide charge early



3. Concentration profiles for Na_2S during modified and conventional batch cooking **(22)**



4. Relative concentration profiles for free hydrosulfide ions during modified and conventional cooking **(21)**, *with 100% corresponding to the total sulfide charge in white and black liquors during the conventional 32% sulfidity cook*

in the continuous cook remains an issue, however.

Batch systems

In modified batch cooking, the chips undergo impregnation with black liquor during the initial stages of the cook. At the end of the cook, wash liquor displaces the spent cooking liquor before blowing or pumping out the contents of the digester. There may also be alkali charge division, but the addition of the bulk of the white liquor is normally after the initial black liquor displacement during the hot liquor fill. It is an option to charge some fresh white liquor at an intermediate time in the cooking stage or adding it with the wash-liquor quench at the displacement stage of the cook.

There are two main suppliers of modified batch cooking equipment, both of which apply similar principles. The major difference between the two technologies is the performance of the black liquor impregnation. One supplier claims that their method of warm liquor followed by hot liquor displacement provides pulp strength advantages. A third supplier initially offered another variation of modified batch cooking. With a merger by this company, one would expect a product rationalization to occur.

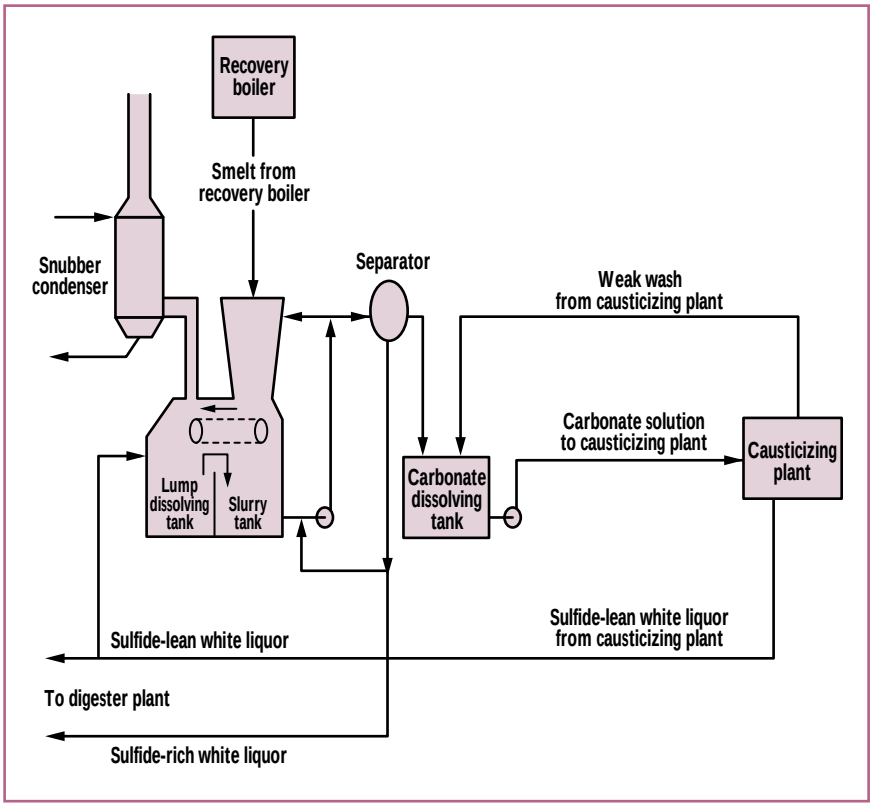
Figures 3 and 4 compare the concentration profiles of sodium sulfide and free hydrosulfide ions during one commercial cooking process *(21–23)*—rapid displacement heating (RDH)—with those of conventional batch cooking. The profiles use measured values from actual mill operations. The other commercial cooking process would show similar trends.

As Fig. 3 shows, the sodium sulfide concentration in the cooking liquor of the modified batch cook is higher during most of the initial and the bulk phases. It is lower in the very beginning of the cook during the warm liquor fill. As Fig. 4 implies, the free hydrosulfide ion concentration is higher in the incoming and outgoing liquors during the initial phase of modified batch cooking. In this modified batch cook at 32% sulfidity, the initial-phase free hydrosulfide concentration is approximately four times higher than a conventional kraft cook at the same sulfidity. It is comparable with that achieved during a conventional kraft cook at approximately 46% sulfidity *(21)*.

As a general observation then, the modified batch cook fulfills the second "rule" to achieve an enhanced level of hydrosulfide concentration at the beginning of the cook. Besides serving the "rules" for improved selectivity, the high strength reported for some displacement batch operation could also be due to superior uniformity in pulping *(24)*. With well-controlled displacements, the distribution of chemicals and heat throughout the digester and throughout each wood chip is probably extremely uniform *(25)*.

RECENT PULPING RESULTS FOR PRETREATMENT OF SOFTWOOD WITH SULFIDE-CONTAINING LIQUOR

Recent pulping work conducted at STFI *(24)* has reaffirmed the principle that pretreating wood chips with sulfide containing liquor to increase sulfide sorption increases selectivity in the subsequent kraft cook. Sorption of sulfide increases with higher hydrosulfide concentration, time, temperature, and concentration of positive ions but decreases with an



***5. Simplified process arrangement* (28)**

increasing concentration of hydroxide ions. These studies *(24)* revealed that the ratio of hydrosulfide to hydroxide ions should be at least six or seven to one to achieve a sufficiently high sulfide sorption. Earlier work *(24)* showed that the better selectivity of a modified batch kraft cook is largely due to the low hydroxide ion and high hydrosulfide concentrations in the pretreatment liquor and the low temperature and long time during pretreatment.

Extensive laboratory trials simulating modified continuous cooking using controlled sulfide profiles investigated the potential for improvements to pulping performance. Adding most or all the sulfide to the beginning of the cook gave the highest hydrosulfide concentrations both in the initial phase and near the transition point from the initial to the bulk delignification phase. The intensified sulfide sorption resulted in better yields and increased viscosities. In subsequent studies involving additional laboratory cooking trials in two locations, there were similar findings *(26, 27)*. According to the authors, it was possible to realize the benefits of sulfide profiling to establish optimum conditions for pulping selectivity in most batch or continuous digesters. These selectivity improvements appear also to be additive to those from the basic modified continuous cooking technologies.

OPTIMIZING THE HYDROSULFIDE APPLICATION SYSTEM DURING KRAFT PULPING

General

There is a strong case for intensifying the sulfide sorption early in the kraft cook. It would provide better selectivity, especially in modified pulping situations where there is strong sulfide depletion during the initial stages. Given the need during most impregnation arrangements to provide a hydrogen sulfide ion to hydroxyl ion ratio of at least six to one or higher to ensure sufficient sulfide sorption, it is apparent that the most suitable liquor available would ordinarily be black liquor. If conditions merit more intensive but shorter time of treatment or a greater selectivity enhancement, however, then the ability to separate the hydrosulfide from the hydroxide of white, green, or black liquors is clearly necessary. There are some alternative concepts *(26)*:

- Pressurized black liquor gasification conceptualized by Kvaerner as a further development of a nearly commercial pressurized gasifier
- Green liquor stripping processes similar to the Tampella recovery system for sulfite liquor making
- Green liquor crystallization commercialized by Ahlstrom in Finland
- Black liquor heat treatment commercialized by Ahlstrom
- Recovery boiler smelt leaching—the proposed process concept.

Of these processes, only green liquor crystallization is fully commercial for kraft liquor making now.

Recovery boiler smelt leaching as the basis for the new process

The proposed liquor-making process *(28)* is a novel method for producing white liquor in separate sulfide-rich and sulfide-lean streams. Conception of the process was to correct or enhance hydrosulfide-related kraft pulping selectivity mechanisms. Its primary use was that a sulfide-rich liquor alone or combined with other liquors could apply to the early phases of a kraft cook and the sulfide-lean liquors later in the cook. The new liquor-making process concept uses the difference in solubility of sodium carbonate and sodium sulfide in the recovery boiler smelt to provide a separation of these two

materials. This separation comes without any external heat requirement or indirect heat transfer. The primary process steps are a smelt leaching operation and a solid sodium carbonate from slurry liquor separation.

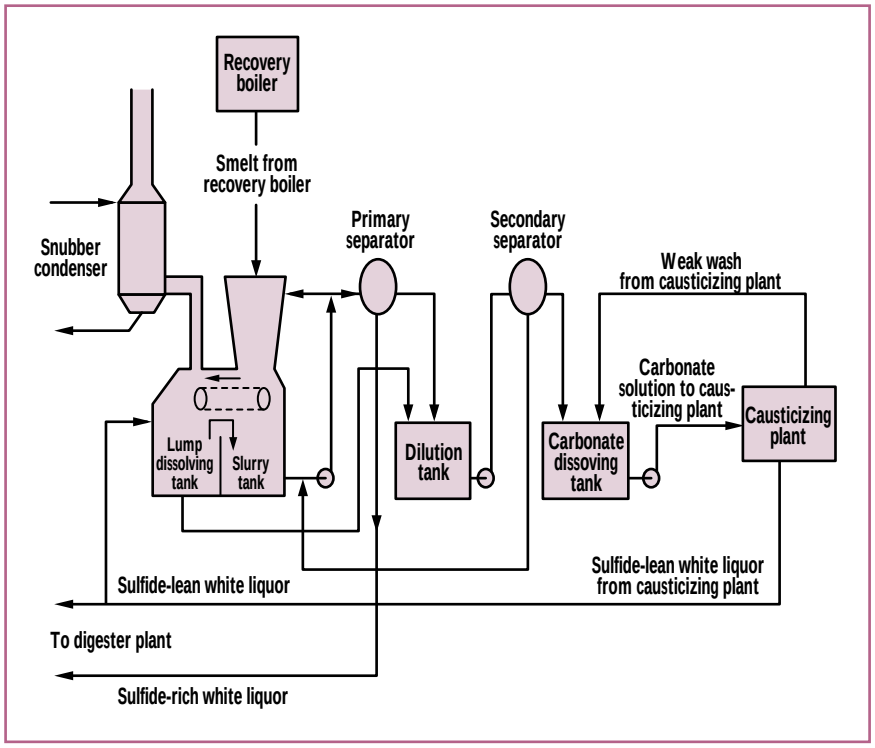
PROCESS DESCRIPTION

Although it is novel, the concept behind the process uses proven and cost efficient subprocesses. **Figure 5** is a simplified schematic of the proposed process. One can follow the process flow from the recovery boiler where smelt pours from the smelt spouts into a bank of smelt hoppers. Here the molten material solidifies through contact with recirculating slurry that flushes the sides of the smelt hoppers.

The slurry largely passes through the moving-bar-type smelt screen to separate oversized lumps from the slurry and carry them to the lump dissolving tank. The accepted slurry collects in the slurry tank.

In the slurry tank, sodium sulfide preferentially dissolves from the smelt particles, while sodium carbonate remains in the solid phase. Pumps recirculate the slurry over the smelt hoppers. A smaller quantity of slurry controlled by slurry density is exported via the carbonate separator feed pumps to the carbonate separators.

Smelt lumps in the lump dissolving tank are introduced to a sidestream of sulfide-lean white liquor produced in the causticizing plant. Sufficient agitation and residence time exists to dissolve the lumps. Liquor overflows from the lump dissolving tank into the slurry tank, with sulfide-lean liquor addition controlled to maintain the level in the slurry tank. If one prefers a sulfide-rich liquor with an even higher sulfidity and lower effective alkali content, it is possible to substitute water or weak wash for the makeup sulfide-lean liquor. The whole process is



***6. Alternative process arrangement* (28)**

under a vapor cap produced by controlled evaporation of water from the slurry.

In the solid bowl decanter centrifuges employed as carbonate separators, the slurry splits into clear, sulfide-rich, white liquor and a cake consisting mainly of solid sodium carbonate. Controlled by liquor density, part of the sulfide-rich liquor proceeds to a sulfide liquor storage tank for use in the digester. The remainder returns to the slurry tank.

The cake from the carbonate separators discharges into the carbonate dissolving tank, where it meets weak wash from the causticizing plant. The resulting solution transfers to green liquor clarification or filtering. In the causticizing plant, sulfide-lean white liquor is produced. Some of this is pumped to the lump dissolving tank. The remainder finds use in the digester, in oxygen delignification, or possibly in bleaching.

A typical layout for a retrofitted or new process system would involve replacing the existing dissolving tank with the integrated slurry tank and lump dissolving tank. The carbonate separators and associated tankage would be in a separate building as close to the recovery boiler as possible. To allow gravity discharge of solid sodium carbonate and sulfide-rich liquor from the carbonate separators, the units would be elevated.

The main process elements such as smelt hoppers, smelt screen, lump dissolving tank, and slurry tank are proven components in a neutral sulfite semichemical recovery process. They will require adaptation to the new process needs that include operation without air infiltration and external cooling under boiling conditions. The equipment will also require scale up to handle the higher smelt flows from the larger scale kraft mills. Due to the high slurry concentrations of the leaching step, one would not expect precipitation of solids such as sodium carbonate

	Conventional	Sulfide-rich	Sulfide-lean	Total
NaOH, *	68.9	150.6	101.2	...
Na_2S*	37.1	181.6	4.8	...
Na_2CO_3*	12.5	trace	21.6	...
Active alkali*	106	332	106	175.5
Effective alkali*	87	241	104	146.0
Sulfidity, % on active alkali	35	54.7	4.5	33.7
Causticity, %	83.5	99.9	82.4	88.6
Percentage of total effective alkali, %	100	49.8	50.2	100

* g/L as Na_2O

I. White liquor compositions

or pirssonite on tank walls or in piping to be as severe a problem as in a system handling a conventional green liquor. Nevertheless, an actual design would include at least dual carbonate separation systems and system allowances for washing or maintenance.

The other main elements of the system—the solid bowl centrifuges for carbonate separation—are also proven components in similar applications such as the separation of brines in the soda ash industry and the separation of sodium chloride from caustic in diaphragm chlor-alkali plants.

Figure 6 shows an alternative process arrangement, if the goal of the operation is to produce as low a sulfur-continuing alkaline liquor as possible. The principal distinguishing feature of this scheme is a series separator arrangement.

IMPACT OF THE LIQUOR-MAKING PROCESS ON MILL OPERATIONS

Liquor properties

Using conceptual process modeling, **Table I** shows typical liquor properties for sulfide-rich and sulfide-lean liquors. For comparison, there is a typical conventional white liquor prepared from the same smelt composition. The following are notable features:

- The sulfidity of the sulfide-rich liquor is 55% compared with 4.5% for the sulfide-lean liquor and 34% overall.
- The combined effective alkali concentration for the novel liquors is approximately 67% higher than for the conventional white liquor. This results in an approximately 15–20% smaller weak black to heavy black liquor evaporation requirement. This is due to two factors: the extremely high concentration of the sulfide-rich liquor and the higher relative concentration of the sulfide-lean liquor. The sodium sulfide is not carried over to the recausticizing system.
- The conversion of sodium carbonate to sodium hydroxide is approximately 6% higher for the new process compared with a conventional case at the same sulfide- lean active alkali and approach to equilibrium. This is due to reprecipitation of sodium carbonate from the portion of the sulfide-lean liquor recycled to smelt leaching.
- The hydraulic load in the green liquor clarification, slaking, causticizing, and white liquor separation systems of the new process will be approximately 76% of that for the comparable conventional case.
- The very low sulfide content of the liquors handled in the recausticizing area will result in lower total reduced sulfur emissions from the lime kiln and lower corrosion rates for process equipment.

KEYWORDS

Alkaline pulping, bibliographies, carbonates, chemical pulping, cooking liquors, hydrosulfides, kraft pulping, leaching, pulping, separation, smelt, sodium carbonate, sodium compounds, sulfides, white liquors.

Energy balance

The new process will not require any steam inputs. Instead, it will reduce the evaporation requirements of a typical mill by approximately 1.4 m^3/a.d. metric ton, with a corresponding reduction in evaporator steam consumption.

The new process will consume some additional electrical energy for agitator, pump, and separator drives. This will be offset by reduced needs in the evaporator and recausticizing areas and significantly reduced needs for a white liquor oxidation system. The net increase in electrical energy demand is approximately 1.5 kW·h/a.d. metric ton.

Warm and hot water balance

In a typical mill situation, the following will affect the warm and hot water balance:

- Decreased production of evaporator condensates by approximately 1.4 m^3/a.d. metric ton
- Heat rejection at the evaporator surface condenser reduced by

approximately 15–20%
- Contaminated hot water needs in recausticizing reduced by approximately 1.5 m^3/a.d. metric ton.

Thus the net available hot water would remain essentially unchanged, but the net warm water produced would decrease by 7–10 m^3/a.d metric ton, reflecting primarily the lower evaporator steam consumption.

Chemicals consumption

The new process will present the possibility to reduce the kappa number when applied in either conventional or modified digesters. The optimum decrease will be highly mill specific, depending upon the bleach sequence, the environmental regulatory situation, and unit chemical costs.

Other impacts

Since one can extend delignification of the brownstock compared with a baseline operation, less bleaching chemicals and lower contaminant discharge rates are possible. Purchased alkali consumption could decrease by using sulfide-lean liquor in the bleach plant extraction stages, possibly with filtrate recycled to the recovery plant. It would be advantageous to oxidize even the greatly reduced sulfide content of the liquor before use in the bleachery. Since only clean caustic with a very low manganese content is suitable for use in peroxide stages, it is possible that the new liquor will not be suitable for peroxide stage use.

Besides enabling enhanced digester operation, the new process could have positive effects on evaporator and recausticizing equipment loadings, steam and water consumption, bleach chemical consumption, and environmental discharges.

Future plans

We conclude that the new process indicates enough promise technically and economically to justify further development. Capital equipment requirements are not excessive considering the potential gains with preliminary calculated returns in an attractive range. At this stage, however, these factors are quite speculative. If the new process can successfully meet the challenges of a pilot demonstration at a mill operation, it could provide a valuable addition to kraft pulp mill liquor-making technology and assist the pulp mill operator in meeting environmental, pulp quality, and economic goals. The new process also fits very well into a plan of evolving toward a closed-cycle mill operation. **TJ**

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The author appreciates the important contributions of Patrik Lownertz of Karlstad, Sweden, in formulating the idea, supervising the pulping verification trials, and delineating the requirements of the new process. He also thanks the British Colombia Science Council and H.A. Simons Ltd. for their financial support of the laboratory program and notes H.A. Simons Ltd.'s continuing support in developing the process concept.

Received for review July 15, 1996.

Accepted Aug. 7, 1996.

Presented at the TAPPI 1996 Engineering Conference.

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