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Removal of Chloride and Potassium from Kraft Chemical Recovery Cycles

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ABSTRACT

The current paper shows how a system for removal of both chloride and potassium may be incorporated in a potential future kraft chemical recovery system, where the traditional recovery boiler has been replaced by a black liquor gasifier. The suggested process involves cooling crystallization of sodium carbonate and sodium bicarbonate from a preferentially sulfide lean green liquor, leaving a stream depleted of useful chemicals but rich in chloride and potassium, that may be led to sewer. The investigation includes a modeling part, where a thermodynamic model has been used to calculate the solubility limits in the green liquor, and an experimental part, where both synthetic green liquor (with a controlled composition) and green liquor taken from a Swedish mill were used. The results show that the suggested process functions well and that both chloride and potassium will be selectively removed from the green liquor, while the useful chemicals will be recovered for reuse in the pulp mill. The size of the system necessary for the suggested process will depend on the concentrations of chloride and potassium that can be tolerated in the process liquor—an example is given showing the technical feasibility of the suggested process.

INTRODUCTION

During the last thirty years the possibility of system closure in a pulp mill by minimizing the waste streams has attracted much attention. An example of such a measure is recycling of bleach plant effluent to the evaporation plant. Such changes inevitably involve internal recycling of waste streams, which in turn increases the risk of accumulation of so-called nonprocess elements

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(NPEs) in the mill. The NPEs are chemicals which enter the pulp mill through the raw materials but which are not useful in the process. Chemicals such as chloride, potassium, and manganese participate neither directly nor indirectly in the pulping process, and must therefore be considered NPEs.

An undisputed fact is that everything that enters the pulp mill must also leave the mill in one way or another. For many of the NPEs, minimizing the waste streams therefore also eliminates one of the ways these chemicals leave the pulp mill, leading to elevated concentrations of NPEs in the process liquors. Thus, it is necessary to study the mechanisms by which NPEs enter and leave a tightly closed pulp mill carefully. It is possible to classify nonprocess elements into two groups. In the first group we find elements that are accumulated in the process liquors, and in the second those that are purged with the green liquor dregs (1). Typically, less soluble chemicals such as calcium, manganese, magnesium, and cadmium are purged with the dregs. However, in the case of carryover of such chemicals to the causticizing process, there is a risk of these chemicals being accumulated in the lime cycle. More soluble chemicals such as chloride, potassium, and aluminum will instead be accumulated in the pulping liquors. For some NPEs it may prove necessary to introduce equipment dedicated to their removal—chloride and potassium are examples of such NPEs for which methods for removal have been studied (2–5).

Much effort was spent during the sixties and seventies to investigate the effect of increased chloride concentration on the process chemistry as a consequence of the idea of "the effluent-free bleached kraft pulp mill," introduced by Rapson (6). Later on, other chemicals started to be considered, such as potassium (7). Nowadays, even trace chemicals in the wood are under study.

A number of investigations of the intake of inorganic chemicals to the pulp mill have been made. Both chloride and potassium normally enter the mill with the wood itself, and in some cases also with the makeup chemicals. The normal intake of both these chemicals is approximately one or a few kilograms of Cl and K per ton of bleached pulp, respectively, but can vary considerably with different species of wood and also with location. More detailed information has been made available in a mill study where a number of inorganic chemicals other than Cl and K were also included (8). Other, more recent studies, describing the intake of NPEs and the levels of NPEs at different locations in the mill are also available (1, 9, 10).

The effects of elevated concentration of chloride in the process liquors have been thoroughly reviewed (9, 11, 12). One of the most noteworthy consequences of elevated chloride concentration is a decreased temperature of solidification of the smelt in the recovery boiler; at 10–20 wt% of NaCl the smelt has a melting point minimum. In the recovery boiler this may lead to a lower average bed level, a thinner layer of solidified smelt on the tubes, and alternation between the solid and liquid phases in the bed. Chlorides are also known to cause general corrosion.

The problems associated with a high concentration of potassium have also been investigated and described in the literature (7, 9). Similar to chloride, most investigations relate the high concentration of potassium to problems in the recovery boiler. The most noticeable influence of an elevated concentration of potassium is a decrease of the melting point of the recovery boiler deposits, which may lead to plugging of the recovery boiler flue gas passages.

Both chloride and potassium have been found to speed up the plugging of the flue gas passages and the fouling of the heat transfer surfaces. This has been explained by the fact that these elements lower the so-called sticky temperature of the deposits. An increase in the rate of sintering of the deposits and the corrosion rate on the boiler tubes has also been noticed (9). Mill studies have been performed by Backman et al. (13).

METHODS FOR REMOVAL OF CHLORIDE AND POTASSIUM

A number of methods for removal of chloride have been suggested, among which some may also be used to solve the problem of high potassium concentration. The simplest and cheapest method involves the removal of chloride and potassium from the recovery boiler electrostatic precipitator dust (4–7, 12, 14, 15). Treating the precipitator dust is an effective way of trying to solve the problems with chloride and potassium, since both these chemicals are enriched in the precipitator dust relative to the process liquors. In a chemical recovery cycle based on black liquor gasification, electrostatic precipitator dust is not collected, and therefore this alternative would no longer be available. However, in the case where a black liquor gasifier is used in parallel to a recovery boiler in order to increase the capacity of the recovery system, this alternative should still be available. Leaching of the precipitator dust was tested in an industrial installation in Harmac Pacific, BC, Canada in 1973 but was soon given up due to serious problems with corrosion and plugging of the piping in the installation. However, in this particular installation, spent sulfuric acid was added to convert Na_2CO_3 to Na_2SO_4 to minimize the losses of Na_2CO_3, and this is probably the reason for the corrosion problems encountered. Careful design considerations need to be made to avoid the plugging problem.

Another process where the precipitator dust is treated for removal of chloride and potassium has been suggested by Maples et al. (16). This system is part of a process called the Bleach Filtrate Recycle (BFR) process, and involves complete dissolution of the precipitator dust, followed by recrystallization of the sodium sulfate content of the dust in an evaporative crystallizer.

After a filtration step the salt cake is dissolved in the strong black liquor and returned to the process whereas the filtrate, enriched in chloride and potassium, is sewered. The BFR process was operated beginning in 1994 as a demonstration plant in Canton, NC, USA, and the process for the removal of chloride and potassium was started up in August 1995 (17). According to figures given for the third quarter of 1996, the installation provides a very good removal of chloride, approximately 95%, whereas the removal of potassium (47%) and the recovery of sulfate (80%) are slightly lower than the design values (17). Champion International shut down the BFR process before selling the mill in 1999.

The evaporation of white liquor as an alternative to purge chlorides was proposed by Reeve and Rapson (18, 19). In the vision of the effluent-free mill, the original idea was to use the NaCl produced to regenerate bleaching chemicals, so this process was named the Salt-Recovery Process. The process of white liquor evaporation, in a number of varieties, has been thoroughly described in the literature (7, 20–22). The basic version involves evaporation of white liquor so that sulfates and carbonates crystallize out initially. Further evaporation also causes NaCl and KCl to crystallize. Different variations of this method can be used to achieve separation of NaCl and KCl or to remove by leaching the rest of carbonate and sulfate that coprecipitates with NaCl and KCl in the second evaporation step. The Salt-Recovery Process was tested in a mill in Thunder Bay, ON, Canada, from 1977 to 1985.

Another method for removing chloride involves crystallization of sodium carbonate (as $Na_2CO_3 \cdot 10H_2O$) from green liquor by cooling and subsequent crystallization of NaCl from the remaining solution by evaporation (23). In this process the lower solubility of Na_2CO_3 at lower temperatures (below approximately 32°C) is used to separate NaCl from Na_2CO_3. It is claimed that 55% of the Na_2CO_3 may be crystallized from the green liquor by lowering the temperature to 10°C, and that as much as 72% would crystallize at 5°C.

Another method of removing chloride and potassium from the recovery system is leaching of the smelt from the recovery boiler (18, 24). By leaching the smelt at 50°C or more, the Na_2S content of the smelt can be removed. The residue is thereafter treated in a cold leach, at around 20°C, to dissolve NaCl and KCl. This method, however, suffers from substantial practical problems (25).

A new method for the purge of chloride ions from precipitator dust has recently been proposed which uses bipolar membrane electrodialysis to split the sodium chloride content of the precipitator dust into caustic soda and hydrochloric acid (26). Rapp and Pfromm simplified the suggested process and performed pilot-plant experiments from which successful removal of both chloride and potassium was reported (27).

PROCESS DESCRIPTION

Gasification of black liquor is an interesting alternative to the conventional recovery boiler. Some of the main reasons for this are the possibility to produce more electricity than using the conventional boiler, a lower risk of smelt–water explosions, and the possibility to achieve a split between sulfur and sodium, thus making it possible to produce tailor-made cooking liquors. In the BLGCC (Black Liquor Gasification Combined Cycle) process of Kværner Chemrec, the black liquor is gasified at high pressure (2–4 MPa) and temperature (900–1000°C) in an oxygen-blown gasifier, producing a smelt and a syngas containing hydrogen sulfide. The smelt is quenched in the bottom of the gasifier, producing a green liquor. Some 25–40% of the H_2S in the black liquor ends up in the syngas. The syngas is led through an absorption–desorption step where H_2S is absorbed in green liquor in the first step, and in the second step H_2S is stripped from the liquor stream leaving the absorption unit, leaving behind a gas stream of H_2S (for production of cooking chemicals), a sulfide lean green liquor, a sweet syngas for production of heat and electricity in a combined cycle power generator, in addition to the already-mentioned green liquor coming out of the quench in the bottom of the gasifier. More detailed information on the gasification process is given by Stigsson (28) and Stigsson and Berglin (29). There are other black liquor gasification concepts available than the one mentioned here; however, the BLGCC process is currently dominant.

A negative effect of the gasification process is that some of the sulfur is produced as $H_2S(g)$ instead of as $Na_2S(aq)$ as in the conventional recovery boiler. When the H_2S is absorbed in green liquor as described above, a corresponding amount of carbonate in the green liquor is converted into bicarbonate. This leads to an increase in lime consumption in the recaustization plant since bicarbonate consumes twice as much lime to form NaOH as does carbonate.

The effect of high levels of chloride and potassium on the gasification process is only partly known. It can be anticipated that the smelt properties will be significantly dependent on the levels of chloride and potassium, like the smelt in the recovery boiler. High levels of chloride may also cause problems with general corrosion.

Figure 1 shows how equipment for removal of chloride and potassium may be incorporated in a kraft recovery system based on gasification of black liquor where a recovery boiler is not present. Only part of the green liquor is drawn off and treated for removal of chloride and potassium after carbonization and desorption of H_2S. The green liquor stream that will be treated must be balanced to keep the concentration of chloride and potassium at the desired level in the recovery system.

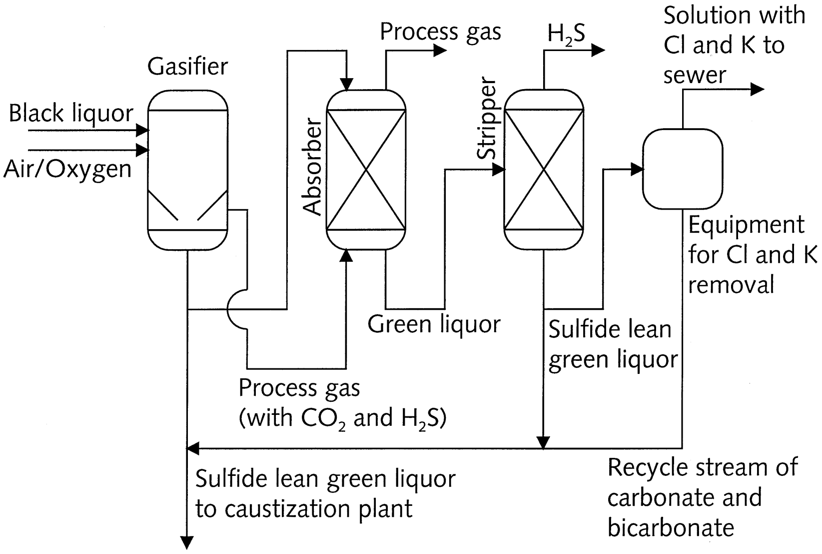

FIG. 1 A simplified schematic of a system for the removal of chloride and potassium in a kraft chemical recovery system using black liquor gasification.

The process for removal of chloride and potassium studied in this work is depicted in Fig. 2. As shown in the figure, the process involves evaporation of the drawn-off green liquor, followed by crystallization. Sodium carbonate and sodium bicarbonate are crystallized at a low temperature in the crystallization step, and the remaining solution is enriched in chloride, potassium, and any sulfide not removed in the absorption–desorption system. Finally, the precipitated crystals are filtered off and the solution is removed from the system.

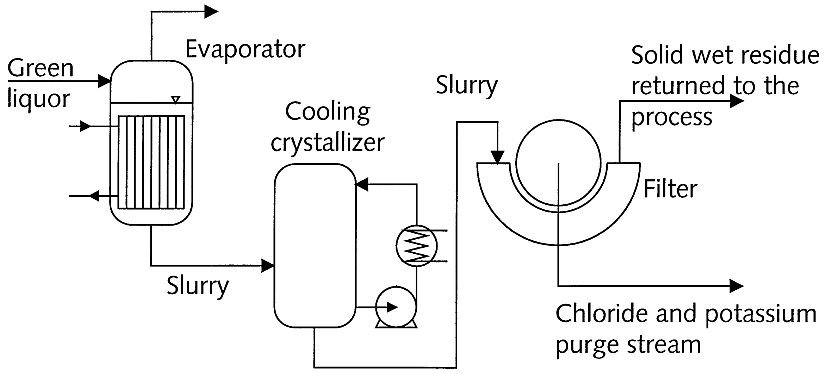

FIG. 2 Suggested process for the removal of chloride and potassium through green liquor cooling crystallization.

MODELING AND SIMULATION

The process described above was simulated using the commercial simulation program Aspen Plus. Chemical equilibrium calculations were performed for the coupled system of chemical reactions, including the different precipitation reactions that were considered possible to occur in the green liquor.

The activity coefficients were modeled using the electrolyte NRTL model (30–32). The model may be used to represent many kinds of mixtures from pure molecular systems (when it reduces to the ordinary NRTL model) to pure fused salts, and it is one of the few models that claims to be valid at higher electrolyte concentrations. Nowadays, the model is widely used in the process industry. In the electrolyte NRTL model the excess Gibbs energy is calculated as a sum of two terms. The first term takes into account the long-range interactions in the mixture due to the electrostatic forces between ions, and is calculated according to an extended Debye–Hückel equation. The second term takes the short-range interactions into account, using the concept of local interaction. The local mole fraction of each species is related to the global mole fraction by an NRTL interaction parameter τ.

Regression of Parameters to Solubility Data

The model parameters needed were the different NRTL interaction parameters τ. These parameters are weakly dependent on the temperature, and they were fitted to the temperature T using three adjustable parameters a, b, and c according to

$$\tau = a + \frac{b}{T} + c\left(\frac{T_{\text{ref}} - T}{T} + \ln \frac{T}{T_{\text{ref}}}\right) \tag{1}$$

where $T_{\text{ref}} = 298.15$ K. Normally, the nonrandomness parameters α that are part of the NRTL model should also be fitted, but it has been proposed to set these parameters to a default value without the performance of the model being affected much (30).

For many species, NRTL parameters were already available in the data bank of the simulation program; however, some parameters were still needed to be regressed (mainly interaction parameters describing the interaction between two ion pairs with a common ion). These regression runs were executed using solubility data as input.

Furthermore, the solubility constants for all salts that may possibly crystallize must be available as a function of the temperature. Aspen Plus offers the possibility to regress the solubility constant K to the temperature using four parameters A to D, where the temperature dependence is given by

$$\ln K = A + \frac{B}{T} + C \ln T + DT \tag{2}$$

TABLE 1

Components Included in the Simulation Model for the Suggested Process for Removal of Chloride

$H_2O(l)$	$Na^+(aq)$	$Cl^-(aq)$
$CO_3^{2-}(aq)$	$HCO_3^-(aq)$	$H_3O^+(aq)$
$CO_2(g)$	$HCl(g)$	$NaCl(s)$
$Na_2CO_3{\cdot}H_2O(s)$	$Na_2CO_3{\cdot}\ 10H_2O(s)$	$NaHCO_3(s)$
$Na_2CO_3{\cdot}NaHCO_3{\cdot}2H_2O(s)$		

Salt solubility data were also used as input for these regression runs.

An important first step in the modeling work is to determine which components and chemical reactions (including precipitation reactions) need to be considered in the simulations. The more the chemistry can be simplified, the fewer model parameters will have to be regressed, which subsequently leads to simplified calculations in the final simulation model for the suggested process. The components that were included in the final model are given in Table 1, and the chemical reactions that were included in the model are shown in Table 2. Since the green liquor coming from the absorption–desorption step is supposed to be lean in sulfide, this chemical was excluded from the simulations.

A very large number of simulations have been performed in this work. Many of the simulations have been devoted to subsystems of the system described above, with the intention of using solubility data available in the literature to regress necessary model parameters.

In the binary systems, i.e., systems with a single salt dissolved in the solvent, the temperature dependence of the solubility constant K for the different salts has been regressed as described in Eq. (2). Solubility data available in the open literature were used as input in the regression runs. The NRTL τ-param-

TABLE 2

Chemical Reactions Included in the Model of the Process for Removal of Chloride

$$CO_2 + 2H_2O \rightleftharpoons H_3O^+ + HCO_3^-$$
$$HCl + H_2O \rightleftharpoons H_3O^+ + Cl^-$$
$$HCO_3^- + H_2O \rightleftharpoons H_3O^+ + CO_3^{2-}$$
$$Na^+ + Cl^- \rightleftharpoons NaCl(s)$$
$$Na^+ + HCO_3^- \rightleftharpoons NaHCO_3(s)$$
$$2Na^+ + CO_3^{2-} + H_2O \rightleftharpoons Na_2CO_3{\cdot}H_2O(s)$$
$$2Na^+ + CO_3^{2-} + 10H_2O \rightleftharpoons Na_2CO_3{\cdot}10H_2O(s)$$
$$3Na^+ + CO_3^{2-} + HCO_3^- + 2H_2O \rightleftharpoons Na_2CO_3{\cdot}NaHCO_3{\cdot}2H_2O(s)$$

eters needed in the simulations were already in the data base of the simulation program. The following binary systems were included in the regression runs:

- $NaCl–H_2O$
- $NaHCO_3–H_2O$
- $Na_2CO_3–H_2O$

The system $Na_2CO_3–H_2O$ can form a number of hydrates. At temperatures up to 32°C the solid phase consists of $Na_2CO_3 \cdot 10H_2O$, and at higher temperatures of $Na_2CO_3 \cdot H_2O$. The strongly decreasing solubility with decreasing temperature should be noted. There is also an intermediate solid phase consisting of $Na_2CO_3 \cdot 7H_2O$, which exists between approximately 32 and 35.4°C. However, we chose to disregard this precipitate to simplify the model.

In the ternary systems, i.e., in this context systems with two salts dissolved in the solvent, it is customary to describe solubility data by plotting the concentration of one of the salts as a function of the concentration of the other for solutions saturated with respect to one or both of the salts. The influence of the temperature is taken into account as a parameter.

In this work, solubility data for the ternary systems have been used to regress NRTL τ-parameters between two anions with a common cation and between two cations with a common anion, respectively, to solubility data for solutions saturated with respect to two salts. The solubility constants already regressed from the binary systems were used in these regression runs.

The following ternary systems were included in the regression runs:

- $NaCl–NaHCO_3–H_2O$
- $NaCl–Na_2CO_3–H_2O$
- $NaHCO_3–Na_2CO_3–H_2O$

As can be seen in Fig. 3, for the system $NaHCO_3–Na_2CO_3–H_2O$ a new salt with the composition $Na_2CO_3 \cdot NaHCO_3 \cdot 2H_2O$, that cannot be formed in the binary systems, appears at temperatures above 25°C. In the temperature range 15–30°C the solid carbonate phase consists of $Na_2CO_3 \cdot 10H_2O$.

Results

The composition of the simulated green liquor is given in Table 3. In a series of simulations, the influence of the degree of evaporation from the green liquor and the temperature of crystallization were investigated. The simulations show that the crystallized solids consist of $Na_2CO_3 \cdot 10H_2O$ and $NaHCO_3$ at temperatures below 25°C, and of $Na_2CO_3 \cdot NaHCO_3 \cdot 2H_2O$ and $NaHCO_3$ at temperatures above 25°C. Furthermore, it is important to note that the process functions reasonably well and that crystallization of NaCl only takes place at 10°C and evaporation to 75%.

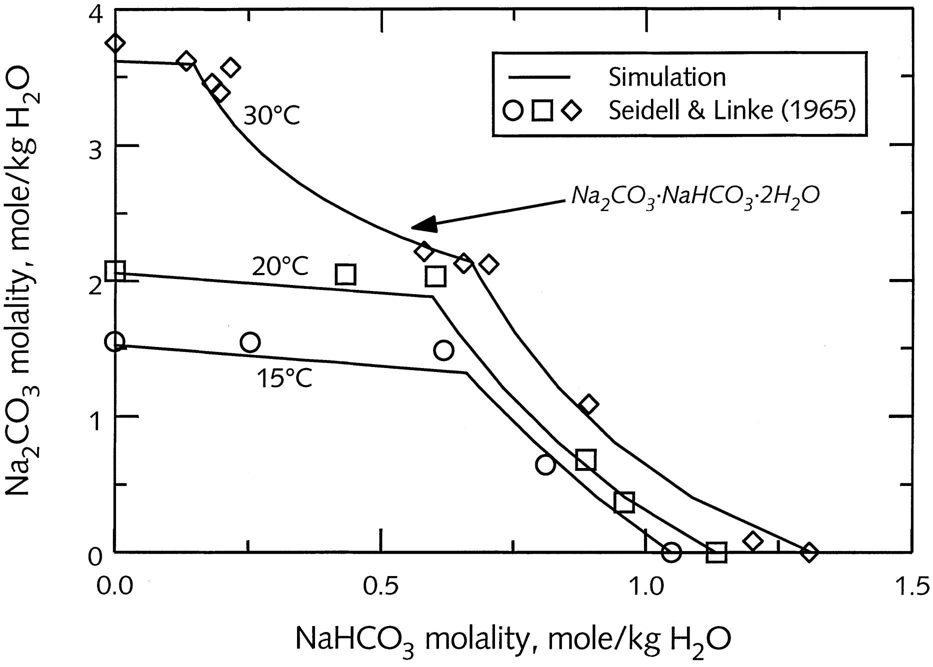

FIG. 3 Comparison between simulation results and literature solubility data for the system $NaHCO_3$–Na_2CO_3–H_2O within a temperature range of 15–30°C. Literature data from Seidell and Linke (33).

Figure 4 shows how much of the carbonate in the treated green liquor can be recycled as a solid to the process as a function of the degree of evaporation and the temperature in the crystallizer. The large influence of temperature is clear when the solubility of the carbonate decreases significantly as $Na_2CO_3 \cdot 10H_2O$ crystallizes instead of $Na_2CO_3 \cdot NaHCO_3 \cdot 2H_2O$. A much larger fraction of the carbonate can be recycled at temperatures below 25°C. Also, the influence of the degree of evaporation is noticeable.

In a corresponding manner, Fig. 5 shows how much of the bicarbonate in the treated green liquor can be recycled to the process. Here, the influence of

TABLE 3
Composition of Green Liquor Used in the Simulation of the Process for Removal of Chloride and Potassium

Component	Concentration (weight percent)
$NaHCO_3$	8.64
Na_2CO_3	10.89
NaCl	1.00
H_2O	79.47

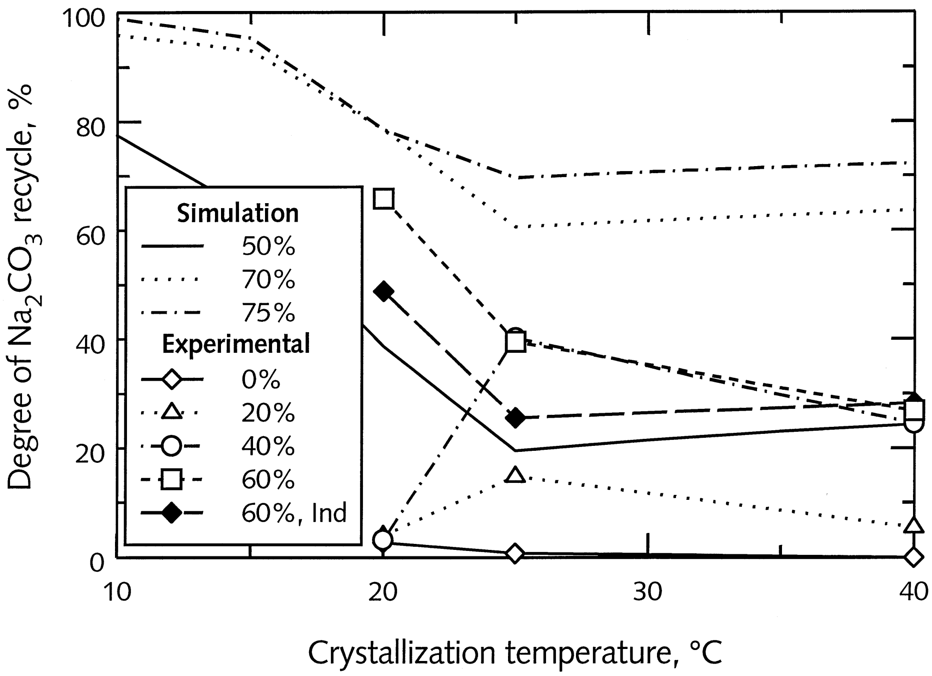

FIG. 4 Degree of recycling of Na_2CO_3 in the treated green liquor to the process as a function of the crystallization temperature and the degree of evaporation. (Industrial green liquor denoted —◆—.)

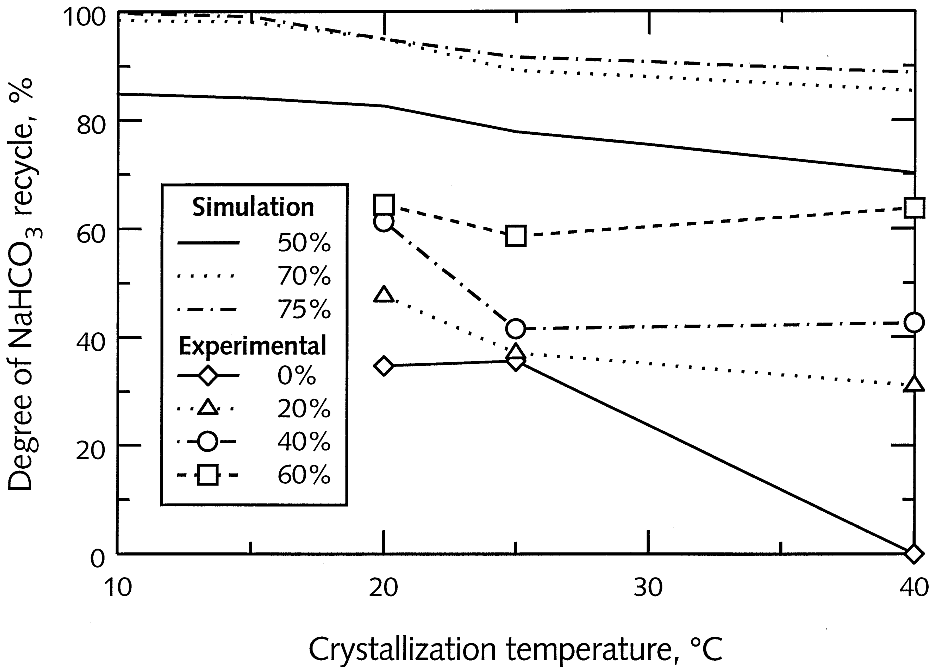

FIG. 5 Degree of recycling of $NaHCO_3$ in the treated green liquor to the process as a function of the crystallization temperature and the degree of evaporation.

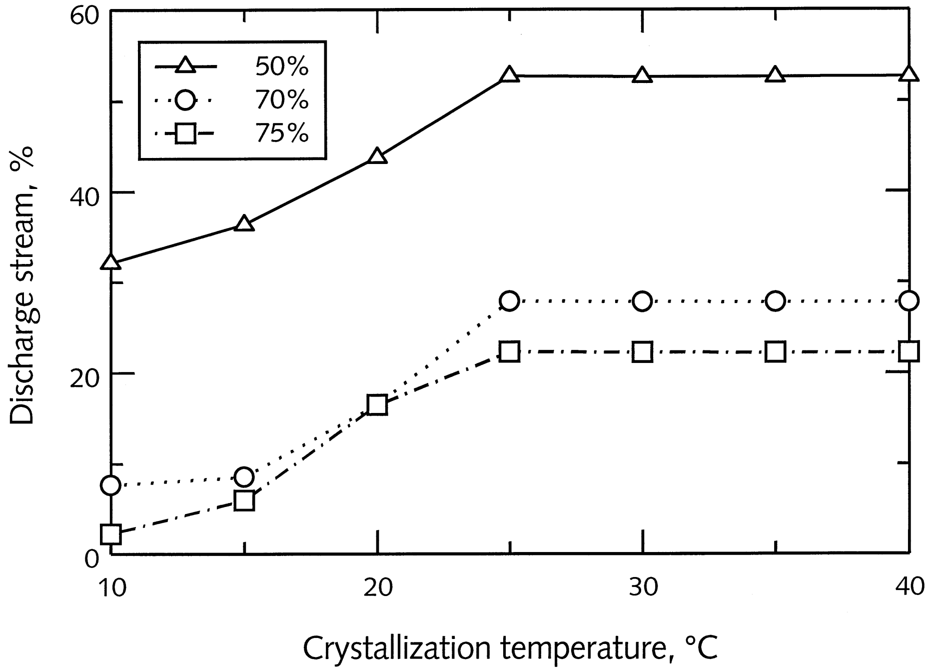

FIG. 6 Fraction of the discharge stream as a function of the crystallization temperature and the degree of evaporation.

the temperature of crystallization seems to be less important than for Na_2CO_3, which is to be expected if the solubilities of the two pure salts are compared. The influence of the degree of evaporation is, however, significant. Again, it is reiterated that the $NaHCO_3$ will crystallize as pure $NaHCO_3$ and as $Na_2CO_3 \cdot NaHCO_3 \cdot 2H_2O$ at temperatures above 25°C, and only as $NaHCO_3$ at lower temperatures.

It is also interesting to note the flow of the liquid stream that has been enriched with chloride in the removal plant and has to be removed. Figure 6 shows the amount of the discharge stream from the removal plant as a fraction of the treated green liquor. Naturally, this stream should be kept to a minimum to minimize carbonate losses, although the main criteria are the acceptable levels of potassium and chloride. As before, we notice the influence of both the temperature of crystallization and the degree of evaporation.

EXPERIMENTAL

Crystallization from Synthetic Green Liquor

An experimental investigation on a laboratory scale has been performed with the purpose of verifying the simulation results. First, precipitation of salt from synthetic green liquor by evaporation followed by cooling was investi-

TABLE 4
Composition of the Synthetic Green Liquor Used in the Experimental Investigation

Component	Concentration (weight percent)
$NaHCO_3$	8.64
Na_2CO_3	10.89
Na_2S	2.12
NaCl	0.21
KCl	0.27
H_2O	77.87

gated. The synthetic green liquor was prepared from pure chemicals. The composition of the synthetic green liquor used in the experiments is shown in Table 4. This composition represents a sulfide-lean green liquor with a relatively high content of bicarbonate.

The parameters investigated were the degree of evaporation (0, 20, 40, and 60 wt% water) and the temperature range in the crystallization step following evaporation (20, 25, and 40°C).

The experiments were performed by preparing the synthetic green liquor and then evaporating the prescribed amount of water by heating. The crystallization was then carried out in a glass container kept at constant temperature in a heated bath. The liquor was stirred using a magnetic bar stirrer during the whole time of equilibration. The residence time for all experiments was at least 48 hours to ensure that equilibrium had been attained. When the experiments were stopped, the liquor was separated from the precipitated solids by filtration.

The liquor phase from the experiments was diluted and analyzed with respect to CO_3^{2-}, HCO_3^-, and S^{2-} by titration with HCl. The solution was also analyzed for Na^+, K^+, and Cl^-. The cations were measured using ICP-ES and the chloride using IC. The solid precipitate from the experiments was dissolved in deionized water and analyzed in the same manner as the liquid phase.

Crystallization from Industrial Green Liquor

Crystallization of sodium carbonate from green liquor supplied by a Swedish kraft mill with a conventional recovery cycle has been investigated at the same conditions as the synthetic green liquor, i.e., at 0, 20, 40, and 60 wt% evaporated water from the green liquor. No desorption of H_2S was performed on the industrial green liquor. Thus, these experiments show how the suggested method would perform in a conventional recovery system. The investigated temperatures of crystallization were 20, 25, and 40°C. The treatment of the samples and the chemical analysis were handled in the same way as in the experimental investigation of the synthetic green liquor.

Results

During the experimental investigation a number of practical problems were encountered. At the crystallization temperature of 20°C, the solid precipitates had a tendency to form large aggregations, and a stronger stirring during crystallization was necessary. In general, the produced crystals were of poor quality and rather hard to filter. In addition, it was noticed that the industrial green liquor was more dilute than the synthetic green liquid, and that crystallization only occurred at 60% degree of evaporation. The results from the investigation are presented in the same way as the simulation results. Thus, the degree of recycling of Na_2CO_3 and $NaHCO_3$ in the treated green liquor is given as a function of the crystallization temperature with the degree of evaporation as a parameter.

Figure 4 shows the results from the experimental investigation for Na_2CO_3. Two of the results, at the crystallization temperature of 20°C and the degree of evaporation of 20 and 40%, seem to be erroneous, and the experiments will have to be repeated. Looking at the simulation results, an increase in the degree of Na_2CO_3 recycle would have been expected when the crystallization temperature was decreased from 25 to 20°C at 20 and 40% degree of evaporation, instead of the behavior indicated by the experimental results. The reason for this deviation is hard to explain but possibly lies in the chemical analysis. Furthermore, the same trend as for the simulation results can be observed: a weak dependence at temperatures above 25°C, with a decreasing solubility at temperatures below that. A comparison with the lines representing the simulation results shows that the results from the simulation and the experiments are of the same order of magnitude. In order to achieve the same degree of recycle of Na_2CO_3, the crystallization temperature will have to be decreased and the degree of evaporation slightly increased. The results for the industrial green liquor show how the suggested method would perform in a conventional recovery system. The experimental results indicate that 70% of the Na_2CO_3 in the synthetic green liquor can be recycled at a crystallization temperature of 20°C and 60% degree of evaporation, with a potential for further recovery at lower crystallization temperatures and/or degrees of evaporation.

Figure 5 shows the corresponding results for $NaHCO_3$. As before, there is some scatter of the points, but less important than for Na_2CO_3. A comparison with the simulation results shows that the recycle of $NaHCO_3$ according to the experimental investigation is lower than predicted by the simulations, although the same trend is observed. The industrial green liquor did not contain any bicarbonate. The experimental results show that nearly 70% of the $NaHCO_3$ in the treated green liquor can be recycled to the recovery system when operating at 20°C and 60% degree of evaporation. Again, there is room for further recovery by decreasing the crystallization temperature and increasing the evaporation.

It is important to note that a good selectivity of removal has been achieved: the chemical analyses have shown that more than 95% of both chloride and potassium in the treated liquor stays in the liquid phase at all the investigated temperatures and degrees of evaporation, both in the investigation of the synthetic and industrial green liquors. As expected, the sulfur values in the treated green liquor did not precipitate.

MILL BALANCES

It is important to calculate the flow rate of the green liquor stream needed for removal of chloride and potassium. Using the results from the simulations and the experimental investigation, the following assumptions have been made: Chloride concentration in the liquor cycle controls the degree of removal for both chloride and potassium, and this concentration is set at 5 g/L chloride in green liquor; The input of chloride to the mill is approximately 1 kg Cl/ton pulp. Thus, about 200 L of green liquor must be treated per ton of pulp.

This investigation suggests that a degree of evaporation of at least 70% and a temperature of crystallization below 20°C are needed to keep the losses of carbonate and bicarbonate to a minimum. This means that approximately 150–200 kg H_2O/ton pulp must be evaporated. At these process conditions it should be possible to keep the losses of both Na_2CO_3 and $NaHCO_3$ in the treated liquor well below 20%. In this estimation the experimental data have been somewhat extrapolated using the results from the computer simulations. It should be reiterated that only part of the green liquor needs to be treated for removal of chloride and potassium.

However, it is clear that the efficiency of the method is strongly dependent on the concentration of chloride and potassium in the green liquor; the lower the concentration that can be accepted, the larger the flow of green liquor for treatment.

DISCUSSION AND CONCLUSIONS

The removal of chloride and potassium from a gasification-based chemical recovery system has been investigated in this work. Through a simulation study and experimental work, the evaporation–crystallization process has been shown to be able to separate chloride and potassium from carbonate and bicarbonate in the green liquor. At the same time as the main part of both chloride and potassium are removed from the system, it should be possible to recycle far above 80% of the carbonate and bicarbonate in the treated green liquor to the pulping process. Experiments performed on a green liquor taken from an industry with a conventional recovery system have shown that 50% of the Na_2CO_3 in the treated green liquor may be recovered.

The simulations performed have not yet included potassium, but it may be postulated that potassium should generally stay with chloride under the investigated process conditions. This is further supported by the experimental results which, as mentioned before, have shown that more than 95% of the chloride and potassium in the treated green liquor could be removed.

Since the removal of both chloride and potassium directly depends on the concentration of these chemicals in the green liquor, the size of the removal system will depend on the acceptable concentration of potassium and chloride in the green liquor. A numerical example has shown that approximately 200 L of green liquor per ton of pulp may have to be treated for the removal of chloride and potassium to achieve a chloride concentration of 5 g/L in the green liquor. The same kind of calculations can easily be performed to take into consideration the potassium concentration. About 5–10% of the treated green liquor ends up in a Cl–K enriched stream which has to be sewered. This stream can be evaporated to precipitate the carbonate together with the potassium and chloride. A leaching step can be employed to recover the carbonate.

Despite the fact that some problems remain to be solved, the main conclusion from this work is that the suggested process can be used to remove both chloride and potassium from the recovery system, and that a thermodynamic model may be used to simulate the process.

FUTURE WORK

Further simulations should be performed where the presence of potassium and sulfide in the green liquor should be taken into account. Simulations with varying green liquor composition should also be performed. It would be particularly interesting to simulate the process for a green liquor without bicarbonate in order to match the experiments already performed on a green liquor taken from a mill with a conventional recovery system. Concerning the experimental work, some experiments need to be repeated, especially at crystallization temperatures below 20°C. Some experiments should also be performed on a synthetic green liquor without bicarbonate, the same as in the simulation work. Furthermore, it would be interesting to study the suggested process on a pilot scale. System design and process integration are factors that need to be carefully studied.

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