

Caustic Soda Production from Green Liquor Using the Green Liquor Splitting (GLS) System

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ABSTRACT

A fixed-resin bed system employing an amphoteric ion-exchange resin was used to separate green liquor from a kraft mill into sodium hydrosulphide-rich and sodium carbonate/hydroxide-rich components. Depending on the conditions used, the separation efficiencies ranged from 80 to 96% for sodium hydrosulphide, 90 to 95% for sodium carbonate and 74 to 92% for sodium hydroxide. Three possible applications for green liquor splitting are discussed. These are: the removal of excess sodium from green liquor (i.e., when alkaline extraction filtrate is recycled to the recovery system in a kraft mill), chemical cross recovery between a semichemical and a kraft mill, and recovery of excess sodium from waste chlorine dioxide generator saltcake.

INTRODUCTION

We have previously reported [1, 2] on the separation of sodium hydrosulphide from sodium hydroxide or carbonate in pulping liquors using an amphoteric ion-exchange resin bed. This separation could provide sodium hydrosulphide-rich and sodium hydrosulphide-poor (caustic-rich) components for extended delignification in kraft pulping. The caustic-rich component could also be used in place of oxidized white liquor in other mill applications, such as oxygen delignification and alkaline extraction stages. However, resin durability studies have shown that the life of conventional resin in white liquor is not sufficiently long for the process to be economically viable. Since conventional resin has an acceptable life when exposed to green liquor, we examined the splitting of green liquor into hydrosulphide-rich and carbonate-rich components in this report. System operation, optimization, resin durability and three possible applications are discussed. These applications are: the removal of excess sodium from green liquor (i.e., when alkaline extraction filtrate is recycled to the recovery system in a kraft mill), chemical cross recovery between a semichemical and a kraft mill, and recovery of excess sodium from waste chlorine dioxide generator saltcake.

EXPERIMENTAL SYSTEM

The main component of the green liquor splitter (GLS) system is a fixed-resin bed, packed with an amphoteric ion-exchange resin. The system has been fully described elsewhere [3]. The two main steps that take place during operation of this system are: sodium hydrosulphide uptake (sorption) and elution of sodium hydrosulphide by water (desorption), as shown in Figure 1.

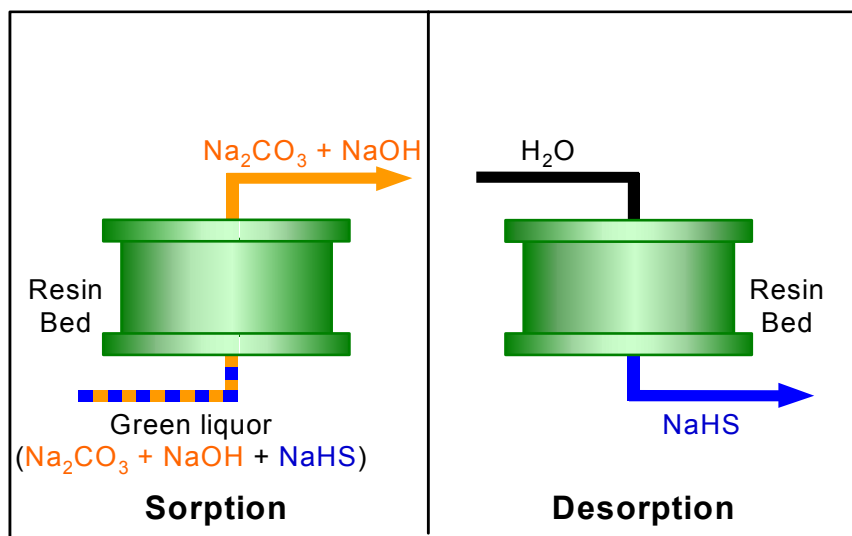


Figure 1. System operation is divided into two steps: a sorption step where NaHS is sorbed by the resin (while Na₂CO₃/NaOH are excluded) and, a desorption step where NaHS is eluted from the resin bed with water.

The system employs Recoflo[®] resin bed technology that has been in use since 1973 for water purification and waste chemical recovery [4, 5]. This technology uses fine particle-size resins, short resin bed heights (7.5 to 61 cm), high flow rates, counter-current regeneration, and short cycle times. Proposed applications of Recoflo[®] technology in the pulp and paper industry include precipitator dust purification (PDP), and generator acid purification (GAP) [3, 6]. The commercial system is a skid-mounted unit that has a fixed-resin bed as the main component. Scale up is accomplished by increasing the diameter of the bed; the largest unit in industrial operation has a diameter of 2.74 m.

In the pilot unit, a resin bed measuring 5 cm in diameter and 61 cm in height was used. In a first step, the kraft mill green liquor ($\text{Na}_2\text{S} + \text{Na}_2\text{CO}_3 + \text{NaOH}$) was fed to the bottom of the resin bed. Given the high pH of this solution, the Na_2S component is in the hydrolyzed form ($\text{NaHS} + \text{NaOH}$). In this step, a sodium hydrosulphide-depleted (sodium carbonate-rich) solution was collected. In a second step, water was fed to the top of the resin bed and a sodium hydrosulphide-rich eluate was collected. The cycle was repeated several times, and samples of the sodium hydrosulphide-rich and sodium carbonate-rich liquors were collected and analyzed once the system had reached steady-state operation. The cycle time is defined as the total time required to complete the sorption and desorption steps as well as the washing steps in between. Cycle time is increased if the resin bed is fouled. Since each step is operated at constant pressure, fouling of the resin bed leads to a reduction in flow and hence, an increase in cycle time.

Analytical Procedures

In North America standard kraft pulping terms [7] are defined as follows: Effective Alkali (EA) is $\text{NaOH} + \frac{1}{2} \text{Na}_2\text{S}$; Active Alkali (AA) is $\text{NaOH} + \text{Na}_2\text{S}$; Total Titratable Alkali (TTA) is $\text{NaOH} + \text{Na}_2\text{S} + \text{Na}_2\text{CO}_3$, all expressed as g $\text{Na}_2\text{O/L}$.

The mill green liquor and the samples taken during the pilot plant experiments were analyzed at room temperature as follows: sodium hydrosulphide concentration was measured by potentiometric titration with mercuric chloride, using a sulphide-selective electrode [8]; the precision of the potentiometric titration was $\pm 1.5\%$. The EA and TTA were determined by a conductometric titration using hydrochloric acid as the titrant [9]; the precision of the conductometric titration was $\pm 2.5\%$. AA was calculated based on the EA and sodium sulphide content; carbonate and sulphate, sulphite, thiosulphate and chloride were measured using Ion Chromatography (IC); sodium and potassium were measured by Atomic Absorption spectroscopy. Multivalent metal ions were measured using Inductively Coupled Plasma (ICP) spectroscopy. The precision of the Atomic Absorption spectroscopy, IC and ICP methods was $\pm 5\%$.

RESULTS AND DISCUSSION

a) Separation of sodium carbonate from a mill green liquor

The composition range for a kraft mill green liquor as supplied by the mill is given in Table I. As-received mill clarified green liquor was allowed to settle in a holding tank at room temperature prior to being processed through a 5- μm cartridge filter and fed to the bottom of the resin bed. Table II shows the composition of a mill green liquor including the multivalent metals. Although the cartridge filter prevented insoluble metal compounds from entering the resin bed, the soluble multivalent metal compounds caused an increase in cycle time after about two weeks of continuous operation. An acid wash step re-established the cycle time.

Depending on the application, the GLS system can be operated in such a way as to maximize sodium hydrosulphide removal or sodium carbonate/hydroxide recovery. The results of four separate runs, designed to meet different objectives are shown in Table III. The amount of all components are expressed as the designated chemical. Although the feed bed volume is different in each of the four runs, each run has the same bed volume for the feed and products. In Run A, with the shortest cycle time, a sodium carbonate product composed of 99.3 g/L Na_2CO_3 , 31.4 g/L NaOH and 4.1 g/L NaHS was obtained. The concentration of NaHS in the carbonate product from Run C, which had a longer cycle time (compared to Runs A and B), was only 1.2 g/L. Run D was designed to have the highest recovery rate for sodium carbonate/hydroxide but, as a result, it produced the lowest sodium hydrosulphide removal rate. As shown in Table III, between 80% and 96% of the sodium hydrosulphide was removed from the green liquor and between 90% and 95% of the sodium carbonate was recovered. Sodium hydroxide recovery was between 74% and 92%. A higher feed flow rate or a shorter cycle time (at the same feed bed volume) means that a smaller system is required to achieve the separation, resulting in lower capital and operating costs. A shorter cycle time, however, results in a higher sodium hydrosulphide residue in the sodium carbonate/sodium hydroxide product.

Table I. The composition range of a kraft mill green liquors based on mill data.
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Green liquor	Concentration range
EA, g/L Na ₂ O	28.8-35.2
AA, g/L Na ₂ O	43.3-52.9
TTA, g/L Na ₂ O	109-119
NaHS, g/L as NaHS	26.2-32.0
Total NaOH, g/L as NaOH	37.2-45.4
Na ₂ CO ₃ , g/L as Na ₂ CO ₃	112.3-113.0
Suspended solids, ppm	100-300

Table II. Composition of an as-received kraft mill green liquor including multivalent metals

EA, g/L Na ₂ O	AA, g/L Na ₂ O	TTA, g/L Na ₂ O	Na, g/L	K, g/L	S, g/L	Cl, g/L	CO ₃ ⁼ , g/L	S ₂ O ₃ ⁼ , g/L	SO ₃ ⁼ , g/L
30.1	43.4	108.5	76.4	7.0	16.6	0.55	66.9	2.55	1.52
Al, mg/L	Ba, mg/L	Ca, mg/L	Cu, mg/L	Fe, mg/L	Mg, mg/L	Mn, mg/L	Si, mg/L	Zn, mg/L	Sus. Solids, mg/L
51.9	1.2	9.3	~0.2	7.0	1.2	4.6	269	~0.3	25

Table III. Comparison of chemical separation efficiencies for four trials employing different cycle times

Run	Cycle time, Minute	Na ₂ CO ₃ , g/L	NaOH, g/L	NaHS, g/L	Na ₂ CO ₃ Recovery, %	NaOH Recovery, %	NaHS Removal, %
(A) Green liquor feed Na ₂ CO ₃ product NaHS product	2.8	109.4 99.3 7.9	42.7 31.4 7.4	32.2 4.1 27.3	90.8	73.5	87.3
(B) Green liquor feed Na ₂ CO ₃ product NaHS product	4.7	112.4 101.1 8.1	40.8 32.7 4.0	30.2 2.6 28.5	90.0	80.1	91.4
(C) Green liquor feed Na ₂ CO ₃ product NaHS product	7.9	110.9 103.8 6.2	42.0 34.7 4.0	31.8 1.2 29.9	93.6	82.6	96.2
(D) Green liquor feed Na ₂ CO ₃ product NaHS product	9.3	114.0 108.0 4.5	44.4 40.8 3.5	32.7 6.4 26.8	94.8	91.9	80.4

b) Resin Durability

Static resin durability studies:

Static durability tests were performed in plastic bottles containing some resins, and filled with green liquor solutions. The bottles were kept under nitrogen to prevent sodium hydrosulphide oxidation. Resin durability was tested at four different temperatures, to determine the upper temperature limit for economic operation of the GLS under mill conditions. Green liquor cooling is required because mill green liquor has a temperature of about 80 to 90 °C, while the internal parts of a standard ion-exchange system begin to degrade at temperatures above 70°C. Apart from room temperature, we evaluated 35 °C to examine the possibility of carbonate precipitation because a metastable range exists between 20 to 35 °C [10]. It is also above this temperature that pirssonite ($\text{Na}_2\text{CO}_3 \cdot \text{CaCO}_3 \cdot 2\text{H}_2\text{O}$) can form in green liquor [11]. During the cooling of green liquor pirssonite can precipitate on the internal surfaces of heat exchangers. Although we did not observe any deposits in the as-received mill green liquor at temperatures between 15 to 20 °C, it is possible that pirssonite may cause scaling over extended operating periods. This scaling tendency depends on the concentrations of TTA in the green liquor, the liquor temperature, calcium concentration, and the efficiency of mixing in the dissolving tank. To prevent pirssonite deposition, it is recommended that the TTA of green liquor be below 90% of the TTA at which pirssonite begins to precipitate [11]. This pirssonite saturation limit will vary from mill to mill because of differences in the sodium salt concentrations in the green liquor. For example, for a particular mill operating at a TTA of 125 g/L Na_2O , the TTA of saturation was calculated to be 130 g/L Na_2O . This indicated that the mill should operate at a TTA lower than 117 g/L Na_2O to prevent scaling [11].

Chemical degradation of the resin depends on the nature of the functional groups, the chemical species present in solution and the operating temperature. The chemical integrity of the resin can be monitored by measuring the total ion-exchange capacity. The total ion-exchange capacity is a measure of the number of ion-exchange groups on the resin that can exchange ions with the surrounding solution.

The green liquor solution contains no oxidants capable of de-crosslinking the resin, but it contains NaHS, which is a powerful nucleophilic agent under alkaline conditions. The resin was exposed continuously to a mill green liquor at room temperature, 35 °C, 60 °C and 90 °C. Figure 2 presents the percentage of the initial total ion-exchange capacity as a function of exposure time. After 360 days, the total ion-exchange capacity dropped by about 15% at room temperature and by 25% at 35 °C. As will be seen in the subsequent section, this decline in the total ion-exchange capacity is not significant. The results for 60 °C and 90 °C (70% and 80% decline after 360 days exposure) indicate that the resin is not durable at higher temperatures. It must be noted here that these results represent a worst-case scenario since, during normal (dynamic) operation, the resin is washed with water after being exposed to the green liquor for about two to three minutes.

Dynamic resin durability studies:

A dynamic resin durability test was conducted to compare the results from static resin durability tests with the performance of the resin under actual operating conditions. The green liquor feed was kept at 60 °C, but the temperature of the solution in the resin bed was about 55 °C. The pilot unit was operated around the clock for 90 days, during which the total anion-exchange capacity of the resin was measured several times. The anion-exchange capacity measured after 90 days showed a loss of 27%, 42% and 48% for the resin at the top, middle and bottom (feed point) of the resin bed, respectively. This is to be expected, since the resin at the bottom of the resin bed is exposed to a higher concentration of NaHS and hence retains a larger fraction of this compound as compared to the rest of the bed. As the green liquor solution moves upward in the resin bed, the remaining sodium hydrosulphide is retained by the resin; by the time the solution reaches the top of the resin bed it is mostly depleted of sodium hydrosulphide. This suggests that the resin at the bottom can be replaced periodically to extend the life of the total resin bed.

The results for the anion-exchange capacity in the middle zone are shown in Figure 2. However, despite the decline in ion-exchange capacity by about 42%, the sodium hydrosulphide removal efficiency remained high at about 98% (Table IV). This indicates that the resin has excess ion-exchange groups and is, therefore, able to maintain performance despite the loss of some of these groups. The degree of resin utilization was found to be only 18% at the start of the experiments and increased to 25% after three months of exposure. Given a capacity loss of 15% per year at room temperature (in static resin durability test), it would take about 3 years (on a linear basis) for the resin capacity to drop by 42%. Prior work with white liquor has shown that the resin bed performance begins to suffer when the resin capacity drops by 50% from the initial value.

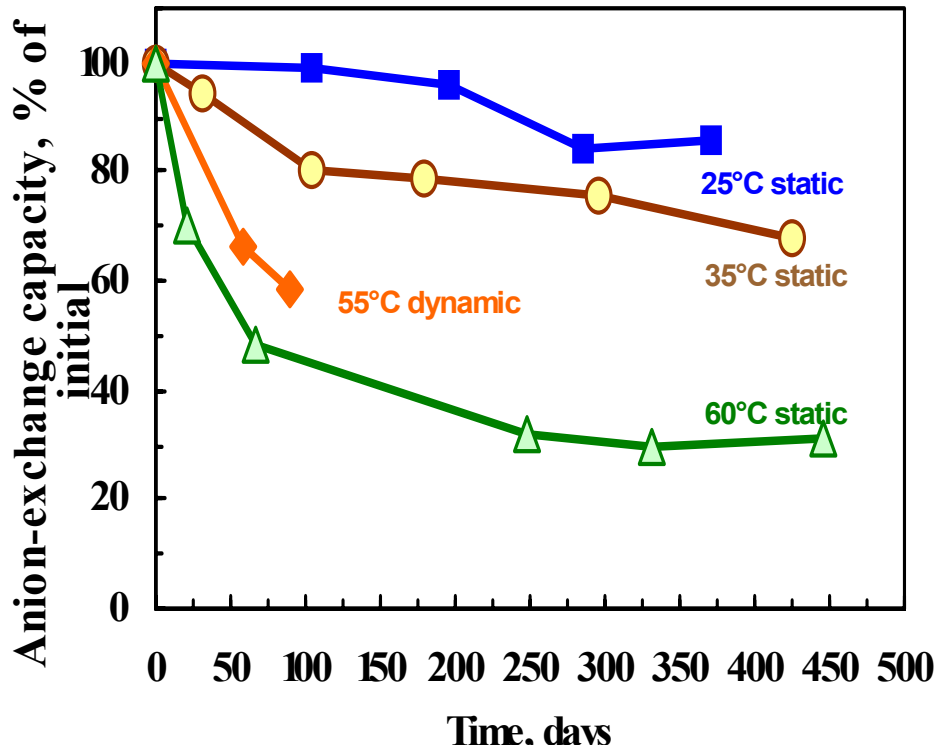


Figure 2. Comparison of static and dynamic resin durability tests in green liquor

	Relative Bed Volume	Na ₂ CO ₃ , g/L	NaOH, g/L	NaHS, g/L
Feed solution	1	118.4	45.1	31.6
Na ₂ CO ₃ -rich product	1	97.1	36.2	0.59
NaHS-rich product	1	15.6	8.8	30.5
% Removal				98
% Recovery		82	81	

c) Applications for green liquor splitting:

Three applications have been identified for green liquor splitting:

1. Removal of excess sodium hydroxide from green liquor

In a kraft mill, an occasion might arise in which the pulping liquor has excess sodium. For example, this could result from the recycle of alkaline bleaching filtrate to a mill with a tight liquor cycle. Ideally, a portion of white liquor should be split to recover the excess sodium in the form of caustic soda. However, because of resin durability problems in white liquor, we propose that a portion of green liquor be split into sodium carbonate/hydroxide- and sodium hydrosulphide-

rich components. The sodium carbonate/hydroxide-rich portion can then be causticized in a separate small causticizing system to provide caustic soda for other applications at the mill (Figure 3). The NaHS solution can either be sent to the weak black liquor or added to the green or white liquor, depending on the mill water balance concerns. In this application, the GLS operation was optimized to produce a sodium carbonate/hydroxide product with a minimum amount of sodium hydrosulphide (see Table III, Run C). This is because sodium hydrosulphide can react and consume hydrogen peroxide in the bleaching extraction stages.

For a green liquor flow of 1.4 L/s or 22 USgpm (corresponding to an excess of sodium caused by filtrate recycle), the equipment cost for a GLS and a small causticizing system (comprising one slaker, three causticizer tanks, one pressure filter and one lime mud mix tank) is estimated at \$1.2 M. The savings in caustic soda recovered in this case (about 12 t/d) would be \$1.47M/year. The operating costs are estimated at about \$0.3 M/year.

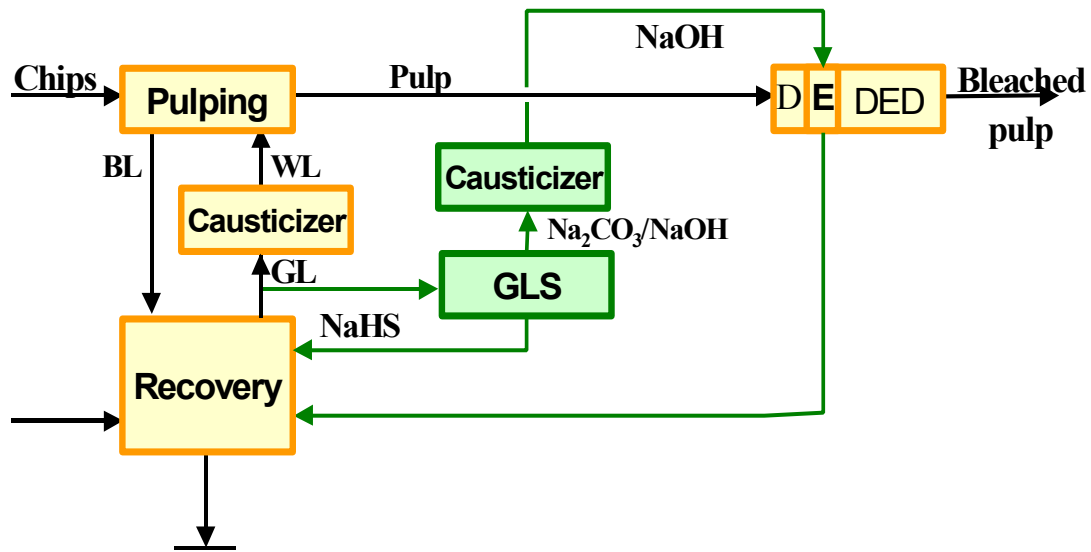


Figure 3. Green liquor splitter (GLS) for caustic soda production

2. Chemical cross recovery between a semichemical mill and a kraft mill

In this application, we examine green liquor splitting with reference to chemical cross-recovery between kraft and semichemical mills. Some semichemical mills that do not have a recovery system rely on chemical cross recovery with a nearby large kraft mill. The spent liquor from pulping at the semichemical mill could provide make-up chemicals for the kraft mill and also produce extra steam because of the organic content. However, at some kraft mills, the input sodium from the spent liquor of the semichemical mill may be in excess of the make-up requirements. In this case, a GLS system can be used to recover the excess sodium as sodium carbonate/hydroxide and provide cooking liquor for a soda mill. We considered the case of a member company NSSC mill that uses sodium sulphite as cooking liquor. The mill does not have a recovery system, instead selling the spent liquor for animal feed preparation. However, this market has disappeared, and the mill had to find an alternative way of dealing with the spent liquor. One option was to cook with green liquor from a large kraft mill owned by the same company, and send the spent liquor back to the kraft mill. The spent liquor would be converted to sodium carbonate and sodium sulphide in the kraft recovery boiler, and thus become part of the green liquor flow produced at the kraft mill. A mill trial was carried out using green liquor for cooking, but the level of Total Reduced Sulphur (TRS) produced was not acceptable. The mill is presently doing cross recovery with the kraft mill, but the kraft mill is disposing of a portion of the excess green liquor (to the effluent treatment system) because of high inventories.

To address the TRS issue, three options were considered: installing an incinerator at the semichemical mill to collect and destroy the TRS, installing an oxidizer to convert the Na_2S in green liquor to $\text{Na}_2\text{S}_2\text{O}_3$ or Na_2SO_4 , and removing sodium hydrosulphide from green liquor using a GLS system and cooking with the separated sodium carbonate solution. In this case, the NSSC process would be replaced by the soda process. The mill obtained estimates for an incinerator, but the cost was found to be too high. Moreover, the degree of conversion of Na_2S to $\text{Na}_2\text{S}_2\text{O}_3$ in a conventional oxidizer is not 100%, while the complete conversion to Na_2SO_4 is expensive because of the high-grade metallurgy required [12]. The estimated equipment cost for a GLS system to process about 50 USgpm of green liquor (as required by the semichemical mill) is about \$1.4M. The chemical savings would be about \$2M for sodium carbonate for the semichemical mill and about \$0.5M for extra steam generation in the kraft mill. The operating costs are about \$0.3M/year.

The challenge in this application was to reduce the sodium hydrosulphide content of green liquor to sufficiently low levels to meet TRS compliance levels (10 ppm for kraft mills). The operation of the GLS unit was, therefore, optimized to reduce the concentration of sodium hydrosulphide (see Table III, Run C). The resulting sodium carbonate solution, containing low levels of residual sodium hydrosulphide, can potentially be used for pulping (Figure 4). This, however, would require the verification of pulp properties, yield and the TRS levels that may be produced due to the residual NaHS content of the sodium carbonate liquor. The residual sodium hydrosulphide can be oxidized to sodium sulphate by the addition of a small amount of hydrogen peroxide. This would cost about \$0.13M/year.

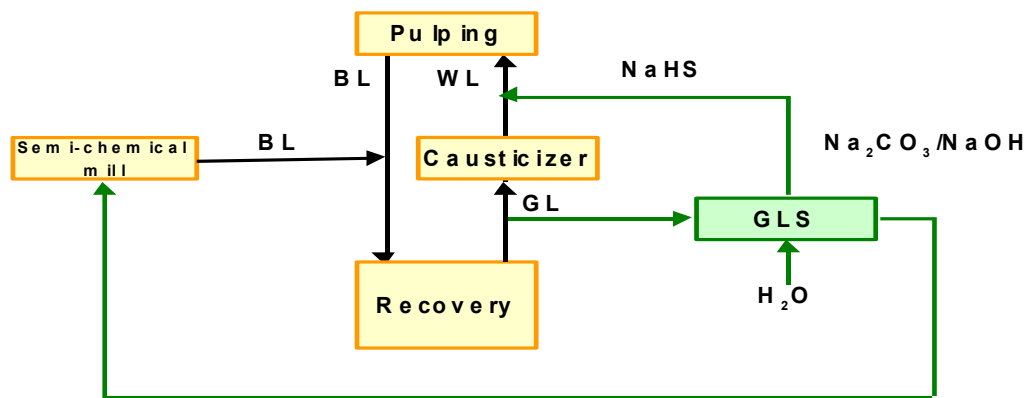


Figure 4. GLS system for chemical cross recovery

3. Recovery of sodium hydroxide from waste chlorine dioxide generator saltcake

With the implementation of ECF bleaching and more closed kraft operation, the requirement for Na-S make-up from the generator saltcake has decreased steadily. Several mills have expressed interest in knowing if it would be possible to recover the sodium value of waste generator saltcake, without upsetting the Na-S balance. To address this issue, we are proposing the process illustrated in Figure 5. In this process, the neutral waste saltcake is added to black liquor. This will be converted to sodium sulphide in the recovery boiler. The resulting green liquor will have a surplus of Na and S in the form of Na_2S . Given the high pH of green liquor, the Na_2S component would be in the hydrolyzed form ($\text{NaHS} + \text{NaOH}$). If a portion of green liquor were to be split using a GLS system, half of the excess sodium and all of the excess sulphur would be separated as NaHS. The other half of the excess sodium would be converted to NaOH. In this way, half of the sodium value in the saltcake will be recovered as caustic soda, which could replace part of the purchased

caustic soda used as make-up. For 30 t/d waste saltcake production, the recovered caustic soda (from 81 USgpm of green liquor) is about 5.3 t/d. The separated NaHS stream can be sold as Na/S make up to other mills, or it can be used in the bleach plant scrubber. In this application, the GLS operation was optimized to reduce the losses of sodium carbonate/sodium hydroxide solution (see Table III, Run D). The estimated equipment cost for a GLS system to process 81 USgpm of green liquor is about \$1.9M. The savings are estimated at \$0.65M/y, while the operating costs are about \$0.4M/y. For this application to be economically viable, a mill would have to be in a position to take credit from the use of the NaHS stream.

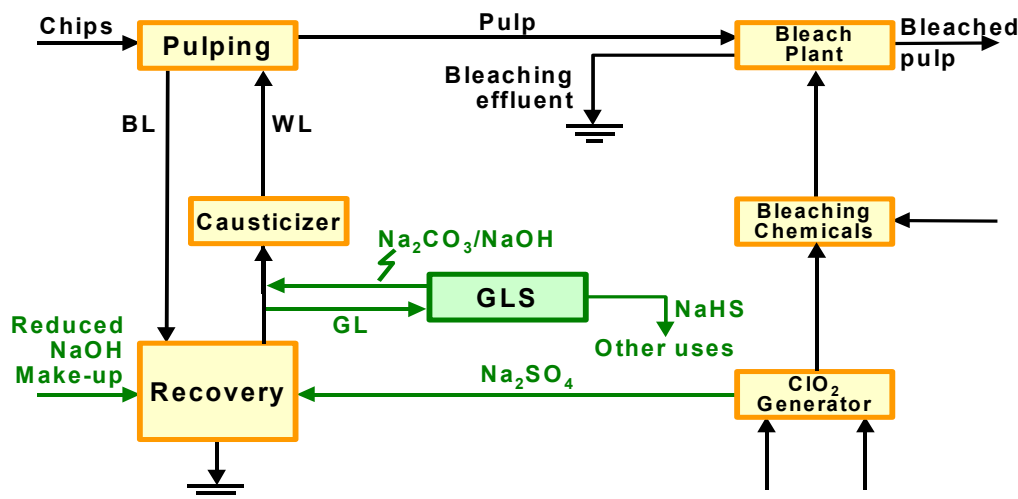


Figure 5. GLS for recovering sodium value from waste generator saltcake

CONCLUSIONS

1. Using a fixed resin bed system and employing an amphoteric ion-exchange resin, sodium hydrosulphide was removed from a mill green liquor. Depending on the conditions used, the separation efficiencies ranged from 80 to 96% for sodium hydrosulphide, 91 to 95% for sodium carbonate and 74 to 92% for sodium hydroxide.
2. Given the low degree of the utilization of the ion-exchange capacity, a resin life of up to three years can be expected if green liquor is cooled to room temperature.
3. Three applications have been identified which will benefit from green liquor splitting. These are: the removal of excess sodium (as sodium hydroxide) from a kraft mill practicing alkaline bleaching filtrate recycle, chemical cross recovery between a kraft and a semichemical mill by providing sodium carbonate for pulping to the semichemical mill, and extracting caustic soda from the waste generator saltcake at a kraft mill.

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