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SIMULTANEOUS CONTROL OF SULFUR AND NON-PROCESS ELEMENTS

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ABSTRACT

A new process concept for removal of potassium, chlorine and sulphur, and simultaneous recovery of sodium was developed. The concept comprises simplified stripping of hydrogen sulphide from green liquor (GLSS), purging of sulphur in elemental form by a liquid redox process, and crystallization of ESP dust together with stripped green liquor. The process allows for simultaneous removal of the mentioned elements with smaller losses of sodium than in earlier ESP dust based processes. The balances of the elements can be controlled independently of each other. The process has been tested in a pilot plant.

Keywords: chlorine, electrostatic precipitator dust, potassium, removal, sulphur.

INTRODUCTION

Potassium and chlorine are detrimental in terms of corrosion of super heaters in the recovery boiler of a pulp mill. Most mills also suffer from surplus of sulphur, which in tall oil recovering mills originates in particular from the use of sulphuric acid, and also from intake of chlorine dioxide generator saltcake. Tightening mill effluent discharge also enhances the problem. In order to manage the sulphur surplus large amounts of recovery boiler precipitator catch and generator saltcake are sewered, resulting in substantial loss of valuable sodium. Sewering of the salts also raises environmental concerns, in particular in inland mills.

Processes based on treatment of recovery boiler electrostatic precipitator catch by crystallization, leaching, cooling crystallization and ion exchange are commercially available [1]. These processes reduce the loss of sodium. Although functional in themselves, they all have the drawback of recovering also sulphur in addition to recovering valuable sodium, thereby increasing the sulphur surplus that frequently was a problem already before. Also, sewering of generator saltcake remains to be a problem. The aim of the development of the new process concept was to find a way to control the balances of all the mentioned four elements, at the same time minimizing sodium loss and reducing environmental impact.

THE BALANCING ISSUE

It is of great importance to consider all the concerned elements, sulphur, potassium, chlorine and sodium, together. Usually, if attention is paid to only one or two of them, problems arise with one of the others. For example, with the standard procedure of sewering ESP dust and generator saltcake, potassium and chlorine are prevented from being built up, and also sulphur can be handled, but substantial sodium values are lost. This way of operation is therefore costly, and also environmentally improper. Introducing a potassium and chlorine removal process improves sodium recovery and environmental performance, but it should not be a surprise if the sulphur balance is upset, since also this element is recovered.

As another example, if a mill sewers ESP dust mainly for control of the sulphur balance, now stops this sewering and replaces it with an internal sulphuric acid plant, sulphur can be controlled and sodium will be saved, but a potassium and chlorine problem quickly arises. These examples show the importance of regarding all the four elements simultaneously.

THE NEW PROCESS CONCEPT

A new process concept for management of sulphur, potassium, chlorine and sodium is presented in **Figure 1**. There are three main process steps: i) simplified stripping of hydrogen sulphide from green liquor (GLSS), ii) oxidizing the hydrogen sulphide to elemental sulphur by a liquid redox process, and iii) evaporative crystallization of stripped green liquor and ESP dust together.

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Stripping of hydrogen sulphide from green liquor can be carried out at atmospheric pressure. Flue gas is introduced in a packed tower with green liquor being circulated a number of times. The following principal reactions are involved:

$$CO_2 + 2OH^- \rightarrow CO_3^{2-} + H_2O \quad (1)$$

$$S^{2-} + H_2O \leftrightarrow HS^- + OH^- \quad (2)$$

$$CO_3^{2-} + CO_2 + H_2O \rightarrow 2HCO_3^- \quad (3)$$

$$HCO_3^- + HS^- \rightarrow H_2S + CO_3^{2-} \quad (4)$$

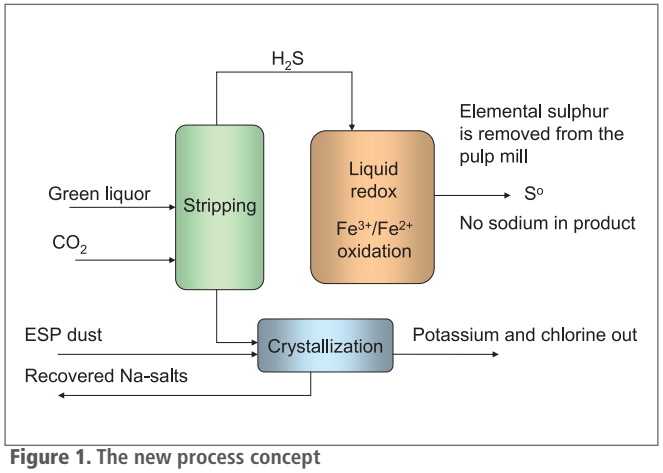

Figure 1. The new process concept

At first, hydroxide is neutralized by carbon dioxide, and carbonate is formed. Further reaction with carbon dioxide produces hydrogen carbonate, which expels sulphide as hydrogen sulphide.

The exhaust gas contains hydrogen sulphide, carbon dioxide and about 80 % nitrogen. The stripper can be operated continuously, batch-wise or semi-continuously. Economic considerations indicate that it is more profitable to use flue gas than pure carbon dioxide.

The gas is taken to a liquid redox process, which is a well-established commercially available technique. The hydrogen sulphide is dissolved in the slightly alkaline scrubbing liquid, and is oxidized with air oxygen to elemental sulphur. Chelated iron ion is used as catalyst. The H_2S undergoes the following over-all reaction:

$$H_2S + 2Fe^{3+} \rightarrow 2H^+ + S^o + 2Fe^{2+} \quad (5)$$

The ferric iron is regenerated by air:

$$2Fe^{2+} + 1/2O_2 + H_2O \rightarrow 2Fe^{3+} + 2OH^- \quad (6)$$

Since the product sulphur is in the form of elemental sulphur, it can be easily removed from the pulp mill without associated losses of sodium. It is also safely transportable. Obviously, it needs to be disposed of in some way, but the primary concern is to get it out from the pulp mill. It can be used for various purposes, like producing sulphuric acid, on site or in a separate plant, in agriculture or in bisulphite production.

It is also possible to convert hydrogen sulphide directly into sulphuric acid. However, since the H_2S concentration in the gas is relatively low in this process, only 1 % – 2 %, as the gas consists of mostly carbon dioxide and nitrogen, a sulphuric acid process would be more costly than a liquid redox process.

There are several potential uses of the stripped green liquor, but the primary one is potassium and chlorine removal. Significant advantages can be achieved by crystallizing it together with ESP dust.

There is a prominent advantage in combining stripped green liquor with ESP dust in crystallization. The solubilities of the involved salts lead to a higher achievable concentration of potassium relative to sodium in the crystallization mother liquor, i.e., the removal stream expelled from the pulp mill [2]. In other words, the sodium loss per removed amount of potassium is smaller. This can be expressed as "sodium loss ratio", Na/K. The more favourable solubility conditions are a consequence of the high carbonate content in the liquor. As such, the process has been called HCC or High Carbonate Crystallization.

When ESP dust alone is dissolved in water, the solution has high sulphate content. As water is evaporated, sodium sulphate and burkeite ($Na_2CO_3 \cdot 2Na_2SO_4$) crystallize, and potassium and chlorine are concentrated in the solution. However, concentrating is possible only up to a limit beyond which glaserite, $K_3Na(SO_4)_2$, precipitates [3]. As a result, potassium will be contained in the solid phase, which is returned to the pulp mill, limiting the efficiency of the removal process [4]. The maximal achievable potassium concentration (Nordic ESP dusts) is in the order of 30 - 35 g/kg, sodium concentration being around 110 g/kg. The sodium loss ratio is therefore at best in the order 3 – 3.5 (weight/weight).

If the stripped green liquor - in which sulphide and hydroxide are replaced or converted to carbonate and bicarbonate -, is used as a solvent for the ESP dust, the carbonate content of the solution is high. In this case, the primary precipitating phase is burkeite. Since burkeite precipitation consumes sulphate, the solution contains less sulphate than in the case of using water to dissolve ESP dust. The consequence of this is that the tendency for glaserite to form is reduced, increasing the solubility of potassium, and allowing potassium to be concentrated to a higher level. In addition, the balance of ionic charges requires that as the potassium concentration increases, the sodium concentration must decrease. This further decreases the Na/K ratio in the solution. Solubility tests and pilot plant runs show a potassium content of around 80 g/kg and a sodium content of around 100 g/kg, giving a sodium loss ratio of

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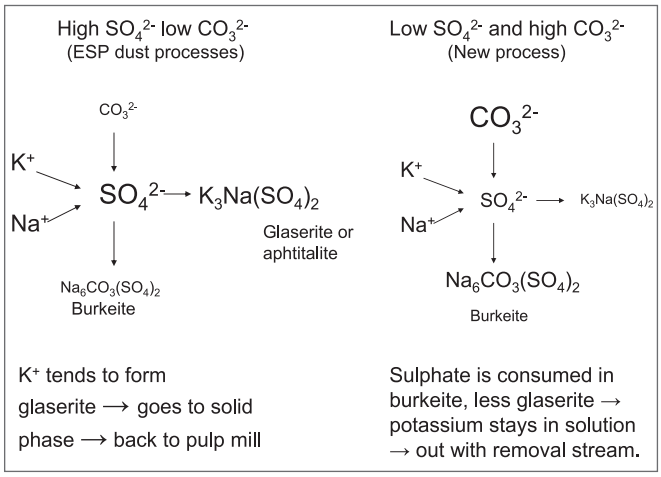

Figure 2. Formation of glaserite in low and high carbonate systems

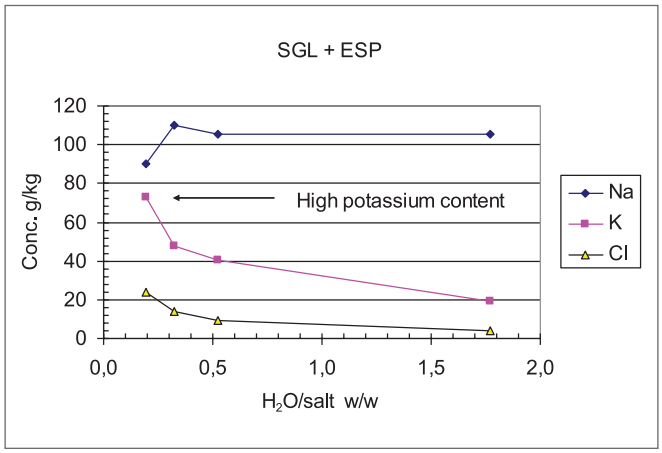

Figure 4. Change of concentrations when ESP was crystallized together with green liquor

around 1.25. Therefore, the amount of lost sodium per removed potassium with the removal stream is considerably reduced with the new process. The situation is illustrated in **Figure 2**.

Figure 3 shows the change in sodium, potassium and chlorine concentrations when ESP dust was dissolved in water, and the solution was evaporated, in this case almost to dryness. The x-axis shows the ratio of remaining water to initially added salt (ESP dust). Evaporation proceeds from right to left.

The figure shows how Na, K and Cl at first are concentrated in the solution, until Na and K begin to precipitate. The Na concentration ceases to rise at about 105 – 115 g/kg, because of crystallization of sodium sulphate and burkeite. Cl continues to be concentrated to high levels relative to the initial concentration, because no chloride containing phases precipitate until evaporation is brought very far. In this experiment there was no evident precipitation, even though there was only about 0.05 kg of water left per kg of initially added dust. The initial Cl-content in the dust was 15 g/kg. It must be emphasized that the chlorine content in ESP dusts from Nordic mills is very low. With dusts from mills with higher Cl content precipitation may occur.

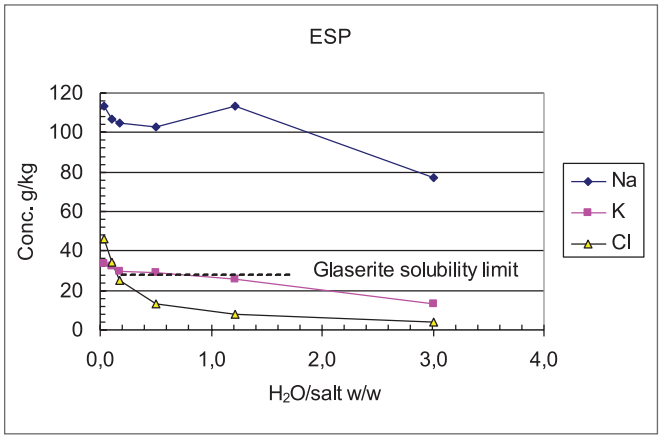

Figure 3. Change of concentrations when ESP alone was crystallized

The potassium concentration ceases to rise at roughly 30 – 35 g/kg, because the solubility limit of glaserite is reached. If solubility would not be restricted by glaserite precipitation, the concentration would rise steeply, just like the chlorine concentration when the water content approaches zero.

Figure 3 is to be compared to the case where - instead of water - stripped green liquor is used to dissolve ESP dust prior to crystallization, which is shown in **Figure 4**. The solution has a much higher carbonate concentration compared to that with water shown in figure 3. In this experiment one part of ESP dust was mixed with four parts of stripped green liquor (w/w). The amount of salts originating from each material was about the same. The solution was evaporated to low water content.

Figure 4 shows how potassium can be maintained in the solution, and concentrated to a higher level, up to about 75 g/kg. At the end of the evaporation, the Na concentration decreases, while K concentration increases to the point their concentrations are close to each other. The sodium loss ratio Na/K in the solution is, therefore, considerably lower, that is more favourable than in the previous case. This means that much less Na will be lost when the solution is purged.

The results in Figures 3 and 4 are applicable to an ash leaching process, as well as a crystallization process. In practice, both crystallization and leaching processes operate at a constant water/salt ratio with continuous feed. The process, therefore, is constantly at a fixed point on the x-axis. A typical range for crystallization is 0,5 – 0,6 and for leaching 0,8 – 0,9.

PILOT PLANT TESTS

Stripping and liquid redox

The whole process concept was investigated by pilot plant tests. Metso's stripping and liquid redox pilot comprises a stripping tower and two scrubbing towers, in which the liquid redox reactions take

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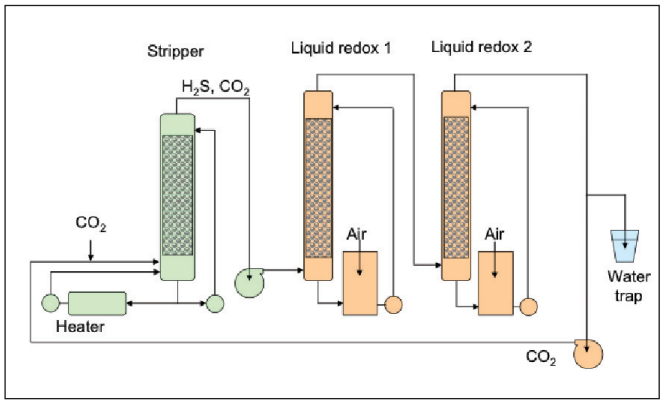

Figure 5. Schematic view of the pilot plant

place. **Figure 5** shows a schematic view. The packing height is 1.6 m in each tower. A volume of about 30 litres can be stripped at a time. The primary method used here was batch wise stripping, but a semi-continuous mode has also been successfully tested, and thus continuous operation is also, in principle, possible. **Figure 6** shows the pilot plant during a test run.

Tests runs were performed with green liquor from two mills, one Nordic and one middle European. In both mills the chloride content in liquor and ESP dust was low, but in the middle European mill the potassium level was high.

Figure 6. Test run with pilot stripping and liquid redox plant

Figure 7. Elemental sulphur obtained in the liquid redox process

Table 1. Analyses of mill materials

Component	Green liquor g/kg		ESP dust g/kg		
	Nordic	European	Nordic	European	Finnish avr. 2004 [5]
Na	77.8	73.1	309	257	289
K	11.4	20.9	59.4	94.9	46
Cl	1.69	0.93	14.0	15.1	6.4
S^{2-}	21.4	19.5	-	-	

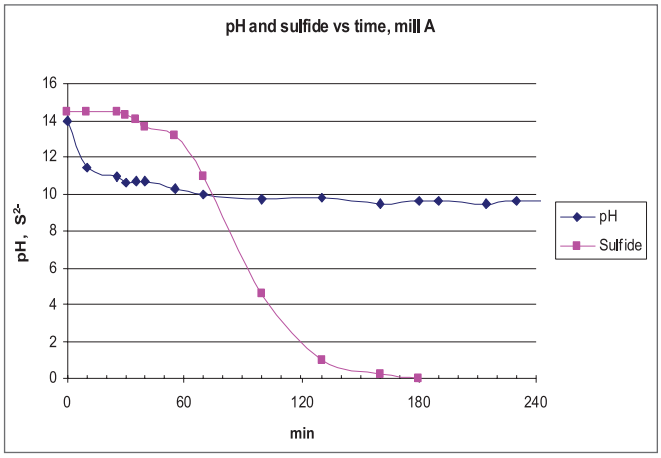

Figure 8. Sulphide and pH at a stripping test

The analyses of green liquor and ESP dust are shown in Table 1. It is important to note that liquor and ESP dust in a pulp mill always is a pair: certain potassium content in the liquor cycle fixes the content in the ESP dust rather precisely. Therefore it is necessary to use dust and liquor from the same mill.

Carbon dioxide from a container was used since there was no recovery boiler flue gas available at the test site. The results of one test are shown in **Figure 8.** Due to restricted space stripping results only for the Nordic mill are presented here.

The initial drop of pH is due to reaction (1). A further drop of pH is buffered by reaction (3), but eventually enough HCO_3^- is formed to expel H_2S. The sulphide content in the solution is essentially eliminated. The reaction time is long due to the low packing height of the small equipment. This causes the solution to stay most of the time in the liquid space at the bottom of the stripper. In a full scale facility the packing layer is considerably higher, and the time required can be shortened.

The liquid redox process was conducted with a solution of $FeCl_3$ and EDTA as chelating agent. Figure 7 shows the sulphur product. The reaction in the liquid redox process takes place rapidly, it is a fairly easy process to perform, and is insensitive to fluctuations in the H_2S content of the gas. Although the pilot plant performed in a packed tower, the commercial variants involve other types of reactors. It has been reported in literature that problems may arise in packed towers due to the sticky nature of the product [6]. In our short period test runs no signs of clogging, attaching to packing or walls, or incrustation were observed.

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Figure 9. Pilot crystallizer

Crystallization

Crystallization tests using stripped green liquor and ESP dust were performed in a pilot crystallizer. The equipment is shown in **Figure 9**. Tests were performed on two dust-liquor mixtures with dust-to-liquor mass ratios of 0.2 and 0.3.

Figure 10 shows the crystal product settles readily, the picture was taken less than 2 minutes after sampling. It can also be filtered easily, as shown in **Figure 11**.

Figure 10. Product crystals, sedimenting

Figure 11. Filtration

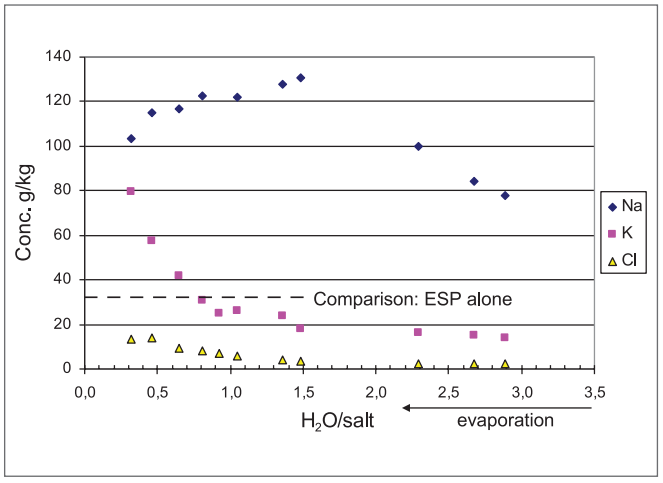

Figure 11. Test results for the Nordic mill

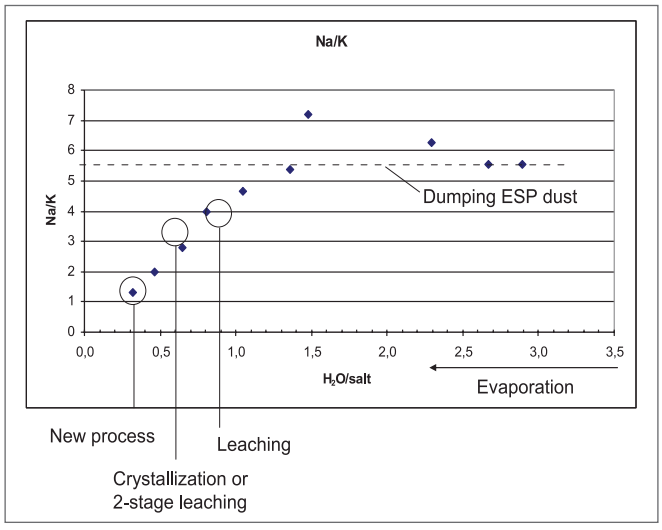

Figure 12. Sodium loss ratio and comparison with other removal processes

Results of sodium, potassium and chlorine analyses for the Nordic mill with the dust-liquor mix ratio 0.2 are presented in **Figure 11**. The results show that potassium was concentrated up to 80 g/kg. This is significantly higher than that achievable when ESP is crystallized alone, without stripped liquor. In the laboratory test presented in Figure 3, where crystallization with ESP dust alone was performed, the potassium concentration did not rise above 30 – 35 g/kg, apparently because of glaserite formation. The pilot tests were in conformance with the laboratory test presented in Figure 4, where a mixture of ESP and stripped green liquor was crystallized.

The results shown in **Figure 11** were obtained in equipment constructed basically as an industrial scale crystallizer, contrary to the lab scale results in Figures 3 and 4. Also, industrial ESP and green liquor were used. Therefore, the results can be expected to correspond rather well to full scale industrial conditions. Similar results were obtained for other runs.

Figure 12 shows the results in terms of sodium loss ratio Na/K. The benefit of the new process is apparent. The sodium loss with each kg of potassium removed is only 1.25 kg, if this stream is used as removal stream.

The results point in the direction that if evaporation would be taken further, the sodium loss ratio could be decreased even more. This may be true, but other factors begin to influence the economy of the process. The less liquid there is present, the more difficult it is to separate all the liquid from the crystals, and this finally impairs the removal efficiency.

A comparison of the sodium loss ratio with other processes is also shown in Figure 12 for the Nordic mill. Dumping ESP dust results in a sodium loss of over 5 kg for each kg of potassium removed. Leaching, two-stage leaching and evaporative crystallization provide sodium loss ratios between 3 and 4. The new process, reaching losses as low as around 1.25 kg, clearly provides a better opportunity to retain sodium in the pulp mill.

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When a mill considers procurement of a potassium and chlorine removal process, questions that usually will be asked are how high the removal efficiency and the sodium recovery are. Removal efficiency is usually expressed as how much of the potassium or chlorine that enters the removal process is actually expelled with the out stream. These questions are only relevant if they are looked at in their right context. By adjustments in the process, i.e., by changing how much water you evaporate in a crystallization process or recirculate filtrate in a leaching process, you can adjust the removal efficiency. This will, however, affect the sodium recovery in the opposite direction. If you evaporate much water, you will get high recovery of sodium, but entrained solution and precipitation of glaserite will impair the removal efficiency, and more potassium and chlorine will be returned to the mills recovery cycle. Thus, the removal efficiency will be lower. You can also adjust to high removal efficiency by evaporating less water, giving less entrained solution and less glaserite formation, but then sodium recovery will decrease. It is more difficult to have both at the same time. This is true for most processes based on fly ash crystallization or leaching. For the mills chemical economy, it is more relevant to ask for the sodium loss ratio, as Na/K or Na/Cl.

APPLICATION TO AN AVERAGE NORDIC MILL

The GLSS and liquid redox processes applied to an example mill of Nordic type would be as follows: the sulphide content in green liquor is on average 23 g/L as S^{2-}.

One cubic meter of green liquor, thus, gives 23 kg of elemental sulphur. The amount of sewered ESP dust is on average 8.4 kg/ADt, containing 1.65 kg of sulphur [5]. The balancing need in an 1800 ADt/d mill is then about 3 tons of sulphur per day. This amount can be obtained from about 130 m^3 of green liquor. This comprises a fraction of the liquor stream of about 2 %. If ClO_2 generator saltcake is to be utilized to an increased extent, a larger volume is required.

The average potassium and chlorine contents in the ESP dust of the average mill in Finland is 46 g/kg and 6.4 g/kg respectively [4]. In the 1800 ADt/d mill this corresponds to 15.1 t of ESP dust. For sulphur balancing, 130 m^3 green liquor or 155 t is needed to be stripped. If 20 % mix ratio is used, 75 t of green liquor is needed for 15 t of dust, leaving a surplus of stripped liquor. This liquor is not wasted. It can be returned to the normal causticization, or be used for production of sulphide free liquor for use in bleaching, or for other purposes. If the goal is to significantly lower the potassium and chloride levels in the liquor cycle, larger amounts of ESP dust and stripped green liquor are needed to be used.

CONCLUSIONS

A study was conducted to examine the new process concept to control the concentrations of the four important elements in the liquor cycle: sodium, sulphur, potassium and chlorine. With most of the earlier processes, controlling only one of these elements has negative effects on one or more of the others. For example, a potassium and chlorine process applied alone may upset the sulphur balance, while dumping ESP dust controls sulphur, potassium and chlorine, but causes large loss of sodium. With the new process concept, the elements can be controlled independently of each other. Sulphur can be purged without associated sodium loss, in eligible quantities and untied to potassium and chlorine removal. Potassium and chlorine can be purged with smaller sodium losses than with earlier processes.

The possibility to purge sulphur independently of the other elements gives an opportunity of better utilizing the generator saltcake from the ClO_2- process. Its sodium content can be recovered to a larger extent. Both ESP dust and generator saltcake sewering can be reduced, improving environmental performance of the mill, thus helping to meet requirements imposed by authorities. ■

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