

A system analysis of the chemical recovery plant of the sulfate pulping process

Part 7. Comments on the smelt dissolver

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SUMMARY: High and uniform quality of green liquor is essential when aiming to produce white liquor of first quality. However, very few papers are to be found dealing with the problems of obtaining green liquor of uniform quality.

In this paper the smelt dissolver and, to a minor extent, the green liquor storage tank were the focus of attention. The study includes measurements carried out on a mill scale smelt dissolver, and some measurements on a green liquor storage tank. Furthermore, dynamic simulations were performed on both devices. Finally, a control study was made of a mill scale smelt dissolver. In this part of the study, the salt concentration was related to the concentration of carbonate in the green liquor.

The findings in this study show that the smelt flow from the recovery boiler is uneven and that the concentration of carbonate in the green liquor leaving the smelt dissolver varies quite considerably. In addition to this the density and the temperature of the green liquor, as well as the temperature in the vent pipe, were shown to follow the variations of the carbonate concentration in the green liquor. However, the carbonate concentrations showed the largest variations.

Measurements of the green liquor leaving the storage tank showed that the carbonate concentration was not even throughout the liquor. Dynamic simulations showed that it was impossible to obtain a homogeneous concentration, even if the liquor in the storage tank was perfectly mixed. The conclusion to be drawn from this observation is that it is necessary to control the smelt dissolver more accurately.

The possibility of doing just this, using a carbonate analyzer, was investigated. Mill studies showed that the green liquor density, temperature and carbonate concentration were more uniform when the carbonate analyzer was used than was the case when a density meter was used. However, both the mill studies and the dynamic simulations showed that the carbonate analyzer used in this study can not give perfect results, as the time lag was too long.

Thus, better and more reliable control of the smelt dissolver could be achieved if it were possible to use an analyzer more sensitive than the density meter normally used, and which incorporated a shorter time lag than the carbonate analyzer used in this study.

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In the sulfate pulp process, pulp is produced by treating wood chips with white liquor. To produce a pulp of high quality at minimum cost, three criteria must be met; the wood chips must be of first quality, the conditions in the digester must be optimal and finally the white liquor must be of first quality. A white liquor is said to be of high quality when both concentration and composition are uniform. Moreover, the concentration of hydroxide and sulfide ions (the active chemicals) must be high compared to the other anions (carbonate, sulfate, thiosulfate, chloride

etc., ions). In order to maximize the hydroxide concentration and minimize the carbonate concentration great efforts were made to control the conditions in the slaker (1, 2, 3), with most of the efforts concentrated on the problem of feeding the correct amount of lime to the green liquor which in turn is fed to the slaker. However, this form of control can only produce white liquor of high quality if both the lime and green liquor are also of high quality. As with its white counterpart, high quality green liquor should be uniform both in terms of concentration as well as composition. In the green liquor system very little can be done to change the composition. In actual fact, the best results are obtained if the composition is remains unaltered, that is, if the oxidation of sulfide ions is avoided. The concentration itself is, however, determined in the smelt dissolver.

At present, the total salt concentration of the green liquor is normally regulated by controlling the density of the liquor. It is well-known that the density of any salt solution depends on the composition, concentration and temperature of the liquor. Taking the composition of a typical green liquor to be the following: 30 g NaOH, 120 g Na₂CO₃, 50 g Na₂S, 10 g Na₂SO₄, 6 g Na₂S₂O₃ and 6 g NaCl per liter, the relationship between concentration and temperature can be calculated (4). In *fig. 1*, the salt concentration is expressed in mol sodium per liter.

The graph (*fig. 1*) shows that a change in the density of 1% results in a change of 7% in the concentration of sodium. Thus the accuracy of the density measurements must be very high in order to achieve proper control of the salt concentration in the green liquor. One instrument which is more sensitive than the density meters normally used is the carbonate analyzer developed at MoDo Development Center (5).

This paper will focus on some of the problems of producing green liquor with a uniform salt concentration. It should be added that the carbonate concentration is expressed as sodium carbonate.

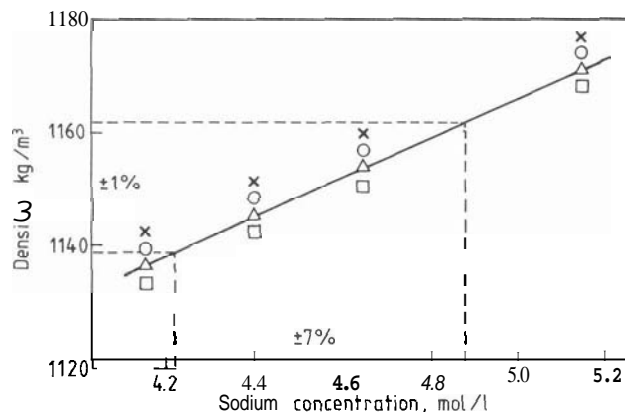


Fig. 1. Density versus sodium concentration for a typical green liquor. × 85°C, ○ 90°C, A 95°C, and □ 100°C.

Scope of the investigation

Since very few papers have been published in this field, it was necessary to start from the very beginning. The investigation can be divided into the following sections:

- The smelt flow from the recovery boiler to the smelt dissolver.
- Measurements carried out on a conventionally controlled smelt dissolver.
- Measurement of sodium carbonate concentration from an unmixed storage tank.
- Computer simulations of the storage tank.
- Computer simulations of regulating the smelt dissolver.
- Mill scale studies of carbonate concentration as the controlling parameter for determining the salt concentration in the smelt dissolver.

The studied green liquor system and the parameters measured

The complete green liquor system in the mill where this investigation was carried out consisted of two smelt dissolver tanks, two green liquor clarifiers and one green liquor storage tank. In this study only the storage tank and one of the smelt dissolver tanks were studied.

The smelt dissolver tank investigated was of conventional design. The vessel was oval in shape and equipped with two side mounted mixers. The smelt is transported from the recovery boiler to the smelt dissolver via three water cooled channels. There are two outlets for transporting the green liquor from the smelt dissolver. When one is being used, the other is descaled by washing it with water. The excess vapor produced in the smelt dissolver is removed via a vent pipe.

The smelt dissolver is controlled by the density readings of the green liquor regulating the flow of weak white liquor being fed to the dissolver, while the liquid level in the smelt dissolver is used to control the green liquor flow from the dissolver.

In all mixing operations it is important to have uniform mixing which ensures that there are no stagnant zones in the tank. This was investigated by studying the concentration values after adding a pulse of lithium salt into the smelt dissolver. Fig. 2 shows the measured data obtained compared with calculations made for a perfectly mixed vessel.

As can be seen, the smelt dissolver studied is as near as is possible to come to a perfectly mixed tank. The residence time was approx. 30 min.

The green liquor storage tank is a conventionally designed storage tank with no mixers installed and has a volume of 5000 m³.

Unless stated, all the parameters measured are in accordance with those in fig. 3, namely temperature, carbonate concentration and density of the green liquor, temperature of both the weak white liquor and in the vent pipe and, finally, the position of the valve controlling the flow of weak white liquor to the smelt dissolver. This last parameter was only measured when the carbonate analyzer was used to control the weak white liquor flow.

Since this study took place in a mill, all the equipment in the investigation was designed for this kind of use. This means of course that the precision of the measurements is not of the highest standard

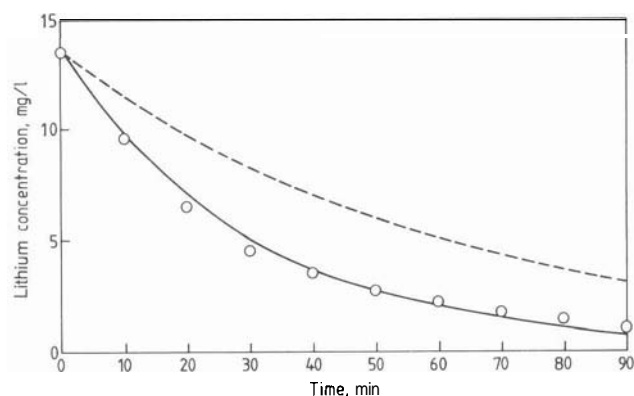


Fig. 2. Pulse response of the smelt dissolver, measurements and calculations. ○ Measured values. — Calculated values, residence time 30 min. - - - Calculated values, residence time 45 min.

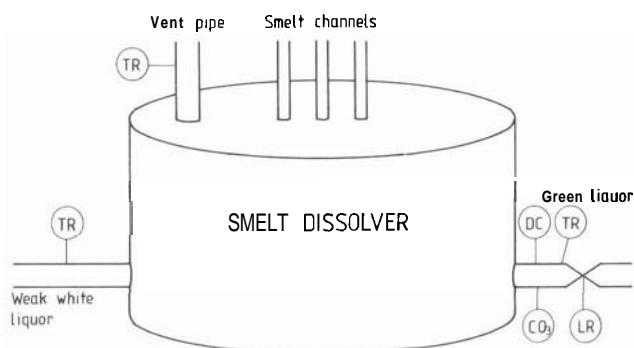


Fig. 3. Measured parameters.

and margins for error in the readings are estimated to be 1% for the carbonate analyzer, 1-2% for the thermocouples and 6-8% for the density measuring device. Since the sensitivity of the devices is greater, it is still possible to record small changes.

Estimation of the smelt flow from the recovery boiler

Since the temperature of the smelt is over 800°C, it is hardly possible to measure the flow directly. However, the smelt flow can be calculated if the sodium concentration of all streams as well as the magnitude of the flows to and from the smelt dissolver, except the smelt flow itself, are all known.

In order to simplify the calculations, various reasonable assumptions were made. The sodium content in the vapor leaving the smelt dissolver was assumed to be zero. Furthermore, since it could easily be shown that the volumetric flow of green liquor was only slightly higher than the volumetric flow of the weak white liquor, these two flows were therefore assumed to have the same value. Finally, since the liquid level was controlled, it was assumed to be constant. Using these assumptions, the smelt flow can be calculated using the equation:

$$S_{sm} = G_g(Na_g - Na_{ww}) / Na_{sm} \quad [1]$$

where

- S_{sm} is the smelt flow (kg/min)
- G_g is the green liquor flow (m³/min)
- Na_g is the sodium content in green liquor (kg/m³)
- Na_{ww} is the sodium content in weak white liquor (kg/m³)
- Na_{sm} is the sodium content in the smelt (kg/kg)

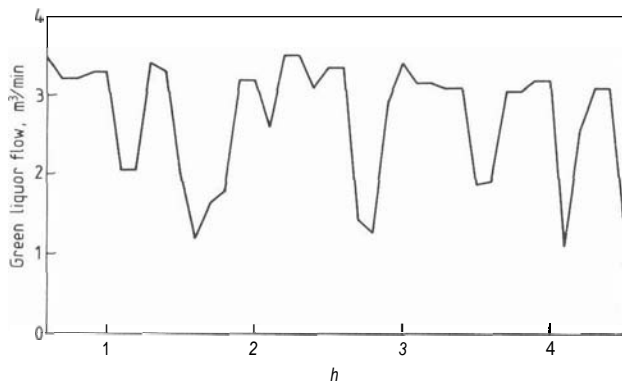


Fig. 4. The flow of green liquor from the smelt dissolver.

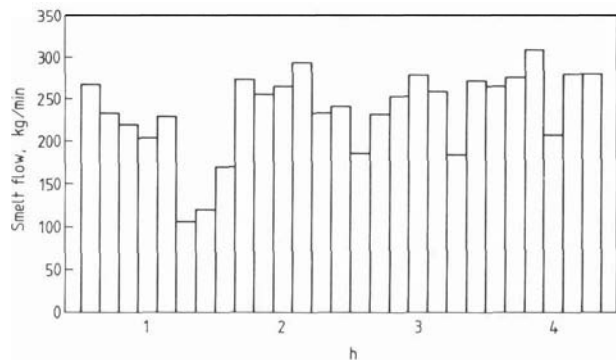


Fig. 5. The smelt flow to the smelt dissolver.

The volumetric flow of the green liquor was measured by continuously adding a specific amount of a lithium salt into the green liquor flow at a position before the pump and a few meters after the pump samples of the green liquor were taken. The concentration of lithium in the samples was measured by flame emission, and the green liquor flow was calculated from the dilution of the lithium. The results are shown in fig. 4. The concentrations of sodium in the smelt, in the green liquor and in the weak white liquor were measured by flame emission. The smelt flow was calculated and the results is shown in fig. 5; the smelt flow varies quite extensively, as can be clearly seen.

Measurements of a standard way of operating the smelt dissolver tank

Measurements were taken for a total of 22 days over a period of 3 months. During this period the mill was shut down, so that the first 11 days were before the stop and the remainder after.

Table 1. Statistics of the parameters measured before and after the stop.

Measurement	Before the stop				After the stop			
	mean	std. dev.	max.	min.	mean	std. dev.	max.	min.
Carbonate conc., g/l	122	11	16	5	114	12	20	3
Density, kg/m ³	1251	13	13	8	1250	11	19	1
Temperature, °C								
green liquor	9	3	4	5	1	9	4	3
vent pipe	8	8	5	9	2	8	7	5
weak white liquor	71	4	2	0	68	5	3	0

Table 1 shows the mean value and the standard deviation before and after the stop as well as the maximum and minimum standard deviations found for each day in each period. The only mean value not similar in both periods is the carbonate concentration. One probable explanation for this that the density meter was adjusted during the stop, and since the regulating is done via the density readings this resulted in the carbonate concentration being affected.

In fig. 6 the standard deviations for each day are expressed as a percentage of the mean value of that day.

The carbonate concentration shows the greatest deviation each day except on day 8, 20 and 21, where the deviations of the vent pipe temperature are greater. If the vent pipe temperature varies more than normal, the green liquor temperature ought also to vary likewise. This is indeed the case for days 8 and 20. Furthermore, on these days the standard deviations for the temperature of the weak white liquor are only 0.6 and 1.2°C respectively. The variations were obviously not caused by variation in the weak white liquor. Variations in the concentration of carbonate and in the density of the green liquor were, moreover, not higher than average, which implies that the smelt flow hardly varies more than normal. A rational explanation for this is, therefore, that the temperature of the smelt varies.

It is interesting to note that the smallest deviation is to be found for the density, and that this is true for all days.

One of the most important results from this period is that a change in the carbonate concentration in the green liquor gave rise to changes in the green liquor density and temperature as well as the vent pipe temperature. Thus, if the carbonate concentration increased the other parameters also increased and vice

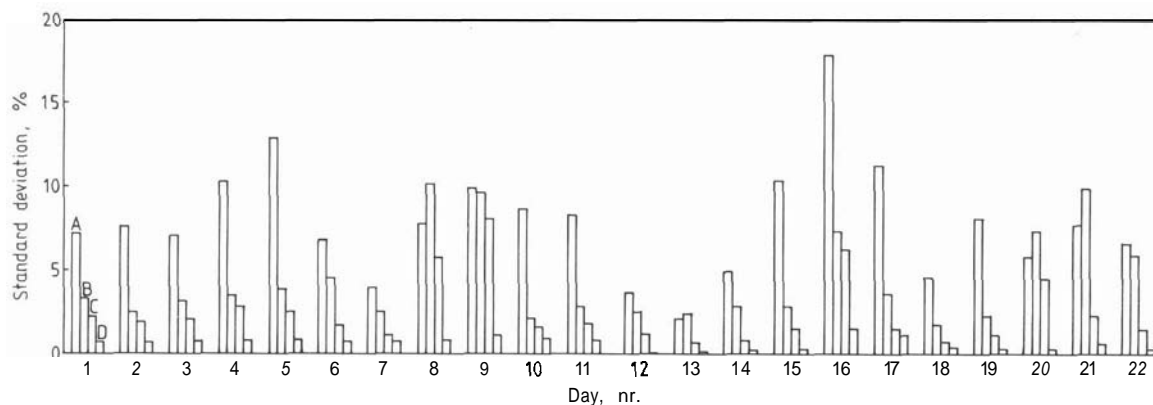


Fig. 6. Standard deviation expressed as a percentage of the mean value per day. A Carbonate concentration. B Vent pipe temperature. C Green liquor temperature. D Density.

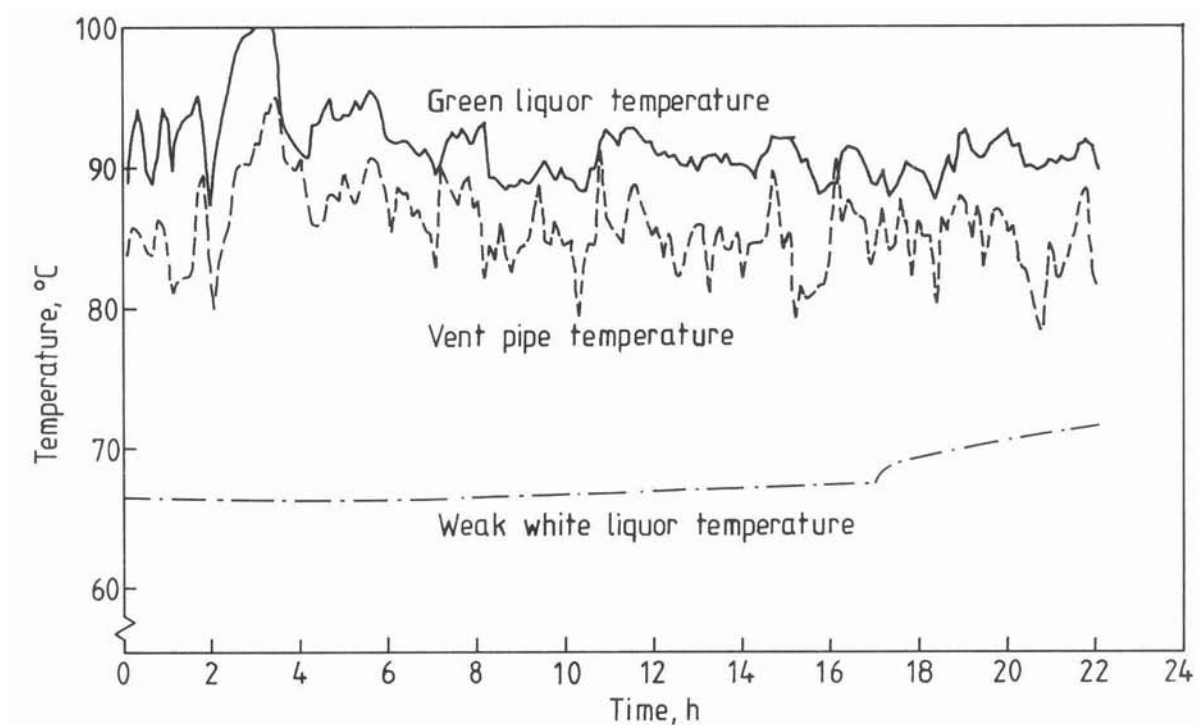
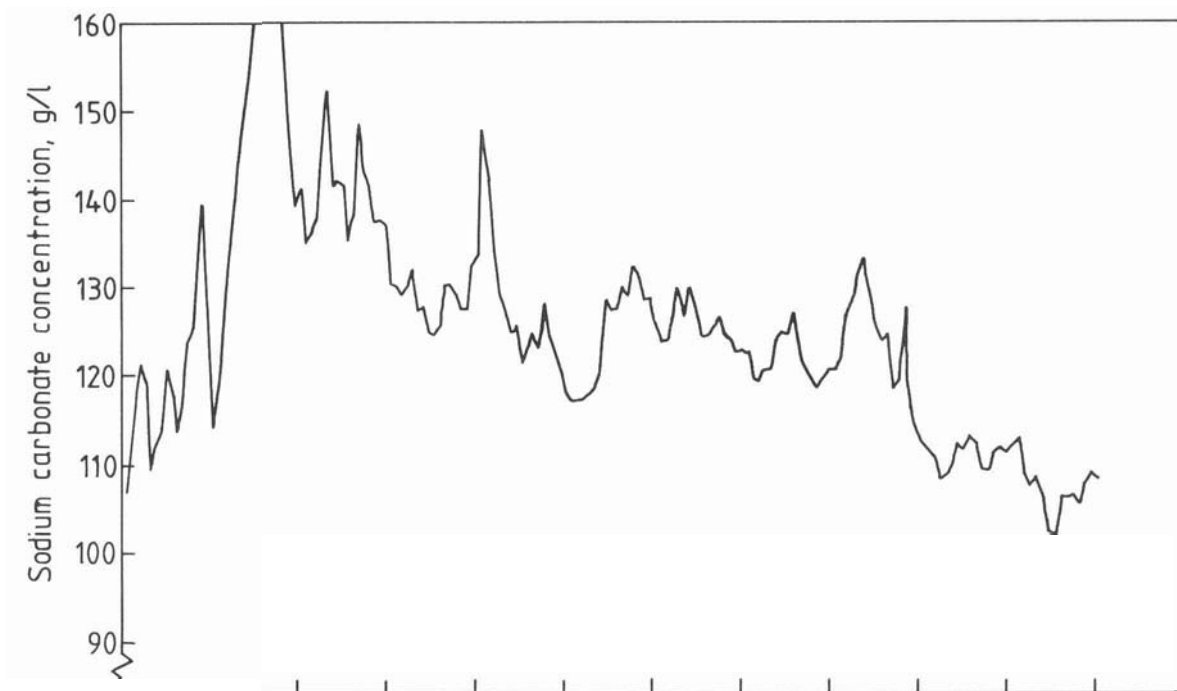
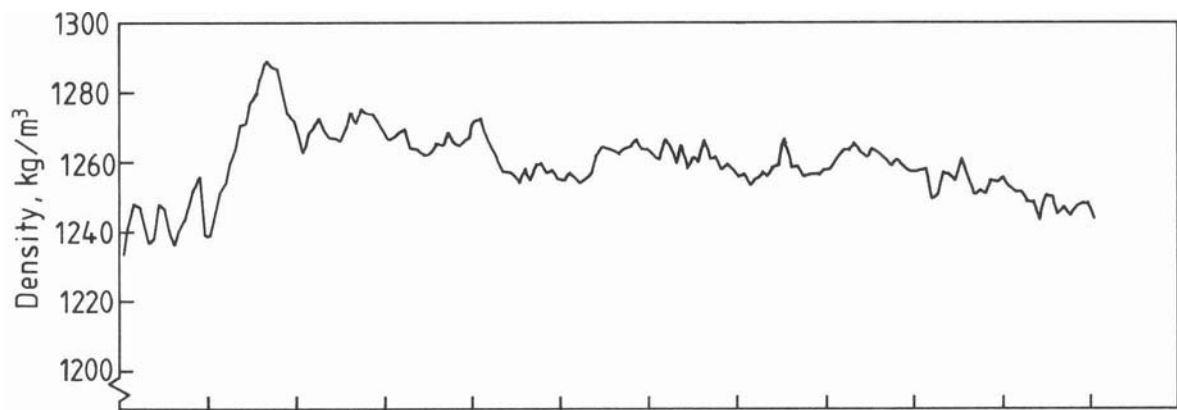


Fig. 7. Variation of the measured parameters for one day.

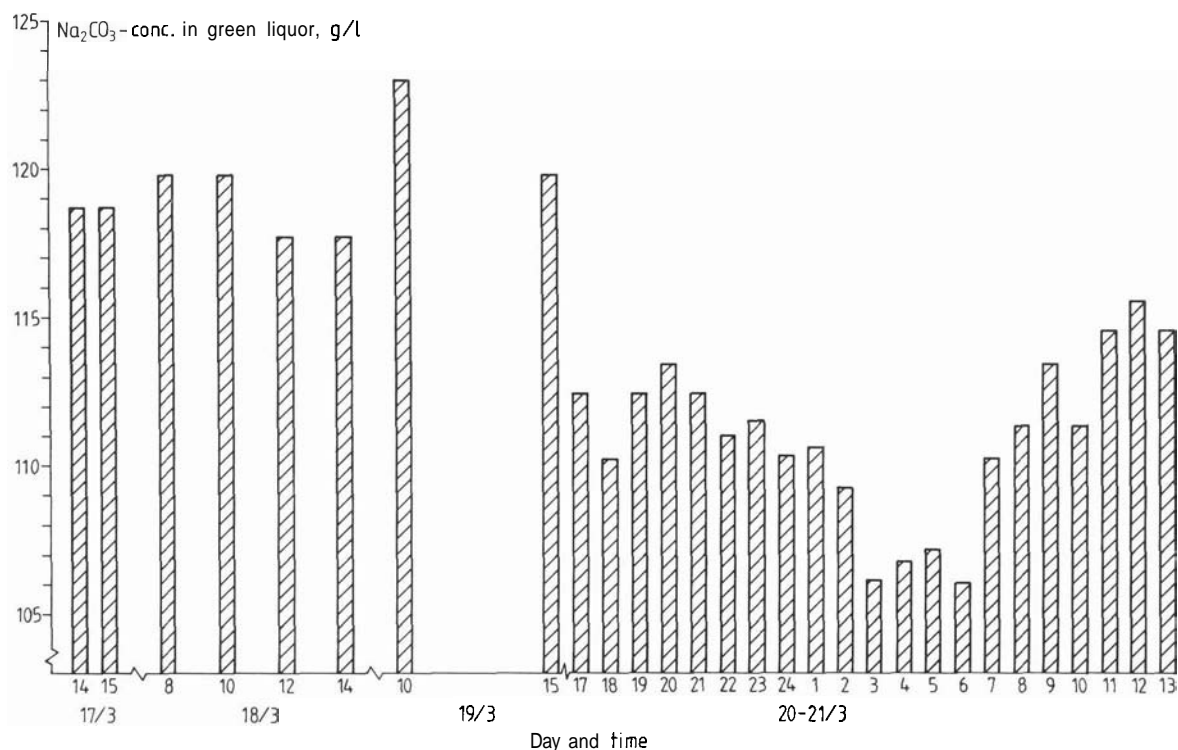


Fig. 8. The concentration of carbonate in the green liquor leaving the storage tank.

versa; an example of this can be seen in *fig. 7*. The same phenomenon was also observed on the other days.

The conclusions to be drawn from the measurements take in this section are as follows:

- Carbonate concentration is the parameter that varies the most.
- Density is the parameter with the smallest variation.
- Parameter variations are interrelated.

The implication here is that it ought to be better to control the total salt concentration of the green liquor by controlling the concentration of carbonate. The temperature of the green liquor or the vent pipe might possibly have been a better choice instead of the density. However, using these two temperatures could have been dangerously problematic since they also reflect the temperature of the incoming weak white liquor and smelt.

The green liquor storage tank

One interesting question is if the green liquor storage tank could be used to smooth out the irregularities in the concentration of carbonate in the green liquor stream from the smelt dissolver tank.

The residence time in the storage tank in this study was approximately 20 hours at maximum green liquor flow and full tank. With this residence time and optimal mixing conditions, the total salt concentration of the green liquor should be quite uniform. However, the tank was not equipped with mixing equipment so that the only mixing involved was that which occurred naturally. Two questions thus arise; is the mixing which occurs naturally efficient enough to smooth out the irregularities in concentration, and if not, could a perfectly mixed storage tank provide the consistency of concentration required?

In order to answer these two questions, both a mill study and some dynamic simulations on a perfectly mixed tank were carried out.

Mill studies

Measurements of the carbonate concentration in the green liquor leaving the storage tank were taken over a period of several days. The results are to be found in *fig. 8*.

This graph shows that the carbonate concentration varied considerably, thus proving that the natural mixing was not sufficient to smooth out these variations.

Simulation of green liquor storage

A dynamic simulation of a perfectly mixed tank with one inlet and one outlet stream is quite simple to make. The material balances are:

$$F_{in} = F_{out} + dM/dt \quad [2]$$

$$F_{in}x_{in} = F_{out}x_{out} + d(Mx_{out})/dt \quad [3]$$

where

- F is the green liquor flow.
- M is the amount of green liquor in the tank.
- t is the time.
- x is the salt concentration in the green liquor.
- in is the inlet stream.
- out is the outlet stream.

These two equations were used with the assumption that the mass flow to the storage tank was constant. In each calculation the size of the perfectly mixed tank was also constant. Data on the carbonate concentration in the inlet stream was obtained from data presented earlier in this paper.

Several different sizes of storage tanks were stud-

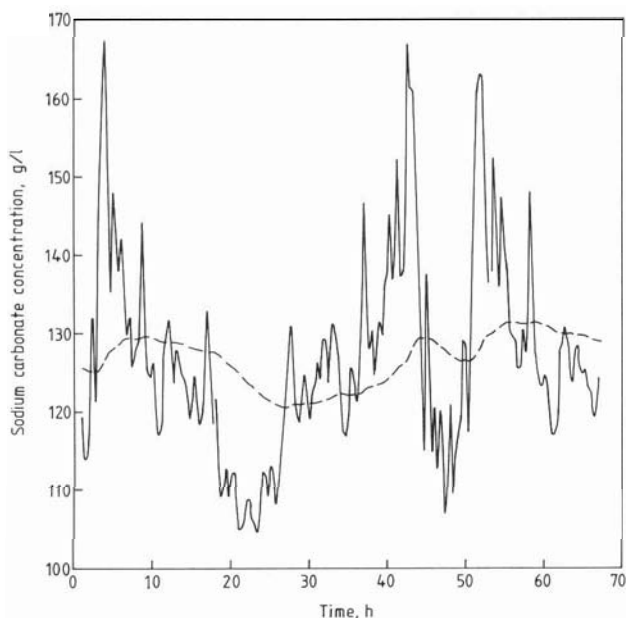


Fig. 9. Simulation of a perfectly mixed storage tank, with large variations of carbonate concentration in the inlet stream. — Sodium carbonate concentration in the inlet stream. — — — Sodium carbonate concentration in the outlet stream.

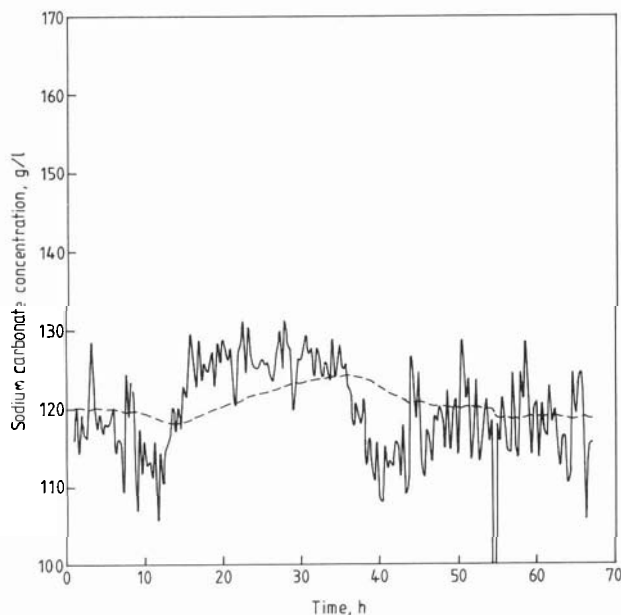


Fig. 10. Simulation of a perfectly mixed storage tank, with small variation of carbonate concentration in the inlet stream. Symbols as in fig. 9.

ied. Fig. 9 and 10 show examples of very large perfectly mixed tanks (5000 m^3), with a residence time of 20 hours. Fig. 9 gives an example when the irregularities in the concentration of carbonate in the inlet stream are very large whilst fig. 10 shows an example with very small irregularities.

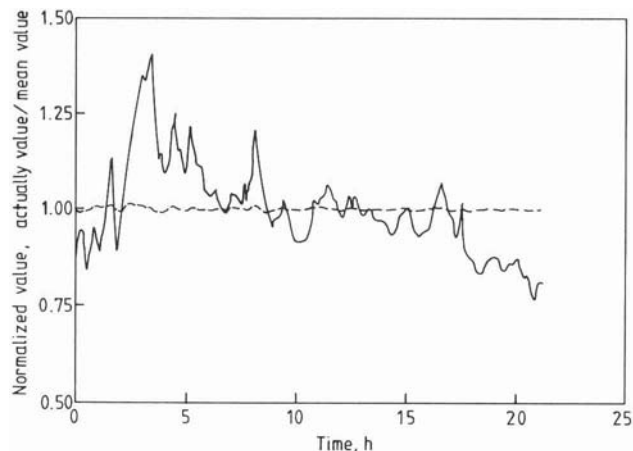


Fig. 11. Controlling the smelt dissolver, with a time lag of 5 minutes. — Smelt flow from the recovery boiler. — — — Sodium carbonate concentration in the green liquor.

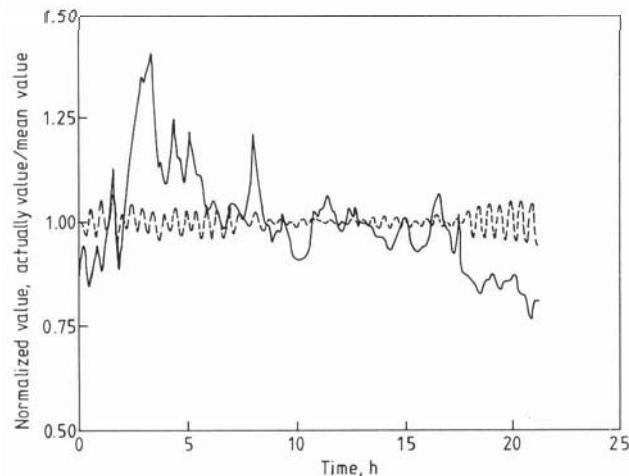


Fig. 12. Controlling the smelt dissolver, with a time lag of 10 minutes. Symbols as in fig. 11.

The conclusion drawn from these results was that it is possible to regulate the rapid fluctuations in the concentration of carbonate, but changes over a long period were impossible to smooth out.

Simulation of controlling the smelt dissolver tank

In order to investigate controlling the smelt dissolver tank a simple dynamic simulation program was developed (see Appendix).

Of great interest in any control system is the influence of the time lag between sampling and control. The time lag is of special interest for this system since the carbonate analyzer employed had a rather long response time (8-12 min) in relation to the residence time of the liquor in the smelt dissolver (30 min).

To simulate a change in the smelt flow as realistic

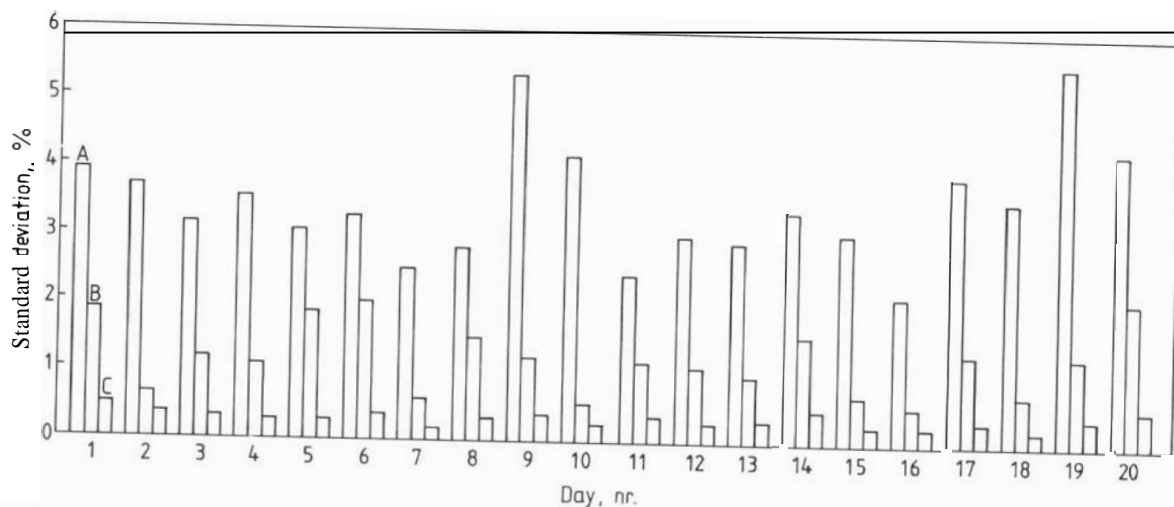


Fig. 13. Standard deviations expressed as a percentage of the mean value (given below between brackets) of that day. A Carbonate concentration (4.9 g Na₂CO₃/l). B Green liquor temperature (1.2°C). C Density (4.2 kg/m³).

as possible, the results from the day discussed earlier were used. The smelt flow for that particular day was calculated from the mass balances using the following assumptions: the density of the green liquor and the carbonate concentration in the weak white liquor and in the smelt were all assumed to be constant.

If the time lag was short, it was easy to control the carbonate concentration in the green liquor, *fig. 11*. But if the time lag was over 8-10 min, the system tended to be unstable, *fig. 12*. This unstable behavior was a result of our ambition to achieve faster control. This behavior can be avoided, but at the cost of having a slow and insufficient control.

Mill scale experiments to control the smelt dissolver with the carbonate analyzer

In order to verify the findings in the foregoing section, arrangements were made to control the smelt dissolver with the carbonate analyzer. A computer was used to sample the values of the parameters and to control the flow of weak white liquor. The control strategy was the same as for a conventional control system. The control algorithm was a conventional PID algorithm. Sampling of the parameters and control was done each minute.

Tests were carried out during this phase of the experiment on 20 occasions. The length of each test was between 2 and 20 hours with the mean value being 8 hours.

Fig. 13 shows the calculated standard deviation of the carbonate concentration, temperature and the density of the green liquor. The mean value for the test period (time weighted) are given below the figure.

The figure shows that the variations are less than half of the variations in the reference period. Interesting to note is that none of the test occasions exhibits a standard deviation greater than the mean value of the reference period.

The variations of the carbonate concentration and the weak white liquor valve opening for one typical test occasion is shown in *fig. 14*.

The sodium carbonate concentration was set at 127 g/l while the calculated mean value was 126.9 g sodium carbonate/l. The amount of smelt coming from the recovery boiler is shown by greater movements of the weak white liquor valve. There is also a smaller but faster movement of the valve; this movement is probably due to self oscillation resulting from the long time lag in the analyzing system and the demands of more rapid control.

We can therefore conclude from this part of the test that:

- It is possible to have a more uniform concentration of the green liquor if a carbonate analyzer is used to control the salt concentration.
- The time lag in the carbonate analyzer used in this study is too long.

Conclusions

In this study it was found that the concentration of carbonate in the green liquor leaving the smelt dissolver tank varied quite considerably. These variations were not reduced in the green liquor storage tank. Calculations showed that the long term variations in concentration were not possible to adjust even if the storage tank was perfectly mixed. However, the short term variations could be smoothed out or eliminated to a certain degree.

It was also found that the variations of the carbonate concentration in the green liquor were due to an uneven smelt flow from the recovery boiler. In addition, the density and the temperature of the green liquor as well as the temperature in the vent pipe followed the variations of the carbonate concentration in the green liquor. However, the carbonate concentrations showed the greatest variations. Thus,

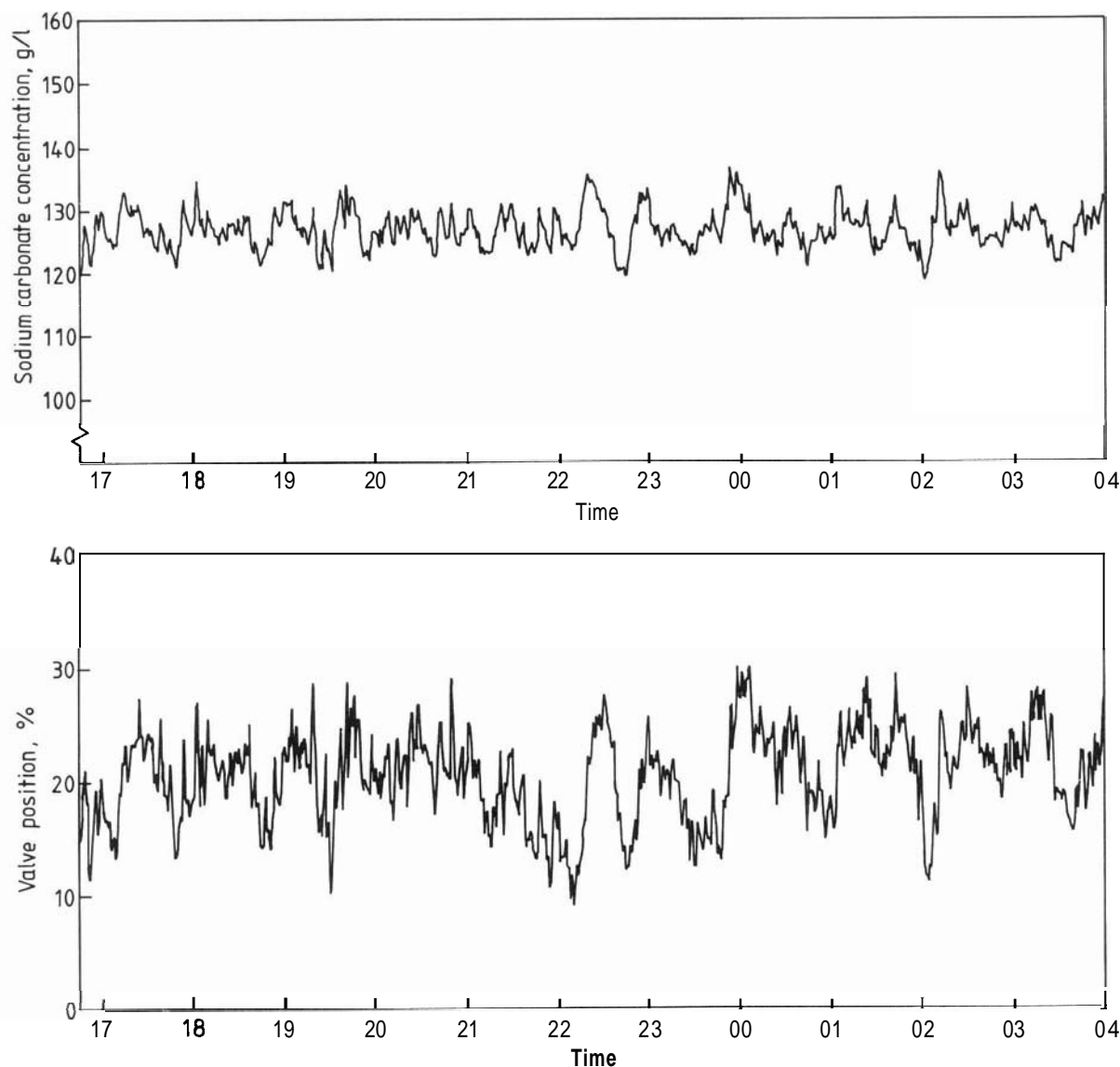


Fig. 14. The carbonate concentration (the upper curve) and the valve opening (the lower curve).

of the parameters investigated, the carbonate concentration ought to be the best parameter to control the strength of the green liquor. This was investigated both in dynamic simulations and by full scale mill tests. The results obtained showed that the carbonate concentration, the density and the temperature of the green liquor became more uniform if the carbonate concentration was used as the control parameter. Unfortunately, the carbonate analyzer used in this study had one drawback, the time lag of the analyzer was too long.

Thus, better and more efficient control of the smelt dissolver could be achieved if the analyzer used were more sensitive than the density indicator normally used today and if it had a shorter delay time than the carbonate analyzer used in this study.

APPENDIX

Equations [4] and [5] show the general form of the material balances of the smelt dissolver.

$$F_{sm} + F_{ww} = F_g + F_{vp} + dM/dt \quad [4]$$

$$x_{sm}F_{sm} + x_{ww}F_{ww} = x_gF_g + x_{vp}F_{vp} + d(x_sM_s)/dt \quad [5]$$

where

- F is the mass flow (kg/s)
- M is the mass in the smelt dissolver (kg)
- x is the mass fraction of sodium carbonate
- sm is smelt
- ww is weak white liquor
- g is green liquor
- s is the smelt dissolver
- vp is the vapor entering the vent pipe

To simplify the equations some reasonable assumptions were made:

- No carbonate in the vapor.
- The amount of vapor generated is constant and subtracted from the flow of weak white liquor.
- The smelt dissolver is a perfectly mixed tank, i.e. the carbonate concentration in the green liquor leaving the smelt dissolver is the same as the carbonate concentration in it.
- A constant carbonate concentration in the weak white liquor and in the smelt.
- The density of the green liquor is constant and the level in the smelt dissolver is constant, i.e. there is no accumulation of mass in the smelt dissolver.

The equations will now be according to the equations [6], [7] and [8].

$$F_{sm} + F_{ww} = F_g \quad [6]$$

$$x_{sm}F_{sm} + x_{ww}F_{ww} = x_gF_g + M_s dx_s/dt \quad [7]$$

$$x_g = x_s \quad [8]$$

The control algorithm is the same as for the dissolver in the mill. Using the above assumptions, the liquid level was controlled by equation [6]. The control of the strength (carbonate concentration) by the weak white liquor flow was performed with a digital PID controller. This kind of controller is normally described according to equation [9].

$$\Delta E = K_p[E(t) - E(t-1)] + K_i E(t) + K_d[E(t) - 2E(t-1) + E(t-2)] \quad [9]$$

where

- ΔE is the necessary adjustment
 $E(t)$ is the error at time t
 K_p is the proportional constant
 K_i is the integration constant
 K_d is the derivation constant

As can be seen, this controller utilizes the three most recent measurements.

The program used for the simulations calculated the material balances each second and the new weak white liquor flow each minute. The valve controlling the weak white liquor flow is assumed to be perfect, though only allowed to have values between 5-95% of maximum flow. An initial estimation of the constants in equation [9] was arrived at using some "rules of thumb" (6, 7). These constants were thereafter adjusted to perform the fastest possible control, free from oscillations.

Acknowledgements

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