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CHEMICAL PULPING

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Abstract—The final discharge to water from a pulping operation depends on the amount of pollutants generated in the process, on the internal process changes made to reduce the pollutants and on the external treatment facilities. This paper mainly deals with the first two concepts.

For comparison the discharge from mechanical pulping and bleaching are briefly discussed. A typical figure for the BOD_7 is 25 kg/tonne of pulp of which 3 comes from wet barking, 12 from the fibre separation (stone groundwood) and 10 from the bleaching operation. The effluent has a low colour and the amount of suspended solids is normally in the range 20–30 kg/tonne of pulp.

In the chemical pulping process 150–600 kg BOD_7/tonne is generated. The lower figure applies to semi-chemical pulping and the higher to the production of viscose pulps. Normally, however, the spent liquor is collected, evaporated and burnt leading to at least 95% reduction of the BOD discharge. The total BOD_7 of the digester and evaporator condensates is 10–12 kg/tonne in kraft pulping and *ca.* 25 kg/tonne in sulphite pulping.

The total BOD_7 and colour from the bleaching of softwood kraft pulp is around 15 and 170 kg/tonne. In the bleaching of sulphite pulp the colour is only about half that from kraft pulp and the BOD_7 slightly lower. The influence of process and operating parameters is discussed. The total discharge (including accidental spills) from kraft and sulphite pulping are summarized.

A number of internal means to reduce the pollutants are reviewed and thin liquor neutralization and oxygen bleaching are presented in detail. Oxygen bleaching (integrated in the liquor system) has the potential of reducing the BOD_7 and colour from the bleach plant by 50%. The limit is presently set by the degree of attainable delignification.

By neutralizing the thin liquor the acetic acid is prevented from flashing to the condensate. An MgO system is discussed. The BOD_7 of the condensates is reduced by 50–70%.

BACKGROUND

In pulp and papermaking the pulping operation generates the largest amounts of water pollutants and has the largest fresh water demand. Depending on the type of process, raw material etc. the discharge ranges from 600 kg BOD_7/tonne of pulp produced to 10 kg BOD_7/tonne. The higher value applies to sulphite viscose pulping and the lower to mechanical pulping.

When discussing the pollutants from the process and how to reduce them the following points should be considered.

1. Process generated pollutants. (i.e. the amount of pollutants formed in the process. Not necessarily equal to the amount discharged).
2. Process changes to reduce the amount of pollutants (discharged).
3. External treatment to reduce the amount of pollutants.

In this context the main emphasis will be placed on the first two points.

Much of the information regarding process generated pollutants comes from a number of studies made at the Swedish Forest Products Research Laboratory. Unpublished material from studies made by EKA and IVL has also been used.

The two measures for polluting discharges used here are BOD_7 (biochemical oxygen demand) and colour. The conversion factor between BOD_7 and BOD_5 depends on the origin of the effluent but as a mean value 1·15 can be used ($BOD_5 = BOD_7/1{\cdot}15$). The *colour* of the effluent is measured at 400 nm and pH 7 and is given in Pt-units. All measures are given on the basis of metric tons of pulp.

MECHANICAL PULPING

The pulping operation

The factors that affect the discharge of dissolved solids during mechanical pulping are treatment temperature, intensity of mechanical action, degree of system closure and wood factors. The higher temperature—and pressure—during the refining process the more of the wood substance is dissolved (Fig. 1). At 100°C i.e. normal groundwood and refiner groundwood manufacture the substance loss is around 2·5%. For thermomechanical pulping it approaches 4% and can reach 10% for board pulps.

The BOD_7-discharge increases linearly with an increase in defibration temperature (Fig. 2). For normal groundwood pulping the value is close to 10 kg/tonne pulp and for thermomechanical pulping up to 20 kg/tonne. Hardboard pulps range from 40 kg/tonne and upwards.

The degree of mechanical action during pulping also seems to have an influence on the BOD_7-discharge (Fig. 3). This diagram summarizes measurements from a number of Swedish groundwood and refiner groundwood mills. When the mills produce a fairly coarse pulp, the discharge is often below 10 kg/tonne. Production of very fine groundwood leads to up to 15 kg BOD_7/tonne.

Bleaching of mechanical pulps

Mechanical pulping thus causes a discharge of dissolved organic substance corresponding to 10–20 kg

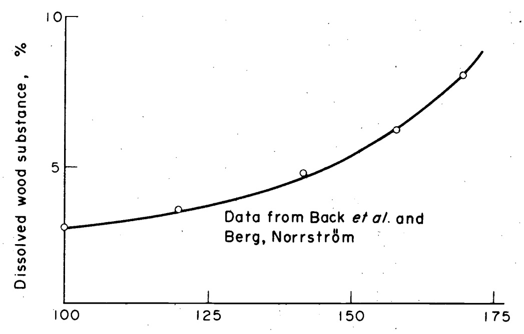

Fig. 1. Dissolved wood substance during defibration of wood at elevated temperature.

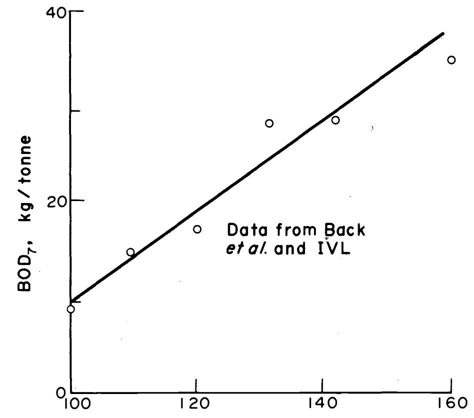

Fig. 2. The BOD_7-value of the dissolved wood substance as a function of defibration temperature.

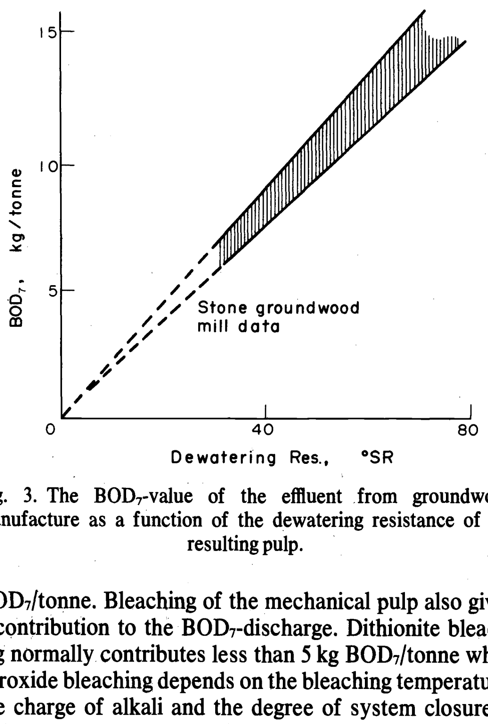

Fig. 3. The BOD_7-value of the effluent from groundwood manufacture as a function of the dewatering resistance of the resulting pulp.

BOD_7/tonne. Bleaching of the mechanical pulp also gives a contribution to the BOD_7-discharge. Dithionite bleaching normally contributes less than 5 kg BOD_7/tonne while peroxide bleaching depends on the bleaching temperature, the charge of alkali and the degree of system closure.

As an example the influence of alkali charge—expressed as final pH during bleaching—on the BOD_7-value is shown in Fig. 4. It must be pointed out that the bleachings were made on laboratory scale with slightly higher than normal alkali profile and with no recirculation of process water. The BOD_7-values are therefore higher than those obtained in mill scale bleaching. Very low alkali charges lead to a BOD_7-value below 10 kg/tonne. At this low alkali charge the bleaching effect is nil or insignificant. To obtain a good bleaching result the final pH should be kept above 9. In that instance the BOD_7-value is 20 kg/tonne and above. Judging from the limited material available there is no difference between thermomechanical and groundwood pulps with respect to BOD_7 discharge during bleaching.

The influence of system closure on the BOD_7 discharge is, however, very marked. In a production line for bleached refiner groundwood water additions are necessary in the refiners and in the screening operations. A

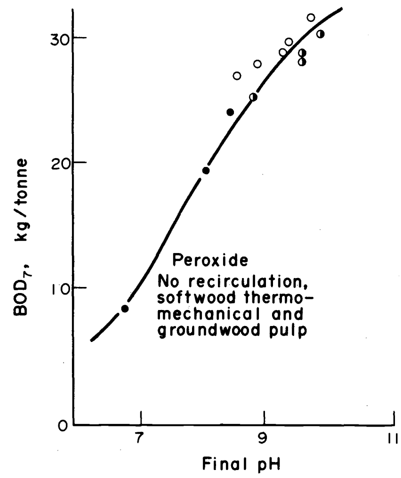

Fig. 4. The BOD_7-value of the spent liquor from peroxide bleaching of groundwood and thermomechanical pulps. No system closure in the bleaching.

higher degree of system closure can be obtained by using water from the dewatering operations for dilution in the refiners and screens. At the same time the effluent volume is—of course—reduced.

Even such a moderate degree of recirculation as 35% reduces the BOD_7-discharge to half its original value (Fig. 5). The reason for this is not completely clear. One important factor is, however, probably the increased amount of dissolved organic substance circulating in the system. This may lead to a slower dissolution of substance from the pulp.

The total BOD_7 from mechanical pulping is thus about 25 kg/tonne of pulp, 3 kg/tonne comes from the wet barking, 12 from the stone or refiner groundwood operation and 10 from the bleaching (Table 1).

There is very little information on the discharge of coloured compounds from the mechanical pulping process. The effluent from barking has a colour in the range 5–40 kg Pt/tonne. The effluents from pulping and bleaching are very low in colour.

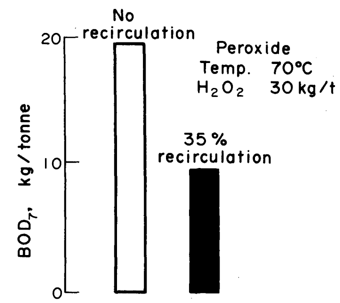

Fig. 5. The BOD_7-value of the spent liquor from peroxide bleaching at 0 and 35% recirculation of the liquor.

Table 1. Discharges from mechanical pulping

Subprocess	BOD_7 (kg/tonne)	Colour (kg/tonne)	SS (kg/tonne)
Barking	3	5–40	7
Pulping	12	Low	15
Bleaching	10	Low	
Total	25	—	22

In a well-kept mill the discharge of suspended solids is around 7 kg/tonne from barking and 15 kg/tonne from pulping and bleaching. The total effluent volume is normally of the order of 30 m^3/tonne.

CHEMICAL PULPING

The pulping operation

The discharges from chemical and semi-chemical pulping are affected by a number of factors. Some of them like washing degree, wood factors, chemical recovery and bleaching variables are self-evidently of great importance to the discharges. Our knowledge on the effect of process, degree of delignification and process variables is, however, rather sparse.

In Fig. 6 the information available in the literature on sulphite pulping has been collected. It shows the BOD_7 of the liquor as a function of the amount of wood substance dissolved during the cook. It includes values both for NSSC and acid sulphite cooks. The NSSC cooks were made on hardwood and the acid sulphite cooks on softwood. It is noteworthy that the values for hardwood and softwood pulping fall on the same line.

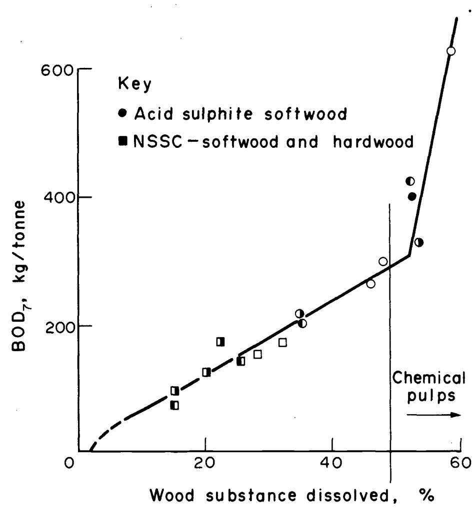

Fig. 6. The BOD_7-value of the spent liquor from sulphite pulping as a function of wood substance dissolved during the cook.

As the pulp yield goes down the BOD_7 of the liquor increases linearly. At the normal yield interval for chemical pulps the BOD_7 is 300–350 kg/tonne. In that region the fairly slow linear BOD_7-increase is turned into a much steeper increase. Dissolving pulps with a yield around 40% thus have a liquor BOD_7 of 600 kg/tonne and above.

The corresponding curve for softwood kraft pulping has a very similar look (Fig. 7). Lack of reliable information makes this curve a bit of guesswork but the main features are probably correct. In the yield range for chemical pulps the BOD_7 is *ca.* 250 kg/tonne and immediately thereafter the steep part of the curve starts. For birch kraft pulps the liquor has a BOD of around 300 kg/tonne in the chemical region.

Right from the curves two observations can be made;

1. The increase in BOD_7 of the liquor seems to be more rapid in the beginning of the kraft cook than in the beginning of the sulphite cook.

2. The rapid increase in BOD_7 toward the end of the cook seems to have approximately the same rate for all three types of cooks.

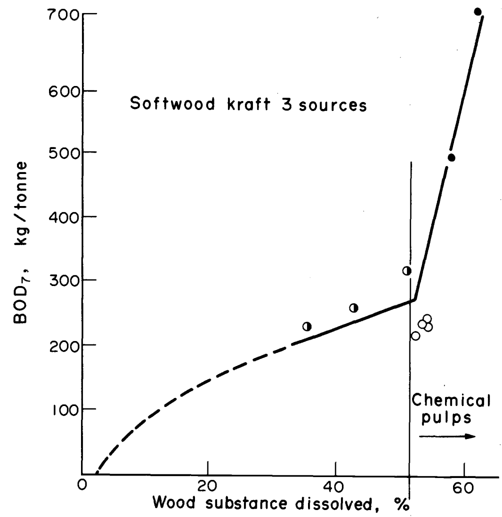

Fig. 7. The BOD_7-value of the spent liquor from softwood kraft pulping as a function of wood substance dissolved during the cook.

Now, what is the practical significance of these curves? The most important feature is no doubt the rapid increase toward the end of the cook. Small changes in pulp yield result in large fluctuations in the BOD_7 of the liquor. Even if the washing stage is very effective and obviously to some extent evens out the variations they still affect the effluent from the screening department. To minimize the effluent BOD_7 the pulp yield should be kept as high and constant as possible.

Today it is very unusual that the spent liquor from the cook is discharged. Instead it goes to evaporation and recovery of the cooking chemicals. The residual organic and inorganic substance that has not been removed in the washing is washed out in the screen and leaves with the screen room effluent.

Earlier, when washing was done primarily to recover cooking chemicals the washing result was expressed as kg Na_2SO_4 leaving the washing stage with the pulp. Today we are more concerned about the discharges that result from the organic substance (Fig. 8).

Above *ca.* 10 kg Na_2SO_4 the relationship between BOD and Na_2SO_4 is linear but the curves are specific for pulp type, pulp Kappa number etc. At low washing losses the relationship becomes nonlinear. The cleaner the pulp the relatively more difficult it becomes to wash out organic substance. The same is valid for birch kraft pulps.

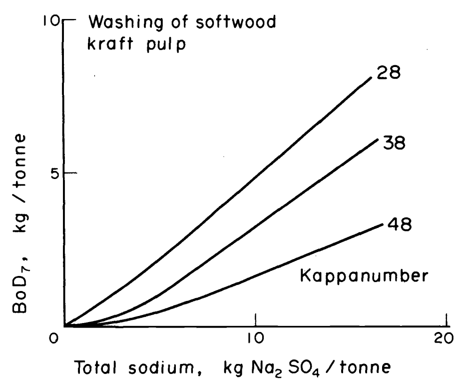

Fig. 8. The BOD_7-value of the liquor remaining with the pulp as a function of degree of washing (expressed as kg Na_2SO_4/tonne). Softwood kraft pulp of Kappa number 28, 38 and 48.

Before leaving the washing-recovery part of the system the BOD-values of the condensates should be considered. During the blow of the cook some of the low molecular weight components of the spent liquor flash off and combine with the digester condensate. For continuous digesters this amounts to 3 kg BOD_7/tonne (Table 2).

Table 2. BOD_7 in condensates from softwood kraft and sulphite pulping

Source	Kraft, kg/tonne Batch	Kraft, kg/tonne Cont	Sulphite, kg/tonne 85†	Sulphite, kg/tonne 95†
Digester	4·9	2·6	5	5
Evaporation	5·5	9·0	22	25
Total	10·4	11·6	27	30

†Degree of washing, %.

For batch digesters it is around 5 kg BOD_7/tonne and the same for kraft and sulphite pulping.

In the evaporation of kraft spent liquor 5 and 9 kg BOD/tonne respectively for batch and continuous digesters goes to the condensates.

In sulphite pulping the total amount of low molecular weight compounds on the degree of washing. At 85% degree of washing 22 kg BOD/tonne goes to the evaporator condensates and at 95% the corresponding figure is 25 kg/tonne.

Bleaching of kraft pulps

In a modern kraft mill with a high washing efficiency and with condensate treatment the bleach plant effluent often presents the highest pollution load. In addition, the bleach plant effluent also normally has a large volume. A number of factors are of importance for the pollution load from the bleach plant; e.g. the washing loss of the incoming pulp, the lignin content of the unbleached pulp, and the bleaching conditions.

A high washing loss of the incoming pulp leads to a high discharge of BOD and colour from the first two bleaching stages. In Fig. 9 the colour of the effluent from the bleaching of a birch kraft pulp is shown. Normally the total colour from the C and E-stages is around 50 kg/tonne.

When the washing loss increases the colour increases in both the chlorination and alkaline extraction stage effluent. In these laboratory bleachings the washing loss was simulated by addition of black liquor. It is interesting to note that the increase in colour is higher than could be expected from calculations when the colour of the black liquor was added to that of the effluent (the line "theoretical"). Components in the black liquor thus react to more intensely coloured compounds during the chlorination.

Both the charge of chlorine in the chlorination and the charge of alkali in the extraction stage influence the pollution load (Fig. 10). At high chlorination temperature an increase in the charge of chlorine leads to a marked increase in the effluent BOD_7. The effect is small, however, at normal temperature and especially when chlorine dioxide is added.

The final pH of the alkaline extraction stage is in most instances kept above 10 (Fig. 11). At lower pH-values the dissolution of chlorinated and degraded lignin from the pulp rapidly decreases. This leads to an increased bleaching chemical demand in the later stages. Within the operating range there is, however, a clear effect on the colour from a change in the charge of alkali.

The total BOD from a bleach plant for fully bleached softwood kraft pulp is around 15 kg/tonne (Table 3). The discharge is evenly distributed on chlorination, first extraction and the final bleaching stages. The total colour is normally *ca.* 170 kg Pt/tonne. Nearly the entire colour comes from the first extraction stage.

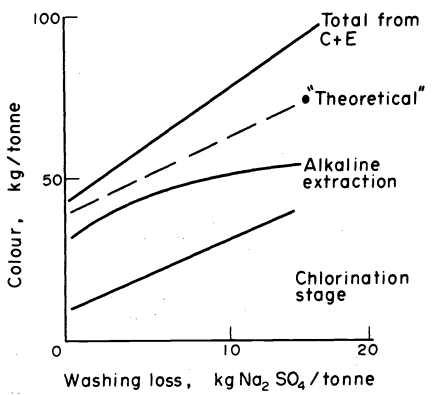

Fig. 9. The colour of the chlorination and alkaline extraction stages effluent as a function of the degree of washing of the unbleached pulp. Birch kraft pulp with a Kappa number = 16.

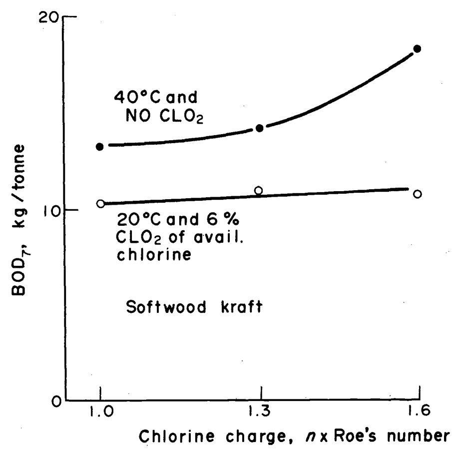

Fig. 10. The BOD_7-value of the chlorination stage effluent as a function of the charge of chlorine. Bleaching of softwood kraft pulp.

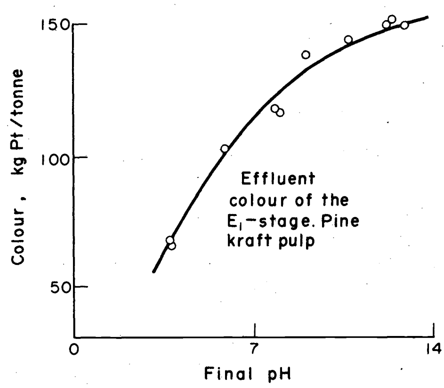

Fig. 11. The colour of the alkaline extraction effluent as a function of the final pH of the stage.

Table 3. Bleach plant effluents

	Softwood kraft		Softwood sulphite	
Stage	BOD_7 (kg/tonne)	Colour (kg/tonne)	BOD_7 (kg/tonne)	Colour (kg/tonne)
C	5	10	6	25
E	5	150	5	40
Final Bleaching	5	10	1	5
Total	15	170	12	70

The BOD from the bleaching of sulphite pulp is 12 kg/tonne. The discharge from the first two stages is dominating. In sulphite pulp bleaching a fairly large part of the colour discharge comes from the first bleaching stage. Total colour is around 70.

The total discharge from chemical pulping

In Table 4 the BOD situation for kraft and sulphite mills with no environmental protection equipment except effective washing, evaporation and recovery of the cooking chemicals is summarized. The calculations have been made for 95 and 98% washing efficiency with respect to BOD_7. 98% efficiency for kraft mills corresponds to 12–14 kg Na_2SO_4/tonne pulp which is a fairly common washing result.

Table 4. BOD_7 Discharges from softwood kraft and sulphite pulping

	Kraft, kg/tonne		Sulphite, kg/tonne	
Operation	95†	98†	95†	98†
Barking			3	3
Evaporation	11	11	30	31
Screening	13	5	18	7
Bleaching	15	15	12	12
Accidental discharges	15	15	20	15
Total	54	46	83	68

†95 and 98% washing efficiency on BOD_7.

For sulphite mills 98% is an exceptionally good result. Even 95% is a very good result which only few mills can reach.

When adding the accidental discharges the total BOD from the kraft line is 54 and 46 kg/tonne. The corresponding figures for sulphite being 83 and 68 kg/tonne. With identical washing result the sulphite mill thus emits 20–30 kg BOD_7 more than the kraft mill. The main reason for this is of course the high BOD of the sulphite condensates.

To further reduce the discharge the following internal changes can be made. In the barking operation dry barking should be applied wherever possible. In those cases where wet barking is necessary the system should be closed with mechanical and chemical treatment of the circulating liquid.

The condensates can be stripped to reduce their BOD. In sulphite pulping the amount of acetic acid going to the condensates should be reduced by neutralizing the spent liquor.

The screen room effluent can be reduced by better washing, closed systems and maybe changed cooking conditions. The bleach plant effluent finally can be diminished by introducing oxygen bleaching and by changed bleaching conditions.

The accidental discharges can be reduced by having proper buffer volumes, by collection of spills, by routines for starting and stopping and by educating the mill personnel.

REDUCTION OF DISCHARGES

In the following a more detailed description is given of thin liquor neutralization and oxygen bleaching.

Oxygen bleaching

In Fig. 12 a closed system for cooking and oxygen bleaching is shown. Washing water is introduced on the radial washer following the oxygen stage and then brought counter-currently to the pulp flow to the brown stock radialwasher and the Hi-heat zone of the digester. The screening system is closed and there is a system for treating the rejects. The only pollutants from the system are those leaving with the oxygen bleached pulp.

The discharges from the final bleaching of the pulp is of course reduced by a more complete delignification in the oxygen stage. The lower limit for the delignification during oxygen bleaching is set by pulp quality criteria (Fig. 13). Concurrently with the delignification a degradation of carbohydrates occur. This degradation can to some extent be controlled by adding inhibitors in the form of soluble magnesium compounds–magnesium complexes.

The practical lower limit is for market pulps around Kappa number 15. Above that only marginal changes in paper characteristics (like tear factor) can be observed.

As a rule oxygen bleaching reduces the discharges of

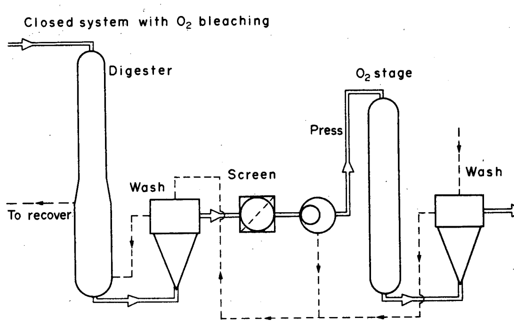

Fig. 12. A system for O_2-bleaching integrated into the washing system.

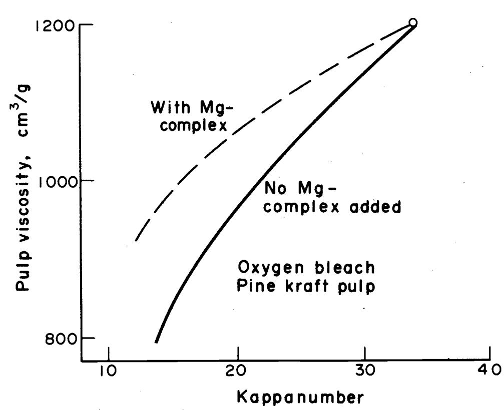

Fig. 13. The intrinsic viscosity of oxygen bleached pine kraft pulp as a function of the Kappa number of the bleached pulp.

Table 5. Oxygen bleaching—colour kg Pt/tonne

Stage	Unbleached†	O_2-bleached‡
C	40	20
E	140	90
HDED	16	7
Total	196	117

†Kappa number 30·1.
‡Kappa number 16·8.

BOD_7 and colour from the bleach plant by *ca.* 50% (Table 5).

Two pulps—one oxygen-bleached to Kappa number 16·8 and one unbleached Kappa number 30·1—were bleached with the sequence CEHDED. The unbleached pulp had an effluent colour of 196 and the oxygen-bleached 117 kg/tonne. Especially the discharge from the extraction stage decreased.

Neutralization of sulphite condensates

The condensates are responsible for a major part of the BOD-discharge from a sulphite mill. To a large extent the BOD is due to acetic acid flashing from the liquor to the condensates during evaporation. By neutralizing the liquor before evaporation the acetic acid reacts to acetates which stay in the liquor. A simplified flow-sheet for a system for neutralization of Mg-base liquor is shown in Fig. 14.

To minimize evaporation costs dry MgO is fed to the thin liquor. The pH of the liquor should preferably be kept above 6. Some retention time should also be provided before the liquor enters the evaporation.

When the pH of the liquor is increased more of the acetic acid stays in the liquor (Fig. 15). At pH-values around 6·5 almost all the acid remains. Normally the neutralization is carried to 85% efficiency.

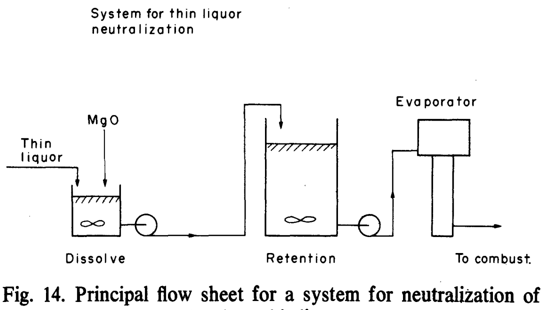

Fig. 14. Principal flow sheet for a system for neutralization of Mg-base thin liquor.

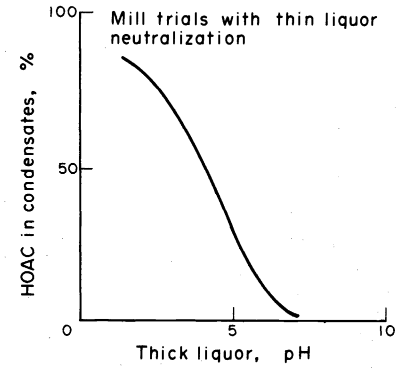

Fig. 15. The percentage of acetic acid carried over to the condensates from the thin liquor as a function of the pH of the thick liquor.

Table 6. Neutralization of thin liquor—BOD_7-reduction in condensates

Type of cook	No neutralization (kg/tonne)		Neutralization (kg/tonne)	
	Total	HOAC	Total	HOAC
Acid	30	19	13	2
Bisulphite	27	16	13	2

The result of spent liquor neutralization on the BOD of the condensates from an acid sulphite and a bisulphite cook is shown in Table 6.

Without neutralization the BOD is 30 and 27 respectively. With neutralization it decreases to 13 of which only 2 kg BOD_7/tonne originates from acetic acid.

CONCLUDING REMARKS

As is evident from this survey our knowledge of processes and discharges have improved tremendously during the last years. Likewise many new internal and external methods to reduce the discharges have been developed.

We need, however, more basic knowledge on the pollutants and their relationship to the processes. We also need effective and economical methods to take care of some specific effluents notably the bleach plant effluent. Future research and development activities should be directed towards these goals.