Oxygen delignification with magnesium as base: a good solution for sulfite pulp

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ABSTRACT *We conducted experiments to compare the use of magnesium as opposed to sodium as base in oxygen delignification. The chemical base used in the oxygen stage should be the same as that used for chip digestion. In other words, for magnesium-based sulfite pulping, $Mg(OH)_2$ or MgO should be used in oxygen bleaching. Pulp that is oxygen delignified using magnesium has a higher yield but a lower average degree of polymerization than pulp oxygen delignified using sodium, because more hemicellulose is dissolved at higher pH. Between the sodium and magnesium used as base for oxygen delignification, there are no appreciable differences in pulp strength, pulp beatability, light-scattering coefficient, and paper apparent density.*

KEYWORDS
Bleaching
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Chlorination
Chlorine bleaching
Chlorine dioxide
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Multistage process
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Oxygen
Peracetic acid
Sequences

Oxygen delignification is one of the most effective and economic techniques for reducing the environmental load from the bleach plant (*1*). Oxygen delignification greatly decreases the lignin content in the pulp prior to final bleaching. Less bleaching chemicals are required in the subsequent bleaching stages, with the result that smaller quantities of chlorinated organic substances are produced.

The effluent from the oxygen stage can be incorporated into the chemical recovery system of the pulp mill. The organic substances dissolved in the effluent can be burned, with the mill gaining the benefit of energy generation. Because of this effluent recovery, the color of waste water discharged from the bleaching plant will also be considerably improved.

As we know, the base used for oxygen delignification in alkaline pulping operations is sodium hydroxide. However, sulfite pulps are often cooked with a magnesium base. In this work, we conducted experiments to compare magnesium and sodium as bases used in oxygen delignification, with regard to pulp qualities and chemical recovery.

Result and discussion

Oxygen delignification reaction

$Mg(OH)_2$/MgO is barely soluble in water [0.086 g of MgO/L of hot water (*2*)]. Mixed with unbleached sulfite pulp, $Mg(OH)_2$/MgO adjusts the pH to the range of 8–9. This basicity is much lower than that in oxygen bleaching

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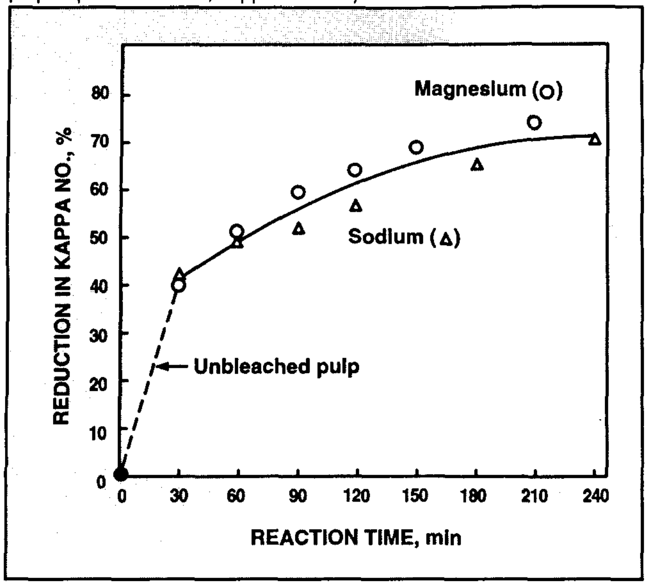
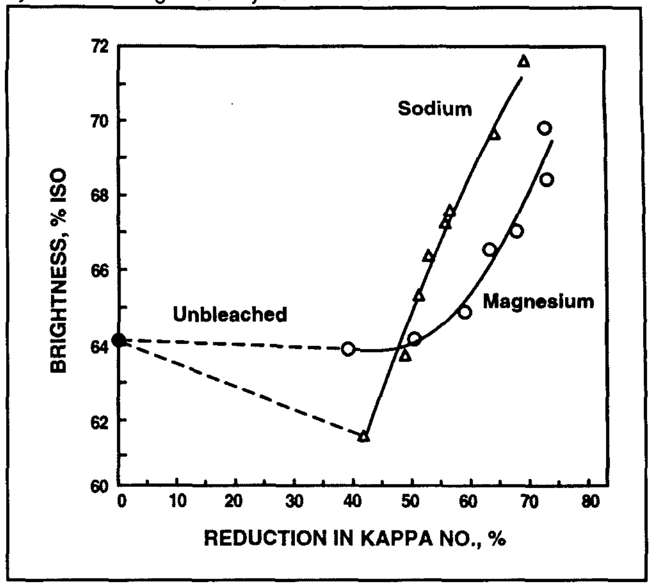
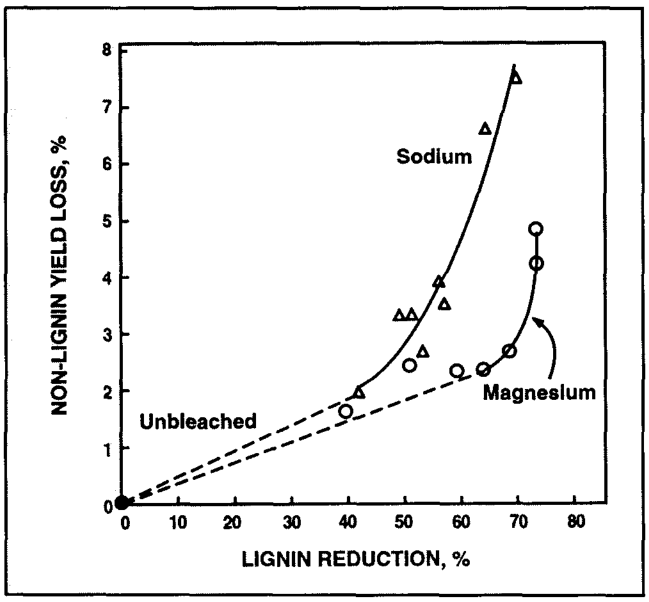
1. Oxygen delignification rates for NaOH and $Mg(OH)_2$ as base (mixed pulp of pine and birch, kappa no. 25.8)



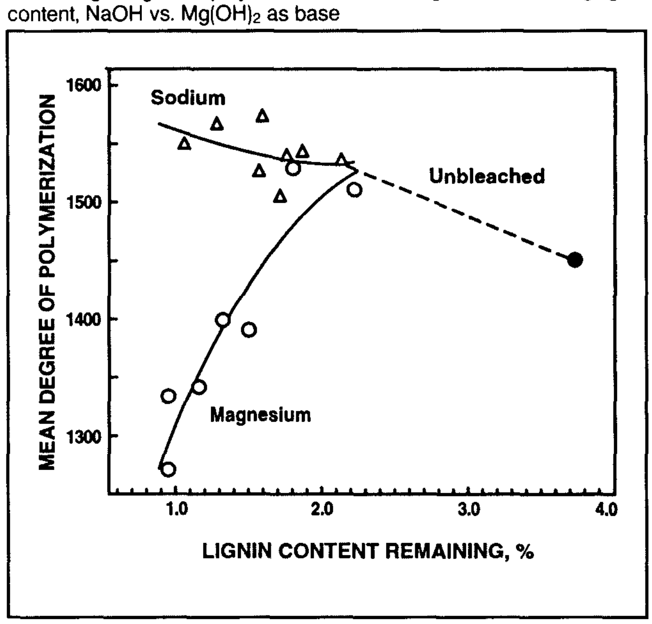
2. Brightness development during oxygen bleaching with sodium hydroxide or magnesium hydroxide as base



3. Nonlignin yield loss with delignification for NaOH vs. $Mg(OH)_2$ as base



4. Average degree of polymerization according to the remaining lignin content, NaOH vs. $Mg(OH)_2$ as base



with NaOH, which has a pH of about 12. Therefore, oxygen delignification with magnesium as base has to be carried out at a higher temperature (120-40°C) than the temperature used for oxygen delignification with sodium as base (90-110°C), if the reaction tower is to be as productive. However, $MgSO_4$ as a cellulose protector is no longer required (*3*). (Mg SO_4 is used in oxygen delignification with sodium as base.)

For oxygen delignification at 135°C using magnesium hydroxide as base, a 90-min retention time will reduce the kappa number by 50-60%, depending on process variables such as oxygen pressure and the amount of base used. This drop in kappa number roughly corresponds to oxygen delignification at 105°C with sodium hydroxide as base, as shown in **Fig. 1**.

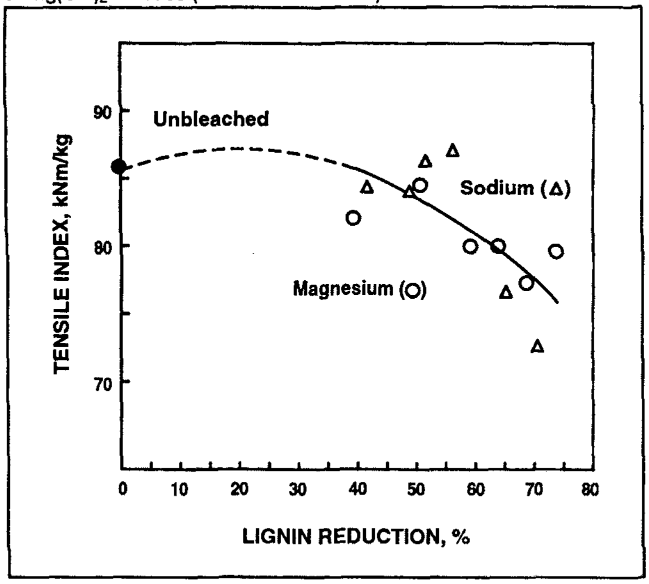
Brightness

Figure 2 presents brightness development based on the extent of delignification during oxygen bleaching with either sodium hydroxide or magnesium hydroxide as base. The raw material used is a bisulfite pulp of pine and birch.

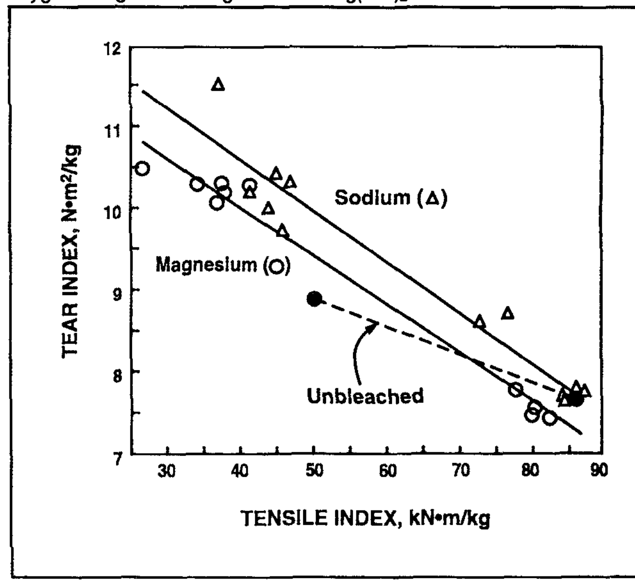
As the figure shows, with magnesium hydroxide, pulp brightness is better than with sodium hydroxide in the first part of the reaction. However, after a reduction in kappa number of about 50%, the pulp brightness with sodium hydroxide as base becomes superior to that with magnesium hydroxide. For softwood, this turning point will come later (*4*).

This phenomenon may be explained if we assume that, during oxygen delignification of sulfite pulp, there is a competition between the two reactions of delignification and alkaline darkening. The alkaline darkening reaction is profoundly favored by

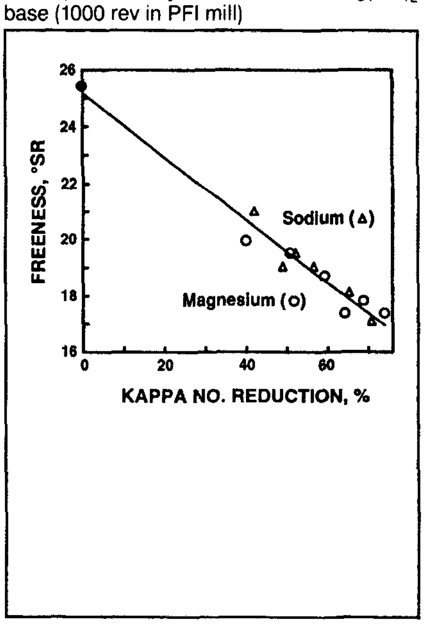
5. Tensile index as oxygen delignification progresses, using NaOH or $Mg(OH)_2$ as base (1000 rev in PFI mill)



6. Relationships between tear index and tensile index for pulps oxygen-delignified using NaOH or $Mg(OH)_2$ as base



7. Pulp beatability, NaOH base vs. $Mg(OH)_2$ base (1000 rev in PFI mill)



higher pH. On the other hand, higher alkaline conditions also help to dissolve the lignin fragments, resulting in a brightness improvement (*4*).

(The brightness sulfite pulp drops during the first 15-30 min of reaction.)

Bleaching yield

As stated, oxygen delignification takes place at a higher pH with sodium than with magnesium. As **Fig. 3** shows, this difference results in greater yield loss for the case with sodium than for the case with magnesium, compared at the same degree of delignification.

The ordinate axis in Fig. 3 indicates the nonlignin yield loss. This quantity is the yield loss minus the yield loss caused by lignin reduction (where percent lignin = 0.147 × kappa no.).

Sulfite pulps cooked in acidic liquors contain large amounts of hemicellulose. This hemicellulose has not been subjected to pH conditions as rigorous as those in alkaline oxygen delignification with sodium as base, and this hemicellulose has not been subjected to alkaline stabilization. Therefore, it is susceptible to alkaline dissolution.

Pulp viscosity

Sulfite pulp that has been oxygen-delignified with sodium as base showed higher viscosity than that oxygen-delignified with magnesium as base. **Figure 4** presents the average degree of polymerization of pulp against the remaining lignin content. The degree of polymerization is calculated according to Eq. 1:

$$DP^{0.905} = 0.75\ V \qquad (1)$$

where

DP = degree of polymerization

V = pulp intrinsic viscosity, dm^3/kg

The difference in the curves is easily explained by the fact that more hemicellulose is dissolved during oxygen delignification with sodium. The dissolution of such low-DP hemicellulose increases the average degree of polymerization of the remaining pulp. However, lower viscosity or polymerization does not necessarily mean low pulp strength.

Pulp strength

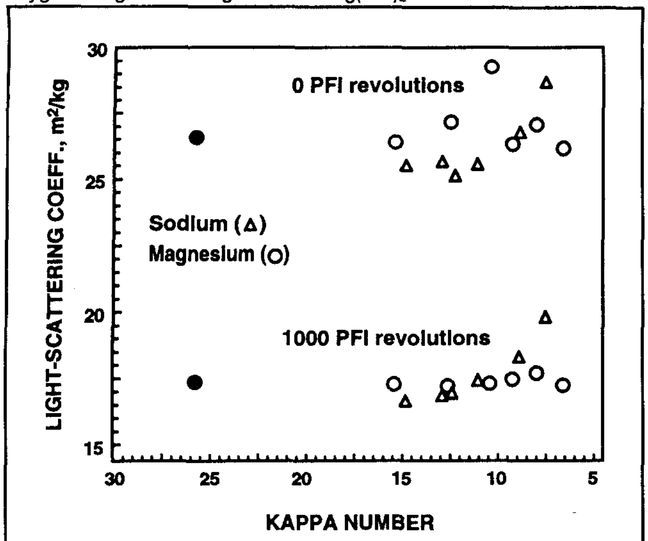
Figure 5 indicates that pulps oxygen-delignified using either sodium or magnesium have about the same tensile strengths at the same degree of delignification. However, pulp from the magnesium-base process may have somewhat lower viscosity or lower average degree of polymerization. This finding supports our hypothesis that lower viscosity results from hemicellulose dissolution rather than from damage to cellulose.

Figure 6 presents the relationships between tear index and tensile index for pulps oxygen-delignified to various percentages of delignification in the range of 35–75%, for both sodium and magnesium used as bases. The difference between these pulps is slight, which may be explained by the fact that the sodium-base oxygen-delignified pulp has a lower yield than magnesium-base oxygen-delignified pulp at the same delignification. More cellulose per unit of pulp results in a somewhat higher tear index.

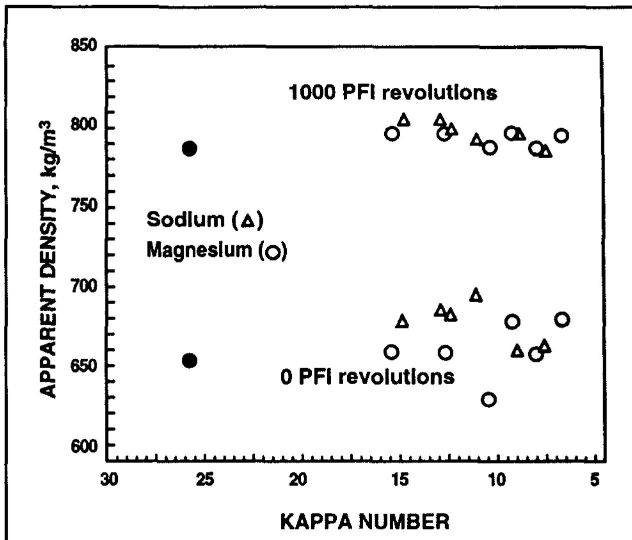
Other pulp properties

Between sodium and magnesium used as base, there are no significant differences in other properties such

8. Pulp light-scattering coefficients for unbleached pulp and pulps oxygen-delignified using NaOH or $Mg(OH)_2$ as base



9. Apparent densities of paper handsheets, NaOH vs. $Mg(OH)_2$ as base



as refinability, pulp-scattering coefficient, and the apparent density of the paper produced.

Two pulps oxygen-delignified using sodium hydroxide or magnesium hydroxide reached the same Schopper-Riegler freeness after beating in a PFI mill (1000 rev) at the same degree of delignification, as illustrated in **Fig. 7**. This figure also shows that the oxygen-delignified pulp is somehow more difficult to beat than the unbleached pulp as a result of less hemicellulose remaining.

Figure 8 shows that there is no significant difference in light-scattering properties between unbleached pulp and the pulps oxygen-delignified with sodium or with magnesium as base, before and after beating. Furthermore, the handsheets formed from these pulps have similar densities, as shown in **Fig. 9**.

Chemical recovery

Figure 10 shows the scheme of the chemical recovery system for a mill using the sulfite pulping process with magnesium as base. Out of the recovery furnace, most of the magnesium ions are in the form of MgO dust, and this major portion of the magnesium is reused for generating cooking liquor.

The recovery system will be simpler if a magnesium-base oxygen-delignification stage is employed rather than a sodium-base oxygen-delignification stage (*3*, *5*). The effluent discharge from the oxygen stage can easily be incorporated into the recovery system of the pulp mill. **Figure 11** illustrates the strategy for incorporating the effluent from the oxygen stage into the recovery system. To decrease the effluent volume and thus the load on the recovery system, the mill can use the effluent from the oxygen stage for washing unbleached pulp before incorporating it into the recovery system.

Nevertheless, if sodium hydroxide is used in the oxygen stage for sulfite pulps cooked with magnesium as base, problems will be encountered as a result of the fact that sodium-magnesium salt deposits on the tubes in the recovery furnace will have lower melting points than pure magnesium salts. This problem will be even more acute if the mill's water system is closed. Besides the troubles for the recovery furnace, sodium salts should be bled out before the recovered magnesium chemicals are reused for cooking, which results in more work and in severe loss of cooking chemicals (*3*, *5*, *6*).

Therefore, the benefits of oxygen delignification can only be fully achieved when the base used for oxygen bleaching is the same as that used for cooking. In other words, magnesium oxygen delignification technology is preferred for sulfite pulps cooked using magnesium as base.

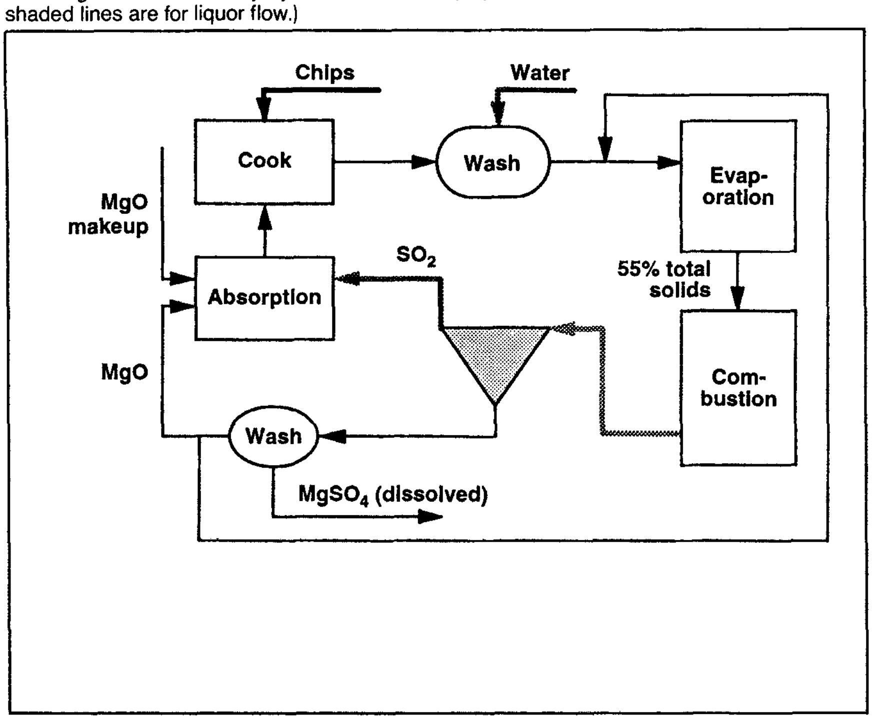
Conclusions

For sulfite pulping with magnesium as base, an oxygen-delignification stage should have magnesium as the base rather than sodium. This match results in a much simpler recovery system.

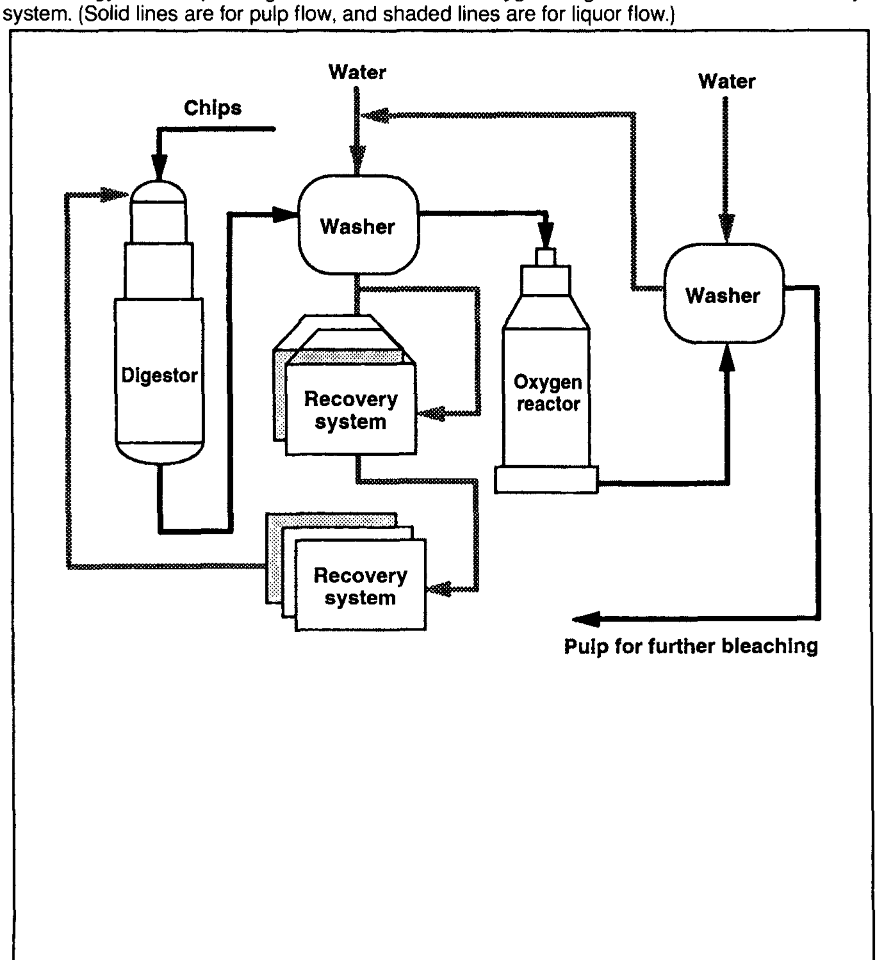
Sulfite pulp can be delignified without strength problems to as high as a 50-70% reduction in kappa number by oxygen delignification using either magnesium hydroxide or sodium hydroxide as base.

Pulp that is oxygen delignified using sodium has a lower yield but a higher average degree of polymerization than pulp oxygen delignified using magnesium, because more hemicellulose is dissolved at higher pH. Between the sodium and magnesium bases used for oxygen delignification, there are no appreciable differences in product properties such as pulp strength, pulp beatability, light scattering, and paper apparent density.

10. Diagram of a recovery system of a sulfite pulp mill. (Solid lines are for pulp flow, and shaded lines are for liquor flow.)



11. Strategy for incorporating the effluent from the oxygen stage into the chemical recovery system. (Solid lines are for pulp flow, and shaded lines are for liquor flow.)



Experimental procedures

Raw material

We used a mill-cooked bisulfite pulp. This pulp was a mixture of pine and birch chips, with a ratio of pine to birch of about 6 to 4. Magnesium hydroxide was used as the base. The kappa number was 25.8, the viscosity was 968 dm^3/kg (71.4 cp), and the brightness was 64.2%.

Oxygen stage

Pulp at 10% consistency was mixed with either NaOH or $Mg(OH)_2$ as base and was transferred to the autoclave, which was pressurized with oxygen to 4 bar at room temperature. The autoclave cylinders were rotated in an oil bath that had been previously heated to reach the reaction temperature of 105°C for sodium hydroxide base or the reaction temperature of 135°C for magnesium hydroxide base. At the end of each reaction time, the autoclave cylinders were rapidly cooled in a water bath, and the pulp was washed.

Pulp analysis methods

Pulp brightness was measured by SCAN-C 11:75, and viscosity was determined by SCAN-C 15:62. Kappa numbers were determined by SCAN-C 24:67. COD was evaluated according to CPPA Standard H.3p.□

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