Use of wetting agents to improve flotation deinking with magnesium oxide

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In the past, alkali such as magnesium oxide and calcium hydroxide have been found to be not as effective in causing fibre swelling or in alkaline flotation deinking as sodium hydroxide. The addition of a wetting agent together with magnesium oxide has been found to increase fibre swelling to near that obtained with sodium hydroxide. The chemistry of the wetting agent was found to be important.
The addition of wetting agent with magnesium oxide in deinking using a Lamort laboratory deinking cell was also found to achieve similar deinking efficiency to that achieved with sodium hydroxide as the alkali source. Similar brightness levels were achieved, but the results indicated that slightly better ink removal efficiency occurred with the magnesium oxide system. The effluent from the magnesium oxide system was also found to have lower dissolved salts content, which is an advantage to mills where salinity is an issue.

Keywords
Flotation deinking, magnesium oxide, wetting agents, ink detachment, fibre swelling, water retention value

Deinking of wastepaper has become increasingly important in recent years and much progress has been made in improving the deinking process. Deinking of newsprint and magazine mixtures involves two key processes: a pulping stage in which ink detachment occurs, and a flotation or separation stage in which ink separation and removal occurs.

The pulping process defibres the paper and disperses the fibres into water to form a pulp slurry. It also detaches the ink from the fibres. This is believed to occur via fibre swelling with alkali.

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Alkaline conditions cause the fibres to swell, take up water and become more flexible. This causes the rigid ink particles on the fibre surface to flake away. This process is enhanced by the saponification of esters in the ink binders under the alkaline conditions (*1*).

There are two possible explanations for this fibre swelling. Many researchers (*2-8*) suggest that the acidic groups present in the fibres, namely carboxyl, sulfonic, phenolic and hydroxyl groups, dissociate in aqueous solution and release counterions. This creates an ion imbalance within the cell wall. Water is drawn into the cell wall by osmotic pressure to equilibrate the ion imbalance. This theory, however, does not explain fully some of the experimental data (*9*). Others (*10*) suggest that differences in swelling behaviour between various alkalis are a result of changes in the hydration shells and the structure of the water molecules around the various ions. This 'flickering cluster theory' has been used to explain the swelling of cellulose (*10*).

Traditionally sodium hydroxide is used as the swelling agent and alkali source in flotation deinking. A high pH is generally required, which results in a highly alkaline effluent that needs to be neutralised producing high salinity. For mills such as Norske Skog Paper, Albury, which have restrictions on the quality of liquid effluent, the high salinity is a problem.

Other alkalis have been found not as effective as sodium hydroxide in deinking and fibre swelling (*11*). This paper describes work undertaken to investigate the effects of different alkali sources and wetting agents on fibre swelling and flotation deinking of newspaper and magazine mixtures compared to the use of conventional sodium hydroxide and fatty acid.

EXPERIMENTAL

Samples of recycled fibre, kraft, TMP and Cold Caustic Semichemical (CCS) pulps were obtained from Norske Skog Paper, Boyer Mill. Newsprint was obtained from the Mercury Press, Hobart. NaOH, MgO, $CaCl_2$ and DTPA were all analytical grade from Aldrich Chemicals. Peroxide was 30% m/v and was obtained from British Drug House. Sodium silicate was technical grade from ChemSupply. Surfactants and wetting agents were obtained from ORICA Chemicals. The surfactant used for reference deinking was a fatty acid potassium soap, while the wetting agents were primary alcohols or alcohol based detergents.

Water retention values

Sufficient pulp, chemicals and deionised water were added to bring the pulp slurry to a stock concentration (s.c.) of 2.5%. The pulp slurry was stirred with a magnetic stirrer for 2 hours then filtered through a wire mesh. The filtered pulp slurry was centrifuged at 2750 rpm for 30 minutes, after which the pulp was weighed, dried and reweighed. The water retention value (WRV), expressed as g water/g o.d. pulp, was determined as follows:

WRV (g/g) = (wet pulp weight - dry weight) / dry pulp weight [1]

Surface tension measurement

A 1% solution of the surfactant was prepared. The surface tension of solutions of varying concentrations, from 0.0005% to 0.05%, was measured using an Analite Surface Tension Meter, which is based on the Wilhemy Plate Method.

Deinking

A 70: 30 mixture of newsprint (aged 2-3 months) and magazines (aged 1-3 years) was pulped in a Lamort laboratory deinker at 50°C and 9% s.c. for 20 minutes using 1% NaOH, 1% H_2O_2, 1% sodium silicate, 0.2% DTPA and 0.04% surfactant. Flotation was carried out at 1% s.c. for 6 minutes using 150 ppm soluble calcium and 0.2% surfactant. Figure 1 shows the Lamort laboratory deinking unit.

Handsheets were prepared from the pulp, after pH adjustment to pH 6, according to AS 1300. 2035: 1993. An Elrepho 2000 Datacolour was used to measure ISO brightness, R700, L*, a* and b*.

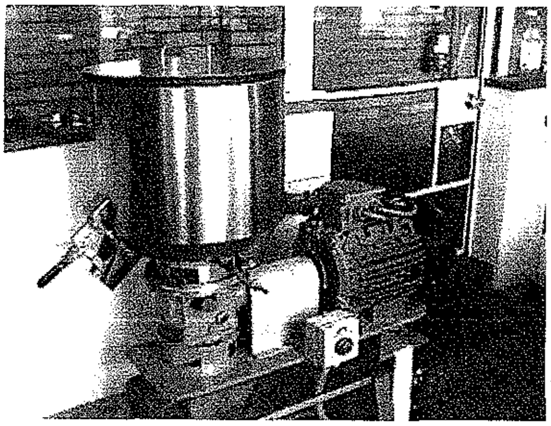

Fig. 1 Lamort laboratory deinking unit.

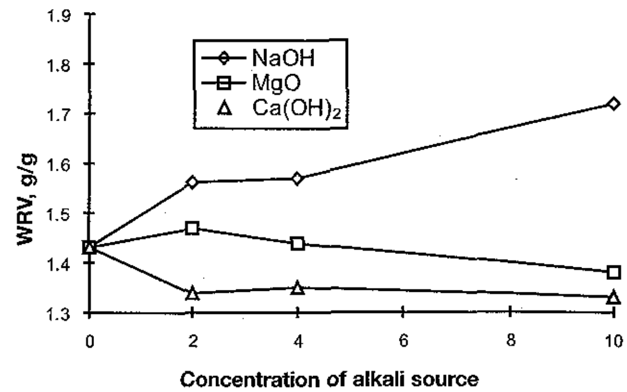

Fig. 2 Effect of different alkalis on the water retention value of TMP pulp.

Conductivity of the filtrate was measured using a Phillips conductivity meter.

RESULTS AND DISCUSSION

Fibre swelling

Effect of different alkali: The water retention value method, developed by Scallan and Carles (*12*), was used to measure fibre swelling. The effect of different alkalis on fibre swelling at varying concentrations of the alkali source was investigated. As shown in Figure 2, the water retention value for TMP pulp, using magnesium oxide and calcium hydroxide, was lower than when using sodium hydroxide, indicating that sodium hydroxide is a more effective alkali for fibre swelling. In the case of sodium hydroxide, the WRV was found to increase as the concentration of sodium hydroxide increased. A slight increase in WRV was observed at 2% MgO, but as the MgO concentration increased further a decrease in WRV occurred. Calcium hydroxide was found to cause a decrease in WRV of the TMP pulp.

The pulp slurry pH was measured and is presented in Table 1.

Addition of both calcium hydroxide and sodium hydroxide increased the pH of the pulp slurry, while the limited solubility of MgO (0.00062 g/100 mL at room temperature and 0.0086 g/100 mL in hot water (*13*)) resulted in a lower pH. These results indicate that fibre swelling is not strictly related to pH but is also dependent on the alkali source. The addition of calcium hydroxide produced the same pH values as the addition of sodium hydroxide, however calcium hydroxide produced a decrease in WRV of the TMP.

One possible explanation for the difference in behaviour between the different alkalis is the differences in the solvation shell around the different cations. Each cation has two hydration regions around it as shown in Figure 3. The first region, know as the 'A' region, is a highly structured layer of immobile clusters of associated water molecules that are immediately adjacent to the charged ion. The second region of more mobile highly reactive monomeric water molecules, which are further from the cation, is known as the 'B' region (*10*). The magnesium ion, having a higher charge/size ratio than the sodium ion, has a smaller 'B' region than sodium ion and so produces less swelling. The calcium ion has a smaller charge/size ratio than the magnesium ion, which would suggest it also has a larger 'B' region than the magnesium ion and so should promote more fibre swelling. The experimental results do not reflect this. One possible explanation for the behaviour of calcium is that it is less hydrolysed than the magnesium ion, so there is less water in both the A and B regions around the calcium ion compared to magnesium.

Effect of wetting agent

Figure 4 shows the effect on WRV of adding different wetting agents to TMP pulp in the presence of MgO. The wetting agents were added in varying concentrations to the pulp, which was then soaked for 2 hours with 2% MgO. Wetting agent WA 1 was found to increase the WRV of TMP at 0.5% addition. Higher concentrations of WA 1, above 0.5%, resulted in a decrease in WRV. The other wetting agents either decreased the WRV of the pulp with MgO or maintained the WRV.

Experiments were conducted in the absence of MgO to investigate the effect of the wetting agent alone on WRV to see if the observed behavior in Figure 4 was a result of the addition of the wetting agent only and not the alkali plus wetting agent. As shown in Figure 5, either very little change or a decrease in WRV occurred for the addition of the other wetting agents. Although WA 2 showed an increase at 2.0% addition, above the 1.0% addition,

Table 1
Pulp slurry pH at varying alkali concentration.

Addition	Sodium Hydroxide	Magnesium Oxide	Calcium Hydroxide
0%	4.47	4.47	4.47
2%	11.93	10.20	11.67
4%	12.24	10.62	11.67
10%	12.74	10.66	12.53

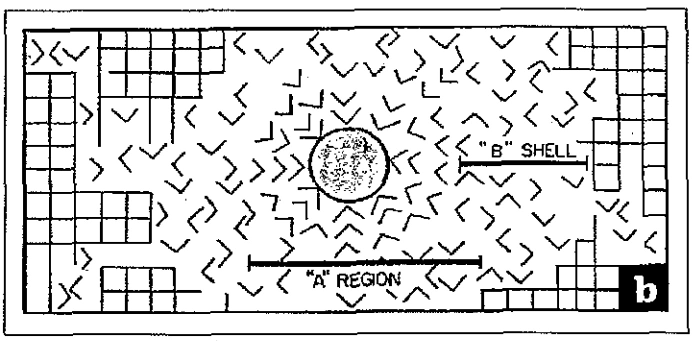

Fig. 3 Diagram of hydration shells around a cation.

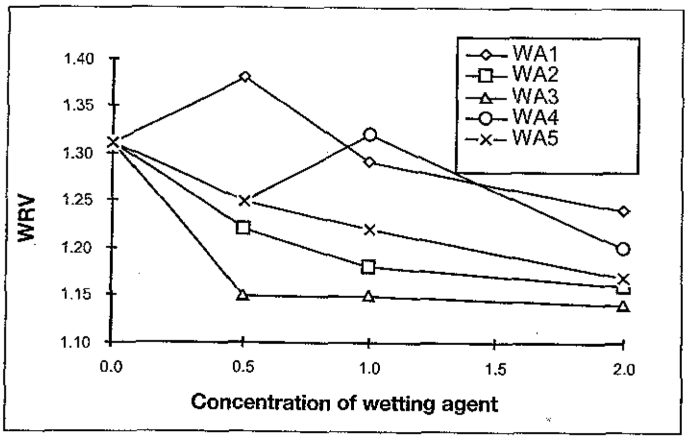

Fig. 4 Effect of wetting agent on the WRV of TMP pulp in the presence of 2% MgO

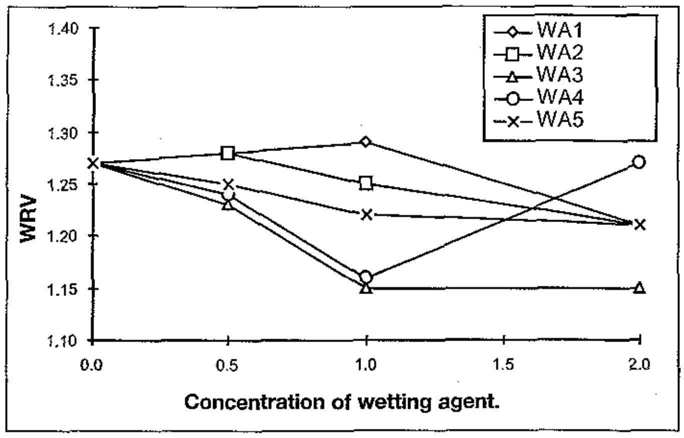

Fig. 5 Effect of wetting agent on the WRV of TMP pulp in the absence of MgO.

no further increase in WRV above the original WRV of the pulp occurred. The results in Figure 5 thus suggest that the wetting agent by itself is not causing an increase in WRV of the pulp.

Further experiments with WA1, at concentrations in the region of 0.1% to 1.0%, were conducted (Fig. 6). A maximum in WRV was observed between WA1 additions of 0.1% and 0.3% on o.d. fibre.

It is believed that the increase in WRV that occurred at 0.1% – 0.5% addition of WA1 to TMP with MgO is due to the wetting agent assisting in the penetration of the alkali into the fibre. The decrease in WRV with the other wetting agents, and at 1% addition of WA1, may be due to the wetting agents reaching and exceeding their critical micelle concentrations. This would affect the wetting ability of the wetting agents.

Flotation deinking

Effect of alkali: The addition of 1% NaOH to the flotation unit was found to produce a brighter pulp than when MgO was used (Fig. 7). NaOH was found to produce a brighter pulp after the pulping stage than MgO. One possible explanation for this is that bleaching of the pulp has occurred in the presence of NaOH, as no ink has been removed at the pulping stage and the brightness handsheets were prepared on filter paper. The MgO system was found to produce a greater difference between the pulping and flotation stage brightness than NaOH. The difference between the pulping brightness and flotation brightness is due to the ink removal that occurs during flotation as the peroxide is diluted in the flotation process and so has no effect on brightness (*11*).

The brightness of pulp from the deinker is controlled by two factors: the lignin chromophores and the ink. At wavelengths longer than 650 nm the reflectance spectra are controlled by the ink alone (*14*), therefore the contribution from the ink alone can be determined from the reflectance at long wavelengths. In this investigation, the reflectance at 700 nm was used as an indication of the ink remaining in the pulp, as this is the maximum wavelength available with the Elrepho Datacolour. This reflectance (R700 nm) can be combined with brightness to determine the separate influences of bleaching and ink.

Figure 8 shows the results of the reflectance readings at 700 nm (R700). As with the brightness results in Figure 6, NaOH produces a higher R700 compared to MgO.

Effect of wetting agent: The addition of wetting agent WA1 was found to improve the deinking efficiency of the MgO system in the Lamort deinker as shown in Figures 9 and 10. An addition level of 0.7% WA1 with 1.0% MgO was found to produce similar deinking to that with NaOH. It should be noted that the wetting agent did not improve the bleaching efficiency of the MgO system as demonstrated by the fact that the brightness and R700 results after pulping are not significantly different and are still lower than for the NaOH system. The wetting agent did appear to further improve ink removal as shown by the increase in brightness and R700 that occurred on addition of 0.7% WA1 with

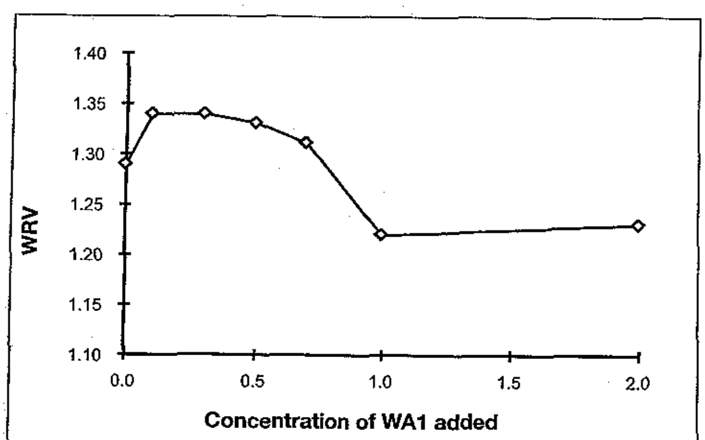

Fig. 6 Effect of wetting agent WA1 addition on the WRV of TMP in the presence of 2% MgO.

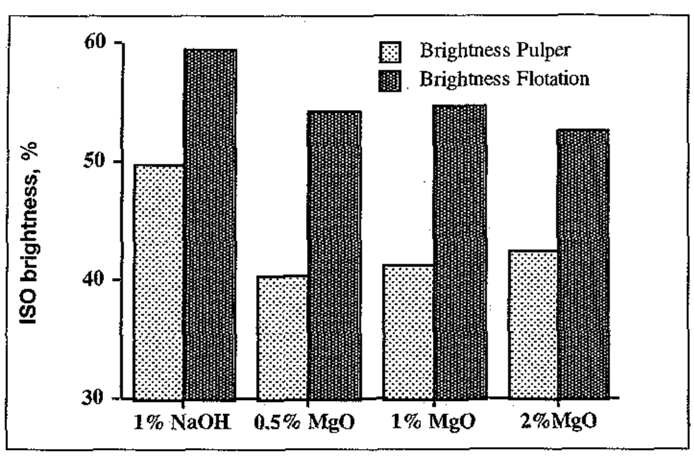

Fig. 7 Effect of various alkali sources on pulp brightness after pulping and flotation.

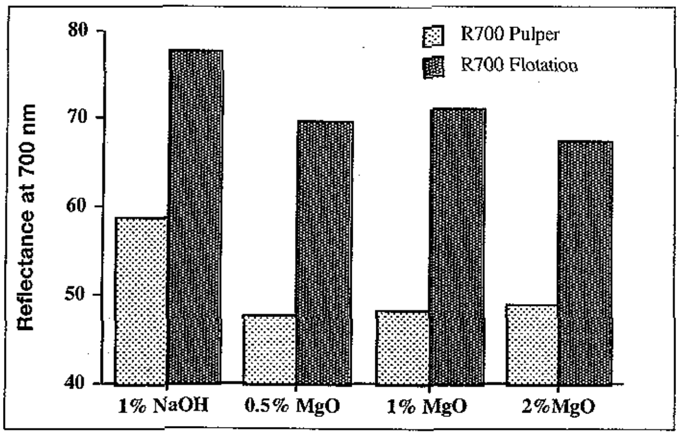

Fig. 8 **Effect of various alkali sources on reflectance R700 after pulping and flotation.**

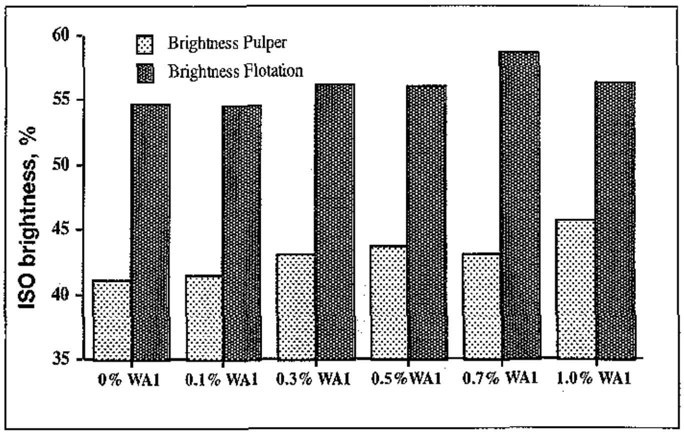

Fig. 9 **Effect of wetting agent and 1% MgO on brightness after pulping and flotation.**

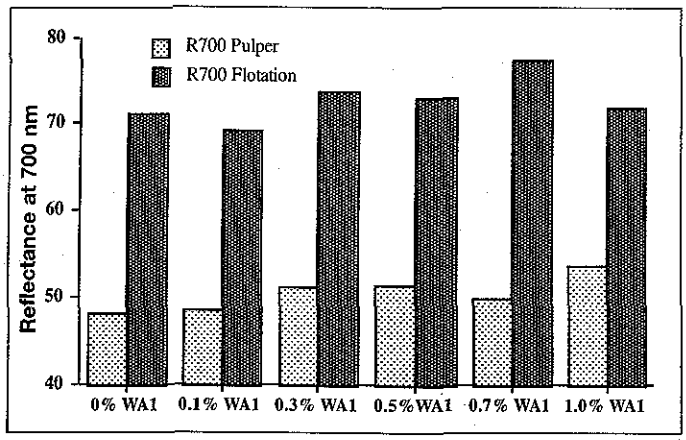

Fig. 10 **Effect of wetting agent and 1% MgO on R700 after pulping and flotation.**

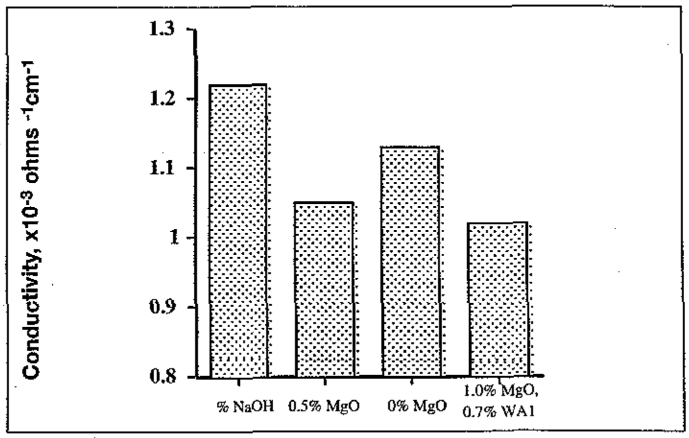

Fig. 11 **Effect of alkali source and wetting agent on conductivity of deinker effluent.**

1.0% MgO.

A series of experiments was also conducted at 0.5% MgO addition. It was found that a lower addition of wetting agent (0.5%WA1) gave the optimum brightness and R700.

Effect on deinking effluent: Figure 11 shows the conductivity measurements of the deinking effluent under various deinking conditions. The use of MgO does produce a less saline effluent as expected. The addition of wetting agent with MgO results in a lower dissolved salt content than for the conventional NaOH system.

Mill Trials

Several successful mill-scale trials have been conducted at the Norske Skog Albury recycled fibre plant using MgO as the sole alkali source and in conjunction with NaOH. Good brightness levels were achieved. Further laboratory work and mill trials are under way to optimise the system and study in more detail the various interactions occurring in the system.

CONCLUSIONS

- The addition of a wetting agent with MgO can improve the fibre swelling ability of MgO to the same as that achieved with NaOH.
- The type of wetting agent used affects the fibre swelling ability of MgO.
- The addition of a wetting agent in the flotation deinking process was found to improve the deinking efficiency when using MgO.
- MgO, and MgO with a wetting agent, produced a less saline effluent from the deinking process than when using NaOH.
- MgO has been found to successfully replace NaOH in the deinking process in mill trials.

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