Ink detachment and redeposition in alkali flotation deinking systems

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SUMMARY

The effective detachment of ink from the fibre surface and the prevention of its redeposition onto the surface before its removal in the flotation cell is important in deinking old newsprint (ONP). Magnesium Oxide (MgO) has been found to be a suitable replacement for sodium hydroxide (NaOH) in flotation deinking in the laboratory but not as effective in mill trials. The reason for the poorer performance is discussed in this paper.

The use of NaOH in the deinking cell was found to produce higher ISO brightness, due to its contribution to peroxide bleaching of the fibres, than when MgO is used as the alkali source. Traditional brightness measurements are thus a poor indication of the deinking efficiency. Measurements of R700 or ERIC are needed to better assess the effect of the different alkalis and other factors on deinking efficiency.

MgO has been found to cause more redeposition of ink onto the fibres than when NaOH is used as the alkali. To overcome this, the addition of soap to the pulper when using MgO is important. The addition of silicate and calcium were found to have a detrimental effect and appear to contribute to ink redeposition. Increasing the surface area of the MgO was found to increase its hydration and also improved the deinking efficiency of the MgO. The addition of the MgO as a hydrated slurry was also found to increase deinking efficiency.

Keywords

Flotation deinking, magnesium oxide, ink detachment, ink redeposition, ERIC effective residual ink concentration, ink removal efficiency

Electron Scanning Microscopy shows that liquid ink forms a thin film on the surface of fibres in newsprint and that there is no morphological characteristics to distinguish inked and non-inked areas (*1*). In the recycling of newsprint this film needs to be removed. This involves the detachment and separation of the ink from the fibre surface and then removal of the ink by either washing or flotation.

Various factors have been identified as affecting ink detachment. These include:

- Type of ink (*2,3*)
- Age of the printed paper (*4,5*)
- Ink application process (*3*)
- Mechanical energy (*6*)
- Chemicals added (*7-9*)

A combination of chemical and mechanical forces is responsible for the detachment of ink from the fibre surface. Most of the ink is believed to be held onto the fibre surface by weak van der Waals forces (*9*). This loosely bound ink is detached through mechanical shear and interfibre abrasion in the pulper. Ink in contact with the fibre surface directly is believed to be held by hydrogen bonding. The use of chemicals is needed to detach these ink particles. Several chemicals are used including alkali and surfactants. Alkali such as sodium hydroxide is added to swell the fibres and soften the ink through saponification. Surfactants are added to help wet the fibres to improve alkali penetration and also to help keep the detached ink dispersed and prevent it from redepositing.

Although there is much reported in the literature about the effect of alkali and other deinking chemicals in the ink detachment and redeposition process (*8,10,11,12-167,9,17-20*), all the work has focused on sodium hydroxide (NaOH) as the alkali source. Our research group has been investigating the use of alternative alkalis such as magnesium oxide (MgO) to replaced sodium hydroxide because of salinity problems (*21-23*) with the Recycle Fibre (RCF) effluent. Mill trials using MgO were conducted and resulted in slightly lower brightness. The poorer performance of MgO has been attributed to several possible reasons including poorer ink detachment and increased ink redeposition in the pulping stage, and also competition between calcium (Ca^{2+}) and magnesium ions (Mg^{2+}) interfering with the calcium fatty acid soap mechanism in the flotation stage.

This paper describes results of research undertaken to investigate ink detachment and ink redeposition in both the MgO and NaOH deinking systems. The importance of the fatty acid soaps and the effect of other deinking chemicals were also studied. Various MgO samples of differing surface area were also compared and the hydration kinetics was investigated in order to see if increasing the solubility of the MgO source might improve its deinking performance.

EXPERIMENTAL

Stock preparation and reagents

Newsprint was obtained from a single batch of specially printed Nornews 45.0 g/m^2 paper from Norske Skog's Boyer Mill. The newspaper was cut into 20 to 30 mm squares and stored in opaque plastic bags at room temperature. The paper was printed on one side only.

Technical grade MgO was supplied by ORICA and sodium silicate was obtained from PQ Silicates. Analytical grade DTPA (Aldrich chemicals), calcium chloride dihydrate (Aldrich chemicals) and hydrogen peroxide (30% solution) were also used. A sample of soap (Olinor 1511-C, 25% solution, Nopco Paper Technology) being used by the Albury mill was obtained from the mill. Two other samples of MgO of varying surface area were obtained from Causmag International. MgO slurry was prepared by adding the required amount of MgO to 100 mL of distilled water and allowing it to hydrate for two hours in a 50°C water bath.

Pulping and flotation deinking

A Lamort Deinkit laboratory pulping and flotation unit was used to carry out pulping and flotation deinking. Pulping was carried out using 750 g o.d. ONP, at a stock concentration (s.c.) of approximately 9% and 50°C with 20 minutes pulping. A 30-minute rest time before flotation was employed. In the flotation stage, the pulp was diluted to 1% s.c. with water at 50°C and a 6 minute flotation time was used. All experiments were carried out in triplicate.

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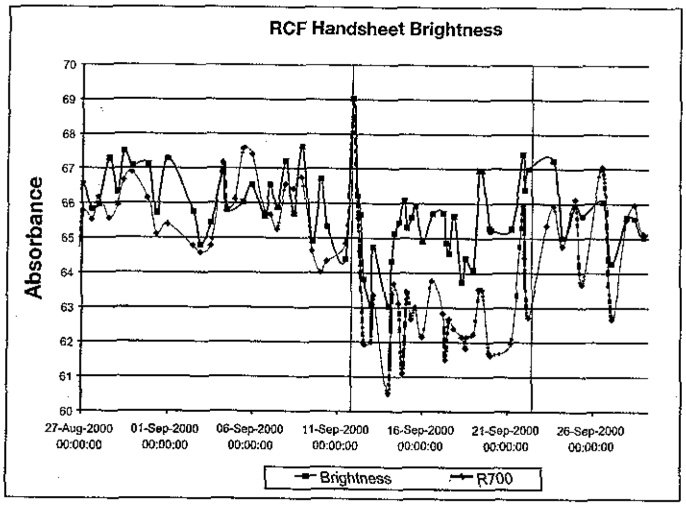

Fig. 1 RCF brightness and R700 during MgO mill trial.

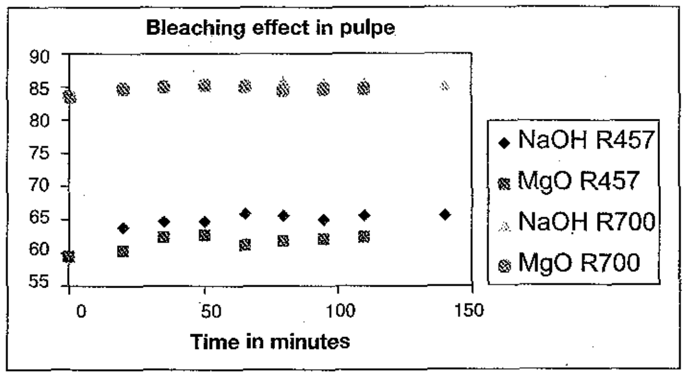

Fig. 2 Effect of alkali source on peroxide bleaching in pulper using 100% unprinted newsprint. (Deinking chemicals: 0.75% NaOH or 0.375% MgO, 0.05% DTPA, 0. 5% sodium silicate, 1.2% hydrogen peroxide, 0.1% fatty acid soap, 20 minutes pulping, 50°C, 8% s.c.).

Optical measurements

Handsheets were made from pulp after the pulping and flotation stages. They were prepared by filtering 5g pulp through No. 4 Whatman filter paper in a 11 cm Buchner funnel. ISO brightness, L*, a*, b* and R_{700nm} were measured using a Datacolour Elrepho 2000.

ERIC measurements

Residual ink concentration was measured using a modification of the ERIC method developed by Jordan and Popson (*24*). Four handsheets from the pulping and flotation stages were made using a British Standard sheet machine. The grammage of each handsheet was $45 g/m^2$. Reflectance measurements of each handsheet, black-backed and self-backed, were made at 700 nm using a Datacolour Elrepho 2000 from which the absorption (k) and scattering coefficients (s) were determined from Kubelka-Munk theory.

The relevant Kubelka-Munk equations used in the calculations are:

$$s = 1/w(1/R_\infty - R_\infty) \ln (1-R_0 R_\infty / 1-R_0/ R_\infty) \quad [1]$$

and this is used to calculate k according to:

$$k = s\,(1- R_\infty)^2 / 2 R_\infty \quad [2]$$

where s = scattering coefficient, w = grammage (kg/m^2), R_∞ = reflectance of opaque pad, R_0 = reflectance over black backing (m^2/kg), k = absorption coefficient (m^2/kg)

The concentration of ink, C_I, is obtained from the following equation:

$$k_R = k_P + C_I k_I \quad [3]$$

where k_R is the measured adsorption coefficient of the recycled fibre handsheets, k_P is the measured adsorption coefficient of the unprinted paper and k_I is the adsorption coefficient of the ink which was assumed to be equal to $12{,}500\ m^2/g$ (*25*).

Ink removal efficiency

Ink removal efficiency was determined by comparing the concentration of ink in the pulper and in the flotation cell:

$$\% \text{ Ink removal} = (C_i^p - C_i^f)/ C_i^p * 100 \quad [4]$$

where C_i^p is the ink concentration in the pulper and C_i^f is the ink concentration after flotation.

Hydration of MgO

MgO samples were hydrated in glass sample vials (1.5g MgO in 9 mL distilled water) for varying times of 3.5 to 240 minutes at 46°C. A 50 mL aliquot of a 1:1 mixture of acetone and ethanol was added to stop the hydration reaction. The samples were then filtered under vacuum and dried at 60°C.

Thermogravimetric analysis of the hydrated MgO samples was carried out using a Setaram TGA 92 thermoanalyser. Samples of 10 mg were heated at a rate of 10°C/min to 25°C, then 5°C/min to 300°C, and then 2°C/min to 420°C. The amount of weight loss due to water elimination was taken between 300 and 420°C. The degree of conversion from MgO to $Mg(OH)_2$ was determined according to Blaha (*26*).

RESULTS AND DISCUSSION

Effect of alkali

Assessment of deinking efficiency is primarily based on the measurement of optical properties of handsheets prepared from deinked pulp. In the past, ISO brightness has been used but it has been shown to be ambiguous in assessing the contribution of residual ink because bleaching reactions also influences it. The reflectance at 700 nm has also been used and is a better measure, as it is not as sensitive to bleaching effects. Peroxide is traditionally added to the pulping stage to overcome alkali darkening due to the alkali. The results of a previous MgO deinking mill trial (Fig. 1) showed that a decrease in the optical properties occurred when using MgO to partially replace NaOH in the RCF plant. This decrease was further investigated to determine how much of it was due to differences in bleaching and how much was due to difference in ink removal.

Figure 2 and Table 1 show the results of some preliminary investigations undertaken to determine the bleaching contribution to the optical measurements of the handsheets prepared from deinked pulp when NaOH and MgO were used as the alkali sources in the pulping stage. Unprinted newsprint was used as the furnish. The optical properties of the paper were measured and are shown as the initial values at the start of the experiment. The paper was pulped in the deinking cell for twenty minutes and then allowed to sit in a water bath at 50°C. The time on the x-axis in Figure 2 corresponds to the total time from the start of the experiment and the time the paper is in contact with the deinking chemicals, that is the pulping time and the rest time.

Table 1
Changes in optical properties of unprinted newsprint when pulped with deinking chemicals after 80 minutes contact time (20 pulping and 60 minutes rest time).

Alkali	ΔR 457	ΔL*	Δa*	Δb*	ΔR700
MgO	2	3	1.2	3.4	1
NaOH	6	6.3	2	5.4	2

The results show that a greater amount of bleaching occurs with the NaOH system than with the MgO system. An increase of 6 units in brightness occurs when using NaOH as the alkali source with 1.2 % peroxide addition compared to 2-unit increase when MgO is used. The results also highlight the fact that the R700 values are not as sensitive to the bleaching effect. A significant change in colour, as measured by the L*, a* and b* of the handsheets was found to occur in the NaOH system.

Ink redeposition is known to occur with increasing time in the pulper when using NaOH as the alkali source. To study the extent of this effect when MgO is used as the alkali source some experiments were undertaken to study the effect of a rest period between the pulping and flotation stage using 100% ONP. A rest period is included in the experiments in order to simulate the retention time in the storage chest after the pulping stage and before the flotation stage in the mill.

The results in Figure 3 show that the deinking efficiency of the MgO system is affected by the amount of time the pulp is left to stand before the flotation stage. In this case the R700 values show a larger decrease than the ISO brightness. These results suggest that a significant amount of ink redeposition is occurring in the MgO system after 30 minutes rest period. All subsequent experiments were then undertaken using a thirty-minute rest period between the flotation and pulping stages to minimise the contribution of rest period on ink redeposition.

Experiments were undertaken to study the effect of the alkali and other deinking chemicals on ink detachment and redeposition. In order to better assess the deinking efficiency the measurement of the Effective Residual Ink Concentration (ERIC) was undertaken using a modified method of measuring the absorption coefficient of 45 g/m^2 handsheets at 700 nm. ERIC is becoming the more widely accepted measurement for deinking efficiency. It has the additional advantage over R700 of being a comparison between the recycled fibre and unprinted paper. The per cent ink removal can then be determined by comparing the difference between the ERIC of the pulping stage and the ERIC after flotation. The effect of the alkali on the % ink removal is shown in Figure 4 while Table 2 summarises the optical properties (ISO brightness, R 700 after flotation and ERIC after flotation). In order to ensure that all detached ink particles were removed, a fatty acid soap (0.1% o.d. fibre) and calcium chloride (150 mg/L) were added to the flotation cell.

Table 2
Effect of alkali on the optical properties after flotation.

Chemicals added to pulper	ISO brightness	R 700	ERIC
No chemicals	46.4 ± 1.0	54.3 ± .5	820 ± 100
0.75% NaOH	48.9 ± 1.2	64.4 ± 2.5	438 ± 107
0.375% MgO	47.7 ± 1.8	60.8 ± 2.6	494 ± 101
0.75%NaOH 0.1% soap	51.0 ± 0..9	67.6 ± 2.2	323 ± 108
0.375% MgO 0.1% soap	50.9 ± 0.1	64.4 ± 0.5	335 ± 16
0.75% NaOH, plus all deinking chemicals	55.3 ± 3.7	67.7 ±1.7	311 ± 76
0.375% MgO plus all deinking chemicals	55.7 ± 1.8	66.1 ± 1.6	365 ± 61

The results in Figure 4 show that a small amount of ink is removed with just water in the pulper. The ink that is removed is only weakly bound to the fibre surface and is removed purely by the mechanical action in the pulper. Addition of alkali improved the ink removal with NaOH removing more ink than MgO. Addition of soap to the alkali improved the per cent ink removal even more, which is also reflected in an increase in R 700 and decrease in ERIC. The addition of soap had a much bigger impact when used with MgO compared to NaOH. The addition of the other deinking chemicals (peroxide, silicate and DTPA) had only a small effect on the ink removal and also other optical properties. The question that needs to be addressed is whether the reduced ink removal with MgO alone is due to less ink detachment or more ink redeposition occurring. The ERIC values alone cannot distinguish between the contribution to the amount of ink present on the fibre surface due to ink detachment or ink redeposition.

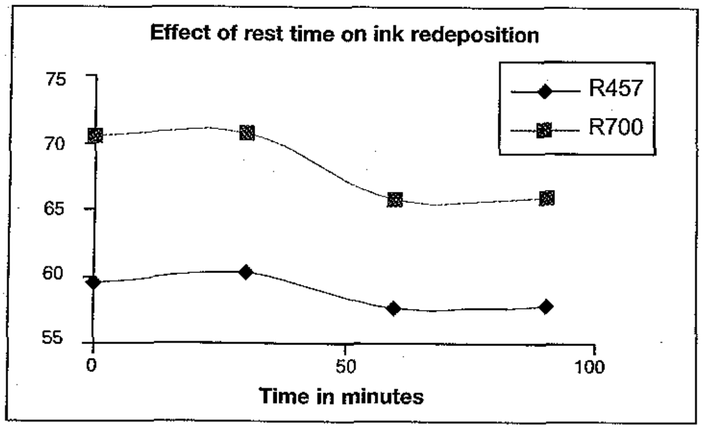

Fig. 3 Effect of rest time on deinking efficiency using MgO as the alkali source and 100% ONP. (Furnish: 70%ONP, 30%OMG; deinking chemicals: 0.75% NaOH or 0.375% MgO, 0.05% DTPA, 0. 5% sodium silicate, 1.2% hydrogen peroxide, 0.1% fatty acid soap, 20 minutes pulping, 50°C, 8% s.c.).

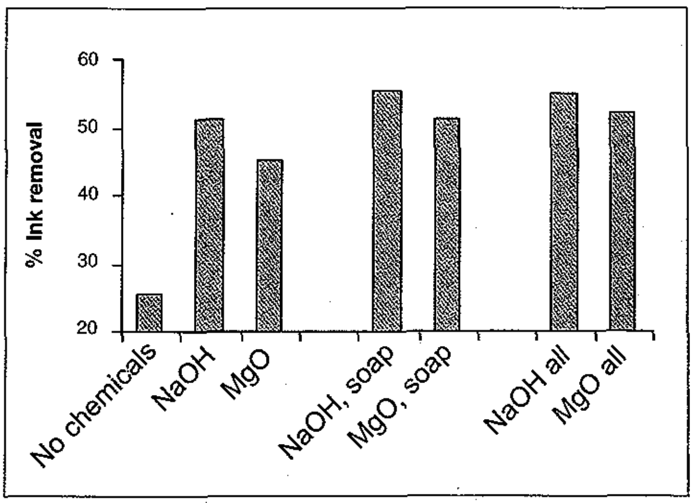

Fig. 4 Effect of alkali on ink removal (%).

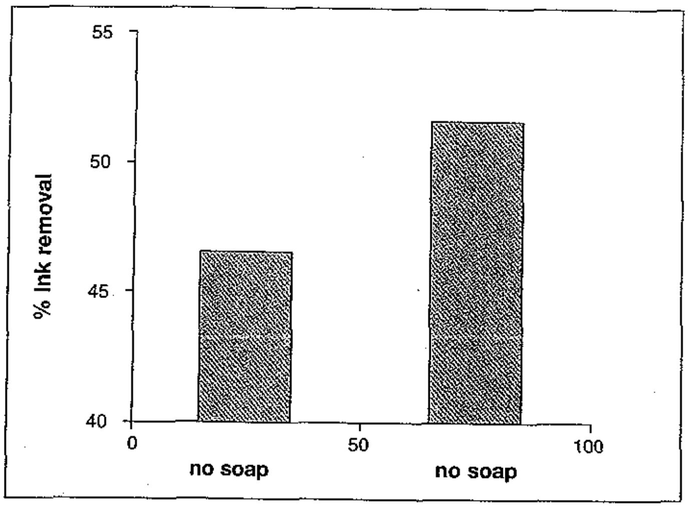

Fig. 5 Effect of soap on ink redeposition using 100% unprinted paper and ink sludge with MgO as alkali.

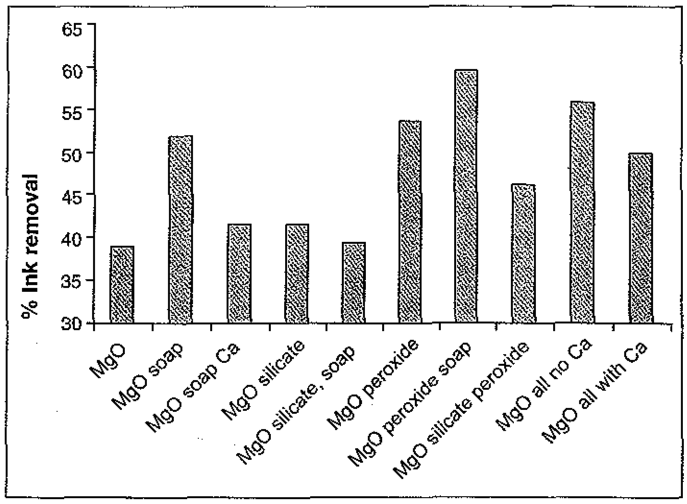

Fig. 6 Effect of deinking chemicals with MgO on deinking efficiency.

To study more fully the extent of redeposition, experiments were undertaken using unprinted newsprint and adding ink sludge to it to see the amount of redeposition of ink onto the fibres that may occur. Figure 5 presents the results of experiments undertaken when MgO was used as the alkali source in the presence and absence of some of the other deinking chemicals. The results show that a greater amount of ink is redeposited onto the fibre surface when MgO alone was used compared to when soap was also added to the pulper. These results along with those in Figure 4 highlight the importance of using soap with MgO to reduce ink redeposition onto the fibre surface.

Ink redeposition is a result of a lowering of the repulsion forces between the negatively charged ink and fibres. Magnesium being a divalent ion has a larger influence on compressing the electrical double layer around the ink and fibres than sodium. It becomes more important then when using MgO to either reduce the process variables that may contribute to redeposition such as pulping time or lag times in chests or add chemicals such as soap that keep the detached ink particles dispersed.

Table 3
Effect of deinking chemicals with MgO on the optical properties after flotation.

Chemicals added to pulper	ISO brightness	R 700	ERIC
0.375% MgO only	47.7 ± 1.8	60.8 ± .2.6	494 ± 100
0.375%MgO, 0.1% soap	50.9 ± 0.1	64.4 ± 0.5	335 ± 16
0.375%MgO, 0.1% soap 150ppm Ca^{2+}	48.8 ± 3.0	60.1 ± 1.9	372 ± 36
0.375%MgO 0.05% silicate	50.2 ± 0.6	62.3 ± 0.5	468 ± 39
0.375v% MgO 0.05% silicate 0.1% soap	50.8 ± 0.8	65.7 ± 0.7	441 ± 56
0.375% MgO 1.2% peroxide	56.2 ± 0.1	63.6 ± 0.5	422 ± 30
0.375% MgO 1.2% peroxide 0.1% soap	58.2 ± 0.4	66.1 ± 0.2	330 ± 27
0.375% MgO 0.05% silicate 1.2% peroxide	56.1 ± 0.2	63.9 ± 0.2	470 ± 51
0.375% MgO plus all deinking chemicals except Ca^{2+}	55.7 ± 1.8	66.1 ± 1.6	365 ± 61
0.375% MgO plus all deinking chemicals 150 ppm Ca^{2+}	55.8 ± 3.8	63.9 ± 2.6	460 ± 85

Effect of deinking chemicals with MgO

The effect of the addition of each of the deinking chemicals to MgO in the pulping cell was further studied to see if interactions between the chemicals might be affecting deinking efficiency. The results are shown in Figure 6 and Table 3.

Poor ink removal is achieved when MgO alone is used and also when silicate or calcium is added with MgO. Good deinking efficiency was achieved when soap was used with MgO and also when peroxide was used.

It appears that the addition of silicate and calcium may be interfering with the soap. Both are known to interact with fatty acid soaps. Calcium in particular will precipitate the soap. This is desirable in the flotation cell. However in the pulper it appears that one of the key roles of the soap is to prevent ink redeposition. If the soap has precipitated then it is unavailable to aid in dispersing the ink particles and preventing them from redepositing. Excess calcium will also encourage redeposition by adsorbing onto the negatively charged ink and fibres and also decrease the electrical double layer repulsive forces allowing the ink to absorb onto the fibres more easily.

Effect of MgO source

MgO has limited solubility and produces a lower pH than the NaOH system. It was hypothesised that the deinking efficiency of the MgO system would be improved by an increase in the degree of hydration. This would mean that more hydroxyl ions would be produced to raise the pH. The rate of hydration of MgO is known to be affected by the surface area *(26)*.

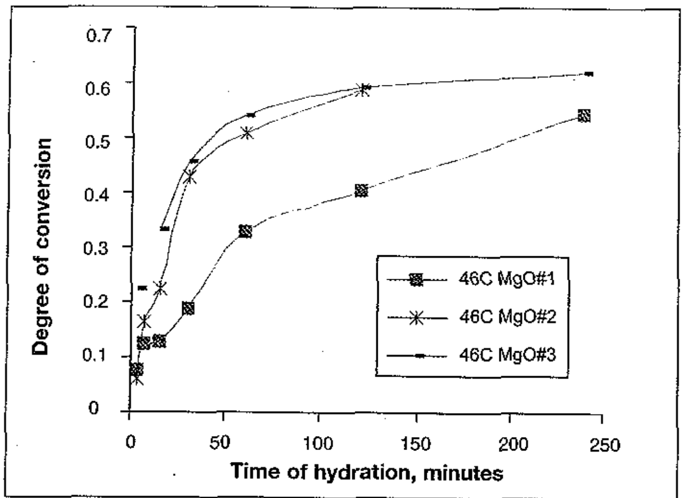

Fig. 7 Extent of hydration of three MgO samples at 46°C.

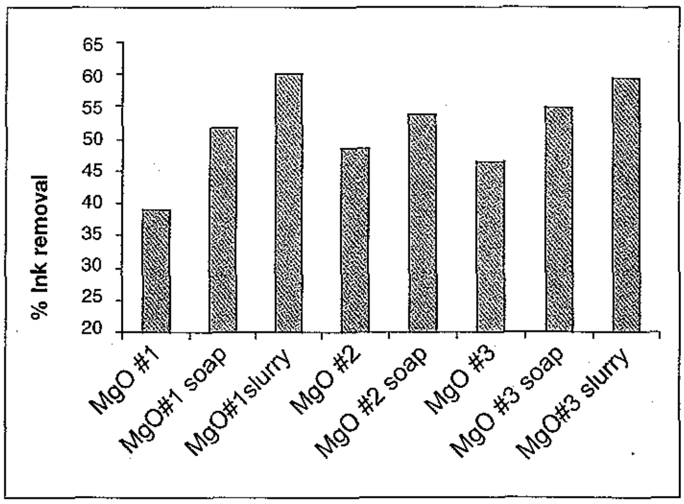

Fig. 8 Effect of MgO type on deinking efficiency.

Table 4
Properties of MgO samples.

Sample	Surface area (m^2/g)	% MgO	Degree of hydration at 46°C, 15 minutes	Pulper pH
MgO #1	35	92-95	13%	9.8
MgO #2	53	98.2	22%	10.4
MgO #3	65	97.4	33%	10.6

Three samples of differing surface area were obtained and their rate of hydration measured by thermogravimetric analysis. Table 4 summarises the properties of the three MgO samples. Figure 7 presents the extent of hydration for the three MgO samples at 46°C.

The sample with the highest surface area was found to have the highest rate of hydration and also produced the highest pH in the pulper of the three MgO samples investigated. The effect of the type of MgO on ink removal efficiency is shown in Figure 8. The samples with the higher surface area did appear to produce slightly higher deinking efficiency when used in conjunction with soap in the pulper. The deinking efficiency was further improved by hydrating the magnesium oxide in 100 mL of distilled water for 2 hours at 50°C before addition to the pulping cell.

CONCLUSIONS

Although MgO has been shown to be a suitable replacement for NaOH in order to reduce salinity from the RCF plant, some problems with poorer deinking efficiency have been experienced. It appears that part of the problem is due to increased ink redeposition. This can be overcome by using soap in the pulper that will disperse the detached ink particles. The presence of silicate and calcium in the pulper were also found to reduce the deinking efficiency. Increasing the surface area of the MgO was found to increase its degree of hydration and raise pH in the pulper. This was found to have a beneficial effect. Hydrating the MgO and adding it as a slurry also improved deinking efficiency of MgO.

ACKNOWLEDGEMENTS

The authors wish to acknowledge the support of ORICA Chemnet and Norske-Skog Paper in providing funds and chemicals. Causmag International is also acknowledged for providing MgO samples. The assistance of Leakhena Hang, a CSIRO Research Scheme student, in experimental work is greatly appreciated.

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Manuscript received for publication 25.8.04.