THEORY AND PRACTICE OF FLOTATION DEINKING

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ABSTRACT

The performance of the preflotation stage of the Norske Skog Skogn DIP mill has been studied over the first year of operation. Process conditions have covered a wider range of process parameters than would normally be expected in an established mill. The main factor affecting free ink removal and filler yield was the process water hardness, and there was a negative correlation between free ink removal efficiency and filler yield. While filler loss was concluded to take place by flotation, physical entrainment seemed to be the main mechanism for fiber loss. An overview of process variables important for mill-scale DIP flotation performance is given.

INTRODUCTION

Although many theoretical considerations and laboratory studies have contributed vitally to the understanding of flotation deinking, not much is published regarding mill-scale effects of various process variables on yield and ink removal efficiency. In an existing mill, the range of variation allowed in full-scale experiments are often limited by the mill's demands on product quality and production volume. Thus, the variations in process conditions that naturally occur in a flotation deinking plant during a start-up phase represent a unique chance to study the performance of the flotation in terms of ink removal efficiency and yield.

The Norske Skog Skogn deinking plant was scheduled for start-up in June 2000, and during the first year, mill conditions have covered a wider range of process parameters than what would normally be expected in an established mill.

Mill overview

The Skogn mill uses a mixture of approximately 30% OMG and 70% ONP. The deinking plant has a design capacity of 170,000 ADT RCP/year, corresponding to 140,000 ADT DIP/year.

The mill uses a two-loop design with alkaline pulping and preflotation (preflotation pH varied between 8.0 and 9.5), and neutral postflotation (pH 7.5-7.8). The process is outlined in Fig. 1. The mill uses a Voith Ecocell flotation unit with 5+2 cells in the preflotation stage and 4+1 cells in the postflotation stage.

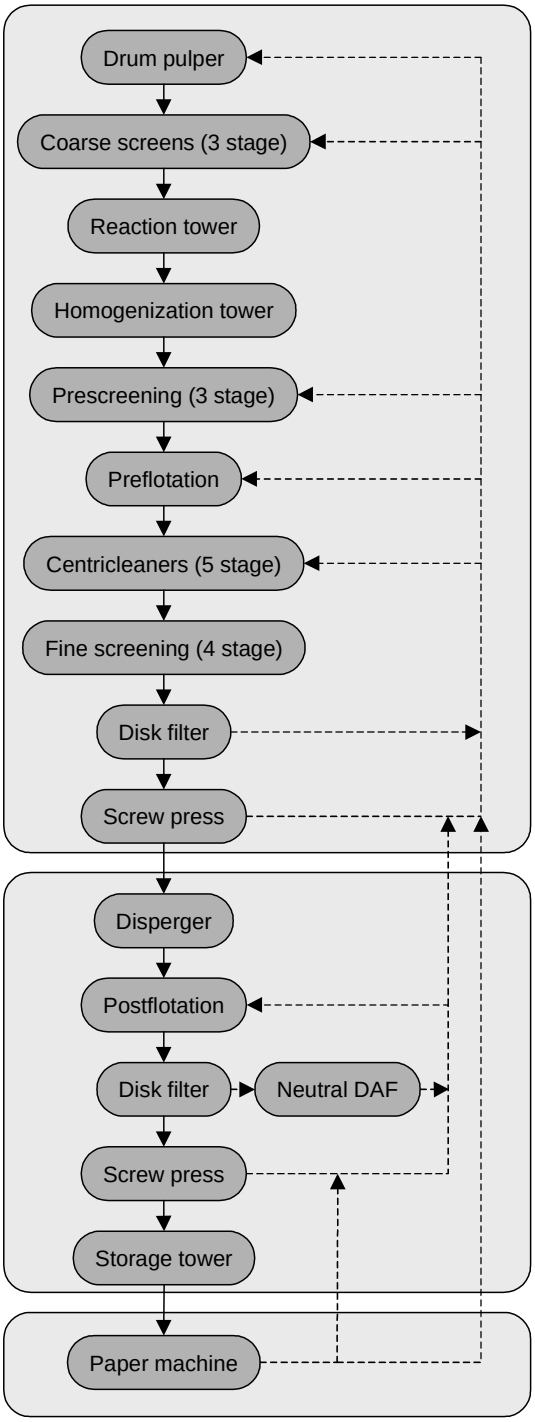

Fig. 1. Process outline of the Norske Skog Skogn DIP mill

Theory of flotation deinking

The chemistry and theory of flotation deinking is well covered in the literature [1-14], so only a few points will be made in this paper. Deinking is basically a two-stage process:

1. Detachment of ink from the fibers and fillers
2. Separation of ink particles from fibers and fillers

In the ink detachment phase, alkali is added to the pulp slurry to detach ink from the fibers. The detached ink parti-

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Table I. Chemicals and dosages

Dosage point	Chemical	Dosage, kg/ADT[a)]	
		Nominal at start-up	May 2001
Pulper	Alkali (NaOH)	8	3.5
	Peroxide	10	5
	Silicate	7	5.5
	Emulsion[b)]	1	2
Before pre-flotation	Lime ($Ca(OH)_2$)[c)]	4	2
	Soap[d)]	4	3
Disperger	Talc	10	8
Storage tower	Sodium hydro-sulfite	0	0

a) As dry matter
b) C16:0, C18:0, C18:1 fatty acids and ethoxylated fatty acids
c) The mill had initially rather soft process water (1-3 °dH), so the addition of Ca^{2+} ions is required for good flotation performance
d) Mixture of C16:0, C18:0 and C18:1 fatty acids, saponified on-site

cles should be dispersed in the water phase, and a surfactant is therefore added to the pulping/ink detachment stage to hydrophilize the ink particles and prevent ink redeposition on the fibers.This surfactant may be anionic (soap or synthetic) or nonionic (normally synthetic). In Europe, a combination of soap and synthetic nonionic surfactants (*e.g.* ethoxylated fatty acids) is often used in the form of a fatty acid emulsion.

During flotation, ink particles should have a hydrophobic surface and the correct size distribution. This is accomplished by adding soap (to the pulper and/or before the flotation) and, if the mill's process water is soft, Ca^{2+} ions, usually in the form of lime milk ($Ca(OH)_2$ slurry). This Ca^{2+} addition may of course cause scaling with other ionic species present in the system (e.g. silicate). The current model for the collecting effect of soap and Ca^{2+} ions is described by Larsson *et al.* [5].

If the first stage in the reaction between ink, soap and Ca^{2+} is the adsorption of soap to the ink particles, one can question the positive effect of non-ionic surfactants. The purpose of the emulsion is to hydrophilize the ink particles, and this may have a negative effect on the adsorption of soap to the ink particles and thus the flotation efficiency. Also, the surfactants may cause steric stabilization of ink particles and increase foaming in the flotation and thus fiber loss by entrainment.

Other chemicals are also used in a flotation DIP mill, and the chemicals used at the Skogn mill are given in Table I. For an overview of their proposed action, see *e.g.* ref [8]

METHODS

Pulp consistency and filler content was measured by vacuum filtering 250 mL pulp samples on ashless "black band" filter paper. The filter pads were dried, weighed and transferred to an oven at 525 °C for at least two hours. The ash was weighed after complete combustion of organic matter, and the filler content of the pulp was assumed to equal to the ash content of the sample after combustion at 525 °C. Clay:carbonate ratio was calculated from the weight difference between samples burned at 525 and 900 °C, respectively.

Brightness and ERIC values were measured on both sides of brightness pads containing approximately 2.5 g OD pulp using a Technidyne Colortouch 2 Model ISO instrument. Both top and bottom side of the pads was measured, and the values were averaged before reporting.

Hyperwash was performed by a modification of the INGEDE 05/1997 standard method for hyperwash of DIP samples, by fractionating a pulp sample on a single-chamber Bauer McNett fractionator equipped with a 200 mesh screen. Hyperwashed pads contained approximately 0.5% ash.

Floatable (free) ink in the samples was calculated according to Eq. 1, and free ink removal efficiency (FIRE) was calculated according to Eq. 2:

$$\text{Floatable ink} = \frac{ERIC - ERIC_{HW}}{ERIC} \cdot 100\% \qquad \text{Eq. 1}$$

$$FIRE = \frac{ERIC(Inject) - ERIC(Accept)}{ERIC(Inject) - ERIC_{HW}(Accept)} \cdot 100\% \qquad \text{Eq. 2}$$

where $ERIC_{HW}$ is the ERIC value of the hyperwashed sample.

Hardness was measured by complexiметric titration on ultrafiltered samples (membrane cutoff of 100,000 amu) to avoid interference from particulate and colloidal Ca-salts. In water loop 1, the content of particulate and colloidal Ca-salts was high enough to give a significant deviation between hardness measured on ultrafiltered samples and hardness measured on samples filtered on a GF/A glass fiber filter. For samples taken in water loop 2, no significant deviation was observed between hardness measurements on ultrafiltered and GF/A-filtered samples.

Yield determination

Determination of mill yields is never a trivial task. The traditional method of yield determination, either for a whole mill or for a single unit operation would be to determine consistencies and volumetric flows across the unit in question. For flotation cells, inject and accept flows are usually given by the process control system, while the reject flow must be determined by manual measurements. The standard method is to use a rectangular bucket at the reject sludge overflow and measure the amount collected for a given time. Collected volume, time and the ratio of bucket length to cell overflow width can then be used to calculate the total amount of reject over a given period of time. Even if this method is fairly reliable, it is rather labor-intensive.

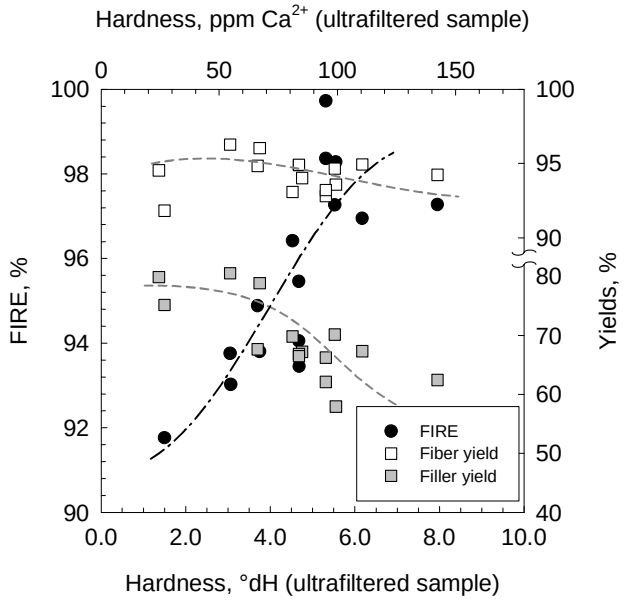

Fig. 2. Free ink removal efficiency and yields as a function of water hardness. Lines are drawn only to indicate apparent trends.

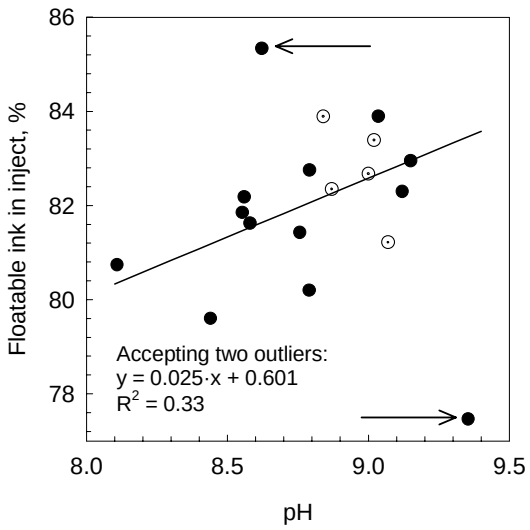

Fig. 3. Ink detachment in the pulper at various pH values. Dotted symbols indicate samples taken using only soap as surfactant in the pulper

In this study, another method has been used. Yields are generally defined by Eq. 3, Eq. 4 and Eq. 5:

$$Y_T = \frac{Q_A}{Q_I} \qquad \text{Eq. 3}$$

$$Y_F = \frac{X_A Q_A}{X_I Q_I} = Y_T \cdot \frac{X_A}{X_I} \qquad \text{Eq. 4}$$

$$Y_W = \frac{(1-X_A)Q_A}{(1-X_I)Q_I} = Y_T \cdot \frac{1-X_A}{1-X_I} \qquad \text{Eq. 5}$$

where Y_T, Y_F and Y_W are total pulp yield, filler yield and fiber (woody material) yield, respectively, Q_I, Q_A and Q_R are the mass flows of pulp in inject, accept and reject, respectively, and X_I, X_A and X_R are the corresponding mass fractions of filler material in the pulp. Assuming that the dilution water does not contain any fibrous or filler material, the mass balance for pulp across the flotation is given by Eq. 6, and the mass balance for filler material across the flotation is given by Eq. 7:

$$Q_I = Q_A + Q_R \qquad \text{Eq. 6}$$

$$X_I Q_I = X_A Q_A + X_R Q_R \qquad \text{Eq. 7}$$

By inserting Eq. 7 into Eq. 6 and rearranging, one gets the following relations for total yield (Y_T), filler yield (Y_F) and fibrous material yield (Y_W):

$$Y_T = \frac{X_R - X_I}{X_R - X_A} \qquad \text{Eq. 8}$$

$$Y_F = \frac{X_A(X_R - X_I)}{X_I(X_R - X_A)} \qquad \text{Eq. 9}$$

$$Y_W = \frac{(1-X_A)(X_R - X_I)}{(1-X_I)(X_R - X_A)} \qquad \text{Eq. 10}$$

This method is only applicable if there is a difference in selectivity for the two pulp components. If the flotation selectivities for fibrous material and fillers are equal, the filler content of accept and reject will equal the filler content of the inject, irrespective of yields. On the other hand, if the selectivity (i.e. the specific yields) for the two pulp components is unequal, a given combination of fiber and filler yields will give one unique set of values for the filler contents of inject, accept and reject. The total yield will of course always be a function of fiber yield, filler yield and inject composition. Yields determined by this method corresponded well with yields obtained through flow measurements, although there was a systematic deviation of about 4%. The correlation coefficient (r^2) was 82%.

RESULTS AND DISCUSSION

Trying to make system from chaos

Analyzing mill data is not always a trivial task, due to the lack of control of all relevant parameters. Generally, one must expect a strong scattering of data, giving the researcher the challenge of extracting useful correlations from highly scattered data. As always, any conclusions drawn from such analyses must be treated with caution.

Using simple two-dimensional plots of performance versus a given process variable, only water hardness seemed to have a significant effect on free ink removal efficiency and filler yield (Fig. 2), while ink detachment seems to be favored by a high pulper pH, as also could be expected (Fig. 3).

Table II. Multiple linear regression results

	Parameter(s)		
	#	Best fit	Effect
FIRE	1	Hardness	+
	2	Hardness	+
		Emulsion dosage	+
	3	Hardness	+
		Emulsion dosage	+
		pH	+
	4	Hardness	+
		Emulsion dosage	+
		pH	+
		Silicate dosage	–
	5	Hardness	+
		Emulsion dosage	+
		pH	+
		Silicate dosage	–
		Reject rate ratio	+
Filler yield	1	Hardness	–
	2	Hardness	–
		Silicate dosage	+
	3	Hardness	–
		Silicate dosage	+
		Inject consistency	+
Fiber yield	1	Inject consistency	+
	2	Inject consistency	+
		Total reject rate	–

Since the hardness had a very strong effect on mill performance, any effects of other process variables were masked by the effect of the water hardness. Thus, multiple linear regression was used to extract secondary process variables influencing the performance of the deinking process. The plots of performance versus water hardness indicated possible non-linear relationships between process variables and mill performance, and since the multiple regression used linear relationships, correlation coefficients will be lower than if a non-linear multiple regression had been used. Still, the correlation coefficients were rather satisfying. For results of the regression analysis, see Table II.

To investigate the validity of the multiple linear regression, a manual stepwise regression analysis was performed. Here, the simple correlation between the most important parameter (hardness) was used to adjust the performance data for the effect of this parameter. The adjusted FIRE and yield data were then plotted against the second most important parameter, and so on. The results from this analysis are summarized in Table III. In the following subsections, these results are discussed in more detail.

Ink detachment

Ink detachment seemed only dependent on the pH in water loop 1. Neither emulsion nor silicate dosage to the pulper seemed to systematically affect the ink detachment.

Table III. Process parameters affecting mill performance, in order of decreasing importance

			Expected	Observed	Comment
FIRE	1	Water hardness	+ +	+ +	a
				0	b
	2	Emulsion dosage	–	+	c
	3	pH	?	(+)	d
	4	Silicate dosage	+	(–)	d
	5	Total reject rate	+	(+)	d
	6	Reject rate ratio (prim/sec)	+	(+)	d
Filler yield	1	Water hardness	– –	0	e
				– –	f
	2	Silicate dosage	+ +	+	
	3	Total reject rate	–	(–)	d
Fiber yield	1	Total reject rate	– –	–	
	2	Water hardness	–	(–)	d
	3	Emulsion dosage	–	(–)	d

a) Below 5.5 °dH (100 ppm $CaCO_3$), as measured on ultrafiltered samples
b) Above 5.5 °dH (100 ppm$CaCO_3$), as measured on ultrafiltered sample
c) Possibly due to increased soap dosage to the system
d) Weak correlation
e) Below 3 °dH (50 ppm $CaCO_3$), as measured on ultrafiltered samples
f) Above 3 °dH (50 ppm $CaCO_3$), as measured on ultrafiltered samples

Ink removal efficiency

As shown in Fig. 2 and Table II, sufficient water hardness is the most important variable for free ink removal efficiency. Also, at low water hardness values there were strong indications of accumulation of soap in water loop 1. Soap dosage should thus be optimized with respect to the hardness of the process water.

Addition of emulsion to the pulper seems to be beneficial for the flotation efficiency. It was expected that surfactants should have a beneficial effect on ink detachment, but the FIRE variable should give a “true” assessment of flotation efficiency. The surfactant added to the pulper was primarily fatty acids, which are saponified in the alkaline environment in the fiber line. An increase of the amount of soap added to the system may increase flotation efficiency, given that the water hardness is appropriate. The apparent positive effect of increasing emulsion dosage may thus be a consequence of an increased dosage of soap to the system. A high pH was also concluded to have a positive effect on ink removal efficiency, however, this correlation is rather weak. Silicate dosage seemed to have a negative effect on ink removal efficiency, possibly due to complexation of Ca^{2+} ions [14].

Total reject rate would easily be expected to give increased ink removal, as is indicated in this study. However, the correlation is weak and the effect is minor compared to the effect of chemical process parameters. The

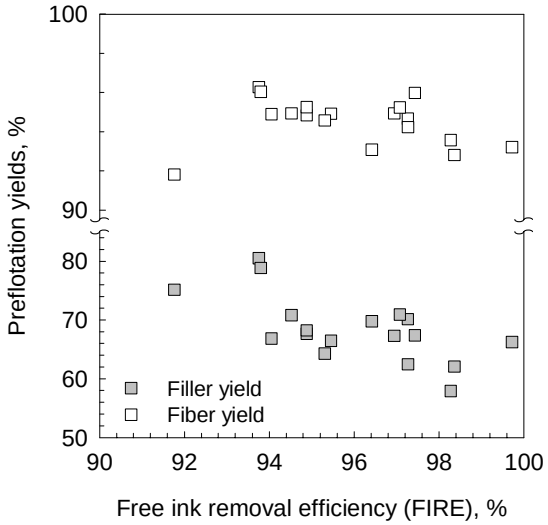

Fig. 4. Yields vs. ink removal efficiency

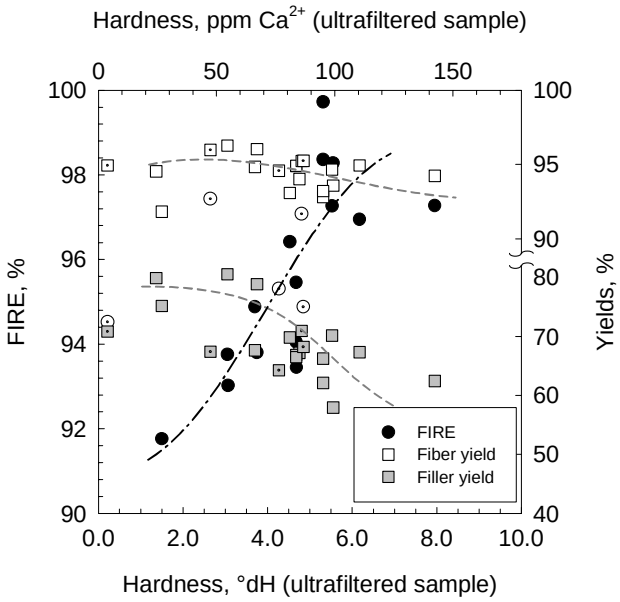

Fig. 5. Ink removal efficiency and yields in preflotation as a function of water hardness, using only soap as surfactant in the pulper. Dotted symbols indicate samples taken using only soap as surfactant in the pulper.

ratio between primary and secondary stage reject rates can also be expected to influence ink removal at a given total reject rate. The parallel between the two-stage flotation system and two cascade-coupled screens is obvious, and for screening systems, maximum pulp cleanliness at a given total reject rate is usually obtained at a high ratio of primary stage to secondary stage reject rate. This also seems to be the fact for this flotation system, however, as for total reject rate, the correlation is weak and the effect is minor compared to the effect of chemical parameters.

Yields

It has been stated that "yield loss often may not scale up well from laboratory tests to mill operations" [3]. To a certain extent, correlations between process parameters and yields observed in this study were consistent with what can be deduced from laboratory experiments.

As previously noted, total yield is the sum of fiber yield and filler yield. Both literature and the data obtained in this study indicate that the mechanisms for stock loss are not necessarily the same for fibrous material and fillers. Thus, fiber yield and filler yield have been treated independently.

Generally, there is an inverse relation between yields and ink removal efficiency (Fig. 4).

Fiber yield

Fiber yield is slightly affected by process parameters, including water hardness (average preflotation fiber yield is 94%, varying from 90 to 96%). However, filler yield varies from 55% to 80%.

Considering that fiber yield seems to depend strongest on total reject rate (Table III), while filler yield depends strongest on chemical parameters as water hardness and silicate dosage (Fig. 2, Table III), there is an indication that the main mechanism for fiber loss is physical entrainment, as has been proposed by other authors [15]. A small amount of fibers may be lost by "true" flotation, as indicated by the slightly decreasing fiber yield with increasing water hardness at hardness values over 3 °dH (50 ppm $CaCO_3$). This is probably due to flotation of partially ink-covered fibers. The fact that the ERIC value for hyperwashed preflotation accept is 86±4% of the ERIC value for the hyperwashed inject further supports the hypothesis of "true" flotation of ink-covered fibers and fiber fragments. Also, hyperwashed secondary stage accepts (which were originally rejected in the primary stage) on average have a 17% higher ERIC value than the hyperwashed inject. This is also a clear indication that ink-covered fibers are enriched in the reject.

The apparent positive effect of consistency on fiber yield (Table II) was concluded to be an artefact caused by the general increase in pulp consistency with time. However, it is interesting to note that although inject consistencies above 15 g/L have not been observed, no adverse effect of high inject consistency can be seen in this study. Some dilution appears in the mixing cell, where the preflotation inject is mixed with secondary stage accept, so the true consistency during flotation is approximately 10% lower than the inject consistency. Apparently, as long as the pulp consistency during flotation is below 13 g/L, yield loss due to increased entrainment of fibers is not a major problem with this flotation cell type.

Filler yield

Both the strong dependence of filler yield on water hardness and the fact that the reject was enriched in carbonate compared to the inject (data not shown) is an indication that filler loss seems to take place by "true" flotation. Considering the zeta potential of clay and carbonate particles in the pH range from 8 to 9.5, one would expect carbonate to float easier than clay, and an enrich-

ment of the reject in carbonate is an indication of "true" flotation of filler particles.

At water hardness values below approximately 3 °dH (50 ppm $CaCO_3$), filler yield seems to be independent of water hardness, while the filler yield decreases with increasing hardness at hardness values above 3 °dH. Na-silicate seems to have a positive effect on filler yield, as may be expected [14]. Increasing the reject rate had a slightly negative effect on filler yield, but, as for free ink removal efficiency, this effect is minor compared to the effect of chemical parameters. This is consistent with the conclusion that filler loss is caused by "true" flotation of filler particles.

From soap and emulsion to only soap

As has been discussed, the usefulness of non-ionic surfactants may be questioned. Also, by the use of OMG as raw material, some non-ionic surfactants are introduced to the process with the paper. The amount of surfactants introduced as a part of the paper raw material has been estimated to the same order of magnitude as the amount of non-ionic tensides added as emulsion.

Since soap generally is a less expensive alternative than emulsion, a mill trial was performed, where emulsion to the pulper was substituted by soap. The results from this trial are shown in Fig. 5. As can bee seen, neither ink removal nor yields seem to be negatively affected by substituting emulsion by soap.

CONCLUSIONS

For the Norske Skog Skogn DIP mill, the single most important parameter affecting ink removal efficiency and filler yield is the water hardness. For good deinking efficiency, a high dosage of surfactant to the pulper, high pH, low silicate dosage, high alkali dosage and a high ratio of primary stage to secondary stage reject rate also seems beneficial. For filler yield, a low water hardness and a high silicate dosage seems beneficial.

Given a good ink detachment, in mill scale, the main mechanism for fiber loss is physical entrainment, although fibers with attached ink seem to float easier than ink-free fibers. The main mechanism for filler loss seems to be flotation, and filler yield can be expected to be inversely related to ink removal efficiency.

Substituting emulsion by soap in the pulper has apparently no negative impact on flotation performance.

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