Environmental benefits of magnesium hydroxide-based peroxide bleaching of mechanical pulp – mill results

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ABSTRACT: The use of a new, technical, high-purity magnesium hydroxide-based peroxide bleaching additive was evaluated in full mill-scale trial runs on two target brightness levels. Trial runs were conducted at a Finnish paper mill using Norwegian spruce (*Picea abies*) as the raw material in a conventional pressurized groundwood process, which includes a high-consistency peroxide bleaching stage. On high brightness grades, the use of sodium-based additives cause high environmental load from the peroxide bleaching stage. One proposed solution to this is to replace all or part of the sodium hydroxide with a weaker alkali, such as magnesium hydroxide. The replacement of traditional bleaching additives was carried out stepwise, ranging from 0% to 100%. Sodium silicate was dosed in proportion to sodium hydroxide, but with a minimum dose of 0.5% by weight on dry pulp. The environmental effluent load from bleaching of both low and high brightness pulps was significantly reduced. We observed a 35% to 48% reduction in total organic carbon (TOC), 37% to 40% reduction in chemical oxygen demand (COD), and 34% to 60% reduction in biological oxygen demand (BOD_7) in the bleaching effluent. At the same time, the target brightness was attained with all replacement ratios. No interference from transition metal ions in the process was observed. The paper quality and paper machine runnability remained good during the trial. These benefits, in addition to the possibility of increasing production capacity, encourage the implementation of the magnesium hydroxide-based bleaching concept.

Application: A magnesium hydroxide-based additive was used successfully for high-brightness peroxide bleaching in a mill trial.

The most effective way of increasing the brightness of mechanical pulp is by using hydrogen peroxide bleaching under highly alkaline conditions. Traditionally, these alkaline conditions have been obtained with the use of sodium hydroxide, with sodium silicate addition for peroxide stability. However, the use of these traditional alkali compounds leads to undesired side effects through the dissolution of organic wood components (e.g., oxidized lignin, hemicelluloses, etc.), which either contribute to the bleaching effluent or are carried over to the paper machine. Increasingly more stringent environmental effluent regulations have emphasized the need for a more effective alkaline peroxide bleaching method that results in a lower organic load.

Early studies have shown that the most suitable replacement of alkali (caustic soda) in mechanical pulp bleaching is magnesium hydroxide ($Mg[OH]_2$) [1-3]. Magnesium hydroxide has been used in mill-scale bleaching trials, and mill conversions have taken place in North America [4-10,17]. Magnesium hydroxide has been promoted for its environmental benefits [4-6], low dosing [6], lower production of anionic trash carryover (which can interfere with paper machine filler retention) [7], and lower oxalate production (which can contribute to paper machine scaling and runnability issues) [8-11].

At Irving Paper (St. John, NB, Canada), a 0.4% reduction in the mill's pulp brightness was achieved on mixed spruce and fir thermomechanical pulp with 1.55% peroxide charge, and the mill's chemical oxygen demand (COD) was reduced by 40% and cationic demand reduced by 20% [6]. The reductions observed in the environmental load have been attributed to lower solubility of magnesium organic acid salts, and to lower pH in the bleaching stage, which removes less of the alkali labile hemicelluloses [6]. Another important factor is the ratio between the COD and biological oxygen demand (BOD_7) of the bleaching filtrate, which can impact the environment. An effluent with a COD:BOD_7 ratio below 10 is considered suitable for microbial wastewater treatment, whereas a higher ratio would reflect a toxic wastewater effluent [12].

Much of the previous work has been performed on North American wood species and at conditions typically used at North American mills, which are different from European mills. Recent results from laboratory trials [4,13] and mill trials [6,14] have been encouraging, and these have motivated a large-scale mill trial in northern Europe. To our understanding, no results have been published on the peroxide bleaching of high initial brightness pressurized groundwood (PGW) using magnesium hydroxide as the alkali source.

In this study, the use of a fortified hydrated magnesia of extremely high purity (BimBright 4500, BIM Finland Oy) was

Grade	NaOH-$Mg(OH)_2$* Replacement Ratio	H_2O_2 Dose (kg on dry pulp metric ton)	NaOH Dose (kg on dry pulp metric ton)	$Mg(OH)_2$* Dose (kg on dry pulp metric ton)	Na_2SiO_3 Dose (kg on dry pulp metric ton)
Low brightness	0%	10.0	10.0	0.0	6.0
	30%	10.0	7.0	2.4	6.0
	50%	10.0	5.0	4.0	6.0
	70%	10.0	3.0	5.6	6.0
	100%	10.0	0.0	8.0	6.0
High brightness	0%	42.0	26.0	0.0	10.0
	30%	42.0	18.2	6.2	10.0
	50%	42.0	13.0	10.4	10.0
	70%	42.0	7.8	14.6	10.0
	100%	42.0	0.0	20.8	10.0
* Magnesium hydroxide-based bleaching additive BimBright 4500					

I. Chemical dosages used in the mill trial.

evaluated in a full mill-scale trial at a Finnish pulp and paper mill. Properties of the bleached pulp and bleaching effluent were determined, with the latter being addressed to assess the environmental benefits of a magnesium-based bleaching stage.

EXPERIMENTAL

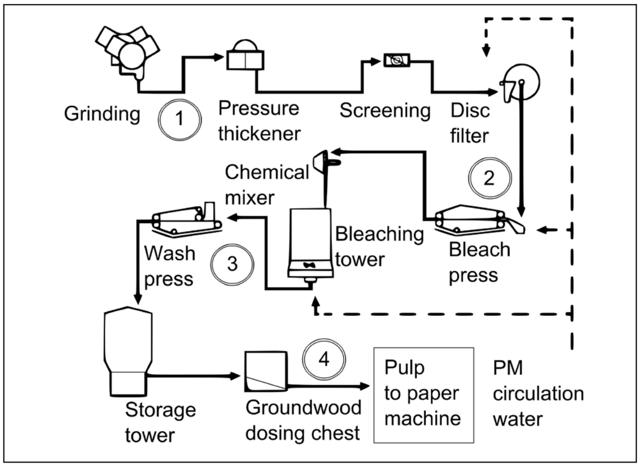
Full-scale trial runs were conducted in a mill using a conventional PGW process with high-consistency peroxide bleaching on Norway spruce (*Picea abies*) in southeastern Finland. Two baseline situations were established using conventional alkaline peroxide bleaching to reach two target brightness levels (0% replacement ratio) (**Table I**) during a 12-day period. In subsequent experiments, the alkali dosing into the peroxide bleaching stage was gradually adjusted from 100% sodium hydroxide to 100% magnesium hydroxide-based additive (Table I) while otherwise keeping the process conditions and chemical dosages unchanged, except for the sodium silicate. This trial phase lasted for 13 days. The pulp was treated with 0.3% dose of diethylenetriamine pentaacetic acid (DTPA) after the screening stage, before the bleach press. The bleaching conditions were as follows: 78°C reaction temperature, 38% pulp consistency, and 128 min reaction time. Bleaching liquor was mixed into the pulp with a mechanical high-power mixer. The post-bleached pulp was acidified. The trial program was first run on a low brightness grade and then on a high brightness grade. Throughout the trial, the pulp was produced at the mill's maximum production capacity and with only small changes in the wood furnish. The initial ISO brightness of the pulp ranged from 62% to 65%. The wood furnish was mostly harvested during the autumn. The trial program was abruptly stopped because of an unrelated mechanical failure in the grinding stage, which spoiled some of the final BOD_7 data collected when the mill was running at 100% replacement with magnesium hydroxide.

Pulp samples were taken directly from the running process, and temperature and pH were immediately measured. The samples were quickly filtered on a Büchner funnel through S&S 597 filter paper of 4-7 μm pore size; the resulting pulp disc and filtrate were recovered for subsequent analyses. The pulp discs were wet-pressed under 400 kPa for 5 min, drum-dried, and conditioned according to ISO 187:1990 "Standard atmosphere for conditioning and testing and procedure for monitoring the atmosphere and conditioning of samples." These discs were used for the determination of pulp ISO brightness using a spectrophotometer (ISO 2470 "Measurement of diffuse blue reflectance factor"). The filtrate samples were analyzed for total organic carbon content (TOC) with a Shimadzu TOC 5050-device (Shimadzu; Kyoto, Japan) according to ISO/CEN EN 1484-3 "Guidelines for the determination of total organic carbon," COD according to SFS 3020 "Determination of chemical oxygen demand in water, oxidation with dichromate," and BOD_7 according to SFS-EN 1899 "Determination of biochemical oxygen demand after n days." In addition, the manganese, iron, and magnesium contents were measured using an atom absorption spectrophotometer according to SCAN-CM 38:05 "Calcium, magnesium, iron, manganese and copper content: Atomic absorption spectroscopy."

To determine the effect of bleaching alkali on the organic carbon load generated in the bleaching stage, ΔTOC was calculated as follows:

$$\Delta TOC_{bleaching}=TOC_{wash\_press\_feed}-TOC_{bleach\_press\_feed} \quad (1)$$

which gives the amount of dissolved organic compounds originating in the bleaching stage, provided that the water used for the pulp dilution contains negligible TOC. Under mill conditions, this naturally is not the case. Large volumes of process water in the paper machine did not have time to fully cycle and reflect the lower generation of TOC in the bleaching stage, so that the measured values of TOC and COD were slightly elevated throughout the process line. The effect of



1. General scheme of the pressurized groundwood plant process flows, equipment, water circulation, and pulp sampling points.

Sampling Point	Sample Description
1	Pressure thickener feed
2	Bleach press feed
3	Wash press feed
4	Groundwood dosing chest

II. Sampling point descriptions and their respective location numbers.

TOC present in the water circulating in the paper machine and pulp mill on the reliability of measurements was considered to be small.

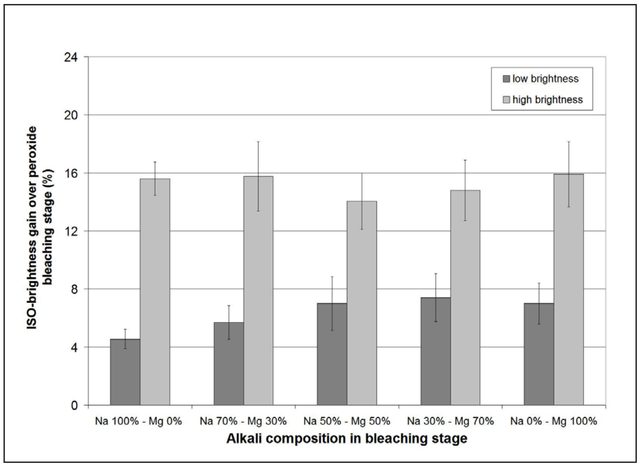
To counteract the cyclic and random variations inherently present in a mill environment, BOD_7 measurements were carried out on combined samples collected over a 24 h period during the trial run at two different experimental points. Otherwise, the sample handling was as described in SFS-EN 1899-1.

Table I presents the alkali dosages used in the mill trial. These values are based on information provided by the chemical supplier (BIM Kemi AB; Stenkullen, Sweden). The magnesium hydroxide–based bleaching additive (BimBright 4500) contained trace impurities: less than 10 ppm iron, less than 5 ppm manganese, and less than 1 ppm copper. The arithmetic mean particle size of the magnesium-based additive was 5.8 µm.

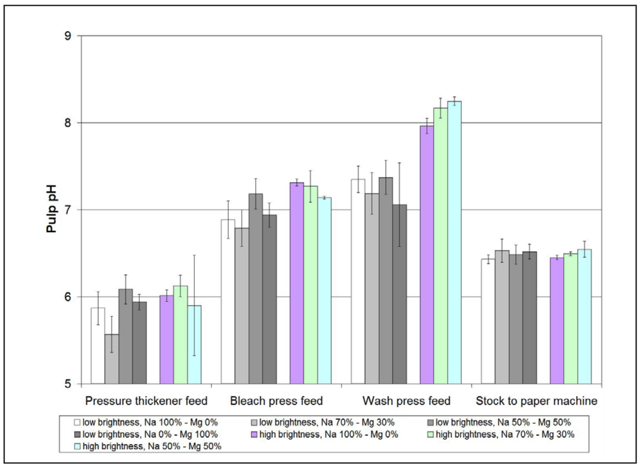
The experimental set-up followed the process flow of the PGW mill. Sampling points were chosen to determine the most important sources of the environmental load in the process. **Figure 1** presents an outline of the PGW process and the locations of sampling points and of circulation water injections, with descriptions in **Table II**.

RESULTS

Figure 2 shows the brightness gain during alkaline peroxide bleaching with different bleaching alkali sources. For the low brightness grade, the bleaching result was improved by more than 2 percentage points when magnesium hydroxide–based alkali replaced more than 50% of the total sodium hydroxide alkali. In the case of the high brightness grade pulp, no obvious effects of the change in alkali composition were seen. The brightness gain was fairly constant at 16% with both alkali systems.

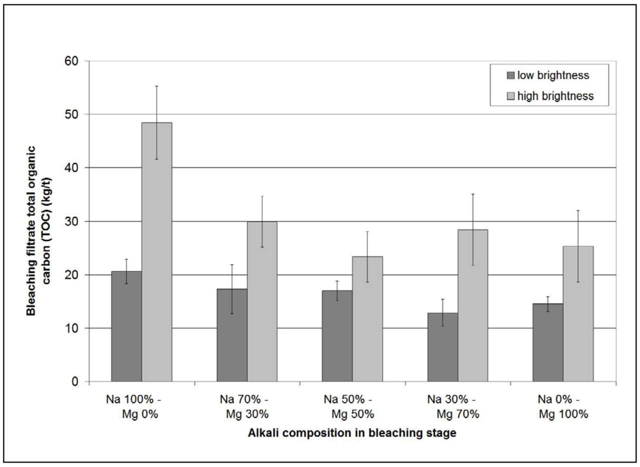


2. The effect of magnesium hydroxide (Mg):sodium hydroxide (Na) ratio in bleaching on the pulp brightness gain between bleach press feed and wash press feed. Pulp mean initial brightness = 64.1%. Error bars represent the 90% confidence interval.

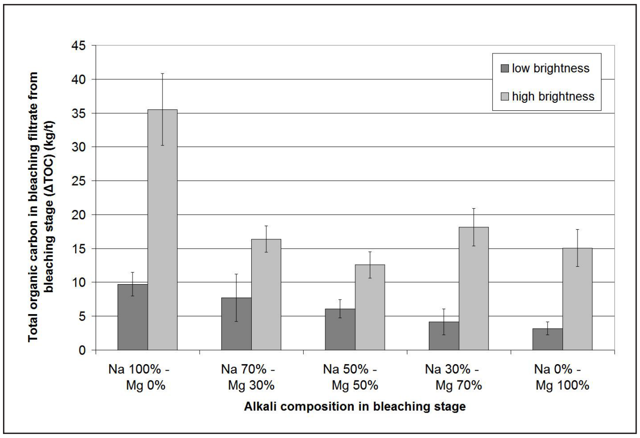


3. The effect of Mg:Na ratio in bleaching on the pH of the dilute pulp suspension. Error bars represent the 90% confidence interval.

Figure 3 shows the pulp's pH at different positions in the pulp line for various magnesium hydroxide:sodium hydroxide ratios in the bleaching stage. The pH of the dilute pulp suspension in the wash press feed varied more than the pH of the pressure thickener feed or bleach press feed. Although the pH of the low and the high brightness pulps differed by as much as one unit in the wash press feed, the changes in alkali composition did not affect the pH of the stock to the paper machine. In fact, the gradual change between monovalent (Na^+) to divalent (Mg^{2+}) cations did not significantly affect the pH



4. The effect of Mg:Na ratio in bleaching on the amount of total organic carbon (TOC) in the effluent from the bleaching stage. Error bars represent the 90% confidence interval.

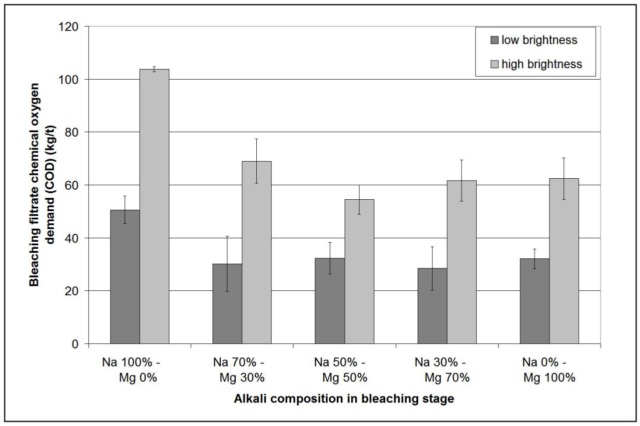


5. The effect of Mg:Na ratio in bleaching on the total organic carbon (ΔTOC) originating from the bleaching stage. Error bars represent the 90% confidence interval.

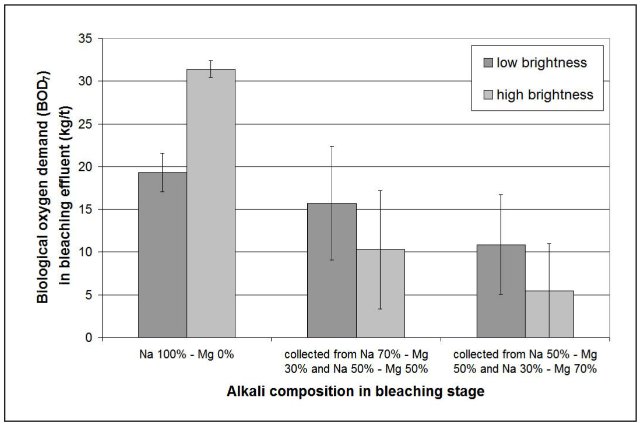
of the stock. This probably is because of the low solubility and wide buffering effect of magnesium hydroxide.

Figures 4 and **5** show the effects of bleaching alkali composition on the TOC in bleaching effluent. When half of the sodium hydroxide was replaced with magnesium hydroxide, a reduction of 50% in the TOC of the high brightness grade pulp effluent was seen. Increasing the proportion of magnesium hydroxide in the bleaching further did not reduce the TOC value. The change in alkali composition also had an effect on the TOC in the bleaching filtrate from the low brightness grade pulp, reducing it from 20 kg/ton to 13 kg/ton.

Figure 6 shows the COD in the bleaching effluent and illustrates the positive effects of replacing sodium hydroxide with magnesium hydroxide. For the low target brightness grade, the reductions of the TOC and COD levels were small because the absolute values were already very low. For the high brightness grade, however, the lower TOC and COD levels obtained with the magnesium-based alkali were clearly visible.



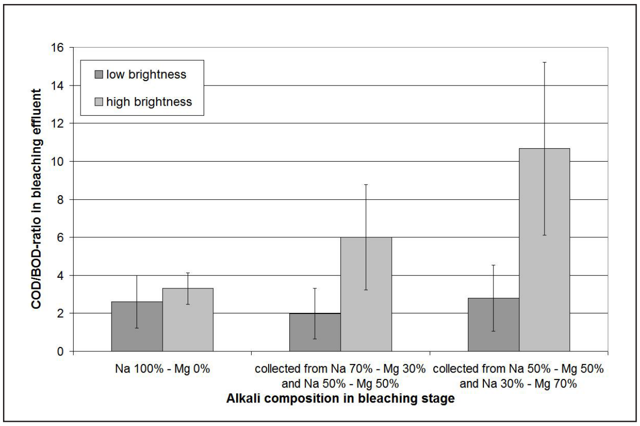
6. The effect of Mg:Na ratio in bleaching on the chemical oxygen demand (COD) of the effluent from the bleaching stage. Error bars represent the 90% confidence interval.



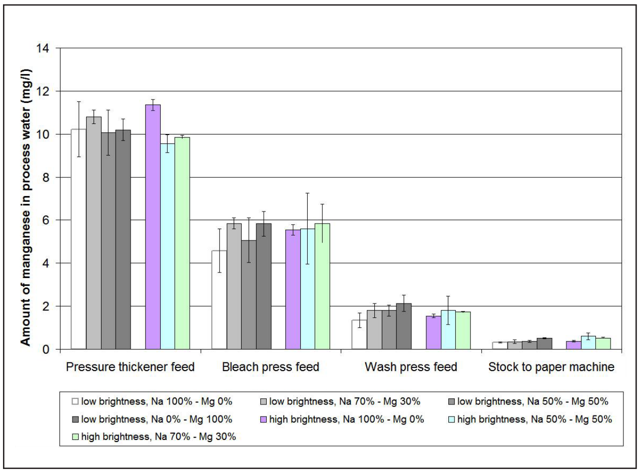
7. The effect of Mg:Na ratio in bleaching on the biological oxygen demand (BOD_7) of the effluent from the bleaching stage. Error bars represent the 90% confidence interval.

The BOD and its relation to the COD of the bleaching effluent were studied on the samples taken for two different replacement ratios. **Figure 7** shows that the overall BOD was lowered sharply as a result of the addition of the magnesium-based alkali on both brightness grades. Despite a large margin of error, the decrease was especially pronounced on the high brightness grade, where BOD_7 decreased from 30 kg/ton to about 12 kg/ton on a combined sample from both 50% and 70% magnesium-based alkali processes. **Figure 8**, on the other hand, shows that although the COD:BOD ratio remained constant and independent of the alkali source on the low brightness pulp, the addition of magnesium-based alkali yielded a higher COD:BOD ratio (>10) than on the high brightness grade.

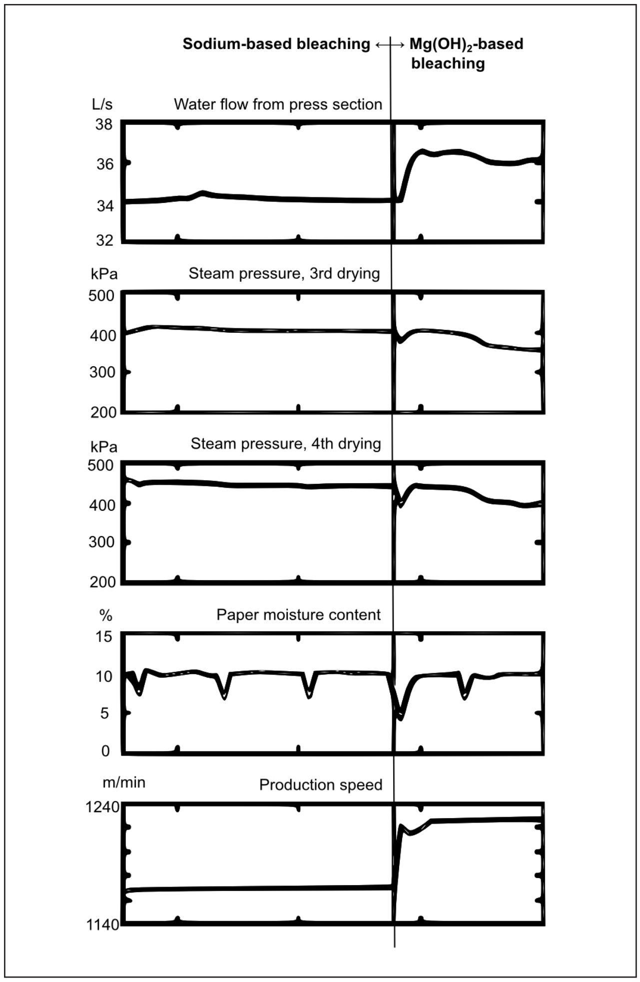
Alkaline peroxide bleaching is highly sensitive for transition metal ions, especially manganese [15], and several grades of commercially available magnesium oxide and magnesium hydroxide contain high amounts of iron and manganese [16]. For this reason, the amount of manganese ions was determined and the results are presented in **Fig. 9**. The amount of manganese in the process water was at its highest at the start



8. The effect of Mg:Na ratio in bleaching on the COD: BOD_7 ratio of the effluent from the bleaching stage. Error bars represent the 90% confidence interval.



9. The levels of manganese in the process water through the process line. Error bars represent the 90% confidence interval.



10. The effect of bleaching alkali change on water flow from the paper machine press section, paper moisture content, and production speed. Data gained from online measurement system of the mill.

of the papermaking process but decreased sharply approaching the paper machine. This amount of manganese was low enough not to interfere with the bleaching or papermaking.

The data presented in **Fig. 10** show that the change of bleaching alkali had slight but measurable positive effects on the papermaking process. With no other adjustments made to the pulping and papermaking process, the water removal on the press section of paper machine was increased, leading to higher production speed.

DISCUSSION

The benefits of using magnesium hydroxide as compared to sodium hydroxide with regard to bleaching efficiency and effluent composition have been discussed by He et al. [4]. Results presented here were in agreement with the results reported by He et al. on the peroxide bleaching of thermomechanical pulp. It is thus probable that in addition to less dissolving of lignin through lower pH in bleaching, magnesium ions reduce the amount of anionic trash by charge neutralization.

To fairly compare the environmental effects of magnesium hydroxide–based alkali, the brightness gain during bleaching has to be considered. On low brightness pulp, the bleaching gain is increased slightly when magnesium is introduced into the process (Fig. 2). On high brightness grade pulp, the brightness gain seems to be slightly impaired with 50% sodium hydroxide and 50% magnesium hydroxide, most likely because of a disturbance in the process flows. Otherwise, the brightness gain remains at a constantly high level. This result is unlike two previously reported results. In one, an ISO-brightness loss of 0.4% was reported in a previous mill-scale study using a commercial technical magnesium hydroxide slurry [6]. In the other, a laboratory experiment with pro analysis-grade magnesium hydroxide gave a brightness decrease of 1.0% [17]. All the measurements of brightness showed a moderate scatter, which is indicated by confidence interval markings.

The cleaner bleaching observed with magnesium-based alkali has been reported to be largely the result of weaker alkalinity and lower pH in the bleaching stage [7]. Figure 3 shows that the pH measured on the dilute pulp suspension in the mill process generally was not affected greatly by the change of bleaching alkali composition. From an environmental point of view, the most important sampling point is the wash press feed. There, it was seen that magnesium-based bleaching with a high peroxide dose (4.2%) led to a slightly higher pH. The reason for the stability of the pH might partially be the large liquid volumes involved in the mill process.

Figures 4 and 5 indicate that, with the low brightness pulp, the environmental load was moderately lowered. The absolute values of TOC in the reference bleaching were low, approximately 20 kg/ton, from which it was lowered by 30%. The change in COD was greater, being 35% less than the reference. With both environmental indicators showing a clear reduction, the brightness result was improved by the use of magnesium hydroxide-based alkali, especially on low target brightness grades.

In the case of the high brightness grade pulp, the lowering of the TOC and COD levels with magnesium-based alkali was clear and sharp, with a 48% reduction of TOC and 37% reduction of COD. These results supported the previously reported laboratory and mill-scale findings [4-6]. Another aspect of the environmental issues of peroxide bleaching is to consider the amount of TOC that originates from the bleaching stage instead of considering only the absolute TOC in the bleaching filtrate. The favorable effect of magnesium-based bleaching on the environmental emissions was particularly evident in Fig. 5; the TOC reductions were substantial, ranging from 21% to 67%, with the substitution of magnesium hydroxide for sodium hydroxide at both brightness levels.

An important characteristic of the effluent was its BOD_7 (Fig. 7). The use of magnesium-based alkali resulted in a lower BOD_7 level, especially with the high brightness grade pulp. Even taking into account the wide margin of error, the decrease in BOD_7 was dramatic (at least 60%).

From the viewpoint of modern effluent treatment, the relation between COD and BOD is equally important [12]. Figure 8 shows that on low brightness pulp the COD:BOD ratio remained almost two, which might be regarded as typical for peroxide bleaching. The replacement of sodium hydroxide with a magnesium hydroxide–based additive on high brightness pulp caused this ratio to rise fivefold, close to the harmful limit. Although the high COD:BOD ratio itself might be considered a disadvantage, the absolute level of the BOD demand was remarkably low.

Certain metal ions, especially transition metal ions, are highly detrimental for peroxide bleaching [15,18-20]. Past mill-scale trials have faced problems with the concentration of transition metal ions in process water originating from the alkaline substances used in bleaching. Depending on the source of the magnesium hydroxide, the amounts of transition metals in commercially available grades have been 900-2000 ppm for iron and 25-50 ppm for manganese. A North American refiner bleaching mill trial was conducted using magnesium hydroxide specified to contain maximums of 100 ppm (0.01%) iron, 100 ppm manganese, and 1 ppm copper [14].

Figure 9 shows that the manganese, which usually originates from the wood raw material, was not excessively carried over to the papermaking process, regardless of the type of bleaching alkali.

In 2006, He et al. [7] reported that multivalent cations that bind to pulp as counter-ions of acidic groups decrease fiber swelling and interfiber bonding. The presence of Mg^{2+} ions in papermaking also has been reported as possibly causing less swelling in fiber cell walls and less bonded sheets compared to the effect of Na+ ions [21]. Hu and Zhang reported that on low (2.0%) alkali doses, using magnesium hydroxide results in a lower water retention value in acidified pulp than using sodium hydroxide in bleaching [22]. The data presented in Fig. 10 show that the bleaching with the magnesium hydroxide-based additive slightly improved water removal on the press section. This also could result from a reduced amount of anionic trash [6,23] from the bleaching stage. In this trial, water removal on the press section was improved by 5%-7%, which allowed a 3%-4% higher production speed. At the same time, the pulp freeness, steam pressure in the paper machine drying section, and paper moisture content remained constant.

CONCLUSION

This mill-scale trial shows that a new, high-purity magnesium hydroxide-based bleaching alkali significantly lowered the environmental load generated by the hydrogen peroxide bleaching stage, without reducing the pulp brightness, paper qualities, or production efficiency. For both target brightness levels, the magnesium hydroxide-based bleaching gave a high brightness with substantially lower TOC, COD, and BOD_7 emissions when the magnesium-based product was half or more of the total alkali used. In the case of the low brightness grade pulp, the magnesium-based bleaching process measurably improved the brightness. Our results were in agreement with previous findings and confirmed that the magnesium hydroxide-based product is an effective alkali source for peroxide bleaching for northern European mills. **TJ**

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Despite the positive changes in the environmental record of the pulp and paper industry, new legislative processes are in motion that are aimed toward reducing effluent emissions in Europe. In mechanical pulp production, the most obvious place for cutting these emissions is the bleaching stage, which has raised interest in non-sodium-based peroxide bleaching in recent years.

In this study, we have implemented the magnesium hydroxide–based bleaching process on high-brightness pulp. High brightness is a long-standing trademark for the northern European (and especially Finnish) printing paper industry. A great deal of effort was paid to ensure a good brightening effect in the mill trial, which called for optimal and exact dosing of chemicals. The observed reduction in the environmental load of bleaching was surprisingly large. This is also the most important finding of this study from the industrial viewpoint. In the near future we are looking for new applications for magnesium hydroxide in pulping processes.

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