Using magnesium hydroxide (Mg(OH)$_2$) as the alkali source in peroxide bleaching at Irving paper

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Abstract: Mg(OH)$_2$ was used to replace sodium hydroxide and sodium silicate in a TMP peroxide bleaching process. Brightness gain with Mg(OH)$_2$ as the sole alkali source is comparable to the caustic/silicate based process. The Mg(OH)$_2$ process produced less anionic trash in the pulp and lower effluent COD content. The sequential addition of chemicals with hydrogen peroxide last was superior to the conventional peroxide bleaching process. Improved economics and performance have been proven in the mill application.

The conventional sodium hydroxide (NaOH)-based peroxide bleaching process is effective in increasing pulp brightness for mechanical pulps. However, as a strong base, sodium hydroxide can cause the dissolution of carbohydrates, particularly hemi-cellulose, into the bleach effluent and is responsible for the increased COD and BOD load to the secondary treatment system. Also, the high alkalinity of the process leads to the formation of a significant amount of anionic trash, which is carried onto the wet-end of the paper machine. This can have negative consequences on papermaking operations, such as increased polymer/additive cost, reduced drainage and decreased product quality.

In recognition of the drawback associated with the NaOH-based peroxide process, peroxide bleaching using weak alkali sources, such as magnesium hydroxide (Mg(OH)$_2$), has received much attention recently. Griffiths and Abbot [1] studied the use of magnesium oxide as the alkali source in a peroxide bleaching of pine TMP, and found that brightness gain is inferior to that of NaOH based peroxide process (about 2 units less at the same peroxide charge). Soteland et al. [2] observed that the size and shape of magnesium oxide particles have a significant impact on the bleaching results and under optimum condition, the magnesium oxide-based peroxide process produced a bleached pulp with about 1.5 units lower in brightness than the NaOH-based process under otherwise identical conditions. Recently, Seuss et al. [3] reported that the application of magnesium hydroxide as an alkali source to bleach mechanical pulps is very attractive. The COD is decreased by 30-40% and the sodium silicate charge can be decreased significantly. Johnson et al. [4] recently concluded many advantages associated with using Mg(OH)$_2$ as the alkali source for bleaching mechanical pulps. In addition to the open literature, there are a number of patents or patent applications on using magnesium oxide or magnesium hydroxide as the alkali source for bleaching of mechanical pulps [5,6].

Irving Paper has made significant progress in decreasing the production cost in its peroxide bleaching stage [7,8], and the effort continues. Most recently, it tested the magnesium hydroxide-based peroxide process at the mill. In this paper, we will report the laboratory and the mill results.

EXPERIMENTAL

Material
Hydrogen peroxide (30% H$_2$O$_2$), magnesium sulfate (MgSO$_4$·7H$_2$O), sodium hydroxide (NaOH)
and manganese sulfate monohydrate (MnSO₄·H₂O) were supplied by Fischer Scientific. Sodium silicate used throughout the study was a clear industrial solution, its Na₂O/SiO₂ molar ratio is 3.1. Diethylenetriamine pentaacetic acid sodium salt (DTPA) was 50% industrial solution. An industrial-grade Mg(OH)₂ slurry (81.2% Mg(OH)₂, the transition metal contents are 1.9 ppm Cu, 797 ppm Fe, and 113 ppm Mn) was supplied by Martin Marietta Magnesia Specialties. The mill chelated TMP with 2.6 ppm Cu, 79.7 ppm Mn, 16.0 ppm Fe, an initial brightness of 55.8% ISO, was received from Irving Paper. Bleached sulfite pulp, used for decomposition trials for Figures 2 - 4, was supplied by a mill in Eastern Canada at 17.7% pulp consistency (1.6 ppm Cu, 25.2 ppm Fe and 1.4 ppm Mn).

Peroxide Stabilization Study

It was carried out with continuous stirring in capped polyethylene containers supported in a constant water bath at 60°C. The initial concentration of hydrogen peroxide was 1.6 g/L. Whenever pulp was needed its consistency was 4%. The total volume of the solution used was 250mL. Unless otherwise stated, the procedure for mixing of solutions simulated the cascade bleach liquor preparation method practiced in industry, that is the stabilizer (DTPA, Na₂SiO₃) the alkali source, and H₂O₂ were mixed together and then the mixture was charged to pulp to which Mn²⁺ had been added.

The extent of the reaction was monitored by withdrawing 5mL samples at specified times, and the residual hydrogen peroxide was determined by following PAPTAC standard testing method, J.16P.

Conventional Peroxide Bleaching

The bleach liquors were prepared by adding, in order, the required amounts of magnesium sulfate, sodium silicate or DTPA (if needed), sodium hydroxide or Mg(OH)₂, and hydrogen peroxide solution to a beaker containing deionized water. Then, the mixed solution was added to the pulp in a polyethylene bag and the pulp slurry kneaded for two minutes. After the required retention time, a liquid sample was taken to determine the ending pH and the residual peroxide. The pulp slurry was required retention time, a liquid sample was taken to determine the ending pH and the residual peroxide.

The P₃ Process [8]

DTPA and Mg(OH)₂ were added to a pulp suspension in a polyethylene bag. After a thorough mixing, the bag, with its contents, was placed into a water bath at 60°C for one minute. Then, the required amount of hydrogen peroxide was added to the bag. Again, a thorough mixing was provided and the bleaching was allowed to continue for 5 hours at 60°C. The subsequent procedures were the same as those in the conventional P process.

RESULTS AND DISCUSSION

H₂O₂ Stability in the Mg(OH)₂ System

We first studied the H₂O₂ stability with an industrial grade Mg(OH)₂ since it contains some transition metals, (see Experimental for details), under typical bleaching conditions.

Figure 1 shows that in Run 1, with industrial-grade Mg(OH)₂ slurry, some peroxide decomposition occurred. This must be caused by the impurities in the system, since no peroxide decomposition was observed in Run 2, with analytical grade magnesium hydroxide.

Na₂SiO₃ or DTPA was then tried as the stabilizer to decrease the peroxide decomposition in the industrial-grade Mg(OH)₂ system. From the results in Figure 2 which show that in Run 1, Na₂SiO₃ was used as the stabilizer at a typical concentration for commercial peroxide bleaching at medium consistency, one can observe that no peroxide decomposition occurred. In Run 2, DTPA was used as the stabilizer at 0.5% concentration, on pulp at 10% pulp consistency, one can find that the peroxide stability was similar to that in Run 1. In Run 3, no stabilizer was used and the peroxide decomposition was extensive. Hence, Na₂SiO₃ and DTPA are good stabilizers to minimize the peroxide decomposition in such a system.

Figure 3 compares Mg(OH)₂ and NaOH systems when using Na₂SiO₃ to decrease the peroxide decomposition. One can observe that silicate is much more effective in decreasing the peroxide decomposition for the Mg(OH)₂ solution than for the NaOH solution. At a silicate charge of 1.5 g/L, there is almost no hydrogen peroxide decomposition under the conditions studied, as indicated in Run 1 for the Mg(OH)₂ process. This is significantly different from the sodium hydroxide based process, which needs much higher silicate to have satisfactory stabilization under otherwise the same conditions. This difference must be attributed to the fact that the Mg(OH)₂ has a mild alkalinity in comparison to NaOH.
The implication from the above results is that for the Mg(OH)₂-based process, the silicate charge (and/or other stabilizers) to achieve effective bleaching would be much less than that in the conventional NaOH process. This is beneficial for reduced bleaching cost and reduced formation of anionic trash. Silicate is an important source of anionic trash during the peroxide bleaching process.

Figure 4 presents the results regarding the use of DTPA as a stabilizer to decrease peroxide decomposition in both Mg(OH)₂- and NaOH-based peroxide processes. For the Mg(OH)₂-based peroxide process the peroxide stability increases with increase in DTPA charge up to 0.5 g/L, thereafter an increase in DTPA results in lower residual peroxide. For the NaOH-based process the same trend is observed however, a higher DTPA charge (2 g/L) is needed to attain the maximum stability. This is in agreement with the study of Qiu [9] who also observed that at a higher pH more DTPA charge is needed to reach the same degree of peroxide stabilization. The decrease in residual peroxide at a very high DTPA charge for both Mg(OH)₂ and NaOH-based peroxide processes can be explained by the peroxide consumption in reaction with DTPA. The reaction of peroxide with tertiary amines is well documented in literature [10].

In summary, the presence of contaminants in the industrial-grade Mg(OH)₂ system induces hydrogen peroxide decomposition, however, it can effectively be reduced with conventional stabilizers, such as Na₂SiO₃ and DTPA. In comparison with the NaOH-based process, the Mg(OH)₂-based process needs substantially lower amounts of stabilizer to reach the same degree of peroxide stabilization.

Laboratory Trials

A comparison of NaOH-based and Mg(OH)₂-based peroxide processes is shown in Table 1. For the Mg(OH)₂ system, three Mg(OH)₂ dosages were tested and the PM process [8] was investigated. The results show that the optimum Mg(OH)₂ dosage is 1% and the conventional mode (the P process), the Mg(OH)₂-based peroxide process gives a slightly lower brightness than the NaOH-based process. The PM process (DTPA and Mg(OH)₂ added to pulp slurry first, and 1 min later, H₂O₂ added), results in a higher brightness and a higher H₂O₂ residue. This confirms that the PM process is applicable to the Mg(OH)₂-based process, and improves the performance of peroxide in bleaching mechanical pulps.

Due to a low alkalinity associated with the Mg(OH)₂-based peroxide process, pulp fibers may not swell to the same extent, which may affect fiber to fiber bonding. This could result in decreased strength properties of the bleached pulp. A comparison of strength properties of the two bleached pulps is shown in Table 2. The difference in tensile, tear and burst are very small. There is also a small increase in bulk (from 2.52 to 2.59 cm³/g). This is quite different from the results obtained from other pulps, such as maple CTMP [11]. A possible explanation is that the freeness of the Irving TMP pulp (spruce/a small amount of fir) is about 70 mL, significantly lower than the BCTMP maple grade (about 350 mL). The pulp fibers of Irving TMP are well developed, and the change in alkalinity from the NaOH-based process to the Mg(OH)₂-based process would have a negligible effect on fiber development for the Irving TMP.

The COD in the bleach process effluent and the anionic

![Figure 4. Peroxide Stabilization with DTPA in Mg(OH)₂-based and NaOH-based processes (4% pulp consistency, 3 ppm Mn²⁺, 1 g/L NaOH, 1 g/L H₂O₂, 60°C, 90 min).](image)

![Figure 5. Comparison of COD in the effluent between the NaOH-based and the Mg(OH)₂-based processes.](image)
trash in the bleached pulp are of significant interest from a practical point of view. The comparisons of COD and anionic trash in the effluent, between the NaOH-based and the Mg(OH)₂-based processes, are found in Figures 5 and 6, respectively. The Mg(OH)₂-based process produces about 20% less COD than the NaOH-based process. The decrease in anionic trash in the bleached pulp is more dramatic, a 40% reduction is noted in Figure 6 for the Mg(OH)₂-based process. Both are related to the much lower alkalinity offered by the Mg(OH)₂-based process.

Mill Trials

Based on the positive results from the laboratory study, a mill trial was conducted at Irving Paper in December 2002. The following two cases were tested:

- The NaOH based process (control run), see Figure 7, 1.55% H₂O₂, 1.0% NaOH, 3.0% silicate (as solution), 60°C.
- The Mg(OH)₂ based peroxide process (Figure 7), 1.51% H₂O₂, 1.0% Mg(OH)₂, no silicate, 60°C.

In the control run, H₂O₂ was added to the pulp slurry via the MC pump #2, while caustic soda and silicate were added via the T-mixer, about one minute downstream from the #2 pump (top Figure 7). For the Mg(OH)₂-based process, Mg(OH)₂ slurry was added via the #2 pump and H₂O₂ via the T-mixer.

The results from the mill trial are summarized in Table 3. The strength properties (tensile, tear) and brightness results were similar between the two processes. It should be noted that the bleaching chemical cost of the Mg(OH)₂-based process is less than that of the NaOH-based process. In addition, the cationic demand of bleached pulp from the Mg(OH)₂-based process was about 15 to 20% lower than that from the NaOH-based pulp. This translates to significant saving in the cationic polymers requirement of the paper machine wet-end operation.

CONCLUSION

The Mg(OH)₂-based peroxide process is effective in improving the bleaching process for mechanical pulp. It decreases bleaching costs while producing bleached TMP with similar optical and strength properties. The PM process makes a significant contribution in this regard. The process has been successfully trialed at the Irving Paper bleach plant. Benefits have been seen throughout the mill, including: i) a lower bleaching cost, ii) decreased COD in the bleaching effluent and iii) decreased anionic trash. Since September 2003, the mill has achieved a significant reduction in the overall manufacturing cost.

REFERENCES


Résumé: Du Mg(OH)2 a été employé pour remplacer l’hydroxyde de sodium et le silicate de sodium pour le blanchiment au peroxyde d’une PTM. Le gain de blancheur avec le Mg(OH)2 comme seule source d’alcali est comparable à celui du procédé caustique-silicate. Le procédé au Mg(OH)2 a produit une pâte ayant moins de déchets anioniques et des effluents présentant une plus faible teneur en DCO. L’ajout successif de produits chimiques, avec le peroxyde d’hydrogène en dernier lieu, a donné un meilleur résultat que le blanchiment au peroxyde classique. L’amélioration des coûts et de la performance ont été confirmés lors de l’application en usine.


Keywords: MAGNESIUM HYDROXIDE, THEMOMECHANICAL PULPS, PEROXIDE BLEACHING, ALKALI, POLLUTION CONTROL.