CALCIUM HYDROXIDE AS AN ALTERNATIVE ALKALI FOR THE OXYGEN BLEACHING STAGE OF KRAFT PULP

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In this study, replacement of sodium hydroxide with calcium hydroxide in the oxygen bleaching stage of commercial Kraft pulping was studied using yellow pine Kraft pulp obtained from a company in the US. The impact of sodium hydroxide, calcium hydroxide, reaction time and temperature on Kraft pulp was evaluated. The sodium hydroxide and calcium hydroxide dosage was varied between 0% and 15% based on oven dry fiber content. The bleaching reaction time was varied between 0 and 360 min, whereas the bleaching temperature ranged between 70 °C and 110 °C. The ability to bleach pulp was measured by determining the Kappa number. Optimum bleaching results were obtained at 2% and 3% calcium hydroxide content. Beyond this, the ability to bleach pulp decreased. The optimum bleaching time for using calcium hydroxide was determined at 40 min, with no significant change in the Kappa number up to 60 min of bleaching time.

Keywords: biomass, biogas, pre-preparation, chemical oxygen demand, hydrothermal treatment, grinding

INTRODUCTION

Since the commercial implementation of oxygen bleaching in 1970 in a South African mill, this process has replaced the use of the chlorine bleaching stage of Kraft pulp.[1,2,3] One of the limitations of using chlorine was the environmental impact caused by residual chlorine pollution in the effluent stream of the pulp and paper mills.[4] The oxygen bleaching process is safe and environmentally friendly, which allows the effluent contents to be burned for energy generation in the Kraft recovery process of paper and pulp mills. This saves energy and further reduces the impact on the environment by not releasing organic compounds in the waste water. In the last 40 years, research work has been done to improve the oxygen bleaching efficiency of chemical pulp. One of the developments that highly contributed to the rapid growth of oxygen bleaching was the discovery of magnesium ions as a cellulose protector agent.[1,5]

Recently, it has been discovered that oxygen bleaching selectivity can be improved by implementing two consecutive oxygen bleaching stages.[3] The first oxygen bleaching stage of this system has a required process time of 20 to 30 min at a process temperature of 80 °C to 85 °C, whereas the second bleaching stage has a higher operating temperature between 90 °C to 100 °C and a reaction time between 40 min to 60 min required for efficient pulp bleaching.[3]

The following requirements should be met to further improve the oxygen bleaching process: low environmental impact, low process cost, the developed system should run safely in a pulp mill, and maintaining low carbohydrate degradation. To achieve the above requirements, the replacement of sodium hydroxide with calcium hydroxide in the oxygen bleaching of Kraft pulp was studied. Calcium hydroxide is well known to be a cheaper commodity than sodium hydroxide.[6,7] Further literature shows that calcium hydroxide effluent has less impact on the environment due to fewer organic compounds, resulting in a 30% drop in chemical oxygen demand (COD) in the effluent as compared to sodium hydroxide use in the peroxide stage.[6,7] By replacing sodium hydroxide with calcium hydroxide, the bleaching equipment does not need to be changed or modified. However, using calcium hydroxide might cause scaling on the interior surfaces of the bleaching equipment or reactor.[8]

This study focuses on the physical and chemical limitations of oxygen bleaching with calcium hydroxide using Kraft pulp.

EXPERIMENTAL

The methodology section describes the equipment, procedures and materials used to investigate the oxygen beaching process using calcium hydroxide as an alternative alkali.

Quantum reactor

For this study, a Quantum reactor was used to perform pulping and bleaching experiments. The Quantum reactor is a three liter pressure vessel. It has a large agitator, which can mix a pulp fiber suspension with a consistency of up to 10%. The agitation is automated, therefore, running time and pause time can be defined. In addition, agitator speed is variable and is set before the reaction starts. The reactor lid has a valve that allows the injection of gases, such as oxygen (O_2) or carbon dioxide (CO_2) used for this study. The bottom of the reactor contains an additional valve. This valve can be used to take a filtrate sample from the reaction or for general cleaning purposes. A pressure gauge and a temperature gauge are helpful to monitor the reaction.

Washing of pulp. Kappa number

A 15 cm Büchner funnel was used to wash the bleached pulp. The Büchner funnel was attached to a 20 liter filter flask, which was connected to a vacuum system. A paper machine former fabric was added to the Büchner funnel instead of a filter paper, to maximize dewatering and prevent clogging of the funnel pores. Bleached pulp was placed in the Büchner funnel and washed with 15 liters of deionized water. By applying vacuum to the Büchner flask, deionized water was forced to move through the pulp cake. After washing was concluded, the pulp was wrapped in a lager paper machine former fabric. With a small press, the wrapped pulp cake was additionally dewatered. After this, the pressed pulp cake was chopped into homogenous small pieces by a crumbling machine. From the homogenized pulp, a pulp pad was made with an 8 cm Büchner funnel. The pulp pad was air dried for Kappa number measurement. The Kappa number and viscosity were measured according to the TAPPI test method T 236 om-06 and T 254 cm-00.[9,10]

Pulp material

For this study, commercial yellow pine Kraft pulp was used. The pulp was taken from the pulping process after the washing stage of the digester. Unfortunately, even after the washing stage of the digester, a high amount of black liquor remained in the pulp. In order to remove the black liquor, the pulp was washed again after the pulp was received. Because of degradation of lignin that occurred during the transport, the pulp used in this study had an initial Kappa number of 11 or 12. The delignification results are correlated to the incoming Kappa number. A high initial Kappa number indicates a higher lignin content, *i.e.* the pulp is easier to bleach, whereas a low initial Kappa number indicates a low lignin content and thus a more difficult to bleach pulp.[11]

RESULTS AND DISCUSSION

In this study, the focus is to replace sodium hydroxide with calcium hydroxide in the oxygen bleaching stage of chemical pulping. Conventionally, sodium hydroxide is used as a base in the oxygen bleaching stage of chemical pulping. Sodium hydroxide has a pH of 13 and a high solubility (1 kg/L). This high pH is important in the bleaching process because a high pH is needed to degrade lignin and create new functional groups, such as carboxylic acids and phenols, which support the solubility of lignin.[12]

Calcium hydroxide also has a high pH (pH 12.6 saturated). Further, calcium hydroxide solubility is extremely low (17.3 g/L). The lower solubility of calcium hydroxide might reduce bleaching efficiency. However, calcium hydroxide is less environmentally damaging and less expensive than sodium hydroxide. By changing alkali concentration, as well as time and temperature, in the Quantum reactor, the performance of sodium hydroxide and calcium hydroxide can be compared.

Concentration of alkali

The relationship between increasing sodium hydroxide or calcium hydroxide concentration and Kappa number is shown in Figure 1, representing the impact of sodium hydroxide in the oxygen bleaching stage at a concentration between 0% and 14%.

Each data point represents one bleaching experiment. Conventionally, the amount of an alkali used in the oxygen bleaching stage is between 2% and 3%. Looking at the sodium hydroxide graph, a reduction of the Kappa number with an increasing amount of sodium hydroxide can be observed. The impact of sodium hydroxide in a bleaching sequence reveals two different trends. First, at a concentration of 0 to 4% sodium hydroxide, a significant drop of the Kappa number can be observed. In this range, a good amount of lignin is removed with a small amount of sodium hydroxide.

Further, with a sodium hydroxide content between 4 and 14%, a less strong reduction of lignin is achieved. A similar behavior is reported in the literature, where a first increase of alkali concentration is reported to lead to a rapid phase of delignification. Further, beyond this rapid phase, an exhaustion of alkali is recognized.

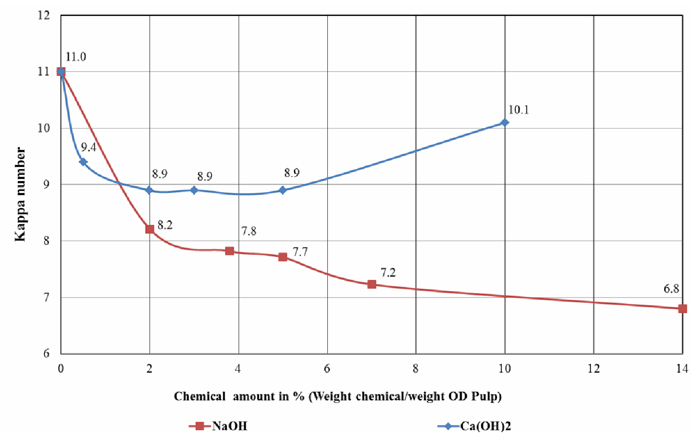

Figure 1: Relation between Kappa number and sodium hydroxide or calcium hydroxide concentration in O-stage, Quantum reactor (90 °C, 90 PSI, 60 min)

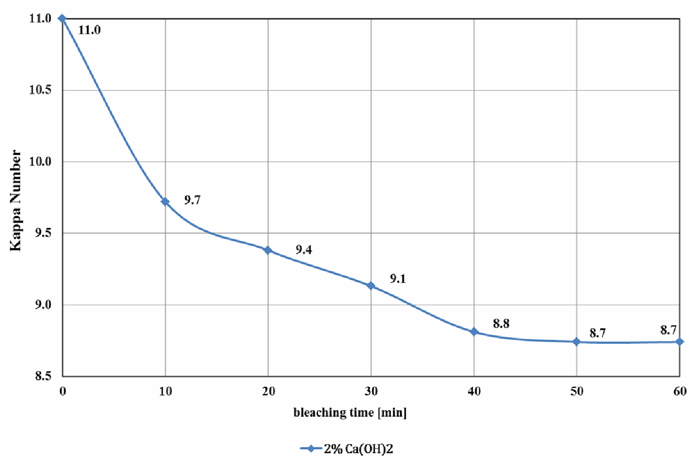

Figure 2: Changes of Kappa number with bleaching time in O-stage, Quantum reactor (90 °C, 90 PSI, 60 min)

The impact of calcium hydroxide at a concentration from 0% to 10% was tested. A concentration between 0% and 2% calcium hydroxide shows a significant reduction in the Kappa number. Between 2% and 5% concentration of calcium hydroxide, there is no change in the Kappa number. Therefore, in this case, the optimum concentration of calcium hydroxide was found between 2 and 5%. Beyond a concentration of 5% calcium hydroxide, the Kappa number begins to increase. This means that beyond 5% calcium hydroxide the bleaching result is negatively impacted. Therefore, the calcium hydroxide study shows that a high amount of calcium hydroxide is not helpful for the oxygen bleaching stage.

In general, it can be said that the most economically and chemically efficient bleaching results for the oxygen bleaching stage is found with 2% calcium hydroxide and 3.8% sodium hydroxide. When 2% calcium hydroxide was compared to 3.8% sodium hydroxide (*i.e.* 1:1 molar ratio), sodium hydroxide had a better pulp bleaching effect as reflected in the lower Kappa number (7.8 Kappa), compared with the pulp bleached with calcium hydroxide that had higher Kappa number of 8.9. Therefore, bleaching pulp with sodium hydroxide led to a 29.1% decrease in

Kappa number, as compared to bleaching with calcium hydroxide, which led to a 19.1% decrease.

Reaction time *versus* bleaching results for calcium hydroxide

Bleaching time is important because it has a direct impact in the reaction kinetics of bleaching. Figure 2 shows a significant decrease in the Kappa number is achieved after 10 min of bleaching with oxygen and 2% calcium hydroxide. Between 10 and 40 min, a weaker decrease in the Kappa number is observed. Further, between 40-60 min the bleaching efficiency starts to flatten out. Under these conditions, a good bleaching result is achieved after 40 min.

Stopping the bleaching after 40 min instead of 60 min reduces the bleaching time by 30%. These results are consistent with a previous report, which found that these types of reactions proceed very rapidly at the beginning and then more slowly over time.[1]

Temperature investigation

Besides bleaching time, temperature plays a major role in bleaching kinetics. In this study, three temperatures were used: 70 °C, 90 °C and 110 °C. Conventionally, in the pulp industry, a temperature of 90 °C is used. The solubility of calcium hydroxide is reduced as temperature increases. Therefore, the concentration of calcium hydroxide is adjusted to reflect this change. A measurement of the ratio of dissolved to not dissolved calcium hydroxide at 90 °C is taken. The same ratio is used for 70 °C and 110 °C. Using a lower temperature reduces heating costs. However, a lower temperature, *e.g.* 70 °C, does not perform as well as a higher temperature, *e.g.* 110 °C (Fig. 3). Using 110 °C helps improve the bleaching result. In addition, the concentration of calcium hydroxide is reduced from 2.8% to 1.6%, a reduction of nearly one-half. Using 50% less calcium hydroxide reduces the negative environment impact and improves material costs; however, more energy would be needed to heat the pulp fiber suspension, which would offset the gains for less chemical usage.

Acid wash study

To displace dissolved organic and soluble inorganic materials after O-stage pulping, a pulp wash study with various wash water pH was performed. Sulfuric acid is used in a concentration of 0.2M to reduce the pH of pulp. By reducing pH, soluble lignin should precipitate in the washing liquid. In addition, literature shows that hydrogen ions of acids can replace the calcium ions that are bonded to the lignin.[13] Different levels of pH were tested to determine if calcium ions can be removed from lignin with a small impact of cellulose degradation.

After O-stage pulp was separated into four smaller samples, the samples were diluted with deionized water and sulfuric acid was added. The washing test revealed that if 2% calcium hydroxide bleached pulp with a pH of 2 and 4 is washed, a reduction in the Kappa number up to 0.4 points (Fig. 4) can be achieved. Further, the washed bleached pulp using 2% calcium hydroxide for bleaching resulted in a final pH of 8.0 and a 0.7 point Kappa number reduction. Washing 5% calcium hydroxide bleached pulp with a pH of 2.0, a 1.7 point reduction in Kappa number was achieved. The bleached pulp washed with pH 4 achieves a decrease of 0.5 Kappa number. Finally, the pulp washed at pH 8.0 achieved a reduction of almost 1 Kappa number.

In general, acid washing can reduce the Kappa number of the pulp by 0.5 to 1.7, depending on the pH.

Sequential runs, bleaching time and calcium hydroxide *vs*. calcium oxide

The focus of this work is to reach a similar bleaching result with calcium hydroxide as with sodium hydroxide. An improvement of bleaching with calcium hydroxide is achieved by sequentially running the oxygen bleaching stage. The first run with calcium hydroxide reduces the Kappa number from 11 to 8.5 (Fig. 5). The second and third bleaching runs reduce the Kappa number to 8.1 and 7.6 respectively.

Bleaching for one hour with calcium hydroxide reduces Kappa number from 11 to 8.5. By increasing bleaching time to three hours, the Kappa number can be reduced from 11 to 8.1. Bleaching pulp for three hours with calcium hydroxide achieves a similar reduction in Kappa number, as 2 sequential runs with calcium hydroxide.

Bleaching with 1.7% calcium oxide shows a similar behavior as bleaching with 1.7% calcium hydroxide. Further, the bleaching result with 17% calcium oxide shows a higher Kappa number than bleaching with 1.7% calcium oxide. This indicates that 17% calcium oxide is less efficient than 1.7% calcium oxide. Even though bleaching with 1.7% calcium oxide achieves the same Kappa number as calcium hydroxide, there might be energy cost savings by selecting calcium oxide. If calcium oxide comes in contact with water, an exothermic reaction takes place. By this reaction, calcium hydroxide is formed. The exothermic heat, by lowering the amount of external energy required to heat up the pulp to 90 °C, might reduce the process cost.

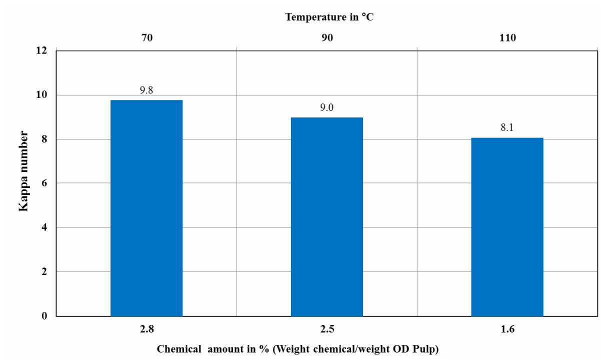

Figure 3: Effect of temperature on Kappa number in O-stage, Quantum reactor (90 PSI, 60 min)

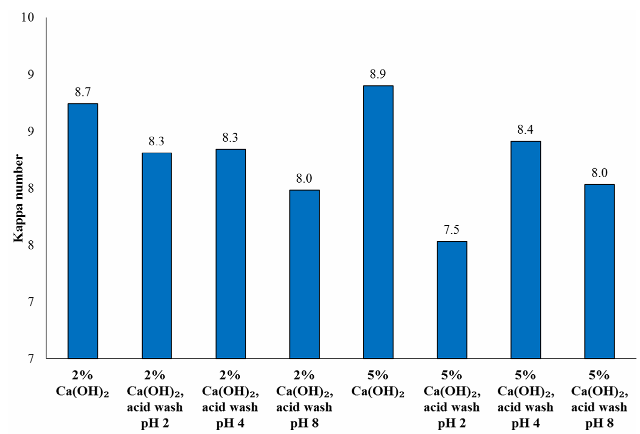

Figure 4: Sequential runs, bleaching time and calcium hydroxide *vs*. calcium oxide

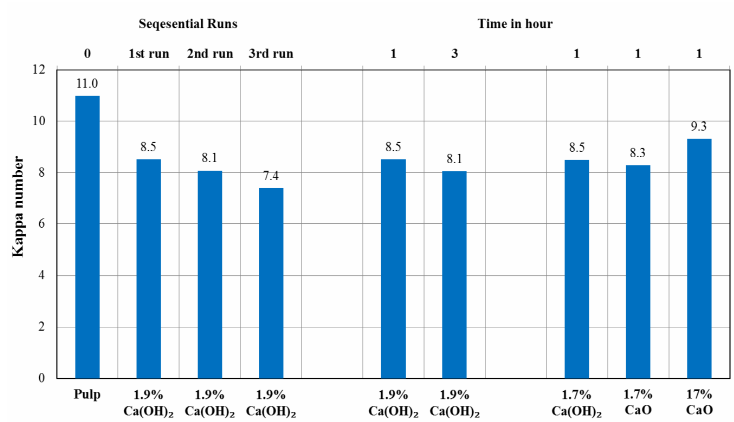

Figure 5: Characteristics of Kappa number through multiple sequence runs with 1.9% calcium hydroxide (a); increasing bleaching time from 1 to 3 h (b); 1.7% calcium hydroxide *vs*. 1.7% calcium oxide and 17% calcium oxide (c) in O-stage, Quantum reactor (90 °C, 90 PSI, 60 min)

CONCLUSION

In this study, replacement of sodium hydroxide with calcium hydroxide in the oxygen bleaching stage of commercial kraft pulps was studied. It was found that calcium hydroxide concentrations of 2% and 3% reached optimum bleaching efficiency for yellow pine Kraft pulps. Beyond this optimum level, the bleaching result was negatively impacted.

Increasing the bleaching time, bleaching temperature, bleaching sequences and sodium hydroxide concentration in combination with calcium hydroxide achieved a positive impact on bleaching efficiency.

One O-stage with calcium hydroxide followed by washing and another O-stage with sodium hydroxide should help to improve the bleaching process, compared to two successive O-stages with calcium hydroxide.

Further research should investigate the environmental impact of the bleaching process effluent streams, such as filtrate and wash water in regard to chemical oxygen demand.

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