

Caustic treatment of OCC for strength improvement during recycling

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ABSTRACT: *This study investigates whether a caustic soaking tower is necessary for OCC. It presents optimum process parameters for soaking. It shows that the components of OCC behave differently during sodium hydroxide treatment. Using optimum conditions, the OCC short span compression index increases 10.6% whereas the linerboard increases 20.4% and the medium increases 11.3%.*

KEYWORDS: *Bibliographies, corrugated boxes, linerboards, mechanical properties, process variables, reclaimed fibers, recycling, soaking, sodium hydroxide.*

As legislation forces the increased use of recycled fibers in paper, the papermaker must find ways to achieve maximum strength from an inferior starting material. It is common knowledge that during virgin fiber drying the cell walls collapse with increasing hydrogen bond formation (1, 2). In subsequent cycles, the existing hydrogen bonds do not all break. This reduces the swelling ability of the fiber. Less swollen secondary fiber is not as flexible as virgin fiber. As a result, the strength potential of the pulp decreases.

During the formation of a new paper sheet, the fiber is not able to form as many fiber-to-fiber hydrogen bonds. This causes lower strength (1). Freeness of recycled

secondary fiber is also lower because of an increase in the fines content. The fines increase the specific surface area and act as fillers. The fines therefore contribute little to the strength, although they significantly affect the drainage properties.

Processes which promote swelling should improve the strength potential of the pulp (3). Sodium hydroxide will improve swelling and can therefore potentially enhance the sheet strength (4-11).

Caustic soaking generally leads to strength improvements in pilot scale studies. In a mill trial, however, the expected strength improvements sometimes do not occur. There is no known explanation for this phenomenon.

We undertook this study to determine the optimum caustic soaking parameters for a 100% recycle facility using a furnish of old corrugated containers (OCC) to produce new linerboard. The work addresses several critical issues. The first is to determine if the optimum soaking reaction time is great enough to require a soaking tower to achieve the best strength improvement for this furnish. Second, it is necessary to determine the optimum process variables of temperature, sodium hydroxide concentration, and consistency. Finally, one must investigate the reasons for the failure of soaking to produce strength improvements in a mill.

Results

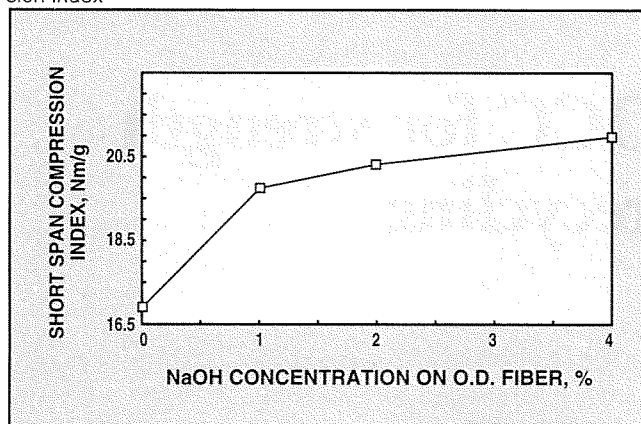
Optimum process parameters for acid papermaking

Figures 1-3 show the process parameters investigated in this study. The optimum parameters are soaking in 2% sodium hydroxide for a minimum of 4 h in the temperature range of 40-70°C. The caustic concentration is 2% sodium hydroxide by weight on o.d. fibers. The consistency can vary from 4-14% without affecting the strength properties. Table I lists a comparison between the strength developed under these conditions vs. the control pulp.

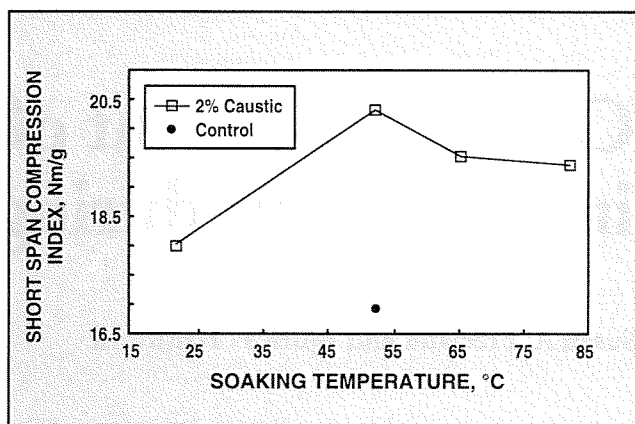
Since the optimum reaction time of 16 h is less than the retention in a

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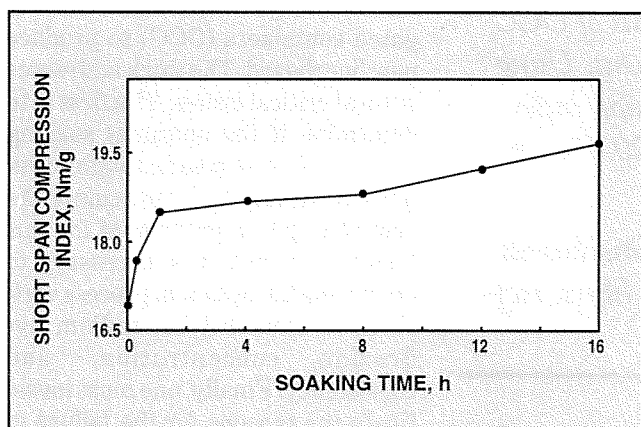
1. Effect of sodium hydroxide concentration on short span compression index



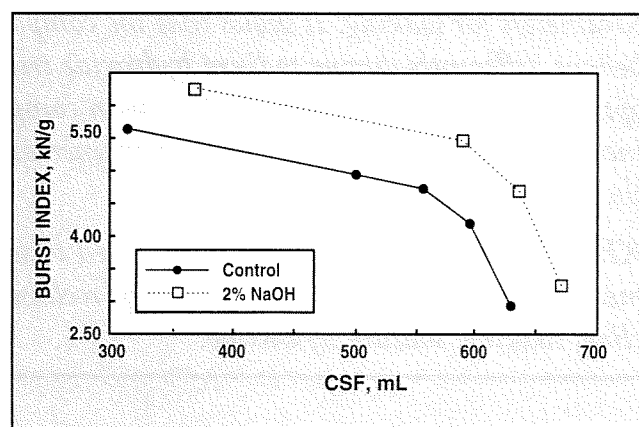
2. Effect of soaking temperature on short span compression index



3. Effect of soaking time on short span compression index



4. Effect of refining on CSF and burst index



commercial soaking tower, a soaking tower is not necessary. It may be possible that the retention in an OCC pulping system is adequate to produce the strength improvements.

Decreasing caliper and increasing density with caustic soaking indicates the sheet is more compact due to an increase in fiber plasticity. The hydroxide ion relaxes the fiber by breaking some of the internal hydrogen bonds which increases flexibility and plasticity. Once the internal hydrogen bonds break, water can incorporate into the fiber creating a swollen fiber. At pH 5.5, however, the water retention value (WRV) decreased due to the reformation of the internal hydrogen bonds. The pulp swelled under alkaline conditions. Washing and acidification of the pulp removed the hydroxide ions

from the fiber forming more hydrogen bonds. The water retention value of the pH 5.5 treated pulp was therefore lower than the untreated pulp. Because of the initial increased plasticity and reduced curl, however, the fibers conform more readily to one another. The sheet density accordingly increases.

The internal bonding and the fiber strength affect tensile properties. Wet zero span tensile, which measures the individual fiber strength, increased by 7.8%. The ratio between tensile strength and dry zero span tensile quantifies the degree of fiber bonding. This ratio increased by 10.6%. As a result of these increases, the tensile index also increased by 11.4%. Z-tensile, which also measures internal bonding of the sheet, increased 19.5%. The internal

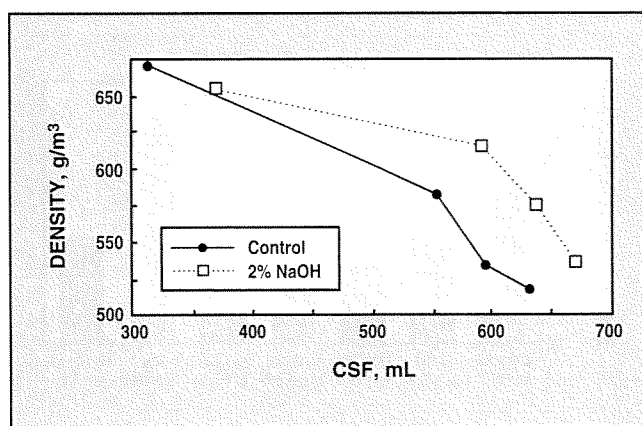
bonding of the sheet increased with sodium hydroxide treatment because of fiber swelling. The swollen fiber has an increased surface area which increases the fiber-to-fiber contact area. As a result, more interfiber hydrogen bonds form, and the internal bonding strength increases.

The lack of an effect on kappa number and yield indicates that delignification and cellulose peeling do not occur to any large extent. The starch content of the pulp decreased due to reaction of the starch with the sodium hydroxide. The fines content did increase, but the increase was not detrimental to the sheet properties.

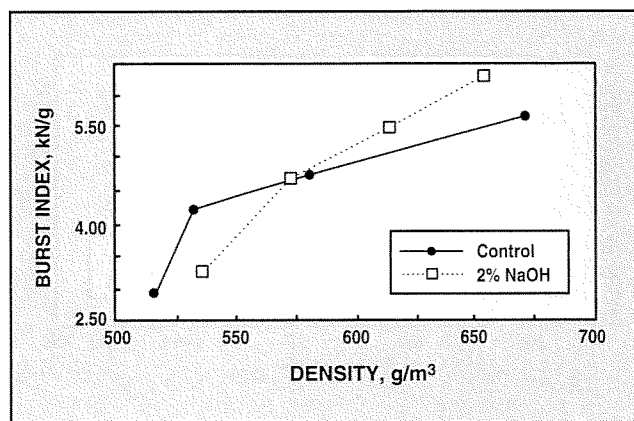
Effect of refining

We beat control and sodium hydroxide treated pulps in a PFI mill dur-

5. Effect of refining on CSF and sheet density



6. Effect of refining on sheet density and burst index



I. Comparison of control and 2% sodium hydroxide treatment on strength properties

	Control	2% NaOH	Change from control, %	2% NaOH	Change from control, %
Test identification no.	6	7		42	
pH	5.5	5.5		11	
Grammage, g/m²	131.7	132.0		130.8	
Caliper, mm	0.250	0.240	-4.00	0.255	2.00
Density, kg/m³	530.4	542.7	2.32	516.2	-2.68
CSF, mL	621	635	2.25	500	-19.48
Burst index, kN/g	2.92	3.31	13.54	4.67	60.21
Short span index, Nm/g	16.86	18.71	11.01	20.57	22.00
Tensile index, Nm/g	34.28	38.17	11.35	47.64	38.96
Wet tensile, Nm/g	1.82	1.84	1.10	1.75	-3.81
Sheet bonding, Nm/g	32.46	36.33	11.93	45.89	41.35
Tensile energy absorption, mJ/g	703	804	14.37	1031	46.60
Elongation, %	2.68	2.80	4.21	3.01	12.23
Dry zero span tensile, kN/g	3.12	3.14	0.64	3.10	-0.51
Wet zero span tensile, kN/g	2.45	2.64	7.79	2.77	13.11
Fiber to fiber bonding ratio	11.00	12.17	10.64	15.37	39.67
Z-tensile index, kN/g	2.28	2.72	19.56	3.50	53.64
Gurley porosity, s	4.8	6.4	33.33	9.4	95.83
WRV, g/g	1.951	1.871	-4.09	2.081	6.64
Kappa no.	87.5	86.4	-1.26	86.4	-1.26
Yield, %	94.1	93.1	-1.06	93.1	-1.06
Fines content, %	0.97	6.33		6.33	
Starch content, wt. %	1.5	1.1	-26.67	1.1	-26.67

ing the soaking treatment. **Figure 4** shows that the strength of the handsheets increased as the CSF decreased. The sodium hydroxide treated samples have a greater strength than the control at the same

freeness. As fibers swell, the surface area to weight ratio typically increases. This lowers the freeness. The conclusion is that the freeness of the sodium hydroxide treated pulp should be lower than the untreated

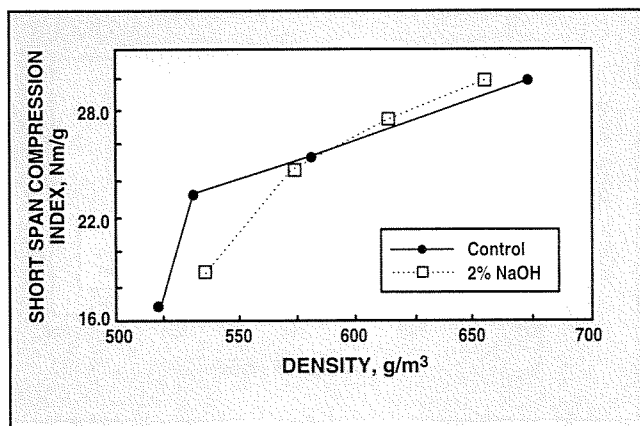
pulp. The treated pulp has higher freeness than the untreated pulp, however, due to the relaxation of the individual fibers. Since the fibers are more relaxed, they suffer much less damage during refining. **Figure 5** shows that this translates into higher freeness after refining and higher sheet density at the same freeness.

At 630 CSF, the burst index is 48% greater for the sodium hydroxide treated handsheets than for the control. The density increased 11%, the short span compression index increased 39%, and the tensile index increased 52%.

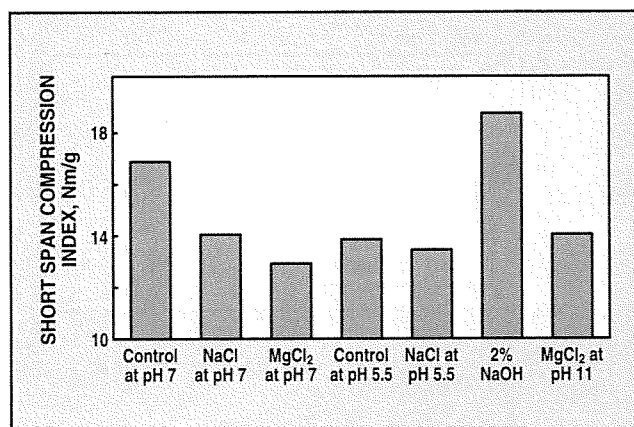
Figure 6 shows that the sodium hydroxide treated pulps develop burst strength at a faster rate than the untreated pulps. At a density of 575 g/m³, the burst index is the same for both pulps. The sodium hydroxide treated pulp required less refining to achieve the same strength, however. As a result, the sodium hydroxide treatment will provide a cost savings during refining, since the strength develops at lower refining cycles.

If sheet density were the only factor contributing to the strength development, the control and sodium hydroxide burst index values would be the same throughout the density range. The treated pulp achieves a larger burst index, however, due to the improved bond area of the swollen fiber. It is not a result of refining. For that reason, the burst index is

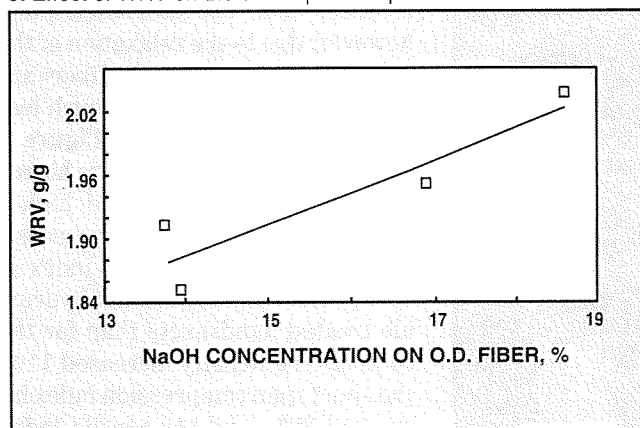
7. Effect of refining on sheet density and short span compression index



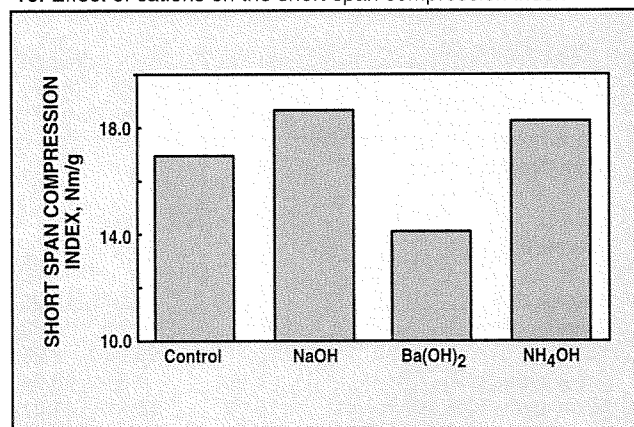
8. Effect of salts on the short span compression index



9. Effect of WRV on the short span compression index



10. Effect of cations on the short span compression index



greater when the sodium hydroxide treatment combines with refining.

The short span compression index has a lower rate of strength development than the burst index, because the short span compression depends more on the sheet density than on the internal bonding. As a result, Fig. 7 shows that the density relates more closely to the short span index. Rate of strength development therefore slows above 575 g/m³.

Strength improvements in the mill environment

Effect of salts

Fresh and white water systems carry various contaminants. The contaminants may affect the swelling and bonding potential of pulp (8, 11, 12, 14, 16). We added several salts to

the soaking step to evaluate the impact of contaminants in the water supply. We added some of the salts to deionized water and others to acid or alkaline slurries.

Figure 8 depicts the effect of salts on the short span compression index. The salts lowered the strength of the sheet for all cases. Magnesium chloride addition to the sodium hydroxide soak gave a poorer performance than the control due to the formation of insoluble magnesium hydroxide reducing the hydroxide ion concentration.

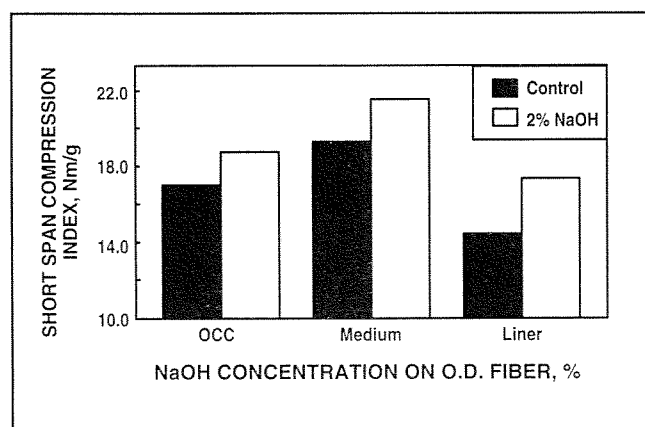
Figure 9 shows the effect of WRV on the short span compression index. As the WRV increases, the short span index also increases. Burst index and tensile index experience the same effect. There is therefore a clear correlation between the strength and the WRV. Any process

which affects the swelling will affect the sheet strength. Since salts are very detrimental to the swelling ability of the fiber, the resulting sheet strength is lower.

Effect of cations on alkaline strength improvement

The proposed mechanism for pulp fiber swelling has indicated that the primary contributors to swelling are the carboxylic acid and the associated counter ion (8-10). Hydroxide ion may also be very important in the swelling mechanism, however. A comparison of various hydroxide ion sources was therefore necessary. Ammonium hydroxide was the selection of a source for an alternate monovalent cation and barium hydroxide the source for a divalent cation. While barium hydroxide has

11. Effect of raw material on the short span compression index



limited solubility, calculations indicated that it gives sufficient hydroxide ion concentrations. **Figure 10** depicts the effect of the hydroxide ion on the short span compression index.

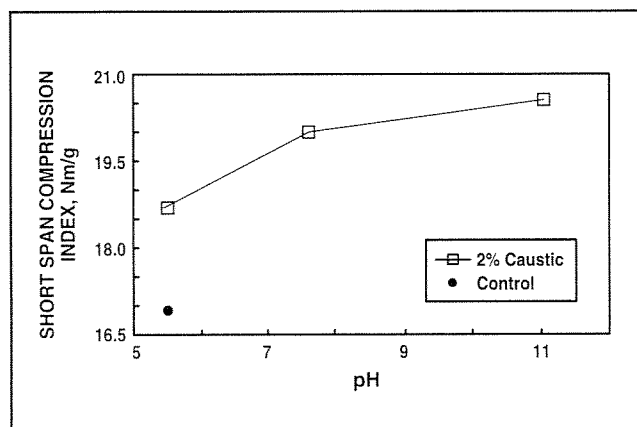
Since previous studies have proposed that divalent cations cause a reduction in strength development (8-11), we used a caustic soaking containing a saturated solution of barium hydroxide to investigate the effect of the barium ion. The pH of the barium hydroxide solution was initially higher than the sodium hydroxide solution. It was the same after soaking which indicates more hydroxide ion consumption during the soaking treatment. Other work reports that the consumption of hydroxide ion is due to the formation of carboxyl groups by the hydrolysis of ester and lactone groups in the pulp (17). The consumption of more hydroxide ion leads to the conclusion that the barium hydroxide should have higher swelling resulting in subsequently greater strength. The barium hydroxide soak resulted in much lower strength than the sodium hydroxide soak, however.

Some researchers propose that multivalent cations reduce the swelling by binding to the carboxylic acid groups and reducing the osmotic pressure (8, 9). One group (11) initially explained the multivalent cation phenomenon resulted from the change in the zeta potential of the

fiber. They later related the effect to the carboxyl content (16). Barium ion will also form large hydrates (13) which would allow the barium ion to bind to the free hydroxyl groups on cellulose. Barium hydroxide precipitates hemicellulose to form insoluble complexes by reacting with the C2 and C3 hydroxyl groups (15). Using all these theories, the barium ion is forming a salt of the carboxylic acid as well as possibly binding to the free hydroxyls of the carbohydrates. Ionization of more carboxyl groups and further hydration of the barium ion reduce the hydroxide ion concentration. During sheet formation, the cellulose is then no longer able to form as many hydrogen bonds, since some of the free hydroxyls bind with the barium ion. The result is lower sheet strength.

We washed pulp treated with barium hydroxide and measured the barium content. Over half of the 15,000 ppm of barium ions in the solution remained with the fiber. If the barium were only present as counterions to the free carboxyl groups, then the concentration of barium ions in the pulp would be closer to 3900 ppm. We based the calculation on 350 meq carboxyl per kg of pulp determined for 66% yield kraft pulp (8). With acid washing of the pulp, the barium concentration decreases to 5500 ppm. This is probably due to the acid removing most of the barium ion from the carboxyls

12. Effect of pH of handsheet formation on the short span compression index



but not removing it from the complex of barium with carbohydrate.

Ammonium hydroxide performed nearly as well as the sodium hydroxide. One expects this since it has a monovalent cation. The resulting strength is slightly lower because the ammonium ion is larger than the sodium ion. It is therefore more difficult to incorporate into the fiber.

Comparison of raw material on strength development

We pulped linerboard from a commercial mill and medium from another commercial source and subjected them to caustic soaking to compare the strength changes of the components to the strength changes of the OCC. **Figure 11** shows the effect of raw materials on the short span compression index.

The short span compression index increased 10.6% for OCC treatment with 2% sodium hydroxide. Treatment of the medium increased the short span compression by 11.3%, while the liner increased 20.4%. The greater strength increase of the liner is probably due to lower lignin content of the kraft liner which allows it to swell more readily than the two stage vapor (TSV) medium. Lignin inhibits swelling by constraining the walls of the fiber and allowing less water into the fiber. Another researcher showed pulp with kappa numbers between 60-90 has the

greatest swelling measured by water retention value (14). The kappa number of the liner used in this study was 69, and the kappa number of the medium used in this study was 103. As a result, the liner had WRV increase of 28% while the medium increased 17%. Lower swelling of the OCC with a WRV increase of 6.6% may be due to the water resistant adhesive used in the corrugating process. Water-resistant adhesives repel water molecules and reduce the amount of water incorporated into the fiber wall.

Effect of sodium hydroxide soaking on the effluent water

Caustic soaking increases the amount of organics in the effluent water. Table II lists the organic contents in the effluent. Total organic carbon (TOC) quantifies the carbon present regardless of structure. BOD measures the oxygen consumed by bacteria as they consume the organics in the water. COD measures the quantity of reducible organics. The results of these three tests are comparable. During caustic soaking, starch from the adhesive solubilizes and enters the effluent stream. Minimal amounts of delignification and carbohydrate peeling slightly increase the organic loading in the effluent.

Increasing the sodium hydroxide concentration increases the BOD. The difference between 1% and 2% sodium hydroxide is not significant, but the difference between 2% and 4% is significant. Even at 4% sodium hydroxide, however, the effluent is much cleaner than the effluent produced in a typical kraft or sulfite process.

Effect of pH of sheet formation

The pH of a papermaking system affects the swelling of the pulp with a concomitant effect on strength. Earlier work showed a maximum WRV for unbleached kraft pulp at pH 10 (14). To assess the effect of pH, we soaked pulp in 2% sodium

II. Fresh and effluent water analysis

	Fresh water	Control	1% NaOH	2% NaOH	4% NaOH
TOC, ppm	<5	336	963	1260	1810
BOD, ppm	<5	230	640	720	1400
COD, ppm	28	866	2880	3870	5200

hydroxide for 4 h at 52°C and 14% consistency. Then we washed it and adjusted it to the desired pH for handsheet formation. Table I compares the paper properties of handsheets made under acid and alkaline conditions. Figure 12 depicts the effect of pH on the short span compression index.

Burst increases 60% over the strength of the untreated pulp compared to 13.5% for pulp at pH 5.5. Short span compression increases 22%, and tensile increases 39%. The internal bonding of the sheet increases 54% as measured by the Z-tensile. Preparing OCC pulp by sodium hydroxide soaking and alkaline papermaking gives a resulting paper whose strength is comparable to that of virgin pulp.

Conclusions

Multivalent cations and salts in a system will hinder the effectiveness of caustic soaking. Every mill must therefore know where any contaminants originate and control their entry into the pulping system. The effect of salts and multivalent cations may partially explain the apparent contradiction in pilot scale and mill trial results.

Since the soaking time of 4 h necessary to achieve the strength is low, a soaking tower is not necessary. Most OCC mills currently have 4–16 h retention time in their high density storage. As long as there is temperature control, the addition of extra storage capacity is not necessary.

Sodium hydroxide soaking of OCC can greatly increase the strength of 100% recycled paperboard. Caustic

soaking can result in energy savings due to reduced refining required to achieve strength. If the papermaking process changes to alkaline, the increase in sheet strength will allow the use of increased OCC content without the use of strength aids such as starch. Several process parameters will need modification to achieve optimum performance from this process. With careful consideration, however, a virgin-like paperboard can result.

Experimental

Materials

This study used 100 pounds of OCC from a commercial box plant. It was an unprinted, combined board of 42 pounds per 1000 ft² double back liner, 26 pounds per 1000 ft² C-flute medium, and 42 pounds per 1000 ft² single face liner. The combined board used water-resistant starch adhesive.

The liner board came from a commercial mill. The kraft liner contained 60% virgin fiber and 40% pre-consumer recycled fiber consisting of machine broke and double kraft lined (DKL) clippings. The virgin fiber contained 43% Douglas-fir, 40% pine, 15% white fir, and 2% other softwoods.

The medium came from a commercial mill. The TSV medium contained 25% virgin fiber, 25% machine broke, 10% tailings as knots from kraft and sulfite mills, and 40% DKL clippings.

Procedure

The combined board underwent hydropulping at 5% consistency and 65°C. The hydropulper was a very

small batch system with a maximum charge of 300 pounds. Extraction plate holes measured 0.625 in diameter. We added two sheets of the combined board at a time with additional water to keep the consistency constant. The hydropulper ran at low intensity for 25 min after addition of all the combined board. After pulping, we dewatered the stock in a 200 mesh screen and then centrifuged it to 30% consistency. We blended the 30% consistency pulp and stored it in plastic lined, 55 gal drums at 4°C until use.

We weighed 304 g of 30% consistency pulp into zippered plastic bags. We prepared a sodium hydroxide solution at the temperature needed for the soaking. We calculated the sodium hydroxide concentration based on the percentage of o.d. fiber. In this way, the ratio of fiber weight to sodium hydroxide content remained constant regardless of consistency. We added the sodium hydroxide solution to the pulp and mixed it thoroughly. We soaked the mixture in a water bath at the desired temperature.

After the desired soaking time, we adjusted the pulp to 3% consistency using deionized water and brought it to pH 5.5 with 50% hydrochloric acid. Then we washed the pulp to remove salt in a 12-in. by 12-in. handsheet mold. The mold had a 200-mesh screen and deionized water. We washed the pulp for 5 cycles of diluting and draining. Then we adjusted the pulp to 0.5% consistency for handsheet preparation. Before making handsheets, we adjusted the pH of the slurry to pH 5.5 with 50% hydrochloric acid.

We prepared 26 pounds per 1000 ft² handsheets in a standard handsheet mold using TAPPI Test Method T 205 om-88. We next conditioned the handsheets and measured physical properties using standard test methods. When refining was necessary, we beat the pulp in a PFI mill using TAPPI Test Method T 248 cm-85. 

Literature Cited

1. DeRuvo, A., Htun, M., and Ehrnorrth, E., *EuCePa 1978 Symposium Proceedings*, EuCePa, Paris, p. 320.
2. Oye, R., Okayama, T., Yamazaki, Y., et al., CPPA, Montreal, p. 191.
3. DeRuvo, A., Farnstrand, P. A., and Hagen, N., *Tappi J.* 69(6): 100(1986).
4. Eastwood, F. G. and Clarke, B., *Paper Tech. & Ind.* 18(5): 155(1977).
5. Kohler, C., 1990 *Fourth Unbleached Kraft Conference Proceedings*, Miller Freeman, San Francisco, no. 14.
6. Hori, H., *Japan Pulp & Paper* 28(4): 27(1992).
7. Eriksson, E. and Sjostrom, E., *Tappi J.* 51(1): 56(1968).
8. Scallan, A. M. and Grignon, J., *Svensk Papperstidn.* 82(2): 40(1979).
9. Katz, S., Liebergott, N., and Scallan, A. M., *Tappi* 64(7): 97(1981).
10. Scallan, A. M., *Tappi J.* 66(11): 73(1983).
11. Cohen, W. E., Farrant, G., and Watson, A. J., *Proc. Aust. Pulp Paper Ind. Tech. Assn.*, 3: (72) 1949.
12. Grignon J. and Scallan, A. M., *J. Appl. Poly. Sci.* 25: 2829(1980).
13. Cotton, A. F. and Wilkinson, G., *Advanced Inorganic Chemistry: A Comprehensive Text*, Wiley, New York, 1980, p. 283-84.
14. Lindstrom, T., in *Paper: Structure and Properties* (J. A. Bristow and P. Kolseth, Ed.), Dekker, New York, 1986, p. 113.
15. Meier, H., *Acta Chem. Scand.* 12(1): 144(1958).
16. Cohen, W. E., Farrant, G., and Watson, A. J., *Proc. Aust. Pulp Paper Ind. Tech. Assn.* 4: 176(1950).
17. Sjostrom, E., *Wood Chemistry Fundamentals and Applications*, Academic Press, New York, 1981.

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