Improving TMP Rejects Refining Through Alkaline Peroxide Pre-treatment for Value-Added Mechanical Papers

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ABSTRACT

We conducted pilot plant trials to clarify the effect of alkaline peroxide pretreatment on TMP rejects. Different alkaline and peroxide charges were applied to the rejects before refining. The study showed that a 2.2% total alkali charge was not sufficient to achieve noticeable energy reduction or physical property improvement. However, at a total alkali charge of 5.2%, alkaline peroxide pretreatment reduced the specific refining energy by 20% to a given freeness, and increased pulp density and tensile strength, most likely as a result of increased fibre flexibility and conformability. With a peroxide charge of 2.9%, the brightness of the refined rejects reached 72%. However, alkaline peroxide pretreatment decreased light scattering and pulp yield.

INTRODUCTION

Mechanical pulps play an important role in the paper industry, not only because of their much higher yield and lower environmental impact as compared with chemical pulps, but also, because of their unique pulp properties, such as high bulk, high light-scattering coefficient, and high opacity [1]. On the other hand, the presence of lignin causes lower sheet strength and reduces the maximum brightness that can be achieved.

In a mechanical pulping process, rejects from screening and cleaning systems contain mainly long fibres and fibre bundles. Rejects refining is a critical step in achieving the desired pulp quality for mechanical value-added papers. The objective of rejects refining is to maximize long-fibre strength and to optimize these long fibres for surface properties. One means of promoting this would be a chemical treatment which would make fibres more flexible.

There are a number of studies on sulphonation of rejects [2–7], but very few reports on alkaline peroxide pretreatment of rejects. Most of the work was reported by Strunk and his colleagues on southern pine TMP and GW rejects for newsprint [8–11]. In general, 10–25% reduction in energy to a given freeness was observed by pre-treating rejects with alkaline peroxide. A retention time of 40 minutes and a temperature of 60°C were found necessary to obtain maximum improvements in pulp properties [9]. When southern pine TMP rejects with a freeness of 462 mL were treated with 4% NaOH and 2% H₂O₂, the tensile index was increased by 20% and the shives content reduced by 50%. However, the bulk was reduced by 18%. A further increase in alkali charge up to 8% did not affect the pulp bulk and tensile strength [9]. In a separate report [11] for southern pine TMP rejects with a higher freeness of 670 mL, 8% NaOH was required to obtain the same 20% increase in tensile. Also, only a 10% decrease in bulk was found with 8% NaOH.

Compared with TMP, alkaline peroxide pretreatment had a larger impact on GW rejects [8]. When the rejects were treated with 7.5% NaOH and 3% H₂O₂, the burst and tensile increased by 50%. This was accompanied by 25% decrease in refining energy. However, the pulp yield was decreased by 1% with every percent alkali used.

For a southern pine TMP newsprint furnish, 4% alkaline peroxide pretreatment of the rejects would allow a reduction of kraft pulp addition from 25 to 15% while maintaining paper strength properties [9]. No data was available for high value-added mechanical paper grades such as SC and LWC.

There is an increasing interest in alkaline peroxide pretreatment of rejects for LWC, SC, and other mechanical high-value papers, due to the potential of reducing refining energy and kraft pulp use, as well as increased demand on pulp quality such as low fibre coarseness, high fibre flexibility, and low shives content. The high surface
requirements of these mechanical high-value papers make the condition of long fibres critical. The negative effect of chemical pretreatment of rejects is reduced opacity and bulk, but this may be compensated by the reduction of kraft reinforcement pulp in furnish, addition of fillers, and less calendering, etc. The balance of the benefits and the detriments requires systematic research on this topic. Compared with newsprint, the mechanical high-value papers have a much higher rejects rate and are usually heavily calendered to achieve target surface properties; therefore, the alkaline peroxide pretreatment on rejects could have a larger impact on these high-value papers.

The objectives of this study are: 1) to clarify the effects of alkaline peroxide pretreatment on TMP rejects, such as refining energy consumption, long fibre development, and pulp properties, and 2) to examine the effects of chemically modified rejects on SCA paper properties when the rejects are combined with mainline accepts and kraft. This paper focuses on the first objective and the subsequent paper will report the results on the second objective.

EXPERIMENTAL

Raw Materials

The TMP screening and cleaning rejects were obtained from an eastern Canadian paper mill and sampled at the dewatering screw press prior to the rejects refiner. Table 1 shows the key properties of the rejects.

<table>
<thead>
<tr>
<th>Table 1. Key properties of the TMP rejects.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Wood species</td>
</tr>
<tr>
<td>Consistency (%)</td>
</tr>
<tr>
<td>Canadian Standard Freeness (mL)</td>
</tr>
<tr>
<td>FQA fibre length (Lw, mm)</td>
</tr>
<tr>
<td>ISO brightness (%)</td>
</tr>
<tr>
<td>FQA coarseness (mg/m)</td>
</tr>
</tbody>
</table>

Alkaline Peroxide Pretreatment Before Refining

The TMP rejects were pretreated with alkaline peroxide before refining. A control run was also done by pretreating the rejects with water at the same temperature and retention time. Target chemical charges on oven dried (o.d.) rejects were 2–7% NaOH and 2.5–4% H2O2 together with 3% silicate, 0.05% MgSO4, and 0.3% DTPA as stabilizers for the alkaline peroxide solution. The alkaline peroxide solution was prepared in a 300 L polyethylene tank just before the trials. The rejects and the chemical solution were mixed by passing the rejects through an atmospheric 36” double-disk refiner (Bauer 400) with the gap wide open. The rejects mixed with alkaline peroxide were retained in a plastic container at ~65°C for 30 minutes. Pulp samples were taken every 10 minutes to measure the pH and H2O2 residues in the pulps.

Refining

After retention, the treated rejects were refined in the same refiner using approximately 1200 kWh/t specific refining energy in the first stage, and then four different energy levels in the second stage. The lowest freeness target of the refined rejects was controlled at about 50 mL and the consistency after the second refining stage was around 20%. Pulp samples were collected at each energy level and were quickly soured in a sodium meta-bisulphite solution to pH around 6. Again, samples were taken to measure the pH and H2O2 residues.

Pulp Testing

The pulp samples were thoroughly washed and screened, and the latency removed before testing. Fibre length and coarseness were measured by a Fibre Quality Analyzer (FQA). Pulp tests were carried out according to PAPTAC standard methods. The content of carboxylic acid groups of the refined rejects was measured by the published method [12].
**Rejects Yield and Effluent Load**

The yield of rejects after alkaline peroxide pretreatment was determined as follows: 30g o.d. unrefined sample was mixed with bleaching chemicals in a Hobart mixer for five minutes and then transferred to a plastic bag. The pulp consistency was adjusted to 28% and the bag was kept in a water bath for 30 minutes at 65°C. After a vigorous disintegration in 3 L deionized water using a Waring blender, the pulp slurry was filtered through a 150-mesh screen with recirculation until the filtrate became clear. The disintegration was repeated with 3 L fresh deionized water and the pulp slurry was left overnight. The slurry was filtered again the next day until the filtrate became clear. All the filtrate was collected and the total solids content was measured which was used in the mass balance later. The pulp pad was put into an oven and dried to a constant weight.

The effluent load was determined using a similar procedure to that described above. After the treatment under the specified conditions (65°C, 30 minutes), the sample was diluted to 5% consistency in a beaker and soured with sodium meta-bisulphite to a pH of around 6. The slurry was filtered through a 150-mesh screen with recirculation until the filtrate became clear. The filtrate was filtered through a Millipore® membrane again and bubbled with air for 40 minutes to remove any residual sodium meta-bisulphite. The collected samples were tested for biochemical oxygen demand (BOD), chemical oxygen demand (COD), and total organic carbon (TOC). BOD and COD determinations were done according to PAPTAC methods H.2 and H.3, respectively. TOC was measured using a Shimadzu TOC-V total organic carbon analyzer.

**RESULTS AND DISCUSSION**

**Specific Energy Consumption**

Figure 1 shows that at a total alkaline charge (TA) of 5.2%, the alkaline peroxide pretreatment on the TMP rejects can reduce the refining energy required to produce pulp at a freeness of 50–100 mL by about 20%. Energy reduction of 10 to 25% to a given freeness was reported when southern pine TMP rejects were pre-treated with 4.8 to 8.8% total alkali and 1.8 to 2.8% peroxide [9]. Groundwood rejects of southern pine and cottonwood also showed similar response to alkaline peroxide pretreatment when pretreated with 7.5% NaOH and 3% H₂O₂ [8]. The decrease in refining energy is most likely due to the fact that under alkaline conditions, fibres swell more than those treated with water only [12–14]. Figure 1 also shows that increasing the total alkali charge to 7.4% did not lead to a further energy reduction. At a 2.2% total alkali charge, the freeness to specific energy relationship was the same as that of the control. This can be attributed to a low swelling degree at a low pH, as supported by the pH profile during alkaline peroxide pretreatment in Figure 2. Compared with the pretreatment with 5.2% and 7.4% total alkaline, treatment with a 2.2% total alkali had a much lower pH during the 30-minute retention time and a lower ending pH at 9. Similarly, it was reported that an alkaline peroxide pretreatment on groundwood rejects of southern pine and cottonwood had a negligible effect on energy consumption when the caustic charge was 4.5% [8].

**Pulp Properties**

The alkaline peroxide pretreatment did not show a significant impact on the fibre size distribution after refining, as shown in Figures 3 and 4. This is in agreement with the reported results on southern pine TMP rejects [9]. However, the alkaline peroxide pretreatment reduced the fibre coarseness of the long fibres (Bauer-McNett P14/R28 fractions), as shown in Figure 5. fibre coarseness influences a wider variety of pulp properties than does fibre length, especially those relating to the surface quality of printing papers [15]. A typical caliper for SCA is 50 µm and the uncollapsed mechanical fibres may exceed half the sheet thickness of SCA [16]. In addition to the apparent influence on smoothness, stiff and uncollapsed mechanical long fibres in LWC and SC furnishes could be collapsed and stressed during calendering and later cause surface roughening upon rewetting in the coating or printing process. The implication of alkaline peroxide pretreatment on surface roughening will be discussed later in this paper.
Figure 1. Alkaline peroxide pretreatment on TMP rejects reduced refining energy to a given freeness when the total alkali charge was 5.2%. No further reduction in refining energy was obtained when the total alkali charge (TA) was increased to 7.4%.

Figure 2. pH profiles during alkaline peroxide pretreatments. Compared with the pretreatment with 5.2% or 7.4% total alkali charges, pretreatment with a 2.2% total alkali had a lower pH during the thirty-minute retention and a lower ending pH close to 9.
Figure 3. Long fibre content at a given total specific refining energy was not significantly affected by alkaline peroxide pretreatment.

Figure 4. Alkaline peroxide pretreatment of rejects had negligible effect on the fines content at a given total specific refining energy.
Figure 5. Alkaline peroxide pretreatment reduced the coarseness of long fibres.

Figure 6 shows that the alkaline peroxide pretreatment significantly reduced the pulp bulk, especially at a higher total alkali charge. Compared with the control at the same refining energy, rejects treated with 5.2% and 7.4% total alkali charges reduced bulk by about 17% and 21%, respectively. Since the fibre size distributions were not affected by the alkaline peroxide pretreatment (Figures 3 and 4), the lower bulk due to the alkaline peroxide pretreatment is most likely the result of increased fibre flexibility and conformability. This is further supported by Figure 7 which shows that the same values of bulk were reached at a higher long fibre content, an indication of more flexible and conformable long fibres for the pulps pre-treated with alkaline peroxide [17]. It is well known that under an alkaline condition, in particular in the presence of hydrogen peroxide, carboxylic groups are generated on the pulp fibres due to the hydrolysis of hemi-cellulose and the oxidation of lignin [12,18–21]. These new acidic groups caused a higher ion concentration in the cell wall than the outside aqueous phase, and thus increasing the osmotic pressure which would draw additional water into the cell wall. Due to the swelling of the cell wall, fibres were softened and became more conformable. Tchepel et al. found that alkaline peroxide treatment reduces the fibre cross-sectional dimension which increases the flexibility of single fibres by lowering the amount of inertia [21]. It was reported that the fibre swelling was linearly related to alkali consumption [12]. At the same refining energy of 2000 kWh/t, Figure 8 shows that the carboxylic content of the pulps increased with the total alkali charge and correspondingly Figure 9 shows that the decrease in bulk of the refined rejects is directly proportional to the total alkali charge. The decrease in bulk also helped decrease the air permeability of the pulps as shown in Figure 10. The higher the total alkali charge, the lower the air permeability. Low air permeability is desirable for SC and LWC papers. For example, lower air permeability will give a better coating holdout for LWC paper.

At a given specific energy or freeness, the TEA was higher when the rejects were pre-treated with total alkali charges of 5.2 and 7.4% compared to that of the control or rejects treated at a total alkali charge of 2.2%, as shown in Figures 11 and 12. Moldenius [22] reported that there is a critical initial pH of 11 below which the strength properties of spruce mechanical pulps are not affected by the alkaline peroxide bleaching. Similar observations were also made by others [14,23,24]. In our study with a total alkali of 2.2%, although the initial pH is 11.3, slightly above 11, there was no strength improvement due to the alkaline peroxide pretreatment. This discrepancy could be explained by the fact that the pH dropped quickly to 10.2 after one minute and then stayed at about 9.5 after two minutes of retention, as shown in Figure 2. The rapid drop of pH in this case could be mainly attributed to the fast peroxide decomposition since the rejects used in this study had 12.4 ppm Mn and had not been chelated before the alkaline peroxide pretreatment. This discrepancy could be explained by the fact that the pH dropped quickly to 10.2 after one minute and then stayed at about 9.5 after two minutes of retention, as shown in Figure 2. The rapid drop of pH in this case could be mainly attributed to the fast peroxide decomposition since the rejects used in this study had 12.4 ppm Mn and had not been chelated before the alkaline peroxide pretreatment. This discrepancy could be explained by the fact that the pH dropped quickly to 10.2 after one minute and then stayed at about 9.5 after two minutes of retention, as shown in Figure 2. The rapid drop of pH in this case could be mainly attributed to the fast peroxide decomposition since the rejects used in this study had 12.4 ppm Mn and had not been chelated before the alkaline peroxide pretreatment. This discrepancy could be explained by the fact that the pH dropped quickly to 10.2 after one minute and then stayed at about 9.5 after two minutes of retention, as shown in Figure 2. The rapid drop of pH in this case could be mainly attributed to the fast peroxide decomposition since the rejects used in this study had 12.4 ppm Mn and had not been chelated before the alkaline peroxide pretreatment. The pH profile during bleaching was not reported in Moldenius’s report [22], but the decomposition of peroxide in his study is expected to be slower than in our study since his pulp was chelated before bleaching and the bleaching was done in the lab with deionized water and as much as 5% silicate.
Figure 6. The alkaline peroxide pretreatment significantly reduced the pulp bulk, especially at a higher total alkali charge.

Figure 7. The same values of bulk were reached at a higher long fibre content, an indication of more flexible and compressible long fibres for the refined rejects pre-treated with alkaline peroxide.
Figure 8. The carboxylic content of the refined rejects increased with the total alkali charge. The measurement of the carboxylic group was done on the rejects refined at a refining energy of 2000 kWh/t.

Figure 9. The decrease in bulk is directly proportional to the total alkali charge in the alkaline peroxide pretreatment. The measurement of bulk was done on the rejects refined at a refining energy of 2000 kWh/t.
Figure 10. The alkaline peroxide pretreatment decreased the air permeability of the rejects pulps.

Figure 11. The alkaline peroxide pretreatment increased TEA at a total alkali charge of 5.2%. However, no further improvement was obtained when the total alkali charge increased to 7.4%.
Figure 12. At a given freeness, the alkaline peroxide pretreatment increased TEA at a total alkali charge of 5.2%. However, no further improvement was obtained when the total alkali charge increased to 7.4%.

Figure 13 shows that at the same refining energy of 2000 kWh/t, the TEA did not increase until the total alkali charge was above 2.2%. There was also no further increase in TEA when the total alkali charge increased from 5.2% to 7.4%, which is in agreement with an earlier study by Sferrazza [9] who reported that increasing total alkali charge from 4.8% to 8.8% had little effect on the paper strength for alkaline peroxide pretreated southern pine TMP rejects. On the other hand, Figure 8 shows that the carboxylic group content increased continuously with the total alkali charge from 2.2 to 7.4%. This insignificant correlation between TEA and carboxylic group content was also observed by others [14,22,23], which was explained by the number of carboxylic groups on fibre surface.

Figure 13. The TEA did not increase until the total alkali charge was above 2.2%. There was also no further increase in TEA when the total alkali charge increased from 5.2% to 7.4%. The TEA measurement was carried out on the rejects refined at a refining energy of 2000 kWh/t.
Strunk et al [8] reported that alkaline peroxide pretreatment with a total alkali charge of 7.5% on groundwood screen rejects resulted in a 50% improvement in physical properties such as breaking length and burst. The screen rejects contained 75% southern pine and 25% cottonwood. The improvements in this case were much more pronounced than the present study and it could be largely explained by the difference in wood species and the existence of hardwood fibres in their rejects. Hardwood fibres contain more hemi-cellulose and less lignin than softwood fibres; therefore, they tend to swell more under alkaline conditions.

The irreversible roughness increase, i.e., the surface roughening, is observed during coating and printing when water is applied onto the paper. This negatively affects the gloss and surface roughness of the final paper. It is generally believed that surface roughening occurs due to the debonding of mechanical long fibre and the recovery of its original tubular shape upon the release of internal stress induced by calendering [4,25–28]. It has been shown that increasing the proportion of long mechanical pulp fibres in the LWC base sheet did not increase the print roughness if the long fibres were thin-walled, flexible, and well bonded [26]. Since alkaline peroxide treatment improved inter-fibre bonding, reduced fibre coarseness, and increased fibre flexibility, this is expected to help reduce surface roughening of the high-value mechanical printing papers. Nurminen [4] has shown that sulphonation of TMP screen rejects helped reduce surface roughening in printing of LWC paper.

Figure 14 shows that alkaline peroxide pretreatment led to a decreased tear index at a total alkali charge higher than 2.2%. As we know, tear index is mainly affected by the long fibre content in the paper (fibre length), fibre strength, and inter-fibre bonding. For those rejects pre-treated with a 5.2% total alkali charge or higher, their long fibre fractions (R14+P14/R28) were similar to or even higher than the untreated rejects at the same energy levels. Fibre strength, which is usually reflected by the zero-span breaking length (Figure 15) is also similar or higher than the control for those pulps pre-treated with a 5.2% total alkali charge or higher. The decrease in tear index can therefore be attributed to the improved fibre flexibility which led to a higher sheet density and better inter-fibre bonding. This will cause fibre breakage rather than pull-out during fracture [29]. Figure 16 shows that tear index decreased with the increase in tensile index. Sulphonated TMP rejects after refining also showed a reduction on tear index [5]. Although the treated rejects had 6.2% higher long fibre (>R30) fraction, its tear index was decreased by 21.7%, compared to the control. Uesaka and his coworkers [30,31] have shown that tensile strength and uniformity are more significant factors than CD tear affecting pressroom runnability. Therefore, the alkaline peroxide pretreatment on rejects is expected to have a positive effect on pressroom runnability.

At a total alkali charge higher than 2.2%, alkaline peroxide pretreatment decreased light scattering of rejects at a given specific energy as seen in Figure 17. The rejects behave more or less like kraft pulp during refining: the light scattering is slightly decreased at a higher refining energy although more fines were generated at the same time (Figure 4). The decreased light scattering was due to the reduced bulk as the result of more flexible fibres and increased inter-fibre bonding. As expected, chemical treatments, such as sulphonation, may also decrease light scattering since such a pretreatment would improve inter-fibre bonding as well. Winberg et al [5] reported that sulphonation pretreatment of TMP rejects resulted in about 40% loss in light scattering when the pulp sulphonate content reached 1.25%.

Although light scattering of rejects was decreased by the alkaline peroxide pretreatment, it is still much higher than that of softwood kraft pulp which has a light scattering coefficient of about 20–30m²/kg. Since alkaline peroxide pretreatment significantly increased tensile strength of the rejects, it is possible to reduce the reinforcement kraft pulp content in SC and LWC paper, therefore, having a positive effect on the light scattering coefficient of the final paper. Also, there is a possibility that less calendering could be used to reach the target surface properties since the treated rejects have a low coarseness and are more flexible and compressible. This will help preserve paper light scattering, opacity, and brightness, especially for heavily calendered papers like SC and LWC. Our results on SCA paper supported this and will be discussed in a subsequent report.
Figure 14. The alkaline peroxide pretreatment decreased tear index at a total alkali charge of 5.2% or higher.

Figure 15. Similar or higher zero-span breaking lengths than control were obtained for the refined rejects pretreated with a total alkali charge of 5.2% or higher.
Figure 16. Tear index decreased with the increasing tensile index.

Figure 17. Alkaline peroxide pretreatment decreased light scattering of the refined rejects at a total alkali charge of 5.2% or higher.
Corresponding to the decrease in light scattering, the alkaline peroxide pretreatment also decreased opacity, as shown in Figure 18. An earlier study [3] showed that sulphonation pretreatment of TMP rejects prior to refining resulted in only a slight decrease (2–3%) in opacity. However, the larger loss in opacity in our case is strongly related to the increase in brightness. As shown in Figure 19, with the alkaline peroxide pretreatment, the brightness of the pulps was increased from 58.6% to 70–73% ISO depending on the chemical charges. A 5.2% total alkali and 2.9% peroxide charge gave a brightness of 72%. Note the alkaline peroxide pretreatment conditions have not been optimized yet and also there was no chelation on rejects before the pretreatment. A higher brightness is one of the most significant advantages of alkaline peroxide pretreatment over the sulphonation process for rejects. For most SC or LWC grades, an ISO brightness of 70–73% meets its requirement. As a result, there is no need to further bleach the rejects.

Figure 18. Alkaline peroxide pretreatment decreased opacity of the refined rejects pulps as a result of increased brightness and decreased light scattering.

Figure 19. Alkaline peroxide pretreatment increased the rejects pulp brightness from 58.6% to 70–73% depending on the chemical charges.
Rejects Yield and Effluent Load

As expected (Figure 20), the alkaline peroxide pretreatment resulted in a decreased pulp yield, which is strongly related but not directly proportional to the total alkali charge. This is attributed to the dissolution of organics, such as hemi-cellulose, extractives, and lignin under the strong alkaline conditions [32–35]. Note the control in Figure 20 and Table 2 was the control rejects that was peroxide bleached after refining to an ISO brightness of 69.4%. The chemicals used in the bleaching were 2.5% total alkali and 1.5% peroxide.

As shown in Figure 20, the refined rejects yield was 97.5% for the control and further decreased to 95.5% at 5.2% total alkali charge. Therefore, compared with the control, there is 2% yield loss which translates into a 1% loss in yield of the TMP pulp if the rejects rate is 50%. An earlier study on alkaline peroxide pretreatment of groundwood rejects found that pulp yield was reduced by about 1% for every 1% of NaOH applied [8]. Sulphonation pretreatment on TMP rejects also showed a yield loss [5].

Corresponding to the yield loss, the effluent load, characterized as COD, BOD, TOC, and cationic demand, was increased at a higher alkali charge (Table 2). For example, the pretreatment with 5.2% total alkali and 2.9% peroxide increased COD by 73% and also almost doubled the BOD as compared with the control. Again, the data in Table 2 are for the rejects stream only. It should be pointed out that for alkaline peroxide pretreatment, the loss of yield, or the dissolution of organics, was also strongly related to the wood species, temperature, retention time, and peroxide charge [33,34,36].

<table>
<thead>
<tr>
<th>Total Alkaline Charge in Pretreatment (%)</th>
<th>Rejects Yield (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>97.5</td>
</tr>
<tr>
<td>2.2</td>
<td>96.0</td>
</tr>
<tr>
<td>5.2</td>
<td>96.6</td>
</tr>
<tr>
<td>7.4</td>
<td>94.2</td>
</tr>
</tbody>
</table>

Figure 20. Alkaline peroxide pretreatment decreased rejects pulp yield which is strongly related but not directly proportional to the total alkali charge. Note the control here was the control rejects that was bleached after refining to an ISO brightness of 69.4% with 2.5% total alkali and 1.5% peroxide.

<table>
<thead>
<tr>
<th>Total Alkaline Charge in Pretreatment (%)</th>
<th>COD (kg/t)</th>
<th>BOD (kg/t)</th>
<th>TOC (kg/t)</th>
<th>Cationic Demand (ueq/L)</th>
</tr>
</thead>
<tbody>
<tr>
<td>2.5%TA+1.5%H₂O₂</td>
<td>55.7</td>
<td>20.7</td>
<td>19.5</td>
<td>0.30</td>
</tr>
<tr>
<td>2.2%TA,2.8% H₂O₂</td>
<td>56.0</td>
<td>18.4</td>
<td>23.0</td>
<td>0.42</td>
</tr>
<tr>
<td>5.2%TA,2.9% H₂O₂</td>
<td>96.5</td>
<td>40.8</td>
<td>30.6</td>
<td>0.51</td>
</tr>
<tr>
<td>7.4%TA,4.3% H₂O₂</td>
<td>123.1</td>
<td>96.7</td>
<td>38.0</td>
<td>0.87</td>
</tr>
</tbody>
</table>

Table 2. Effluent characteristics from the alkaline peroxide pretreatment of rejects.
CONCLUSIONS

Pilot plant trials were conducted to clarify the effect of alkaline peroxide pretreatment on TMP rejects. In general, a 5.2% total alkali seems to be the optimal and 2.2% is not enough to change the freeness-energy relationship. At a total alkali charge of 5.2%, alkaline peroxide pretreatment reduced the specific refining energy by 20% to a given freeness, increased pulp density and tensile strength, most likely as a result of increased fibre flexibility and conformability. The alkaline peroxide pretreatment had a negligible effect on fibre length and its distribution under the current experimental conditions. Without chelating and washing before refining, refined rejects reached an ISO brightness of 72% with 5.2% total alkali and 2.9% peroxide. A detrimental effect of the alkaline peroxide pretreatment is reduced light scattering and pulp yield.

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Importance of Rejects Refining

• Rejects are mainly coarse fibers / fiber bundles

• Objectives of rejects refining
  – Further develop fibers to maximize strength
  – Develop fibers for improved surface properties
  – Reduce shives

• Ways to improve rejects refining
  – Low-intensity refining
  – Chemical treatment
    • Sulfonation
    • Alkaline peroxide
Why Pre-treat Rejects Before Refining?

- Limited reports on alkaline peroxide pre-treatment (APT) of southern pine TMP or GWD rejects for newsprint
  - Reduced refining energy
  - Increased strength
  - Reduced light scattering and opacity
  - Low rejects rate of 10-30%
  - Typically little or no kraft in newsprint
  - Lightly calendered
Renewed Interest in APT of Rejects

• Renewed interest in APT of TMP rejects for mechanical high value-added grades such as LWC and SC
  – Potential of reducing refining energy and kraft
  – Increased demand on pulp quality such as low fiber wall thickness and high fiber flexibility
  – Rejects rate as high as 50%
  – Heavily calendered for high smoothness
Objectives

• Clarify the effects of alkaline peroxide pre-treatment on rejects refining
  – Energy consumption
  – Fiber development
  – Pulp property
  – Yield and effluent load

• Generate pulps for handsheet study on SCA
Alkaline Peroxide Pre-treatment (APT)

- TMP rejects from Screening and fractionation
- Spruce/fir
- Freeness: 399mL CSF
- Lw: 1.682mm
- Brightness: 58.6% ISO
- Coarseness: 0.181mg/m

- Total Alkaline (TA): 2 – 7.5%
- NaOH: 1.7 – 7.2%
- H$_2$O$_2$: 2.5 - 4%
- MgSO$_4$: 0.05%
- DTPA: 0.3%
- Silicate: 3%
Experimental Schematics

TMP screen & cleaner rejects

Mix with alkaline peroxide in a refiner

65ºC, 30 min

Rejects refining

Rejects refining

Rejects screen

Combine with accepts

Bleaching

Combine with bleached accepts, and kraft to make handsheet

Mainline accepts

Bleaching

Combine with kraft to make control handsheet
Sprout Bauer 36” Atmospheric Refiner
APT Reduced Refining Energy at a Given Freeness

**TA: Total Alkaline Charge**

- Control
- 2.2% TA, 2.8%H2O2
- 5.2% TA, 2.9%H2O2
- 7.4%TA, 4.3%H2O2
APT Not Affecting Fiber Size Distribution

![Graph showing Total Specific Energy (kWh/t) vs Bauer-McNett R28 % and Bauer-McNett P200 % for different treatments.

- Control
- 2.2% TA, 2.8% H2O2
- 5.2% TA, 2.9% H2O2
- 7.4% TA, 4.3% H2O2]
APT Reduced Coarseness of Long Fibers

![Graph showing the relationship between Total Specific Energy (kWh/t) and P14/R28 Coarseness (mg/m) for different treatment conditions. The graph includes data points for Control, 2.2% TA, 2.8% H2O2, 5.2% TA, 2.9% H2O2, and 7.4% TA, 4.3% H2O2 treatments. The trend lines indicate a decrease in coarseness with increased specific energy.]
Increased APT treatment
APT Increased Carboxylic Content
(for pulps refined by the same SEC of 2000 kWh/t)
Specific Volume vs. TA in APT
(for pulps refined by the same SEC of 2000 kWh/t)
TEA vs. Refining Energy

Control

2.2% TA, 2.8% H2O2

5.2% TA, 2.9% H2O2

7.4% TA, 4.3% H2O2

TEA (mJ/g)

Total Specific Energy (kWh/t)
Tear vs. Refining Energy

Tear Index (mN·m²/g)

- Control
- 2.2% TA, 2.8% H₂O₂
- 5.2% TA, 2.9% H₂O₂
- 7.4% TA, 4.3% H₂O₂

Total Specific Energy (kWh/t)
Fiber Strength vs. Refining Energy

Zero-Span Breaking Length (km) vs. Total Specific Energy (kWh/t)

- **Control**
- **2.2% TA, 2.8%H2O2**
- **5.2% TA, 2.9%H2O2**
- **7.4%TA, 4.3%H2O2**
Tensile vs. Tear Index

- Control
- 2.2% TA, 2.8% H2O2
- 5.2% TA, 2.9% H2O2
- 7.4% TA, 4.3% H2O2
APT Increase Pulp Brightness

![Graph showing the relationship between ISO Brightness and Total Specific Energy (kWh/t)].

- **Control**: 
  - 2.2% TA, 2.8% H2O2
  - 5.2% TA, 2.90% H2O2
  - 7.4% TA, 4.3% H2O2
Light Scattering vs. Refining Energy

![Graph showing light scattering coefficient (m²/kg) versus total specific energy (kWh/t). The graph includes four different treatments: Control, 2.2% TA, 2.8%H₂O₂, 5.2% TA, 2.9%H₂O₂, and 7.4%TA, 4.3%H₂O₂. The data points are plotted on the graph, and the lines show a trend.]
# Negative Effect of APT on Rejects

<table>
<thead>
<tr>
<th></th>
<th>Control rejects subsequently bleached</th>
<th>APT rejects</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Chemical doses &amp; brightness</strong></td>
<td>2.5% TA+1.5% H$_2$O$_2$ 69.4% ISO</td>
<td>5.2% TA+2.9% H$_2$O$_2$ 71.8% ISO</td>
</tr>
<tr>
<td><strong>Reject yield (%)</strong></td>
<td>97.5</td>
<td>95.5</td>
</tr>
<tr>
<td><strong>COD (kg/t)</strong></td>
<td>55.7</td>
<td>96.5</td>
</tr>
<tr>
<td><strong>BOD (kg/t)</strong></td>
<td>20.7</td>
<td>40.8</td>
</tr>
<tr>
<td><strong>Cationic demand (ueq/L)</strong></td>
<td>0.30</td>
<td>0.51</td>
</tr>
</tbody>
</table>
Summary

• Compared with the control, APT with 5.2% TA and 2.9% H₂O₂
  – Reduced 20% refining energy to a given freeness
  – Reduced fiber coarseness and increased fiber flexibility/conformability
  – Increased TEA
  – Bleached rejects to ISO brightness > 70%
  – Reduced light scattering
  – Decreased yield and increased effluent load
Thanks for your attention!
pH Profile During the APT

Fresh liquor

0 min. retention

10 min. retention

20 min. retention

30 min. retention

After refining

- 2.2% TA, 2.8% H2O2
- 5.2% TA, 2.9% H2O2
- 7.4% TA, 4.3% H2O2