INTRODUCTION

A research program directed toward utilization of hardwoods by producing papermaking pulps at near groundwood yields but with processing potential was undertaken at the Forest Products Laboratory (FPL) in the immediate post-World War II period. This program continued the FPL investigations that had led to the FPL semichemical pulping process.

The first study in the program, begun in late 1947, involved treatment of wood chips with water and steam followed by fiberizing in a disk refiner. The pulps were suitable for application to corrugating medium as reported in May, 1949 (1). A preliminary study of pulping with mineral acids at low temperatures started at the same time proved unpromising.

Another research project, which started in late 1948, considered the use of caustic soda of moderate strength on wood chips at ambient temperature. This project resulted in the development of the so-called "cold soda semichemical" (CSSC) process, more properly designated as cold soda chemimechanical process (cold soda CMP). The first publication on this process appeared in August, 1950 (2). This process was successfully demonstrated in a trial at the NSSC mill of Green Bay Pulp & Paper Co., Green Bay, Wisconsin, and was subsequently used there commercially from 1951 to 1952 (3). The product was corrugating board. This was the first CMP operation.

The purposes of this report are: 1. To record the circumstances of the origin and development of the FPL cold soda CMP process; 2. To note the growth and decline of commercial cold soda pulping in the U.S.; 3. To point out the short time for transfer of the experimental technology into mill practice; 4. To discuss the nature and mechanism of the cold soda process from new experimental information; and 5. To review recent literature on the process.

Historical

A cold soda-type process was patented in Germany in 1919 by Erich Opferman for producing pulp from straw, reeds and other nonwood plant materials by simultaneous treatment with alkali at ambient temperature and mechanically fiberizing in a kollergang, stamp mill or other fiber separation means (4). In 1935 Robert Woodhead patented in Australia a chemical-mechanical pulping process based on treatment of wood chips (specifically Australian eucalyptus) with an alkali or alkaline salt (specifically caustic soda) with subsequent disintegration of the chips in a rod or ball mill (including a kollergang) to produce a coarse pulp for wrappings and news (using 2% NaOH) and a fine pulp for printings and writings (using 8-10% NaOH) (5). Although the patent also mentions the beater and Jordan as Fiberizing equipment, the disk refiner, the heart of the modern semichemical-type processes, was not recognized. As far as is known, neither the Opferman nor the Woodhead processes were ever developed commercially (6).

FPL Cold Soda Pulping Process Development Studies

FPL publications on cold soda pulping in the period of 1950-1958 involved extensive investigations of the variables of the process as outlined below (2, 7, 8, 9).

Independent Variables:

Wood - Aspen and 17 northern, southern and western hardwoods, spruce, northern fir; chip size; chip moisture content.
Treatment - Presteaming; time, temperature, pressure (including vacuum impregnation) and alkali concentration; liquor/wood.
Fiberizing - Degree (freeness), disk refiner; roll-type fiberizer.
Brightening - Brightening agents (calcium hypochlorite, sodium peroxide, sulfur dioxide included); optical properties; special use tests.

Dependent Variables:

Pulp - Yield; chemical consumption; freeness; pulp strength properties; optical properties; special use tests.

Mill Application of FPL Cold Soda CMP Process

The FPL cold soda process moved into full commercial production about six years after the first publication in 1950 with the exception of the 1951-1952 temporary, partial production in the NSSC mill noted previously. The chronological order of the
Establishment of the nine U.S. mills in the period of 1950–1960 is given in Table 1. Nine cold soda mills were also started up and operated in foreign countries, including Australia (Tasmania), Japan, Argentina, Colombia and Italy (10).

Increased utilization of hardwoods from a fiber resource standpoint was an important factor in the U.S. industry during the 1950–1960 period. This circumstance was favorable to considering the cold soda process as a means for increasing the use of hardwoods in northern and southern mills.

The U.S. and foreign mills differed considerably in their pulping systems, as described below, although all involved the two-stage, semichemical-type configuration of impregnation and fiberizing steps.

Chronology. A chronology of the FPL publications on cold soda pulping and the U.S. mill applications over the 1950–1960 period is given in Table 1.

The records of longevity of the cold soda operations cannot be completely established, but it is known that by 1969 only one of the original U.S. cold soda mills was still in operation (27) and this mill terminated its cold soda pulp production in 1986 (19). The three mills in Tasmania (the first in 1957 (29, 30, 31)) and others in Japan have continued operating to this day (32, 33, 34). A cold soda pulping operation in Spain, making pulp for use in coated papers, was patented in 1981 with operation in 1984 (35).

Hardwood utilization. The FPL publications showed that the cola soda process was flexible as to hardwood species (2). This facility was important to mills dependent on softwoods and wanting to diversify their fiber base into the hardwoods. Thus, the northern mills used aspen (poplar), beech, maple and birch and the southern mills pulped gum and oak. The Tasmanian mills used eucalyptus and the Japanese cold soda mills used indigenous mixed hardwoods. The new Spanish mill also uses eucalyptus (35).

Pulping systems. The nine cold soda pulp mills as of 1960 (Table 1) used a variety of systems for special chip preparation, impregnation of the caustic reagent, pressing for pre-fiberizing and spent liquor recovery and fiberizing in one to three stages. This same variety extended to the thickening before papermaking used the screens and cleaners of the period.

The pulping systems themselves were of the following types:

Chip fractionators in some mills to produce small chips.

Caustic impregnation is globe digesters or live-bottom bins; cyclic pressure in batch vessels; inclined and horizontal tube continuous pressure impregnator; and spray application before chip fractionator, press and fiberizers with intermediate retention.

Continuing Investigations of Cold Soda CMP Pulps and Pulping

Pressing in screw pressers for prefiberizing and spent liquor recovery.

Fiberizing in vertical disk refiners in one to three stages.

Screening and cleanings with standard equipment.

Brightening hardwood cold soda pulps from the brightness range of 40-45%, depending on the wood species, to a brightness level of 60–70% by the application of sodium chlorite (yield loss of 2-5%), peroxide, sodium or hydrogen with appropriate buffering, and sodium hydroxide in methods adapted from groundwood brightening.

Spent Liquor Recovery and Disposal. Cold soda pulping operations in 1960 generally fortified spent caustic treatment reagent for subsequent reuse. Wash water was usually recycled as dilution water at the refiners, screens and cleaners. The reactions products, once the system was in equilibrium apparently passed out in the white water or, as discussed below, in the pulp itself. Since the mills mostly had low pulp capacity (Table 1), the environmental effect was ignored. An exception was a relatively large mill of 200 tons per day, employing a cross recovery arrangement with its associated kraft mill (36). The caustic spent liquor and the necessary sulfuric acid were added to the concentrated black liquor as a replacement for salt cake make up. The BOD, for cold soda pulping is reported as being 200 lb/ton of pulp (26).

Chemical Composition of Pulps. The first FPL publication on cold soda CMP pulping of aspen showed the yield loss, which increased with increased alkali consumption, was concentrated in the hemicellulose fraction (2). The solution of wood substances by the cold soda reagent has also been described as being small amounts, 5–10% of lignin and carbohydrates, with a pulp yield of 90–93% (uncorrected for fiber fragments) (37). Another reference claims the loss of a small amount of lignin but mostly hemicelluloses (other than extractives), largely acetyl groups; sodium ions may exchange for calcium ions (38). Another source also indicates that acetyl groups, in addition to hemicellulose (pentosan), and some lignin are lost (10).

Recent tests show that the principal hemicellulose lost is xylan (Table 2). Glucan and Klason lignin showed no change; there was a slight loss in acid soluble lignin. A commercial PMP pulp made from hot extracted aspen chips treated with a low percentage of sodium hydroxide (2%) exhibited only a very small decrease in xylan content (Table 2).

An experimental aspen, well-washed cold soda pulp had a sodium content (determined by inductively coupled plasma (ICP spectroscopy) of 318 ppm (39). This compares with the sodium content of the aspen...
wood used of 39 ppm. (An average hardwood figure is 70 ppm and softwoods 50 ppm (40)). In contrast an unwashed NaO₂-brightened CMP pulp had a sodium content of 11,14 ppm.

Morphology of Cold Soda Pulp Fibers. The mechanism of cold soda pulping has been described as a differential swelling causing increases in middle lamella thickness and fiber section area and a greater decrease in lumen area which result in stresses which, on mechanical fiberizing, result in failures between the middle lamella, primary and secondary walls causing exposures of fibrils for bonding (10, 37, 41). Microscopic examination of cold soda pulp shows largely undamaged fibers with exposed secondary walls and some fine matter; (38). The amount of fine material increases with the degree of fiberization at the expense of long fibers. SEM shows microfibrils of irregular outline due to adhering non-cellulosic and lignin particles (41).

Current SEM studies at the FPL of aspen cold soda CMP, groundwood and kraft pulps at low magnification (25X) show the cold soda pulp to be less macerated and fiberillated than the groundwood pulp and more like the delignified and fiber-separated kraft pulp except for the fiber bundles in the cold soda pulp (Figs. 1, 2, and 3). At a considerably higher magnification (5,000X) the cold soda pulp exhibits fractured inner fiber structures and exposed inner surfaces due to stresses of swelling released by fiberizing (Fig. 4). These exposed inner surfaces account for the enhanced fiber bonding characterizing the pulp.

Cold Soda Process Developments. The early 1980's Spanish high-yield eucalyptus operation (stated as a chemithermo-mechanical process (CTMP) but in reality a CMP mill) employs a patented impregnation in several towers with caustic soda plus additives and fiberising of the treated chips in a two-stage disk refiner system; there is a great overall similarity to the FPL process (35).

A Wisconsin mill makes an ultra-high-yield pulp from aspen in a system involving pressing steam chips treated with surfactant and chelating reagents before refiner addition of caustic soda and hydrogen peroxide (2 and 15%, respectively) in making a pulp suitable for use in carbonless paper (42).

A U.S. patented hardwood CMP process employs a two-stage treatment with caustic soda and sulfite in making a pulp strong for its grade. This is yet another variation of the FPL procedure (43, 44).

A Russian patented CMP process (species is not given in abstract) includes sulonation of a well-treated cold soda pulp (6-9% caustic soda) to produce a pulp suitable for newsprint of improved properties (45). Up to 59% is used with groundwood.

CONCLUSIONS

The FPL hardwood-based cold soda chemimechanical pulping process, as first published in 1950, had its first commercial application in 1951-52 in a modified NSSC corrugating mill and its first production in a custom-designed CMP mill in 1956.

By 1960 there were nine cold soda mills each in the U.S. and in foreign countries making ultra-high-yield (85-95) hardwood pulps for use in printing papers (including newsprint) and paperboards. Nine years later, however, there was only one U.S. and two or three foreign mills operating, the others having been converted to other CMP or NSSC processes or terminated due to changing industry needs.

Investigations of cold soda CMP technology continue; a new eucalyptus cold soda CMP mill started up in Spain in 1984. Up to 62% of the pulp is used in writing paper.

It is concluded that the cold soda CMP process served a useful purpose as a transition process in the growth of U.S. and world production of hardwood pulps.

LITERATURE CITED

6. Woodhead, Robert, In a brief meeting with J. N. McGovern at the Forest Products Laboratory about 1950, Robert Woodhead produced a scrap of yellowish paper of a new type, indicating it was of cold soda pulp origin.
18. Forest Products Laboratory, List of cold soda pulp mills in the U.S. (April, 1961).
34. Ito, Takeshi and Hiroshi Tsuchiya, Empirical comparison between cold soda chemi-groundwood pulp (C-GCP) and hot sulfite chemi-groundwood pulp (H-GCP) in the newsprint mill. 1975 International Mechanical Pulping Conference, San Francisco (June 16-20).
42. Beatty, James, Development of alkaline peroxide CH pulp. Presented at Lake States TAPPI. Appleton, Wisconsin (Feb. 12, 1985).
ACKNOWLEDGEMENTS

The services of M. J. Effland and T. A. Kuster, Forest Products Laboratory, in providing chemical analyses and SEM photomicrographs, respectively, are greatly appreciated.

Table 1. Chronology of Cold Soda CMP Development and U.S. Commercialization.

<table>
<thead>
<tr>
<th>Year</th>
<th>Mill Identification</th>
<th>Mill Location</th>
<th>Product Type</th>
<th>Daily Tons</th>
<th>Wood Species</th>
<th>Brightening Agent</th>
<th>Disposition of Operation</th>
<th>References</th>
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<tr>
<td>1950-1958</td>
<td>FPL publications on process developments including variables and product applications</td>
<td>Green Bay, WI</td>
<td>Corrugating, liner</td>
<td>17</td>
<td>Hardwoods</td>
<td>Hypochlorite</td>
<td>--</td>
<td>2,7,8,9</td>
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<tr>
<td>1951</td>
<td>Green Bay P&amp;F Co.</td>
<td>Green Bay, WI</td>
<td>Corrugating, liner</td>
<td>30</td>
<td>Aspen</td>
<td>-</td>
<td>Reverted to NSSC</td>
<td>10</td>
</tr>
<tr>
<td>1956</td>
<td>Gould Paper Co.</td>
<td>Lyons Falls, NY</td>
<td>Publication papers</td>
<td>40</td>
<td>Mixed birch, beech, maple</td>
<td>Sodium hypochlorite</td>
<td>Converted to CMP</td>
<td>11,12,13</td>
</tr>
<tr>
<td>1956</td>
<td>Stone Container Corp.</td>
<td>Coshocton, OH</td>
<td>Corrugating</td>
<td>55</td>
<td>Poplar, soft maple, willow, local hardwoods</td>
<td>-</td>
<td>Converted to NSSC</td>
<td>14,15</td>
</tr>
<tr>
<td>1956</td>
<td>Diamond-March Co.</td>
<td>Ogdensburg, NY</td>
<td>Molded products</td>
<td>35</td>
<td>Softwood</td>
<td>-</td>
<td>Converted to secondary fiber</td>
<td>16</td>
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<tr>
<td>1957</td>
<td>Bowaters Southern Paper Corp.</td>
<td>Calhoun, TN</td>
<td>News</td>
<td>200</td>
<td>Oak</td>
<td>Hypochlorite</td>
<td>Terminated (1986)</td>
<td>17,18,19</td>
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<tr>
<td>1957</td>
<td>Coosa River Newsprint Co.</td>
<td>Coosa Fines, AL</td>
<td>News</td>
<td>50</td>
<td>Sweetgum, oak</td>
<td>Hypochlorite</td>
<td>Terminated</td>
<td>17,20</td>
</tr>
<tr>
<td>1958</td>
<td>Champion Paper &amp; Fibre Co.</td>
<td>Pasadena, TX</td>
<td>Publication papers</td>
<td>30</td>
<td>Gum, oak</td>
<td>Peroxide</td>
<td>Terminated (1961)</td>
<td>21,22</td>
</tr>
<tr>
<td>1959</td>
<td>Packaging Corp. of America</td>
<td>Filer City, MI</td>
<td>Foodboard</td>
<td>60</td>
<td>Aspen</td>
<td>Peroxide</td>
<td>Converted to NSSC</td>
<td>23,24</td>
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<tr>
<td>1960</td>
<td>Continental Can Company</td>
<td>Augusta, GA</td>
<td>Foodboard</td>
<td>125</td>
<td>Hardwoods</td>
<td>Peroxide</td>
<td>Terminated</td>
<td>25,26</td>
</tr>
<tr>
<td>1969</td>
<td>Last cold soda CMP mills in operation (Bowater)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
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<tr>
<td>1986</td>
<td>Last U.S. cold soda mill terminated (Bowater)</td>
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<td></td>
<td></td>
<td>28</td>
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<tr>
<td>1987</td>
<td>Four CMP mills listed in 1987 Lockwood's Directory</td>
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<td>28</td>
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Table 2. Chemical Compositions of Aspen Wood and CMP Pulps (39).

<table>
<thead>
<tr>
<th>Material</th>
<th>Yield - %</th>
<th>Lignin - %</th>
<th>Carbohydrates - %</th>
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</thead>
<tbody>
<tr>
<td></td>
<td>Klassen</td>
<td>Acid Sol.</td>
<td>Glucan</td>
</tr>
<tr>
<td>Wood</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>FPL Cold</td>
<td>91.1</td>
<td>19.3</td>
<td>51.8</td>
</tr>
<tr>
<td>Soda CNF</td>
<td>(X.91)²</td>
<td>(17.6)</td>
<td>(47.2)</td>
</tr>
<tr>
<td>Comm'1, PMF ³</td>
<td>94 ⁷</td>
<td>18.8</td>
<td>46.9</td>
</tr>
<tr>
<td>(X.94)⁴</td>
<td>(17.7)</td>
<td>(3.9)</td>
<td>(44.1)</td>
</tr>
</tbody>
</table>

1 Aspen wood and pulps.
2 TAPPI T 222.
3 TAPPI Useful Method 250 (October, 1976).
4 High Performance Liquid Chromatography (HPLC).
5 Numbers in parentheses are on original wood basis.
6 Peroxide Mechanical Pulp (PMF); steamed aspen chips extracted with surfactant and chelating agents and treated at refiner with caustic soda and hydrogen peroxide.
7 Estimated.
Fig. 1. Aspen cols soda (25X).

Fig. 2. Aspen groundwood (25X)
Fig. 3. Aspen kraft (25X).

Fig. 4. Aspen cold soda (5,000X).