

¹Use of Borate in Semi-Chemical Pulping

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ABSTRACT

The original neutral sulfite semichemical (NSSC) pulping process used sodium sulfite as the principle cooking chemical, but had the disadvantage of sulfur emission problems. Considerable research was conducted to investigate the use of other chemicals including sodium hydroxide, but was not completely satisfactory because of high chemical costs. Several mills adapted a sodium carbonate based process but experienced slower pulping and reduced physical properties.

The objective of this research is to study the use of borate as a pulping chemical in sodium carbonate semi-chemical pulping. The experimental plan included digester cooks, one with pure sodium carbonate, and the other with partially borate autocausticized sodium carbonate.

It was found that without heating the borate and sodium carbonate, the effect of borate was similar to that of sodium carbonate. Mixtures of sodium borate and sodium carbonate were then heated up to 850 °C, which is below the melting point of these salts. This was done to simulate the processes occurring in a fluidized bed reactor (a common recovery system in sodium carbonate semichemical pulping). At 850 °C, there was a slight reaction between sodium carbonate and sodium borate. This reaction resulted in the production of sodium hydroxide, which tended to increase the pulping rates and the resulting paper strength properties.

INTRODUCTION

In the United States, the semi-chemical process was first used in 1925. This process was ideally suited for the production of hardwood pulp with yields between 60-80% for bleached and unbleached pulps respectively. Among the semi-chemical pulping processes, Neutral Sulfite Semi Chemical (NSSC) pulping process was most popular.

There were many reasons for pulp mills to switch over from NSSC process to sodium carbonate pulping. Four key reasons for this conversion are:

1. End products of the decomposition of liquors from the NSSC process include hydrogen sulfide and sulfur dioxide. Both of these chemicals are malodorous and corrosive.
2. Generally, the recovery of NSSC spent liquor is not economical because of the high capital cost of recovery equipment and the low heat yield in the recovery process. (1)
3. The markets for the salt cake by-product made at the mills burning spent NSSC liquor in fluidized bed incinerators are poor. (2)
4. There are high chemical costs involved in NSSC pulping because the sodium sulfate and soda ash cannot be recycled. (2)

Dillard, et al. claims that there are several advantages when sulfur is removed from the pulping system including: (3)

1. Simplified recovery.
2. Increased pulp yield.
3. Improvement in the removal of water on the paper machine up to 5% with a corresponding reduction in steam usage.

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4. The total pulping chemical usage is reduced thus reducing the cost.
5. The load on mill evaporators is decreased up to 25%.
6. The mill and surrounding areas are freed from all unpleasant odors from the sulfur containing products formed by NSSC process.
7. The absence of sulfur containing reducing agents in spent liquor helps to reduce aqueous effluent problems.
8. Problems related with dreg formation and disposals are eliminated.
9. The recovery furnace smelt obtained by removing sulfur from the pulping system is much less sensitive to smelt-water interactions.

Dixon, et al. (4) claims a process of cooking wood with sodium carbonate alone under pressure and Heritage, et al. (5) claims a pulping process where sodium hydroxide alone is used as a pulping agent. It was observed that the use of sodium carbonate alone results in slow pulping requiring more chemical which is less economical where as if sodium hydroxide alone is used as pulping agent, it extracts more of the desirable hemicelluloses required for corrugating medium, which reduces the sheet strength properties.

Hanson, et al. (2) describes three major approaches to no-sulfur pulping:

1. Owens-Illinois Process: In this process, the active pulping agents are a mixture of sodium carbonate and sodium hydroxide. Makeup chemical for the process is sodium hydroxide. Some potassium hydroxide also may be included in Kraft-type incinerators to improve smelting properties.
2. Soda ash process: The active pulping agent is sodium carbonate. The spent liquor from the process is successfully burned in fluidized bed incinerators, and the recovered sodium carbonate is recycled back to pulping.
3. Modified soda ash process: Soda ash (sodium carbonate) along with small amount of caustic soda (sodium hydroxide) makeup is used.

The three no-sulfur methods mentioned above use similar chemicals in different ratios of sodium carbonate to sodium hydroxide. The pulp properties, degree of delignification, refining horsepower and quality vary significantly depending on the ratio used. (2)

Although there are several good advantages to the above no-sulfur processes, there are some disadvantages. (2), including:

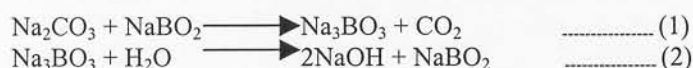
1. Slight sacrifice in either pulp quality or pulp yield may be observed compared to NSSC process.
2. The cost of sodium hydroxide is high.
3. The color of the obtained medium is darker than the conventional NSSC pulp (but this is of minor importance).

Apart from the above three non-sulfur pulping methods, the use of anthraquinone has also been tested in NSSC pulping. It is observed that anthraquinone has a marked influence on NSSC pulping particularly when pine is used as the wood source. There has been of particular interest in Finland and South Africa for the use of pine neutral sulfite pulps as a replacement for kraft pulps. Anthraquinone helps to enhance the rate of lignin removal without the use of high chemical applications, elevated temperatures or prolonged cooking times. Some evidence also indicates that NSSC-AQ pulp from *pinus radiate* can be successfully used as a replacement for the long fiber (Southern Pine) kraft in corrugating medium and linerboard applications. (6)

Pulping properties of borates:

In autocausticizing the removal of carbon dioxide occurs in the recovery furnace (7, 8). Theoretically, borate fulfills the definition of autocausticizing and so called autocausticizable borate.

The equations that defend the autocausticizability of borate are:



Borate pulping seems to be advantageous from the energetic point of view. Also, the contribution of borate to the toxicity of effluent seems to be negligible (8). There is laboratory evidence showing no accelerated corrosion of steel due to the replacement of hydroxide-carbons with borate.

It is suggested (7) that the application of borates may be advantageous in other pulping processes. Also in research conducted at Western Michigan University, it was observed that the properties of pulp changed in many ways by the addition of borate in cooking chemicals. Here, it was found that the addition of borate increased yield, tensile strength, tear strength, burst strength, and reduced the amount of screened rejects (9, 10).

EXPERIMENTAL

The objective of this research is to study the use of borate as a pulping chemical in sodium carbonate semi-chemical pulping. Experiments were performed on a laboratory scale and are divided into sections, which are summarized as below:

1. Collection of materials and chemicals required for project
2. Air-drying the wood chips to the room conditions.
3. Pulp preparation
4. Washing
5. Disintegration in Waring blender
6. Determination of yield
7. Pulp screening
8. Pulp refining
9. Preparation of handsheets
10. Pulp testing

1. Collection of materials and chemicals required for project

The supplies needed for the experiment include mixed hard wood chips, sodium carbonate and sodium metaborate. Menasha Corporation supplied the hardwood chips, technical grade sodium carbonate was purchased and U.S. Borax supplied sodium metaborate.

The equipment employed for the experiments included: M&K digester, PFI refiner, oven, British handsheet making apparatus and TAPPI testing equipment. All the equipment is available in the laboratories of Department of Paper Engineering and Paper Pilot Plant at Western Michigan University.

2. Air drying the wood chips to the room conditions

To ensure that the wood chips did not deteriorate during the course of the research, they were air dried at room temperature.

3. Preparation of pulp

Oven Dried (OD) mixed hardwood chips were fed into the cooking vessel of M/K digester. The liquor to wood ratio maintained was 4:1 with the chemical charge of 10% (as sodium oxide). The continuous heaters were turned on allowing the cook to pressurize. The heating was continued until the temperature reached 100°C and held for 15 minutes. After this, the heating was continued until the temperature reached 170°C, the digester was held for 30 minutes at 170°C and then cooled down to 100°C in 20 minutes. The pH of cooking liquor before and after cooking is determined.

4. Washing

After cooking, the wood chips were washed with cold water for 5 minutes to remove surface black liquor.

5. Disintegration in Waring blender

The washed chips were disintegrated in two batches in Waring blender with 2500 ml of hot water (temperature around 48°C) on low speed for 5 minutes. After disintegration, the chips/pulp were washed with cold water on Nobel sheet making apparatus. Following washing, the pulp was collected in plastic bag with a sample taken aside for yield determination.

6. Determination of yield

The moisture content of the sample taken from plastic bag in the above step was determined. From the moisture content of the sample obtained, the total yield of the pulp collected in the plastic bag was measured.

7. Screening of pulp

The pulp was then screened on laboratory vibrated slotted screener. The screened yield and rejects were determined. The freeness was measured using a Canadian Standard Freeness tester.

8. PFI mill processing of pulp

The moisture content of the accepts obtained from screening was determined. Based on this moisture content, three samples of 300 gm of wet pulp with 10% consistency were prepared. These three samples were refined using PFI refiner for 1000, 2000 and 3000 revolutions. After PFI refining, the freeness of the samples was measured.

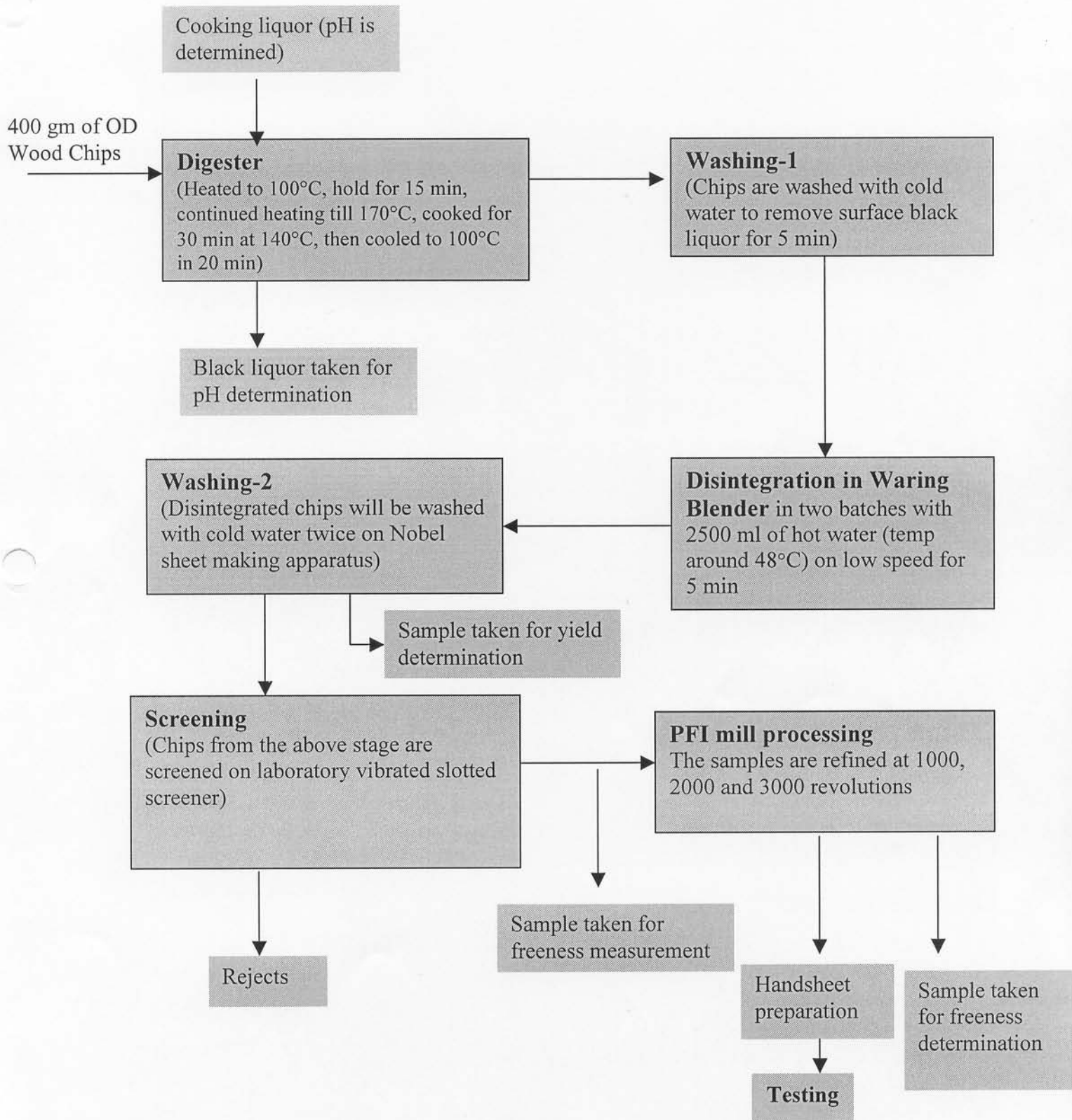
9. Preparation of handsheets

In order to determine the strength properties of pulp, handsheets were prepared from the pulp following TAPPI standard procedures. The consistency of the pulp for making handsheets was adjusted so that the basis weight of the prepared handsheets was around 150 g/m² (air-dried weight).

10. Pulp testing

The handsheets were allowed to condition over-night in the testing lab. Then they were cut to test specimens according to TAPPI standards to determine tensile strength, tear strength, brightness, and burst strength.

Block diagram of the experimental procedure that is followed for part-I of the project:



Since in semi-chemical pulping, the sodium carbonate is commonly recovered in a fluidized bed furnace, this process was simulated in the laboratory by heating the borate/sodium carbonate mixture to temperatures below their melting point (750 to 850 °C). When autocausticizing is practiced with borate in the kraft process, sodium metaborate reacts with sodium carbonate in the char bed at temperatures above 900 °C in the recovery furnace forming trisodium borate. This trisodium borate when dissolved in water gives sodium hydroxide regenerating sodium metaborate. The formed cooking liquor is used for pulping.

Mixtures of sodium carbonate and sodium metaborate were used by on a 10% autocausticizing ratio. The mixture of borate and carbonate was first dissolved in water and then dried in oven at 105 °C. This resulted in the evaporation of all water and ensured uniform and proper mixing of carbonate and borate. The resultant mixture of carbonate and borate was then placed in a tubular alumina reactor and the reactor placed in a muffle furnace. The mixed salts were heated to temperatures ranging from 750 to 850°C for 60 minutes. Since a product of this reaction is carbon dioxide, the extent of reaction was determined by measuring the weight loss. In all cases, only minor changes in weight loss were observed (a few percent), but the loss was greater at 850 °C.

After heating, the required amount of mixture (such that chemical charge for cooking is 10% based on sodium oxide content) was taken and cooking liquor was prepared. The further part of the experiment is similar to the one described in first part.

Totally six handsheets were prepared for each pulp at basis weight of 150 g/m². The tensile strength and burst strength were measured twice for each of the four sheets for a total of 8 readings from each pulping experiment. The tear strength of each sheet was measured for a total of 4 readings from each pulping experiment.

RESULTS AND DISCUSSION

The cooking experiments for this project were conducted in two different cooking vessels of same M/K digester, which is available in lab. So, to confirm the reproducibility of these two cooking vessels, two pulping experiments were conducted with pure sodium carbonate as pulping chemical. The results, showing the physical properties of the handsheets from these pulps, are shown below in Figures 1 through 4. Since no borate was used, these pulping experiments were named for convenience purposes as 0% AC –Left and 0% AC-Right. (Denoting the pulps obtained from left and right vessels of the M/K digester).

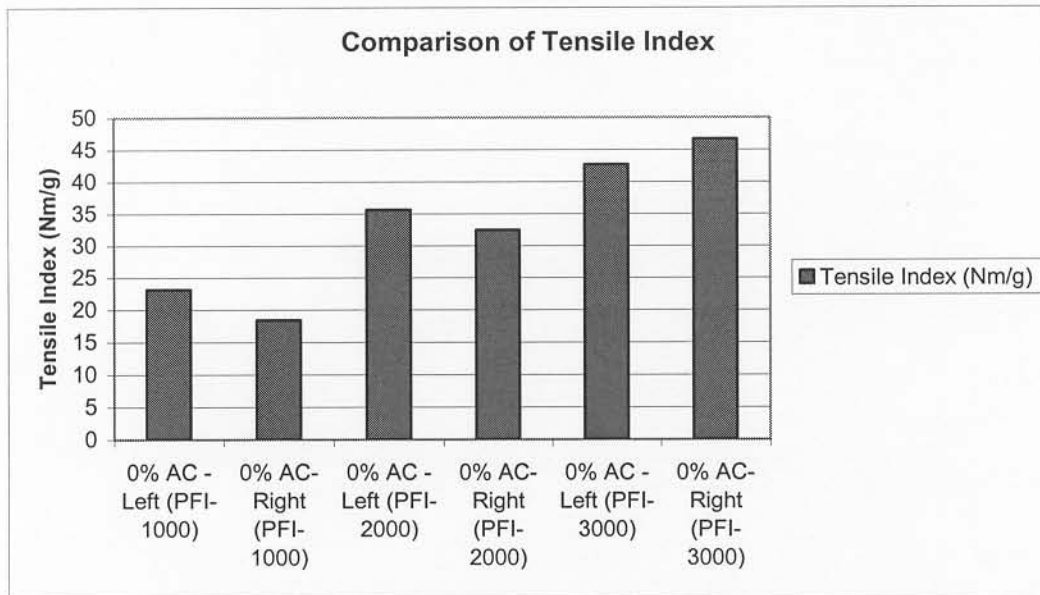


Fig. 1. Comparison of Tensile Strength Properties for Handsheets Prepared from the Left and Right reactors at PFI Refining from 1000 to 3000 Revolutions.

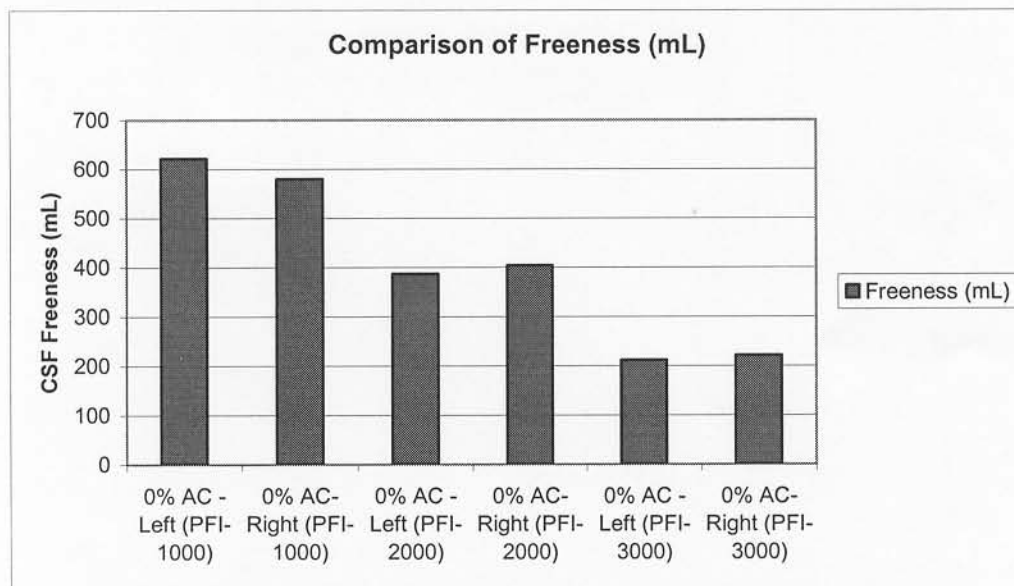


Fig. 2. CSF Freeness values for the pulps obtaining by pulping with 0% AC chemicals at PFI refining from 1000 to 3000 revolutions.

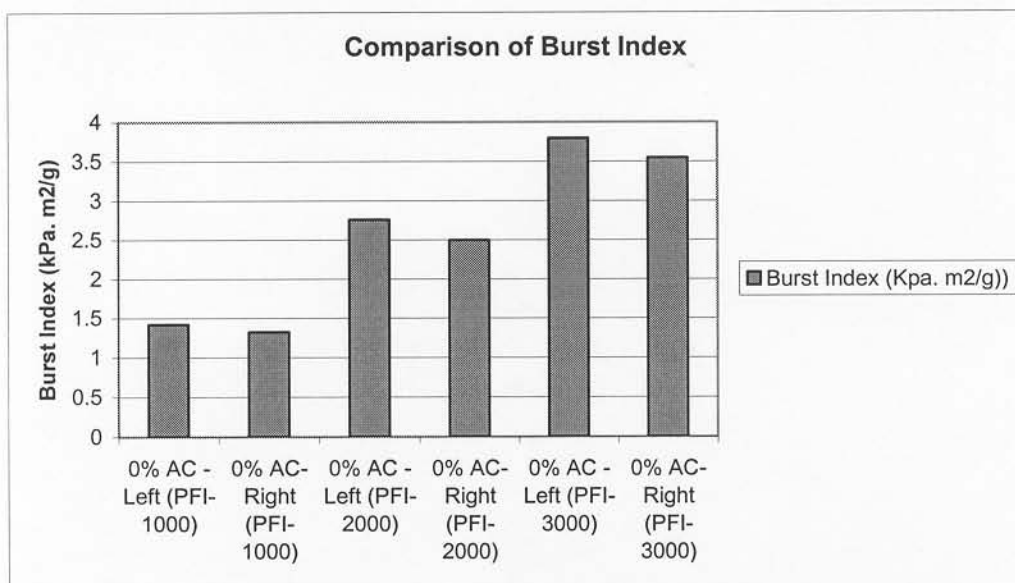


Fig. 3. Comparison of Burst Index values for the pulps obtaining by pulping with 0% AC chemicals at PFI refining from 1000 to 3000 revolutions.

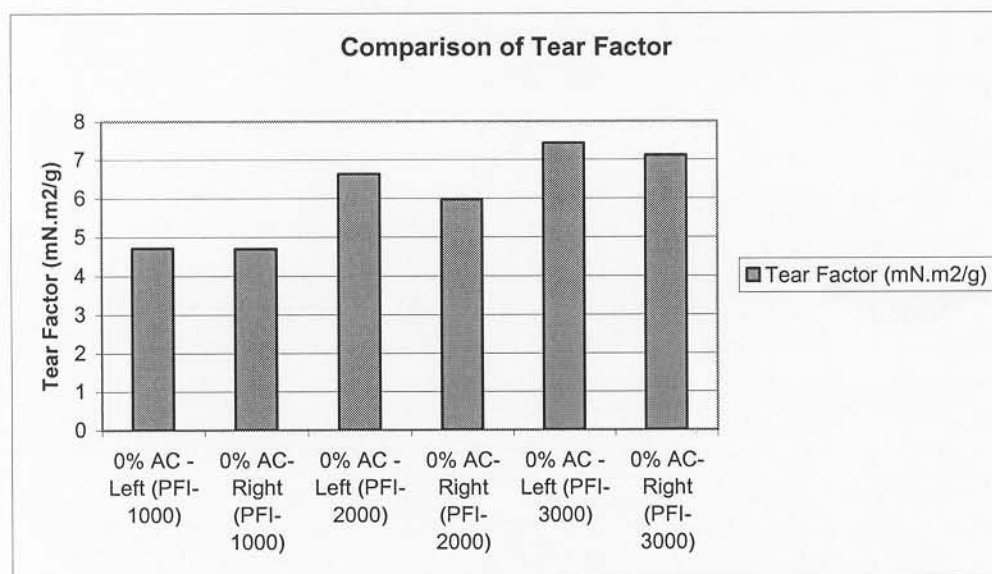


Fig. 4. Tear Factor values for the pulps obtaining by pulping with 0% AC at PFI refining from 1000 to 3000 revolutions.

The above graphs confirm the reproducibility of the M/K digester, which is used for pulping experiments. Since the results seem to be statistically similar, the two pulping experiments carried out in the left and right vessel of digester can be considered as 0% AC- trial 1 and 0% AC-trial 2.

After confirming the reproducibility for pulping with no borate present, pulping experiments were conducted for 10% borate addition with no heating and for 10% borate addition with heating. The results from these pulping experiments are shown in Fig. 5 through 7.

Table-1 Properties of pulp obtained from cooks with 0% AC, 10% AC and 10% AC-heated chemicals

CSF FREENESS (mL)								
	0% AC - Trial 1	0% AC - Trial 2	10% AC - Trial 1	10% AC - Trial 2	10% AC heated - Trial 1	10% AC heated - Trial 2	Std.Dev	Average
PFI-1000 rev	622	580	578	554	562	560	24.787	576
PFI-2000 rev	387	404	403	397	395	327	29.31	385.5
PFI-3000 rev	212	222	187	232	208	154	28.155	202.5
TENSILE INDEX (Nm/g)								
	0% AC - Trial 1	0% AC - Trial 2	10% AC - Trial 1	10% AC - Trial 2	10% AC heated - Trial 1	10% AC heated - Trial 2	Std. Dev	Average
PFI-1000 rev	23.19	18.43	17.126	17.77	27.664	23.79	4.2045	21.33
PFI-2000 rev	35.64	32.49	31.98	34.59	40.625	33.82	3.1276	34.86
PFI-3000 rev	42.652	46.66	45.75	41.94	50.204	47.51	3.0942	45.79
BURST INDEX (kPa.m2/g)								
	0% AC - Trial 1	0% AC - Trial 2	10% AC - Trial 1	10% AC - Trial 2	10% AC heated - Trial 1	10% AC heated - Trial 2	Std. Dev	Average
PFI-1000 rev	1.421	1.324	1.223	1.464	1.516	1.307	0.1098	1.376
PFI-2000 rev	2.527	2.818	2.527	2.818	2.647	2.255	0.213	2.599
PFI-3000 rev	3.795	3.543	3.544	3.728	3.595	3.258	0.1869	3.577
TEAR FACTOR (mN.m2/g)								
	0% AC - Trial 1	0% AC - Trial 2	10% AC - Trial 1	10% AC - Trial 2	10% AC heated - Trial 1	10% AC heated - Trial 2	Std. Dev	Average
PFI-1000 rev	4.714	4.703	6.797	6.489	6.247	5.241	0.9276	5.699
PFI-2000 rev	6.628	5.97	6.797	6.489	6.345	5.261	0.5594	6.248
PFI-3000 rev	7.432	7.117	7.151	6.479	6.201	5.298	0.7913	6.613

Figures 5 and 6 shows the effect of borate addition on the pulping yield and freeness.

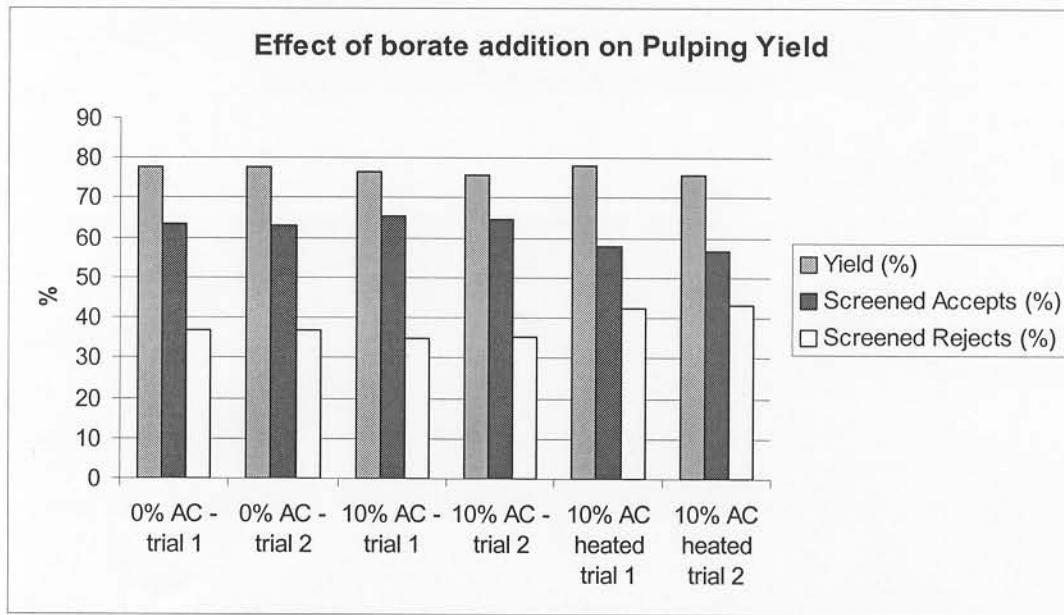


Fig. 5. Effect of borate addition on pulping yield for the pulps prepared using 0% AC, 10% borate addition with no heating (10% AC) and 10% borate addition with heating. (10% AC-heated).

The total yield obtained for all pulps was close to 76-78%. This shows that the yields of all the above pulps are approximately the same, which implies that the addition of borates without heating or heated below the melting point of chemicals does not greatly affect total yield.

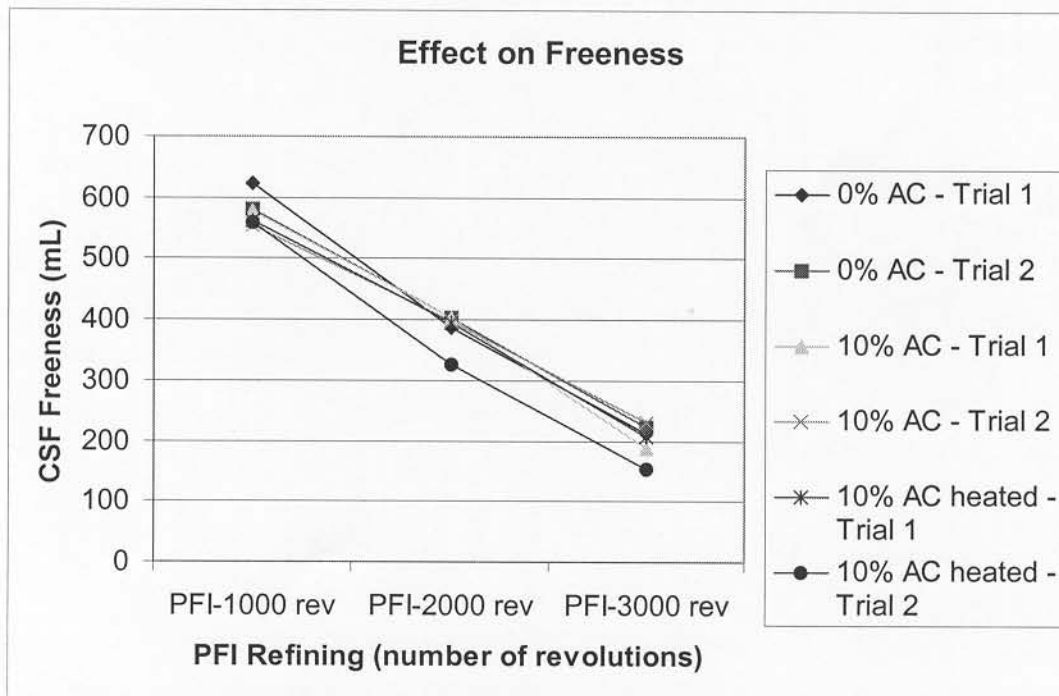


Fig. 6. Effect of borate addition on Freeness for the pulps prepared using 0% AC, 10% AC and 10% AC-heated chemicals and refined at PFI 1000 to 3000 revolutions.

The CSF freeness values were measured for the pulps to determine if any changes due to pulping could be observed after refining. A slight decrease in freeness values is observed for the pulp obtained using 10% AC-heated chemicals. This suggests that this pulp refines more easily.

Figure 7 shows the tensile index for handsheets produced with pulp from 0% AC, 10% borate addition with no heating (10% AC) and 10% borate addition with heating (10% AC-heated)

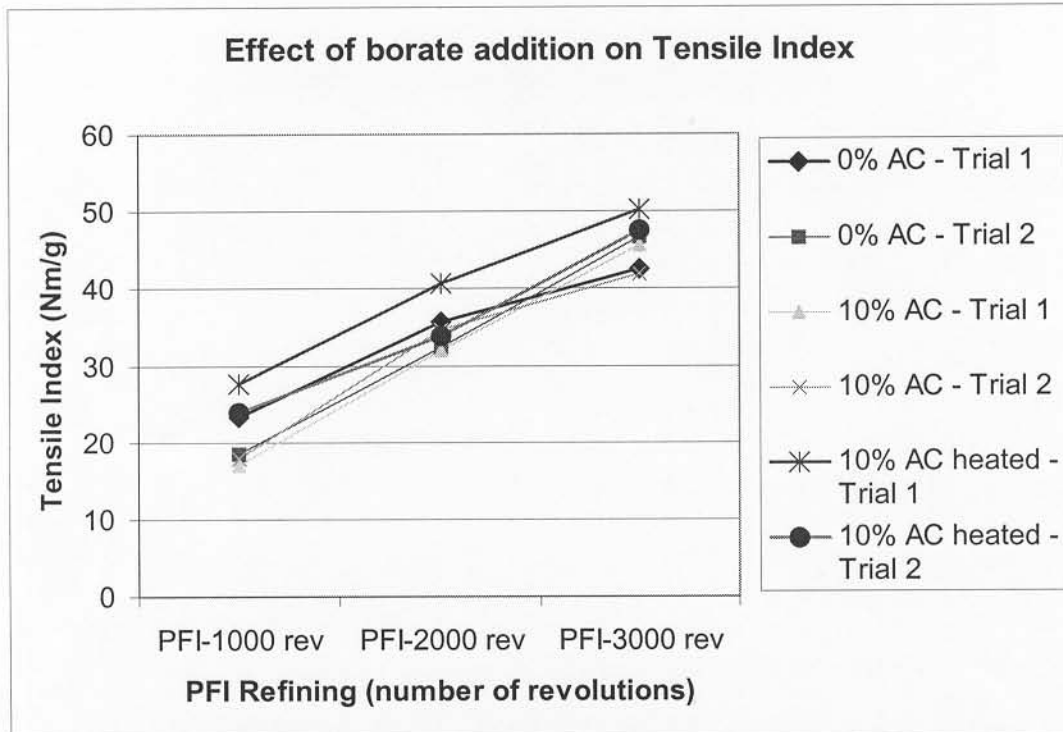


Fig.7. Comparison of tensile index values for the handsheets prepared with pulp from 0% AC, 10% borate addition with no heating (10% AC) and 10% borate addition with heating.(10% AC-heated).

The tensile strength tends to increase when heated borate is used in pulping chemicals. This could be due to the formation of sodium hydroxide when borate and carbonate was heated at 850°C and dissolved in water (from Equation (2)). This sodium hydroxide formed attributes higher pH to the cooking liquor and increased delignification in the pulp thus helping in better bonding which in turn increases strength. The pH of the cooking liquor obtained from heated chemicals is close to between 11.7-12.0 where as the pH of the other cooking liquors from 10% AC unheated and 0% AC chemicals is between 11.1-11.3 (shown in Figure 8).

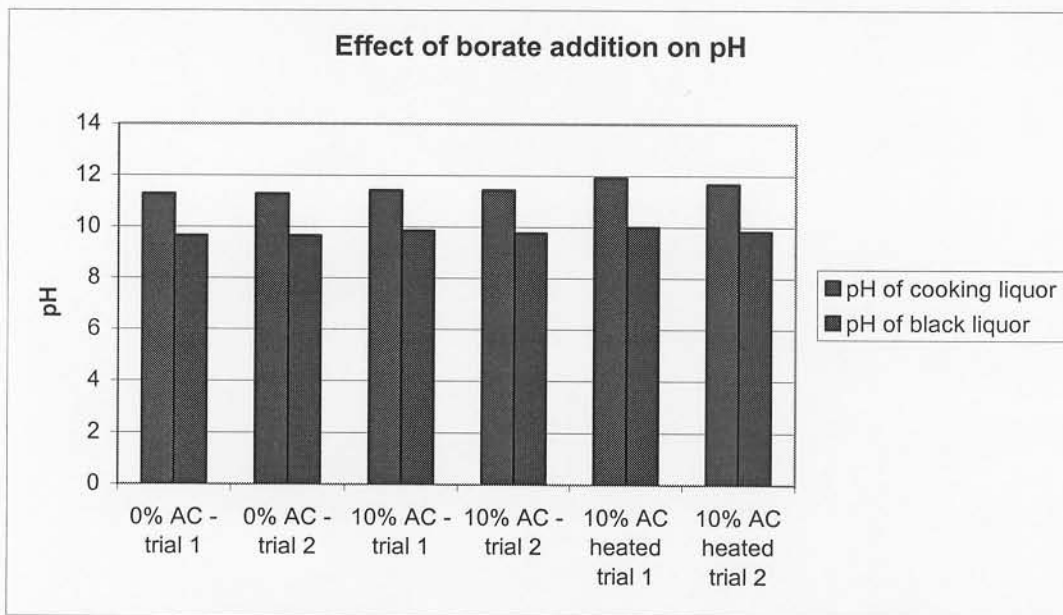


Fig. 8. Effect of borate addition on pH in cooking and black liquors of 0% AC, 10% AC and 10% AC-heated pulping processes.

The burst index for the three pulps refined to 1000, 2000 and 3000 revolutions in the PFI mill are shown in Figure 9.

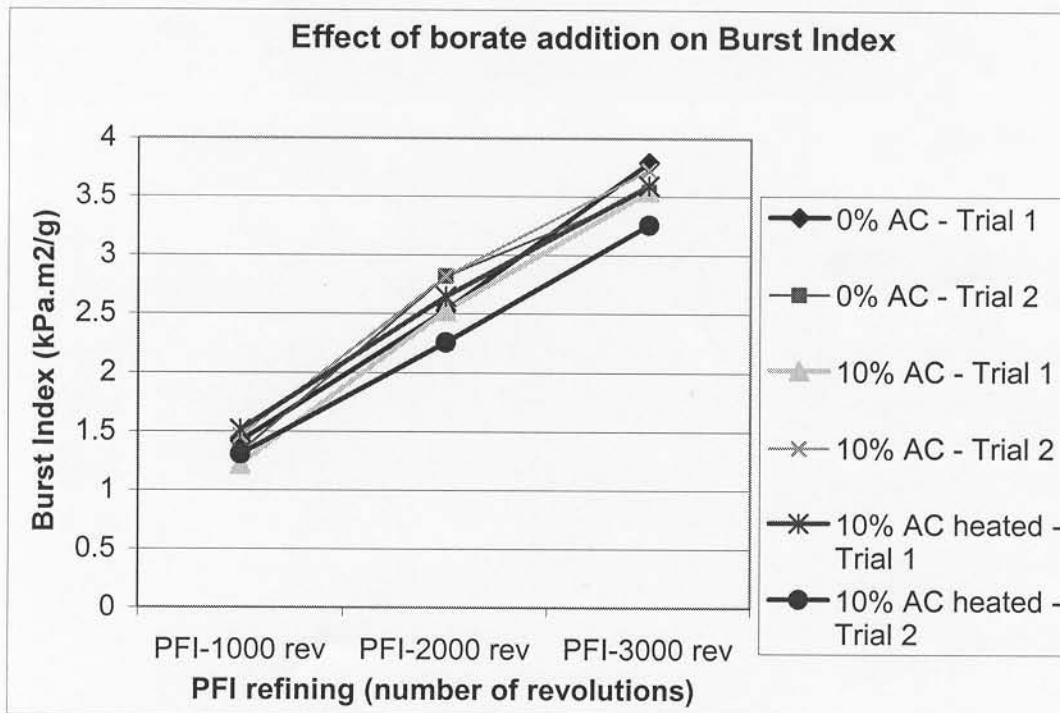


Fig. 9. Effect of borate addition on burst index for the handsheets prepared with pulp from 0% AC, 10% borate addition with no heating (10% AC) and 10% borate addition with heating. (10% AC-heated).

The burst index of the pulp does not seem to change much with the addition of borate. The burst index is a good indication of the bonding strength of the fibers in the handsheet. For pulps obtained from chemicals

consisting of heated carbonate/borate mixture and refined at higher number of revolutions, the burst strength seems to be relatively poor indicating the reduced bonding potential of the fibers.

The effect of borate addition on the tear factor is shown in Fig. 10.

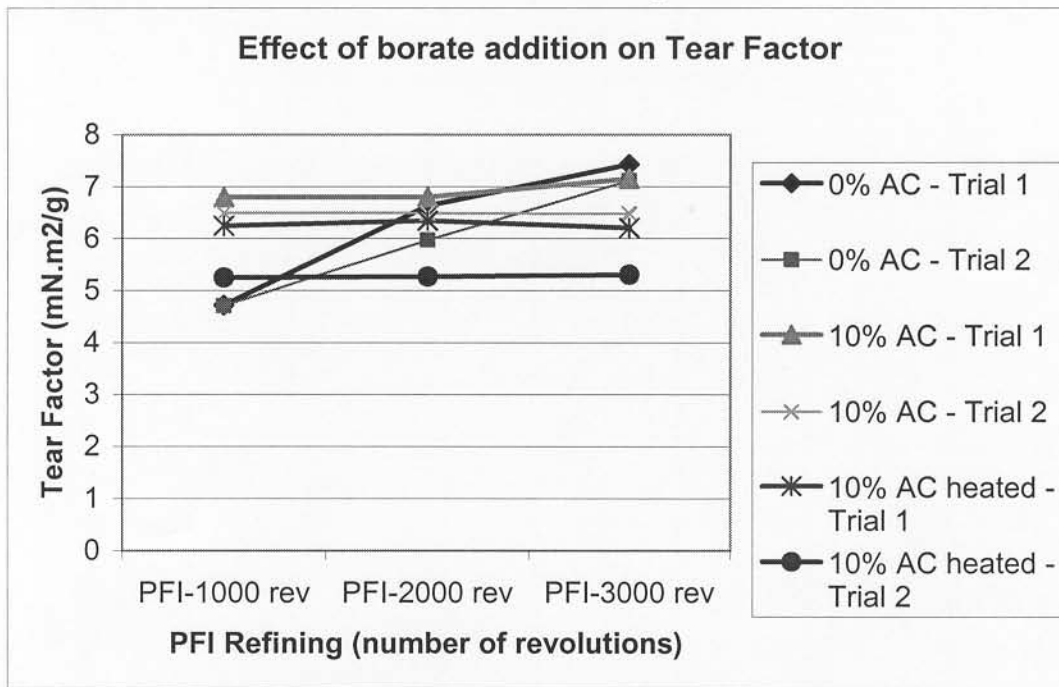


Fig. 10. Effect of borate addition on tear factor for the handsheets prepared with pulp from 0% AC, 10% borate addition with no heating (10% AC) and 10% borate addition with heating.(10% AC-heated).

For the pulps refined at lower number of revolutions, tear factor tends to increase with the addition of borate. This indicates that these pulps refine more readily.

Conclusions

1. In general, the addition of borate had only minor affects on the pulping and the strength properties. This likely occurred because the reaction of borate with carbonate is very slow below the melting point of salts.
2. Without melting, borate provides a buffering effect during pulping similar to that of sodium carbonate.
3. There is no significant effect on the total yield with the addition of smaller quantities of borate.
4. The addition of borates slightly increased the pH of cooking liquor and black liquor.
5. Freeness is not greatly affected by pulping with borate chemicals.
6. Burst strength is not greatly affected by the addition of borate.
7. Tensile strength is slightly increased when pulped with heated borates.
8. Tear strength is increased upon the addition of borate at low refining levels.

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