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ALUM PRETREATMENT OF HIGH-YIELD SULPHITE

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THE sulphite operation in the Quebec North Shore Paper Company at Baie Comeau was converted to a high-yield sodium bisulphite pulping system in 1970. It consisted of a regular two-stage refining sequence with intermediate washing and a separate reject-refining arrangement.

The first pulp produced, at a pulp yield of 64 per cent, was very shivy in spite of the fact that the deckered freeness was 640 CSF. The power input was 0·92 MJ/kg (13 hpd/o.d.t.). The dry-strength values were good. However, the paper-machine operation was adversely affected and the percentage of screen rejects was increased in an attempt to obtain a cleaner pulp. The additional refining produced some improvement in the paper-machine operation but it was not comparable to that obtained with the low-yield pulp.

A number of modifications were made to the system during 1971 and 1972 with some improvement being obtained in the paper-machine operation. The paper-machine operating efficiency was still inferior to that for the low-yield pulp.

A single-stage refining trial was carried out in January 1973 and the pulp yield was increased at the same time in order to be able to apply more refining power. The pulp yield averaged 69 per cent and the power input was 1·15 MJ/kg (16·2 hpd/o.d.t.) for a deckered freeness of 503 CSF. This power requirement was low for the pulp yield and freeness level obtained. The trial had an adverse effect on the paper-machine operation and the mill reverted to low-yield pulping. At the same time a thorough study of high-yield pulping was initiated to determine, if possible, why a high yield pulp could not be produced at Baie Comeau that would not have an adverse effect on the paper-machine operation. Positive results had been obtained at other Eastern Canadian newsprint mills.

Under the chairmanship of A. A. Robertson

High-yield evaluation

An examination of data obtained on samples of high-yield pulps obtained from different mills, summarised in Table 1, indicated some very interesting trends. The dry-strength values for the samples from Baie Comeau were at least comparable and in some cases superior to the other pulps. The high freenesses of the Baie Comeau pulps correlated very well with the low wet-web strengths, the stiffness of the fibres and the reported low power inputs. The low wet-web results could not be predicted from any of the dry-strength data. However, the hourly mill tests showed deckered freenesses in the range of 570–600 CSF compared to the 665–675 CSF results obtained after a time delay of 2–3 days. This increase in pulp freeness with time was not being obtained for the other high-yield pulps.

Refining trials done in our own Research Department and at PPRIC indicated that superior pulp characteristics could be obtained at higher freenesses and with a higher power input than reported by the mill.

The data indicated a possibility of a discrepancy in the freeness values and the low power input.

Freeness study

Extensive work done by the Baie Comeau operating personnel indicated that:

(i) the freeness values obtained by the mill and the Research Department on the same pulp sample and done on the same day were comparable,
(ii) there was no air entrainment in the pulp which would cause a higher freeness,
(iii) the freeness drop across the refining system was uniform,
(iv) the freeness of the high-yield pulp increased with time and the increase was very rapid for the first three days, and
(v) the addition of calcite or alum produced an immediate increase in freeness and then there was a further gradual increase.

The data developed indicated that the high-yield problem might be associated with the mill water supply.

The fresh water at Baie Comeau is very soft, i.e. 10 ppm $CaCO_3$ and the pH is 6·5. The sodium cation present on the high-yield fibre is not stable in the pH range of 4–5 and it is readily replaced by a hydrogen ion. The ion exchange produces a high-swollen and very slippery pulp that is very difficult to refine. This suggested that it would be desirable to reduce the swelling characteristics of the fibre and to make the high-yield material more resistant to refining. A refining study was indicated. Alum was selected for the study because the trivalent ions were more stable than the monovalent or bivalent ions in the operating pH range of 4–5.

TABLE 1—COMPARISON OF HIGH-YIELD PULPS

Mill	*Freeness*	*Burst index*	*Tear index*	*Breaking length*	*Dry stretch (%)*	*Bulk* (cm^3/g)	*Hypo No.*	*Wet-web stretch (%)*
Dalhousie	560	6·6	7·0	10 210	1·9	1·53	22·1	4·4
Thunder Bay	565	6·1	7·2	9 280	2·3	1·74	22·0	3·8
Price Bros.	625	5·1	8·1	8 790	1·9	1·66	21·2	3·8
Beaupre	645	6·3	7·1	10 430	2·2	1·69	23·8	3·5
Fort William	573	5·6	8·0	9 110	2·2	1·76	21·4	4·2
Iroquois Falls	676	5·8	7·3	9 350	2·1	1·73	20·3	—
Port Alfred	670	4·2	9·5	7 110	1·7	1·82	2·26	3·3
Belgo	698	4·7	8·7	7 740	1·8	2·02	23·1	2·7
Pine Falls	652	5·3	7·6	8 860	2·1	1·76	—	—
Bowaters	665	6·0	8·6	8 420	1·8	1·71	—	2·7
Baie Comeau (1971–72 Average)	682	5·9	9·9	9 370	2·2	1·83	—	2·8

TABLE 2—LABORATORY REFINING—EFFECT OF ALUM ADDITION

				Wet-web		*Dry strengths*					
Run No.	*Alum (kg/t)*	*Power applied (MJ/kg)*	*Freeness (CSF)*	*Breaking length*	*Stretch (%)*	*Bulk* (cm^3/g)	*Burst index*	*Tear index*	*Breaking length*	*Stretch (%)*	*Water retention*†
1	0	0·50	750	85	2·1	2·06	5·5	10·9	6 830	2·5	1·95
2	10	0·90	728	98	2·2	1·96	5·3	11·2	6 750	2·6	1·76
3	15	1·39	713	90	2·9	1·86	5·5	10·7	7 230	3·0	1·75
4	20	1·84	684	92	3·4	1·89	5·2	14·5	6 090	3·3	1·64
5	25	2·04	709	90	4·1	1·76	5·3	12·0	6 380	3·0	1·64
6	0*	—	—	85	2·2	2·01	4·5	11·7	5 860	2·3	1·68

* 15 kg/t alum added to refined pulp from run No. 1.
† Grams water retained by 1 g oven dry pulp after centrifuging for 30 minutes at 900 g.

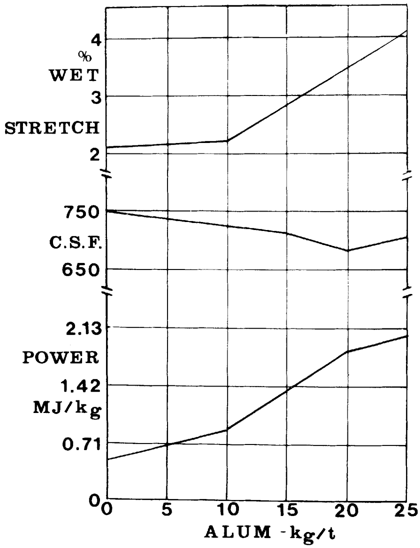

Fig. 1.

Refining study

It was found that a high-yield pulp had a capacity of combining with the aluminium from approximately 20 kg of alum per ton of pulp. This compressed the electric double layer surrounding the fibre and reduced both the fibre charge and the amount of bound water.

The effect of an alum addition on the fibre-to-fibre friction was determined by passing alum-treated, high-yield pulps through a 30 cm laboratory Sprout-Waldron refiner at the rate of 2 tons per day and at 10 per cent consistency. Two refining passes were used with plate separations of 0·51 mm and 0·25 mm, respectively. Different amounts of alum were used. In one instance, alum was added to the refined pulp. The data obtained are summarised in Table 2 and some are illustrated graphically in Fig. 1.

Any change in refining characteristics had to be due to a change in fibre-to-fibre friction, since the feed rates, plate clearances and refining consistencies were kept constant. The results obtained indicated that significant changes in fibre-to-fibre were obtained and that a minimum addition of 15 kg/o.d.t. was required. The power input increased from 0·50 MJ/kg to 2·04 MJ/kg for only small variations in pulp freenesses. The wet-web stretch increased from 2·1 to 4·1 per cent (an increase of 95 per cent). The addition of alum after refining had no significant positive effect on the wet-web characteristics.

TABLE 3—LABORATORY REFINING—EFFECT OF ALUM—ADDITION AT DIFFERENT YIELD LEVELS

Hypo No.	Alum addition (kg/t)	Freeness (CSF)	Power input (MJ/kg)	Burst index	Tear index	Breaking length	Wet-web Tests: Stretch (%)	Wet-web Tests: Breaking length
12·6	0	600	1·28	7·0	6·7	8 200	5·2	110
	20	600	1·53	7·6	7·3	9 000	6·1	121
	0	570	1·53	7·9	7·9	9 300	5·9	119
	20	570	1·74	8·4	8·0	9 400	6·3	127
17·1	0	630	1·17	8·1	7·3	8 900	3·6	110
	20	630	1·58	6·3	8·2	8 400	4·5	105
	0	580	1·53	8·8	7·6	9 700	4·3	122
	20	580	1·95	8·0	7·6	9 300	5·2	113
22·7	0	690	1·39	—	6·9	—	3·0	95
	20	690	1·60	6·5	8·1	8 300	3·4	79

Changes in the dry strength were erratic and did not indicate a significant effect. However, examination of photomicrographs of the resultant pulps indicated significant differences. The alum addition, prior to refining, produced longer and thinner fibres that appeared to be more flexible. The improvement obtained in fibre characteristics was similar to that obtained by increasing the refining consistency.

The results of another study evaluating the effect of alum addition on pulps at three different hypo numbers are summarised in Table 3. In each case, the alum addition increased the power requirement to reach a given freeness and increased the wet-web stretch. The effect on the burst and tear indices varied.

The increase in the wet-web properties and the work by Pearson(1) and Mardon(2) on the relationship of wet-web properties to paper machine runnability justified a mill trial.

Mill data

THE mill trial started with alum addition to low-yield, sodium-bisulphite pulp in order to ensure that an alum addition in the sulphite mill would not have any adverse effect on the paper-machine operation. When this had been completed, the pulp yield was increased to over 60 per cent. Table 4 summarises some data that show the effect of adding 15 kg/t of alum per ton of pulp at two yield levels. In both instances, the alum addition increased the power requirement to reach a given freeness and, at the same time, higher percentages of long fibres (retained on a 14 mesh screen) were obtained. The dry-strength values were relatively unaffected by the alum addition. A patent has been obtained on this process.(3)

The improvements obtained were encouraging but higher values were desirable. Two effects were evaluated—(1) higher alum addition and (2)

TABLE 4—EFFECT OF ALUM ADDITION ON LOW-YIELD AND HIGH-YIELD BISULPHITE

	Low		*High*	
Alum addition (kg/t)	0	15	0	15
Accepted pulp yield (%)	53·4	52·3	63·5	60·6
Hypo No.	13·8	13·8	22·0	20·7
Total refining power (MJ/kg)	0·2	0·3	0·82	1·13
Freeness (CSF)	575	588	520	591
Bulk (cm^3/g)	1·62	1·62	1·65	1·65
Tear index	9·3	9·5	8·7	8·4
Burst index	6·9	6·7	6·7	6·5
Breaking length	10 000	9 970	10 130	10 600
Fibre classification				
Retained on 14 mesh (%)	13·2	19·5	24·4	28·8

higher stock temperature. The data obtained are summarised in Table 5. Increasing the alum addition from 15 to 25 kg/t increased the power requirements to maintain a given freeness, increased the percentage of long fibre present and produced a small increase in wet-web characteristics. The drainage characteristics were also improved because higher pulp consistencies were obtained on the disc filter and additional groundwood white-water was utilised.

TABLE 5—EFFECT OF INCREASING ALUM ADDITION AND REFINING TEMPERATURE (MILL DATA)

Alum addition (kg/t)	15	25	25
Pulp yield (%)	58·3	61·4	60·3
Hypo No.	21·5	21·4	20·8
Total refining power (MJ/kg)	1·10	1·41	1·26
Refining temperature (°C)	2	2	27
Freeness (CSF)	578	579	576
Bulk	1·73	1·70	1·67
Tear index	10·0	9·9	9·3
Burst index	6·5	6·1	5·9
Breaking length	9 720	9 580	8 190
Fibre classification, retained on 14 mesh (%)	27·8	30·6	27·2
Wet-web strength			
Breaking length	131	137	148
Stretch (%)	2·5	2·7	2·8

Increasing the stock temperature going to the refiner from 2° C reduced the power requirements from 1·41 to 1·26 MJ/kg and decreased the long fibre fraction. However, the wet-web characteristics showed an additional small improvement.

Paper-mill data obtained when the alum addition was 15 kg/t are summarised in Tables 6 and 7. Paper-machine speed and production efficiency increased and the number of breaks decreased with a lower percentage of chemical fibre. Paper formation, wire mark and paper roughness improved while linting was not adversely affected. The moisture content did not change.

Recent analyses of laboratory data and a review of a paper by Haglund

TABLE 6—PAPER-MILL DATA

	Without alum	*With alum*
Sulphite yield (%)	63·0	64·0
Sulphite content (%)	24·9	24·1
Production (tons/day)	1 050	1 165
Paper machine speed (average m/m)	711	743
Production efficiency (%)	85·0	88·7
Breaks per day	41·4	33·2

TABLE 7—NEWSPRINT QUALITY

	Without alum	*With alum*
Moisture (%)	6·9	7·0
Roughness—top	71	66
bottom	76	71
Formation*	55·1	51·8
Wire mark	12·9	10·7

* Q.N.S. Formation Tester

et al.[4] indicated that the optimum addition of alum for a given yield has not been determined and that the alum addition required for the optimum effect could increase with increasing yield. Additional work is being contemplated.

Notes

THE first reference to this work was contained in a paper prepared by Leask *et al.*[5] in 1974 and additional information was given in a second paper by Shaw *et al.*[6] in 1975.

Acknowledgement

To D. Page of PPRIC for his helpful discussions.

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Transcription of Discussion

Discussion

Mr K. Bradway As I understand it you add the alum before refining.

Mr R. A. Leask That is right. There is about half a minute between the time that the alum is added to the cooked chips and when it enters the refiners.

Bradway My reason for asking this is that the alum effect that you see in terms of freeness could just as well happen after refining and I was wondering if it is essential to have the alum introduced before the refining in order to get the observed results?

Leask Yes. Actually if you look in the preprints you will see that we did refining work where we added alum before refining and in one case we added the alum after refining. We did not get the same effect at all and there was quite a significant difference. Actually it is also interesting in the mill, as soon as we added alum to the stock and made no change on the refining set up, the power consumed increased very substantially. If you also look at the fibre classification with the alum addition, our long fibre percentage was substantially higher than without the alum.

Dr J. Grant Did you measure the pH values corresponding with the alum additions? They might have shown some interesting correlations, I think.

Leask No.

Dr A. A. Robertson This is an interesting paper in that it deals with a problem that is probably related to electrokinetics but is in an area that is not generally recognised. The more usual areas are those of zeta potential and its effects on coagulation, deposition or retention, that is the effect of electrokinetics on small particles. It also has an effect on large particles, but mechanical and hydrodynamic effects are so much greater that the only way

Under the chairmanship of A. A. Robertson that it shows up is in the friction coefficient and the ease with which large fibres slip over one another. Here the electrokinetic effects affect the friction and I think that Leask has attributed the improved behaviour to an increase in friction during refining.

Dr D. A. I. Goring I would just like to ask whether you are sure it is an electrokinetic effect? Could the alum be dehydrating the fibre, and producing an increase in interfibre friction or an increase in the friction between the refiner plates and the fibre and thereby allowing one to get more energy into the pulp? It seems to me that the fibre is slippery because it has on its surface a gel of, perhaps, sulphonated lignin; is that right? The alum might be causing this gel to dehydrate a bit and thus make the fibre less slippery?

Leask I don't know, all I know is that it works. I have no explanation for the mechanism.

Dr D. H. Page Leask and I have discussed this many times and I would like to put forward two possible explanations. On the one hand we have the possibility of having sulphonate groups close to the surface and these are satisfied generally by sodium ions which are hydrated. The fibre is therefore slippery and soaplike. If these ions are replaced by aluminium then there is the possibility of salt cross links between one fibre and another which may last for a sufficiently long time to affect the frictional force. On the other hand there is the possibility of changing the structure of the fibre in the same way, and this would change the ease of putting energy in. I am inclined to think that the surface effect is the most important.