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DEWATERABILITY OF A MODEL PRIMARY SLUDGE

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Introduction

Sludge dewatering and disposal is a major environmental problem facing pulp and paper mills. As environmental regulations are stiffened, the situation is expected to worsen. At present, approximately one-half the cost of building and running a waste treatment plant is devoted to sludge handling.

At this same time, more and more mills are searching for ways to recover fiber from their waste effluents. Some uses have been found for sludges and research devoted to sludge utilization continues. However, basic to any sludge management strategy is the ability to produce a sludge cake with low moisture content.

It had previously been thought that only the sludge fiber size distribution controlled dewaterability. Based on work done at the Institute several years ago, it was believed that the chemical makeup of sludges may also influence dewaterability. Accordingly, a research program was undertaken to determine the relationship between sludge chemical composition and dewaterability. We have found that the chemistry of the sludge, as opposed to simple fiber size distribution, may be the factor controlling dewaterability. Work is continuing in our laboratories on practical means to achieve sludge cakes with low moisture contents.

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Abstract

Sludge dewatering and disposal is a major environmental problem facing pulp and paper mills. Little is known of the factors which make some primary sludges difficult to dewater. The objective of this study was to determine the relationship between sludge chemical composition and dewaterability. Based on results obtained, it appears that chemical composition plays a key role in determining sludge dewaterability. It was previously thought that dewaterability was primarily a function of particle size distribution.

Introduction

Although pulp and paper mills have continually searched for means to increase utilization of fiber resources, a significant amount is still lost to the waste water stream (1). This fiber eventually is physically removed from the waste water stream either by a sedimentation or flotation unit operation. The concentrated slurry, now known as the primary sludge, is further processed to reduce the moisture content prior to final disposition.

Because the cost of sludge disposal continues to escalate (2,3) and because there is a growing concern over the proposed laws regulating the land application of sludges (4), many workers are investigating alternative uses for primary sludges (5-7). Basic to the economics of any sludge

management strategy is the ability to produce a sludge cake of low moisture content.

Little is known of the mechanisms by which hydrous sludges are able to bind large quantities of water. Atalla (8) hypothesized a relationship between not only the fiber size distribution but also the chemical composition of the fibers and their ability to be dewatered. Brecht and Strittmatter (9-11) also found a relationship between the dewaterability of model sludges and both the fiber size distribution and the ash content of the sludge.

It is generally accepted that sludges containing large proportions of long fiber are easier to dewater than sludges containing only fiber fines. However, the effect of fiber chemical composition has not been fully elucidated. This study was undertaken in order to further investigate the relationship between the chemical composition of a model primary sludge and its dewaterability characteristics.

The experimental approach taken was to pulp a softwood species using a mild delignification procedure which minimized the loss of other wood components. The fibers were then subjected to progressively stronger solvents in order to selectively remove the water and alkali extractable components. After milling and size classification, each fiber size group was tested for dewaterability by a modified centrifugal water retention test method and by the standard Buchner funnel specific resistance to filtration test method. By simultaneously varying both fiber size and chemical composition, it became possible to perform a regression analysis which indicated the relative importance of chemical composition and fiber size to dewaterability.

Experimental

Wafers, of dimensions 0.75" x 0.25" x 0.015", were prepared from a freshly harvested bolt of Southern loblolly pine (Pinus taeda L.).

Holocellulose was isolated from the wafers by the following procedure. After room temperature extraction for 3 days in 1:1 chloroform/ethanol, approximately 100 g.a.d. wafers were placed in a 4-liter beaker and 3-liter distilled water and 45 g NaClO₂ (Olin, technical grade) were added. The pH was adjusted to 4.0 ± 0.2 with 4N acetic acid. At this point, a vacuum was applied to ensure penetration of the chemicals into the wafers. The mixture was then gently stirred for one hour at $30 \pm 2^\circ\text{C}$ at which time the temperature was raised to $40 \pm 2^\circ\text{C}$. Delignification was continued until a test wafer fell apart when concentrated NaOH was added to it and when the methoxyl content remained constant. When delignification was complete, usually in about 4 days, the pulping liquor was decanted and the wafers washed in distilled water and neutralized. During washing, the chips were defiberized; this material was then termed holocellulose.

The prepared holocellulose was then extracted at 20°C for 24 hours in distilled water. Excess pulping chemicals were the main component of the extract liquor. A sample of fiber was taken for physical testing.

The fiber was then extracted at 75°C for 3 hours in distilled water. The main component extracted was pectin. A sample of the fiber was taken for physical testing.

The remaining fiber was extracted with Ba(OH)₂/NaOH, 1% NaOH, and finally 15% NaOH according to the method of Beelik, et al. (12). This

procedure permits the selective extraction of hemicelluloses from holocellulose. Xylans are the main component of the $\text{Ba}(\text{OH})_2/\text{NaOH}$ extract liquor while galactoglucomannan is dissolved in the 1% NaOH extract liquor. Glucomannans are dissolved in the 15% NaOH extract liquor. After each extraction a sample of fiber was taken for physical testing.

The extracted fiber samples were freeze dried and put through a Wiley mill for size classification. Screen sizes used were 80, 100, 150, and 200 mesh.

Carbohydrate analysis was done by the method of Borchardt (13).

A modified Centrifugal Water Retention test method was adopted from Thode, *et al.* (14).

The Buchner funnel specific resistance to filtration test was done according to standard techniques (15).

Results and discussion

The carbohydrate composition of the fibers after each extraction is given in Table I. These values compare quite favorably with those given by Beelik, *et al.* (12) for western hemlock and grand fir species. As predicted, the content of xylose dropped precipitously after the $\text{Ba}(\text{OH})_2/\text{NaOH}$ extraction. After each extraction, carbohydrate composition was as expected.

Table II shows the results of the Centrifugal Water Retention (CWR) tests. This test was chosen because it gives reproducible results and requires small samples. Since the holocellulose could be produced in only small quantities, small sample size was a desirable test feature.

The CWR test consists, in essence, of placing a small amount of pulp slurry in a specially designed centrifuge tube and centrifuging at 2800 g for 15 minutes. The cake is then carefully removed from the centrifuge tube and the moisture content is determined. All free and most of the interstitial water is removed during centrifugation and only the water chemically associated with the solids remains.

The results of the CWR tests should not be interpreted in absolute terms. Rather, trends in the data are of more significance. As can be seen, as more wood components are extracted within a particular size category, the solids content increases, indicating greater ease in dewaterability. Because these extraction steps selectively remove hemicelluloses, the large difference between the solids content of the hot water and $\text{Ba}(\text{OH})_2/\text{NaOH}$ extraction steps in all mesh sizes suggests that removal of some hemicelluloses may be governing the dewatering process.

The results of the Buchner funnel tests are given in Table III. It was hoped that this test would provide more easily interpretable data since the test is used to design vacuum filtration equipment. It was disappointing to find that differences between the values are too small to draw any firm conclusions. However, looking at the data as trend indicators, reveals much the same as the CWR test. The only difference is that there is an increase in resistance (indicating a more difficult to dewater sludge) between the 1% and 15% NaOH extraction step. It is thought this may be due to swelling of the fibers after hemicelluloses are removed. A major difference between the CWR and the Buchner funnel tests is the magnitude of the mechanical forces exerted on the fibers; much more force is used in the CWR test. This would allow more

of the interstitial water to be removed and permit small differences in chemically bound water to be observed.

The correlation coefficient (r^2) from the analysis of variance tests are shown in Table IV. A correlation coefficient greater than 0.90 was considered very significant. As can be clearly seen, there were no clues to the relationship between chemical composition and specific resistance to filtration. Somewhat surprisingly, not even mesh size could be correlated with dewaterability.

Arabinose and xylose content in the fibers shows a high correlation with CWR. Total hemicellulose also shows a high correlation; this could be an experimental artifact in that the total hemicellulose content for loblolly pine is dominated by xylose. The experimental procedure suffers from a limitation because it is not possible to change the order of hemicelluloses extracted. Thus, it is not possible to determine if the high correlation of CWR to xylose is due to the presence of xylose on the fiber or to its order of removal from the fiber. Once again, mesh size was not shown to be statistically significant.

These results may be used to suggest reasons for differences in dewaterability between mill primary sludges. For example, it is thought groundwood sludges are difficult to dewater because of the large fines content. These results indicate the problem may be due to the high hemicellulose content of this high yield process. Conversely, low yield kraft primary sludges are usually quite easy to dewater; this could be due to the low hemicellulose composition of the sludges.

This investigation has suggested that the chemical composition of

primary sludges may be more significant than fiber size distribution in relation to dewaterability. One practical question which has not been addressed is whether all size fractions within a particular sludge have the same chemical composition. As mills close their white water systems, this may have an adverse impact on treatment plant operation. Another question is whether mills who use more than one type of pulp may experience problems in chemical dewatering aid addition because the sludge characteristics have changed due to differences in chemical composition between furnishes. Work on these issues continues in our laboratories.

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I. Carbohydrate composition of fibers after indicated extraction

Extraction	Weight Percentage				
	Arabinose	Xylose	Mannose	Galactose	Glucose
Chloroform/ethanol	1.1	5.0	12.2	2.2	43.4
Cold water	0.8	7.0	13.4	2.0	62.0
Hot water	0.8	6.9	13.5	1.9	62.7
Ba(OH) ₂ /NaOH	0.3	2.8	14.9	1.6	70.7
1% NaOH	0.2	2.2	15.4	1.0	67.5
15% NaOH	0.0	1.0	13.2	1.0	77.1

II. Solids content of cake (%) after centrifugal
water retention test

Mesh	Extraction				
	Cold water	Hot water	Ba(OH) ₂ /NaOH	1% NaOH	15% NaOH
80	37.5	38.9	47.8	50.6	54.0
100	35.5	35.8	44.8	49.1	52.6
150	34.3	35.0	44.2	46.8	52.3
200	35.2	33.7	43.8	46.3	49.7

III. Specific resistance of fibers to filtration

Mesh	Specific Resistance $\times 10^{-8}$ (sec ² /g)				
	Cold water	Hot water	Ba(OH) ₂ /NaOH	1% NaOH	15% NaOH
80	2.4	2.3	2.1	0.6	1.6
100	4.5	2.1	2.2	1.0	1.6
150	7.2	3.3	2.6	1.3	1.4
200	4.7	3.1	0.7	1.6	1.3

IV. Analysis of variance results

Variable	<u>r²</u>	
	CWR	Specific Resistance
Arabinose	0.94	0.48
Xylose	0.93	0.49
Mannose	0.10	0.19
Galactose	0.85	0.49
Glucose	0.79	0.33
Total hemicellulose	0.91	0.40
Mesh size	0.04	0.02