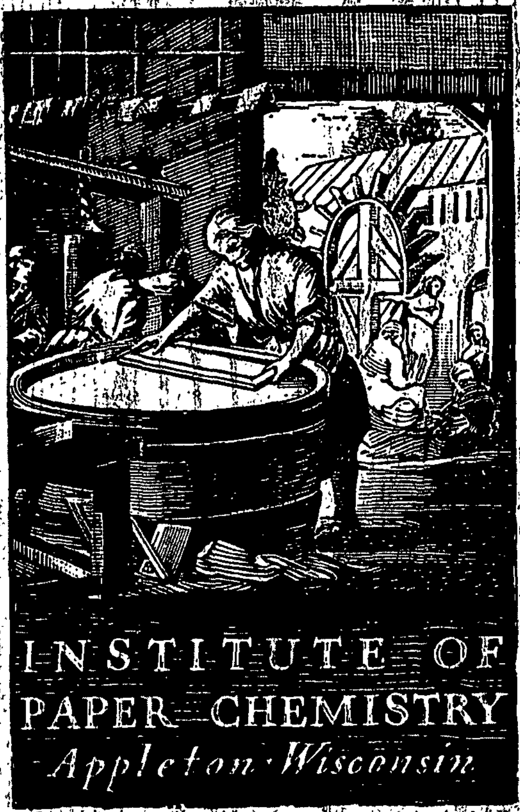

HYDROUS SLUDGES: FURTHER CHARACTERIZATIONS AND A MODEL SYSTEM

Project 2962

Report Two

A Progress Report

to

NATIONAL COUNCIL OF THE PAPER INDUSTRY FOR AIR AND STREAM IMPROVEMENT, INC.

February 29, 1972

THE INSTITUTE OF PAPER CHEMISTRY

Appleton, Wisconsin

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SUMMARY

The effort during the second period of the program was devoted to more detailed characterization of sludges from the Lufkin mill of Southland Paper Mills, Inc., and to development of a model system based on groundwood pulp from the same mill.

Over the range of solids contents which permit characterization by centrifugal sedimentation measurements, the groundwood and its fractions duplicated, to a remarkable degree, the dewatering behavior of the sludges and fractions of the sludges.

Chemical analyses demonstrated that, for both the sludges and the groundwood, the finer fractions have a higher content of water-swellable polysaccharides. The differences between the compositions of the fines and the coarser fractions are, however, greater for the sludges than for the groundwood.

INTRODUCTION

The second period of this investigation has been devoted to more detailed characterization of sludges from the primary clarifiers of the Lufkin facility of Southland Paper Mills, Inc., and to comparison of the sludges with a sample of the groundwood pulp used in the mill. The characterization and the comparison with the groundwood pulp were based on mechanical fractionation followed by chemical analyses and sedimentation studies on individual fractions. Some attention was also given to further refinement of the methods used to characterize the dewaterability of sludges.

It was established during the first period, and discussed in detail in the first report (1), that the major components of the sludges obtained from four different mills were pulp-derived solids closely approximating some of the constituents of the pulps in use at these mills. It was also demonstrated that the behavior of the sludges is closely approximated by the behavior of a groundwood pulp. Chemical analyses revealed some correlation of sedimentation behavior with content of pectic substances. And it was shown that centrifugal sedimentation behavior is a sensitive indicator of differences between the sludges which are related to their dewatering behavior.

The sludge from the Lufkin mill, designated as Sludge A, was chosen for extensive investigation because it was the least easily dewatered. In the current period, additional samples of sludge from the Lufkin mill were investigated, and these have been designated Sludges A-2 and A-3.

It was noted in Report One that a model system based on groundwood pulp would be considered. A sample of southern pine groundwood pulp was obtained from the Lufkin mill for use in this exploration. This sample has been designated groundwood SP. In addition, to provide a basis for comparison, some of the tests were carried out on a sample of northern aspen groundwood. This sample has been designated groundwood NA.

Two of the questions posed in the concluding section of Report One have been central to the effort during the current period. The first is whether the mechanical fragmentation of the fibers in the grinding process is accompanied by a size-related chemical differentiation. The second is whether a particular size fraction of a sludge dominates the behavior of the whole or whether the latter is essentially a composite of the patterns of behavior of all its fractions.

CHARACTERIZATION

FRACTIONATION

The first step in the characterization of the systems investigated was a mechanical classification. The double classification procedure used was similar to that described previously (1). The results are shown in Fig. 1 and Table I.

TABLE I

BAUER-McNETT CLASSIFICATION

Coarse Screens	Sludge A-2	Sludge A-3	Groundwood SP	Groundwood NA
On 14 mesh	2.0	1.6	0	0
Through 14, on 20 mesh	4.0	4.0	5.3	0.8
Through 20, on 35 mesh	5.2	5.0	10.8	7.1
Through 35, on 60 mesh	7.9	9.3	17.9	26.8
Through 60 mesh, by diff.	80.9	80.1	66.0	65.3
Fine Screens				
On 60 mesh	17.0	19.0	29.4	18.2
Through 60, on 100 mesh	6.3	6.2	12.2	15.0
Through 100, on 150 mesh	6.7	5.0	15.2	18.4
Through 150, on 200 mesh	5.2	4.8	6.7	7.6
Through 200 mesh, by diff.	64.8	65.0	36.5	40.8
Through 200 mesh, corrected for 14-60 mesh retention	62.7	64.1	31.9	24.3

The outstanding feature of the sludges is their much higher content of fines (through 200) and lower content of most other fractions. The papermaking process is clearly selective in its capacity to retain fibers. Fibers retained

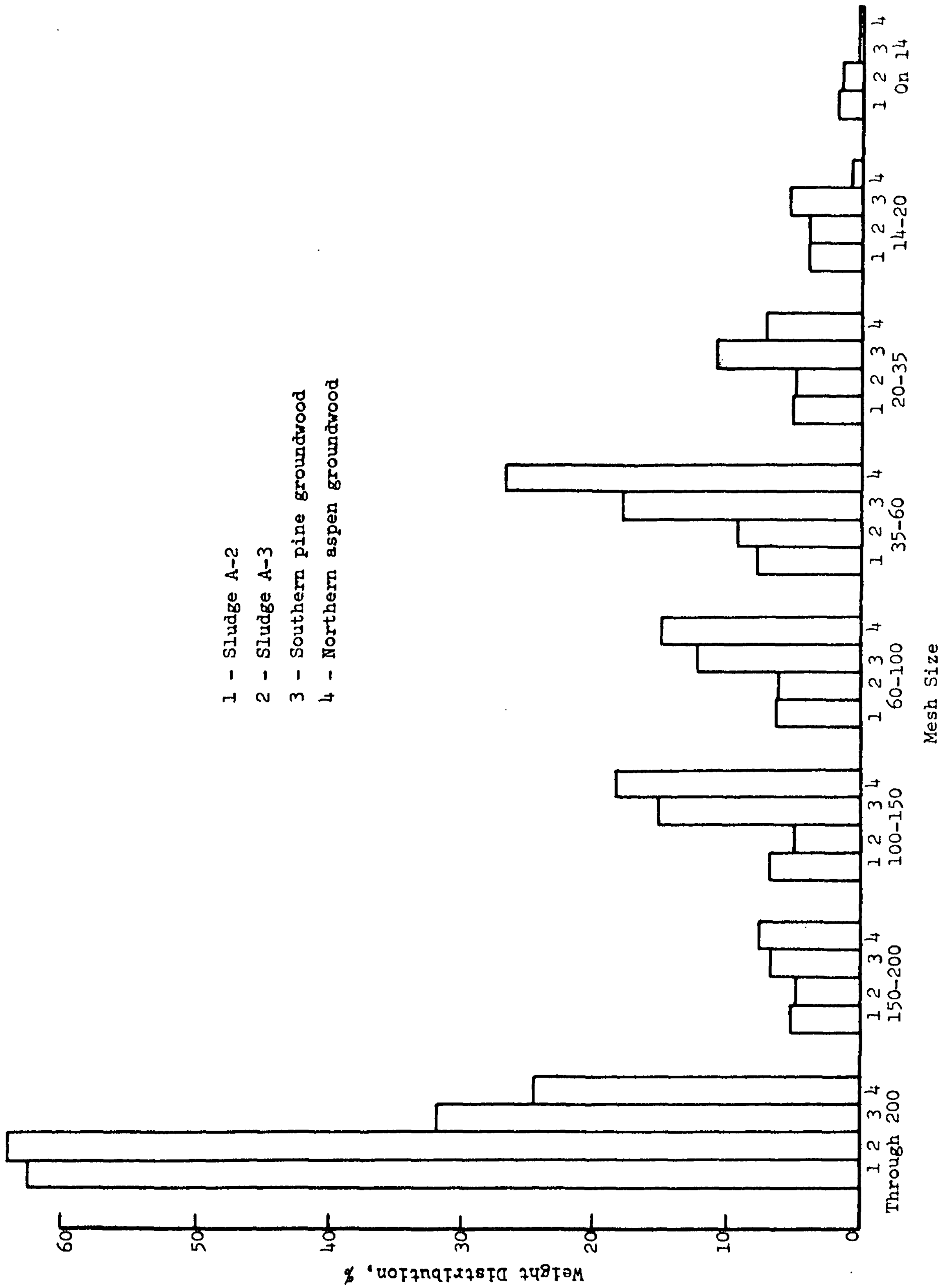

Figure 1. Bauer-McNett Classification of 2 Sludges and 2 Groundwood Pulps

on 150 mesh, or coarser, screens are lost to the effluent stream at a much lower rate than finer fibers.

While the separation into eight fractions obtained in the double classification is essential to developing a view of the particle size distribution, it did not seem desirable to subject all the fractions to the types of analyses contemplated for further characterization. A coarser fractionation was therefore carried out to provide samples in large enough quantities for these studies. This consisted of a classification producing three large fractions. The first, designated 'on 60,' includes all particles retained on a 60-mesh screen. The second, designated 'through 60,' includes all particles passing through a 60-mesh screen. The third fraction, designated 'through 200' includes all particles passing through a 200-mesh screen, and is the only one having a corresponding fraction in the finer fractionation reported above. The analyses to be described below were, in every instance, carried out for the three large fractions as well as for the unfractionated sample designated 'whole.'

CENTRIFUGAL SEDIMENTATION

As noted in Report One, centrifugal sedimentation was found to be sensitive to variations in the nature of the suspension, and provides a basis for comparison of sedimentation characteristics. This technique was applied to characterizing the fractions of the sludges and groundwoods prepared as noted above. The centrifugations were carried out at rotational speeds of 250, 500, and 750 r.p.m. It was found that optimum resolution of the curves occurs for centrifugation at 500 r.p.m., corresponding to a relative centrifugal force (g) of 55 at the tip of the centrifuge tubes. The data chosen for graphical presentation in this report are the sedimentation curves at 500 r.p.m.

Figures 2 to 5 show the sedimentation curves of the three major fractions and of the whole sample for the two sludges and for both groundwood samples. Two features stand out. The first is the great similarity of the curve for the sludges and groundwood SP. The second is the degree of resolution of the curves for all three samples. The fractions of the hardwood groundwood NA, in contrast, do not result in well-resolved sedimentation curves.

Figures 6 to 9 provide a comparison of the sedimentation behavior of the same size fractions from Sludge A-2 and groundwood SP. It is clear that although differences in sedimentation rates are observed, these differences are quite small.

CHEMICAL ANALYSES

The fractions of Sludges A-2 and A-3 and of groundwood SP were also subjected to chemical analyses. The results are shown in Tables II, III, and IV. The sugar analyses are of particular interest because they indicate the relative abundance of cellulose, hemicelluloses, and pectic substances. Other constituents, particularly lignin, have also been determined.

A number of important observations emerge from the chemical analyses. The first is the clear indication of significant variation of composition with particle size. The magnitude of this variation is greater for the sludges than for the groundwood SP, although even in the latter the differences are quite significant. The other observations are related to the nature of the variation in chemical composition with particle size. Among these, the variation of glucan content is the most important. The increase of glucan content with

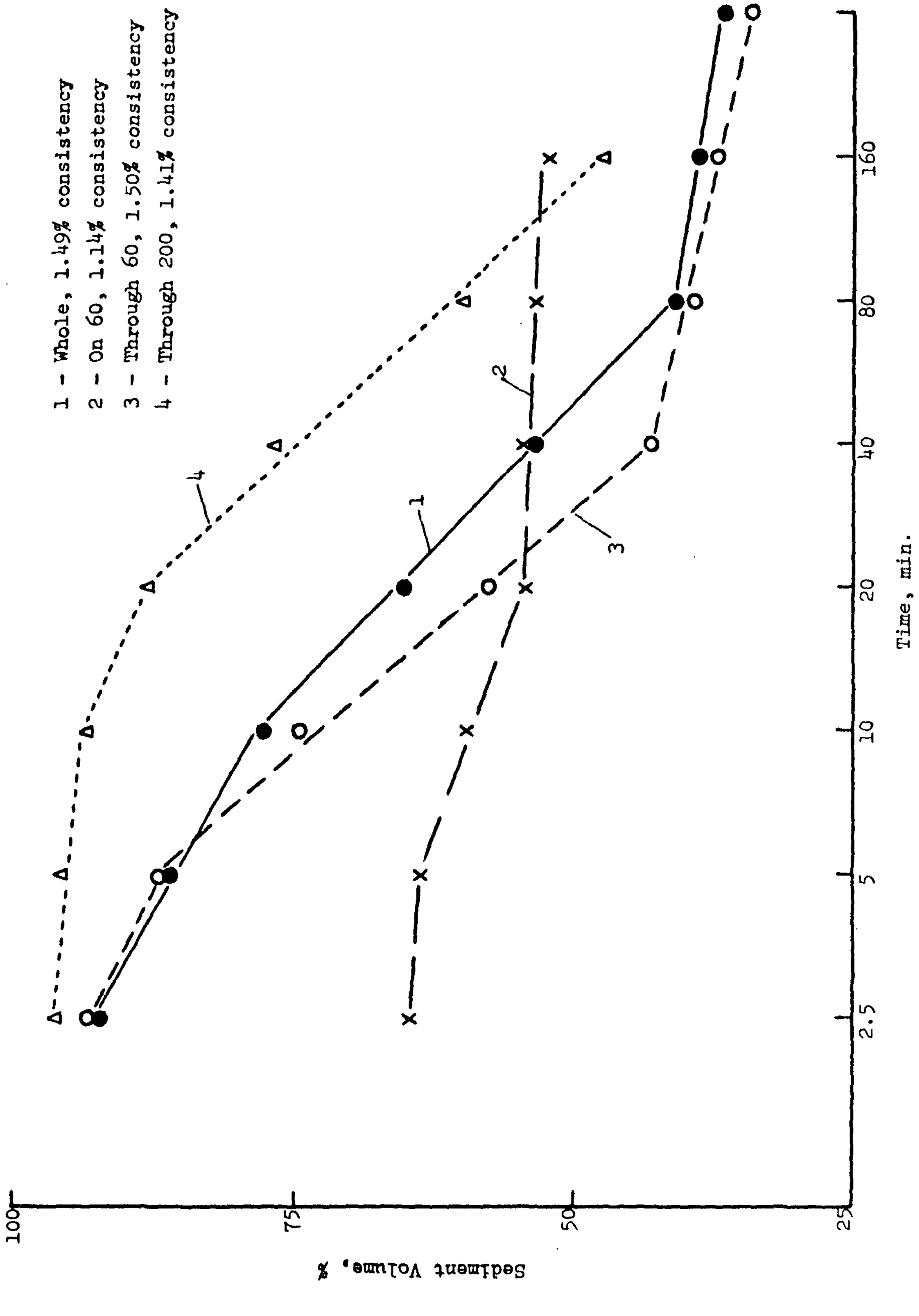

Figure 2. Centrifugal Sedimentation, Sludge A-2 and Fractions, 500 r.p.m.

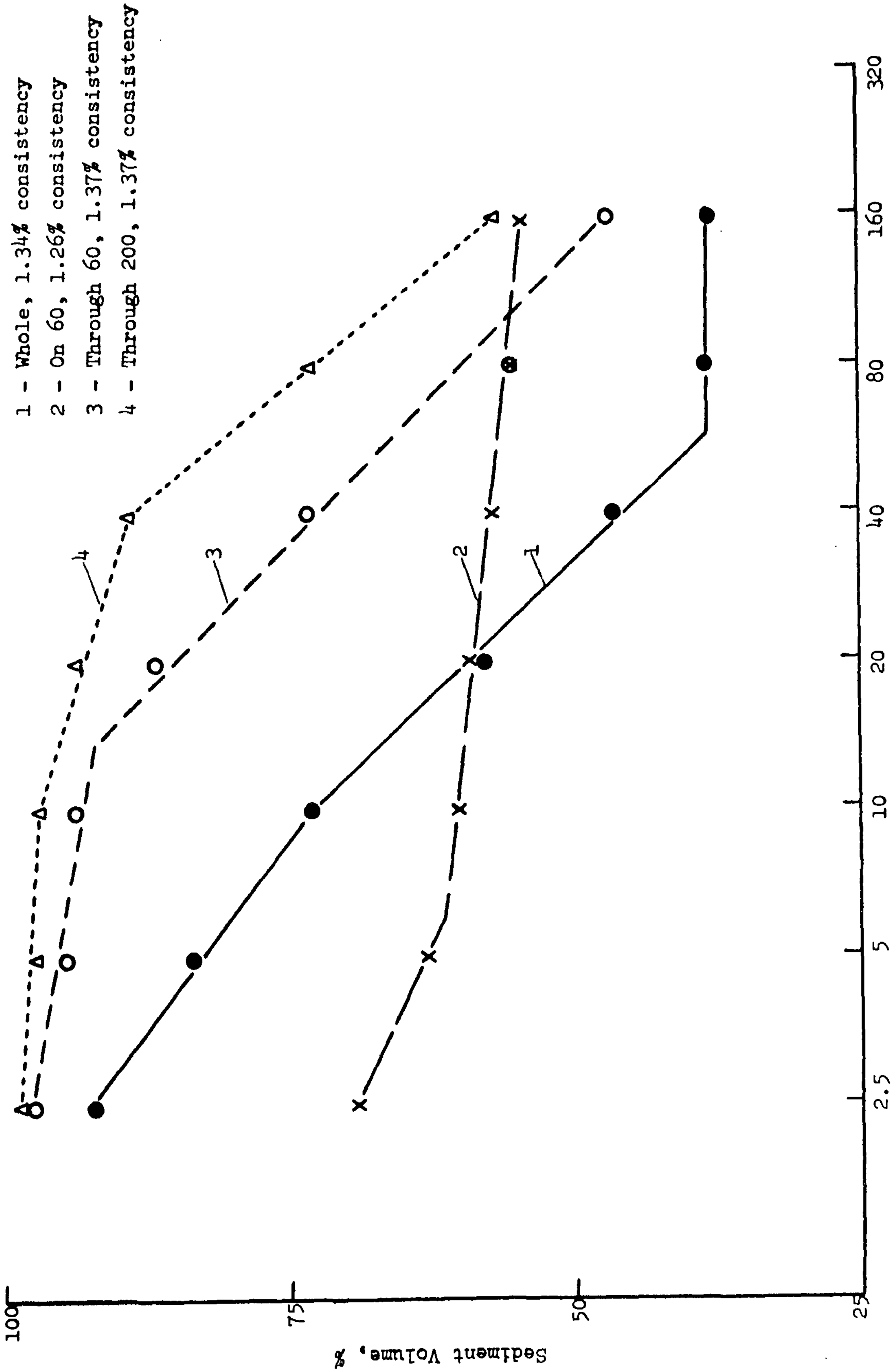

Figure 3. Centrifugal Sedimentation, Sludge A-3 and Fractions, 500 r.p.m.

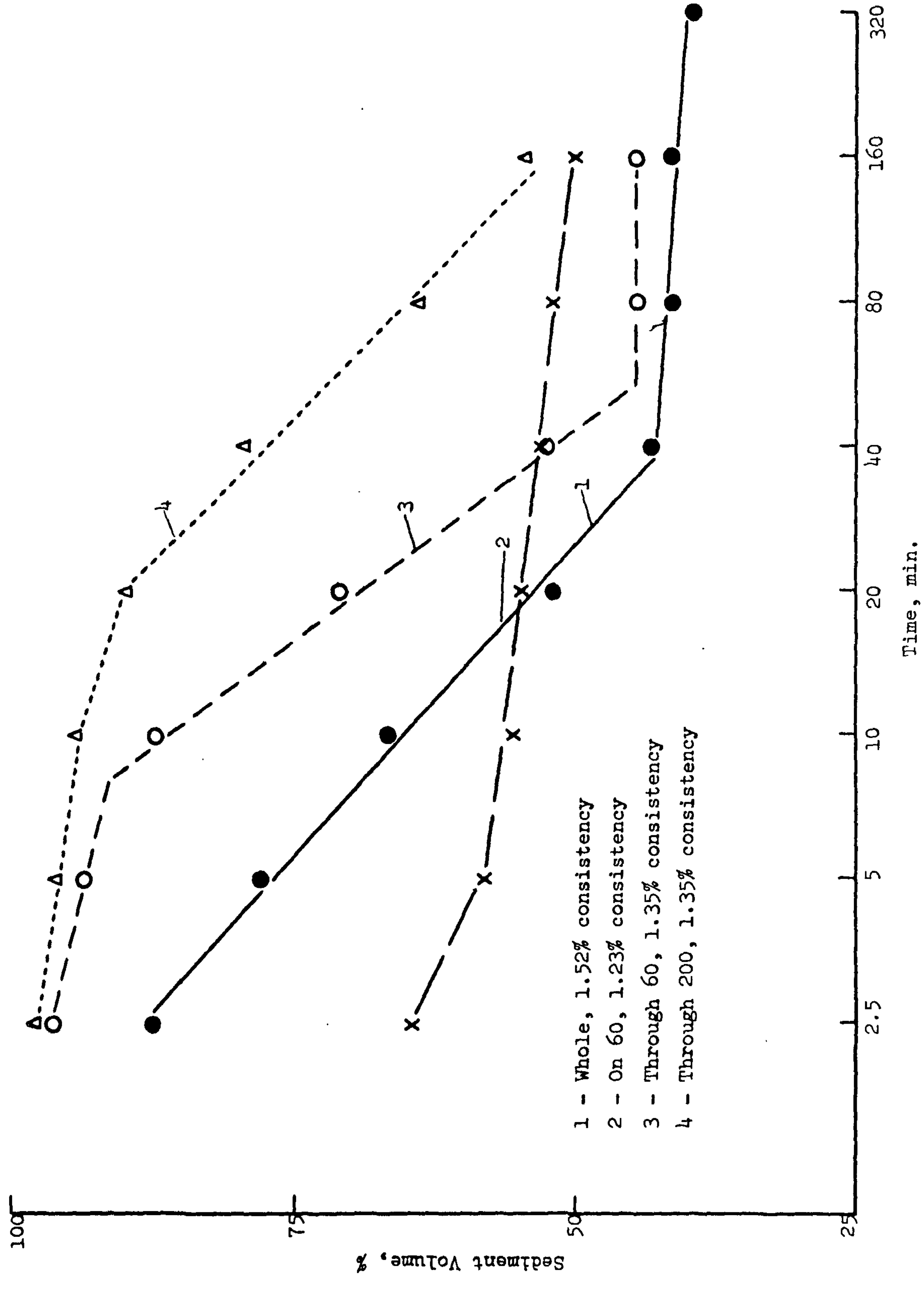

Figure 4. Centrifugal Sedimentation, Southern Pine Groundwood and Fractions, 500 r.p.m.

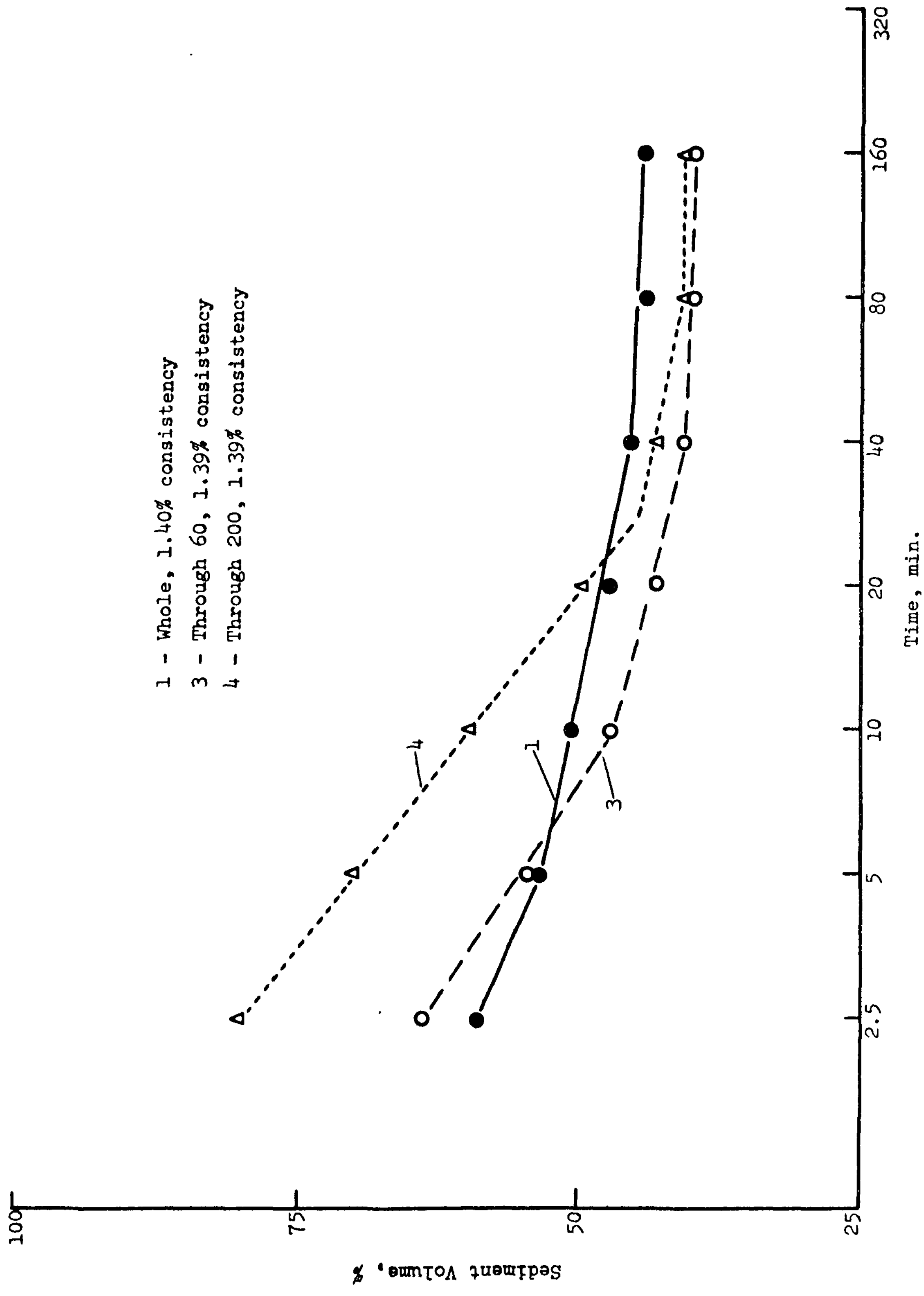

Figure 5. Centrifugal Sedimentation, Northern Aspen Groundwood and Fractions, 500 r.p.m.

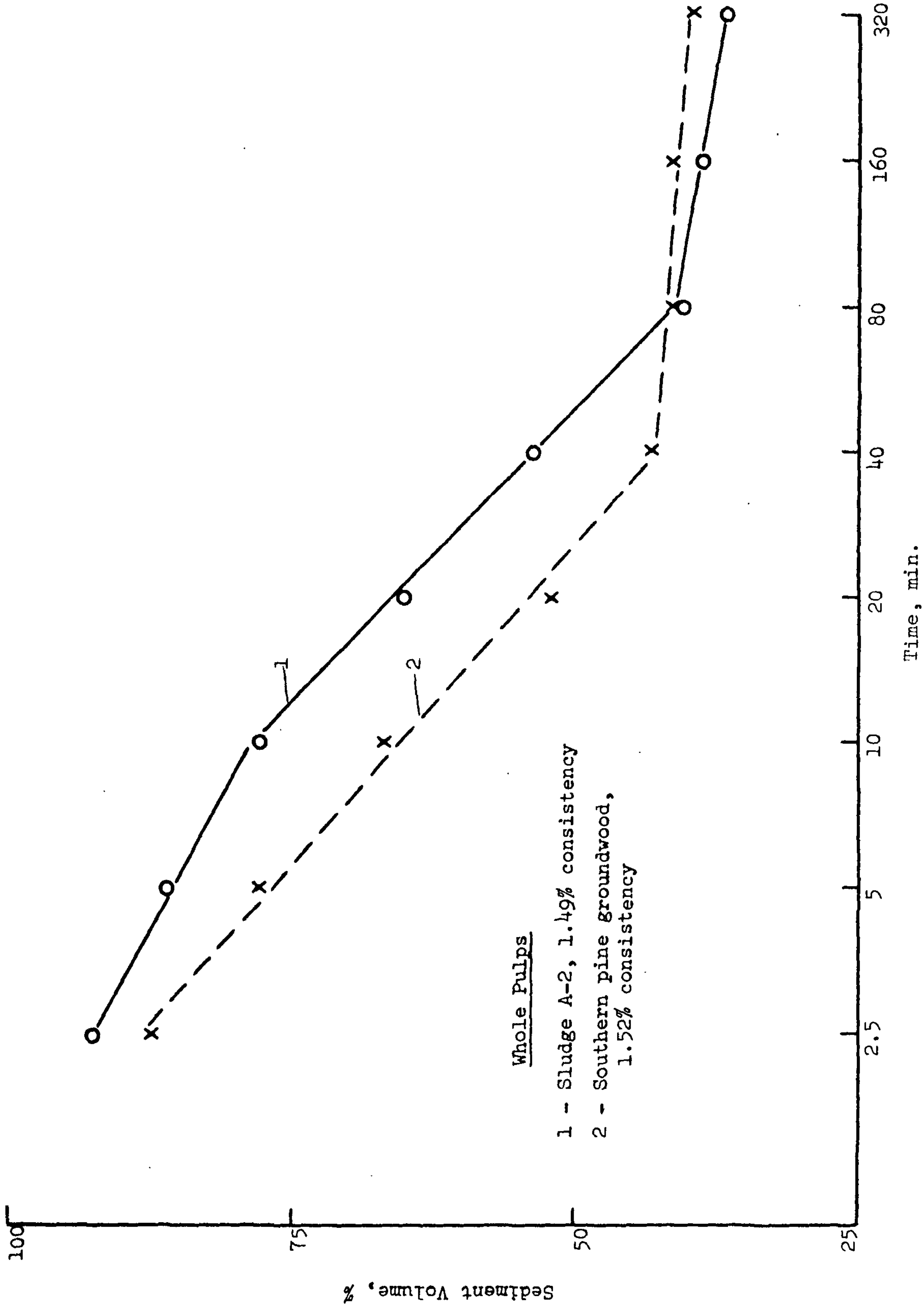

Figure 6. Centrifugal Sedimentation, Sludge A-2 and Southern Pine Groundwood, 500 r.p.m.

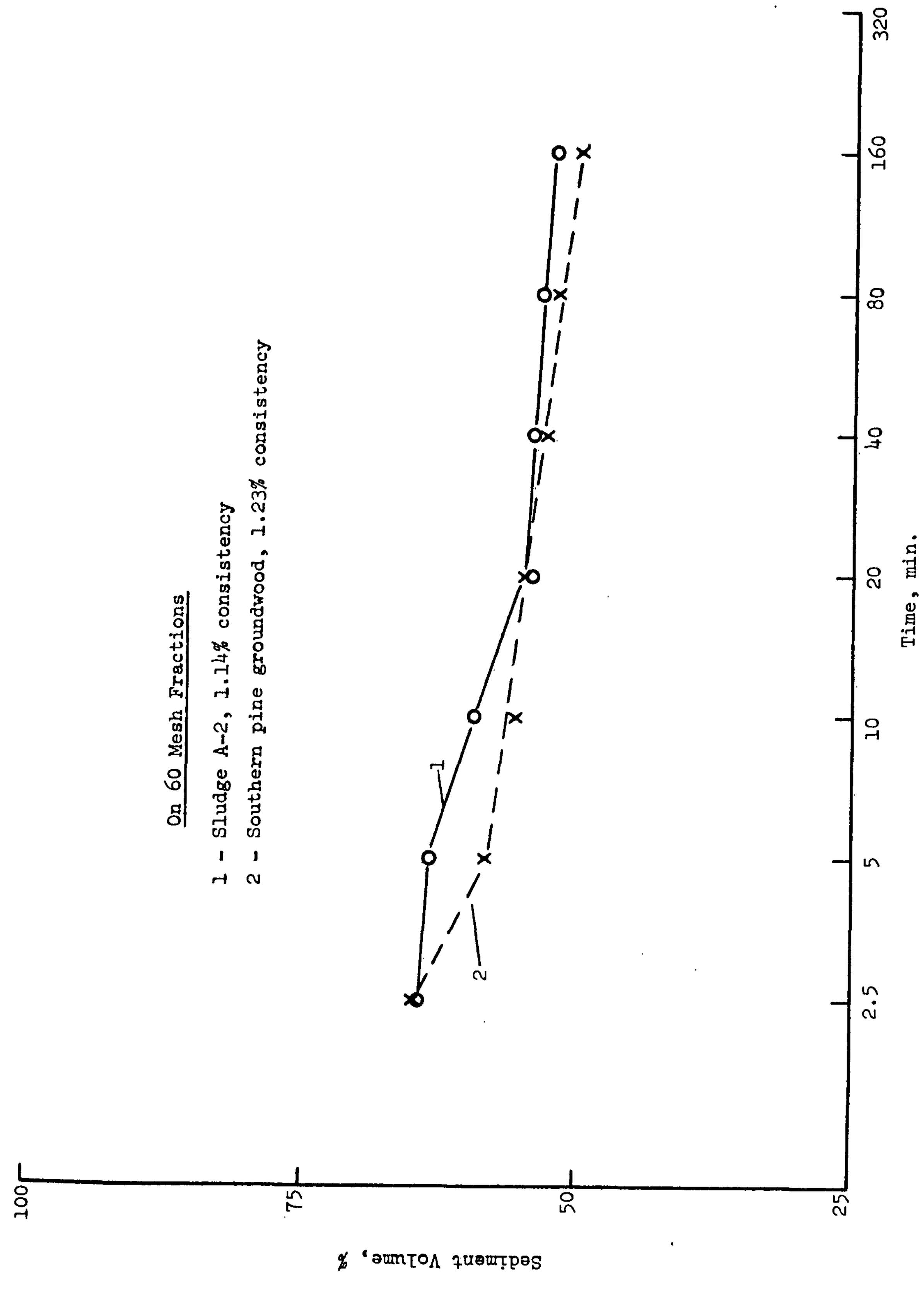

Figure 7. Centrifugal Sedimentation, On 60 Mesh Fractions of Sludge A-2 and Southern Pine Groundwood, 500 r.p.m.

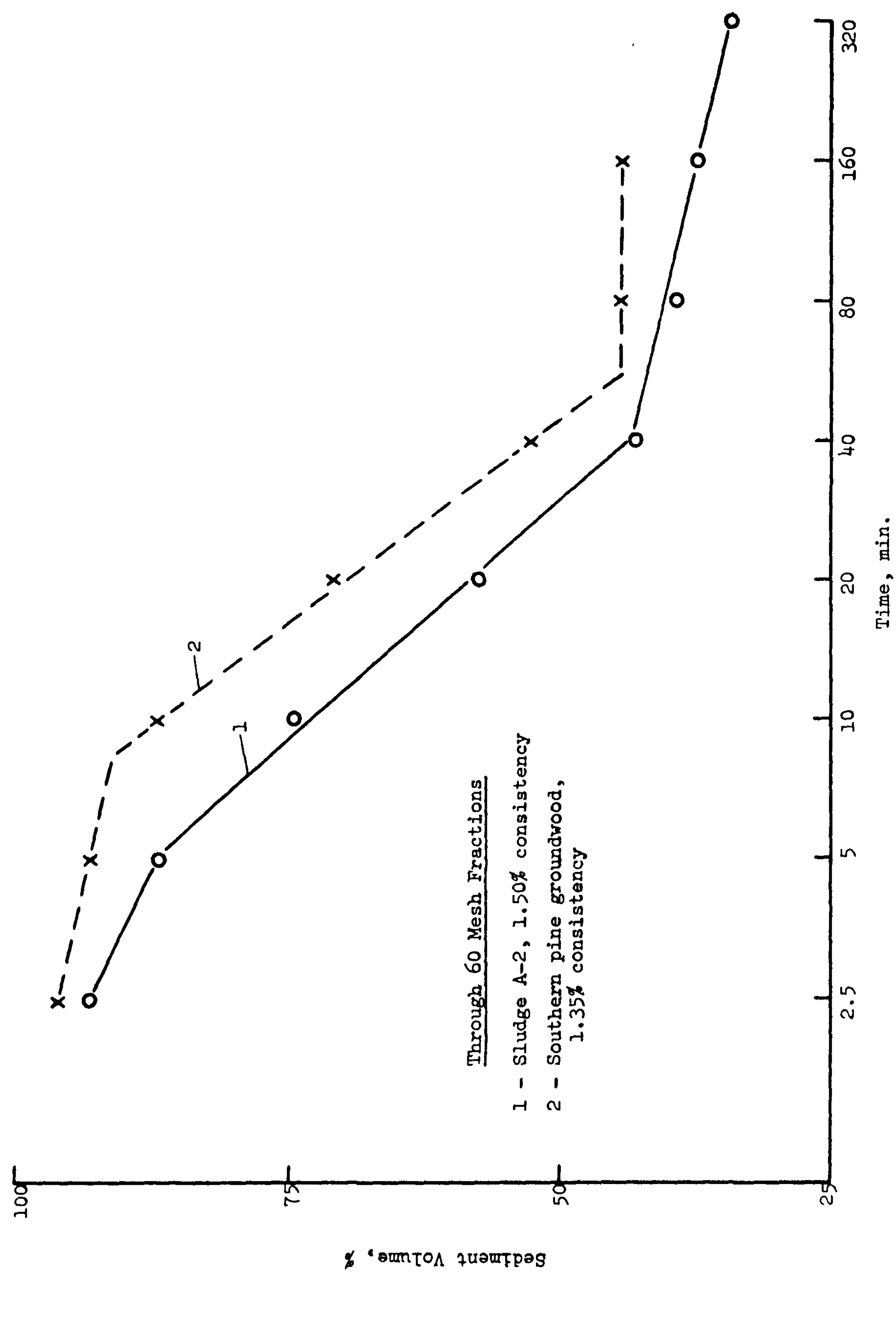

Figure 8. Centrifugal Sedimentation, Through 60 Mesh Fractions of Sludge A-2 and Southern Pine Groundwood, 500 r.p.m.

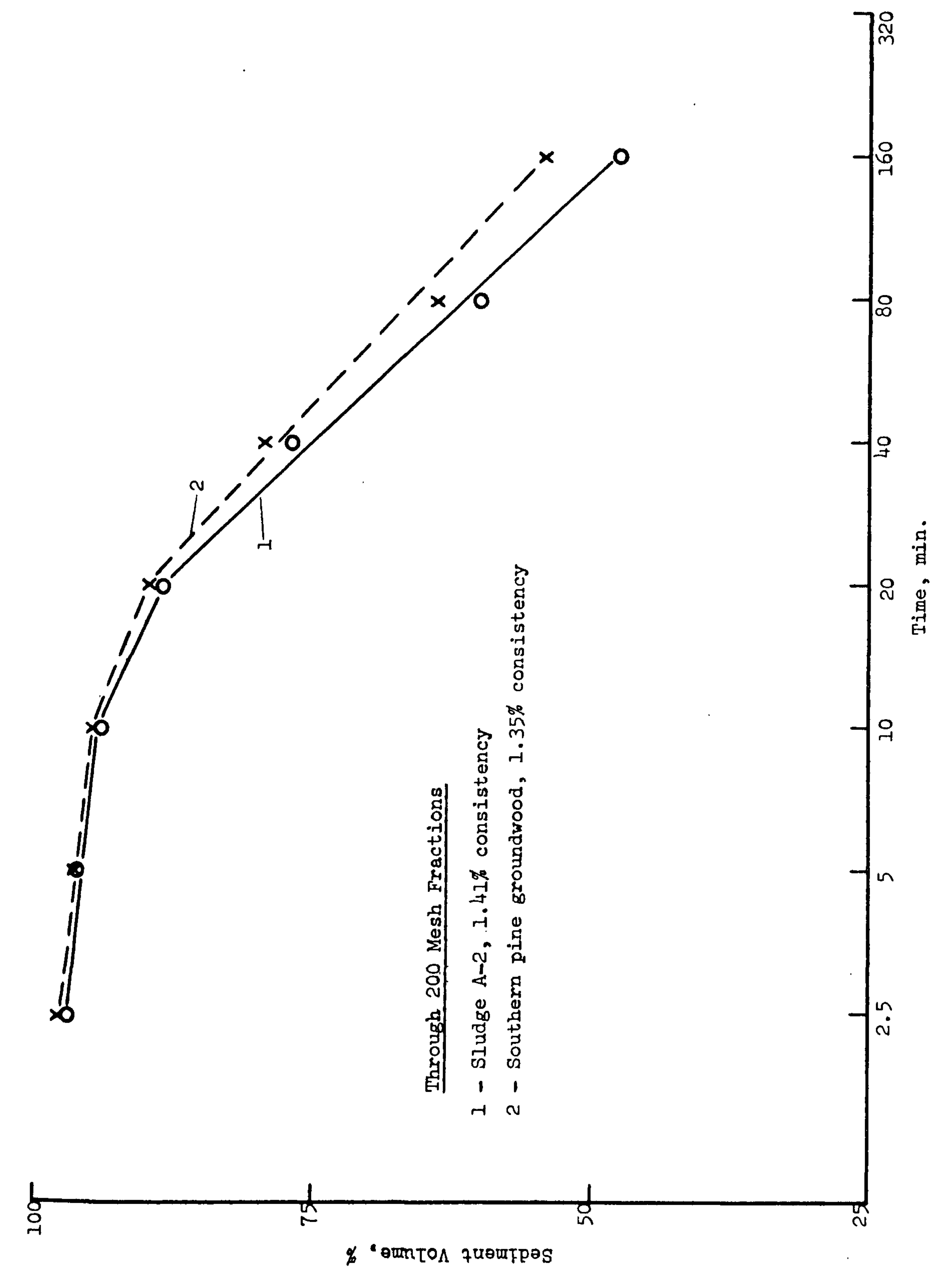

Figure 9. Centrifugal Sedimentation, Through 200 Mesh Fractions of Sludge A-2 and Southern Pine Groundwood, 500 r.p.m.

particle size suggests an increase of the cellulose content relative to the hemicelluloses. Also noteworthy, however, is the inverse relationship between particle size and lignin content.

TABLE II

CHEMICAL ANALYSIS — SLUDGE A-2

	Whole, %	On 60, %	Through 60, %	Through 200, %
Araban	1.1	1.0	1.3	1.3
Xylan	5.2	7.05	5.8	5.6
Mannan	7.9	10.65	8.4	8.0
Galactan	2.7	1.85	2.8	3.4
Glucan	34.5	52.4	35.9	32.1
Galacturonic anhydride[a]	0.47	0.405	0.54	0.65
Lignin	25.1	18.8	27.4	29.3
Nitrogen	0.16	0.055	0.155	0.15
Extractives (alcohol-benzene)	11.0	3.81	8.52	9.85
Ash	2.94	1.10	2.96	2.73

[a]Pectin contains approximately 80% galacturonic anhydride.

Results are based on moisture-free fractions.
Analyses include components of interest to the study. Totals are less than 100%.

TABLE III

CHEMICAL ANALYSIS — SLUDGE A-3

	Whole, %	On 60, %	Through 60, %	Through 200, %
Araban	1.0	1.0	1.1	1.1
Xylan	5.3	7.2	5.1	4.8
Mannan	7.6	11.0	7.2	6.6
Galactan	2.4	1.9	2.8	2.7
Glucan	33.1	49.9	31.7	28.3
Galacturonic anhydride[a]	0.34	0.10	0.23	0.29
Lignin	24.0	19.8	25.5	26.0
Nitrogen	0.20	0.04	0.25	0.32
Extractives (alcohol-benzene)	12.1	1.3	11.8	14.2
Ash	5.2	1.6	5.4	6.0

[a]Pectin contains approximately 80% galacturonic anhydride.

Results are based on moisture-free fractions.
Analyses include components of interest to the study. Totals are less than 100%.

TABLE IV

CHEMICAL ANALYSIS — SOUTHERN PINE GROUNDWOOD

	Whole, %	On 60, %	Through 60, %	Through 200, %
Araban	1.3	1.1	0.8	1.3
Xylan	6.7	6.5	6.2	5.7
Mannan	11.3	12.4	10.4	9.0
Galactan	3.3	2.0	3.3	3.5
Glucan	40.9	43.1	38.9	34.7
Galacturonic anhydride[a]	0.36	0.26	0.36	0.43
Lignin[b]	27.56	25.55	28.68	32.18
Nitrogen	0.06	0.03	0.08	0.07
Extractives (alcohol-benzene)	4.18	0.86	2.63	2.42
Ash	0.77	0.66	1.26	1.76

[a]Pectin contains approximately 80% galacturonic anhydride.

[b]Not corrected for ash.

Results are based on moisture-free fractions.
Analyses include components of interest to the study. Totals are less than 100%.

DISCUSSION

The results summarized above suggest a number of conclusions related to the nature of the systems under study as well as the course of further investigations with a model system.

MODEL SYSTEMS

A comparison of both centrifugal sedimentation results and chemical analysis data for the two sludges and groundwood SP indicates that the groundwood system approximates the sludges closely enough to establish the validity of its use as a model system in further investigations. It is true that differences in particle size distribution, and in the range of variation of chemical composition, do occur between the groundwood SP and the sludges. These differences can be adequately accounted for, however, at this stage in the investigations. Thus, the hypothesis put forth in Report One concerning the development of a model system seems to be valid.

A broader implication of the comparison of the sludges with groundwood SP is that a basis may be developed for understanding the dewatering properties of mill sludges in terms of the dewatering behavior of fractions of the pulps in use at the source mills. The close correspondence between the behavior of fractions of the sludge and those of the groundwood (Fig. 6 to 9) indicates that mechanical classification can contribute to developing the relation between the behavior of the two types of systems.

SEDIMENTATION

The measured sedimentation rates for the different fractions can be interpreted in terms of both chemical and mechanical factors. The chemical differences result in differences in the density differential which in turn contributes to the balance of mechanical effects which determine the observed sedimentation rate.

The most obvious purely mechanical effect is the variation in surface-to-volume ratio associated with variation in particle size. The higher surface-to-volume ratio for the smaller particles will result in a higher ratio of viscous drag to inertial forces. Thus, sedimentation of smaller particles will occur more slowly entirely apart from any differences in constitution.

The chemical difference which is likely to influence the density differential is the balance of carbohydrate content between cellulose and the hemicelluloses. The higher hemicellulose content of the smaller particles is likely to result in increased swelling by water thus bringing the specific gravity of the particles closer to that of water.

The two factors listed as contributing to the slower sedimentation of small particles (i.e., surface-to-volume ratio; hemicellulose-to-cellulose ratio) seem to be coupled in a complex manner. This is brought out in comparisons of sedimentation curves for the whole systems with those of the fractions. Thus, for both sludges and groundwood SP the sedimentation curves for the whole system begin at a level intermediate between those of the smaller and larger fractions, but in each case the final part of the whole-system curve is at a level significantly below the level for the largest (on 60) fraction. The shape of the curve for the 'on 60' fraction suggests the possibility of a 'brush-pile effect' mechanically inhibiting further compaction.

CHEMICAL ANALYSES

It was noted above that the increased hemicellulose content would result in greater swelling. This observation is in part based on the nature of the hemicelluloses involved.

Two galactoglucomannans are known to occur in southern pine (2). Of these, one contains approximately 0.1 galactopyranose residues per 3 mannopyranose residues, and is soluble only in strong caustic solution. The other has 1 galactopyranose residue per 3 mannopyranose residues, and is soluble in water. Examination of the galactan-to-mannan ratio for the different fractions reveals a consistent pattern for the two sludges and the groundwood SP. The ratio of galactan to mannan is about 0.17 for the 'on 60' fractions, and ranges from 0.37 to 0.42 for the 'through 200' fractions. Clearly the content of the water-soluble galactoglucomannan increases as particle size decreases. And it is anticipated that the greater water solubility contributes to hydration of the particles.

Another constituent closely related to the hemicelluloses is pectin. Although it occurs in smaller quantities than the hemicelluloses, it is important because of its capacity to bind large amounts of water. The content of pectin is also found to increase as particle size decreases. Thus, it appears likely that the higher pectin content also contributes to greater hydration of the smaller particles.

Consideration of the potential roles of the galactoglucomannan and the pectin indicates that, in addition to investigation of the ratio of the other polysaccharides to cellulose, some attention must be given to the nature of the particular polysaccharides involved.

FUTURE DIRECTIONS

The results obtained so far in the current program suggest that further refinement of the nature of the observations is desirable. A sedimentation procedure more directly related to the capacity of the sludge to bind water at a molecular level would permit clearer distinction between the hydration properties of the fractions. In addition, the nature of the relationship between sugar analysis and capacity for hydration needs to be explored.

SEDIMENTATION

The weakness of the sedimentation procedure used so far is that, in the limit, i.e., at long periods of centrifugation, the process may be dominated by mechanical compaction effects which have little or nothing to do with binding of water within the particles. In Fig. 2 to 4 it is seen that, at long periods, the 'on 60' fraction attains a lower degree of separation than the other fractions. This is in spite of the fact that in the early stages it separates far more rapidly than the other fractions. The 'brush-pile' effect was suggested above in explanation of this observation. The figures also show that the curves for some of the other fractions approach the same slope as the 'on 60' curve at long periods, although this occurs at a higher level of separation. This too suggests a mechanical effect since greater compaction of the smaller particles can be anticipated. Thus, it appears clear that although the centrifugal sedimentation experiments provide valuable information concerning the early phases of separation of the sludges and their fractions, continuation beyond a separation corresponding to approximately 4 to 5% solids brings into dominance mechanisms unrelated to hydration of the particles. A new technique is thus being evaluated.

The technique under study is that developed by Thode, et al., at the Institute in order to measure the changes in hydration capacity which accompany beating of chemical pulps (3). Though a number of centrifugal methods have been described in the literature, the method of Thode, et al, was chosen because the special equipment developed for its application is readily available at the Institute.

The method is essentially a technique for centrifugal filtration. The suspension to be tested is made to drain through an appropriate screen, resulting in the formation of a pad. The pad and the supporting screen are then transferred to a specially designed centrifuge head assembly which enables spinning in the International Centrifuge, Model V. A relative centrifugal force of 3000 g. is possible in the present arrangment. After spinning for a fixed period, the pad is removed and weighed, then oven dried and weighed again. Final solids contents of 15 to 30% are possible with this technique. Preliminary exploratory experiments indicate that this technique is indeed sensitive to the capacity of the fibers to bind water.

CHEMICAL ANALYSES

As noted above, the analyses carried out so far have indicated that components which arise from hygroscopic polysaccharides do occur in larger quantities in the smaller particles. These results are consistent with the hypothesis that such polysaccharides are an important factor in the dewatering problem, but the evidence remains indirect in nature. The chemical approach which is currently under development is intended to provide more direct evidence concerning this point.

The approach chosen is an adaptation of the procedure used by Banerji and Thompson in investigations of hemicelluloses (4). The pulp is subjected to a mild chlorine delignification in order to minimize the loss of soluble polysaccharides. This is followed by extraction with water and caustic solutions of increasing strength to remove, in stages, the various polysaccharides.

In the present program, the delignification has been modified to further reduce the loss of polysaccharides, by carrying out the chlorination and extraction in organic media. This phase has been successfully accomplished, and a lignin level of about 1.0% has been attained.

The next phase, projected for the near future, will involve extraction by aqueous, and aqueous caustic media of increasing strength, followed by two types of observations. In the first, the capacity of the residual pulp to bind water will be measured, using Thode's 'centrifugal water retention' method, after each stage of extraction. The second type of observation will be a sugar analysis carried out on the polysaccharides solubilized at each stage. Thus, it is hoped that the polysaccharides responsible for hydration of the sludge particles will be identified directly.

It is anticipated that success in the program as projected should lead to general relationships between hemicellulose content of pulps and the hydration properties of the sludges resulting from operations utilizing the particular pulps.

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