INSTITUTE OF
PAPER CHEMISTRY
Appleton · Wisconsin

HYDROUS SLUDGES.
A PRELIMINARY CHARACTERIZATION

Project 2962

Report One

A Progress Report

to

NATIONAL COUNCIL OF THE PAPER INDUSTRY

FOR AIR AND STREAM IMPROVEMENT, INC.

March 5, 1971

THE INSTITUTE OF PAPER CHEMISTRY

Appleton, Wisconsin

HYDROUS SLUDGES. A PRELIMINARY CHARACTERIZATION

Project 2962

Report One

A Progress Report

to

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

March 5, 1971

TABLE OF CONTENTS

THE INSTITUTE OF PAPER CHEMISTRY

Appleton, Wisconsin

HYDROUS SLUDGES. A PRELIMINARY CHARACTERIZATION

SUMMARY

The effort during this opening period of the program has been directed at a preliminary chemical and mechanical characterization of representative sludges.

The ~~pulps~~ sludges were found to consist of pulp-derived matter to a greater extent than had been anticipated. It was also found that a model system based on groundwood pulp closely approximated the behavior of the sludges.

The chemical analyses supported the hypothesis, put forward in the proposal for this work, concerning the presence of significant amounts of pectic substances.

INTRODUCTION

The effort during this opening period of the program has been directed at characterizing the sludges received from four mills which have been chosen, in consultation with Dr. I. Gellman of the National Council of the Paper Industry for Air and Stream Improvement, Inc., to provide representative samples for our investigation. The sludges received are presumed to be taken from the underflows of primary clarifiers. The mills supplying the sludges are: Southland Paper Mills, Inc., Lufkin, Texas; International Paper Company, Mobile, Alabama; Bowaters Southern Paper Corporation, Calhoun, Tennessee; and Kimberly-Clark Corporation, Coosa Pines, Alabama. The sludges from these mills are labelled Sludges A, B, C, and D, respectively, and this designation will be used in the following discussion.

Sludge A was from the mill identified by Dr. Gellman as experiencing the greatest difficulty in dewatering operations. This sludge, in fact, had the lowest consistency when received, and had undergone very little separation in transit. Samples B, C, and D had been requested from other mills to provide a basis for comparison. Sludge D had the highest consistency when received, and was the most readily separated by sedimentation.

The investigations carried out were in two areas. A series of gravitational and centrifugal sedimentations were carried out to explore the separation of the sludges in potential fields. Simultaneously a broader experimental program was pursued to develop chemical and mechanical characterization of the sludges. The most detailed investigations were carried out on Sludge A. Sludge D was the one most often used as a basis for comparison.

SEDIMENTATION STUDIES

The sedimentation studies were of two types. Initially, sedimentations in the gravitational field carried out in graduated cylinders were emphasized. At a later point, sedimentations carried out in a laboratory centrifuge at speeds up to 2500 r.p.m. were found more informative.

GRAVITATIONAL SEDIMENTATION

The sludges were initially compared in a gravitational sedimentation experiment carried out after dilution of Sludges B, C, and D to the same consistency as that of Sludge A. Differentiation between the sludges was qualitative, indicating that Sludge A was indeed the slowest separating. Additional samples of the sludges were then diluted to a consistency of 0.3% and allowed to settle in the gravitational field. The separation behavior is shown in Fig. 1. It is clear that A is the most 'difficult' sludge and D the 'best behaved.' Dr. Gellman's expectation (1) that Sludge A would be the least easily dewatered by sedimentation was thus confirmed. On the basis of these results, Sludge A was chosen for subsequent investigation and Sludge D chosen as the basis for comparison in the search for key factors.

The next sequence of studies explored the effect of a variety of treatments on the sedimentation behavior of Sludge A. The treatments included washing with both cold and hot water, and a variety of chemical treatments both alkaline and acid. The chemical treatments were usually followed by neutralization and washing. Washing was carried out by dispersion in fresh water, centrifugation, and decantation of the supernatant.

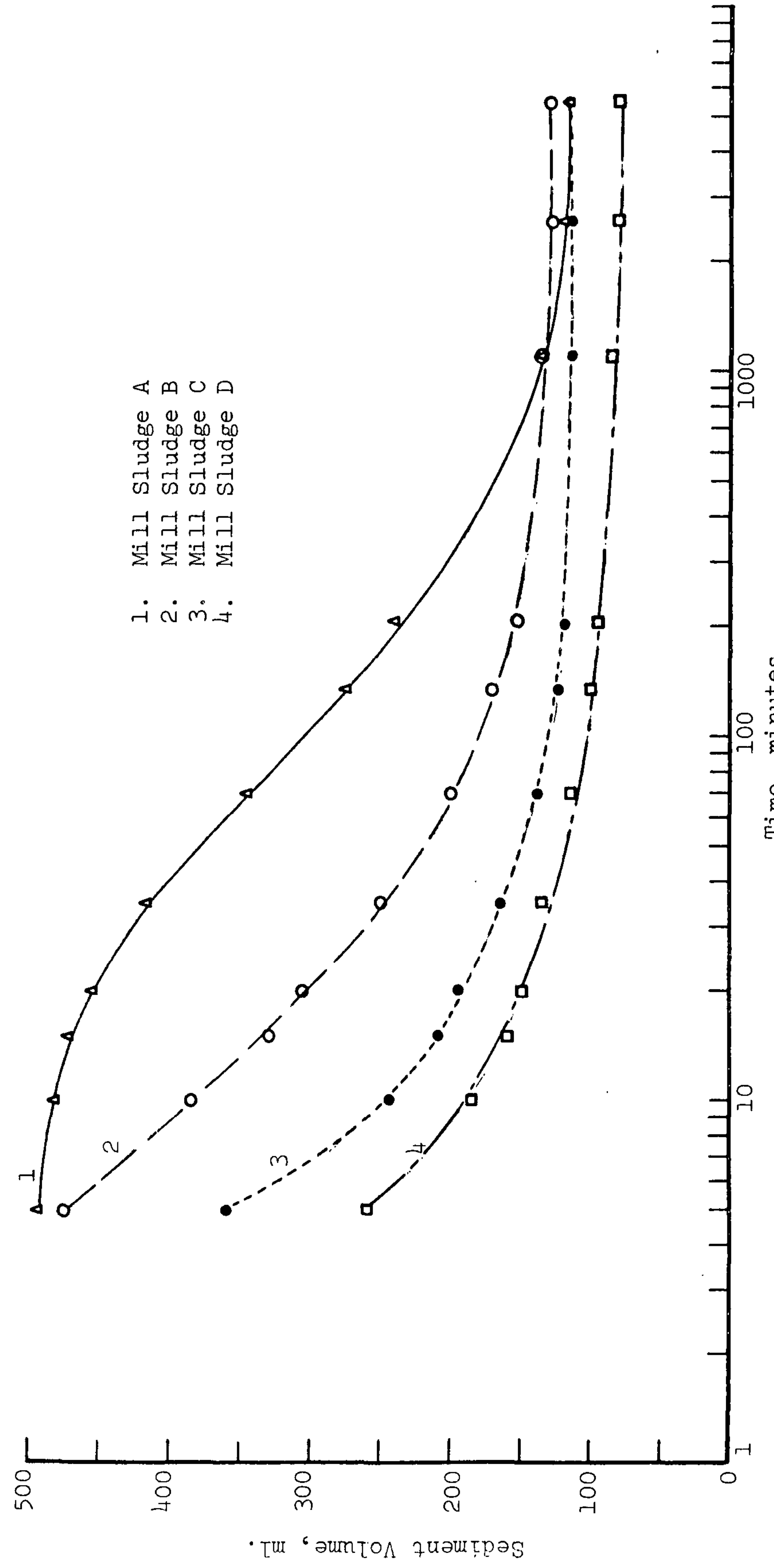

Figure 1. Comparative Settling Tests of Diluted Sludges (500 ml. at 0.3% Consistency)

The treatments are listed in Table I, which also includes indications of the results. The last two columns show the level of the sedimentation interface after approximately one day and one week. The most notable result of this series of experiments is that none of the treatments produced significant changes in the sedimentation behavior. The greatest compaction after one week occurred in the sample treated with 0.5M sulfuric acid for two hours at 123°C. Almost half of the nonvolatile residue in this sample was solubilized.

TABLE I

CHEMICAL TREATMENTS OF SLUDGE A

Treatment	Nonvolatile[a] Residue, % After Treatment	Settling at 40°F. Level of Interface in 100-ml. Cylinder Overnight	1 Week
None	1.05	95	84
4 Cold water washes	0.92	88	71
Hot water wash	0.91	85	69
Wash 1% NaOH	0.93	87	70
Wash 4% NaOH	1.22	85	69
SO_2 saturation + steam bath	--	89	85
3.7% Alum	--	97	94
Heat at 90°C.	--	90	85
2.5N HCl, 30 minutes at 100°C.	--	84	79
SO_2 saturation + 2 hr. at 123°C.	1.07	88	75
0.5M H_2SO_4 + 2 hr. at 123°C.	0.72	68	52

[a] Since the treatments have unpredictable effects on the nonvolatile residue the initial consistency was held constant and the % nonvolatile residue determined after the treatments. Where values are not given the determination was not made.

At this point the results of the microscopic and classification studies (to be described below) became available, and thought was given to the question of a model system. It appeared that a groundwood pulp might provide a suitable model system. A sample of groundwood (Canadian spruce) was available and was, therefore, used in preliminary sedimentation experiments analogous to those outlined in Table I for Sludge A. The treatments and results are outlined in Table II. The most significant observation is that the behavior of the groundwood slurry is very similar to that of Sludge A. Though a similarity of behavior was anticipated, the degree observed was surprising.

TABLE II

CHEMICAL TREATMENTS OF GROUNDWOOD

Treatment	Nonvolatile[a] Residue, % After Treatment	Settling at 40°F. Level of Interface in 100-ml. Cylinder	
		Overnight	1 Week
None	1.42	91	89
Water wash	1.42	95	89
Wash 1% NaOH	1.45	87	83
Heat at 90°C.	1.46	82	77
SO_2 saturation + 2 hr. at 127°C.	0.98	65	63
0.5<u>M</u> H_2SO_4 + 2 hr. at 127°C.	1.03	57	52

[a]Since the treatments have unpredictable effects on the nonvolatile residue the initial consistency was held constant and the % nonvolatile residue determined after the treatments.

CENTRIFUGAL SEDIMENTATION

It had been noted during centrifuge washing operations that the degree of compaction of the sediments attained in the centrifuge is much greater than that observed in gravitational sedimentation. It was thought, therefore, that measurements of sedimentation rates in the centrifuge would provide additional information on the sedimentation behavior of the sludges.

Results of the first trial by this technique are shown in Fig. 2 in which are plotted the sedimentation curves, at 500 r.p.m.*, for Sludges A, B, C, and D, all adjusted to a consistency of 1.4%. The curve for Sludge A, which consists of two linear regions, suggests that two different mechanisms dominated in sequence. The curve for Sludge B is similar to that of A, but the difference between the slopes of the two segments is not as great. Although the data for Sludges C and D could also be interpreted in terms of two linear regions, the differences between the two regions are not sufficiently pronounced to be convincing on their own.

The results of the initial experiments were considered encouraging enough to warrant further development of this technique. Other rotational speeds were tried and it was found that the speeds between 250 and 750 r.p.m. result in a suitable range of sedimentation rates.

*The relative centrifugal force (G) at the tip of the tube is 55 at a rotational speed of 500 r.p.m. It must be kept in mind that, because the centrifuge tube has a finite height, G is not constant throughout. The corresponding values of G at other rotational speeds are 14 and 125 for speeds of 250 and 750 r.p.m., respectively.

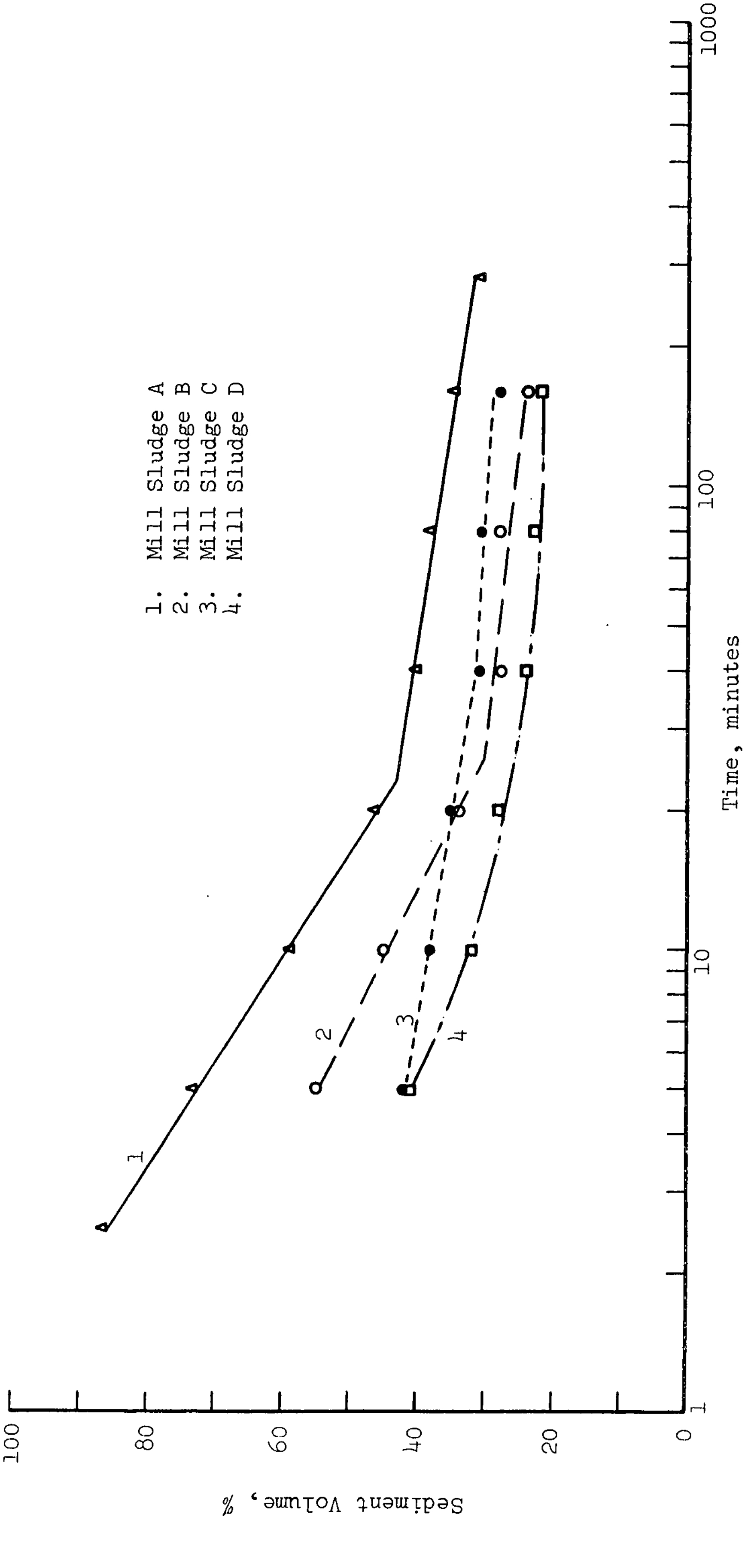

Figure 2. Sediment Rates of 4 Sludges (1.4% Consistency, 500 r.p.m.)

The next series of experiments were a comparison of Sludge A and the groundwood pulp at 250, 500, and 750 r.p.m. The results are shown in Fig. 3. Two features are revealed in these sedimentation curves. The similarity between the behavior of Sludge A and the groundwood pulp noted in the gravitational sedimentation is observed again here. Thus, at any one rotational speed, the sedimentation curves of the sludge and the pulp are quite close. The second notable feature is that the separation of the sedimentation curves into two regions seems to depend on the rotational speed. The pattern of variation for the groundwood pulp is more consistent than that for Sludge A.

It seems clear from the results obtained so far that the centrifuge sedimentations are more sensitive to variations in the nature of the sludges than gravitational sedimentations. The linearity of the sedimentation curves on semi-logarithmic coordinates suggests that the controlling mechanism may lend itself to analytical description. Further exploration of centrifugal sedimentation is indicated.

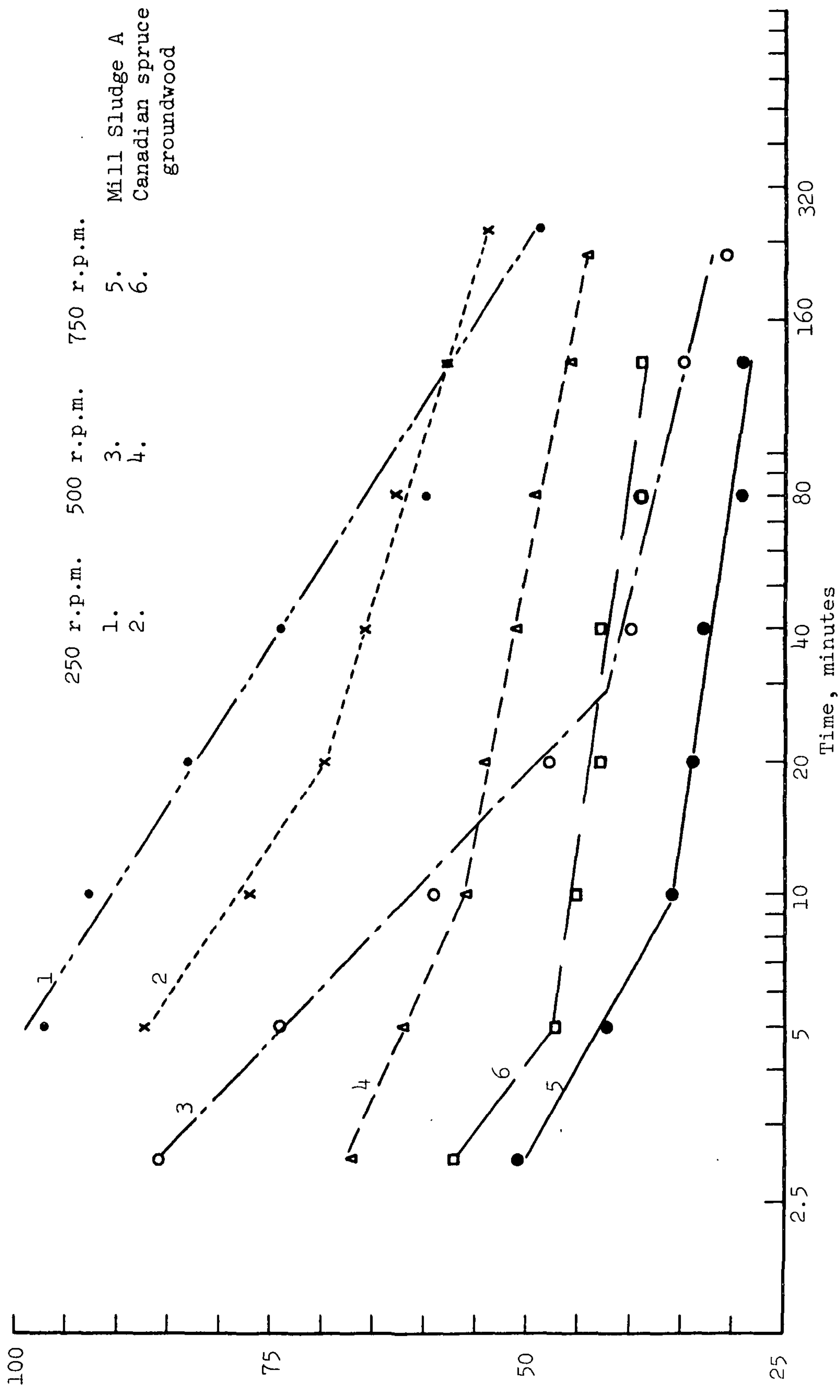

Figure 3. Centrifugal Sedimentation of Sludge "A" and Groundwood

CHARACTERIZATION

The characterization of the sludges involved a number of mechanical and chemical methods. Microscopic examination provided qualitative information on the solids content, particularly pulp-derived components. Classification on the Bauer-McNett fiber classifier gave indications of the particle size distributions. Filtration-resistance measurements also gave evidence, though of an indirect nature, concerning the mechanical character of the sludges. The chemical analyses established the major components of the sludges and provided some insight into the factors which determine their behavior. Some rheological measurements were made as well, but the results have not been conclusive.

MICROSCOPIC EXAMINATION

Microscopic examination of the sludges revealed that, in all cases, at least 90% of the solids are wood pulp fibers and fines. In both Samples A and D, pulp-derived solids are in fact in excess of 95% of the total solids. The groundwood content of three of the sludges is quite high, ranging from 71% in Sludge D to 95% in Sludge A. The fourth sludge, B, has a groundwood content of only 14%.

Distinguishing features of Sludge A are that it has the highest groundwood content and that it is the only sludge in which the pulp-derived components are entirely of southern yellow pine. Sludges C and D are mostly of southern yellow pine, but both contain small quantities of hardwoods. Sludge B has a hardwood content of 39%. More detailed descriptions are given in the report from the Fiber Microscopy Laboratory, attached as Appendix I.

CLASSIFICATION

Classification using a Bauer-McNett fiber classifier was undertaken in search of some relationship between sedimentation behavior and particle-size distribution. Slurries from each sludge were put through the classifier twice, once using 14-, 20-, 35-, and 60-mesh screens, and once using 60-, 100-, 150-, and 200-mesh screens. A comparison of the results for Sludges A and D is shown in Fig. 4. The most striking feature is that Sludge D, the 'better behaved' sludge, has the larger fraction passing through the 200-mesh screen. Indeed, it is the largest fraction for any of the sludges. Considering all four sludges, the fraction passing through 200-mesh screens is approximately twice the fraction expected for a typical groundwood.

The results of the classification experiments are tabulated in the report from the Pulp Laboratory, attached as Appendix II.

FILTRATION

Filtration experiments were of two types, both preliminary in nature. In the first series it was established that Sludge A can be clarified by repeated passage through Whatman No. 1 filter paper. A number of other filtrations were carried out using finer grades of Whatman filter paper as well as Millipore filters. Although variations in rates were observed, and some were very slow, the sludge did not plug the pores and prevent further filtration.

The second series of studies consisted of constant rate filtration studies carried out in the Engineering Laboratory, also on Sludge A. The specific surface and the specific volume were evaluated. Similar studies on other related systems

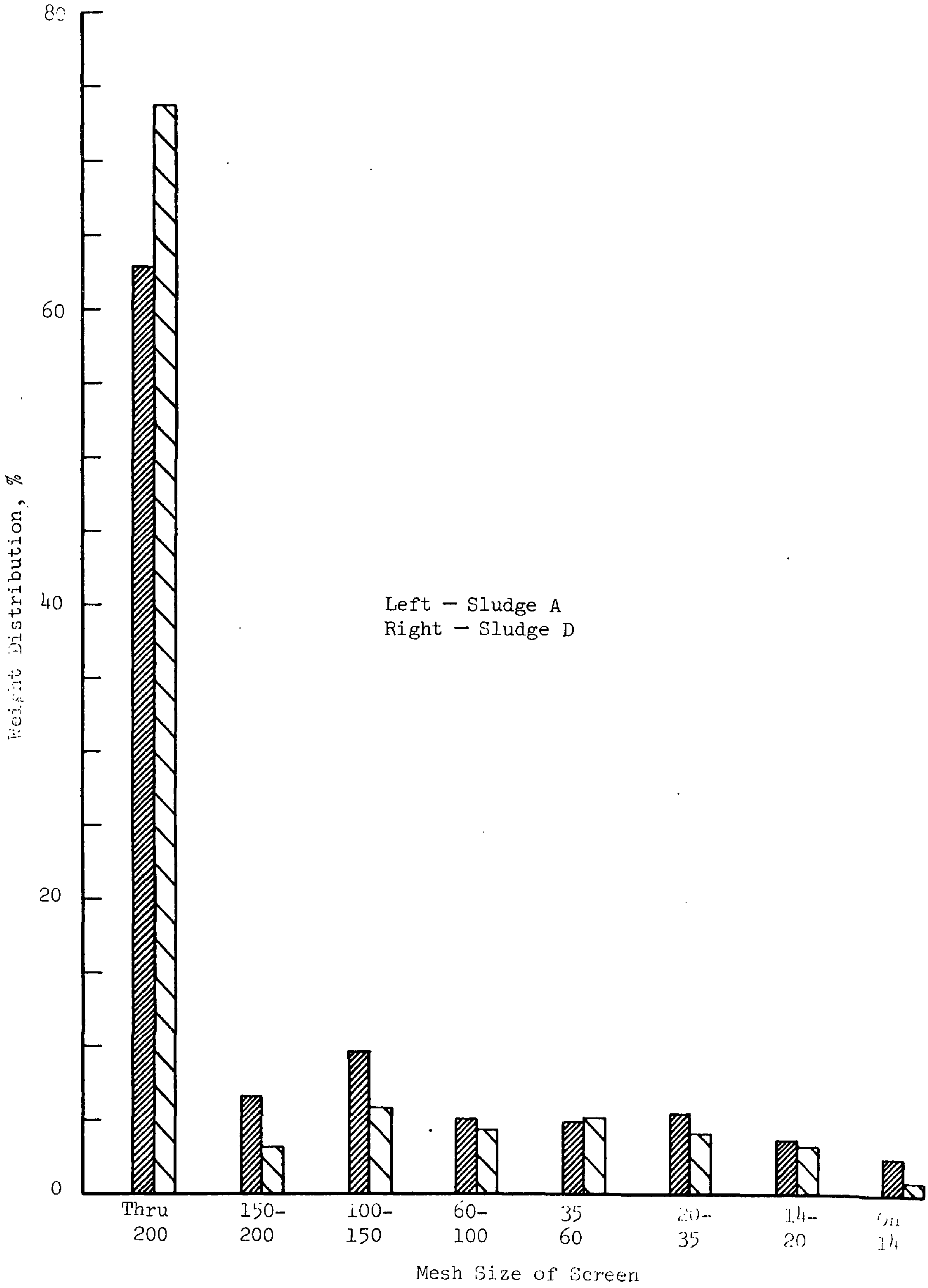

Figure 4. Bauer-McNett Classification of Sludges "A" and "D"

may be necessary to provide a basis for comparison. This approach needs further exploration.

CHEMICAL ANALYSES

The chemical analyses of the sludges were of two types. Initially, a sugar analysis was carried out on each of the sludges. Subsequently, more comprehensive analyses were carried out on Sludges A and D.

Results of the sugar analyses are listed in Table III. Of particular interest are the relatively high values of galacturonic anhydride, indicating that pectic substances do in fact survive in large enough quantities to be significant factors in the hydration of the sludges. When taken relative to the total carbohydrate content of each sample, the amount of galacturonic anhydride observed for Sludges B, C, and D are approximately what one would observe for a mature wood. The relative value for Sludge A is approximately 20% higher than the value expected for a mature wood.

The sugar distributions are generally consistent with the results of the microscopic examinations, if the latter are translated with the aid of data on wood species composition (2). Comparison of the mannan-to-xylan ratios reveals a relatively low value for Sludge B, reflecting its higher hardwood content. The distributions for Sludges A, C, and D are consistent with a very high southern pine fraction.

The analyses on Sludges A and D were extended to include lignin, nitrogen, alcohol-benzene extractables, and ash content. In addition, the analyses were repeated for the fraction of each of the two sludges which passed through 200-mesh screens. The results are compared in Table IV.

TABLE III

SUGAR ANALYSES

	Sludge A		Sludge B		Sludge C		Sludge D	
	Solids, %	Carbohydrates, %	Solids, %	Carbohydrates, %	Solids, %	Carbohydrates, %	Solids, %	Carbohydrates, %
Rhamnan	0.09	0.236	<0.05	<0.1	0.1	0.187	0.05	0.122
Araban	0.8	2.1	0.7	1.4	1.2	2.24	0.7	1.71
Xylan	3.9	10.23	6.2	12.38	6.3	11.8	4.4	10.78
Mannan	6.0	15.78	4.4	8.78	8.9	16.7	5.8	14.2
Galactan	2.2	5.78	1.3	2.59	2.9	5.42	2.2	5.38
Glucan	24.4	64	36.8	73.4	33.3	62.3	27.1	66.3
Galacturonic anhydride[a]	0.72	1.82	0.75	1.5	0.80	1.5	0.62	1.52

[a]Pectin contained about 80% galacturonic anhydride.

TABLE IV

COMPARISON OF SLUDGES A AND D

	A		D	
	Sludge, %	Fines, %	Sludge, %	Fines, %
Galacturonic anhydride	0.72	--	0.62	--
Rhamnan	0.09	0.1	0.05	--
Araban	0.8	0.9	0.7	0.8
Xylan	3.9	4.4	4.4	4.4
Mannan	6.0	5.5	5.8	5.1
Galactan	2.2	2.5	2.2	2.1
Glucan	24.4	25.3	27.1	25.0
Lignin[a]	24.7	--	23.0	--
Nitrogen	0.71	0.9	0.11	0.08
Alcohol-benzene extractives	13.0	10.7	10.7	7.1
Ash	13.8	13.8	20.9	27.7

[a]Due to uncertainties in initial determinations of lignin these were repeated for the sludges. The fines samples were not sufficient for a second determination. The comparison of sludges and fines noted in the body of the report is based on the relative values of the initial determinations.

The fines of both sludges are quite similar in composition to the sludges themselves, except that the fines are lower in extractables in both cases. There are indications that the lignin contents of the fines are also lower than those of the sludges. The sugar analyses of Sludges A and D are very similar to each other. The outstanding differences between the two sludges are that the ash content of D is almost twice that of A, and that the nitrogen content of A is 8 to 10 times that of D. The relatively high nitrogen content of A may reflect the presence of biological sludges recirculated to the primary clarifier in small quantities in Mill A. The presence of small amounts of biological growth had been noted during the microscopic examination.

OTHER EXPLORATORY WORK

As indicated earlier, some rheological measurements were made. The difficulty encountered was that the heterogeneity of the sludges led to segregation in the immediate neighborhood of the viscometer rotor. As a consequence, the viscosity reading did not reach a steady state. If it had, it would have been more indicative of the viscosity of the interstitial liquid than that of the sludge as a whole. It was thought that the viscosity of the liquid should be investigated separately to establish whether soluble polymeric matter contributes to its properties. A sample of the supernatant liquid from a centrifugation was chosen for viscosity studies. To eliminate the influence of any dissolved low molecular weight materials, the sample was dialyzed for a number of days. In the course of the dialysis some of the dissolved material precipitated. The dispersion was filtered and the filtrate concentrated. An additional amount of material precipitated. Thus, a substance which is not very soluble in water was precipitated by both dialysis and concentration. Since the sample of sludge had been in our possession for some months at this time, it was decided that further pursuit of this matter should be delayed until we receive a fresh sample of the sludge. We would then be in a position to explore the matter of dissolved solids with more confidence.

Another area which has been explored in a preliminary way is the application of NMR spectroscopy to measurement of the accessibility of pulp-derived matter to hydration. Here the trials have been confined to the groundwood pulp chosen as a model system. If this technique is successful it will be applied in future work.

CONCLUSIONS

The most important conclusion at this stage in the program is that the major constituent of each sludge is pulp-derived matter closely related to the nature of the pulps in use at the source mill. The fraction of the solids content of the sludges which is of this type is much larger than had been anticipated.

The second major conclusion is that the behavior of the sludges is quite closely approximated by that of a groundwood pulp. The sedimentation studies, both with and without chemical treatment, and both in the gravitational field and in the centrifuge, support this conclusion. The results of the chemical analyses are also consistent with this conclusion.

Among the results of the chemical analyses the most notable is the finding that significant amounts of pectic matter (tabulated as galacturonic anhydride) are in fact retained in the pulp-derived matter. This is consistent with the basic postulate put forth in the proposal for this work, concerning the presence of swellable polysaccharides in solid residues. The relatively high content of galacturonic anhydride is consistent with the postulated role of the pectic substance in stabilizing the hydrated state of the sludges. Also consistent with this postulation is the observation that the relative amount of pectic substances is highest in Sludge A. Other aspects of the results of the chemical analyses reflect the constitution of the pulp-derived components as determined from microscopic examination of the sludges.

Primary among the results derived from the sedimentation studies is the observation that centrifugal sedimentation behavior is a sensitive indicator of differences between the sludges which are related to their dewatering behavior. The linearity of the semilogarithmic graphing of the sedimentation curves implies a regularity in the mechanisms which determine the rates.

FUTURE WORK

The directions for future work are derived from the primary conclusions outlined above. Thus, it appears that the most logical choice for a first model system would be one consisting of southern pine groundwood. Such a system would certainly closely approximate the chemical constitution of the sludges. To obtain a close match to the mechanical condition of the sludges, it would probably be necessary that the groundwood pulp be classified and blended to correspond to the classification of the sludges. Such a matching of the mechanical state of the sludges is not considered necessary at this stage, however.

The present projection is that a sample of groundwood pulp will be obtain from Mill A to be used as primary material. This pulp will be classified by the same procedure indicated above for the sludges. The centrifugal sedimentation behavior of the different fractions will then be investigated. In addition, chemical analyses will be carried out on selected fractions to find out whether the pattern of mechanical fragmentation accomplished in the grinding process is accompanied by a chemical differentiation. Particular emphasis will be placed on the content of pectic substances. The objective of both components of the projecte program is to find out whether a particular size fraction of the groundwood pulp determines the sedimentation behavior of the whole, or whether the latter is essentially a composite of the pattern of behavior of all its fractions.

Though the interstitial liquids received little attention during the initial phase outlined in this report, the effort in this area will be expanded upon receipt of fresh samples of sludge. The phenomena observed during dialysis and concentration will be investigated further.

Modifications of the NMR technique are under way. If these are successful they will be applied to studies of the hydration of the different fractions of the groundwood pulp used in the sedimentation studies projected above.

LITERATURE CITED

1. Dr. I. Gellman, National Council for Air and Stream Improvement, Private communication.

2. Browning, B. L., The chemistry of wood. Chap. 3. N.Y., J. Wiley & Sons, 1963.

THE INSTITUTE OF PAPER CHEMISTRY

S. C. Nagel

S. C. Nagel, Research Fellow

Rajai H. Atalla

Rajai H. Atalla, Research Associate

John W. Swanson

John W. Swanson, Director
Division of Natural
Materials & Systems

APPENDIX I

MICROSCOPIC EXAMINATION OF SLUDGE SAMPLES

The results of a microscopic examination of the four submitted sludge samples are as follows:

SLUDGE B

Fiber Analysis

Pulp	Fiber Count	Weight Factor	Refined Count	Weighted Percentages
S. W. unbl. kraft	135	1.5	202	43
S. W. bl. kraft	44	1.5	66	14
H. W. kraft	195	0.7	136	39
Groundwood	50	1.3	65	14

Species Identification and Comments

S. W. kraft — species of southern yellow pine — 100%
H. W. kraft — species of gum, oak, yellow poplar, beech, and evergreen magnolia

The sample contains a large number of fines which are principally hardwood parenchyma cells and groundwood flour, mucus, and fibrils. The groundwood fines gave a strong test for lignin with phloroglucinol. These fines are not included in a quantitative fiber analysis of a normal hardwood or groundwood pulp. The groundwood fines in this particular sample could account for 50% by weight of the total solids content of the sample. The amount of the fines fraction could, of course, be determined by screen classification.

It is estimated that 90+% of the solids content of the sample is made up of wood pulp fibers and fines.

Some starch granules are present in this sample.

SLUDGE A

Fiber Analysis

Pulp	Fiber Count	Weight Factor	Refined Count	Weighted Percentages
S. W. bl. kraft	9	1.5	14	5
Groundwood	190	1.3	273	95

Species Identification and Comments

S. W. kraft — species of southern yellow pine — 100%
Groundwood — species of southern yellow pine — 100%

Same comments as made for the groundwood furnish of Sludge B. The solids content of the sample is made up principally (95+%) of groundwood and groundwood fines (i.e., wood flour, mucus, dust, and fibrils).

A small amount of biological growth was observed in this sample.

SLUDGE C

Fiber Analysis

Pulp	Fiber Count	Weight Factor	Refined Count	Weighted Percentages
S. W. bl. kraft	30	1.5	45	10
H. W. unbl. kraft	16	0.6	10	2
Groundwood and screenings	260	1.5	390	88

Species Identification and Comments

S. W. kraft — species of southern yellow pine
H. W. kraft — species of oak and yellow poplar
Groundwood — species of southern yellow pine

The solids content of the sludge sample is 95-100% wood pulp.

SLUDGE D

Fiber Analysis

Pulp	Fiber Count	Weight Factor	Refined Count	Weighted Percentages
S. W. unbl. kraft	60	1.5	90	22
H. W. kraft	50	0.6	30	7
Groundwood	230	1.3	299	71

Species Identification and Comments

S. W. kraft — species of southern yellow pine
H. W. kraft — species of oak and yellow poplar
Groundwood — principally species of pine with a small percentage of hardwood species

The solids content of the sludge sample is also probably 95+% wood pulp.

APPENDIX II

FIBER CLASSIFICATION

INTRODUCTION

Four pulp slurries were submitted by Mr. Nagel for fiber classification. Aside from an understanding that the material was essentially composed of paper mill "sludges," nothing was known of the fiber length distribution. Efforts were made to develop the maximum amount of information, using a Bauer-McNett fiber classifier as a test instrument.

EXPERIMENTAL

Each sample was given a single pass through the Bauer-McNett fiber classifier housed in the Chemical Engineering Laboratory. This machine is normally fitted with 14-, 20-, 35-, and 60-mesh screens, so these were employed for the initial examination. The fraction passing the 60-mesh screen was caught and a sample was filtered for inspection. The fractions retained on each screen were washed into a Buchner funnel containing a tared filter paper and the captured material was oven dried. The filter papers and their contents were delivered to Mr. Nagel for his inspection. The fractionation data are given in Table V.

TABLE V

INITIAL FIBER CLASSIFICATION TESTS

Sample	C	B	D	A
On 14 mesh, %	4.7	17.3	0.8	2.4
On 20 mesh, %	7.8	6.3	3.2	3.6
On 35 mesh, %	9.6	5.2	4.0	5.3
On 60 mesh, %	9.5	5.3	5.1	4.8
Through 60 mesh, % (by difference)	68.4	65.9	86.9	83.9

The screens in the classifier were replaced in such a manner that the finest in the series described in Table VI was installed in the first tank. The remaining tanks were fitted with 100-, 150-, and 200-mesh screens in that order. The fraction passing the 200-mesh screens was caught in a large container and several gallons were set aside for later concentration of the solids. The material drained from the tanks after the test (performed as described in T 233 su-64) was dried on the muslin used to collect it. The accumulations were later scraped from the cloth and presented to Mr. Nagel for his inspection.

TABLE VI

BAUER-McNETT CLASSIFICATION TESTS — NO. 2

Sample	C	B	D	A
On 60 mesh, %	32.4	33.9	14.4	21.3
On 100 mesh, %	6.3	4.0	4.2	5.0
On 150 mesh, %	6.0	4.2	5.8	9.6
Through 200 mesh, % (by difference)	52.5	55.7	72.4	57.6

A part of the concentrated fines (through a 200-mesh screen) were saved in slurry form for possible microscopic inspection and about 10 liters were passed through filter paper and the solids were dried on a hot plate. The filter paper and the solids were given to Mr. Nagel.