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MINES BRANCH INVESTIGATION REPORT IR 73-71

SEPARATION OF WOOD FIBRE-CLAY WASTE FOR REUTILIZATION IN A PAPER PLANT

by

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MINERAL PROCESSING DIVISION

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A. Winer* and S. R. Rao**

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SUMMARY OF RESULTS

A wood fibre-clay waste, from a fine-paper plant was separated into its components. The best separation was made by means of a differential flocculation technique, at pH 8, using a cationic flocculant. Washing the recovered wood fibre removed more of the adhering clay. The best products obtained were:

(a) 81 per cent wood fibre, 19 per cent adhering clay, in the flocculated portion, and

(b) 78 per cent clay, 22 per cent wood fibre, in the unflocculated portion.

There was some loss of wood fibre in the differential flocculation process, which increased during washing of the clay from the wood fibre. This loss could be minimized by careful control of the various stages of the process. A proposed schematic flowsheet for the differential flocculation process is included.

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INTRODUCTION

A preliminary cost calculation showed that substantial savings could accrue to a fine paper plant if the clay-wood waste from the process could be separated and recycled.[1] There are a number of these plants in Canada and because of interest by industry and because the Mines Branch is interested in the utilization of solid mineral wastes a project was initiated to determine whether separation of wood fibre from clay was feasible.

EXPERIMENTAL WORK

Composition of Waste

A sample of waste material, a mixture of wood fibre and clay, was obtained from an Ontario paper plant. Microscopic examination showed the clay to be held in a fibrous network. Examination of the sludge by scanning electron microscope showed not only the fibrous network but also the close adherence of the clay to the surface of the wood fibre. Also visible was the small particle size of the clay, assumed to be kaolin, and the relatively large size of the wood fibre. Figure 1 shows a sample of the waste which had been freeze-dried for better dispersion and Figure 2 a sample which had been oven-dried at 250°C.

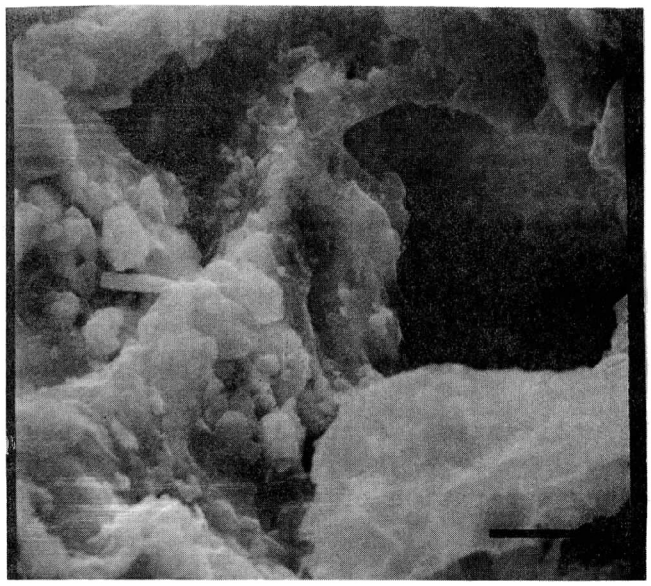
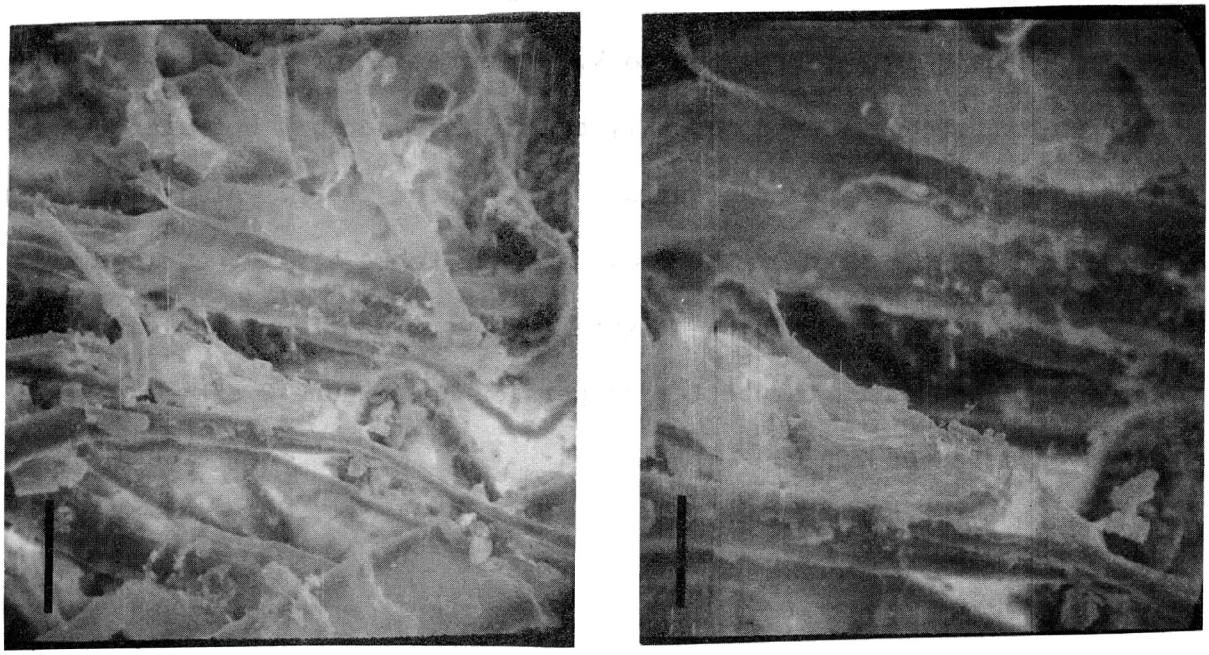


Figure 1. Electron scanning photomicrographs of "as received" wood fibre-clay waste material, freeze-dried. x 2000.



(a)
x 300

(b)
x 600

Figure 2. Electron scanning photomicrographs of "as received" wood fibre-clay material dried at 250°C.

Preliminary Studies

Preliminary experimentation[2] included the following:

(1) effect of pH; effect of dispersion,
(2) effect of comminution; release of clay from the fibre using ultrasonics, Waring blender, Abbé mill,
(3) effect of additives, such as Tide, Aerosol OT, Polyhall M402,
(4) effect of separation by settling, centrifuging screening,
(5) effect of flotation.

The best combination of methods for separation of the wood fibre-clay mixture was: Abbé mill grinding, screening-off of the fibre, then settling the fibre and decanting the clay suspension.

Additional Studies

Following an analysis of the results of the preliminary studies it was decided to concentrate further experiments in the following areas.

(1) Tabling
(2) Variable Speed Centrifugation
(3) Differential Flocculation.

For these studies it was desirable to more accurately determine the pH at which dispersion of the waste was best. This was done using an automated potentiometric titrator.

Electrokinetic Measurements

A potentiometric titration technique, developed by Sirois, Alexander, Page and Winer[3] was used in conducting this study. The apparent isoelectric point (IEP) of the slurry was determined from the titration curves. The curve based on these results (Figure 3) showed that the IEP of the mixture was about pH 10. The strongly basic portion of the titration curve is not shown.

At pH 12 the material dispersed well but the possibilities existed (a) that chemical interaction could occur at this high alkalinity, and that (b) partial hydrolysis of the flocculant would occur. Lower alkalinity, i.e.,

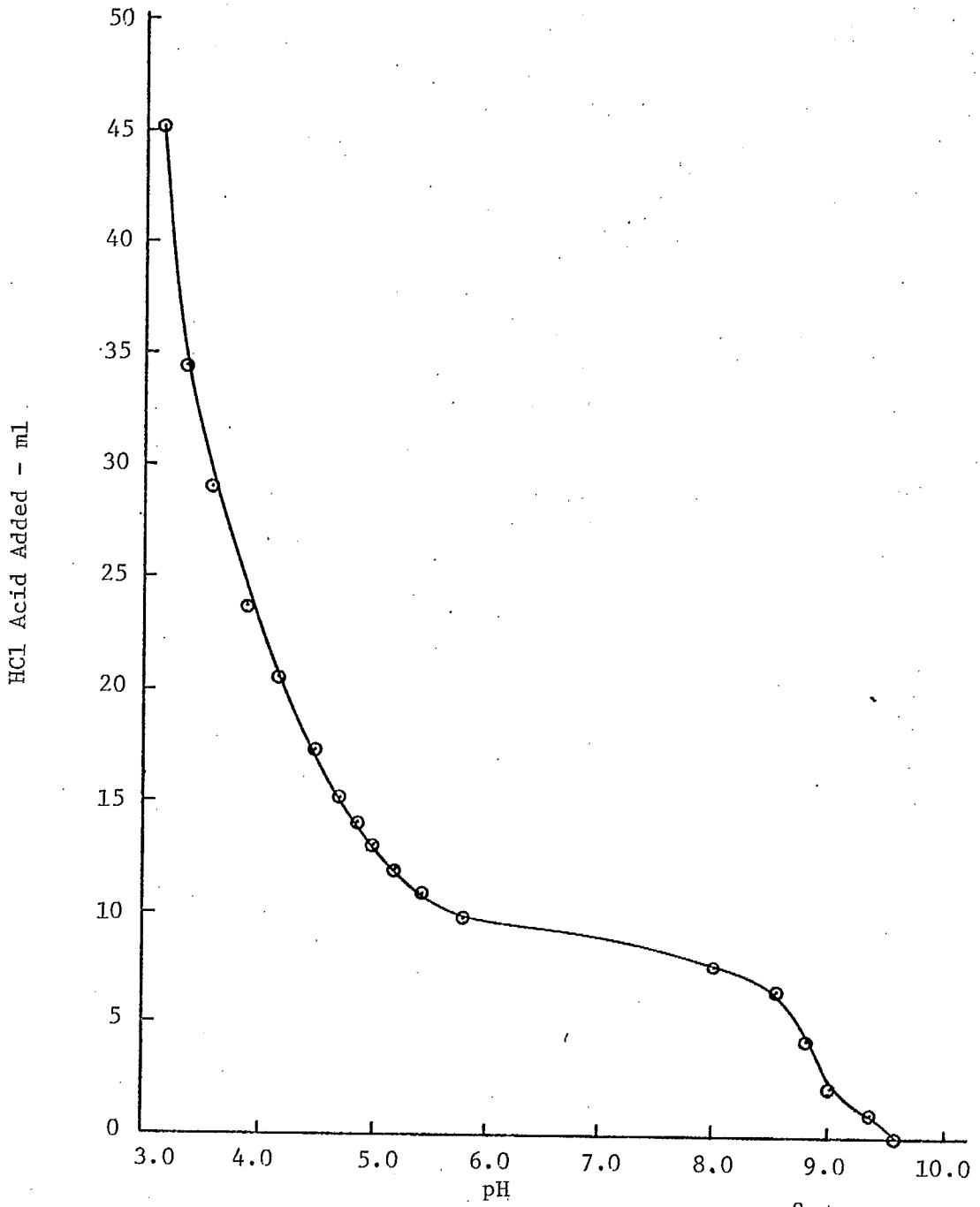


Figure 3. Effect of Cumulative Additions of 10^{-2}N HCl. on pH of wood fibre-clay slurry.

a pH of 8, was usually used because it was sufficiently distant from the IEP and still allowed good dispersion of the slurry.

Tabling

Preliminary experiments to separate the fibre-clay mixture were made using a Wilfley table. The waste mixture was first conditioned in a Denver flotation machine. Flow rates, table inclination and pH were varied but only small amounts of clay were separated from the fibre. This study was therefore terminated.

Variable Centrifugation

Nine slurries, at pH 12, consisting of different weights of the fibre-clay waste were prepared. These were separately centrifuged at three speeds, in the range 540 to 3180 rpm for periods of 1, 5, and 15 minutes.

Two distinct phases were noted after centrifugation in all the tests, with the best separation occurring at the lower speeds. However, because of the mechanical entrapment of the clay by the fibre this method was not entirely satisfactory and this part of the study was terminated.

Other Methods of Dispersion

Intensive mechanical and ultrasonic methods were used to aid in the dispersion of the dilute suspension. Best results were obtained by the addition of NaOH to the suspension to pH 8, which was then dispersed, first by using an ultrasonic probe for 15 min and then by shearing for 2 min in a Waring Blender.

The results of these tests are summarized in Table 1.

TABLE 1

Summary of Results

Dispersion and Sedimentation of Wood Fibre-Clay Waste at pH 8 and 12

Test No.	Sample (0.25 per cent solids)							
	1	2	3	4	5	6	7	8
pH of suspension	8.1	12.0	8.1	12.0	8.0	12.0	8.2	12.1
Ultrasonic probe, min	0	0	15	15	0	0	15	15
Waring blender, min	2	2	2	2	2	2	2	2
Sedimentation, min	60	60	60	60	60	60	60	60
Unsettled Fraction								
Per cent clay	63.2	65.9	74.8	62.8	71.6	69.1	70.6	63.3
Per cent fibre	36.8	34.1	25.2	37.3	28.5	30.9	29.4	36.7
Settled Fraction								
Per cent clay	36.4	37.7	34.4	38.3	35.7	39.5	36.1	39.2
Per cent fibre	63.6	62.3	65.6	61.7	64.3	60.5	63.9	60.8

These results show that Test No. 3 gave the best separation of the constituents. The ultrasonic probe did not appear to play a significant role because Test No. 5, without ultrasonic aid, showed almost as good a product separation. It appears that pH plays the predominant role in this case.

These methods of dispersion were also considered not satisfactory and therefore differential flocculation studies were initiated.

DIFFERENTIAL FLOCCULATION

Flocculant Considerations

Flocculants have been employed for a number of separation processes in recent years. Their differential action is based on preferential adsorption of the flocculant on one of the constituents. Adsorption is generally attributed to the surface charges on the suspended solid which is opposite to that on the flocculant ion. Negatively charged particles would, therefore, require cationic flocculants for successful flocculation. A number of additional factors, which are not yet fully understood, may complicate flocculant action. These include the fineness of the solid materials, the degree of mechanical entrapment, and the degree of dispersion of the two or more solids present in the mixture. The choice of flocculant is, therefore, empirical to an extent, although it is often possible to make a reasonable selection if, e.g., the surface chemistry and other physical chemical characteristics of the mixture are known[4]. Where this information is lacking, an electrokinetic study is often helpful.

Electrokinetic Considerations

The apparent isolectricpoint (IEP) of a two-component mixture has been previously discussed by Rao and Sirois[5]. Although their work was based on a mixture of metallic and oxide constituents, the writers believed that the theory could be extended to other two-component, non-metallic mixtures. The theory would imply that at pH 10 the net surface electrical charge of the clay-fibre mixture is zero, which would result in their remixing.

Preliminary Tests

Based on the above considerations, a few laboratory tests were conducted to determine the pH at which the clay-fibre lumps broke down and dispersed. Tests were then performed using cationic and anionic flocculants. The subsequent separation tests were conducted using the flocculant which had the best visually-indicated effect.

An aqueous clay-fibre slurry containing two per cent solids was used in the initial tests to determine the degree of dispersion at different pH values. Lumps of the solid material broke down progressively with vigorous stirring at all pH values. The best dispersion, however, occurred at pH 12 with the solids present in very small lumps.

Although pH 12 and 8 were both considered, because of the reasons previously discussed in the section "Electrokinetic Measurements", it was decided to conduct the experiments at pH 8.

Flocculation Tests

Clay (kaolin) and the wood fibre are both surface-negative and it therefore was appropriate to use a cationic flocculant and determine its effect. The cationic reagent Hercofloc 813* was selected. This is a polyacrylamide of low molecular weight.

A stock solution of 100 ppm was prepared, i.e., 0.1 g/1000 ml water. Five grams of freeze-dried material were suspended in 400 ml of water and the pH adjusted to pH 8, using KOH. One hundred ml of the suspension was transferred into a separate beaker, 5 ml of the flocculant solution was then added during stirring. Final flocculant concentration in the beaker was 5 ppm. Flocculation was rapid.

*Hercules Inc. Wilmington, supplied by Harrison and Crossfield, Toronto, Ontario.

The supernatant unflocculated portion was decanted and filtered to remove solids. The flocculated portion was washed with distilled water and separated. Both solids were freeze-dried and examined by scanning electron microscope. The photomicrographs showed that the unflocculated portion was essentially clay with almost no fibre. The flocculated portion consisted of fibre, but close examination of the photomicrographs could not conclusively prove that clay was not present on the surface of the fibre. To determine this point and to explore the practical feasibility of separation of the two solids by differential flocculation, larger samples were used in the subsequent tests.

Large Scale Tests

Flocculation tests with greater amounts of sample were made as follows:

Test 1. Three hundred grams of the as-received waste material were suspended in water in a 24-litre container, adjusted to pH 8, and stirred until the solids were well dispersed. Flocculant stock solution (1200 ml) was added and the stirring was continued for 30 min. Flocculation occurred rapidly and the suspension was allowed to settle for 10 minutes. The unflocculated portion was then decanted and evaporated to recover the solids. The flocculated portion was freeze-dried for ease of photomicrographing. The solids content from both flocculated and unflocculated portions were analyzed for the amount of constituents,i.e., clay and wood fibre, as follows:

After drying at 110^{o}C the material was weighed accurately. The dried material was then fired to constant weight in a crucible for 2 hours at 1000^{o}C. After desication, the fired dehydroxylated material was reweighed and the clay content determined. The wood fibre was determined by difference

$$\text{i.e., per cent clay} = \frac{100^*}{86} \times \frac{\text{wt of fired material}}{\text{wt of dried sample}} \times 100$$

per cent wood fibre = 100 - per cent clay

* ratio of natural/ignited clay.

Test 2. In another test, 300 g of the original material was suspended in 24 litre of water at pH 8, the suspension stirred until well dispersed and allowed to settle. Settling was relatively rapid, a matter of minutes. The supernatant (unsettled) portion was decanted. More water was added to the settled portion, which was then stirred for 30 min, and allowed to settle. The unsettled portion was decanted and added to the supernatant portion. More water was again added (24 litre) to the settled portion, stirred until the material was suspended, and then 300 ml of the flocculant stock solution added. After stirring for 15 min, the supernatant liquid was again decanted and added to the previous decanted portion. The clay in the supernatant portions was coagulated by adding 10 g of alum ($Al_2(SO_4)_3 18\ H_2O$) per 20 litre of suspension. The clay was then recovered by decantation followed by filtration.

Each fraction, filtered and flocculated, was analyzed as before to determine clay and wood contents.

Test 3. This test was similar to Test No. 2 except that no flocculant was used.

Test 4. This test was similar to Test No. 2, but the concentration of flocculant used was less.

Test 5. This test was similar to Test No. 2, but the concentration of flocculant was less.

In two cases, washing of the flocculated portion was performed three times, using clean water, to determine whether the clay could be washed from the fibre.

RESULTS AND DISCUSSION

Figures 4 and 5 are scanning electron photomicrographs of the separated materials.

Figure 4. Flocculated portion of separated material, 400X

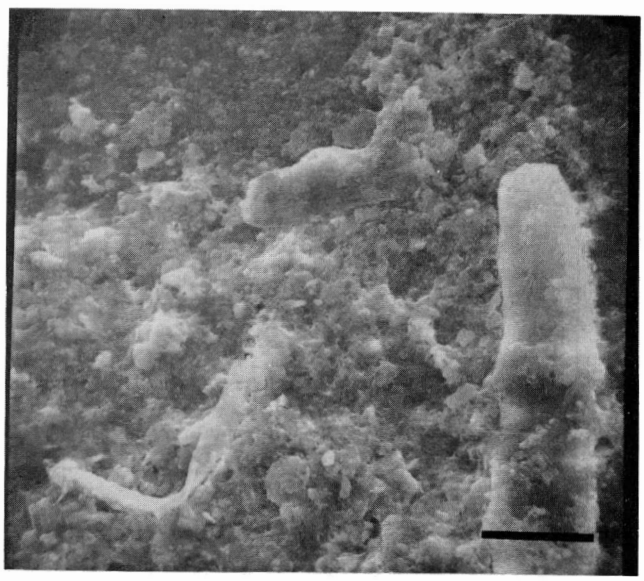


Figure 5. Unflocculated portion of separated material, 500X

Tables 2 and 3 summarize the results for the differential flocculation experiments.

TABLE 2

Results of Differential Flocculation Tests

Original Sample (Dry 110°C)
Wood Fibre = 60.7 per cent by weight
Clay = 39.3 " " " "

Stock Reagent Added		Sample Wt (dry)	Distribution		Floc + Unfloc Material (dry)	Flocculated Portion			Unflocculated Portion			Material Losses Dry Wt Basis		
							Wood Fibre	Clay		Wood Fibre	Clay	By Differential Flocculation Total	Distribution	
ml	Wt per cent	g	Wood Fibre 0.607 x wt g	Clay 0.393 x wt g		Floc Portion Wt (dry) g	Wood Fibre Wt (dry) g	Clay Wt (dry) g	Unfloc Portion Wt (dry) g	Wood Fibre Wt (dry) g	Clay Wt (dry) g	g	Wood Fibre g	Clay g
1200	0.12	102.9	62.5	40.4	98.9	96.5	61.0	35.5	2.4	0.78	1.62	4.00	0.64	3.36
300	0.029	102.9	62.5	40.4	100.7	73.9	55.5	18.5	27.2	4.90	22.3	2.19	1.90	0.30
0	0	17.2	10.4	6.74	-	9.7	7.83	1.87	Clay discarded		-	-	-	-
150	0.014	102.9	62.5	40.4	100.5	73.5	53.3	20.2	27.0	6.50	20.5	2.40	1.90	0.50
0*	0	17.2	10.4	6.74	16.0	13.4	9.18	4.18	2.66	0.49	2.17	1.13	0.73	0.39
50	0.014	34.3	20.8	13.5	31.9	18.6	14.0	4.65	13.3	4.45	8.88	2.40	2.36	0.04
50*	0.014	34.3	20.8	13.5	30.9	18.8	15.2	3.63	12.1	2.62	9.46	3.44	3.05	0.41

*Three washings performed on the flocculated portions.

TABLE 3

Summary of Results for Differential Flocculation on a Per Cent Basis

Reagent Added ml	Reagent Added Per Cent by Wt. (Dry Basis)	Flocculated Portion		Unflocculated Portion		Material Loss (Dry Basis)		
		Wood Fibre Per Cent	Clay Per Cent	Wood Fibre Per Cent	Clay Per Cent	Total Per Cent	Distribution	
							Wood Fibre Per Cent	Clay Per Cent
1200	0.12	63.2	36.8	32.4	67.6	3.88	0.62	3.26
300	0.029	74.9	25.1	18.0	82.0	2.13	1.75	0.38
0	0	80.8	19.2	Clay portion discarded		-	-	-
150	0.014	72.5	27.5	24.3	75.7	2.33	1.85	0.48
0	0	68.7	31.3	18.3	81.7	16.6	10.8	5.8
50	0.014	75.0	25.0	33.4	66.6	7.00	6.88	0.12
50	0.014	80.7	19.3	21.7	78.3	10.03	8.86	1.17

*Three washings performed on the flocculated portion.

Results indicate that the cationic flocculant tends to preferentially flocculate the wood fibre. With higher concentration of flocculant, however, significant amounts of clay are also flocculated along with the fibre. Although both the clay and wood fibre are negatively charged at their surfaces, the preferential flocculation of wood fibre could be attributed to its lower charge as compared with clay. The zeta potential of kaolin has been given as around -45 mV[6, 7] at pH 8, and that of wood occurs in the range -22 to -32 mV[7], depending upon the source and nature of the wood. Furthermore, the zeta potential of wood drops to -10 mV[7] when it is treated with polyacrylamide. The cationic flocculant, it is assumed, thus performs two functions: (1) by adsorption at the fibre surface, it lowers the surface charge, and (2) it subsequently gives rise to large flocs by a bridging mechanism causing the dispersed particles to cluster. In fact, the lowering of charge appears to facilitate the bridging and formation of flocs. The clay present is not as easily flocculated because of the much larger negative charge present. Neutralization in this case is necessary to promote clustering. This occurs if a larger concentration of flocculant is introduced. Hence, with sufficiently low concentrations of flocculant, wood fibre could be preferentially flocculated. The unflocculated portion would contain a high proportion of concentrated clay.

Tests in which three further washings of the flocculated wood portion were performed (Table 2 and 3) indicate that washing removed part of the clay, increasing the fibre concentration from 75 to 80 per cent.

Losses of material by the differential technique were studied to determine where they occurred. The amounts of the wood fibre and clay constituents in the dried, as-received, sample were compared to the amounts of clay and wood fibre in the flocculated and unflocculated portions (Tables 2 and 3).

This showed that the wood fibre was the major contributor to the losses and that these losses occurred mainly in the flocculated portion, probably during the washing procedure.

This was confirmed by the results of the last two runs shown in Tables 2 and 3. Here, also, the wood fibre (flocculated portion) contributed to the major loss, but the sample that was washed three times showed a much greater loss. The inference is that washing the clay from the wood fibre also removed some of the fine fibres.

Although increased washing apparently results in increased loss of material, the amount of wood fibre in the flocculated portion increases in relation to the clay. The clay in the washings can then be discarded or precipitated. Here, there is an economic trade-off. Careful attention to the stages of flocculation, precipitation, and filtration can very likely decrease material losses.

CONCLUDING REMARKS AND RECOMMENDATIONS

From the considerations above, treatment would begin at the effluent stage, say in a settling tank. The aqueous effluent containing the wood fibre and clay could perhaps be treated on a semi-batch basis because of the rapid settling caused by the cationic reagent used.

The unsettled or unflocculated portion containing the clay would be pumped or siphoned off and the clay precipitated by the addition of a small amount of alum. The water would be removed by filtering or centrifuging then neutralized and reused. The clay (kaolin) could be centrifuged or recycled by other means to the papermaking process without further moisture removal.

The water used for washing the wood fibre would contain clay and this could be removed, if so desired, by further additions of alum followed by centrifugation or filtration. The economics of the process would determine this aspect of the procedure. The wash water with or without the clay could then be returned to the plant water repurification system for reuse in the paper processing.

A flowsheet of the proposed process is shown in Figure 6.

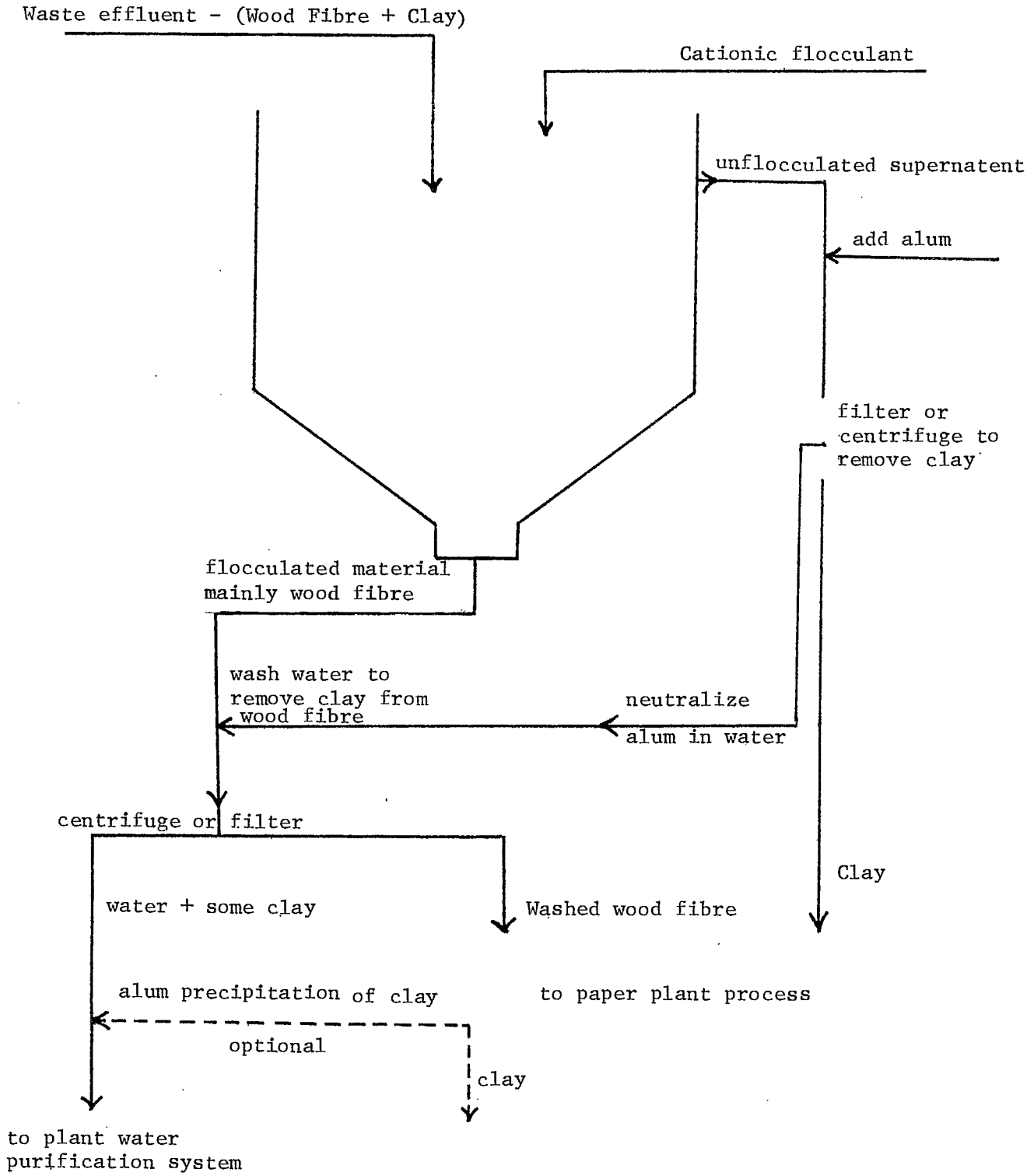


Figure 6. Schematic flowsheet for separation of wood fibre-clay from paper plant waste by differential flocculation.

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