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Western Michigan University

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UTILIZATION OF DEINKING WASTE /

A Senior Thesis

Conducted under the supervision of

Dr. R. H. Diehm, Professor of

Pulp and Paper Technology,

Western Michigan University,

Kalamazoo, Michigan

Submitted June 9, 1959

Richard H. Jones
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LITERATURE SURVEY

Introduction

In research aimed at utilization of sludge obtained from primary sedimentation of deinking mill wastes a literature study was made to determine what has been done toward meeting these ends and what new lines of thought needed investigation.

Our first thought in a literature survey was to find out the nature of the deinking sludge. It was found that the composition of deinking solid varies greatly from mill to mill and is determined by the waste paper used. A commercial laboratory analysis showed that the sludge is principally clay and fibrous materials (Table I)(1).

As early as 1931 suggestions for utilization of deinking sludge were made. These suggestions outlined plans for using the clay portion of the sludge as paper stock, filler for paper board, and as a cement for molded products (2).

Kalamazoo River Improvement Company

Since 1931 the basic work on sludge utilization has been done by the Kalamazoo River Improvement Company and the National Council for Stream Improvement of the Paper and Paperboard Industries Incorporated. Two approaches were used in the develop-

TABLE I

RATIONAL ANALYSIS OF DEINKING SLUDGE (1)

Constituent	Per Cent "as is"	Basis	Kaolin	"Free" Water	"Cellulose" (C ₁₂ H ₂₂ O ₁₁)u	Carbon Black	Titaniz (TiO ₂)	Balance Unassigned
SiO ₂	27.45		27.45					0
Al ₂ O ₃	23.90		23.30					0.60
Fe ₂ O ₃	0.45							0.45
TiO ₂	2.13						2.13	0
H ₂ O			(8.23)	(1.74)				- -
C	14.74				10.73	4.01		0
H	3.36	0.91	0.19		1.64			0.62
O	21.98	7.32	1.55		13.11			0
S	0.12							0.12
N	- -							- -
Per cent Ash	59.80							- -
L.O.I. 900°F.	33.68							- -
F.M. 105°C.	1.74							- -
Unassigned	5.87							5.87 *
Total	100.00	58.98	1.74	25.48	4.01	2.13		7.66

* A significant fraction of the "Unassigned" is probably CaCO₃ as indicated qualitatively by acid test.

ment work in utilization of deinking sludge. One was the conversion of solids into products that could be used in papermaking, and the other was studying other industries as potential consumers of modified sludge solids. The mineral content of the sludge suggested the use of the sludge as an industrial filter and extensive work was carried out in the fields of industrial filler, and also building materials and velamation of clay.

The work of Newton and Nadleman gives the cost of calcination, a comparison of the abrasiveness of calcined sludge and commercial clays, particle size determination of calcined and ball-milled sludges, an evaluation as a coating pigment and relationships between brightness and inceneration time. "All of the grinding tests reduced the particle size of calcined sludge to the range of filler clays and commercial calcined clays used in paper making. However, the particle size obtained by both dry and wet ball-milling was coarser than commercial clays." The cost of these processes is relatively high however (3). Palladino, Morgan and Irving have presented numerous data pertaining to the sediable and volitile portions of the sludge. Palladino also

investigated the use of the sludge as a preservation material (4). Also, use of deinking sludge in cement products and as a lightweight aggregate was investigated by Nadleman and Newton (3). Drexel studied the use of additives to reduce the viscosity of the sludge in a thesis at Western Michigan University (5).

Since calcination studies proved not too promising, it was decided to try to use the principles of froth flotation as a method of separating the dark carbon like materials from the fiber and clays which might be useable. Newton carried out studies with pine oil and kerosene before his work for the Kalamazoo River Company ended. The result of this work is shown in Table II (3).

Lester Beeman in a senior thesis at Western Michigan University carried out extensive research on removal of the carbon from deinking sludge by froth flotation. Attempts were made to remove carbon from clay and cellulose with a fatty acid, a soap of the same fatty acid and oleic acid as collector. Pine oil, aliphatic alcohols and long chain alcohols were used as frothers and sodium silicate as a depressant. It was found that a fatty acid

without a depressant gave the best results. In attempts to float clays and cellulose from carbon, coco amine and tallow diamine were used as collectors. The same frothers were used with starch as a depressant. The best results were obtained using the diamine and starch (6).

Since this thesis will continue with flotation of the dark colored particles in the sludge, or the flotation of the fibers and clays the remainder of the survey was spent on the flotation principle.

Froth Flotation

Flotation refers epecifically to the art and science of separating solid particles from each other in a liquid pulp, or suspension, by means of air bubbles. In froth flotation (by far the most usual form as opposed to bulk oil flotation and skin flotation) a froth is formed by introducing air into a pulp which consists of the finely divided particles and water, to which a frothing agent has been added. Those minerals that have an affinity for air bubbles rise to the surface in the froth and are thus removed from those that are com-

TABLE II
COMPARISON OF PINE OIL AND KEROSENE
AS COLLECTORS OF CARBON BLACK

COLLECTOR	FOAM		TAILINGS	
	Brightness (Percent)	Ash (Percent)	Brightness (Percent)	Ash (Percent)
Pine Oil	39.0	56.2	46.5	54.1
50-50 Mixture				
Pine Oil and Kerosene	32.5	63.8	52.5	49.0
Kerosene	32.5	67.9	53.0	49.3

pletely wetted.

Chemical Factors

Collectors

In principle, flotation depends on the relative wettability of surfaces (7). A flotation system consists of a liquid, a gas, and some particulate material. The surface of the material may exhibit a natural nonwettability, but it usually must be treated with various flotation reagents in order to produce the desired degree of wettability or nonwettability. These reagents are called "collectors". They are divided into two classes - - - anionic and cationic (8). The anionic class is selective to those minerals which have a high concentration of positive surface charges. The cationic class is selective to those minerals which have a high concentration of negative surface charges.

Anionic collectors are used in the great majority of present day ore flotation operations. They are grouped into classes based on the active or polar groups (7), the most common of which are sulfhydrylic (mercapto) or carboxylic. The sulfhydrylic class includes types such as xanthates and thiophos-

phates with the general structural formulas:



R = alkyl group M = alkali metal or ammonium ion

The carboxylic collectors are principally fatty acids or their soaps.

Cationic collectors include quaternary ammonium, pyridinium, quinolinium or sulfonium salts and amine derivatives of fatty acids. The amines are the most versatile of all known reagents for non-metallic mineral separations (8). The development of those cationic reagents during the last 15 to 20 years has been the major factor in the advance of the field of non-metallic mineral separations.

Every collector should possess the following characteristics (8):

- a) It must possess a greater affinity for the particle that is being concentrated than for the other particle constituents of the pulp.
- b) It must be relatively or completely soluble in water, or compatible with a particle-water pulp.
- c) It should be non-corrosive.
- d) It should be quite stable chemically.

- e) It must be a potent collector which has the ability to promote speedy and rapid flotation of particles with a minimum of contact time preceding flotation.

The polar end of the collector attaches itself to the mineral surface either by chemical or physical absorption; the nonpolar unreactive end is oriented away from the mineral surface. The result is a hydrophobic coating at the mineral surface which permits attachment to the air bubbles. It is this surface condition which permits the floating of minerals which normally sink in water.

Quite often both cationic and anionic collectors are used in consecutive circuits under entirely different conditions to produce a satisfactory process.

Modifiers

If other ions are present in solution, in addition to the hydrogen and hydroxyl ions, they exert profound effects on the attachment of collector ions to the mineral surfaces and thus give rise to a large class of so-called "modifying reagents" (7).

Modifying agents may be classed in one of the following groups, according to their functions (9):

pH control

Depressant

Activator

Sulfidizer

Disperser of deflocculator

Protective colloid

Examples of pH control agents are lime, soda ash, and sulphuric acid. Where it is desirable to carry out flotation on the alkaline side and lime can be used, this low cost material is preferred. Soda ash is usually used where lime may be objectionable. Sulfuric acid is the usual agent for control of pH on the acid side.

Lime, sodium cyanide, and certain dichromates are examples of depressants. These reagents prevent the attachment of the collecting ion to the particle surface. Depressants are necessary where it is desirable to prevent flotation of one mineral normally floatable along with another being removed.

Certain modifying agents, termed activators, serve to bring about the attachment of collectors

to particles by means of an ionic bridge. When a material has been depressed or is not normally floatable an activator is used to bring about its active flotation.

Sodium Sulfide is the common sulfidizing agent. Sulfides are easily floated with xanthate type collectors.

Gangue, at times, may be of such a nature as to contain materials having a tendency to flocculate or clump, or hold together to such an extent as to interfere with efficient flotation of the desired material. Then, it becomes necessary to apply deflocculators and dispersants, and protective colloids are then used to hold them in the dispersed state. Sodium silicate is used as a dispersant. Starch, Casein, and glue are examples of materials used to disperse both gangue and carbonaceous materials and to serve as protective colloids to prevent reflocculation.

Since the reactions under consideration take place at the surfaces of minerals, and also since only a partial monomolecular layer is required to produce flotation in most cases, the quantity of

dissolved ion necessary to affect the reactions is very small. No fixed rule can be given to the amounts of flotation agents to be used. The optimum quantity varies with the material being beneficiated.

Physical Factors

Once the particle has been prepared with a water-repellent surface, it must be brought into contact with an air-water interface in such a manner that it will remain at that interface long enough for a separation to be effected. The most common method of producing these conditions is by the use of froth flotation, in which air bubbles are introduced into a pulp in any of a variety of ways.

A good flotation bubble must be small, and it must not join the other bubbles until it gets to the top of the slurry (10). Flotation engineers have determined that bubble structure is an important factor in flotation recovery (11). Experience proves that it is the surface area - - not the size of the bubbles - - which controls recovery. Small bubbles are desirable because they are more active

and expose a greater surface area.

Frothers

When the coated bubbles rise to the surface, they must remain stable a sufficient time for the froth to be removed. To produce a froth that will be persistent enough to allow a separation, a number of frothing agents may be used. Frothers are chemicals that ionize to a very slight extent in water and only very slightly (10). One ion must be hydroxyl, as bubbles in water have their surfaces composed in part from these hydroxyl ions. The mating ion forming the rest of the frother should be a chemical chain, generally a carbon hydrogen chain. The most commonly used frother is pine oil (an impure terpineol $C_{10}H_{17}OH$). Amyl alcohol, other long chain alcohols, phenol, cresylic acid, creosote, and others are also used. Aliphatic alcohols containing five to ten carbon atoms are frothers which have more recently found application in this field. Frothers function by changing the surface tension of the liquid (7). The froth serves a secondary purpose in providing a zone in which

the unfloated mineral particle (pulp that has been mechanically entrapped) will drain away from the flotation concentrate.

Excess frother will reduce the selectivity by producing too much froth, or, in extreme cases, will destroy the froth completely (7).

Conditioning

Most minerals can be floated from their ores quickly after addition of the flotation agents to the pulp. However, some ores require conditioning before flotation takes place. In some cases, this conditioning is simply a matter of allowing longer contact time between flotation agents and mineral particles before flotation sets in. In other cases, the pulp must be given a preflotation attrition before the surface of the mineral particle can accept the collector agent (3).

Particle size

The particle diameter of carbon black (the average diameter) probably does not exceed 0.1 micron (14), while clays range in particle diameter from .05 micron to 20 microns (15). Coating clays

contain from 70 to 95% particles which are finer than 2 microns (16).

Fine particles in the near-collodial size range are difficult to recover by flotation. This is due in part to the mechanical difficulty of bringing fine particles into contact with air bubbles (12) and in part to the fact that the surfaces of fine particles are not the same as a freshly produced surface. Gaudin and Malezemoff (13) postulate that fine particles have a surface older on the average than coarse particles. Thus, some ores require a scrubbing or attrition treatment to expose fresh mineral particle surfaces to the collector agent.

Water Supply

Water supplies in adequate quantity and purity necessary.

Equipment

Froth flotation cells are classified in accordance with the mode of introduction of the gas as: (a) agitation cells in which air is drawn down by a vortex caused by a rotating impeller; (b) sub-aeration cells in which air is introduced by suction or by blowing through or to the base of a

rotating impeller; (c) cascade cells in which air is introduced by tumbling of the pulp; and (d) pneumatic cells in which air is introduced directly by blowing.

In agitation cells the design and speed of the impeller precisely controls the number and size of the bubbles (10).

Variables

The common variables during operation are (7):

Height of the pulp in the cell

Degree of aeration

Pulp density

Temperature of the pulp

A relatively lower depth of pulp means a deeper froth layer and usually results in a cleaner overflow.

A more intense aeration may provide a greater probability of particle-bubble contact, but may also result in a concentrate containing more undesirable impurities.

Pulp density is important in both chemical and mechanical consideration. It determines reaction time and the quantity of reagent required to give

the desired reagent concentrations; hence, chemical factors argue for higher pulp densities. On the other hand, mechanical factors place definite limits on the optimum density. Flotation is normally more rapid and complete in denser pulps, but concentrate grade is lower; however, there are some exceptions to this rule (17).

Temperature of the pulp has an effect on the rate of reagent reaction. Usually, Flotation is carried out at the temperature assumed by the pulp. In some cases, however, it is necessary to raise the temperature of the pulp in order to accelerate the slow action of the collector at the normal temperature (6).

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Experimental Design

The experimental work was carried out in three parts. Since carbon black has a positive charge and clay and cellulose fibers have a negative charge, the first part of the experimental work was to separate carbon from sludge using anionic type collectors and the principles of froth flotation.

The second portion of the experimental design was to bleach the tailings of the flotation experiments with an oxidation and reducing bleach.

The final work was the calcination of the higher brightness portion of the flotation experiments at the lowest possible temperature to obtain a high brightness product and a comparison of this product and commercial filler clays as to brightness and particle size.

The brightness of the deinking waste was taken before and after flotation. In this way a comparison could be made as to how much has been removed from the deinking waste. Brightness samples of the original deinking waste were collected on filter paper by means of a small buchnes funnel, Brightness samples of the floated deinking sludge were

obtained by removing a portion of the clay-cellulose fraction from the flotation machine. These samples were then filtered and dried in the same manner as the original deinking waste.

All brightness tests were made with the Photovolt brightness tester.

It was assumed that any system which showed promise of a good separation in a single stage operation could be improved by a multiple stage operation.

Equipment

The equipment used in the flotation experiments consisted of a laboratory size Fagergren Flotation machine of the batch operated type. The flotation chamber is of 3000 gram capacity and air is introduced by direct agitation. An impeller speed of 1800 RPM was used in all experiments.

Part I

Flotation of Carbon from Clay and Cellulose

Collectors

Aero Promoter 708 - a fatty acid
Octyl Alcohol
Hydrogen Peroxide
Sodium Peroxide
Sodium Borate

Frothers

Pine Oil- an impure terpeneol
Aero Froth 63 - Higher aliphatic alcohols
Aero Froth 80 - long chain alcohol
Aero Froth 65 - water soluble synthetic frother

Depressants

Sodium Silicate
Starch
Citric acid
Tannic acid

Experiments Part I

<u>Exp.</u> <u>No.</u>	<u>Collector</u>	<u>Amount</u> <u>lb/ton</u>	<u>Frother</u>	<u>Amount</u> <u>lb/ton</u>	<u>Depressant</u>	<u>Amount</u> <u>lb/ton</u>
1	AeroPromoter 708	0.5	Pine Oil	0.1	-	
2	" "	"	" "	"	Sodium Sil.	1.7
3	" "	"	Aero Froth 63	"	-	
4	" "	"	" " 80	"	-	
5	" "	"	" "	"	Sodium Sil.	1.7
6*	Octyl Alcohol	"	Pine Oil	"	Starch	0.5
7*	" "	"	" "	"	Citric acid	"
8*	" "	"	" "	"	Tannic acid	"
9*	" "	"	Aero Froth 63	"	Starch	"
10*	" "	"	" "	"	Citric acid	"
11*	" "	"	" "	"	Tannic acid	"
12*	" "	"	Aero Froth 65	"	Starch	"
13*	" "	"	" "	"	Citric acid	"
14*	" "	"	" "	"	Tannic acid	"
15*	" "	"	Aero Froth 80	"	Starch	"
16*	" "	"	" "	"	Citric acid	"
17*	" "	"	" "	"	Tannic acid	"
18**	Hydrogen Peroxide	0.5	Pine Oil	0.1	Starch	0.5
19**	Sodium Peroxide	"	" "	"	"	"
20**	Sodium Borate	"	" "	"	"	"
21**	Sodium Peroxide) Octyl Alcohol)	"	" "	"	"	"

* Pretreatment with sodium chloride (0.5 #1 ton)

** Pretreatment with alum (0.5 #1 ton)

Part II

Bleaching of Flotation Products

Chemicals used.

Sodium hypochlorite

~~Z~~inc Hydrosulfite

Experiments:

Flotation experiments giving the best results were bleached with the above chemicals. The hypochlorite bleach was for 30 minutes at 25°C, 5.25% on pulp. The hydrosulfite bleaching was done at 160°F, for one hour, 1% on pulp.

Part III

The tailings from the flotation experiments were calcined at the lowest temperature giving a high brightness product. The ash content, brightness (Toppi 646-M54) and particle size 649-SM-54 was compared to commercial filler clays.

Data

Samples of both the original deinking waste and the clay cellulose fraction of the floated, were collected on filter paper and air dried. Brightness readings were taken with a Photovolt brightness tester. The results of these determinations are shown in Table I. The bleaching experiments were carried out as stated and these results are shown in Table II.

The calcination of the tailings was carried out at 1100°F and a comparison of the product with commercial products is shown in Figure 1, and the accompanying graph.

All flotation experiments were carried out at a PH of 6.7 to 7.0, at a consistency of 1.5 to 2.5%, by weight, of deinking waste. The temperature was that assumed by the pulp. The pulp was stirred for five minutes after addition of flotation reagents before air was introduced, and flotation time varied from 12 to 20 minutes.

The calcination experiments were carried out at 1100°F in a muffle furnace checked for temperature with a thermo couple and potentiometer.

TABLE NO. I

Results of Brightness Determination- Flotation Experiments

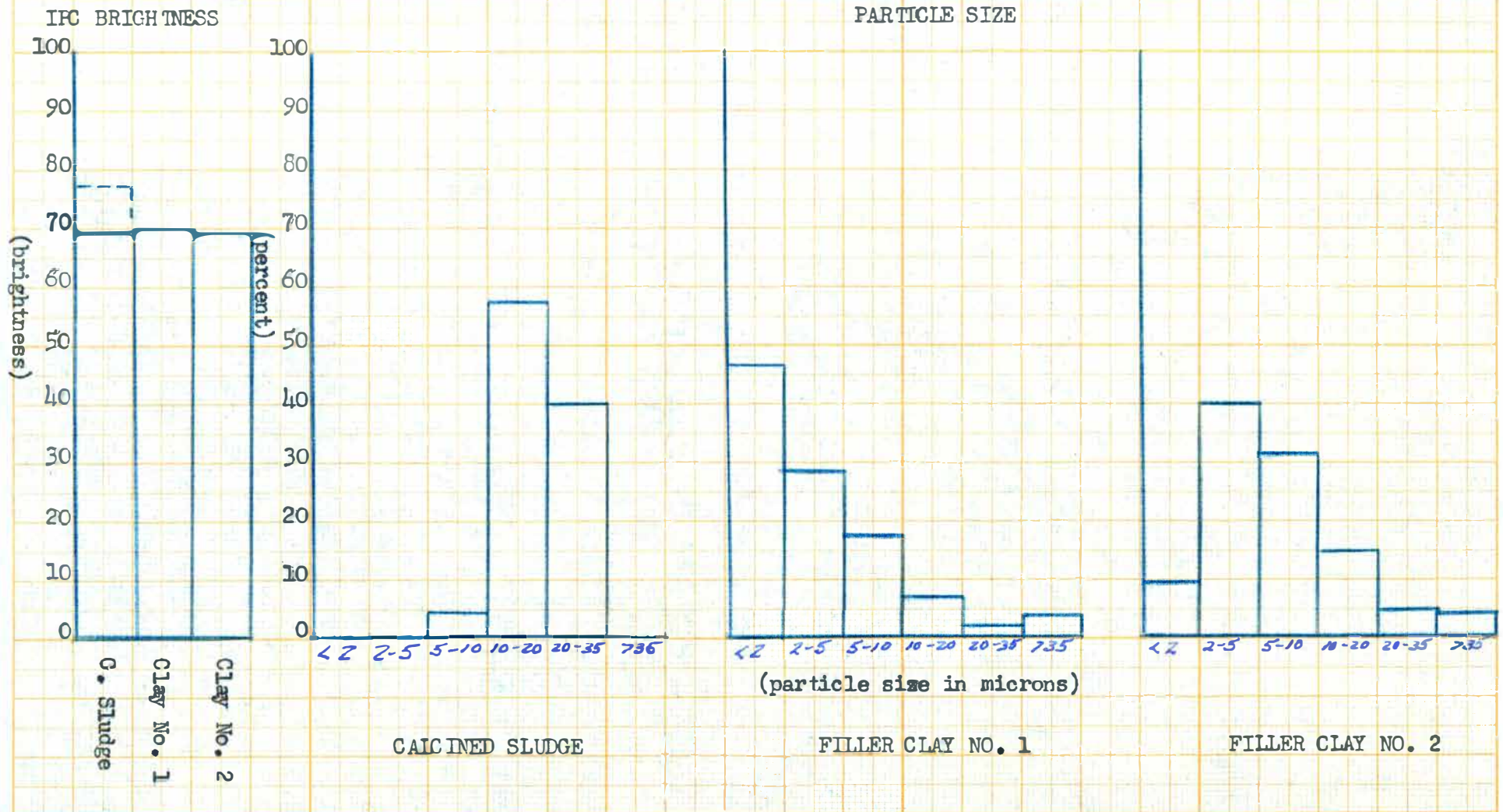
Experiment No.	Tailings Bright.	Froth Bright.
1	60.0	50.0
2	44.0	44.0
3	47.0	43.0
4	50.0	43.0
5	46.0	45.5
6	58.5	46-52
7	59.5	49-54
8	57.5	44-52
9	59.0	48-54
10	59.0	46-54
11	57.0	45-56
12	61.0	45-52
13	60.0	49.0
14	no good	turned brown
15	59.0	42-54
16	58.5	44-48
17	no good	turned brown
18	58.5	56.0
19	59.0	54.0
20	59.0	56.0
21	60.0	49.0

TABLE NO. II

Results of Brightness Determination- Bleaching Experiments

Process	Brightness
Before flotation	48.0
After flotation	59.0
Hypochlorite bleaching	61.5
Zinc hydrosulfite bleaching	62.0

Comparison of Calcined Sludge and Commercial Filler Clays No. 1 and 2



SUMMARY

The flotation experiments showed very little deviation in results from experiment to experiment. The increase in brightness ranged from 10.5 to 12 points. The change in brightness of the froth was slight. The ash content of the tailing ranged from 32.8 to 33.1%, while the froth was from 46 to 51.0 ° from the original 57.0.

The bleaching of the high brightness pulp showed little or no substantial increase in the brightness of the pulp.

The calcination product was near the range of commercial filler clays particle size, and compared favorably in brightness.

CONCLUSIONS

On the basis of these experiments it is believed that a definite and useful separation of carbon black from clay and cellulose fiber can be made, and this allows calcination to a high brightness product at a lower calcination temperature.

The experiments also indicate that bleaching has no apparent value for obtaining a higher brightness product.