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Zeta Potential and Its Affects on the Washing Stages of Newsprint Deinking

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ZETA POTENTIAL AND ITS AFFECTS ON THE WASHING STAGES OF NEWSPRINT DEINKING

by

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ABSTRACT

The use of zeta potential as a parameter in the washing stages of newsprint deinking is discussed. Previous research provided the temperature, time, and consistencies used in the hydropulper and washing stages. The research carried out tried to determine whether or not zeta potential can be used as a way of increasing the effectiveness of the washing stages. By varying the zeta potential with chemical additives it was found that very little correlation could be seen between the zeta potential and the brightness resulting from the flotation cell and sidehill screen washings.

It was also determined that the microelectrophoresis method of measuring zeta potential has no validity when used to measure fiber charge if the fines in the system do not have the same charge as the fibers.

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INTRODUCTION

The use of secondary fiber as an economical means of extending high cost virgin fiber has long been established. In the recycling process some waste papers are more easily deinked than others. Newsprint is an example of one of the more complicated wastes to be used. Ink used in newsprint is generally comprised of carbon black and linseed oil. Because of the lack of charge on carbon black particles it is difficult to deink by conventional methods. This lack of charge is where this study takes hold.

It has been shown how the electrokinetics of a system can contribute to the dispersing capabilities of that system. This investigation will try to show how zeta potential affects the washing stages of newsprint deinking. Two different washing methods (sidehill screen and froth floatation) will be evaluated at varying zeta potentials. Zeta potential variation will be obtained by the use of selected chemical additives. Evaluation will be made on the brightness of the deinked stock.

Another reason newsprint was selected for this study is because of its low filler content. Unlike a coated magazine stock which uses many fillers and additives, newsprint is relatively free from these constituents which affect zeta potential.

DEINKING

Many different deinking systems are used in the world today. No set pattern or 'correct' method is known. Although each system is designed for a specific purpose, each follows a basic format.

The first step usually consists of cooking the stock with deinking chemicals in a hydropulper. Many chemicals can be used depending upon the nature of the stock and its end application.

The next step is the removal of the suspended ink particles and other impurities. Prescreening and pre-cleaning to remove large-surfaced impurities is a must. The removal of ink is done with screens or a floatation process. One of the most efficient types of screens is the sidehill washer.

Sidehill Screen

The stock starts at the top of the sidehill screen and is allowed to flow downwards on the screen which is angled to 45 degrees with respect to the horizontal. As the stock travels down the screen the screen causes the fibers to roll rather than slide down. This rolling action allows the fibers to expose a larger surface area which results in cleaner stock. As the stock rolls down the screen it loses water, chemicals, fines, and

ink particles. Printing ink particles and fiber stock are separated on the basis of the differing particle size by wash filters in a number of series-connected stages. Most sidehill washers are set up with counter-current flow in order to conserve water usage as this is its major drawback along with loss of fines.

Flotation Cell

The other type of washer is the flotation cell. This follows the principle of selective floatation and utilizes the physical properties of the differing wettability for the separation of the ink particles to be removed from the suspension. Soaps, the alkali salts of fatty acids, are used to reduce surface tension which contributes to frothing on the boundry layer of water and air. These soaps contain a hydrophobic end- the fatty acid component, with a negative charge, and a functional group, hydrophilic- with a positive charge (Fig. 1). The hydrophobic end faces the ink particles which have a poorer wettability and thus lifts them off. Therefore, the air bubbles can more easily deposit on the ink particles and rise to the surface, while the fibers remain in the suspension.[14] As air enters the bottom of the flotation cell it is subjected to turbulence by a propeller which disperses it into the stock as tiny bubbles. The adhesion of ink particles

to the air bubbles is a function of two parameters- particle size and the degree of wettability. The measure of wettability is called contact angle(Fig. 2). Contact angle can be controlled by the use of frothers (soaps) as discussed earlier.

MECHANISM OF ZETA POTENTIAL

Once the ink particles have been released from the fibers they may still retain some affinity for those fibers. This affinity (if existent) is due to the charge of the particles.

Cellulose fibers in paper stock solutions behave very much like colloidal suspensions and are held in stable suspension due to the electrokinetic potential between the fibers and the suspending medium (e.g. water). Suspended colloidal particles in a fluid generally possess an electrical charge which is responsible for the stability of the colloidal suspension. Most colloidal particles have a negative charge in an aqueous medium and hence are surrounded by stationary positive charges. This is surrounded by a diffuse layer of positive and negative charges to keep the whole system at electrical neutrality. The zeta potential is the difference between the charge of this movable layer and that of the bulk of the suspending liquid. It is defined as the potential existing at the plane of shear which exists when the particle is moved through the liquid under the influence of an electric field.

The theory of the electric double layer deals with the distribution of counter-ions (ions of opposite charge in the fluid near the particle) and co-ions in the

locality of the charged surface. The particle acquires its surface charge by ionization and/or preferential ion adsorbtion. The adsorbed ion layer is represented by a continuous distribution of charge over this surface. The oppositly charged ions (counter-ions) are drawn to the colloid by electrostatic attraction, while thermal agitation, mechanical shear, and Brownian movement tends to distribute them uniformly throughout the solution. In the absence of mechanical shear, thermal agitation, and Brownian motion, sufficient counter-ions would become firmly attached to the surface of the colloidal particle to neutralize its charge. Usually thermal agitation is present in paper stock solutions prohibiting formation of this compact double layer. The combined affect of electrical forces and thermal agitation is, therefore, to create a 'diffuse' electrical double layer (often referred to as the Gouy-Chapman double layer[12,16,17])(Fig. 3).

This simple picture of the double layer of charges neglects several important facets of the problem. For one, not all of the counter-ions and solvent molecules are mobile. Narrow layers of charges remain fixed in a region close to the surface of the particle. Stern[12,17] introduced a correction for the finite size of the ions in the first layer adjacent to the charged surface.

Stern also considered the possibility of specific ion adsorbtion giving a compact layer of counter-ions attached to the surface by electrostatic and Vander Waals' forces strongly enough to overcome thermal agitation. The total double layer is, therefore, considered to be divided into two parts. A compact Stern layer, and a diffuse layer, the two layers being in equilibruim (Fig. 4). The potential charge in the Stern layer increases with electrolyte concentration. It is possible with polyvalent counter-ions, for reversal of charge to take place within the Stern layer.

The plane of shear demarks the region between the fixed and mobile solvent molecules. The potential at the plane of shear is the zeta potential. It is the potential at the surface separating the immobile part of the double layer from the diffuse part. It is a simultaneous measure of the charge of the diffuse double layer (per unit surface of the colloid) and of its extent away from the surface. The zeta potential is therefore related to the force and distance over which the particles can repel each other.

Measurement of zeta potential by electrophoresis is widely used. Electrophoresis refers to the movement of the charged particles relative to a stationary liquid by an applied potential gradient. The velocity at

which these particles migrate at a regulated voltage is called its electrophoretic mobility (E.M.). This E.M. can be measured using a microscope, regulated voltage, timer, and a keen eye. Electrophoretic mobility is measured in microns per second over volts per centimeter. The microns per second is the velocity of the particles as timed against the microscope eyepiece grid. The volts per centimeter is the applied voltage across the glass cell divided by the length of the cell. If every measurement is taken at the same length (1000 microns), the voltage is kept constant, and the cell length is also kept constant, E.M. is then a function of the time it takes to travel the 1000 microns. This results in ease of measurement of the electrophoretic mobility which is related to zeta potential by the fact that the velocity at which these charged particles migrate towards their oppositely charged electrode is directly related to the charge of the particles. Electrophoretic mobility is an indirect measurement of zeta potential, which is normally measured in units of millivolts.

The main use of zeta potential to date in the paper industry has been for retention on the wet end of paper machines. It has been found that when zeta potential is controlled, better retention and improved drainage result. This is done by bringing the system

close to its isoelectric point (zero zeta potential). If the charges in a system can be minimized, the attraction-repulsion forces are also lost. It is for this reason that zeta potential has become a familiar term with wet end chemists.

In deinking, if the ink can be kept as far away from the fibers as possible it will enhance the washing stages. The zeta potential can be regulated to achieve this repulsion and it is hoped that this paper will be able to substantiate this claim.

EXPERIMENTAL PROCEDURE

Three pre-lab cooks were run to determine which cooking chemicals would be best suited for this research.

A lab mixer with a heated jacket was used to simulate actual conditions of the hydropulper. All cooks were run at 120°F for 45 minutes. Eighty grams of Kalamazoo Gazette newsprint was repulped in two liters of water.

The following table lists the chemicals used in the lab cooks:

	1% $NaSiO_2$	1% NaOH	1% $Na_2H_2O_2$	1% $CaCO_3$
Cook #1	X			X
Cook #2		X	X	X
Cook #3	X	X	X	X

All cooks contained 0.01% Triton X-100 as a surfactant.

All three cooks separated the ink from the fibers equally well. The following table shows the optical results obtained from Noble and Wood handsheets:

Cook	G.E. Brightness	Opacity
1	50.6	97.0
2	52.5	98.0
3	52.5	98.6

Due to the nature of this research, that of charge

distribution, and the fact that all three cooks performed equally well in separating the ink from the stock. I felt that the first cook should be used for the completion of this work. The fewer chemicals used the better chances of the work being representative of what is actually taking place.

Pilot Plant Cook

Stock used for the major portion of this research was prepared from 220 pounds of Kalamazoo Gazette newsprint cooked for one-half hour with the cooking chemicals from Cook #1. This was done in W.M.U.'s Paper Recycling Plant (See Appendix 1). The stock was then dewatered to a consistency of 8.0% through a horizontal screw press. The stock was then stored in plastic bags in fiber drums at a temperature of 45°F. A preservative was added in the hydropulper to help keep the stock from going bad.

This stock had a brightness of 45.2 compared to the 50.6 brightness of the smaller lab cook.

Measurement of Zeta Potential

The Hercules Electrophoretic Mobility Equipment was used to measure the E.M. of the charged particles for this study. This equipment consists of a microscope with dark field illumination, a voltage supply,

timer, and a cell apparatus (See Appendix 2).

Samples to be measured are strained through 100 mesh screens so that only fines and small particles in the system will be measured for charge. Cellulose fibers are too large to show reliable electrophoretic movement and also tend to settle to the bottom of the cell. Therefore, the fibers are filtered out and measurements are made on the cellulose fines and other small particles in the system. The small particles are assumed to have the same surface charge as the fibers and large particles in the original unfiltered sample.

Flotation Cell Washing

The Voith-Morden laboratory model flotation cell was used as one type of washing method (See Fig. 5).

Each washing ran 45 minutes and contained one-half gram of Ivory Snow. No collector was used. The Ivory Snow was used as a soap to promote bubble formation.

A consistency of 0.80% to 1.0% was used in the flotation cell. One-hundred and fifty grams of bone dry stock was diluted in 15 liters and agitated thoroughly before being added to the cell.

The air intake was adjusted to keep a constant head of foam so that the raised ink particles were carried away in minimal time.

Sidehill Screen

A laboratory sidehill screen with a 80 mesh screen was used as the other type of washing method investigated.

Stock was washed down the screen at a consistency of 1.0% with the screen at a 45° angle from the horizontal. Each stock was washed down the screen three times to assure adequate washing.

After each stock had been washed, Noble and Wood handsheets were made and G.E. Brightness was measured.

Chemical Additives

The following chemical additives were used to adjust the zeta potential of each stock sample:

1. DuPont Aluminum Complex 101
2. Sodium Pyrophosphate
3. Thorium Nitrate
4. Potassium Ferrocyanide
5. Triton X-152 (non-ionic)
6. Triton X-100
7. Silver Nitrate

These chemicals were either chosen because they had been suggested by articles in the literature search or the author had a curiosity as to its affect on the stock.

When the additives were added in smaller amounts, no substantial differences in zeta potential were seen. Only when larger amounts were added (See Appendix 3) would the zeta potential of the stock make a significant

change. Once this change in zeta potential occured, it was difficult to get the charge to change further by adding more of the additive. This is the reason the isoelectric point of the system was never looked at. To get to the isoelectric point it would be necessary to add an additive that would reverse the charge on the fibers. The additives used in this study that reversed the charge on the fibers did not pass through the isoelectric point. The zeta potential went from highly negative to highly positive without becoming neutral first.

OBSERVATIONS

For each stock sample the zeta potential, charge of individual particles (positive or negative), and final brightness was measured.

Additive	Particle Charge	Zeta Potential	Flotation Cell Brightness	Sidehill Screen Brightness
1	+	19.4 mV	50.2	49.7
2	-	34.9	48.6	50.6
3	-	15.2	48.9	48.9
4	-	23.9	48.8	49.3
5	-	13.8	48.6	49.6
6	+	23.0	48.3	50.5
7	+	19.6	27.4	———

The reason for the very low brightness value on the Silver Nitrate (#7) stock can be accounted for by looking at the wood chemistry of lignin. The silver ions attacked the color groups of the lignin in the groundwood which produced the brown stock.

When the flotation cell was used with stocks that had positive particle charge, a large fiber loss occured. When the reversal of charge took place it appears to have made the fibers have a greater affinity for the air bubbles created in the flotation cell. This reversal of charge must be looked into more thoroughly to determine what is actually taking place. A large fiber loss makes this reversal of charge an unwanted situation.

Graph 1 plots zeta potential vs. brightness for the sidehill screen and Graph 2 for the flotation cell.

These graphs show very little correlation between zeta potential and the washed brightness of the stock. From the graphs it can be seen that the difference between the highest and lowest values is roughly a point and a half of brightness. These values are within experimental error considering lab technique and the instrument making the measurement.

When the chemical additives were added to the stock, the fines in the system will accept or change charge greater than would fibers due to their larger surface area. The fines are what the microelectrophoresis method of zeta potential measures. When the charge is measured on the fines it does not necessarily mean that the fibers have also attained this charge. The stock was classified with the Clark Classifier and 24% of the stock passed a 100 mesh screen to be classified as fines.

Most of the fines are lost in both types of washings so that any correlation between fine charge, zeta potential of the system, and final brightness is probably non-existent.

CONCLUSIONS

This research found very little correlation between zeta potential and the washing of Kalamazoo Gazette newsprint. This was due, at least in part, to the method used in measuring zeta potential (that of microelectrophoresis) and the large percentage of fines in the system.

Microelectrophoresis is probably not a reliable indicator of washing efficiency where the stock has a high percentage of fines even though zeta potential does have practical applications in wet end papermaking.

RECOMMENDATIONS

Due to the large fraction of fines in the stock used, the microelectrophoresis method of measuring the zeta potential should not have been used. If a more valid way of measuring the charge on fibers is developed this area is indeed in need of more research. A more thorough study as to the affects of charge on fibers and their relationship to flotation cell washing is needed to make valid conclusions.

The mechanism of charge reversal is another place where further investigation is necessary. Whether it was only the additives I chose which undergo this untypical type of reaction, or all chemicals which reverse charge, should be looked into further.

GRAPH 1 SIDEHILL SCREEN

GRAPH 2 FLOATATION CELL

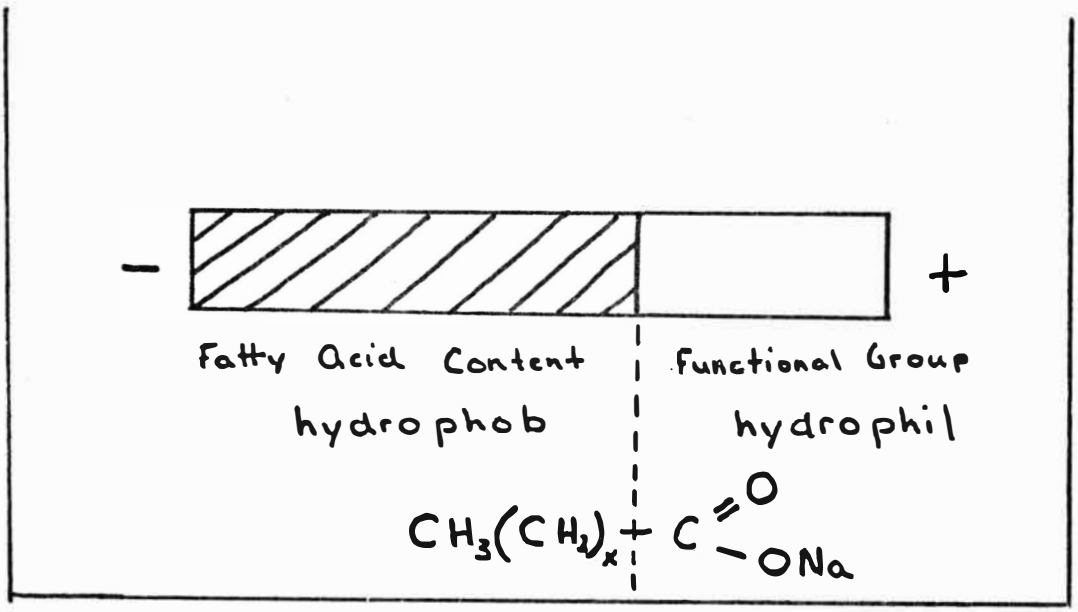

−
+
Fatty Acid Content
hydrophob
Functional Group
hydrophil
$CH_3(CH_2)_x$ + C(=O)−ONa

Fig. 1

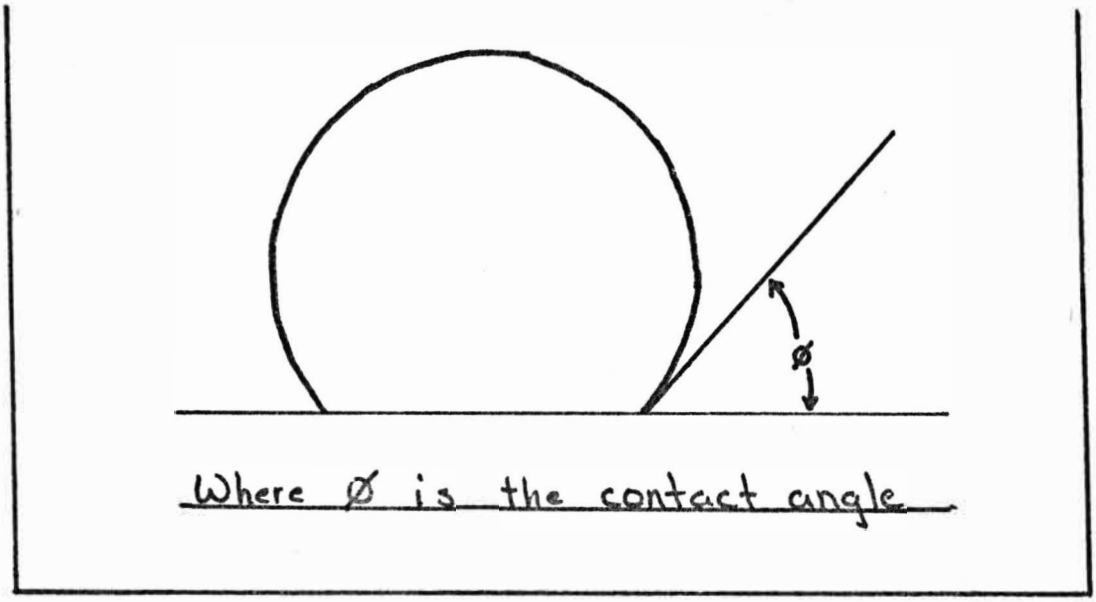

ø
Where ø is the contact angle

Fig. 2

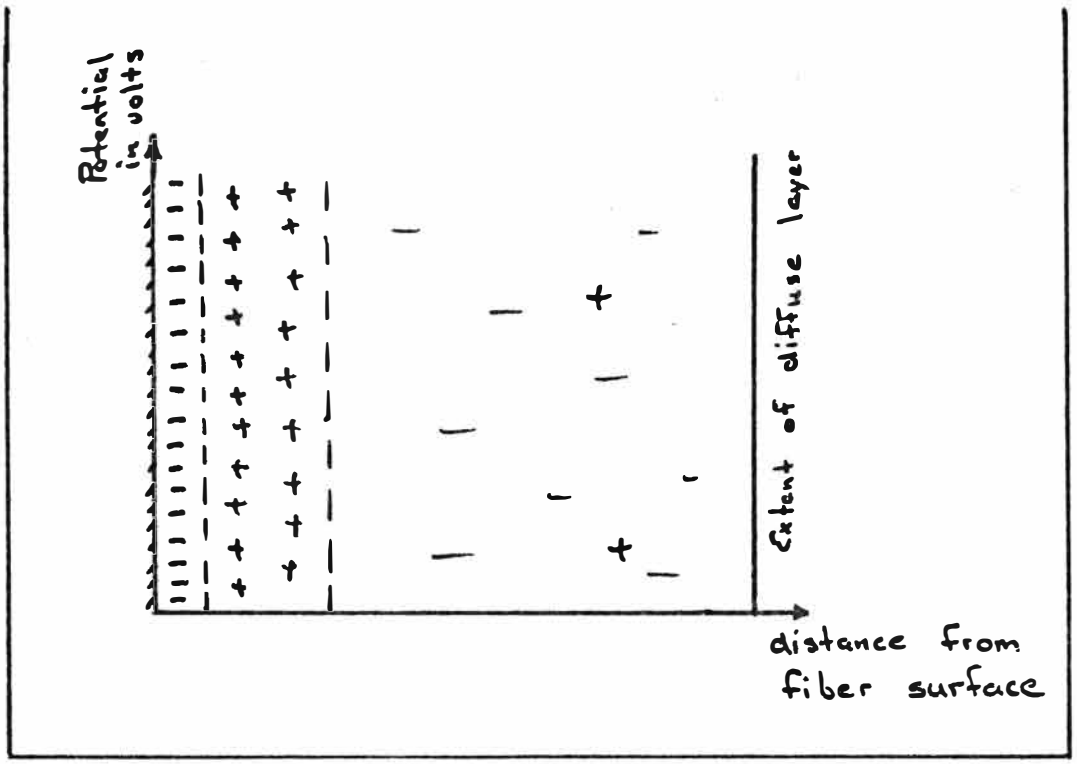

Potential in volts
Extent of diffuse layer
distance from fiber surface

Fig. 3

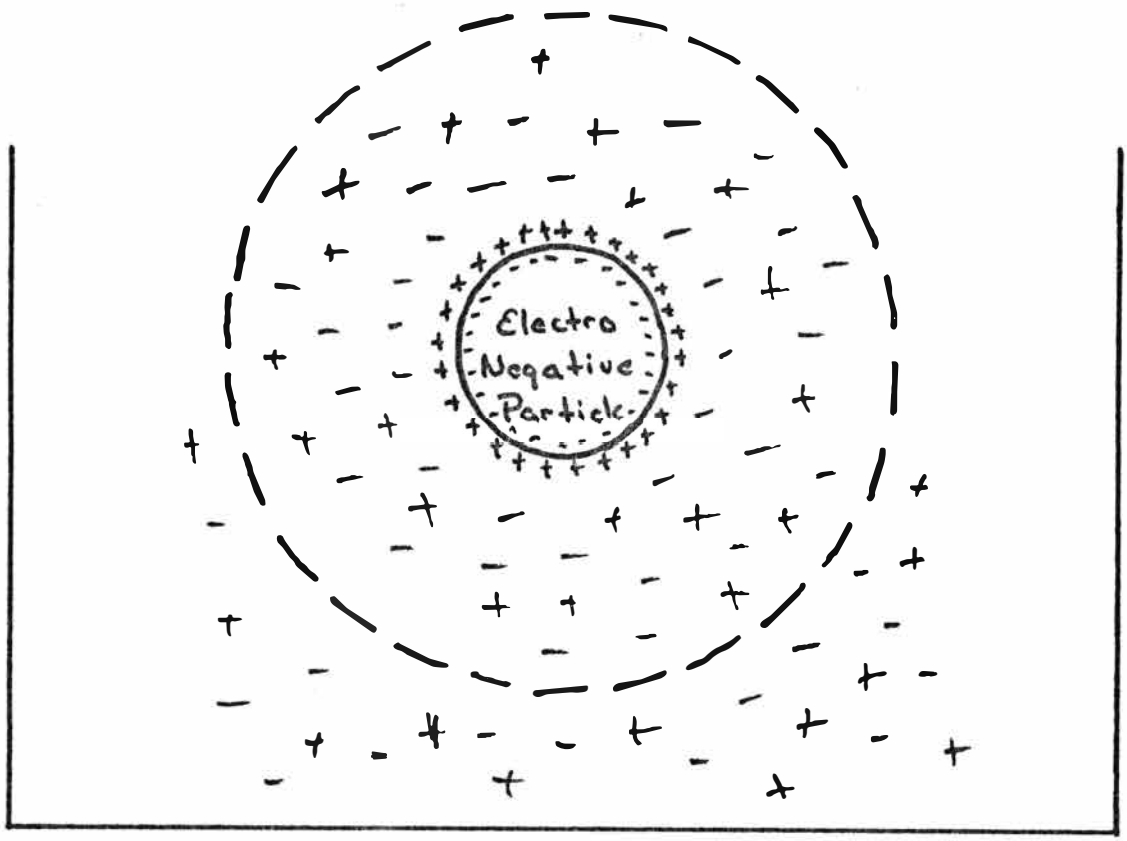

Electro
Negative
Particle

Fig. 4

LAB MODEL OF FLOTATION CELL

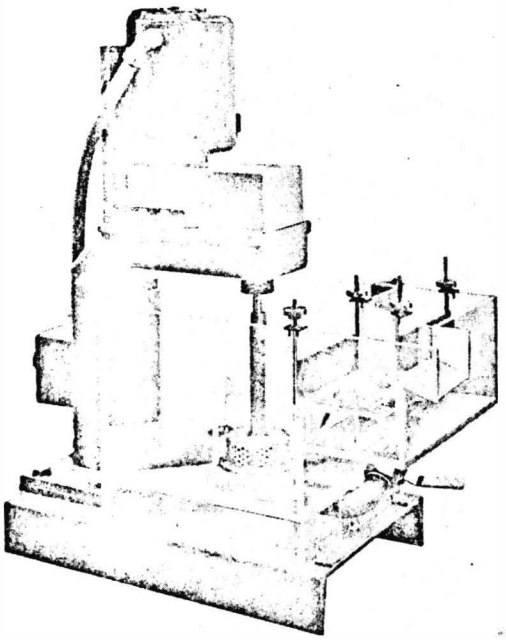


Fig. 5

APPENDIX 1

Pilot Plant Hydropulper Cook

Stock used for this research consisted of 220 pounds of Kalamazoo Gazette newsprint cooked for one-half hour in our recycling plant's hydropulper. For a consistency of 6.0%, 3667 pounds of water (440 gal.) was added. For cooking chemicals, 2.2 pounds each of calcium carbonate and sodium silicate were used. The cook also contained 0.01% Triton X-100 as a surfactant. The cook was run at a temperature of 120° F. A Vineland Chemical Co. preservative, Slimacide V-10, was added in the hydropulper to help keep the stock from going bad. The stock was then dewatered to a consistency of 8.0% through a horizontal screw press. The stock was then stored in plastic bags inside of fiber drums. The drums were stored at a constant temperature of about 45° F.

The recycling plant's hydropulper is six feet in diameter and has a maximum capacity of 250 pounds of dry pulp. A 60 H.P. motor turns the hydropulper.

APPENDIX 2

Determination of Electrophoretic Mobility

Measurement of zeta potential was done using the Hercules Electrophoretic Mobility Equipment. The equipment measures the electrophoretic mobility of the charged particles which can be converted to zeta potential which will be shown later.

A microscope with dark field illumination was used so particle movement could be seen easier.

A suspension of small particles (having been screened through a 100 mesh screen) is placed in a thin flat glass cell and particle movement is observed in the microscope.

Direct current is applied across external copper electrodes immersed in saturated copper sulfate solution. These reversible electrodes prevent gasification and polarization at higher current flows. The voltage drop across the flat glass cell is measured by platinum electrodes inserted at each end of the measuring cell. An integral timer was used to time the movement of particles across a calibrated grid in the microscope eyepiece.

The velocity of the particles is proportional to their surface charge. If the speed of the particles is observed, their relative charge can be calculated:

$$\text{Electrophoretic Mobility (E.M.)} = \frac{\text{particle speed in microns/sec}}{\text{voltage gradient in volts/cm}}$$

From the electrophoretic mobility, the zeta potential on the electrical double layer can be approximated;

$$\text{Zeta Potential (Z.P.)} = \text{E.M.} \times (4\pi\ell/D)$$

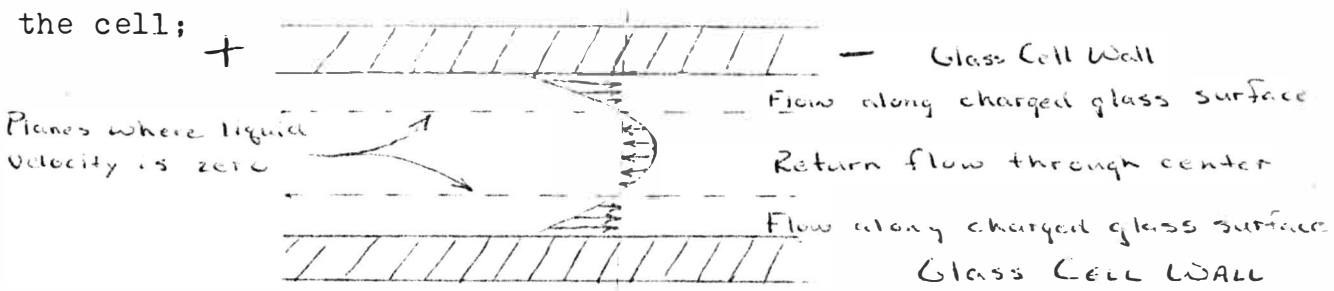
Where,

ℓ = Viscosity of liquid
D = Dielectric constant of liquid

or for spherical particles in water,

Z.P. (millivolts) = E.M. x 12.8

But, the movement of particles in the glass cell is also influenced by electroosmosis, the movement of the liquid along the charged glass surface. Since the cell used is closed, the flow of liquid along the walls is counterbalanced by a return flow in the center of the cell;



As noted in the diagram, there are two positions where the liquid velocity due to electroosmosis is zero. These are known as the stationary planes and it is only at these planes that electrophoresis measurements are made.

For flat glass cells of the type used, the stationary planes are located 20% of the depth of the cell from the inside top and bottom surfaces. In practice, the top stationary plane is always used because of difficulty in seeing the particles in the bottom stationary plane against a background of settled particles on the bottom of the cell.

When making measurements the voltage across the platinum electrodes was adjusted to 43 volts. The eye-piece grid was calibrated in 100 micron squares. Ten divisions equals 1000 microns. The cell length was 3.2 centimeters. The E.M. equals:

$$\text{E.M.} = \frac{1000/\text{ time in seconds for 10 divisions travel}}{43 \text{ volts}/\ 3.2 \text{ cm}}$$

$$= 75/\ t \text{ in seconds for 10 divisions of travel}$$

The units of E.M. are microns/sec/volt/cm. When making E.M. measurements, the particle motion was timed for 10 divisions of travel. Then the simple equation 75/t gives the E.M. measurement which can easily be converted to zeta potential (millivolts).

APPENDIX 3

Chemical Additives

The following table shows the amounts of chemical additive used to acquire the zeta potential used:

Chemical Additive	Quantity	Z.P.
1	30 ml	+19.4 mV
2	30 gm	-39.4
3	10 gm	-15.2
4	25 gm	-23.9
5	10 ml	-18.8
6	35 ml	+23.0
7	10 gm	+19.6

The quantities indicated were added to the stock after it had been diluted in the 15 liters of water before being washed

The zeta potential for unprinted Kalamazoo Gazette newsprint was -25.8 mV. That of printed Gazette newsprint was -20.2 mV. The ink reduced the zeta potential of the stock by 5.6 mV.

The Kalamazoo Gazette uses a letterpress press on all of its newsprint. On inserts and other specials it uses the offset process.

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