Electrochemical potential in papermaking significance and an instrument for measurement

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Introduction

The importance of the electrokinetic potential in the wet-end chemistry of papermaking system has long been acknowledged. The magnitude and nature of potential have a significant effect on the retention of pigments, dyes, internal size, wet strength resins, as well as on drainage and on flocculation during paper making. The studies conducted by various scientists indicate that maximum retention and drainage occurs at the electrophoretic mobility potential level of near zero. Measurement of in-plant electrokinetic potential is difficult task, therefore, process control by zeta potential is not commonly used in paper mills. The effect and variation of electrokinetics in the paper making system can be easily interpreted by the measurement of potential, if it can be measured regularly and/or continuously, which calls for the need of a low cost and robust instrument giving direct relationship with electrophoretic mobility potential.

Scope

The measurement of electrokinetic potential at papermaking process stages will give the overall picture of wet-end chemistry in a papermill. Visualizing the process requirements, it was decided to choose a measuring technique which could give the linearly related va'ues at follow ng process variables —

- Consistency variation from 0.2% to 1%
- pH variation of 4 to 6.5
- Temperature variation in range of 20 to 45°C
- Particle size variation of 30 um to 3000μm
- Suitable for heterogeneous particle shapes and sizes

The technique should also be good to provide :-

Information feed back within short time of 5 min to 30 minutes to bring an effective contol in the continuous process.

- Within acceptable accuracy range.
- Sample could be used as such, without any modification.
- Should be simple enough to be used by process persons with wide technical/scientific background (Engineers, Scientists or Science graduates).
- The equipment could be used with minimum of human error.
- The equipment should be for online measurements.

Application

Colloidal particles have some electrochemical charge. The magnitude and nature of charge is dependent on both, the media and the particle composition. This electrochemical charge controls the state of colloidal particles being either in coagulated or dispersed condition. Papermaking suspension consists of negatively charged fibers/fines. The magnitude of charge of pulp fibers is in the range of (—) 9 mV to (— 20 mV and the chemical additives used in papermaking are in the range of (–) 5 to (–)40 mV, when measured by zeta meter. Papermaking furnishes give poor retention, drainage and formation, due to their repulsive potential range. Cationic charge neutralizing chemical such as Alum and Wet Strength additives can reduce the charge of the papermaking furnishes in the range of -5 mV to +5 mV, where the repulsive effect is suitably diminished and the coagulation effect is maximized.

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The measurement technique available for measuring zeta potential identified for use in papermaking industry are :

(i) Moving boundary electrophoresis
(ii) Microelectrophoresis
(iii) Streaming potential

Microelectrophoresis are being used in research application since a long time. Sophisticated and precision instrument for microelectrophoresis measruements are available. It was decided to purchase one such instrument. A electrophoretic mobility meter was purchased from Zeta Meter Inc, USA, model Zeta Meter 3+ to measure the zeta potential in the laboratory.

Experiments on Two Identified Techniques Moving Boundary Electrophoresis

For making measurements on moving boundary electrophoresis, a glass apparatus was constructed Fig. 1. Wire electrode made of platinum were placed in the side tubes of the apparatus. Electricfield to the suspension was applied through these electrodes. Platinum wire electrodes were used in the arms of the U–tubes for measuring the applied electric field. These separate electrodes were employed for applying and measuring the electric field so as to avoid any disturbance by reaction products generated at the working electrodes. A variable D. C. supply (0–300 V DC) was connected with the working electrodes.

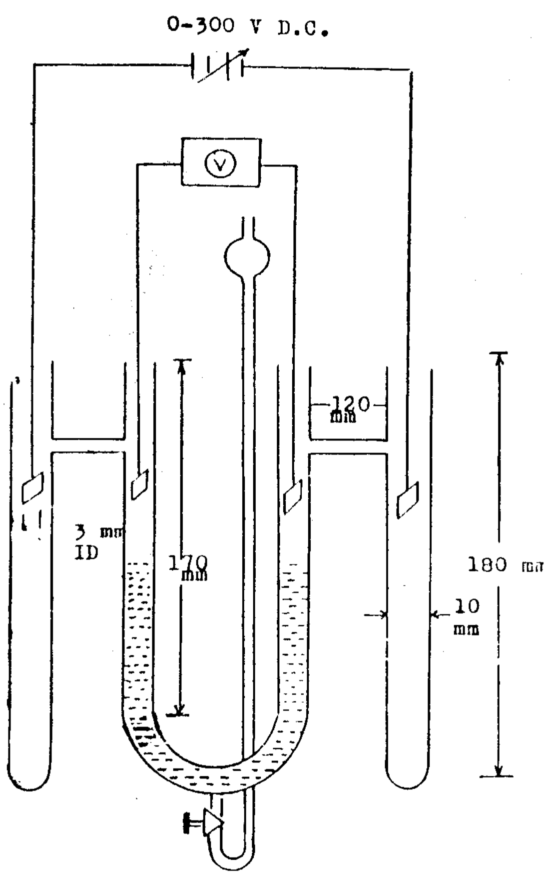

Fig. 1
Apparatus Used for Moving Boundary Electrophoresis

After numerous observations on moving boundary electrophoresis, it was realized that accurate measurements would be difficult with this method. Practical difficulty observed in this method were :

- Poor boundary formation
- Low consistency requirement
- Large time requirements and difficult to use
- Not suitable for hydrated papermaking furnishes.

Streaming Potential :

The streaming potential is the voltage difference developed between the ends of a capillary tube or across the porous diaphragm, when liquid in a suspension is forced to flow by an externally applied pressure difference P. An expression relating streaming potential E_S to applied pressure P and the zeta potential may be given as follows [1] :

$$\pi = (4 n E_S X)/(PD) \ldots\ldots\ldots\ldots\ldots I$$

Where π represents Zeta Potential, n, is the coefficient of viscosity, X the specific conductance and D the dielectri constant.

Streaming potential method can be used in paper making industry due to following reasons :

(1) Fibrous suspension can form plug, which is necessity for measurement of streaming potential in paper making furnishes.

(2) It makes the measurement on whole suspension (fines and fibers) as such without any modification in the sample.

(3) This method offers promising scope for online application, if sample can be drawn automatically at regulated interval from the process.

(4) It can be used for shop-floor measurements and can be developed for a continuous system.

Since this method can be conveniently used in paper making industry for the measurement of electrokinetic potential in the papermaking industry, the method was persued.

Development of streaming potential cell principle of operation

The operation of streaming potential measuring cell is to form a pad of fibers/fines while pumping white water through the cell, and to measure the electrical charge flow with water in terms of streaming potential across the pad. This value, plus the conductance and temperature parameter, can be used to calculate zeta potential. The apparatus for measuring streaming potential of pulp suspensions was initially designed as shown in Fig. 2. It consisted of a glass tube fitted with a disk plug made of porous glass. Wire electrodes made of platinum were fixed at equal distance from the porous plug for measuring potential across the plug. To ensure intimate electrical contact between the electrodes and the fluid, further to reduce electrode-fluid inter facial capacitance, surface area was increased by making them rough and porous. This is done by platinizing the electrodes.

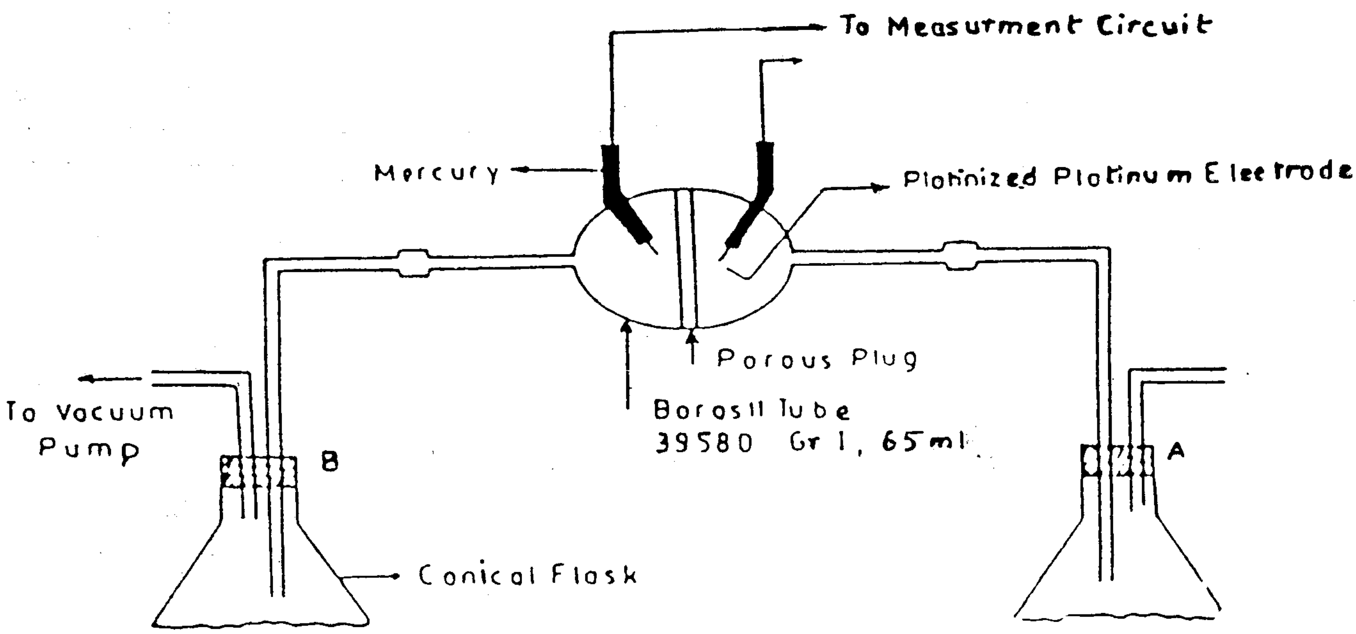

Fig. 2. FIRST CELL USED FOR MEASURING STREAMING POTENTIAL

Amplifier Circuit

The value of streaming potential is small, the streaming potential signal is needed to be amplified. The amplifier circuit used is shown Fig. 3. The circuit makes use of a high performance operational amplifier (ICL 7650 S). The opamp is chopper stabilized and offers exceptionally low input offset voltage and is extremely stable with respect to time and temperature. The maximum input current drawn by the opamp is only 10^{-11} amperes. The gain of the circuit is five. Voltage at the output of the amplifier was measured by connecting a sensitive digital voltmeter.

Problems Faced with the above Glass Tube

Several operational problems were encountered with the use of apparatus. The porous plug fitted glass tube developed problems like leaking through periphery of the plug with glass surface and choking of plug. Replacement of the plug is not possible as it requires facilities for glass blowing. The tube is also

FIG. 1 Apparatus Used for Moving Boundary Electrophoresis

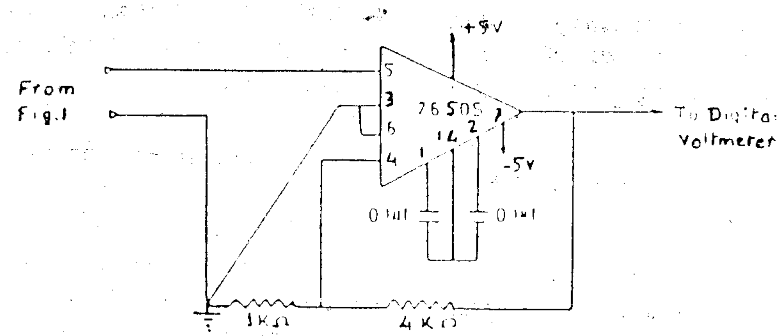

Fig 3 AMPLIFIER CIRCUIT USED WITH CELL

quite fragile and needs to be handled carefully. Some inaccuracies in the results were attributed to these operational problems. In view of the above observations, decision was taken to modify the streaming potential cell.

Further platinum Anode and platinum cathode are applicable for system having a specific conductivity up to 1000 umhos/cm. Papermaking suspension are of high specific conductivity (up to 1700 umhos/cm near isoelectric point), where these platinum electrodes are not good, therefore in the modified apparatus it was required to modify the electrodes also.

Modification in Cell and Electrode Design

In the modified apparatus shown in Fig. 4, the glass tube fitted with porous plug was replaced with a fabricated acrylic cell. A fine synthetic screen was employed in place of the porous diaphragm. The screen is fitted inside the cell using rubber rings. The cell is constructed in two parts. Each part consist of one electrode chamber. These parts are joined together using clamps and can be easily separated for cleaning or replacement of screen. Platinum +ive and platinum—ive electrodes are replaced by molybdenum Cylinder anode. which is more suitable for high ranges of specific conductivity (2) and a platinum Rod cathode. Platinum rod cathode is a rugged bullet shaped electrode made of platinum-iridium to minimize interaction with the suspension.

Measurement Method

When a constant vacuum in applied across the porous plug, specimen starts to flow in the cell. voltage

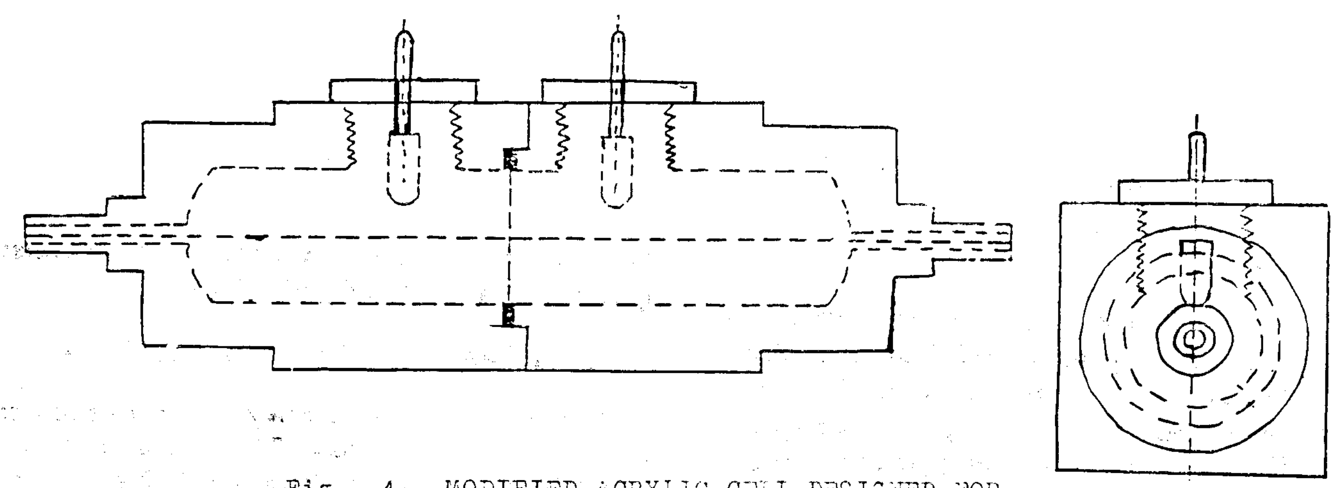

Fig. 4. MODIFIED ACRYLIC CELL DESIGNED FOR STREAMING POTENTIAL MEASUREMENT

Fig. 4 MODIFIED ACRYLIC CELL DESIGNED FOR STREAMING POTENTIAL MEASUREMENT is measured when the vacuum is stable after some time. Then vacuum is released and the voltage is measured again with liquid stationary in the tube. The difference between the two voltage readings is divided by the gain of the circuit represents the streaming potential of the specimen suspension.

5. Data acquisition system

Controlling of vacuum pump operation, keys, automatic measurement of streaming potential, specific conductivity and automatic calculation of zeta potential was done by 8085 microprocessor interfaced with a personal computer. An overall schematic block diagram of the system is shown in the Fig 5. The system hardware can be broadly divided into three sections :

(1) First section consist of streaming potential cell, amplifier circuit and signal conditioner for specific conductivity and temperature measurement.

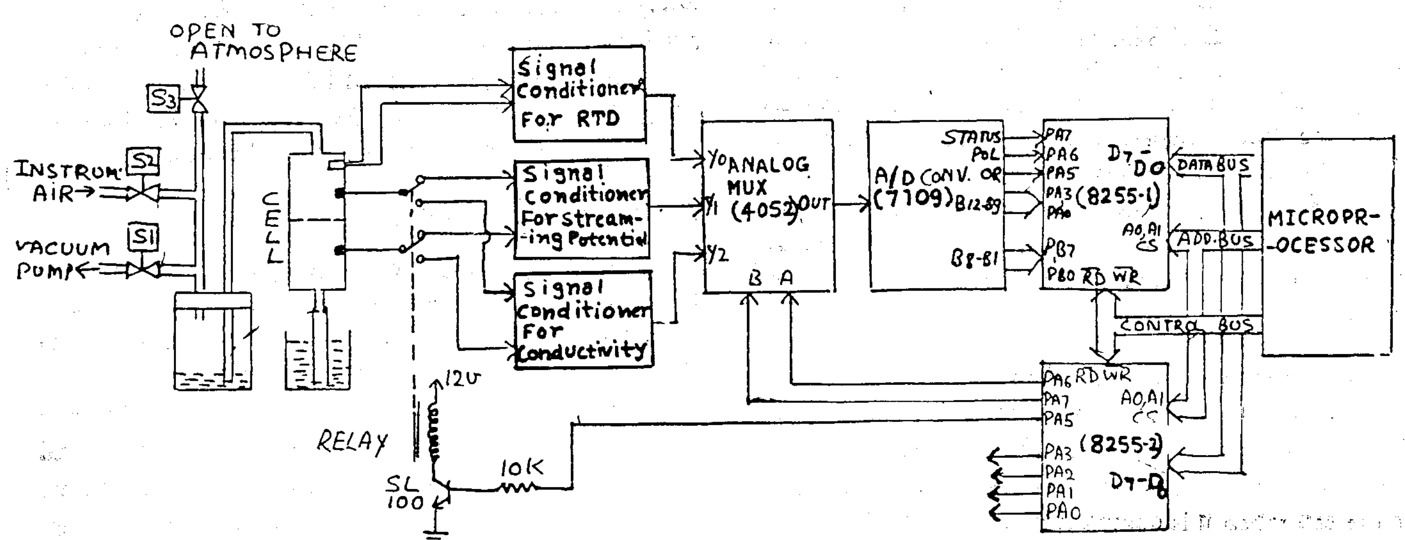

Fig. 5 DATA ACQUISITION SYSTEM

(2) The second section is the interfacing section, the following are the main components of this interfacing section.

(a) **Analog Mux** :—The interface is multi channel, i.e. it allows data collection from three input signals. These are signal for streaming potential specific conductivity and temperature signals. We use a 4052, 8 channel analog mux, which allows up to 8 input signal simultaneously. The particular input to be sampled is collected through software under the user control.

(b) **Analog to digital converter:**—Physical signals are normally available in analog form and these need to be processed digitally by Microprocessor/PC. So ADC is needed. To provide reasonable accuracy it is suggested to use 7109, 12 bit ADC.

(c) **Programmable Peripheral interface (8255):**—In order to read the digital signals given by the ADC, a minimum of 14 bit buffer is needed to hold the data. Some buffers are also needed for pump, keys, relays, mux etc. Rather than selecting normal latches (buffers) we propose using two programmable peripheral chips which provide some flexibility in the proposed data acquisition interface. The intel 8255 programmable peripheral interface is used, because it is directly compatible wi h the 8085 microprocessor and IBM PC bus signals.

(3) Third section consist of 8085 based microcomputer with peripheral chips and PC.

(a) **8085 based microcomputer:**—is used to control the vacuum pump and keys and for measuring streaming potential, specific conductivity and temperature data in a desired manner through a programmable peripheral interface. We used a EC— 85 microcomputer. EC— 85 is an advanced microprocessor designed by professional Electronic products.

(b) **PC:**—The PC used in the system is based on intel 8088. All the standard hardware features are incorporated within PC.

System Operation

First the software controls relay, in such a way that cell connects it's electrodes to streaming potential amplifier circuit. Now the program controls pumps and keys in such a way that liquid starts to flow in cell, developing a signal across the electrodes. This signal is automatically fed to analog mux. Depending upon the select input of the mux this signal is fed to the ADC converter. When ADC finishes conversion of this data it informs 8255 (1) through the status line. Microprocessor then reads the converted sample through port A and B of 8255 (1) and store it in the memory of microprocessor. Now the program controls pump and keys in such a way that liquid come to stationary position. Signal across the cell is again fed to the analog mux. From the analog mux it is fed to the ADC. When conversion finishes, microprocessor reads it and store it in the memory. This procedure is repeated again and depending upon the no of measurements.

Now the program controls the relay in such a way that cell automatically connects its electrodes to the specific conductivity circuit.Further pump and keys are controlled in such a way that liquid starts to flow in the cell when it is completely filled signal appears across the electrode is fed to the specific conductivity circuit. Output of this circuit is fed to the mux. Depending upon the select input of the mux this conductivity signal is fed to the ADC converter when conversion finishes microprocessor reads this signal and store it in the memory.

We have now streaming potential and specific conductivity data, which gives Zeta Potential Value the using the equation —I in programmed microprocessor and displays the value.

Observation

Measurement made at Laboratory

Raw Material/Pulp Used

Three types of bleached pulps were used for measurements in laboratory. They were Hardwood pulp (100% Eucalyptus), a typical commercial mix of long and short fiber pulps (70% Eucalyptus. 18% Bamboo and 12% Pine) pulp and a Bagasse pulp.

Sample Preparation

For studies, (—) 70 fraction of 0.3% consistency samples were prepared from air dried and stored pulps. To prepare slurry of 0.3% consistency, the pulp was soaked for few hours in distilled water and then disintegrated. Consistency of slurry was measured using filter paper and was corrected to exact value of 0.3%. The slurry was then divided into 500 ml samples. Predetermined amount of electrolyte solutions (Poly aluminum chloride grade 18/5 from Grasim Industries Ltd.) were added in these samples. After adequate stirring, the samples were subjected to fractionation on Dynamic Retention Jar Mark IV using stainless steel 70 mesh wire. Reason for the use of (—) 70 fraction has been discussed in our earlier publication [3].

Results and Discussion

Streaming potential of the samples was determined from the apparatus discussed above. Same samples were used for investigations on Zeta Meter 3+. Conductivity of the samples was measured separately by zeta meter 3+. Zeta potential was calculated by making use of equation by taking dielectric constant and viscosity coefficient equal to that of the distilled water. Fig. 6. and Fig. 7. represent the curves showing nature of Zeta potential with variation in electrolyte (PAC 18/5) content. The calculated zeta potential values from Streaming potential apparatus data are shown with continuous lines. The dotted lines represent the Zeta potential values from the Zeta meter 3+. It is evident from the curves that although there is a difference in the values of zeta potential obtained by the two methods, the nature of curves is identical, however, variations can be seen at low poly aluminum chloride contents. Specific conductivity of the samples are low in this region. It is believed that the surface conductivity phenomenon plays an important role with low conductivity samples and the errors in this region are due to the fact that surface conductivity has been taken to be negligible. The observations made on two commercial pulps, thus confirming the similarity of curves by the two methods and the versatility of the apparatus.

Measurement on industrial furnishes

Sample of various process stages of papermaking was taken from the mill. Zeta potential values of

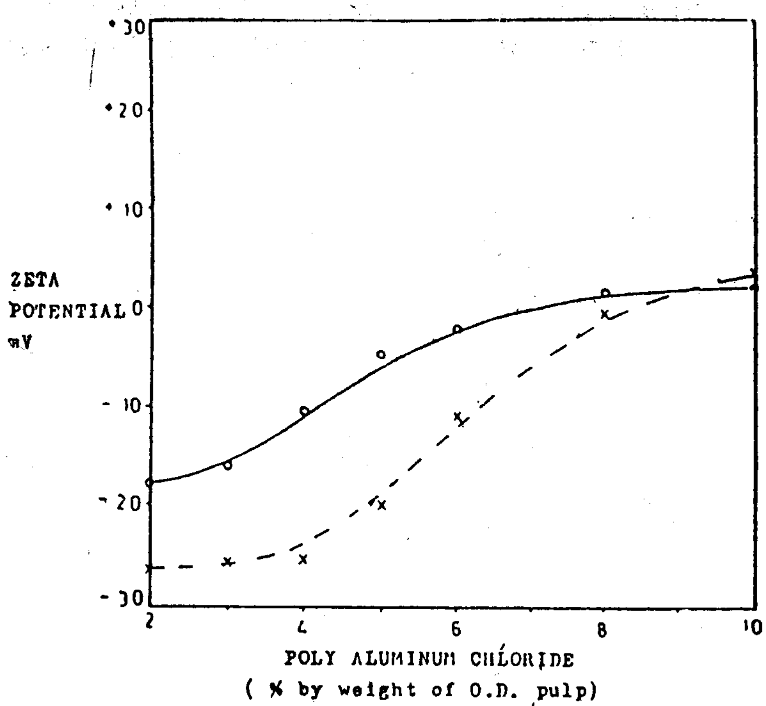

Fig. 6. Polyelectrolyte vs Zeta Potential For Commercial mix pulp (70% Long & 30% Short Fibers)

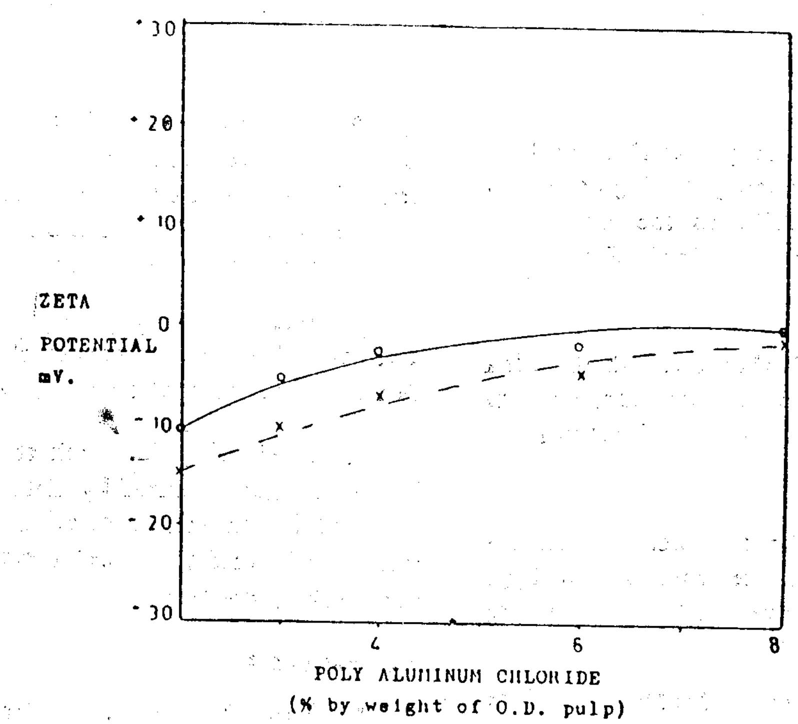

Fig. 7. Polyelectrolyte vs Zeta Potential for Eucalyptus pulp

these samples are measured by using Zeta meter 3+ and also calculated using streaming potential apparatus. The zeta potential values from both the apparatus are plotted in the Fig. 8.

3. Streaming potential measurement are very fast, so gives the ability to make continuous adjustments to the electrokinetic properties of a papermaking furnish in real time.

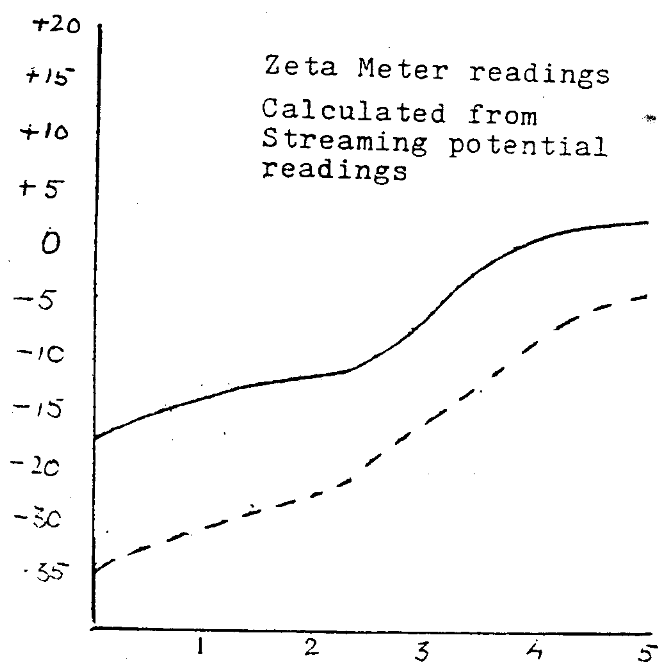

Fig. 8. Zeta Potential Values from Different process stages at mill testings

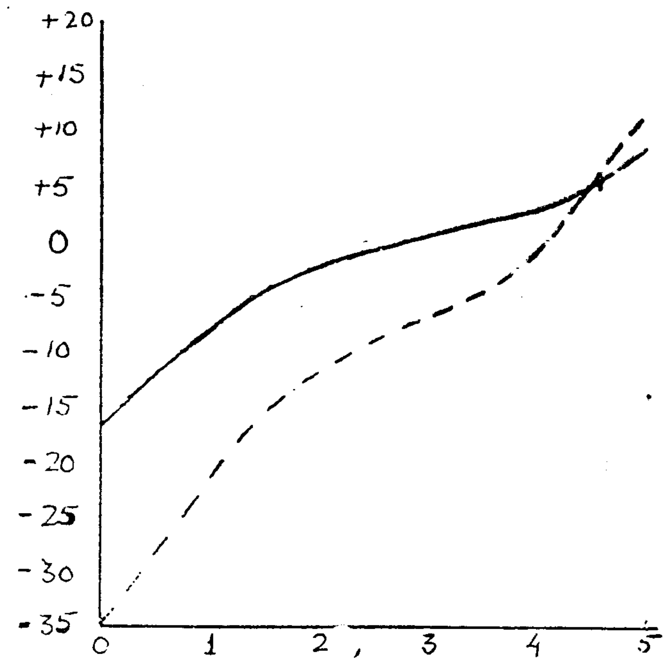

Fig. 9. Zeta Potential values of mill sample with polyelectrolyte

Some measurements of zeta potential from both the apparatus are made by adding varying amount of poly aluminum chloride (PAC). to the samples of various stages and these are plotted in the Fig. 9.

Results and discussion

It is evident from the fig that although there is a difference in the values of zeta potential from both the apparatus but the nature of the curve is identical.

Conclusion

1. This instrument make measurements on suspension of concentration ranges from 0.2 to 1%., where other conventional methods of measuring zeta potential are difficult to operate.

2. This instrument is very useful for suspensions near zero charge, where the sample coagulates rapidly. Such a state makes measurements difficult by other and conventional methods of measurements.

4. Conventional methods of measurements are used to measure the zeta potential of very small particles. The streaming potential measurement can be made on fine and long fibers alike and thus process back water can be used without any modification.

5. The proposed streaming potential system operates under direct computer control via a standard interface thus no human error involved.

6. Isoelectric point reach at same dose of polyelectrolyte when measured by Zeta meter or streaming potential instrument. Streaming potential measurements can be used to determine cationic demand of any papermaking syestem.

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Application of zeta potential for retention optimization on bageasse pulp

IPPTA Vol—3, No. 3, SEPT 1991