STUDIES ON THE UPGRADING CELLULOSE PULPS BY ELECTRODIALYTIC TREATMENT

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Experimental investigations were carried out to study the feasibility of upgrading pulps by electrodialytic treatment, with particular reference to deashification of pulp, to be utilized in the manufacture of dissolving and filtration grades of pulp. Different pulp systems, bagasse, mixed hardwood and cotton linter, were subjected to electrodialytic treatment in three compartment and multicompartment electrodialysers with copper plate as cathode and platinum foil as anode, cellophane paper being used as semi-permeable membrane. Influencing process parameters, current density, pulp consistency and residence time were studied and optimised. For all systems, deashification pattern was observed to be asymptotic in nature giving increased initial rate followed by considerable drop. Electrical energy consumption was increased considerably beyond fifty percent deashification level in case of bagasse and hardwood pulp samples, while for cotton linter pulp, economical deashification level was reached at above seventy percent deashification level. Electrodialytic treatment was found to have pronounced effect on the removal of extractive content from cotton linter pulp, along with deashification.

INTRODUCTION

One of the bottlenecks in the manufacture of finer grades of pulps to be utilized for rayon and filter paper grade, is due to ash and other cationic impurities. In spite of two stage pulping followed by elaborate screening, washing and multistage bleaching (upto seven to eight stages), it becomes difficult to remove cationic impurities below a certain level required for the same. This problem is particularly acute when dissolving grades of pulp are made based on high silica content cellulosic raw materials like bamboo, bagasse etc.

Electrodialytic treatment of cellulose pulps were suggested by Kantor[1] for the reduction of ash content. Investigations carried out by Korolev and Kitaeva[2] indicated feasibility of removing considerable amount of ash content of pulp by electrodialysis (ED) treatment. Voluminous work[3-6] carried out recently on the versatility of the ED technique in the field of black liquor fractionation indicated possibility of its application in the field of de-ashification of cellulose pulps. Availability of synthetic membranes having sufficient degree of mechanical sturdiness and selectivity has rendered the electrodialytic technique feasible on commercial scale.

An attempt has been made in the present work to study the feasibility of deashification of different pulp systems having higher silica content by electrodialytic treatment.

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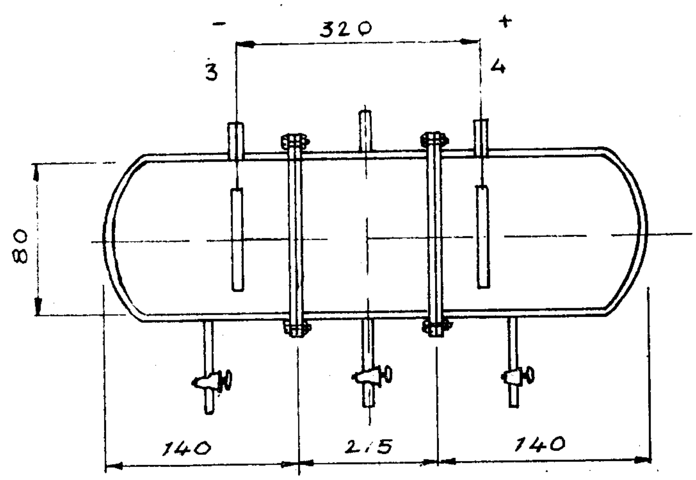

FIG 1 THREE-COMPARTMENT ELECTRODIALYZER

NO	NAME OF PART	MATERIAL	NOS
1	ELECTRODIALYZER	PERSPEX/ GLASS	1
2	FLANGES	C. I.	4
3	CATHODE	COPPER	1
4	ANODE	PLATINUM OR GRAPHITE	1

All dimensions in mm

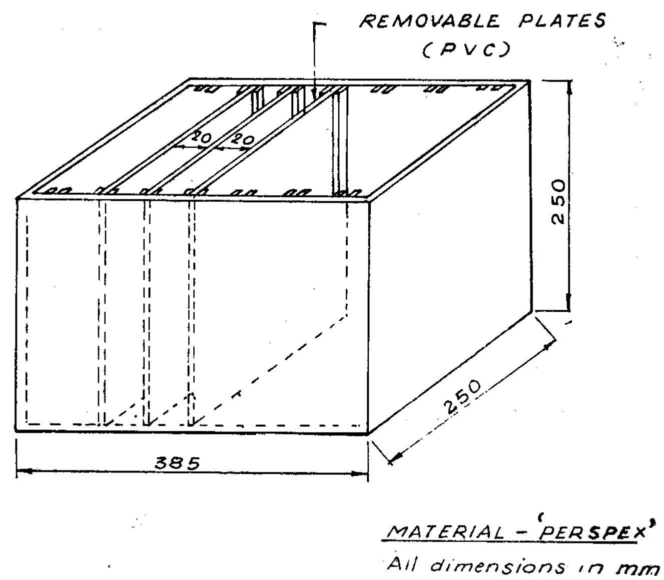

FIG 2 MULTI COMPARTMENT ELECTRODIALYZER

PLAN OF THE WORK AND EXPERIMENTAL PROCEDURES

Experimental investigations were carried out in a three compartment electrodialyzer as per fig. 1 and confirmed in multi-compartment unit according to fig. 2. The ED unit consisted of perspex compartments, with copper plate as cathode, and platinum as anode plate, separated from the middle compartment by cellophane paper as membrane. The pulp sample was taken in the middle compartment and subjected to electrodialysis by applying D.C. voltage across the two electrodes. Deashification rate was measured by taking out pulp samples at an interval of 1/2 to 1 hr. and analysed with regard to ash content according to TAPPI standard procedure.

The following influencing process parameters were studied during ED operation and optimum conditions arrived.

(i) Current density
(ii) Pulp consistency
(iii) Residence time

The effect of electrodialytic treatment upon the degree of deashification was studied for the following systems:

(i) Mixed hardwood pulp
(ii) Bagasse pulp
(iii) Cotton linter pulp

Mixed hardwood pulp was obtained from Gwalior Rayon Ltd., Nagda. Bagasse pulp was made in the laboratory by soda pulping and conventional bleaching. Cotton linter pulp (second cut) was prepared in the laboratory by soda cooking in presence of 'surf' as surface active agent.

Analytical procedures for the estimation of lignin, pentosans, and extractive content was in accordance with TAPPI standard procedures.

RESULTS AND DISCUSSION

Different systems were subjected to electrodialytic treatment in order to study the following objectives.

(1) The effect of electrodialytic treatment on the removal of cationic impurities present in various pulp systems.
(2) To study the effect of ED on the removal of anionic impurities, and neutral substances including lignin, pentosan, extractives and other acid radicals.
(3) Optimisation of process parameters which influence the electrodialytic deashification of pulp.
(4) To study the effect of degradation, if any, in terms of reduction of pulp viscosity during ED treatment.

System A: Mixed Hardwood pulp sample

The pulp samples as per the analytical report consists of the following:

% ash	—0.34
% Pertosam	—3.5
% Resins and fats	—0.3
Viscosity, CP	—13.0

Optimization of current density

The ED treatment of pulp sample under different current densities is presented in fig. 4. It indicates

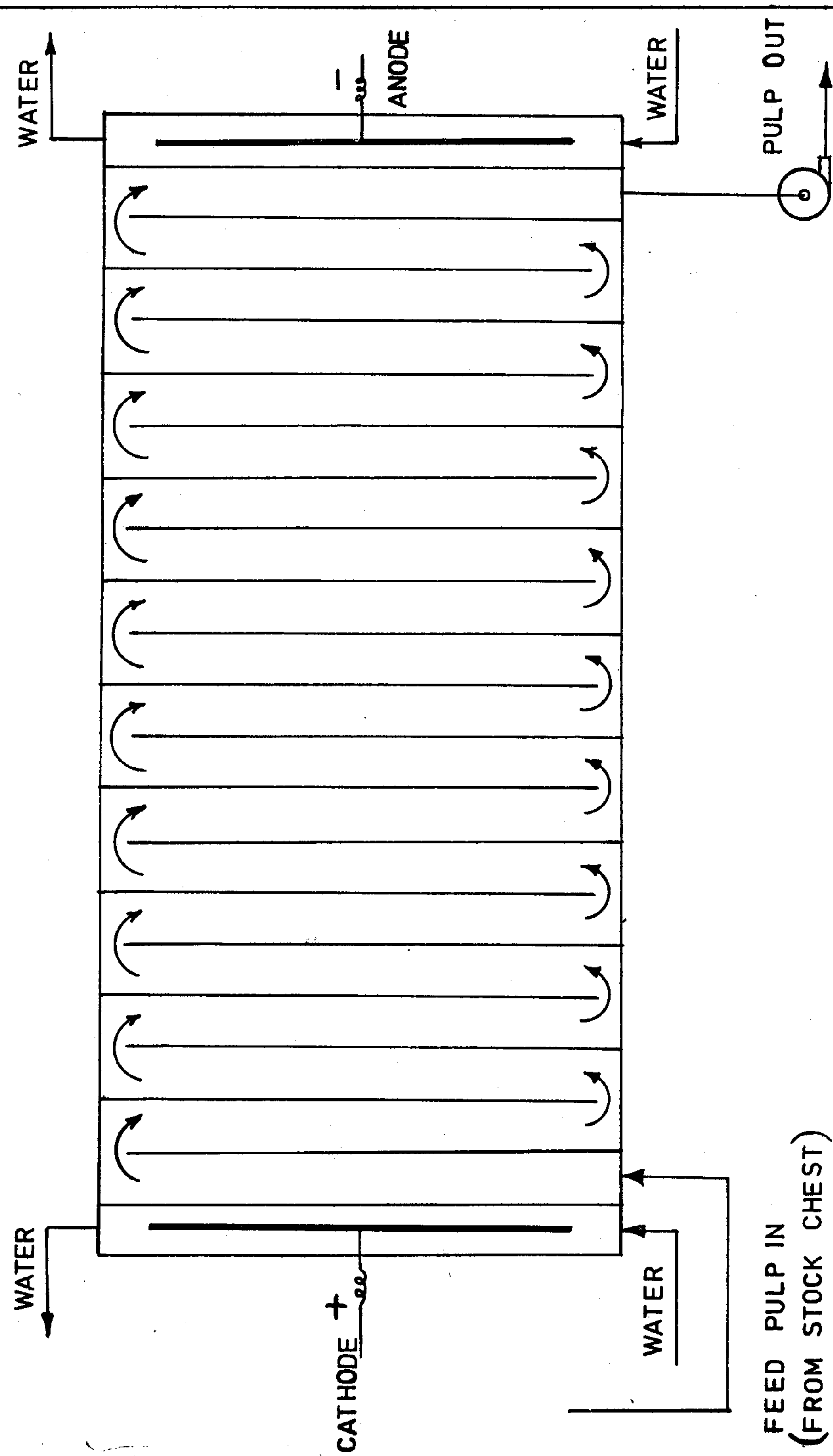

FIG. 3 **MULTICOMPARTMENT ELCTRODIALYSER**

increased deashification rate with ED time which after reaching to a maximum value assumes asymptotic nature. This pattern is observed upto the current density of 5 m A/cm^2 beyond which the deashification rate falls down and again assumes asymptomatic shape. As for example when current density is increased from 2 to 5 m A/cm^2, deashification rate is increased from 30 per cent to 42 per cent after one hour's electrodialytic treatment. After subjecting it to 2 hrs. ED time deashification rate is increased from 37 per cent to 52 per cent while after 3 hrs. operation deashification figures are 40 per cent and 54 per cent. It is indicated from the same figure that beyond a current density of 5 m A/cm^2 for the sample under study deashification rate is lowered and that is mainly attributed to concentration polarisation mechanism of which may be explained as follows:

Concentration polarisation starts when current density goes above the limiting current density (^{i}lim) which is reached when ion starvation takes place at the interface between the membrane and the solution. This results from the ions being removed electrically through the membrane at a faster rate than, they can be replenished from the bulk of the solution by diffusion, mixing or electromigration in the solution. Due to this effect a concentration gradient is built up (fig. 5).

For practical purpose this gradient may be considered to be effective over a small distance δ extending into the bulk of the solution which can be assumed to be of uniform concentration, δ being defined as the thickness of the diffusion layer and has been determined for various types of electrode processes. From theoretical consideration limiting current density can be estimated from the following expression:

$$^{i}lim = \frac{DF \cdot C_s}{(1-t_s^+)}$$

where

D= Diffusion constant of cation in soln. (equiv./cm^2 per unit concentration gradient)

F= Faraday constant

t_s^+= Transport number of cations in solution.

Significance of this expression is that ^{i}lim represents the largest current density which can be employed for the process in question i.e. the diffusion of the cations under consideration through the cathode membrane if it is assumed that δ remains constant.

The current can exceed ^{i}lim but if it does so polarisation occurs. The potential will increase to a value which permits other energetically less favourable process to take place. As the current increases above ^{i}lim the extra current will at first be carried by anion passing through the cathode membrane and vice versa, thus the overall current efficiency (with respect to the desirable process) is decreased considerably. At yet higher current densities current will be carried by hydrogen and hydroxyl ions from the dissociation of water. It seems probable that limiting current density is reached during deashification of pulp suspension when current density is increased beyond 5 m A/cm^2.

The higher the applied current density lower is the cell area to achieve the desired degree of ion transfer (cation transfer during deashification) and therefore lower is the capital cost and cost for membrane replacement. On the other hand energy cost goes on increasing in proportion to the current density with respect to the removal of a particular ion. More over current efficiency drops down significantly at higher values of current density due to concentration polarisation as mentioned above.

Consequently there must be an optimum current density for each system including electrodialytic deshification of pulp systems which is the first and the most important variable that should be established experimentally.

Based on this it is recommended to use 5 m A/cm^2 as the optimum current density for the electrodialytic deashification within a practical limit. Experimental investigations indicate 2 hrs. ED time as the optimum value taking into consideration degree of deashification achieved.

Effect of pulp consistency on the degree of deashification

Influence of pulp consistency on the degree of deashification is shown in fig. 6. According to this deashification rate under different consistencies follows asymptomic path i.e. rapid deashification rate followed by considerable decreased rate. Pulp consistency was varied from 0.5 to 2 per cent and it was observed from the figure 6 that deashification rate was increased from 29 per cent to 5o per cent under similar electrodialytic conditions when the consistency is varied from 1 per cent to 1.5 per cent Referring to same figure it is evident that consistency higher than 1.5 per cent does not give any significant effect so far as the deashification rate is concerned. Decreased rate of deashification at higher consistency is attributed to higher density effect and the physical hinderance to the diffusing ion to either side. Taking all these factors into consideration it is concluded that 1.5 per cent consistency is recommended to be best suited for practical operation.

Since in a continuous electrodialytic operation size of ED unit is proportional to the residence time, additional degree of deashification obtained is insignificant as compared to the additional expenditure incur-

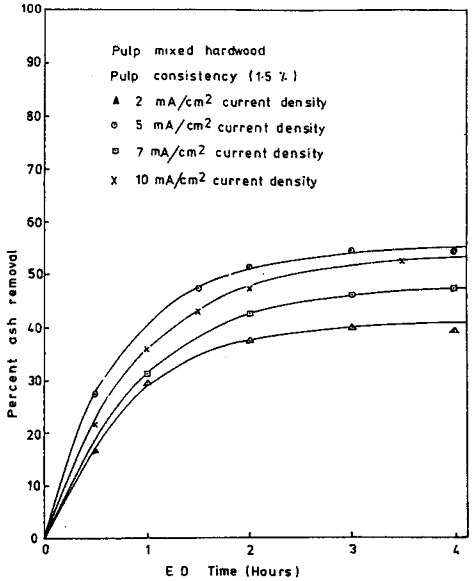

FIG 4 OPTIMIZATION OF CURRENT DENSITY DURING ELECTRODIALYSIS

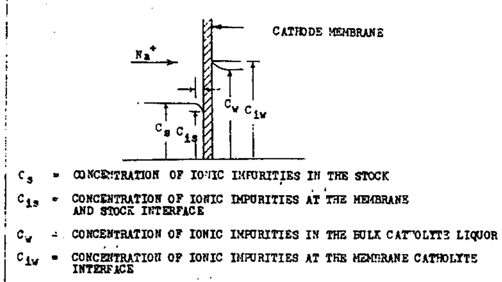

FIG. 5 CONCENTRATION PROFILES ACROSS THE CATHODE MEMBRANE

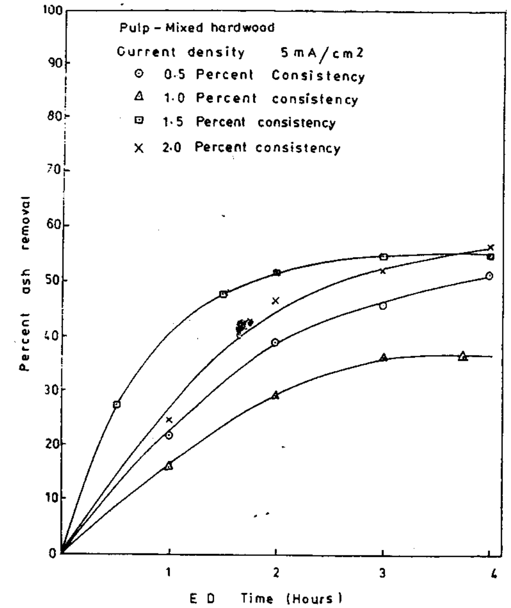

FIG 6 OPTIMIZATION OF PULP CONSISTENCY DURING E D

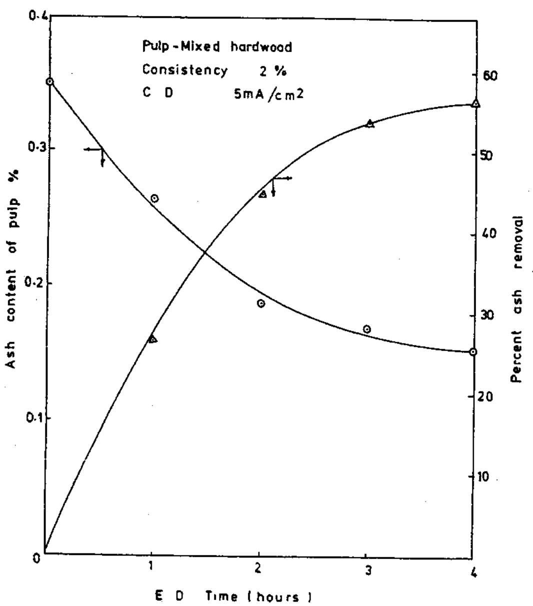

FIG 7 EFFECT OF E D TIME ON DEASHIFICATION OF PULP AND PERCENT ASH REMOVAL

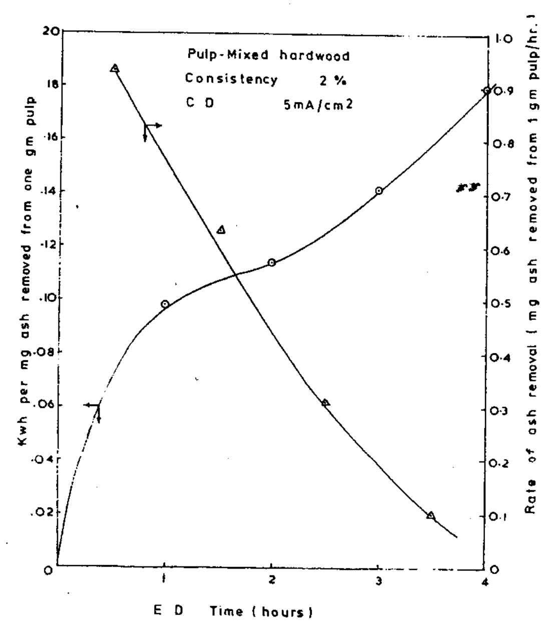

FIG 8 EFFECT OF E D TIME ON POWER CONSUMPTION AND DEASHIFICATION RATE

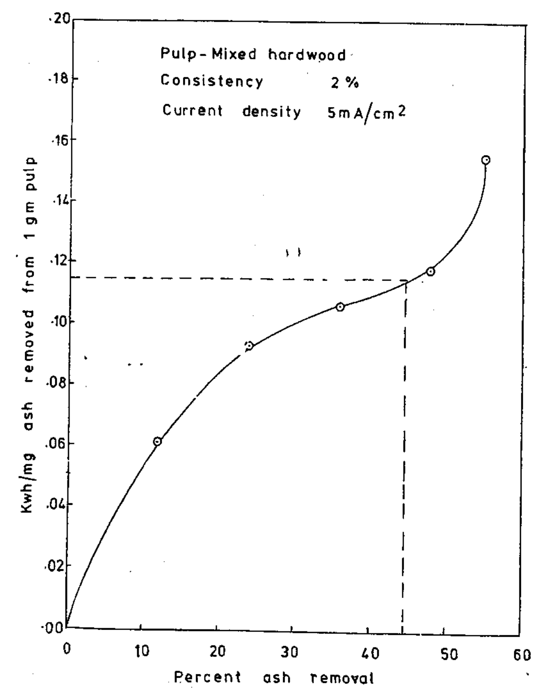

FIG. 9 EFFECT OF POWER CONSUMPTION ON THE DEGREE OF DEASHIFICATION

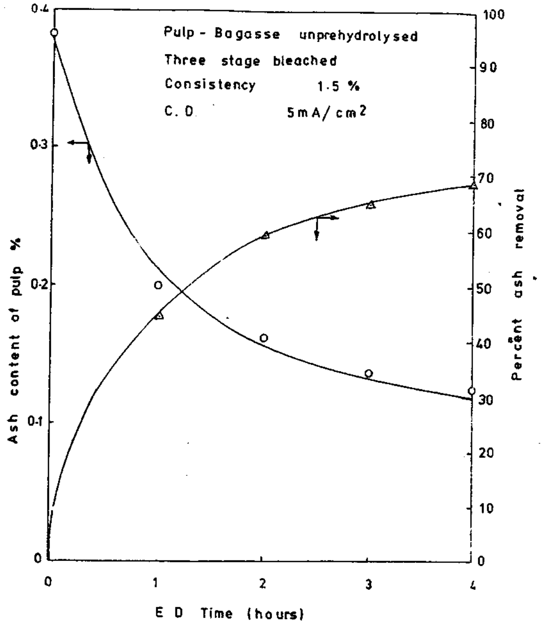

FIG.10 EFFECT OF E D TIME ON DEASHFICATION OF PULP AND PERCENT ASH REMOVAL

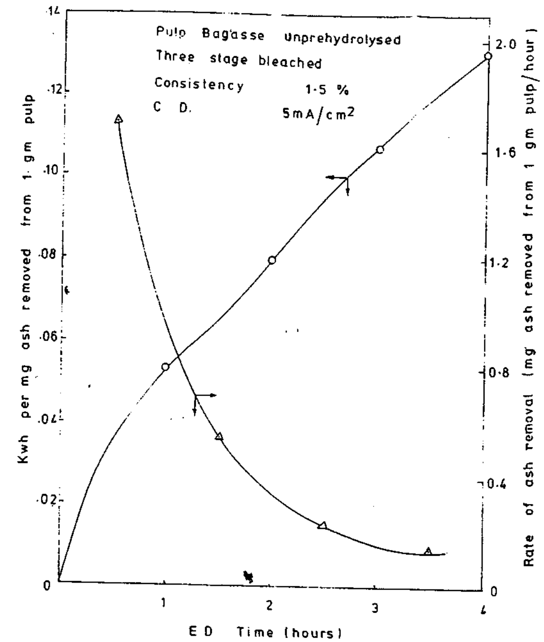

FIG. 11 EFFECT OF E D TIME ON POWER CONSUMPTION AND DEASHIFICATION RATE

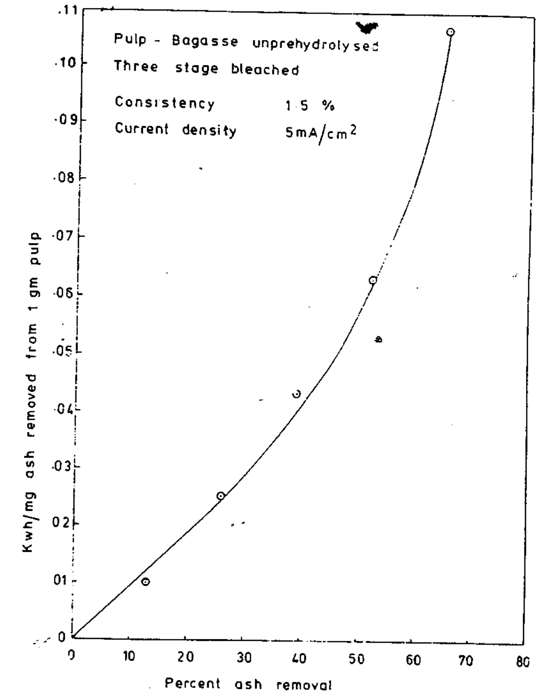

FIG 12 EFEECT OF POWER CONSUMTION ON THE DEGREE OF DEASHIFICATION

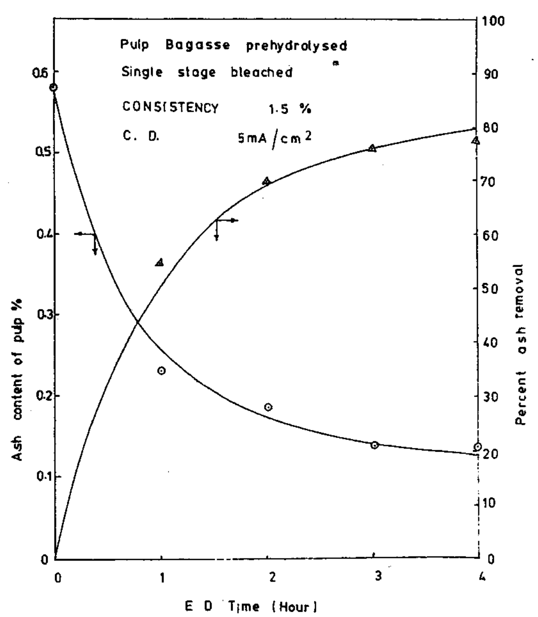

FIG.13 EFFET OF E D TIME ON DEASHIFICATION OF PULP AND PERCENT ASH REMOVAL

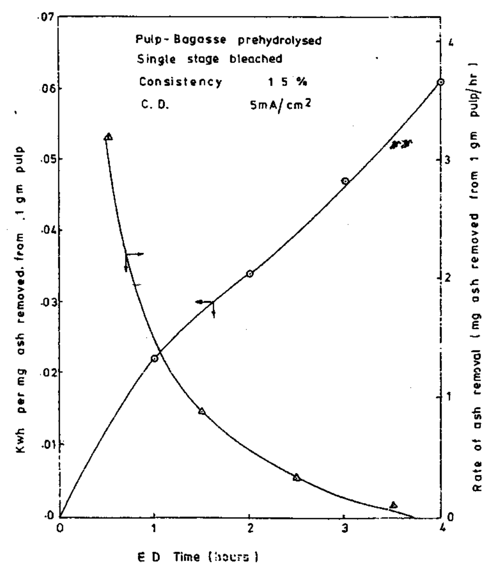

FIG. 14 EEFECT OF TIME ON POWER CONSUMPTION AND DEASHIFICATION RATE

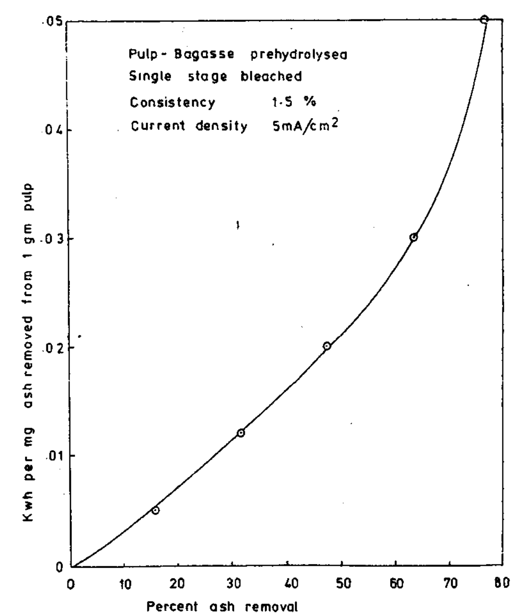

FIG. 15 EFFECT OF POWER CONSUMPTION ON THE DEGREE OF DEASHIFICATION

red in the installation of larger sized unit. As for example based on fig. 6 an additional 5 percent deashification is achieved by increasing the ED time from 1.5 to 2.5 hr. i.e. by increasing the residence time by 60 percent. Taking these factors into consideration it is suggested to have 1.5 hr. as the ED time to achieve the most economic level of deashification.

Pulp ash content and percent ash removal data under optimum electrodialytic condition for mixed hardwood pulp is presented in fig. 7. It is evident from this figure that deashification level required for rayon grade pulp i.e. pulp ash content of 0.15 percent can not be achieved within the practical limit of ED residence time.

Power consumption during deashification by ED is presented in fig. 8 and 9. By referring to fig. 9, it is evident that beyond a deashification level of 48 percent power consumption per unit (mg.) is increased tremendously. As for example power consumption at 48 percent deashification is 0.11 KWh while at 56 percent deashification power consumption is increased to 0.15 i.e. power consumption is increased by 40 percent while deashification is improved by only 16.5 percent.

System B: (i) Bagasse pulp by alkali boiling (without prehydrolysis) following by three stage bleaching (C-E-H):

Deashification degree in terms of reduction of ash content in pulp together with percent ash removal during electrodialysis operation is presented in fig. 10 while power consumption under different degree of deashification is shown in figure 11 and 12. By referring to these figures it is evident that deashification and power consumption follow similar pattern as is observed in case of mixed hardwood. Based on similar considerations it is advisable not to go beyond 45 percent deashification level and ED time of 2 hrs. because of rapid increase in power consumption and rapid fall of deashification rate after 45 percent deashification.

In case of bagasse pulp obtained by acid prehydrolysis followed by alkaline boiling and one stage bleaching (hypochlorite) deashification curve is found to be of similar nature i.e. initial rapid rate of deashificaion followed by considerable decrease beyond 45 percent ash removal. When power consumption figure for this system (fig. 14) is compared with that of unprehydrolysed bagasse pulp (fig. 11) under similar electrodialytic conditions it is observed that there is pronounced decrease of electrical energy requirement. By referring to fig. 12 and 15, it is seen that power requirement in case of unprehydrolysed pulp is of the order of 0.057 KWh/mg ash removed at 50 percent deashification level, while energy consumption is found to be 0.021 KWh/mg ash in case of prehydrolysed pulp under similar electroliadytic conditions. Based on these experimental investigations and their comparative evaluation it is concluded that electrical energy requirement could be decreased enormously to achieve same degree of deashification if bagasse pulp is obtained after prehydrolytic treatment.

System C: Cotton Linter (second cut) pulp obtained by soda pulping in presence of 'Surf' as surface active agent followed by one stage (hypochlorite) bleaching:

Rate of deashification and power consumption under optimum electrodialytic conditions is presented in fig. 16 and 17. These experimental results indicate that deashification follows two step pattern i.e. initial rapid rate followed by rapid fall. When these data are compared with that of other systems reported earlier cotton linter pulp is found to have higher rate of deashification. It is also significant that deashification level can be reached beyond 70 percent within the electrodialytic time of 2 hrs. With regards to electrical energy consumption during ED it is observed that cotton linter pulp requires considerably smaller amount of power as compared to other systems. By referring to these figures power requirement is found to be .0145 KWh/mg ash removal (fig. 18) as compared to .0210 in case of prehydrolysed bagasse pulp and .057 in case of unprehydrolysed bagasse pulp. Alongwith deashification during ED it is observed that considerable amount of extractive content is removed in case of cotton linter system. Based on this higher level of deashification and extractive removal, it seems it is possible to upgrade the cotton linter pulp for the manufacture of quantitative grade filter paper.

In order to study the effect of electrodialysis upon the quality of pulp with particular reference to degradation effect, if any, investigations were carried out to study the degradation effect in terms of reduction in pulp viscosity by using FeTNa as solvent and measuring the time of efflux through U tube viscometer ('B') for different concentrations of pulp solution. The results are plotted in fig. 19. According to this figure giving the relationship between reduced viscosity data before and after electrodialysis it is observed that degradation effect is negligible, since there is no decrease in the intrinsic viscosity of the pulp (intercept on yaxis).

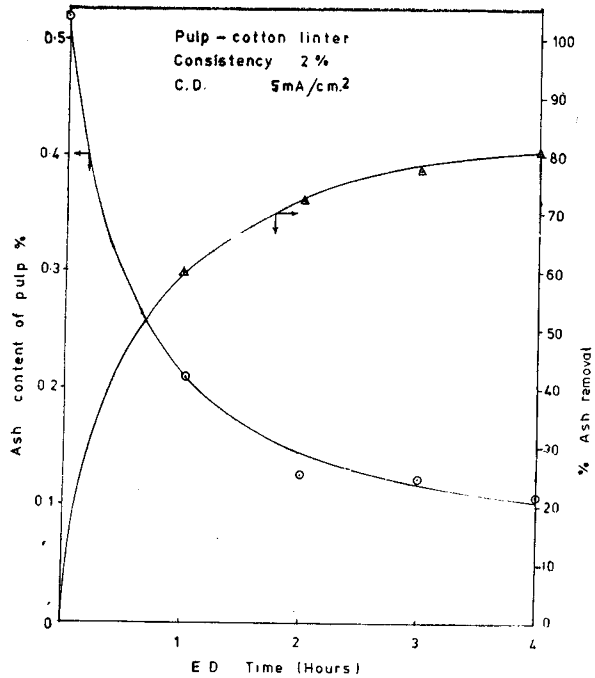

FIG. 16 EFFECT OF E D TIME ON DEASHIFICATION OF PULP AND PERCENT ASH REMOVAL

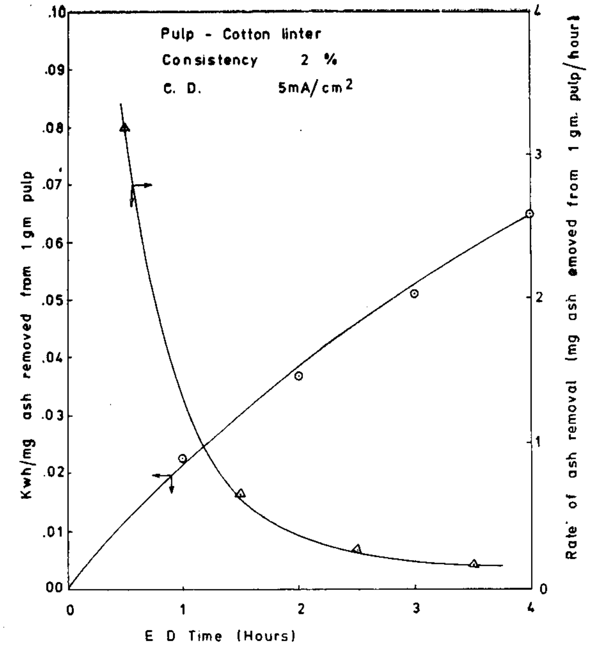

FIG. 17 EFFECT OF E D TIME ON POWER CONSUMPTION AND DEASHIFICATION RATE

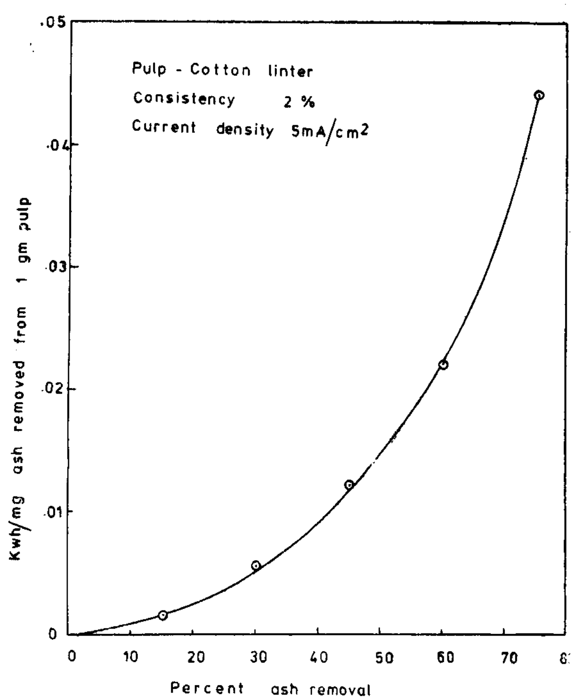

FIG. 18 EFFECT OF POWER CONSUMPTION ON THE DEGREE OF DEASHIFICATION

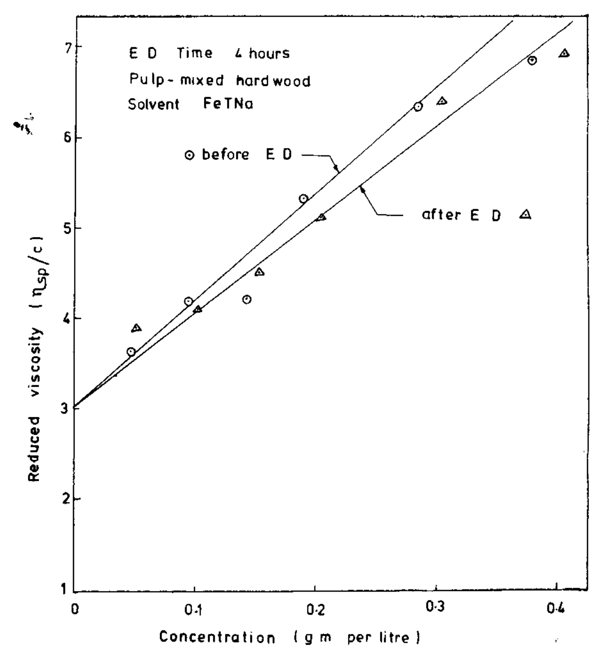

FIG. 19 EFFECT OF ELECTRODIALYSIS ON THE D P OF PULP

Working principle of a commercial electrodialysis unit for the deashification of pulp is explained diagrammatically in fig. 3. Optimum residence time, say 1-1/2 hr. is to be attained by passing the pulp suspension through diffrent compartments. separated between cathode and anode as shown in the figure.

CONCLUSIONS:

Based on the critical assessment of the experimental investigation on the upgrading of pulp by ED technique, the following conclusions are made.

(1) For electrodialytic deashification of pulp systems following optimum process conditions were observed.

  (a) Current density – 5 m A/cm^2
  (b) Pulp consistency – 1.5 percent
  (c) ED time – 1-1/2 hrs.

It is recommend to carry out further work on pilot plant scale to confirm optimum operating conditions obtained on bench scale experimental investigations which might be used to design the commercial electrodialysis unit for the upgrading of pulps.

(2) Deashification pattern during ED treatment follows in two steps initial rapid deashification rate followed by considerable decrease giving an asymptotic shape to the deashification curve.

(3) In case of bagasse and hardwood pulps deashification level beyond fifty percent is not practicable due to uneconomical deashification rate requiring high residence time.

(4) Cotton linter pulp furnishes over seventy percent deashification within a reasonable ED time of 2 hrs. giving pulp suitable for the manufacture of rayon and quantitative grade filter paper.

(5) Considerable reduction cover seventy percent) of pulp extractive content is observed in case of cotton linter during electrodialysis treatment.

(6) Degradation effect of ED on pulp quality is found to be negligible for all systems studied.

(7) Electrodialysis offers insignificant effect on the removal of pentosans and lignin contents of pulp.

(8) Acid prehydrolytic treatment before alkaline pulping renders bagasse pulp more amenable to electrodialytic treatment requiring considerably less amount of power consumption to achieve same degree of deashification.

ACKNOWLEDGEMENT

One of the authors (KKM) wishes to offer grateful thanks to the Director and the Head of the Chemical Engineering Department, Indian Institute of Technology, Bombay, for giving financial support in the form of a Post Graduate Scholarship, resulted in the completion of a research project, a part of which is presented in the present communication.

REFERENCES

1. Kantor, L.A., 'Reduction of Ash content and Partial Bleaching of Sulfate Cellulose through Electrodialysis' Bumazh Prom., **18,** No. 12, 16-20 (1940) (C.A. Vol. 38, 1944, 16387).
2. Kitaeva, S. Kh. and Korolev, V.V., 'Deashing Pulps by means of electrodialysis', (Moscow Fillial Central Paper Research Inst.); Bumazh. Prom., **32,** No. 6, 4-7 (1957) C.A. Vol. 52, 1958, 3336f.
3. Mintz., M.S., Lacey, R.E., and Lang, E.W., 'Separation of Pulping Liquor Components with Electrodialysis Process', Tappi, 50, No. 3, 137-145 (1967).
4. Dubey, G.A., Mc Elthinney, T.R., and Wiley, A.J., 'Electrodialysis—a new unit operation for recovery of values from spent sulfite liquors' Tappi, 48, No. 2, 95-98 (1965).
5. Yean, W.Q., and Goring, D.A.I., 'The separation of Lignin Sulfonates from Hemicelluloses by Electrophoresis convection', PPRIC Tech. Report No. 328, May 1963, Tappi, Vol. 47 16 (1964).
6. Joshi, V.S., Ph.D., Thesis; Chemical Engineering Deppt., Indian Institute Technology, Bombay (1970).