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**INFLUENCE OF IONIC STRENGTH AND pH  
OF DISPERSED FEEDS ON MICROFILTRATION**

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*The influences of particle shape,  $\zeta$ -potential and size with change of pH and ionic strength on permeate flux during the microfiltration of model dispersions (two different china clays with mean particle sizes 3.5  $\mu\text{m}$  and 1.5  $\mu\text{m}$ ) on flat sheet ceramic membranes ( $\text{ZrO}_2$ , mean size of pores 0.2  $\mu\text{m}$ ) have been studied. The experimental filtration system and the dispersion characterisation experiments are presented. The results of the experiments show that  $\zeta$ -potential of the particles has considerable impact on the magnitude of the cake resistance and hence on the permeate flux. The effects are especially pronounced during the microfiltration of dispersion in the area close to isoelectric point of dispersion, where the dispersion has tendency to instability and the particles tend to aggregate. The effects resulted in higher porosity filter cakes (deposits) and a lower value of filter cake resistance, and hence to a permeate flux that increased to double the value of a non-treated dispersion. These observations are caused by the particle interactions.*

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## Introduction

The influence of particle properties on the filtration of dispersions has long been recognised [1–6]. Studies of many different aqueous dispersions have established that the characteristic properties of the feed such as particle charge [7–9], particle size distribution [10] and particle shape [11–14] can all influence filterability. Crossflow membrane processes for liquid feed streams are complicated by the phenomena of membrane fouling and of concentration polarisation in the liquid boundary layer adjacent to the membrane surface. Concentration polarisation and membrane fouling are major concerns in the successful use of a membrane based separation operation, as their net effect is reduction of permeate flux, which results in loss of productivity. Therefore, it is important to reduce or control concentration polarisation and fouling in membrane processes and to enhance the permeate flux.

There are many methods to reduce the effects of fouling. One of them is based on influencing the electrical interaction between particles. The pH value has significant influence on permeate flux, especially in the proximity of isoelectric point (IEP) of some colloidal dispersions, where they have a tendency to be unstable and hence sediment. The effects of pH and salt concentration on microfiltration permeate flux have been reported by a number of researchers.

Kwon *et al.* [15,16] investigated the thickness of the double diffuse layer and its influence on microfiltration. They found that the thickness of the double diffuse layer is closely related to the ionic strength of the solution. Elzo and Huisman [17] filtered silica particles with a mean size of 0.5  $\mu\text{m}$ , using inorganic membranes (mean pore size of 0.2  $\mu\text{m}$ ) made of  $\alpha\text{-Al}_2\text{O}_3$ . They studied the influence of some physical-chemical factors (e.g. pH, salt concentration and its valence) on the permeate flux, and found that permeate flux depended on the surface charge of the dispersed particles and on the surface charge of the membrane surface. They concluded that the isoelectric point causes a decline of the permeate flux. Huisman *et al.* [18] studied the influence of  $\zeta$ -potential of three different ceramic membranes ( $\text{Al}_2\text{O}_3$ ,  $\text{ZrO}_2$  and  $\text{TiO}_2$ ) on the process of microfiltration of silica particles. They performed measurements for two values of pH, thus using two  $\zeta$ -potentials; one solution was acid and the other alkaline. They found that the  $\zeta$ -potential of neither the dispersion nor the membrane surface influenced microfiltration.

The aim of this study is to determine which operating parameters are involved in flux enhancement and to establish a link between electrochemical parameters, shape of particles and cake resistance.

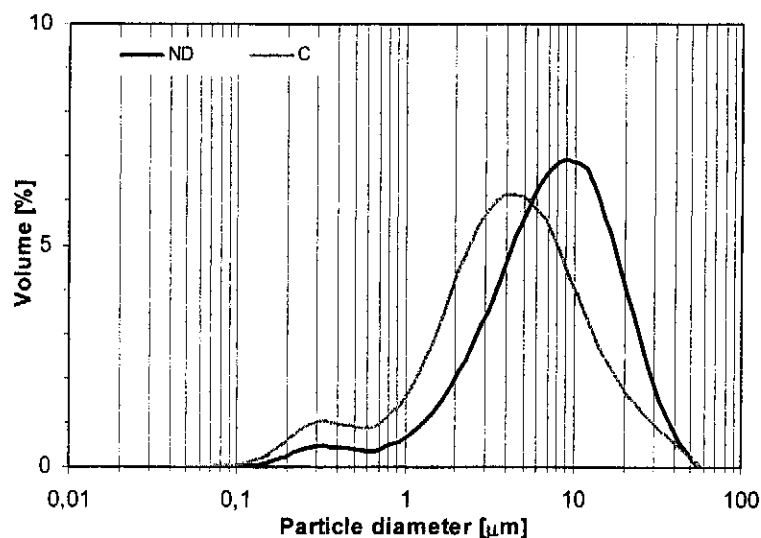


Fig. 1 Particle size distributions of non-treated china clay dispersions

## Experimental

### Membranes

The membranes used in the filtration experiments were flat sheet ceramic membranes. They consisted of thin layer of  $ZrO_2$  deposited on the surface of an Inconel support mesh (these were originally supplied under the trade name Ceramesh). The characteristics of the membrane are: length,  $L = 0.06$  m; width,  $W = 0.04$  m; nominal pore size,  $d_p = 0.2$   $\mu\text{m}$ ; mean membrane resistance,  $R_m = 6 \times 10^{11}$   $\text{m}^{-1}$  (obtained from water flux measurements) and membrane surface area,  $A_m = 2.4 \times 10^{-3}$   $\text{m}^2$ . A new membrane was used in each experiment, and before each run the pure water flux was measured with deionised water.

### Dispersions

The microfiltration experiments were carried out with an aqueous dispersion of two different china clays. The trade names (ND and C) of each china clay are used as the identifier. Dispersions were prepared by mixing the dry powder into deionised water in an ultrasonic bath. The pH values were adjusted using hydrochloric acid, and the ionic strength was changed by using  $\text{Na}_3\text{PO}_4$  which is also a dispersant for the china clay. The concentration of dispersant was 0.5 % w/v.

Figure 1 shows the particle size distributions of both types of china clay when dispersed in water with no chemicals added.

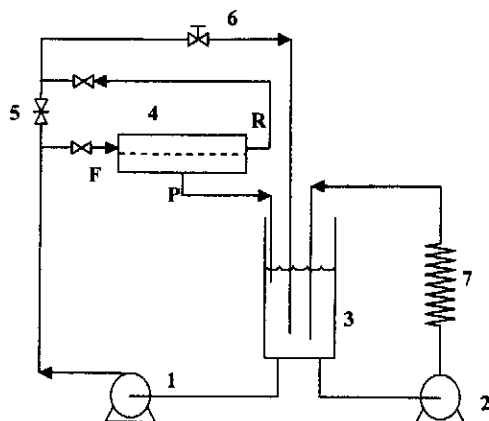


Fig. 2 Scheme of filtration apparatus: 1 – peristaltic pump; 2 – membrane pump; 3 – stock tank; 4 – membrane module; 5 – bypass valve; 6 – needle valve; 7 – heat exchanger; F – feed; P – permeate; R – retentate

### Filtration Experiments

The microfiltration experimental apparatus used is shown schematically in Fig. 2. The circulating loop was constructed of stainless steel and contained a fifteen litre feed suspension reservoir, pump and the membrane module. This loop was also equipped with a pressure and flow monitoring system. The crossflow velocity was controlled using the speed of the pump, and the operating pressure (and hence trans-membrane pressure) in the loop was controlled by a needle valve downstream of the filter unit; both parameters were varied independently. The second flow loop was used for regulating the temperature of the suspension.

In the experiments, two different china clay suspensions were used, each with a concentration of 5 % by weight at various pH and with or without surfactant,  $\text{Na}_3\text{PO}_4$ . During all the tests, the filtration was run at a constant crossflow velocity of  $1 \text{ m s}^{-1}$  and a constant pressure of either 100 or 200 kPa.

Before each filtration experiment the resistance of membrane was measured. The membrane was placed into the membrane module, and deionised water was circulated in the test loop at a pressure 100 kPa and a velocity of  $1 \text{ m s}^{-1}$  for about 30 minutes. During this time a stable value of the permeability of the membrane to water was observed. From the measured permeate flow rate, the membrane resistance  $R_m$  was calculated from

$$R_m = \frac{\Delta P}{\mu_p J_w} \quad (1)$$

where  $\mu_p$  is dynamic viscosity of the permeate,  $J_w$  is the permeate flux for deionised water and  $\Delta P$  is the transmembrane pressure.

After this measurement, the dispersion was placed into the reservoir and the filtration was started, the operating pressure as well as feed velocity were adjusted by the regulation system. The stock dispersion was kept at a constant temperature of 25 °C. The permeate flux was measured every 5 minutes during the first hour, and every 10 minutes during the second hour. The experiment was stopped after obtaining a constant permeate flux. The adjustment of pH value was performed 18 hours before the filtration experiments, to allow stable equilibration conditions to be reached in the dispersion (that is, an equilibrium state of particle-particle interactions). After each set of experiments the unit and the membranes were rinsed with deionised water and the pure water flux was measured again under the conditions of initial test until the steady state was attained. From this value the membrane resistance was calculated again. The fouling tendency of the membrane can be calculated from the difference between the two resistances (that is the “before” and “after” filtration resistances). However, our membranes showed no fouling.

The total filtration resistance  $R_t$  was calculated from

$$R_t = \frac{\Delta P}{\mu_p J_\infty} \quad (2)$$

where  $J_\infty$  is the steady state permeate flux. The difference between the total filtration resistance and the membrane resistance is filter cake resistance  $R_c$ .

### Particle Size and $\zeta$ -Potential Measurements

The particle size distributions were measured using a MasterSizer (Malvern Instrument Ltd., UK).

The  $\zeta$ -potential measurements were carried out on a ZetaSizer (Malvern instrument Ltd., UK). The stock dispersion was diluted to the concentration of 1 kg m<sup>-3</sup> using permeate, in order to retain the same solution conditions (pH, salt concentration) that existed during filtration. The  $\zeta$ -potential of the particles was calculated from a measurement of the electrophoretic mobility using

$$\zeta = \frac{\mu u}{\varepsilon_0 \varepsilon_r} \quad (3)$$

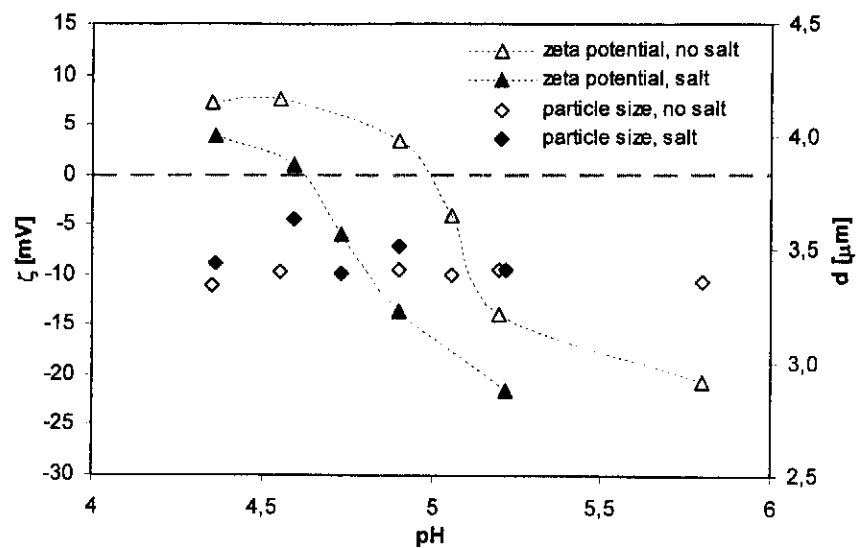


Fig. 3 Influence of pH value on  $\zeta$ -potential and particle size of ND china clay

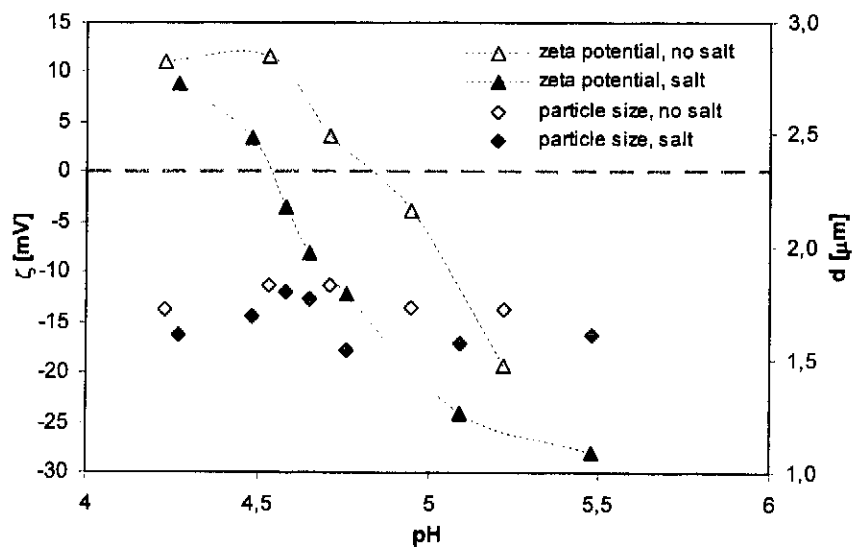


Fig. 4 Influence of pH value on  $\zeta$ -potential and particle size of C china clay

where  $u$  is the mobility of the particles,  $\mu$  is the dynamic viscosity and  $\epsilon_0$  and  $\epsilon_r$  are permittivity of free space and relative permittivity of the liquid.

## Results and Discussion

All the data are plotted for both china clays separately. The experiments focussed on the areas close to isoelectric point of the dispersions; hence the range of pH value used was from 4 to 6 for both china clays.

### Particle Size and $\zeta$ -Potential Measurements

The results obtained are plotted as the  $\zeta$ -potential and particle size vs. the pH range. From Figs 3 and 4 we can observe that the  $\zeta$ -potential of each dispersion was strongly dependent on the pH value of dispersion. Further, the added salt ( $\text{Na}_3\text{PO}_4$ ) can move the isoelectric point. The influence of pH value on the particle size was negligible.

Figure 3 shows the  $\zeta$ -potential and particle size of ND china clay particles, with and without salt. From this figure is seen that the IEP of non-treated ND china clay is about pH 5; after adding the  $\text{Na}_3\text{PO}_4$ , the IEP reduced towards a more acid solution at pH 4.6. The influence of pH on particle size is again small; the average particle size is about 3.5  $\mu\text{m}$ .

Figure 4 shows the  $\zeta$ -potential and particle size of china clay C particles, with and without salt. The particle size of this dispersion is smaller, about 1.7  $\mu\text{m}$ . However, there are some influences of pH on the value of the particle size, which increased slightly in area close to the IEP. The IEP of the non-treated dispersion was about pH 4.8 and after adding the salt the isoelectric point reduced to pH 4.5.

### Filtration Experiments

Figures 5 and 6 show the results from the crossflow microfiltration experiments performed at various pH values for non-treated and treated dispersions. The results are plotted as the steady state value of permeate flux vs. the pH.

As can be seen in Fig. 5, all the data curves show similar trends. All curves have a maximum permeate flux at the isoelectric point of the dispersion. At negative  $\zeta$ -potentials, less than about  $-20$  mV, the filtration pressure conditions did not affect permeate flux significantly. The difference between permeate flux values at the different pressures increased around the IEP of the dispersion for both treated and untreated dispersions. The dispersion was unstable close to the IEP, which is probably the reason why the value of permeate flux increased. The effect of the salt treatment was to reduce the permeate flux, which coincided with a reduction of the zeta potential through salt addition (Fig. 3). The particle-particle and particle-membrane interactions around the IEP have considerable influence on microfiltration processes, especially on the creation of filter cake; in conven-

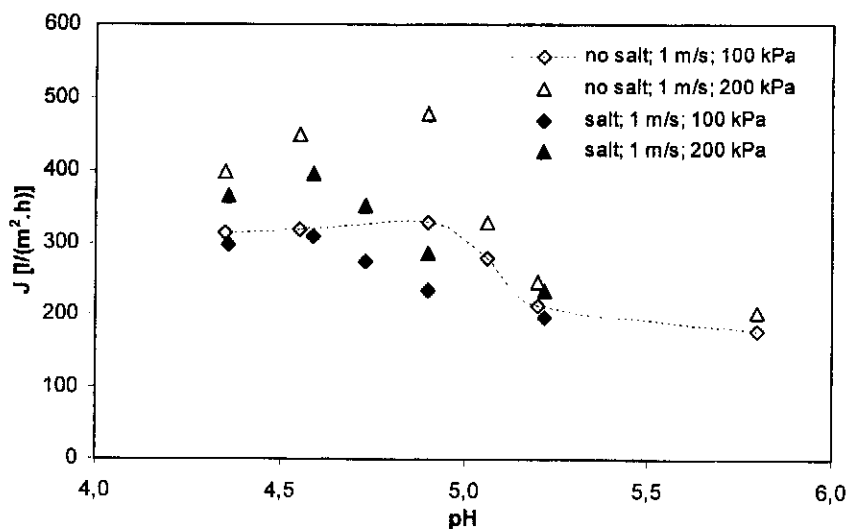


Fig. 5 Influence of pH value on steady state permeate flux (ND china clay)

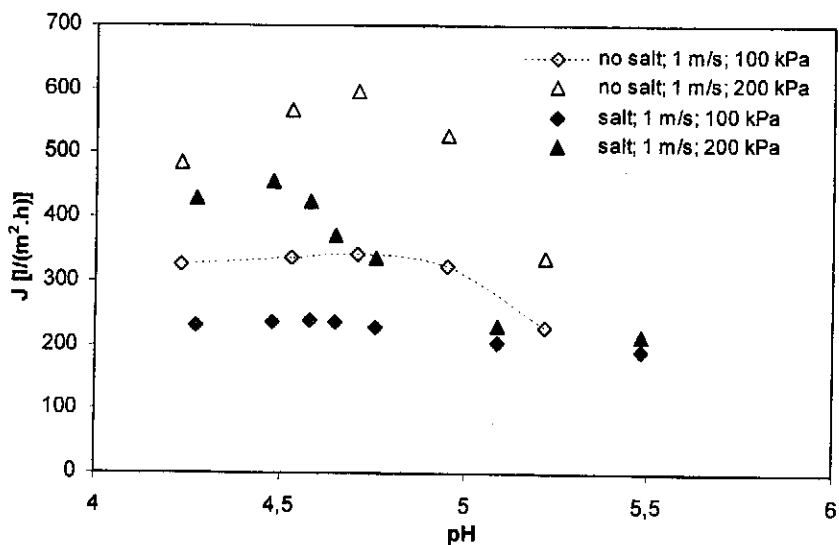


Fig. 6 Influence of pH value on steady state permeate flux (C china clay)

tional filtration, filtering a dispersion close to its IEP is known to lead to a bulkier (more porous) cake that possesses a higher permeability [19].

Figure 6 shows the influence of pH on the steady state permeate flux for china clay C. Although the general trends are similar to those observed for the ND



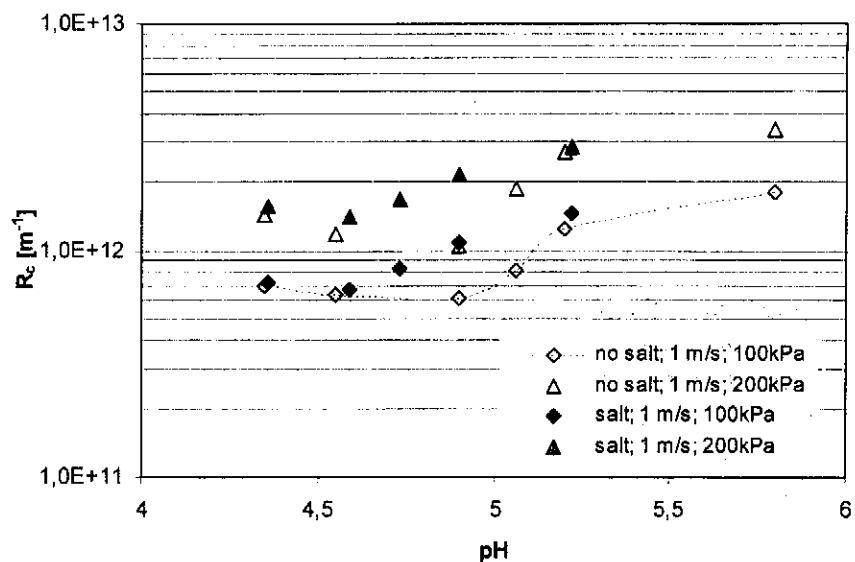


Fig. 7 Influence of pH value on filter cake resistance (ND china clay)

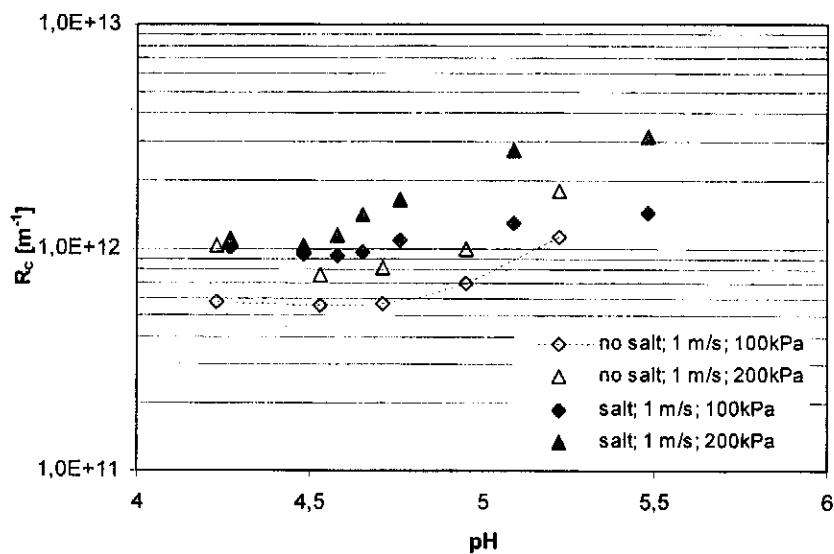


Fig. 8 Influence of pH value on filter cake resistance (C china clay)

clay, it can be seen that the permeate flux is nearly constant when filtering the salt treated dispersion at a pressure of 100 kPa. At higher pHs, the zeta potential again overcomes the effect of the presence of salt and causes the steady state fluxes to be similar for treated and untreated feeds. At lower pHs, salt treatment causes a

flux reduction. Since Fig. 4 shows no aggregation effect closer to the IEP, it seems likely that the surface chemistry of the clay and the resultant particle-particle interaction had a dominant influence on filter cake structure for treated suspensions.

### Filter Cake Resistance

Figures 7 and 8 show the influence of pH and ionic strength on the resistance of the filter cake for both china clay dispersions.

The effects of pH, salt addition and transmembrane pressure show similar trends. The minimum value of the filter cake resistance occurred in the proximity of the IEP for each clay. This phenomenon is caused by the particle interaction where the particles have the least tendency to disperse; close to the IEP the dispersion had a tendency to be unstable (although Figs 3 and 4 show no significant aggregation). However, the weak repulsion between the particles apparently resulted in higher porosity filter cakes and thence to a lower value of filter cake resistance (a phenomenon that is well known in cake filtration [19]).

### Influence of $\zeta$ -Potential on Permeate Flux

Figure 9 shows the flux decline curves for non-treated china clay ND and for the

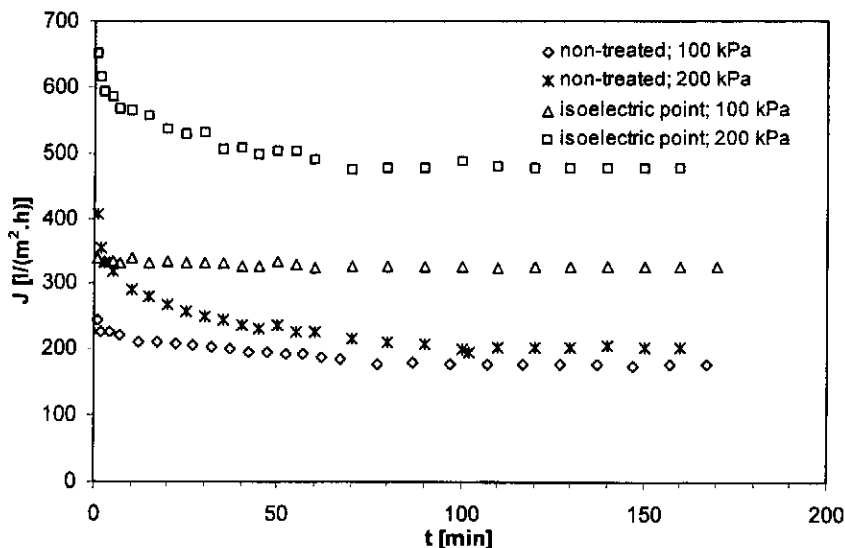


Fig. 9 Influence of  $\zeta$ -potential value on permeate flux (ND china clay; no salt)

same dispersions at their IEP. At the IEP, the rate of filtration was roughly double the rate for the non-treated dispersion at its natural pH. At the IEP the steady state flux also tends to be reached more rapidly, indicating that an equilibrium thickness of deposit was formed faster.

## Conclusion

The results of the experiments show that the  $\zeta$ -potential of particles has important effects on the permeate flux. This is especially pronounced during microfiltration of the dispersion when it is close to its isoelectric point, when the value of permeate flux increased to about double the value of non-treated dispersion. This is due to the particle interactions; close to the isoelectric point the dispersion had a tendency towards instability although no particle aggregation was evident. It resulted in either deposition of a lower thickness of cake or of one with a higher porosity, thereby leading to higher values of permeate fluxes and lower filter cake resistances.

## Acknowledgements

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## Symbols

$A_m$	membrane surface area, $m^2$
$d_p$	nominal pore size, m
$J_p$	permeate flux for deionised water, $m\ s^{-1}$
$J_\infty$	steady state of permeate flux, $m\ s^{-1}$
$L$	length of membrane, m
$\Delta P$	transmembrane pressure, Pa
$R_c$	filter cake resistance, $m^{-1}$
$R_m$	membrane resistance, $m^{-1}$
$R_t$	total filtration resistance, $m^{-1}$
$W$	width of membrane, m
$\epsilon_0$	permittivity of free space, $F\ m^{-1}$
$\epsilon_r$	relative permittivity of the liquid
$\mu$	dynamic viscosity of liquid, Pa s
$\mu_p$	dynamic viscosity of permeate, Pa s
$u$	electrophoretic mobility, $m^2\ V^{-1}\ s^{-1}$
$\zeta$	zeta potential, V

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