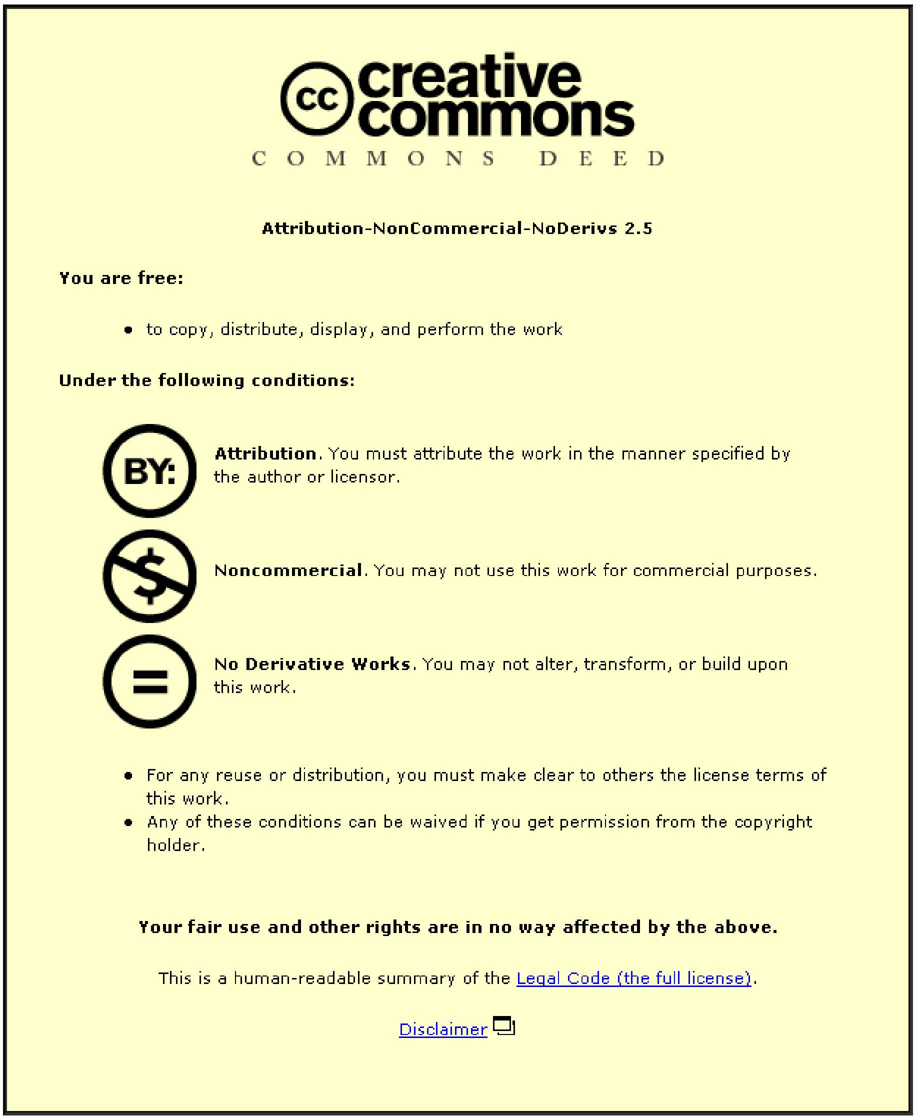

UNDERSTANDING FLUX DECLINE IN CROSSFLOW MICROFILTRATION – PART II: EFFECTS OF PROCESS PARAMETERS

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ABSTRACT

Further results from an experimental study of membrane fouling and permeate flux decline during crossflow microfiltration are presented. A computer controlled microfilter and a variety of well characterised particulate solids and polymeric membranes were used to acquire a range of data over typical operating conditions. Example data highlight influences of the process parameters filtration pressure, crossflow velocity, suspension concentration, and particle surface charge, and demonstrate the interdependence of the process operating conditions with particle size, size distribution and shape. Many of the results obtained are discussed with respect to existing literature data which are apparently contradictory, but the current data provides explanations for these contradictions and enable conclusions to be drawn.

KEYWORDS

Membranes; Fouling; Microfiltration; Pressure; Crossflow velocity; Particle properties

INTRODUCTION

This paper is the second in a series reporting the results from experimental and theoretical studies aimed at understanding fouling processes and their effects in crossflow microfiltration. Part I[1] presented experimental data which showed the various and complex interacting effects of particle size and size distribution and membrane pore size. The present paper delineates the roles of the main process parameters which, for this purpose, are the trans-membrane pressure difference (hereinafter referred to as the filtration pressure), crossflow velocity, and suspension concentration and pH. The effects of these parameters were also found to be dependent on particle size and size distribution, and cannot be discussed without reference to the particle properties. This highlights the interdependence of processing conditions on the basic properties of the particles and their surrounding fluid.

EXPERIMENTAL TECHNIQUES

Several particle systems, suspensions and polymeric microfiltration membranes were identified and characterised[1] for use in this work. The membranes chosen included track etched (e.g. Nuclepore PC), homogeneous cast (e.g. Sartorius CN) and asymmetric cast (e.g. Domnick Hunter Asypor) types; these were characterised in terms of pore size, pore shape and permeability through standard laboratory techniques[1,2].

The particles were chosen for their range of size, shape and surface charge characteristics. More complete descriptions of the characterisation procedures were provided in Part I[1]. The range of parameters studies for the work in this paper are summarised in Table 1 and Figure 1. The particulates showed 50% particle sizes ranging from 0.5 to 27.5 μm when dispersed in double distilled water and significantly differing surface charge characteristics depending on suspension pH (Figure 1). Both anatase and china clay are typical of relatively high surface charge materials and could be expected to show pronounced effects of surface charge when aqueous suspensions were microfiltered. Calcite and aragonite, however, are more typical of low surface charge solids

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when dispersed in aqueous media. Some difficulty was experienced in reliably measuring the electrophoretic mobility, and hence ζ-potential, of the calcite suspensions. It seems that the surfaces of calcite particles are extremely sensitive to even small changes in their solution environment. Factors such as ageing and suspension concentration have been reported to alter surface properties sufficiently to account for apparently similar suspensions exhibiting quite different surface charge characteristics, both in terms of sign and magnitude, when tested by different workers[3-6]. However, the data presented in Figure 1 for calcite are in accordance with the published literature and sufficiently reliable for the current purpose.

Leaf Filter Tests

Constant pressure leaf filter tests were performed to evaluate the compression characteristics of the test suspensions. For the lower pressure tests up to 410 kPa (60 psi) a conventional (constant) pressure driven leaf filter was used which comprised a 0.2 μm rated Sartorius CN membrane with an effective filtration area of 82 cm^2. The tests above 410 kPa (60 psi) were performed using a piston press operating at constant pressure. This apparatus comprised a vertically mounted cylinder having an internal bore of 43 mm and length 193 mm, with the base end closed by the semi-permeable membrane supported on a porous sinter plate[7,8]. Constant pressure was applied to the solid/liquid mixture in the cylinder by a pneumatic piston and the piston movement and volume of filtrate were recorded continuously. Data were obtained for all the suspensions over the pressure range 100 to 10,900 kPa (15 to 1600 psi) and analysed to give information such as specific cake resistance and voids ratio. For the suspensions tested the results showed that the magnitude of both specific cake resistance and voids ratio were dependent on the properties of the dispersed phase. Average specific cake resistance α_{av} was found to be largely independent of the concentration in the original feed and increased as the applied pressure Δp increased; the resulting correlations between α_{av} and Δp are shown in Table 2. Voids ratio generally decreased with an increasing applied pressure, and the magnitude of the voids ratio was also affected by the initial concentration of the feed suspension. For example, with anatase suspensions and otherwise identical experimental conditions, the value of cake voids ratio at the end of the consolidation phase was reduced from 7.8 to 1.2 as the feed concentration was increased from 0.33% v/v to 30% v/v.

Microfiltration Tests

The equipment and test procedures used to assess membrane fouling behaviour was described previously[1]. Briefly, the computer controlled apparatus comprised a recirculation circuit where the process suspension was pumped through a crossflow microfilter incorporating a 24 cm^2 planar geometry membrane and returned to the feed tank. The filtration pressure, crossflow velocity and feed stream temperature were maintained at preset values through appropriate transducers and control circuitry and the feed and filtrate flow rates were monitored for the duration of a test.

MICROFILTRATION TEST RESULTS

The matrix of properties shown in Table 1 were investigated for the range of membranes and feed suspensions. The sample data shown in Figures 2 to 12 highlight the effects of the filtration pressure, crossflow velocity, suspension concentration, particle shape and surface charge. Many more similar data were accumulated that confirm the effects shown.

Effects of Filtration Pressure

Figure 2 illustrates the typical effects of raising the filtration pressure whilst keeping the other experimental conditions constant. With the filtration of a relatively ‘large’ particle size feed suspension an increased filtration pressure resulted in an improved filtration rate. Whilst such an outcome could have been expected, and deduced from Darcy's law, the data highlight an important aspect. Darcy's law indicates that the flow rate of a liquid through a porous body, such as a cake or fouling layer, is directly proportional to the applied pressure gradient. The data illustrated in Figure 2 show that in a permeate flux is not proportional to the hydraulic pressure gradient applied during filtration; frequently, in fact, only small increases in flux are observed for quite substantial increases in pressure, particularly when feeds contain higher proportions of particle fines. In the context of this series of papers the terms ‘fouling layer’ and ‘cake’ are used to differentiate between fouling mechanisms. The former refers to a stochastic mechanism whereby an essentially irreversible penetration of particulates into the membrane pore entrances occurs; the latter is associated with the largely reversible, shear limited, deposition of particulates at or near the membrane surface[1]. These two apparently independent phenomena occur simultaneously, and respectively they account for the rapid initial flux decline and the subsequent progressive flux reduction observed in the microfiltration of particulate suspensions.

When the particle size of the suspension was reduced from a 50% size of 27.5 μm to 2.7 μm by grinding prior to filtration the improvements in flux obtained by raising the filtration pressure were reduced. There was also a general tendency for an equilibrium flux to be established more rapidly at lower filtration pressures. It is established in ultrafiltration[9,10], and there are reports of similar effects in microfiltration[11,12], that a raised filtration pressure can lead to increased fouling and will not always produce an improved filtration performance. The potential improvement to be gained by raising the pressure can be fully compensated by an increase in the flow resistance of foulants at or near the membrane pore throats. Figures 3 and 4 illustrate how this phenomenon is readily observed when suspensions containing finer particulates, such as anatase, are filtered. Whilst a majority of the tests performed, such as the sequence shown in Figure 3, showed at least some improvement in filtrate flux at higher pressures a few experiments also indicated that an increased filtration pressure may, on occasion, have a detrimental effect on flux performance. For anatase suspensions at a pH = 4, where the charge at the particle surface is close to the iso-electric point (IEP), an increased filtration pressure was seen to improve filtrate flux slightly. Any potential for greater flux improvement was offset by the tendency to form a higher resistance deposit with the result that the fluxes recorded after two hours filtration were often (for practical purposes) identical. Although this indicates that similar degrees of fouling had occurred irrespective of the pressure difference, the extent to which either reversible cake formation or irreversible, stochastic fouling by particulates occurred is difficult to quantify. With higher pH anatase suspensions (Figure 4) where the particulates in the feed are close to their maximum surface charge an increased pressure produced a flux performance reduced to the extent that filtration essentially stopped after a few hundred seconds when the pressure was raised above 10 psi (68 kPa). It is known from and other work[8] that deposits of anatase formed on membranes are likely to pack to a higher porosity if a higher surface charge is present on the constituent particles. (At a filtration pressure of 500 kPa (74 psi), the porosity of an anatase cake at pH = 9 is 0.846, and at pH = 4 it is 0.571). The effects shown in Figure 4 can therefore be explained by the fact that the suspension was well dispersed at pH = 9.0. When the particles in suspensions are better dispersed, the fine particles in the distribution were able to penetrate the larger pores in the membrane (see Figure 5).

Some further effects were observed when china clay suspensions, with concentrations up to 2% v/v, were filtered at different pressures. There was little difference in flux performance over the pressure range 0 to 50 psi (340 kPa) and it would seem that the platelet shape clay particles forming the cake layer(s) were orientated in the shear field above the membrane and subsequently deposited with their ‘faces’ parallel to the membrane surface, creating a layer of low permeability. The results obtained with china clay demonstrate that an increased pressure does not always increase the filtration rate, and that particle shape is a factor to be considered in this context. In contrast, the data obtained with ground calcite which has a rhomboidal shape showed that for a suspension with a similar 50% particle size (to the china clay) a significant increase in flux level could be achieved by raising the filtration pressure under otherwise identical test conditions. Here, the particles deposited on the membrane formed a more open structure through which the liquor from the feed stream could flow more readily.

Effects of Crossflow Velocity

When tests were performed at various crossflow velocities some unexpected results were produced. Figures 6 and 7 show data obtained for ground and unground calcite suspensions respectively under otherwise identical filtration conditions. With the ground suspension the expected result was obtained, that is, an increased crossflow velocity produced an improved filtration flux. Here the additional shearing forces generated at the higher velocities caused a thinner layer of particulates to accumulate at the membrane; a result confirmed through flow visualisation[13]. However, when the challenge stream contained a greater proportion of larger, unground, particles the filtration rate was seen to fall with increasing crossflow velocity despite a substantial thinning of the fouling layer at the higher crossflows[13]. This unforeseen, although not entirely unknown[14,15], phenomenon could be repeated using other particulate materials of different shape and surface charge characteristics such as aragonite and a variety of membrane types. A possible explanation for the phenomenon might be in terms of a particle classification near the filtering surface. It is known that the membrane deposits which appear during microfiltration are formed from the finer particle species present in the feed stream[1,16]. The axial velocity gradient which is generated across the flow channel would seem to cause a preferential deposition of the finer material from the feed stream at the septum surfaces. Whilst the mechanism(s) by which the classification occurs is debatable and difficult to identify there may be contributions from factors such as preferential removal of larger particles from the foulant layers by the scouring action of the crossflow stream and possibly lateral particle migration in the crossflow stream[17] (the pinch effect). The deposits responsible for fouling could thus have a resistance considerably higher than that which might be expected from a simplistic approach.

The results obtained with the unground calcite suspensions may be explained partially by particle classification effects. As the crossflow velocity was increased more of the larger particles, which were potential foulants, remained in the feed. Hence, the particulates deposited at or near the membrane surface were composed of progressively finer species which formed higher resistance ‘cakes’ and caused lower filtration rates. The experimental data shown in Part I[1] give some possible credence to the classification hypothesis.

The results presented in Figures 6 and 7 suggest that for a given suspension there will exist a critical size (and size distribution) where crossflow velocity should have little or no effect on the flux decline curve. Figure 8 confirms that such a situation can be achieved in practice. Here, a sequence of experiments were performed at three crossflow velocities (0.8, 1.5 and 2.3 m s^{-1}) using a number of calcite suspensions exhibiting different mean particle sizes. The particles in suspension had unimodal size distributions with median sizes of 24.3, 17.1, 10, 5.2 and 2.6 μm respectively[1]. Each of the points, and hence lines, plotted on Figure 8 shows the difference in flux levels after two hours filtration between a ‘high’ and a ‘low’ crossflow velocity experiment. A positive y-axis value indicates that the higher crossflow velocity gave improved flux levels. From the diagram it is seen that for the calcite suspensions tested (at a concentration of 0.033% v/v) the transition between flux up or down with increasing crossflow occurred at a 50% size in the region of 5 to 10 μm. When a corresponding sequence of tests were performed at the higher concentration of 0.33% v/v a more clearly defined transition occurred at a 50% size nearer to 20 μm. Further experiments using a suspension concentration of 1.8% v/v showed the transition point higher still at a 50% size nearer to 24 μm for otherwise similar test conditions. These results imply that specifying a particle size alone as a characterising parameter is insufficient to determine where the transition will occur. Furthermore, this data casts doubt on the validity of existing microfiltration models which use a mean particle size, none of which can seemingly account for such a phenomenon through their basic governing equations[18-24]. Furthermore, it is suspected that for smaller (mean) particle size suspensions the increased/decreased flux phenomenon with crossflow velocity can be observed at higher crossflows than those available with the microfiltration system used for the tests described here.

Many of the effects of changing the crossflow velocity on filtration flux are directly attributable to the particle size and size distribution of the dispersed phase. Whilst they can be repeated using a range of membranes of differing structure and polymer type a number of other factors are worth highlighting. When finer suspensions are filtered an equilibrium flux is often established more rapidly at lower crossflow velocities. If the crossflow velocity is raised the filtration flux can under some process conditions be seen to continually decline over the period of an experiment (a similar phenomenon has been sparingly reported in ultrafiltration work[25]). At the lower crossflow velocities the shear caused by the crossflowing stream would seem insufficient to overcome the forces which cause particles to accumulate at the membrane. The increased permeation through the membrane at higher crossflows (for finer dispersions) would certainly tend to influence the particulates in the flowing suspension to a greater extent than at low crossflows, although other factors such as different combinations of pore plugging/blocking mechanisms may affect the fouling processes. It is recognised that in ultrafiltration it is more common to find molecular species in solution, and the rate and extent of fouling is then probably determined by molecular attractions between the membrane and the foulant. Molecular foulants have not been studied in the work being reported in this paper.

The effectiveness of crossflow velocity was also influenced by the surface charge characteristics of the particles in the feed stream. When anatase suspensions were filtered at a pH = 2.45 corresponding to a low surface charge (and ζ-potential) there was a tendency for particles to agglomerate. The deposit formed on the membrane surface was more readily influenced by the shearing action of the crossflowing stream. However, when the surface charge is higher such as at pH = 10.0 for anatase the deposit formed during filtration was more difficult to remove by increasing the crossflow. The feed particles here are likely to be well dispersed and penetrate the pores of the membrane. This type of deposition is difficult to remove by shear flows. Similarly, when yeast suspensions were filtered little improvement in flux performance was observed with increased crossflow due to the formation of cohesive, compressible fouling and cake layer(s).

Effects of Suspension Concentration

The typical influence of suspension concentration on filtration performance is shown in Figures 9 and 10. Whilst all of the data collected for different solids systems and membranes showed similar trends in terms of flux decline a number of points are worth noting. The general effect of increasing the solids concentration of the feed suspension was to lower the filtrate flux. However, in several cases similar fluxes were recorded, particularly at longer filtration times, for different suspension concentrations. This was primarily a consequence of the more rapid establishment of an equilibrium flux at higher feed concentrations, an effect which was more pronounced at smaller particle sizes. Such flux phenomena were particularly apparent when the challenge stream was a china clay suspension. Over the concentration range 0.033-2.0% v/v almost identical fluxes were seen after a few hundred seconds filtration. Such results contrasted the sequences of experiments performed to evaluate the compression characteristics of the test suspensions. In these experiments a ‘deadend’ filtration technique was employed where the challenge stream flowed perpendicular, rather than tangential, to the filtering medium. Here, raising the concentration lowered filtrate flux but flux levels between tests at different concentrations were always significantly different at longer filtration times. These results suggest that the phenomenon in crossflow filtration of similar flux levels at different concentrations may be solely a consequence of the shear field generated by the crossflowing stream at the membrane surface and its effects on the alignment and packing of the particles.

When the feed stream is more concentrated there is a preference for filtration to occur with particles bridging membrane pores rather than plugging them. If a more dilute suspension is considered, however, there is a tendency for pore plugging to occur to a more significant extent. During the initial stages of microfiltration the results suggest that for different feed concentrations the fouling mechanisms can be significantly dissimilar with pore blocking and bridging occurring to various extents. However, after an initial period the permeate fluxes become similar due to the higher flow resistances of the cakes formed compared with the membrane. This also implies that the fouling layer may change structure and composition throughout the filtration.

Influences of Particle Shape

Although the qualitative effects of particle shape are highlighted throughout this paper it is worth noting a few further points here. The influence of particle shape is difficult to isolate and quantify experimentally due to the problems of identifying the representative particle size for the feed and reproducing this size in an alternative solid. Several texts[26,27] have examined the general problem of shape and proposed the use of equivalent particle diameters. None of these have gained a universal acceptance and no direct comparisons between feeds of different particle shape have been attempted here. However, under some circumstances irregular shape can have a significant effect on flux performance in microfiltration due to the apparent orientation of particulates at the membrane surface. For example, with china clay suspensions, which comprise platelet shape particles, there was almost no flux improvement when the filtration pressure was raised from 10 (68) to 50 psi (340 kPa). Similarly, for china clay there was a marked insensitivity to feed concentration over the range 0.033 to 2.0% v/v. Both of these results are almost certainly influenced to some extent by the irregular shape of china clay whereby the cake or dynamic membrane formed during filtration is predominantly composed of particles lying with their faces parallel to the membrane surface. The unpredictable nature of particle shape was observed when microfiltration experiments were performed with another irregular shaped particle, aragonite. Despite its acicular shape, aragonite exhibited very similar filtration performance (in terms of trends) to its polymorph calcite which has a rhomboidal shape. Thus, whilst the influence of particle shape can be demonstrated, attempts to predict its effects *a priori* are both qualitatively and quantitatively difficult due to inherent complexities.

Effects of Suspension pH/Particle Surface Charge

When suspensions such as calcite were microfiltered at the pH's corresponding to zero and maximum (negative) particle surface charge virtually no change was detected between the individual flux decline curves. This is not surprising as the calcite tested exhibited a relatively low maximum surface charge (≈ -20 mV) and large median size (≈ 2.6 μm); here surface effects play only a minor role and hydrodynamic forces dominate the formation of fouling layers. Figures 11 and 12 show the effects of pH on the filtration of anatase suspensions at two different concentrations with the pH's again spanning the points corresponding to near zero and peak ζ-potential. Anatase, which can exhibit a relatively high ζ-potential (≈ -55 mV) and small median particle size (≈ 0.5 μm) in aqueous suspension, was found to be significantly more sensitive to changes in pH and particle surface properties than materials such as calcite. At higher concentrations in particular, where surface forces have a greater influence due to the closer proximity of particles in the feed, a near order of magnitude difference in filtrate flux levels could be observed between high and low pH experiments.

It is well documented that ‘stable’ high ζ-potential suspensions are invariably more difficult to filter than ‘unstable’ low ζ-potential systems[6,28]. High surface charge particles in suspension are well dispersed by mutually repulsive electrostatic forces and form cakes or fouling layers of high resistance during filtration. For the initial period of a filtration test any particles which are discrete due to high surface charge and within the immediate vicinity of the membrane will tend to move with the fluid flow streamlines toward the membrane pore throats where they become potential foulants. These particles are likely to penetrate the relatively open pore entrances on the membrane surface, leading to irreversible fouling via the stochastic process described earlier. However, near the point of zero surface charge (IEP) particles in suspension tend to agglomerate, due mainly to attractive Van der Waals forces, and the fouling deposit formed during membrane filtration has a lower overall resistance. Here the stochastic irreversible fouling of the pores is less prevalent and the cake layer formed over the surface of the membrane plays a more significant role in determining flux levels.

DISCUSSION

The previous paper in this series[1] discussed the importance of particle and membrane pore size to fouling potential. It was highlighted that whilst some observations had been made, no systematic investigation of particle and pore size effects in microfiltration had been reported. The authors consider that a similar statement is also true for the remaining process parameters described here. In the past researchers have attempted to quantify the influences of the process parameters to the fouling propensity of microfiltration membranes[29-31]. Some have investigated the filtration of particulate, mineral based suspensions, others the filtration of biological or related suspensions with a range of polymeric membranes whilst yet more have provided data for ceramic microfiltration membranes. None of the existing literature, however, would seem to have tackled the long standing requirement for an extensive, coordinated research programme, aimed at understanding the fundamentals of fouling in microfiltration. The lack of such an undertaking has inevitably led to the publication of apparently contradictory results in the literature. Two of the more pertinent contradictions are discussed here.

Most authors have recognised the importance of the basic operating parameters such as filtration pressure and suspension concentration and it has often been inferred that crossflow velocity (or shear rate at the membrane surface) is the most important. Whilst it has been realised by some researchers increasing the filtration pressure can often lead to a reduced filtration performance, most reports (and all too often industrial practice) persist with the notion that crossflow velocity should be increased to a maximum in order to achieve the best separation performance. The data shown in this paper clearly indicate that for MF an increased crossflow can readily induce a lower filtration rate. The effect of crossflow velocity would appear to be influenced by the size and range of particle sizes in the feed, the solids concentration at which a test is performed and the relative influence of the surface forces present on the suspended particulates. Moreover, flux rates can be observed to either rise or fall with increasing crossflow when only the solids concentration is altered for otherwise identical experimental conditions. The latter suggests that in a representative microfiltration the influence of an individual operating parameter is inter-dependent with one or more of the others and illustrates the danger of relying on purely theoretical models and unrealistic experimental data to interpret fouling phenomena. The authors have previously noted[1] the prevalence of theoretical models and computer simulations in the more recent literature, many of which are either uncorroborated by experimental data or are claimed to be proven with experiments performed at wholly unrealistic flow conditions. Comparisons of these models with the more realistic experimental data presented in Figures 2 to 12 indicate poor agreement for both flux decline and equilibrium flux levels and will be the subject of a future paper. A minority of the already limited experimental data published previously indicate how crossflow can be detrimental to flux performance in MF[14], however, these results appear to have been obtained with only one type of challenge stream and were difficult to interpret at the time. This is not surprising given our current lack of understanding for fouling phenomena and such findings undoubtedly lead to a certain amount of confusion. What is clear, however, is that microfiltration should not necessarily be performed at the highest available pressures and crossflows. Indeed there would currently appear to be a growing research effort undertaking experimental work in MF (and UF) to determine both the effects of pulsed pressure and crossflow whereby fouling is reduced through the use of non-constant operational variables[15,32-34] and the coupling of low crossflows and pressures with imposed force fields[35]. Many of these research programmes require further development but give further indication of how the process conditions must be carefully considered in relation to the challenge stream and tailored accordingly to avoid unnecessary membrane fouling and wastage of pumping energy.

The data presented in this paper regarding the effects of particle surface charge may at first sight appear contradictory to established theories. When particles in suspension exhibit a significant ζ-potential they are likely to be well dispersed due to mutually repulsive (long range) forces. Thus a cake, or particle layer, formed from such particles is often found to exhibit a higher porosity than a cake formed by particulates close to their IEP where short range attractive forces are more dominant and promote higher packing densities[7,8]. If this reasoning is correct then flux rates should be a minimum at the IEP of the feed. Such an effect has been previously observed with the membrane filtration of BSA and monodisperse silica feeds[36,37]. It is noted in passing, however, that the form (shape) of BSA protein macromolecules can change with pH and silica spheres are often sterically stabilised or coated in some other way in aqueous suspension to keep the individual particles discrete. The data shown in Figures 11 and 12 illustrate that for the microfiltration of polydisperse mineral suspensions the opposite effect can occur and flux rates are observed to be a maximum in the vicinity of the IEP. This apparent contradiction with (predominantly) UF data is unlikely to be due to any major difference in basic experimental procedures and is perhaps best explained in terms of particle agglomeration. Near the IEP of the feed the net inter-particle attraction is greatest and will tend to induce the particles in the feed to agglomerate. Thus the solids challenging the membrane pores are likely to be significantly larger than the primary particle size with the result that layers will tend to form on the membrane surface rather than in the membrane pores. and the overall flow resistance observed will be lower. In a related technique, flocculation with polyelectrolytes prior to microfiltration has been shown to increase flux by inducing the formation of flocs and promoting solids deposition at the membrane surface[38]). Moreover, with less penetration of particles into the pores occurring near the iso-electric point of the feed the filtrate quality tended to be improved (Table 3). The results obtained with all the solids types tested suggest that whenever possible crossflow membrane filtration should be performed with the particles in the feed suspension at or near the point of lowest surface charge. Such an effect can be produced by altering the pH and/or ionic strength of the solution environment surrounding the particles.

CONCLUSIONS

When considering the advances made in membrane filtration research over the previous decades it is perhaps surprising to recall that microfiltration is the oldest of the membrane separation technologies. Whilst some progress has been made toward understanding fouling in MF, the development of the process towards industrial viability has been slow and the number of applications relatively few. Whether the development problems have been a result of industrial pressure to find a ‘quick’ solution, the apparent need to investigate complex feed streams, or a lack of academic or industrial interest is difficult to determine. However, the growing potential markets for MF[39] suggest that solutions to fouling problems are now required. The data presented in this paper have been obtained in a systematic manner and illustrate how we may begin to understand more of the fundamentals of fouling. The results are summarised in Table 4 and these descriptions highlight how seemingly complex phenomena can be investigated using carefully characterised materials and controlled experimental techniques. At several points throughout this paper, however, conclusions have been deduced from the results of a relatively large number of experiments. Whilst this is the best technique currently available to attempt a fuller understanding of fouling, it is recognised that filtration experiments by themselves represent a ‘black box’ approach where reasoning is often inferred rather than directly observed. For instance, the structure of fouling and cake layers is thought to change continuously during microfiltration due to factors such as particle capture/loss and consolidation. Until such hypotheses are proven a full picture of membrane fouling is unlikely to be obtained; further papers in this series will cast light into the black box!

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FIGURES AND TABLES

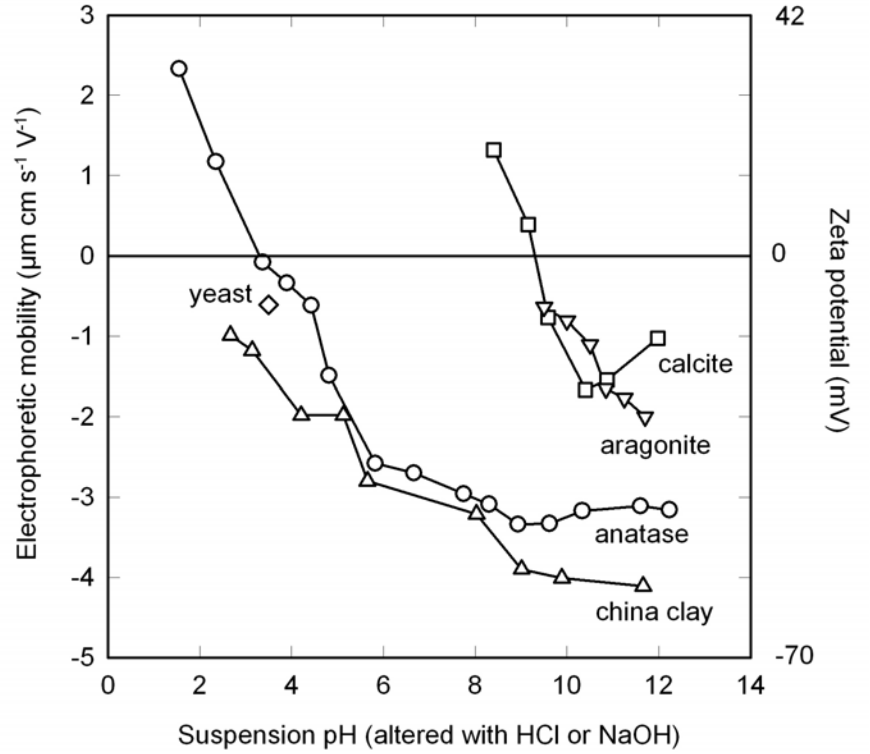

Figure 1: Electrophoretic mobility vs. pH for the test suspensions.

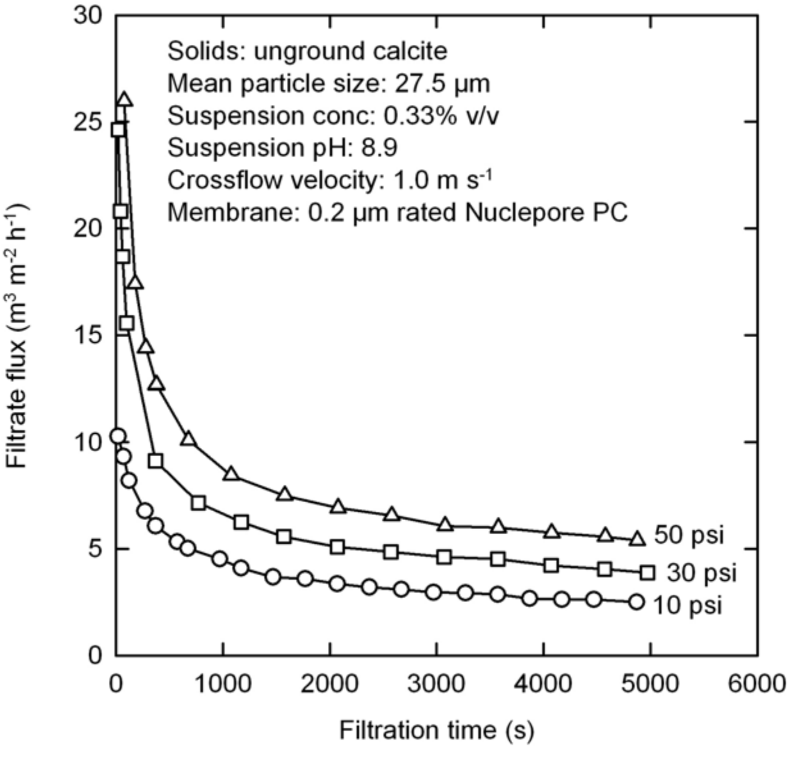

Figure 2: Effect of pressure on flux decline for calcite suspensions.

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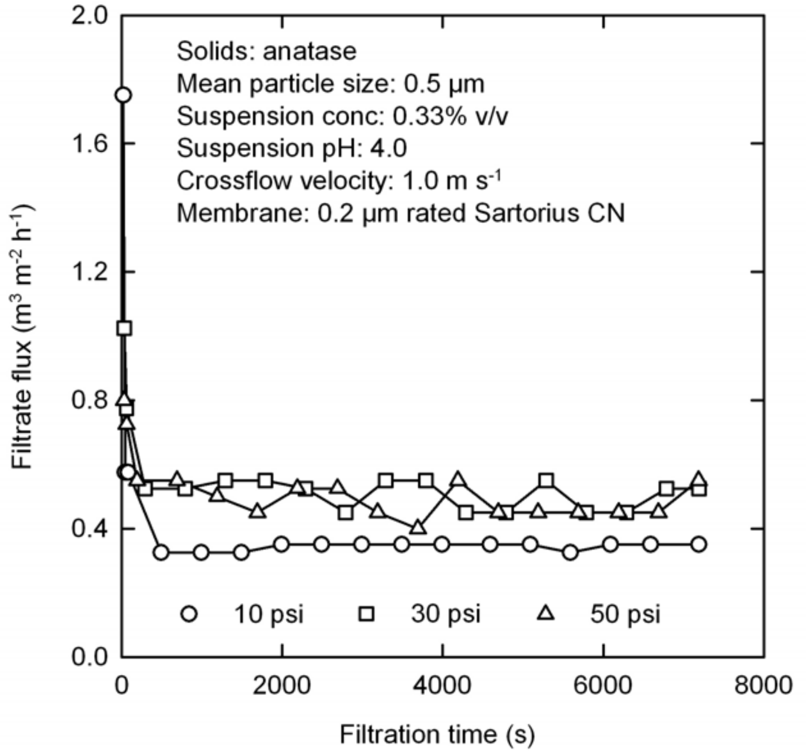

Figure 3: Effect of pressure on flux decline for anatase suspensions at the pH corresponding to the isoelectric point.

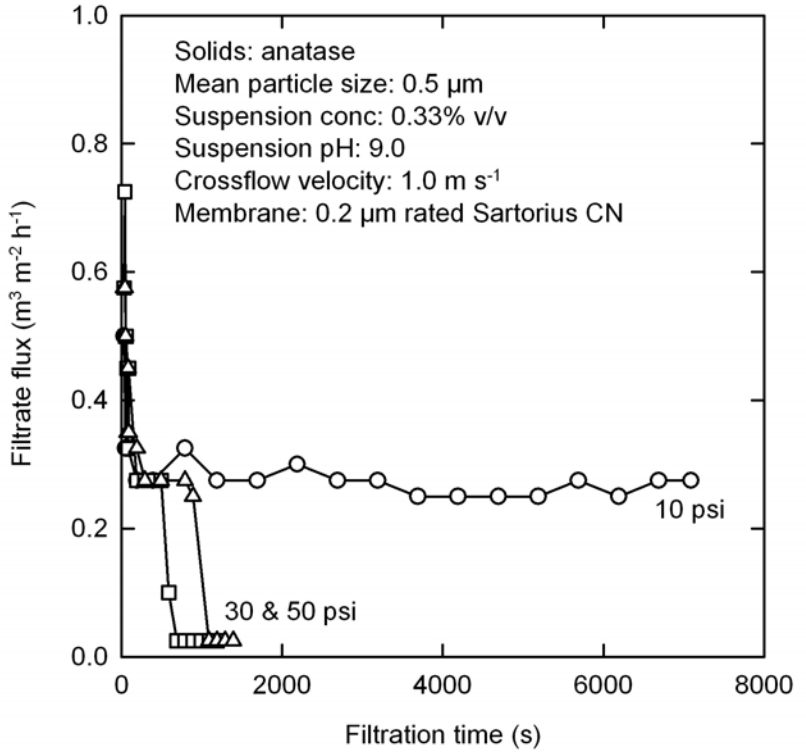

Figure 4: Effect of pressure on flux decline for anatase suspensions at the pH corresponding to the point of maximum particle surface charge.

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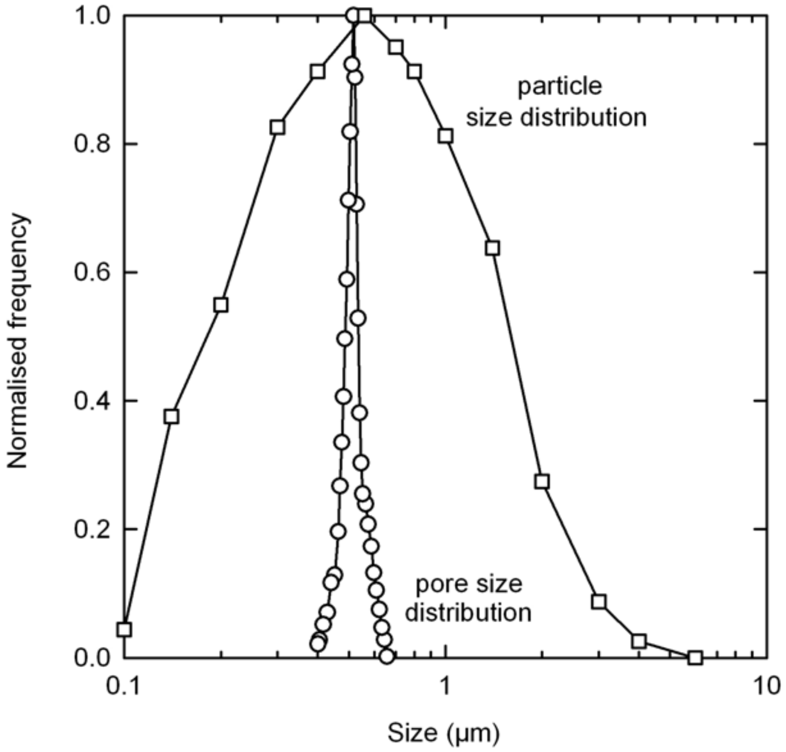

Figure 5: The overlaps between the particle and pore size distribution of an anatase suspension and a 0.2 µm rated Sartorius CN membrane.

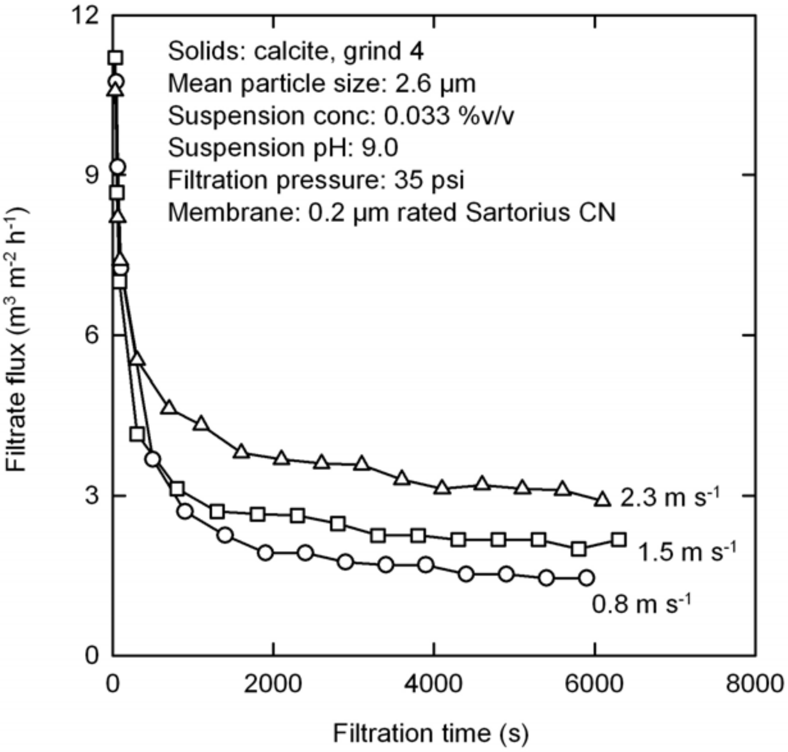

Figure 6: Effect of crossflow velocity on flux decline for finer calcite suspensions.

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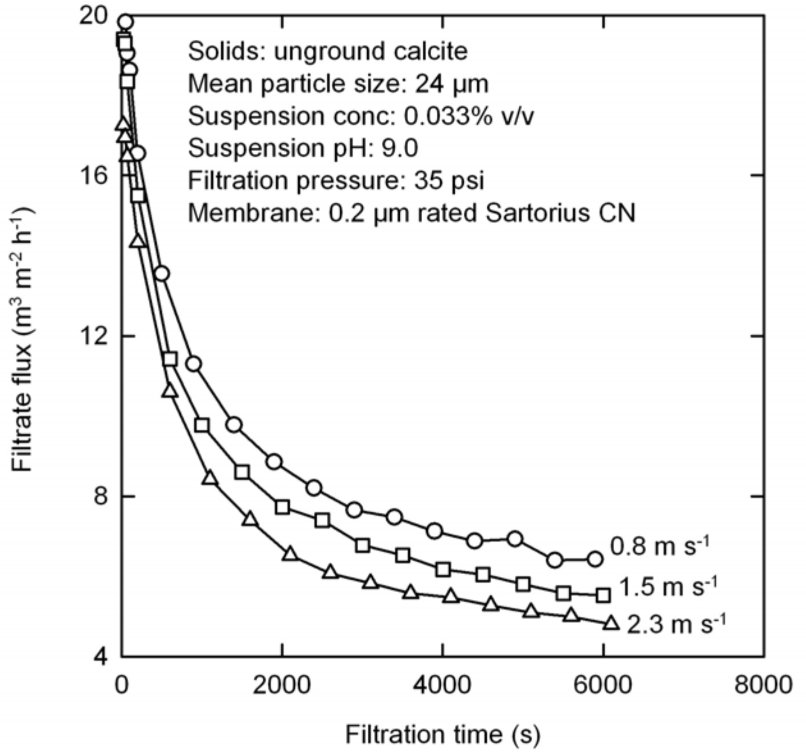

Figure 7: Effect of crossflow velocity on flux decline for coarser calcite suspensions.

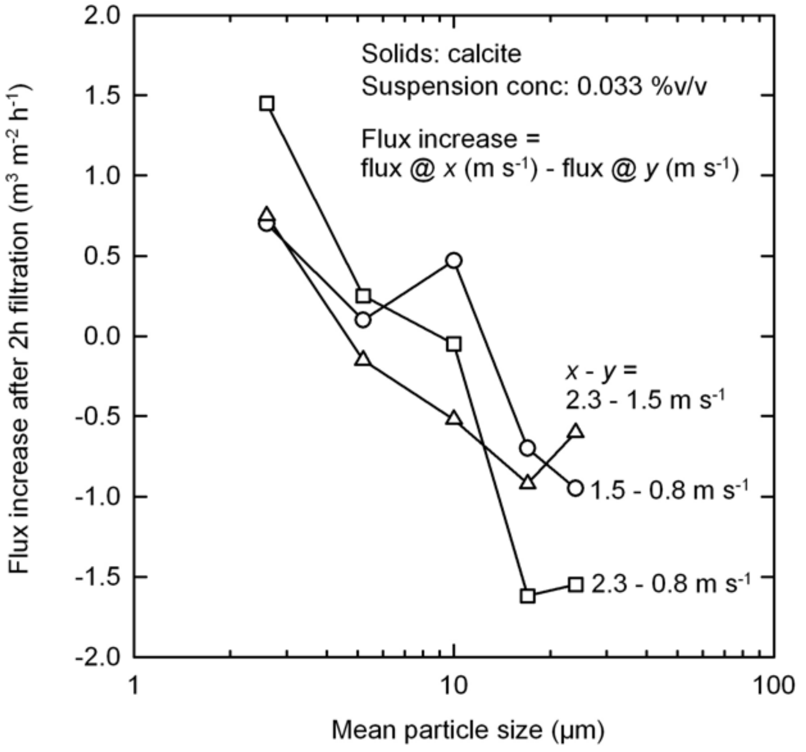

Figure 8: Effect of crossflow velocity and particle size on flux decline for low concentration calcite suspensions.

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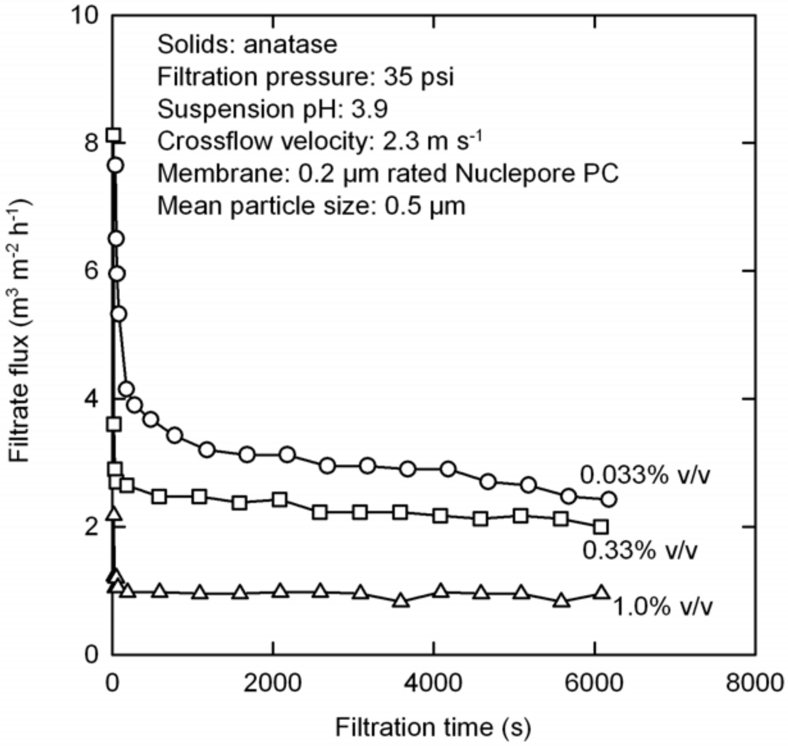

Figure 9: Effect of feed concentration on flux decline for anatase suspensions.

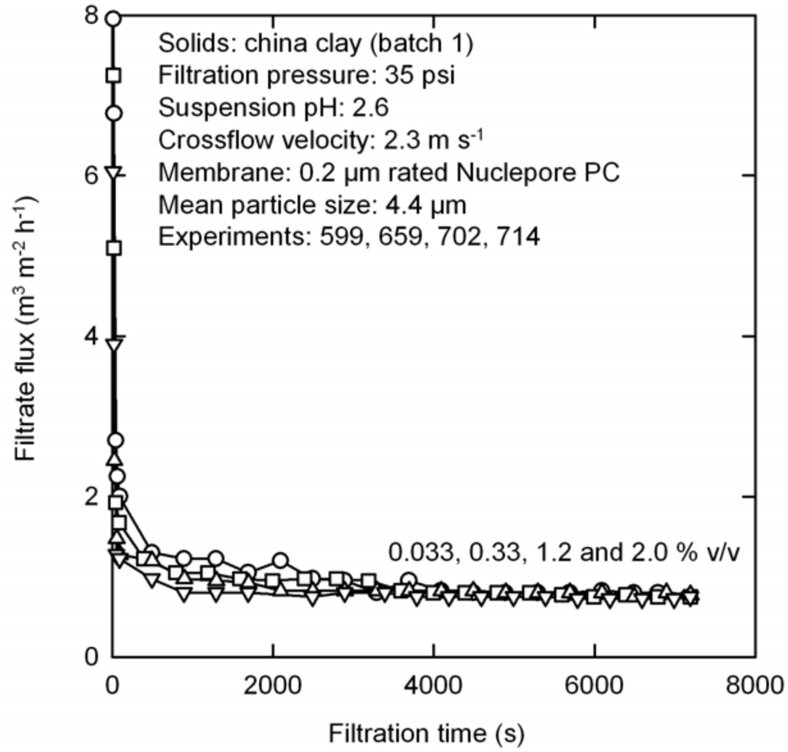

Figure 10: Effect of feed concentration on flux decline for china clay suspensions.

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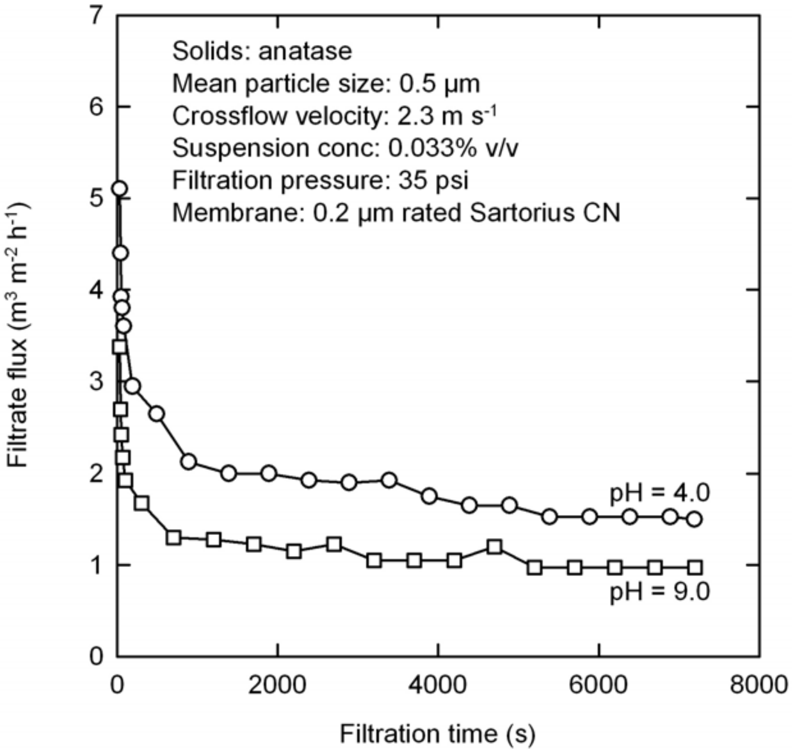

Figure 11: Effect of pH on flux decline for low concentration anatase suspensions.

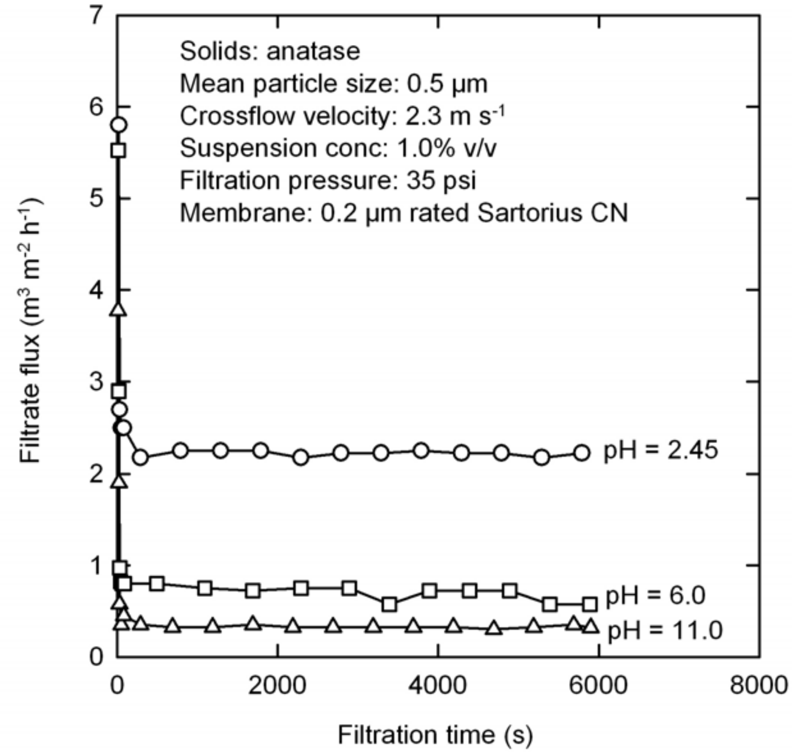

Figure 12: Effect of pH on flux decline for high concentration anatase suspensions.

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Property	Calcite	Anatase	China clay	Aragonite	Yeast
Particle size[1] (μm)	2.6 → 27.5	0.5	4.4	1.9 → 10.1	6.7
Particle shape	rhomboidal	tetragonal	platelet	acicular	oblate spheroid
ζ-potential (mV)[2]	0 → -20	+10 → -55	-10 → -55	-11.3	-8.5
Pore rating (μm)	0.2 → 10	0.2 → 5	0.2 → 10	0.2 → 10	0.2 →5
Solids conc. (% v/v)	0.033 → 1.8	0.033 → 1.0	0.033 → 2.0	0.033 → 1.65	0.0006 → 0.0015
Crossflow (m s^{-1})	0.8 → 2.3	0.8 → 2.3	0.8 → 2.3	0.8 → 2.3	0.8 → 2.3
Pressure (psi)	10 → 50	10 → 50	10 → 50	10 → 50	10 → 50

[1] 50% size quoted; [2] pH altered with HCl or NaOH

Table 1: Some material properties and the range of experimental conditions examined.

Dispersed phase	Mean size (μm)	pH	$\alpha_{av} = \alpha_0 \Delta p^n$	
			α_0	n
calcite	27.5	8.9	$4.6\text{x}10^6$	0.49
calcite	2.6	8.9	$5.4\text{x}10^9$	0.32
anatase	0.5	3.9	$1.6\text{x}10^{12}$	0.07
anatase	0.5	9.1	$1.6\text{x}10^{12}$	0.1
china clay	4.4	2.5	$7.4\text{x}10^{10}$	0.25
china clay	4.4	10.5	$6.9\text{x}10^{10}$	0.51
aragonite	10.1	9.2	$7.7\text{x}10^8$	0.22
yeast	6.7	3.5	$1.3\text{x}10^5$	>1

Δp in kPa

Table 2: Some compression characteristics for the test suspensions.

Membrane rating (μm)	Feed solids conc. (% v/v)	pH	Crossflow (m s^{-1})	Permeate quality
0.2	0.033	3.9	0.8, 1.5, 2.3	clear throughout tests
1	0.033	3.9	0.8, 2.3	clear throughout tests
1	0.033	9.1	2.3	clear throughout test
5	0.033	3.9	0.8	clear after 8 mins.
5	0.033	3.9	2.3	clear after 8 mins.
10	0.033	3.9	2.3	cloudy throughout test
0.2	0.33	3.9	0.8, 1.5, 2.3	clear throughout tests
1	0.33	3.9	0.8, 1.5, 2.3	clear throughout tests
1	0.33	9.1	2.3	clear after 20 mins.
5	0.33	3.9	0.8	clear after 45 mins.
5	0.33	3.9	1.5	clear after 25 mins.
5	0.33	3.9	2.3	clear after 17 mins.
10	0.33	3.9	2.3	cloudy throughout test
1	1.0	3.9	2.3	clear after 2 mins.
1	1.0	9.1	2.3	cloudy throughout test

Table 3: Effect of filtration conditions on permeate quality for anatase suspensions and Nuclepore PC membranes.

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Property	Comment
Suspension pH	When the representative particle size of the feed was sufficiently large hydrodynamic forces dominated and suspension pH/ionic strength had a negligible effect on flux decline. With reduced particle size surface forces are more dominant and at high particle ζ-potentials, fluxes were lower than those recorded at or near the iso-electric point. Differences in flux levels were accentuated at higher feed concentrations and could be up to an order of magnitude. Filtrate quality and thus solids retention were generally improved near the iso-electric pH where lower ζ-potentials exist and particle dispersion is likely to be poorer.
Suspension concentration	At raised suspension concentrations fluxes were generally lower and equilibrium was established more rapidly. The fluxes recorded at longer times were often similar over a range of concentrations. The latter phenomenon was exaggerated when the representative feed size was smaller and particularly noticeable when the feed stream was china clay (and the particle shape was plate-like).
Crossflow velocity	When the proportion of particle fines in the feed was high, an increased crossflow led to thinner cakes and higher overall fluxes. The flux improvements were more significant near the iso-electric pH of the feed and reduced at pH's closer to the point of maximum particle surface charge where fouling deposits appeared to be more cohesive. A pseudo-equilibrium flux was established more rapidly at lower crossflows whilst filtrate clarity generally improved at higher crossflows. With reduced proportions of fines and larger particle size feeds an increased crossflow produced more extensive fouling and lower flux levels. The size transition between flux increase or decrease with crossflow was dependent on the feed concentration.
Filtration pressure	For the largest particle size suspensions tested (50% sizes 24-27 μm) there was a significant improvement in flux with increased pressure; an effect that was exaggerated at lower suspension concentrations. The influence of pressure on flux levels was reduced for feeds with smaller median sizes and higher concentrations and some feeds containing particulates of irregular shape.
Particle shape	The influences of irregular particle shape were difficult to quantify or predict, however, significant effects on flux decline could be observed.

Table 4: Summary of the influence of process parameters in microfiltration.

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