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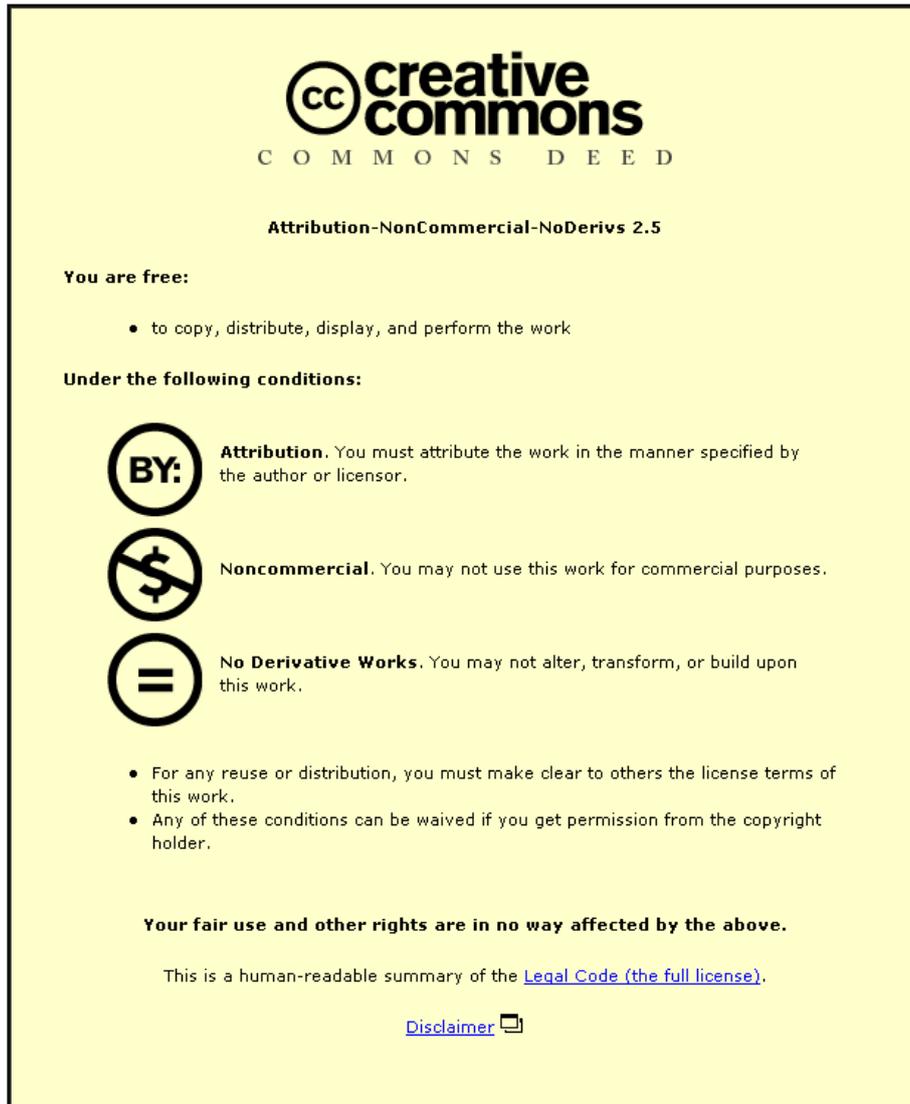
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FACTORS AFFECTING THE FOULING OF MEMBRANES IN CROSSFLOW MICROFILTRATION

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ABSTRACT

Results from an on-going research programme are presented which illustrate the factors affecting the fouling of polymeric microfiltration membranes by colloidal and fine particulate matter. Experimental data obtained from a computer controlled crossflow apparatus show how flux decline is influenced by a matrix of particle, suspension, membrane and process parameters. Relevant variables such as feed concentration, crossflow velocity, filtration pressure and suspension pH are delineated and separated to highlight the salient features of the crossflow process. The results obtained to date from the project explain some of the anomalies which have been reported in the published literature and indicate ways in which process design can be improved.

INTRODUCTION

Crossflow microfiltration has recently been attracting much interest from process industries wishing to treat aqueous feed streams. Whilst some apparently successful applications have been reported¹ it is acknowledged that the fouling problem associated with membrane processes is poorly understood and prevents more widespread use of the technology². Previous work relating to microfiltration has generally not taken due account of all the relevant variables. Research programmes have often used ill-characterised, complex feed streams containing mixtures of molecules and particulates, either or both of which may be membrane foulants in combination or in their own right. A full understanding of membrane fouling cannot be obtained unless all the variables are properly delineated, and separated out in an appropriately designed experimental programme using a well controlled filtration apparatus. The work presented here represents a step in this direction. The paper is essentially divided into two sections. The first section concentrates on the characterisation tests which provided background knowledge regarding the properties of the particles, suspensions and membranes used in the microfiltration experiments. The second describes the filtration apparatus and the results of the crossflow experiments.

CHARACTERISATION TESTS

The suspensions and membranes subsequently tested in the microfiltration experiments were characterised through a series of independent tests using a variety of commercially available laboratory instruments. The properties measured are summarised in Table 1.

Membrane Characterisation

Both Nuclepore polycarbonate (PC) and Sartorius cellulose nitrate (CN) flat sheet membranes have been examined. These were considered to be representative of the range of microfiltration membranes currently available. Nuclepore PC membranes are manufactured via a nuclear track etching technique which produces a structure of predominantly discrete, cylindrical pores randomly dispersed over a thin sheet. Sartorius CN membranes, on the other hand, are produced by a casting process which yields a much thicker microporous membrane with a tortuous pore structure. The membranes were available in a range of pore size ratings and scanning electron micrographs confirmed the homogeneous structures described.

The pore size distributions of the membranes were measured with a Coulter porometer. Unsoiled samples of the membranes used in the filtration experiments were tested in accordance with ASTM-E 1294-89³ and the results are shown in Figures 1 & 2. They highlight an interesting phenomenon. The Nuclepore membranes exhibited narrow pore size distributions around mean values close to the manufacturer's quoted ratings. However, the Sartorius membranes demonstrated mean pore sizes somewhat different from the quoted ratings. For instance a 0.2 μm rated membrane had a mean pore size of 0.56 μm whilst an 8 μm rated membrane of the same type yielded mean and maximum pore sizes of 3.6 μm and 5.8 μm respectively. The pore size distributions were found to widen for both membrane types at larger pore size ratings. This perhaps indicates the difficulties experienced in manufacturing larger pore size membranes with 'tight' size distributions.

The permeability and 'clean water flux' of the membranes were measured in a pressure driven permeameter. For each sample the permeation rates corresponding to a series of applied pressure differences were determined, and Darcy's Law used to give its permeability. These tests were performed with double distilled water at 20°C. Table 2 gives the membrane characterisation data.

The data in Table 2 show that both permeability and clean water flux increased for membranes with larger pore size ratings, there being nearly two orders of magnitude difference in the permeabilities of 0.2 μm and 10 μm rated Nuclepore polycarbonate membranes. Sartorius membranes were considerably more permeable than the corresponding Nuclepore ones with there being approximately an order of magnitude difference in permeability between equivalently rated membranes.

The contact angles between various aqueous suspensions and the membranes were also measured to give an indication of membrane wettability. The novel technique involved the use of a high magnification lens and camera coupled to a video system capable of taking and storing 400 frames per second⁴. Both Nuclepore PC and Sartorius CN membranes were found to be hydrophilic; the measured contact angle fell with time as water from the droplet introduced onto the membrane surface progressively penetrated the membrane pores. Tests were performed over a range of pH values using double distilled water and samples of the suspensions from the microfiltration tests. Whilst the magnitude and rate of change of the contact angle were dependent on the material properties of the membranes neither pH nor the presence of the solids tested significantly affected the contact angles measured.

Particle Characterisation

The particle size distributions were evaluated using laser-based Malvern instruments. Two mineral powder types were considered, calcite (calcium carbonate), supplied as an analar grade by BDH, and anatase (titanium dioxide) obtained from Tioxide PLC in an uncoated form. No cleaning or washing of the powders was performed prior to any test. The measured particle size distributions for the powders dispersed in double distilled water are shown in Figure 3. The smallest mean size was exhibited by anatase with most of the particulates in the region of 0.5 μm . By contrast the unground calcite suspension had a mean size of approximately 24 μm and an apparently much wider distribution. To obtain a range of mean sizes calcite suspensions were wet ground in a ball mill for periods of up to one day. Over a 24 h period the mean size would typically be reduced to around 2.6 μm .

The particle shapes of the powders were examined with a scanning electron microscope. Calcite, in both its ground and unground forms, exhibited a rhomboidal shape whilst anatase resembled an oblate spheroidal form.

Suspension Characterisation

The effect of pH on particle surface charge was determined using a Malvern Zetasizer. Calcite has a relatively low surface charge with the points of zero and maximum negative zeta potential (-24 mV) corresponding to the pH's 8.9 and 10.6 respectively. Anatase is typical of a high surface charge material and the pH's 3.9 and 9.1 represent the zeta potentials of 0 mV and -47 mV respectively when hydrochloric acid (HCl) and sodium hydroxide (NaOH) are used to alter the solution environment pH.

A Carrimed controlled stress rheometer was used to investigate suspension rheology. The behaviour of the suspensions were found to be Newtonian, as might be expected from the relatively low solids concentrations.

CROSSFLOW MICROFILTRATION EXPERIMENTS

A matrix of properties have been investigated for the range of suspensions and membranes described in the characterisation tests. The effects of the variables shown in Table 3 were delineated from each other by selection of the experimental test conditions.

Experimental Apparatus

The equipment used to assess membrane fouling behaviour is shown schematically in Figure 4. The unit comprised a flow circuit in which suspension of a known, essentially constant, composition was pumped continuously through a crossflow microfilter at a predefined crossflow velocity and trans-membrane pressure. These desired filtration conditions were maintained by two electrically operated proportional control valves. The valves were linked to a computer via electronic control circuitry which monitored conditions at various points within the flow circuit using suitable transducers. When a deviation from the desired conditions was detected the control valves moved to compensate and thus maintain a constant filtration pressure and crossflow velocity. The temperature of the process suspension was also regulated using a plate type heat exchanger positioned in the feed tank. In this way it was possible to investigate the effects of the filtration pressure up to 50 psi and the crossflow velocity up to 3 m s^{-1} whilst keeping the feed at a temperature of $30 \pm 2^\circ\text{C}$.

The purpose built microfilter was constructed from plastic and stainless steel (as was the rest of the flow circuit and ancillaries) and consisted of a supported 24 cm^2 flat sheet membrane positioned to form one side of a rectangular flow section. During an experiment the suspension flowed through this volume and tangential to the membrane. The filtrate produced was returned to the feed tank via a flowmeter.

Prior to the start of a filtration test the process suspension, made to a known concentration from either a dry powder and double distilled water or in the case of a ground sample from a diluted slurry, was stirred in the feed tank for several minutes to produce an homogeneous mixture. The suspension pH was altered if necessary using the electrolytes NaOH or HCl. The test was then performed at the desired filtration settings with data recorded and permanently stored by the computer on floppy disk. Each test was run for a maximum of two hours or until the membrane fouled to such an extent that the flow rate could not be recorded satisfactorily.

DISCUSSION OF EXPERIMENTAL RESULTS

When a filtration test commenced a sharp fall in filtration rate from the clean water flux was observed. The rapid, essentially irreversible fouling of the membrane⁴ during this period can be attributed to particle polarisation at or near the filtering surface. After the initial rapid fouling the rate of flux decline progressively lessened until after some time an equilibrium filtration rate was observed in most experiments. Here, the additional fouling toward equilibrium is largely reversible

and apparently due to the formation of surface particulate layers. When the equilibrium state is reached the particles forming the fouling layer(s) are seemingly in a state of 'dynamic equilibrium' whereby they are leaving and joining the layer at the same rate⁵.

Effects of Filtration Pressure

Figure 5 shows the typical effects of raising the filtration pressure whilst keeping the other experimental conditions constant. In most cases it was found that an increased filtration pressure resulted in an improved filtration rate. This would be expected from Darcy's law which indicates that flux is directly proportional to the applied pressure gradient. The influence of pressure was found to be more substantial when the feed contained a greater proportion of larger particles; these suspensions forming less resistant membrane deposits during filtration. For finer calcite and anatase suspensions the improvement in flux obtained by raising the filtration pressure was less. It is well established in ultrafiltration⁶, and there are reports of similar effects in microfiltration⁷, that an increased filtration pressure 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 the fouling layer at or near the membrane surface. In extreme circumstances an increased pressure can cause filtrate flux to fall. Figure 6 illustrates this for anatase suspensions filtered at a pH where the feed particles exhibited high surface charge. In such a case the membrane deposits are compressible (more so than at low charge⁸) and an increase in pressure above 10 psi caused the deposit to compact and become less permeable.

Effects of Crossflow Velocity

When tests were performed at various crossflow velocities observed effects were dependent on the particle size in the feed. With the finer particle suspensions the expected result was obtained, that is, an increased crossflow velocity produced an improved filtration flux. However, when the feed stream contained a greater proportion of larger, unground calcite particles the filtration rate was seen to fall with increasing crossflow velocity⁴. At intermediate feed particle sizes the influence of crossflow can be negligible over a range of velocities. Similar effects of particle size and crossflow can be demonstrated with a range of membrane types and suspension concentrations and are almost certainly attributable to particle classification effects at or near the septum surface.

Effects of Suspension Concentration

The general effect of increasing the solids concentration for all types of feed suspension tested was to lower the filtrate flux. However, in several instances similar fluxes were recorded at longer filtration times for different suspension concentrations over the range 0.033-1.8% v/v. This was primarily a consequence of the more rapid establishment of an equilibrium flux at higher feed concentrations and was exaggerated at smaller particle sizes.

Effects of Suspension pH

The effects of pH were determined at pH's which traversed the range between the points of zero and peak surface charge. For calcite, which exhibits a relatively low zeta potential in combination with a 'large' particle size, there was virtually no change in flux performance between similar experiments performed at low and high surface charge. With anatase, which can exhibit a high zeta potential and 'small' particle size in aqueous suspension, a more significant influence of solution environment was found (Figure 7). At higher concentrations in particular, where surface forces have more influence, approximately an order of magnitude difference in filtrate flux levels could be observed between high and low pH experiments. The results suggest that whenever possible membrane filtration should be performed with the particles in the feed suspension at or near the point of zero surface charge; this improves both flux levels and filtrate clarity.

Effects of Particle Size

Figure 8 shows the typical effects of changing the mean particle size of a calcite suspension on flux decline. With a smaller particle size there was a tendency for the filtrate flux to be reduced more rapidly at the start of filtration and an equilibrium or pseudo-equilibrium flux to be established sooner. The fluxes recorded at longer filtration times for 'large' and 'small' particle systems were often similar in magnitude, particularly at higher crossflow velocities. Other tests showed that particle fines constitute a major proportion of the fouling layer(s) formed in crossflow microfiltration. The particle classification effects induced by the crossflow coupled to the frequent lack of formation of a true filter cake makes identification the particles responsible for the formation of fouling layers difficult.

Effects of Membrane Pore Size

Membrane pore size was found to affect filtration performance to an extent dependent on a number of factors. In experiments using feeds with a majority of particulates larger than the membrane pore sizes only a minimal effect of pore size on flux performance was observed. For instance, two otherwise identical tests performed with 0.2 μm & 10 μm rated Nuclepore PC membranes and a 27 μm mean size calcite feed gave virtually identical fluxes after 10 minutes filtration⁴. The result is perhaps surprising when one considers that there are two orders of magnitude difference in the permeabilities of the two membranes (see Table 2). Figure 9 shows the typical effect of filtering a finer calcite suspension with different pore size membranes. Here, the pore ratings (and sizes) traversed the mean size of the particles in the feed and a fall in filtrate flux (due to internal pore fouling) was observed as the membrane pore rating was increased to diameters larger than the particles' size. These results, and other with anatase, suggest that it was the fouling layer(s) formed during filtration which predominantly determine flux performance and not membrane permeability.

Effects of Membrane Type

Identical tests were performed using Nuclepore PC and Sartorius CN membranes of the same rating. Despite the obvious differences in membrane construction the flux declines recorded were almost identical. Moreover, similar results could be obtained over a range of experimental conditions using both calcite and anatase. Although this stage of the investigation is still in its preliminary stages it would seem that the polymeric membrane may only act as a support for the 'dynamic membrane' formed during filtration and it is the latter which largely determines flux performance (in the absence of adsorption).

CONCLUDING REMARKS

The work reported in this paper is part of an integrated series of projects being carried out at Exeter on membrane filtration, aimed at providing a fundamental understanding of fouling. These involve both extensive experimental work, using appropriately designed programmes and equipment, and theoretical modelling. Whilst the experimental programme is not yet complete the initial findings have gone some way to explaining some of the anomalies which currently exist in the literature. It would appear that the fouling in crossflow microfiltration occurs due to two apparently independent mechanisms; one reversible and the other largely irreversible. Whilst the degree to which each occurs is currently being quantified it has been shown that many, often inter-related, parameters affect filtration performance. Until these relationships and the basic principles of fouling are fully understood a complete picture of membrane filtration will not be obtained.

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FIGURES AND TABLES

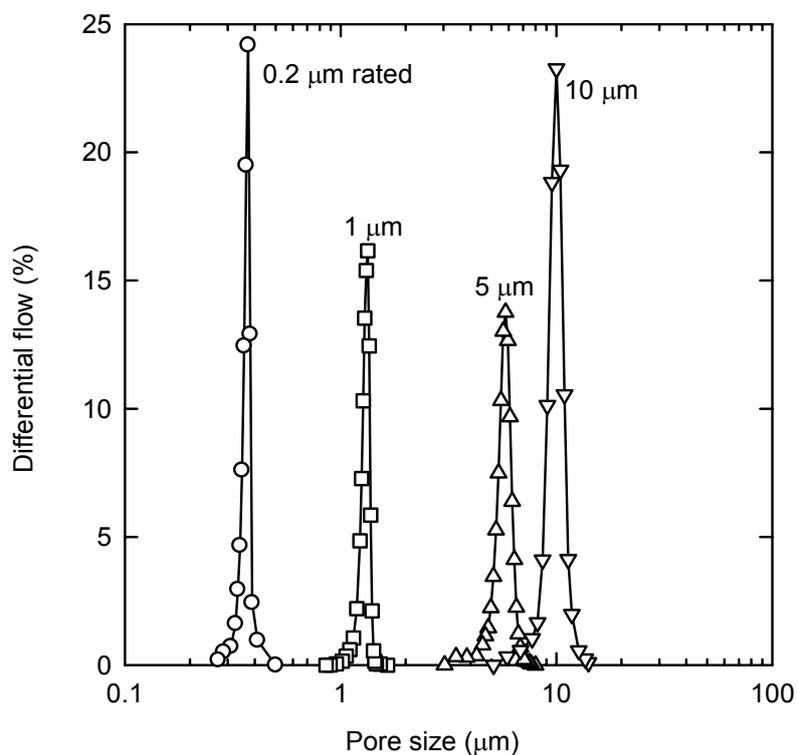


Figure 1: Pore size distributions of Nuclepore PC membranes.

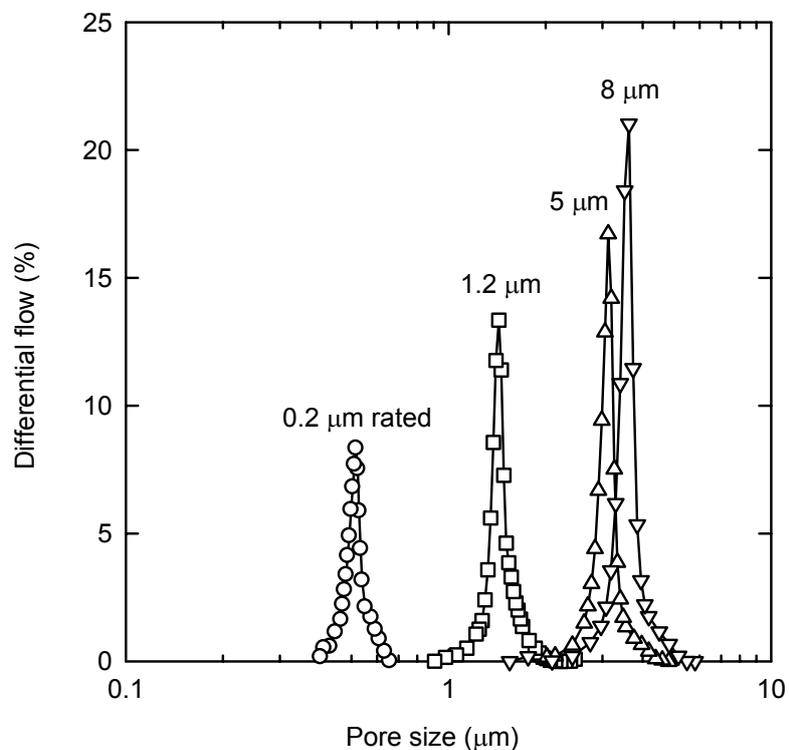


Figure 2: Pore size distributions of Sartorius CN membranes.

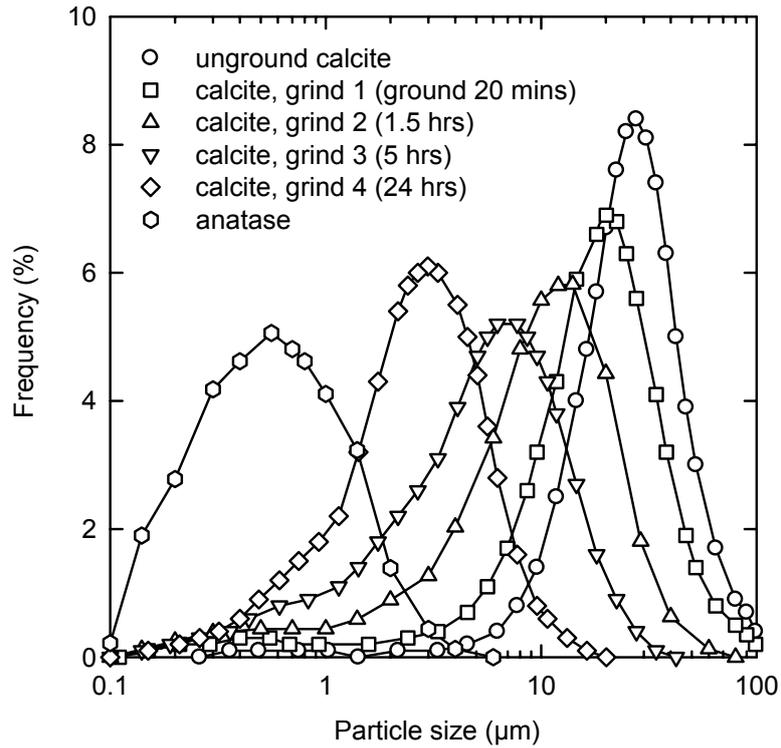


Figure 3: Size distributions for calcite and anatase.

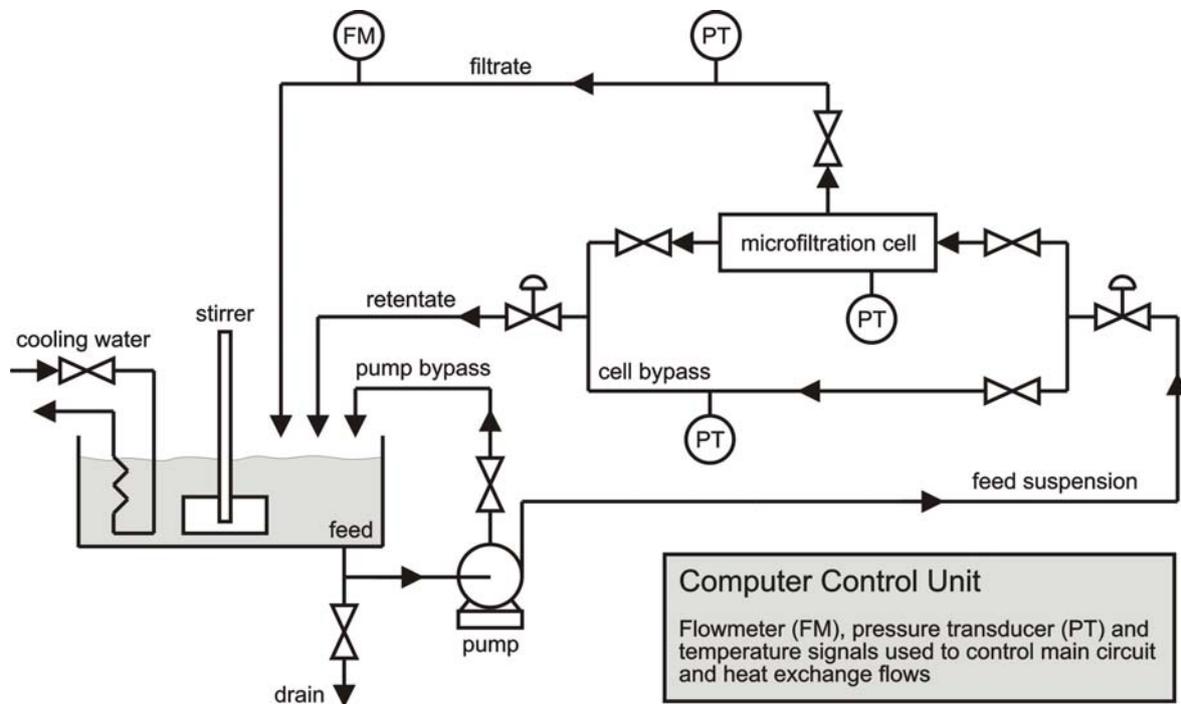


Figure 4: Schematic of the crossflow microfiltration unit.

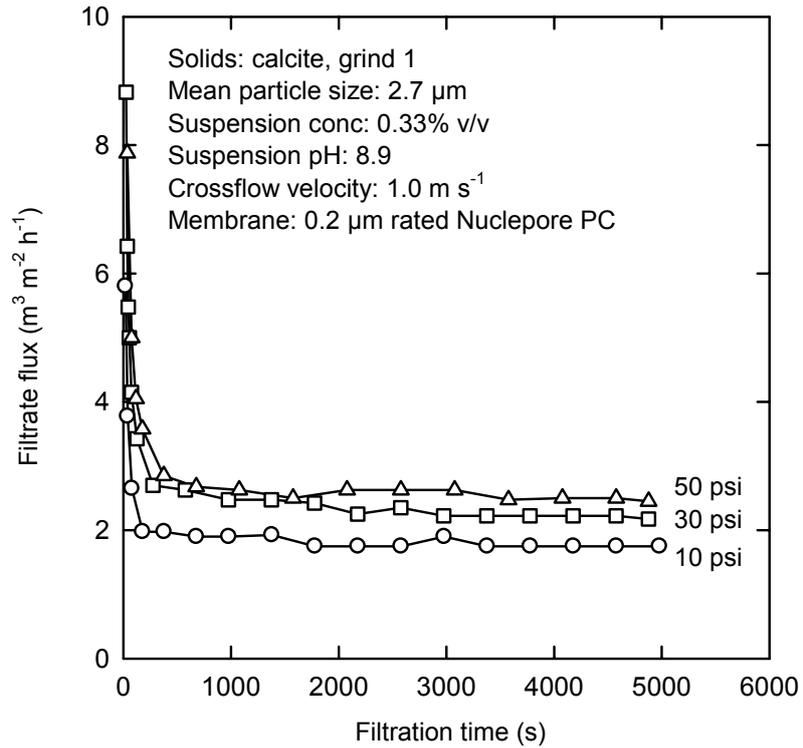


Figure 5: Effect of pressure on flux decline for calcite suspensions.

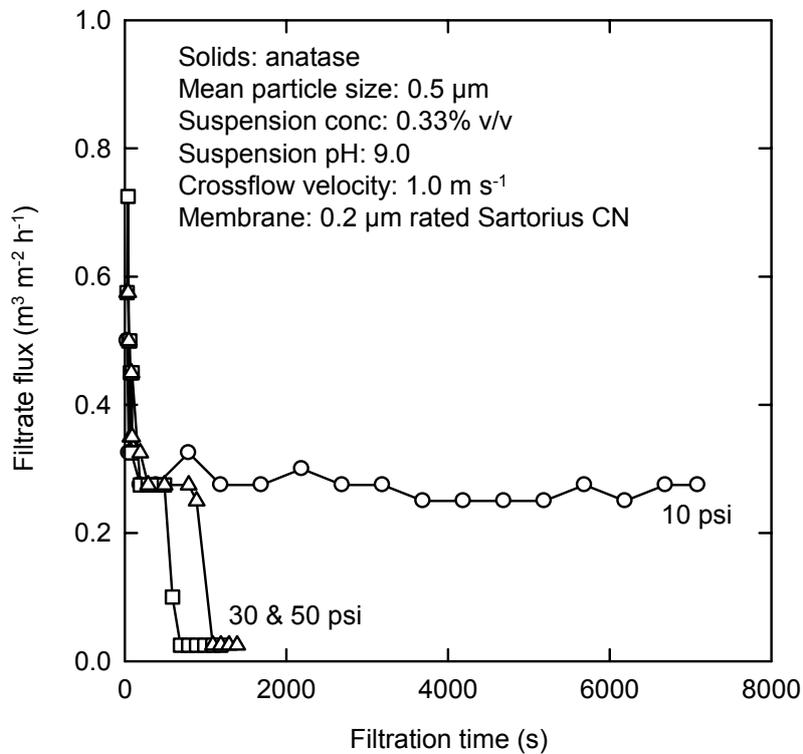


Figure 6: An effect of pressure on flux decline for anatase suspensions.

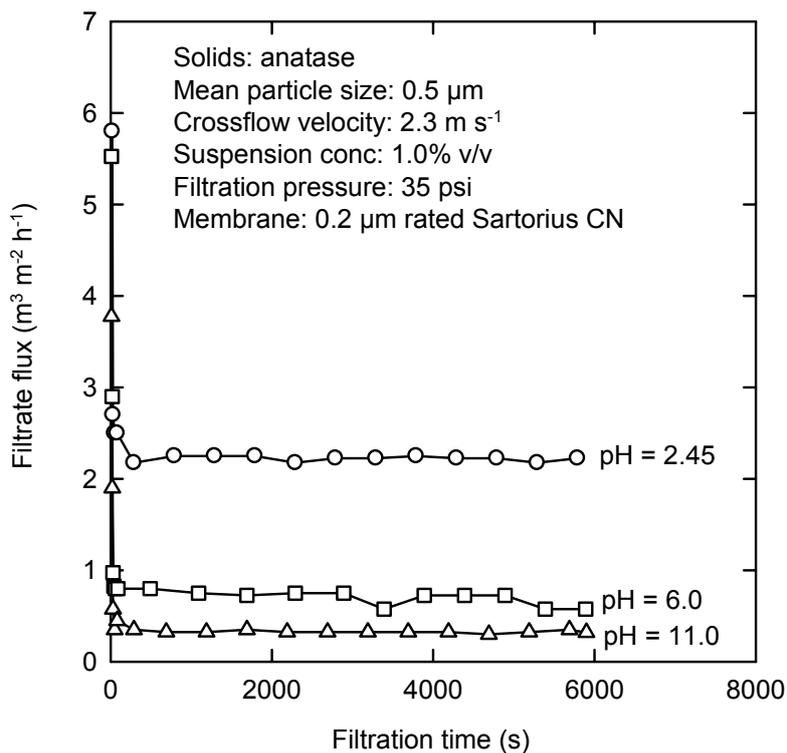


Figure 7: The influence of suspension pH on flux decline for anataze suspensions.

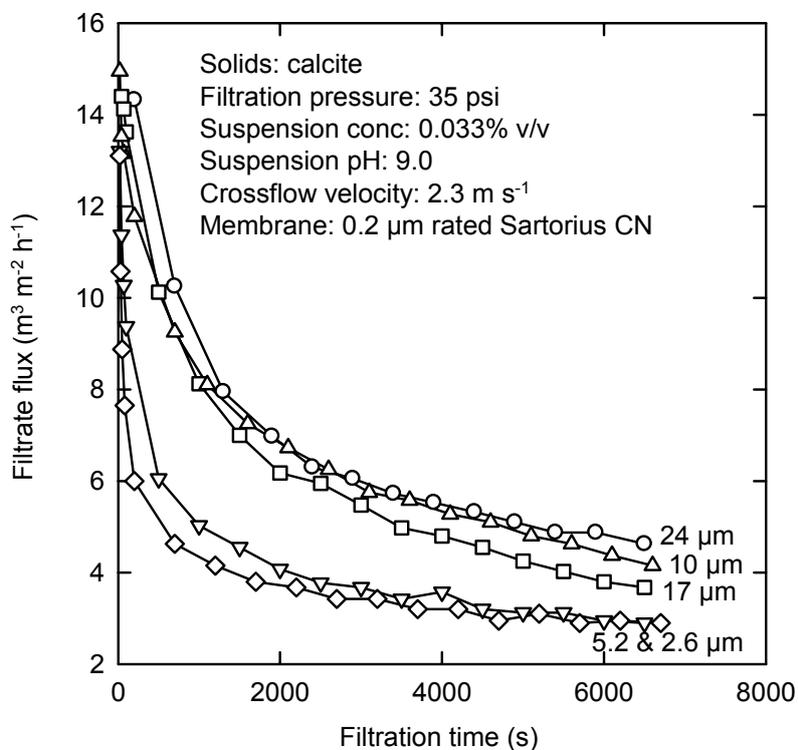


Figure 8: Typical effect of mean particle size on flux decline for calcite suspensions.

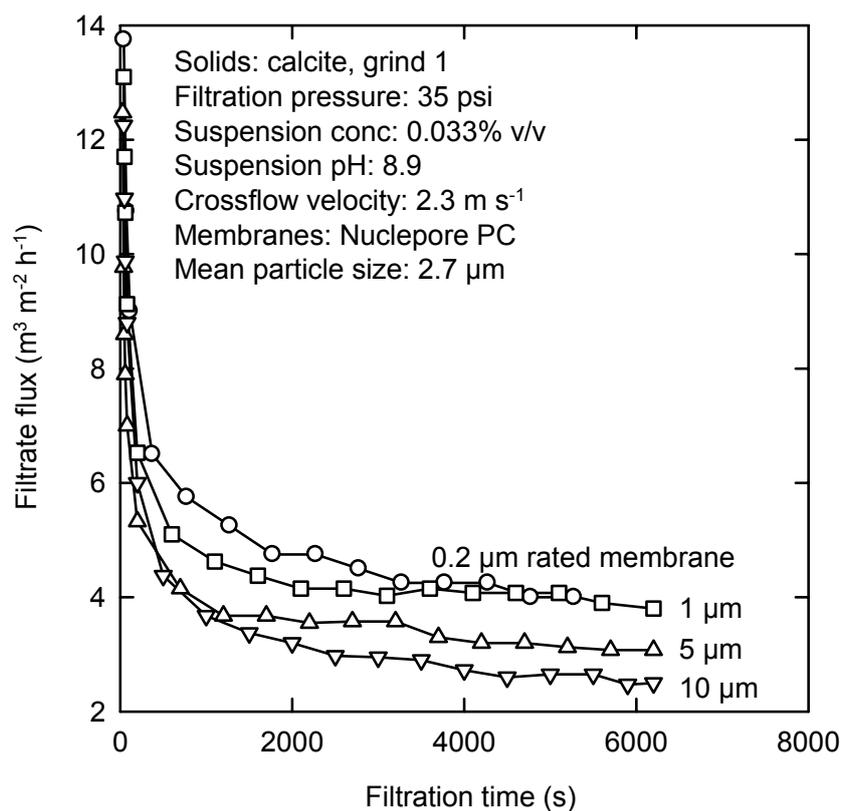


Figure 9: Effect of membrane pore size on flux decline for fine calcite suspensions.

Particle/process stream	Membrane
Size/size distribution	Pore size/size distribution
Particle shape	Asymmetry
pH - ζ -potential relationship	Pore shape
Rheology	Wettability
	Permeability

Table 1: Parameters evaluated in the characterisation experiments.

Membrane type and rating (μm)	Thickness (μm)	Clean water flux at 10 psi ($\text{ml cm}^{-2} \text{min}^{-1}$)	Permeability (m^2)
Nuclepore PC (10)	10	456	1.1×10^{-14}
Nuclepore PC (5)	10	390	9.4×10^{-15}
Nuclepore PC (1)	11	56.4	1.5×10^{-15}
Nuclepore PC (0.2)	10	11.2	2.7×10^{-16}
Sartorius CN (8)	140	355	1.2×10^{-13}
Sartorius CN (5)	140	198	6.7×10^{-14}
Sartorius CN (1.2)	140	136	4.6×10^{-14}
Sartorius CN (0.2)	130	15.9	5.0×10^{-15}

Table 2: Membrane thickness and permeability data.

Feed stream	Membrane	Process parameters
Particle size	Pore size	Solids concentration
pH (surface charge)	Pore shape	Crossflow velocity
	Polymer type	Filtration pressure

Table 3: Matrix of properties examined in the filtration experiments.