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UNDERSTANDING FLUX DECLINE IN CROSSFLOW MICROFILTRATION – PART I: THE EFFECTS OF PARTICLE/PORE SIZE

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ABSTRACT
Experimental data have been obtained from a computer controlled crossflow microfiltration apparatus. Polymer membranes of differing properties were characterised and used to filter aqueous suspensions carrying colloidal and fine particles of known shape, size, surface charge and chemical composition. The characterisation and experimental procedures are described and sample flux decline curves presented. By changing the size and size distribution of the feed and the pore size of the membrane in a systematic manner, the importance of the pore/particle size ratio to fouling is illustrated. The data obtained explain some of the apparent anomalies which have been presented in previous publications and highlight some important design criteria for membrane installations.

KEYWORDS
Microfiltration; Membranes; Fouling; Characterisation

INTRODUCTION
The separation of solid/liquid systems has become an important topic in both industry and academia. The former is driven by ever stricter legislation from governments and international bodies to manufacture their products with a minimum of damage to the environment whilst attempting to maintain their own competitiveness in the market place. This need for improved efficiency (at a realistic cost) has fuelled research not only into existing separation methods but also provided the impetus to develop new technologies. These technologies, frequently invented and nurtured in the laboratories of academic institutions, address the growing problem of processing feed streams, and perhaps more importantly waste streams, containing finer particulates. The development of the pressure driven membrane processes reverse osmosis, ultrafiltration and more recently microfiltration, promised to solve the problems inherent with other separation techniques. Whilst reverse osmosis is now becoming the 'standard' method for the desalination of sea water, microfiltration, and to a lesser extent ultrafiltration, are still struggling to become widely accepted as viable processes. Although some apparently successful applications have been reported it is acknowledged that the fouling problems associated with micro- and ultrafiltration are poorly understood and prevents the more widespread use of the technologies – although it is recognised that ultrafiltration is now becoming more widely accepted in, for example, the dairy industry.

Crossflow microfiltration was originally perceived as a method of dewatering aqueous suspensions, with particulates typically in the range 0.05-30 μm, by utilising shear generated forces to prevent the formation of deposits or cakes at the filtering surface. Despite the use of crossflow velocities up to 8 m s⁻¹, the shear rates generated at the membrane surfaces are frequently insufficient to prevent significant fouling by particulates; the rapid decline from the relatively high membrane clean water fluxes at the start of filtration and the subsequent low quasi-steady flux levels which follow being the undesirable consequences. Whilst researchers have in the past attempted to alleviate fouling through, for example the use of imposed force and rotational fields, many others have attempted to understand the fundamental reasons for flux declines and fouling mechanisms in crossflow filtration processes. Experimental research programmes, although setting out with
the best intentions, have often struggled with the need to use 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. As a consequence the published literature is often conflicting and confusing to the extent that problems understanding the effects of even basic parameters such as crossflow velocity and filtration pressure remain unresolved. Theoretical work\textsuperscript{13-21}, which appears to have been particularly prevalent in the microfiltration literature recently, has suffered as a result of the conflicting experimental data. The models produced, whilst tackling an inherently complex problem, seem to be acclaimed successful or otherwise on their ability to interpret flux decline data and not on the correctness of their description of the particle and deposit dynamics. The latter has always been an assumption of the chosen model, and has been claimed to be appropriate if interpretations of the former happen to turn out to be of the right order of magnitude. Attempts to substantiate the assumptions have usually been by recourse to fresh experimental observations of particles in wholly different flow and compositional environments (or in some cases no experimental verification has been offered at all). This ‘black box’ approach to modelling must be judged in terms of the applicability of the models to real systems. Previous work\textsuperscript{22} has shown that even the best of the existing models\textsuperscript{23}, which is perhaps surprisingly an empirically derived relation between flux and process parameters rather than a more rigorous model derived from fundamental principles, can only reliably predict flux performance within two orders of magnitude of the true value.

The above considerations, taking previously published work into account, suggest that there is a need for a coordinated experimental research programme which examines the fundamental aspects of membrane fouling. This paper describes the results of part of such a programme were the matrix of variables which most affect the microfiltration of aqueous suspensions are properly delineated and investigated using a well controlled filtration apparatus. The characterisation and experimental procedures used are described in detail and the results of the microfiltration experiments presented through typical flux decline curves. The extensive experimental work involved in the research programme necessitates that only the effects of particle size and membrane pore size on flux decline are described in detail here. The effects of the other process variables known to influence microfiltration will be related in future papers.

**EXPERIMENTAL TECHNIQUES AND PROCEDURES**

The experimental programme may be conveniently divided into two parts. The first, involved work to characterise the properties of the particles, suspensions and membranes and the interfacial interactions between them with the parameters shown in Table 1 measured using commercially available laboratory test equipment. The information acquired from the characterisation tests was subsequently used to aid the analysis of the microfiltration experiments and assess membrane fouling for the range of process conditions examined.

**Membrane Characterisation**

The range of organic microfiltration membranes available commercially in a flat sheet form was initially examined to identify septa with differing structures, material properties and pore size ratings. Many different membranes were subsequently characterised, the Nuclepore (polycarbonate, PC) and Sartorius (cellulose nitrate, CN) membranes which were available in a range of pore size ratings from 0.2 \( \mu \text{m} \) to 10 \( \mu \text{m} \) being typical examples. The micrographs shown in Figures 1 and 2 highlight the distinct differences in the structures of these membranes. Nuclear track etched Nuclepore PC membranes have a structure composed of series of predominantly cylindrical pores dispersed in what appears to be a random manner. Single, discrete pores are of an almost uniform diameter through the membrane whilst doublets, triplets and greater coincidences have a variable shape in both their axial and radial directions. The homogeneous Sartorius CN membranes are produced by a casting process and thus exhibited quite different tortuous structures composed of matrices of interconnected pores.
The pore size and pore size distributions of the membranes were measured with a Coulter porometer. The instrument uses compressed air to displace a flourinated hydrocarbon wetting fluid (trade name Porofil) from the pores of the test specimen. As the air pressure is increased the wetting fluid is displaced from progressively smaller pores and the total air flow rate through the membrane can be related to the pore size. Unsoiled samples of the membranes were tested in accordance with ASTM E1294-89 and sample results are shown in Figure 3 and Table 2. Whilst Nuclepore PC membranes exhibit fairly narrow pore size distributions around mean values close to the manufacturer's quoted ratings, the other membranes tested demonstrated mean pore sizes somewhat different from the quoted ratings. For instance a 0.2 μm rated Sartorius CN membrane has an average mean pore size of 0.51 μm and an 8 μm rated membrane of the same type has mean and 90% pore sizes of 3.6 μm and 4.2 μm respectively where the ‘90% size’ indicates the pore size below which 90% of the total possible flow through the membrane occurs. The range of pore sizes found in the membrane samples widened considerably for the larger pore ratings and more variation was observed in the 90% than the 10% pore size. This perhaps indicates the difficulties experienced in manufacturing larger pore size membranes with ‘tight’ size distributions.

In addition to pore size and size distribution, a number of other membrane characteristics were evaluated and the results are summarised in Table 3. Although full descriptions are not pertinent to the present work a few points are worth emphasising. There is a clear indication that significant differences exist in the permeability of ‘large’ and ‘small’ pore size membranes (e.g. ~10² change between 0.2 μm and 10 μm rated Nuclepore PC membranes) though the reasons for the sometimes large difference between measured and manufacturer quoted values are rather less obvious. The porosities and typical thicknesses quoted for the membranes give an indication of the primary mechanisms by which removal of solids is achieved during filtration. Track etched Nuclepore PC membranes rely to a significant extent on a ‘sieving’ process whereas cast Sartorius CN membranes utilise their tortuous structure to provide more depth filtration when conditions allow.

Suspension Characterisation

A range of powders and a yeast were identified for use as challenge streams in the microfiltration experiments. They included the minerals calcite (CaCO₃), anatase (TiO₂) and china clay, and are considered to encompass the range of properties required to examine and evaluate the parameters which most affect the microfiltration of particulate suspensions. These systems were chosen primarily for their different size, shape and surface charge characteristics, whilst at the same time being representative of ‘real particulates, rather than being idealised such as latex or silica spheres. All behaved in a Newtonian manner over the region of suspension concentrations tested.

The size and size distributions of the chosen particle systems dispersed in double distilled water were evaluated using Malvern Auto- and Master- Sizer laser light scattering instruments and the results are summarised in Table 4. The powders were of an Analar (or equivalent) grade and used without further cleaning or washing in both the characterisation and microfiltration experiments. The smallest mean size of the suspensions tested was exhibited by anatase with most of the particulates in the region of 0.5 μm. A typical china clay suspension had a larger mean size of 4.4 μm and a correspondingly wider distribution. In contrast the unground calcite had a mean size of 24.3 μm respectively and an apparently very wide size distribution when dispersed in water. When the calcite was wet ground in a ball mill the mean size was reduced. To obtain a range of mean sizes the grinding time was varied over the period 0-24 h where the mean size would typically change by an order of magnitude. The unimodal suspensions obtained through wet grinding were also combined in the appropriate proportions to give bimodal suspensions of nominally similar mean sizes but widely differing size distributions such as those shown in Figure 4.
The effect of pH on particle surface charge, and hence $\zeta$-potential, was also determined for the powder dispersions with a Malvern ZetaSizer. The suspension pH was altered with the same electrolytes used in the filtration tests (HCl and NaOH) and double distilled water was used as the dispersing medium. The rhomboidal shape calcite particles have a relatively low surface charge in aqueous suspension with the points of zero and maximum negative $\zeta$-potential occurring at the pH's 8.9 and 10.6 ($\zeta = -20 \text{ mV}$) respectively. Conversely, the tetragonal shape anatase is typical of a high surface charge material where the zero and peak negative $\zeta$-potentials occur at the pH's 3.9 and 9.0 ($\zeta = -60 \text{ mV}$). The platelet shape china clay particles show a steadily increasing negative ‘average’ $\zeta$-potential with increasing pH ($\zeta = -54 \text{ mV @ pH} = 10$) and an isoelectric point in the pH region 0-2. This, however, belies the complicated distribution of surface charge on china clay where in some aqueous solutions the ‘faces’ of a china clay particle have a predominantly negative charge whilst the ‘edges’ exhibit a positive charge.

Microfiltration Apparatus and Test Procedure

The equipment used to assess membrane fouling behaviour is shown schematically in Figure 5. 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 vary the filtration pressure over the range 0-50 psi and the crossflow velocity 0-3 m s$^{-1}$ whilst keeping the feed at a temperature of 30±2ºC.

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 an enclosed rectangular section. During an experiment the process suspension flowed through the rectangular space thus formed and tangential to the membrane to generate shear forces at the filtering surface. The filtrate produced during filtration was collected in a suitable compartment behind the membrane and returned to the feed tank via a flowmeter and piping.

Prior to the start of a microfiltration test the process suspension, made to a known concentration between 0.033% v/v and 2% v/v from either a dry powder and double distilled water, from a diluted slurry (in the case of a wet ground sample) or incubated and grown for a period of days (in the case of yeast), was stirred in the feed tank for a suitable time to produce an homogeneous mixture. The suspension pH was then altered if necessary using the electrolytes hydrochloric acid (HCl) or sodium hydroxide (NaOH) and the resultant mixture stirred continuously. No other dispersants or flocculants were added. The membrane chosen to achieve the separation was cut to size from a larger sheet and mounted in the microfilter pre-wetted with double distilled water. The test was performed at the desired filtration settings with the relevant data permanently stored by the computer. 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.

The matrix of properties shown in Table 5 were investigated for the range of membranes and feed suspensions. The sample data shown in Figures 6-12 highlight the effects of particle size, particle size distribution and membrane pore size on flux decline. Many more similar data were accumulated that confirm the effects shown.

MICROFILTRATION TEST RESULTS
Whilst the parameters shown in Table 5 affected the microfiltration of the suspensions to an extent dependent on their relative magnitudes, the tests showed almost without exception the same general characteristics. When the filtration test commenced a sharp fall in filtration rate from the clean water flux was observed. The rapid fouling of the membrane during this period can be attributed to the accumulation of particulate matter at or near the filtering surface (i.e. due to particle ‘polarisation’ or to cake formation), the particulates being drawn toward the filtering surface by the convective flow of filtrate through the septum. After the rapid initial fouling the rate of flux decline progressively lessened until a near equilibrium filtration rate was observed in most experiments. Here the shearing action generated by the crossflowing stream seemingly prevented further significant deposition of matter at the fouling layer/membrane surfaces.

The Formation of Fouling Layers

When a pseudo-equilibrium flux state is reached in microfiltration it has been suggested that the particles forming the fouling layer(s) are possibly in a state of ‘dynamic equilibrium’ whereby particles are leaving and joining the layer(s) at the same rate20. Romero and Davis20 attributed this to a phenomenon which they called ‘shear induced hydrodynamic self diffusion’, which formed the basis of much of the theoretical work published in recent years. It is hypothesised that a concentrated layer, part of which may be mobile and part stationary depending on the flow conditions in the flow volume above the membrane. The formation of dynamic membranes has been observed30 in a complimentary experimental programme using a high speed, high magnification video system capable of operation at recording speeds up to 400 frames per second and optical resolutions of ~2 μm. Layer build-up was examined for a range of process conditions whilst monitoring flux performance. When larger particle feeds such as unground calcite were filtered the majority of the particulates comprising the fouling layers were deposited within a few seconds of the start of filtration; the resultant, predominantly stationary, layer having a surface unevenness between one and three particle diameters. At the ‘rough’ surface of the deposit particles flowing with the free stream (close to the surface) were observed to roll and jostle between sites along the surface to become permanently lodged or occasionally move back into the free stream. When finer particle feeds such as ground calcite or anatase were filtered a stationary layer was again rapidly established after filtration was initiated, however, here no saltation motion was observed and particles within three (particle) diameters of the deposit surface could be seen to undergo an erratic rolling motion. In conjunction with this erratic motion a moving ‘front’ of particles could sometimes be observed to travel at a low velocity in the direction of the crossflow over the stationary fouling layer already deposited on the membrane. Thus, it would appear that for the process conditions typically found in ‘real’ microfiltration systems, shear induced hydrodynamic self diffusion only tenuously describes the phenomena which are observed in practice.

Fouling by particulates appears to be due to two apparently independent mechanisms which occur simultaneously. The first accounts for the initial sharp decline in permeate flux and is irreversible for all practical purposes, and due to the rapid deposition and capture of the finer particles from the suspension and their subsequent penetration into the pores of the membrane. This is a stochastic process, dependent on localised hydrodynamic conditions close to the pore entrances. The second mechanism is largely reversible and causes further particulate layer(s) to form above the membrane surface; the so called ‘dynamic membrane’.

From hereon we shall refer to the first mechanism where particle penetration occurs and which is largely irreversible as ‘fouling by particulates’, and to the second which is reversible as ‘cake formation’. The nature of the ‘cake’ formed in crossflow filtration processes is not to be confused with that which results from conventional deadend filtration. Unlike a conventional cake which has its thickness limited by the available pressure and whose limiting thickness is approached as the available hydraulic pressure is dissipated as a cumulative drag at the surface of the particles as the fluid passes through the cake, one formed in microfiltration (or ultrafiltration) has its thickness limited by the shear forces at the free surface. When the sum of the cohesive forces between the particles and the drag acting on the particles at the free surface, causing the particles to remain in
the cake, is equal to the shear forces tending to remove particles from the cake, the cake can be said to have a pseudo constant thickness. Hence, in deadend filtration the filtrate flux tends to zero as the limiting thickness of the cake is reached, but in crossflow filtration this flux condition is frequently not reached and a finite flux can be associated with the limiting thickness. When a gel, rather than a cake, is formed at the surface of the membrane, then a flux close to zero can be found when the limiting cake thickness is reached (this is more common in ultrafiltration than it is in microfiltration).

Effects of Particle Size

Figures 6 and 7 show the typical effects on flux decline of changing the median particle size of a calcite suspension by wet grinding prior to filtration. As a general rule a reduced particle size in the feed resulted in lower overall flux levels being recorded. However, the situation is complicated by a number of factors. With a smaller 50% particle size there was a tendency for the filtrate flux to be reduced more rapidly at the start of filtration and a pseudo-equilibrium flux to be established sooner. Thus, the fluxes recorded at longer filtration times for ‘large’ and ‘small’ particle systems were often similar in magnitude, particularly at higher crossflows (and possibly higher concentrations) where the flux performance did not necessarily follow the simple ‘smaller size gives lower flux’ relationship. Crossflow velocity has been shown to affect the filtration of particulate suspensions in different ways. For feed suspensions containing a higher proportion of larger particles, a raised crossflow velocity caused the filtrate flux to fall to lower values – this can be observed by comparing Figure 6 and 7. Here, the seemingly preferential deposition of finer particle species at the septum surfaces introduces a classification effect and the layer(s) responsible for membrane fouling can have a resistance considerably higher than that which might be expected from a simplistic approach. As the crossflow velocity is raised the fouling layer is thought to become composed of progressively finer particle species which form higher resistance deposits leading to lower filtration rates. With smaller particle systems a raised crossflow has the opposite effect of improving the filtration rate. At intermediate particle sizes there can exist situations where increasing the crossflow over the range 0-3 m s\(^{-1}\) does not significantly affect filtrate flux rates. A higher crossflow velocity will tend to move the fluxes recorded for different particle size feeds closer together and may thus result in the flux recorded for the smaller particle size system sometimes being above that measured for the larger (e.g. Figure 7).

Effects of Particle Size Distribution

It seems likely that the fouling layers formed during the filtration of different particle size systems will be of a different structure and composition. In conventional deadend filtration, where the bulk suspension flow is normal to the filtering medium, smaller particle systems usually form cakes with a higher resistance to filtration than large particle systems. For crossflow microfiltration, however, the situation is not as clear due to the particle classification phenomena described previously. Such an effect in combination with the lack of true cake formation makes identifying the particles responsible for the formation and structure of the cake layer more difficult to quantify. Although previous attempts have been made to measure the size distributions in cake layers, perhaps a more reliable insight can be gained by testing the filtration performance of suspensions with the same 50% size but differing size distributions. The data shown in Figure 8 for low concentration and crossflow were acquired using calcite suspensions with a nominal 50% size of 10 μm (see Table 4). The flux decline curves for mixes 1 and 2 and mixes 3 and 4 are essentially identical and exhibit flux levels below that recorded for the experiment performed using the suspension designated ‘grind 2’. What is interesting to note here is that mixes 1 and 2 are both partly composed of a suspension with a 50% size of 5.2 μm (grind 3) whilst mixes 3 and 4 both have a component from a suspension with a 50% size of 2.6 μm (grind 4). These results support the hypothesis that it is the smaller particles in the feed which are predominantly responsible for the formation of the fouling layer in or on the membrane.

It therefore follows that some size fraction less than the 50% percentile should be used to characterise the feed as this is more indicative of the fouling potential of the feed. When either the crossflow velocity or suspension concentration is raised the flux decline curves for the different size distribution feeds tend to come together at longer filtration times and near identical flux declines are observed for the suspensions shown in Figure 8 when filtering with a crossflow of 2.3 m s\(^{-1}\) and a suspension concentration of 0.33% v/v. When the magnitude of either of these two operating parameters is raised the flux performance achieved is essentially 'de-sensitised' to the influences of particle size distribution and the similar fluxes achieved after a short initial differential period suggest that the fouling layers have similar properties and are perhaps composed of particles with similar sizes and size ranges.

The influence of particle fines is perhaps most clearly illustrated in Figure 9. The three sets of data on the graph show the flux decline curves for calcite suspensions exhibiting 50% sizes of 2.6 \(\mu\)m, 9.9 \(\mu\)m and 24.3 \(\mu\)m respectively. The suspension with a 50% size of 9.9 \(\mu\)m was composed of a mix of suspensions with median sizes of 2.6 \(\mu\)m and 24.3 \(\mu\)m respectively. The near identical flux performance between the 2.6 \(\mu\)m and 9.9 \(\mu\)m median size suspensions confirms that only a certain proportion of the feed, that is the fines, determine the fouling rates. This result was confirmed with a sequence of tests using mixtures of anatase and calcite suspensions were even the addition of small amounts of anatase powder to otherwise pure calcite suspensions resulted in significantly lower flux rates.

**Effects of Membrane Pore Size**

Membrane pore size was found to affect filtration performance to an extent dependent on a number of factors. Figure 10 shows the typical effects of filtering a feed suspension with a majority of particulates significantly larger than the pore sizes present in the membrane septum. Here, 0.2 \(\mu\)m and 10 \(\mu\)m rated Nuclepore PC membranes were used to filter unground calcite suspensions having 50% sizes in excess of 20 \(\mu\)m. It is immediately obvious that for the given experimental conditions the fluxes recorded for both membranes are very similar with perhaps only the initial stages of filtration showing any discernible difference. The result is perhaps surprising when one considers the permeabilities of the two membranes (see Table 3). The characterisation experiments showed that there are approximately two orders of magnitude difference in the permeabilities of 10 \(\mu\)m and 0.2 \(\mu\)m rated Nuclepore PC membranes with intermediate pore size ratings somewhere between. Thus, in a simplistic sense it would be reasonable to assume that the use of more permeable membranes would produce improved filtration rates whilst allowing macromolecules and maybe some fines to pass through the membrane with the filtrate. The fact that little difference in filtration rates or filtrate clarity were observed with unground calcite suspensions and various pore size membranes suggests that here it was the fouling layer formed at the membrane surface during filtration which played the most significant role in determining flux performance.

When suspensions of finer particulates were filtered using different pore size membranes further effects were observed (see Figure 11). Whilst in some cases virtually no difference in flux performance could be detected (in particular for china clay suspensions where the situation is complicated by particle shape effects) the majority of tests indicated that increasing the membrane pore size caused a reduced filtration performance both in terms of flux levels and visual quality of filtrate. Here it seems that particulates were fouling the membrane pores internally, as well as at the pore throats, to an extent dependent on the overlap between the particle and pore sizes present in the feed stream and membrane respectively. The filtrate quality usually improved with filtration time as the deposit on or in the membrane gradually formed and the clarity was often further enhanced at higher crossflows. In the case of these finer suspensions it seems that membrane fouling was influenced to a greater extent by the mechanical interactions between the internal surfaces of the membranes and the particles forming the fouling layers, rather than merely the formation of surface cake layer.
Although the effects of membrane pore size described were observed in the vast majority of tests a couple of the experiment sequences gave rather curious, but pertinent, results. Figure 12 shows that for the given experimental conditions a 5 μm rated membrane gave a flux significantly higher than the 0.2 μm, 1 μm and 10 μm rated membranes. The filtrate produced during the test with the 5 μm membrane also remained cloudy throughout the course of the filtration whilst the other three tests all produced visually clear filtrates; in some cases after a few minutes filtration. That these data could be repeated using different batches of membranes (i.e. result could not be explained by faulty samples or the presence of pin-holes in the membrane) is curious, however, similar types of behaviour were observed for a sequence of data obtained from experiments with yeast and have been occasionally reported in ultrafiltration literature\textsuperscript{33}. It would seem that for certain combinations of process conditions and pore to particle size ratios some membranes will not produce a high rejection when comparisons between the particle and pore sizes present in the challenge stream and membrane respectively suggest they should.

DISCUSSION

A recent review of crossflow microfiltration of cell suspensions has been presented by Lojkine \textit{et al.}\textsuperscript{34}. It is confirmed by that review that particle size effects and particle-pore interactions have not been the subject of systematic experimental studies taking into account all the main variables in the process, but what observations have been made are from investigations of a limited range of parameters. Nonetheless, some important observations have been made, and it is noted that in general the mean size of the particles found in the cake layer is less than that of the feed particles\textsuperscript{6,32,36-38}, this is confirmed by the present work. Fischer \textit{et al.}\textsuperscript{36}, filtering calcium carbonate slurries, also found that the size of the particles in the cake layer decreased as the crossflow velocity increased, leading to a reduction of the permeate flux with increased crossflow velocity even though the cake thickness was decreased. Contradictory results also exist in the literature. For example, Sims \textit{et al.}\textsuperscript{39} found that flux increased when the particle size of \textit{Aspergillus niger} suspensions was reduced from 20-850 μm to 20-150 μm. It is conceivable that this is due to a reduction of the packing density in the cake layer, as it is well known that a wider size distribution will lead to a tighter packing density\textsuperscript{40} and a higher cake resistance\textsuperscript{41}. It has also been noted that permeate flux increases with particle size when filtering kaolin slurries\textsuperscript{42}.

The extent of particulate fouling in crossflow microfiltration is related to a matrix of feed stream, membrane and process parameters. The microfiltration experiments showed that among the more important of these are the particle size of the feed and the membrane pore size. When the particle size which is representative of the fouling potential of the feed stream is large in comparison with a ‘representative’ membrane pore size, cake formation by particulates is the predominant mechanism causing flux decline. When the converse is true, however, and the pore size is large in comparison to the particle size, pore penetration by particulates occurs to a degree dependent on the overlap between the size distributions of the solids in the feed and the pores in the membrane. Fouling in this latter instance occurs through a combination of surface and internal pore blockage.

The fouling and cake layer formed during crossflow filtration has previously been recognised as being an important factor in determining flux decline\textsuperscript{35}. It has been proposed that three distinct classes of cake (referred to as the dynamic membrane by Murkes \textit{et al.}\textsuperscript{35}) can be identified, with the ratio of a mean particle size in the feed to the mean pore size in the membrane determining the type of ‘dynamic membrane’ formed (Table 6). The classification reproduced in Table 6 is quite self-evident when the particle and pore size variations are both monosized and have no variance. However, in reality the distinction between classifications is not clear-cut as both particle and pore sizes possess associated distribution densities. This was in fact the case in the present work. Nonetheless, the following general observations can be made: (i) the formation of the cake layer on the membrane occurs rapidly when filtration is initiated, and (ii) once formed the cake acts as the filtering medium which rejects the remainder of the dispersed phase(s). The degree to which any of Murkes\textsuperscript{35} proposed dynamic membrane types forms in a test is unclear, however, it is
reasonable to suppose that the filtrations performed with finer particle suspensions involved a significant degree of internal pore blocking (i.e. fouling) by particulates, while experiments with coarser feed streams may have shown more pore bridging and plugging phenomena. Although these terms say nothing quantitative (or even qualitative) about the static or dynamic nature of any cake or fouling layer, similar effects of pore and particle size could be demonstrated with a wide range of particle systems and membrane types used in this work. This indicates that it is not membrane structure that is of prime importance in crossflow microfiltration but rather the interaction between the larger membrane pores and the particle fines in the feed. The relation between these two parameters can determine the degree of internal, largely irreversible, membrane fouling and pore penetration found in any given filtration and points to the need for a clearer definition of the term 'particle fines'. In the context of crossflow microfiltration, particle fines may be considered to be those particulates forming the fouling layer(s) which have sizes similar to or smaller than those of the pores in the filtering surface. The extent to which these particulates influence the flux performance and filtrate clarity is dependent on their number relative to the number of pore entrances in the membrane. When more concentrated suspensions are filtered, there are likely to be more particles (on average) challenging each pore entrance with the result that most deposition will occur at the pore throats near the membrane surface in contact with the feed stream. If more dilute suspensions are considered there will be a lower number of particulates approaching each pore with the consequence that particles have an enhanced probability of entering the pores to cause internal blockage.

McDonough et al. carried out experiments with colloidal silica (mean sizes 0.024 μm and 0.046 μm) and polystyrene lattices (0.19 μm and 0.58 μm), and found that filtrate (or permeate) flux first decreased and then increased with particle size (the minimum flux was obtained with 0.046 μm spheres). They attributed this behaviour to electrical and double layer interactions – these parameters also formed part of this study and will be discussed in Part 2 of this series of papers. The hypothesis advanced in the preceding paragraphs is equally as applicable to McDonough’s data as it is to the data presented here, and when combined with electrokinetic arguments may provide a more complete explanation of his observations.

The shear induced classification of particulates at the membrane surface means that the median particle size of the feed stream is a poor indicator of fouling potential. It would be more appropriate to specify some other size percentile as a representative measure and it is proposed here that the 10% percentile of the cumulative undersize distribution of the particle sizes in the feed should be used. The microfiltration experiments pointed to this. The 10 percentile particle size, together with the 90 percentile of the cumulative undersize number distribution of the pore sizes in the membrane, are considered to provide more reasonable estimates of fouling potential. By utilising such an argument, the data presented in Figures 6-12 (and other similar collections of data) can be illustrated in a way which emphasises the importance of the relationship between pore and particle size in microfiltration. For a data sequence, where for instance membrane pore size is varied and all other experimental conditions remain constant, it is possible to construct a plot similar to Figure 13. Here, the ratio of the 90% pore to 10% particle sizes are plotted against filtrate flux after 2 h filtration at three different crossflow velocities. When the pore to particle size ratio << 1, particles which are relatively large compared to the pores in the septum form predominantly cake layers on the membrane surface. As the ratio approaches one challenging particles will tend to lodge in the pore throats and flux levels will fall. For ratios >> 1 particles approaching the pores are more likely to be trapped internally such that irreversible fouling and lower flux rates ensue.

The selection of a membrane for a given duty must be performed with care. It would seem prudent to attempt to exclude particulates from the internal pore passages of the membrane to enhance both flux performance and rejection. When the membrane is selected such that most of the particles in the feed stream are large in comparison to the membrane pores, cake formation will predominate and provided the membrane permeability is not too low the structure of this deposit, and not the membrane permeability, will control the flux levels achieved. If the membrane is chosen such that there is a significant overlap in the larger membrane pore and finer particle sizes
then more severe fouling is likely to occur. Furthermore, should membrane regeneration be required and cleaning procedures such as backflushing are employed, the removal of particulates from membrane pores will prove more troublesome than the removal of surface deposits.

CONCLUSIONS

The descriptions given in this paper highlight some of the major trends observed in the characterisation and microfiltration experiments. Although the general effects of particle and pore size and their inter-relations are given in Table 7, these statements only summarise part of an integrated series of projects relating to membrane filtration, aimed at providing fundamental understanding and technical solutions to the fouling problems associated with particulates. The remainder of the results concerning particulate fouling will be published in future papers and it is envisaged that, together with a more appropriate model, a new approach to the design and sizing of crossflow microfilters will be produced. Few of the data considered in this paper are independent of each other in any 'real' filtration problem and the task of developing a global model to account for the interactions of all the basic parameters (as well as any chemical changes at the membrane/feed interface(s)) is daunting. Until there is a fundamental understanding of such interactions and their contributions to the fouling process, no complete picture of membrane filtration will be obtained.

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Science and Engineering Research Council under the auspices of the Specially Promoted Programme in Particle Technology to fund a part of the work presented in this paper.
FIGURES AND TABLES

Figure 1: The topography and cross-section of a 1 μm rated Nuclepore PC membrane.

Figure 2: The topography of a 1.2 μm rated Sartorius CN membrane.
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Figure 4: Size distributions of the calcite suspensions with a mean particle size of 10.1±0.18 μm.
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Figure 6: Effect of particle size on flux decline for calcite suspensions at lower crossflow velocity.
Figure 7: Effect of particle size on flux decline for calcite suspensions at higher crossflow velocity.

Figure 8: Effect of particle size distribution on flux decline for calcite suspensions at low crossflow and concentration.
Figure 9: Effect of particle fines on flux decline for calcite suspensions.

Figure 10: Effect of membrane pore size on flux decline for unground calcite suspensions.
Figure 11: Effect of membrane pore size on flux decline for anatase suspensions.

Figure 12: An effect of membrane pore size on flux decline for china clay suspensions.
Figure 13: Influence of pore/particle size ratio on filtrate flux for calcite (grind 4) suspensions and Nuclepore PC membranes.
Table 1: Parameters evaluated in the characterisation experiments.

<table>
<thead>
<tr>
<th>Particle/process stream</th>
<th>Membrane</th>
</tr>
</thead>
<tbody>
<tr>
<td>Particle size</td>
<td>Pore size</td>
</tr>
<tr>
<td>Particle size distribution</td>
<td>Pore size distribution</td>
</tr>
<tr>
<td>Particle shape</td>
<td>Pore shape</td>
</tr>
<tr>
<td>pH, ζ-potential relationship</td>
<td>Asymmetry</td>
</tr>
<tr>
<td>Rheology</td>
<td>Permeability</td>
</tr>
<tr>
<td>Compression characteristics</td>
<td>Wettability</td>
</tr>
</tbody>
</table>

Table 2: Average pore size and variations in ten samples taken from 293 mm membrane circles.

<table>
<thead>
<tr>
<th>Membrane type</th>
<th>Rating† (µm)</th>
<th>90% size variation (µm)</th>
<th>50% size variation (µm)</th>
<th>10% size variation (µm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Nuclepore PC</td>
<td>10</td>
<td>11.70 (+3.11/-0.73)</td>
<td>10.26 (+0.65/-0.27)</td>
<td>8.99 (+0.33/-0.29)</td>
</tr>
<tr>
<td>Nuclepore PC</td>
<td>5</td>
<td>6.00 (+0.12/-0.12)</td>
<td>5.56 (+0.10/-0.11)</td>
<td>5.03 (+0.12/-0.10)</td>
</tr>
<tr>
<td>Nuclepore PC</td>
<td>1</td>
<td>1.32 (+0.02/-0.03)</td>
<td>1.26 (+0.02/-0.04)</td>
<td>1.17 (+0.02/-0.03)</td>
</tr>
<tr>
<td>Nuclepore PC</td>
<td>0.2</td>
<td>0.364 (+0.007/-0.008)</td>
<td>0.351 (+0.008/-0.007)</td>
<td>0.323 (+0.008/-0.006)</td>
</tr>
<tr>
<td>Sartorius CN</td>
<td>8</td>
<td>4.15</td>
<td>3.63</td>
<td>3.24</td>
</tr>
<tr>
<td>Sartorius CN</td>
<td>5</td>
<td>3.51</td>
<td>3.15</td>
<td>2.82</td>
</tr>
<tr>
<td>Sartorius CN</td>
<td>1.2</td>
<td>1.66 (+0.05/-0.03)</td>
<td>1.45 (+0.03/-0.02)</td>
<td>1.33 (+0.04/-0.04)</td>
</tr>
<tr>
<td>Sartorius CN</td>
<td>0.2</td>
<td>0.58 (+0.05/-0.03)</td>
<td>0.51 (+0.04/-0.02)</td>
<td>0.46 (+0.02/-0.02)</td>
</tr>
</tbody>
</table>

†manufacturers designation

Table 3: Miscellaneous membrane characterisation data.

<table>
<thead>
<tr>
<th>Property</th>
<th>Nuclepore PC</th>
<th>Sartorius CN</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ratings (µm)</td>
<td>0.2-10</td>
<td>0.2-8</td>
</tr>
<tr>
<td>Pore size variation with pH</td>
<td>not tested†</td>
<td>none for pH's 2.3-11.5</td>
</tr>
<tr>
<td>Measured permeability (m²)</td>
<td>2.7-110 x10⁻¹⁶</td>
<td>5-120 x10⁻¹⁵</td>
</tr>
<tr>
<td>Stated permeability‡ (m²)</td>
<td>4.8-600 x10⁻¹⁶</td>
<td>4.7-180 x10⁻¹⁵</td>
</tr>
<tr>
<td>Pore density (pores cm⁻²)</td>
<td>3000-1x10⁵</td>
<td>not applicable</td>
</tr>
<tr>
<td>ζ-potential</td>
<td>-ve for pH's 2-11 ²⁷</td>
<td>-ve for pH's 2-12 ²⁸</td>
</tr>
<tr>
<td>Typical porosity (%)</td>
<td>10</td>
<td>75</td>
</tr>
<tr>
<td>Typical thickness (µm)</td>
<td>10</td>
<td>135</td>
</tr>
<tr>
<td>Wettability (contact angle)</td>
<td>hydrophilic* (53°)</td>
<td>hydrophilic (31°)</td>
</tr>
</tbody>
</table>

†due to design limitation of porometer, ‡by manufacturer for water permeation
*known to be coated during manufacture

### Table 4: Particle size data for powders dispersed in double distilled water.

<table>
<thead>
<tr>
<th>Solids</th>
<th>Suspension pretreatment (and designated name)</th>
<th>10% size (μm)</th>
<th>50% size (μm)</th>
<th>90% size (μm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>calcite</td>
<td>unground</td>
<td>11.03</td>
<td>24.31</td>
<td>45.59</td>
</tr>
<tr>
<td>calcite</td>
<td>wet ground 20 mins (grind 1)</td>
<td>5.17</td>
<td>17.10</td>
<td>36.35</td>
</tr>
<tr>
<td>calcite</td>
<td>wet ground 1.5 h (grind 2)</td>
<td>1.86</td>
<td>9.97</td>
<td>23.22</td>
</tr>
<tr>
<td>calcite</td>
<td>wet ground 5 h (grind 3)</td>
<td>1.01</td>
<td>5.23</td>
<td>13.12</td>
</tr>
<tr>
<td>calcite</td>
<td>wet ground 24 h (grind 4)</td>
<td>0.77</td>
<td>2.52</td>
<td>5.68</td>
</tr>
<tr>
<td>calcite</td>
<td>unground + grind 3 (mix 1)</td>
<td>2.49</td>
<td>10.15</td>
<td>31.53</td>
</tr>
<tr>
<td>calcite</td>
<td>grind 1 + grind 3 (mix 2)</td>
<td>1.96</td>
<td>10.16</td>
<td>28.99</td>
</tr>
<tr>
<td>calcite</td>
<td>unground + grind 4 (mix 3)</td>
<td>1.31</td>
<td>9.93</td>
<td>38.32</td>
</tr>
<tr>
<td>calcite</td>
<td>grind 1 + grind 4 (mix 4)</td>
<td>1.28</td>
<td>10.29</td>
<td>31.90</td>
</tr>
<tr>
<td>anatase</td>
<td>-</td>
<td>0.20</td>
<td>0.54</td>
<td>1.49</td>
</tr>
<tr>
<td>china clay</td>
<td>-</td>
<td>0.79</td>
<td>4.42</td>
<td>14.24</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Feed stream</th>
<th>Membrane</th>
<th>Process parameters</th>
</tr>
</thead>
<tbody>
<tr>
<td>Particle size</td>
<td>Pore size</td>
<td>Solids concentration</td>
</tr>
<tr>
<td>Particle size distribution</td>
<td>Pore shape</td>
<td>Crossflow velocity</td>
</tr>
<tr>
<td>Particle shape</td>
<td>Pore asymmetry</td>
<td>Filtration pressure</td>
</tr>
<tr>
<td>pH (surface charge)</td>
<td>Surface charge</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Polymer type</td>
<td></td>
</tr>
</tbody>
</table>

### Table 5: Matrix of properties examined in the microfiltration experiments.

### Table 6: The proposed classification of dynamic membrane types.35

<table>
<thead>
<tr>
<th>Particle (x) and pore (d_p) sizes</th>
<th>Comments</th>
</tr>
</thead>
<tbody>
<tr>
<td>x &gt; d_p</td>
<td>A ‘dynamic membrane’ forms on the membrane surface with little pore penetration by particulates (designated Class 1).</td>
</tr>
<tr>
<td>x &lt; d_p</td>
<td>Pore penetration by particulates occurs here to cause internal fouling of the membrane. As the foulant layers accumulate so the rejection of the membrane improves (Class 2).</td>
</tr>
<tr>
<td>x ≈ d_p</td>
<td>With similar particle and pore sizes the ‘dynamic membrane’ is formed both in the pores due to penetration and around the pore throats (Class 3).</td>
</tr>
<tr>
<td>Property</td>
<td>Comment</td>
</tr>
<tr>
<td>--------------------</td>
<td>------------------------------------------------------------------------------------------------------------------------------------------</td>
</tr>
<tr>
<td>Particle size</td>
<td>At smaller particle sizes filtrate fluxes were generally lower and equilibrium was established more rapidly. The presence of even a small percentage of fines significantly lowered flux rates. At higher crossflows and longer filtration times similar fluxes were often observed for a range of suspensions with differing median size.</td>
</tr>
<tr>
<td>Size distribution</td>
<td>Influence most pronounced at low crossflow and concentration where feeds containing the greater proportion of fines gave the lower filtration rates. At higher crossflows and concentrations, where the effective number of particles challenging each pore was increased, the effects on flux performance were negligible.</td>
</tr>
<tr>
<td>Membrane pore size</td>
<td>Little influence on flux or rejection when the majority of the particles in the feed were significantly larger than the pores in membrane. Filtrate quality and flux levels often worse when a significant proportion of the particles in the feed were close to or smaller than the membrane pores. If the pore sizes in the membrane were much larger than the particles in the feed stream, flux rates improved to higher levels although solids rejection was very poor. In a minority of tests poor rejection was observed when comparisons of pore/particle size suggested that filtrate clarity should be good.</td>
</tr>
</tbody>
</table>

Table 7: Summary of the influence of particle/pore size in microfiltration.