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An Experimental Study of Particulate Retention by Microporous Membranes in Liquid Filtration

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An experimental study of particulate matter retention by 0.1, 0.22, 0.45, and 0.65 μm rated membrane filters during liquid filtration has been made with polystyrene latex spheres using an automated filter test system and a laser particle counter. The filtration during particle loading tests was found to begin with a sieving dominant regime followed by a transition regime and a cake filtration regime as particles accumulate inside the filter pores and on the filter surface. For latex sphere sizes that are equal to the nominal pore size of the filter, the initial filter efficiencies were found to range from 97 to 99.9%. Complete retention($>$99.9999999%) was achieved for a range of particle sizes that are 2 to 3 times the rate pore sizes of the filter.

Key Words : Liquid Filtration, Sieving, Cake Filtration, Membrane, Laser Particle Counter, Latex Spheres.

1. Introduction

Particulate matter in liquids is one of the most important contributors to particulate contamination in many industrial processes. For example, semiconductor manufacturing, pharmaceutical and biological processing, and sterile filtration utilize filtration for particle removal from process liquids. Liquids may contain various suspension contaminants : organics, bacteria, silica, particulates, ionic impurities, and dissolved gases. In the case of liquid chemicals, the particle concentration in even very clean chemicals may be thousands of times higher than the corresponding concentrations in gases. For example, typical particle concentration($>$0.5 μm in diameter) of bottled process chemicals is from 1,000 to 50,000 particles/liter, while for air in a class 10 clean room the particle concentration is less than 0.4 particles/liter for particles $>$0.5 μm(Lee, 1992).

Liquid filtration can be described as the separation of solids from liquids by passing a suspension through a permeable medium which retains the particles. The only effective mechanism that can be relied upon to remove suspended particles in a liquid is sieving, although the actual efficiency of filtration will be modified by charge effects due to electrical double-layer, adhesion, adsorption, and hydrophobic or hydrophilic properties of the filter. For this reason, the actual performance of a filter for liquid filtration must be studied experimentally.

The dominant particle capture mechanisms in liquids are sieving and cake filtration. In sieving, if the size of the particles present is larger than the pore opening in the filter, the particles will be captured and retained. The mechanism is also known as mechanical sieving or straining. Retention by sieving will theoretically be unaffected by the test or process conditions. In cake filtration, the accumulation of a thick layer of collected particulate material on the upstream face of the filter provides a porous medium through which the liquid must pass. A very important factor in cake filtration is the permeability or the resistance of the cake, which is determined by the properties

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of the filtered particles and the structure of the cake formed.

Membrane filters are widely used for filtration and they have been shown to be highly effective in reducing the particulate concentration levels in both gases and liquids (Brock, 1983; Rubow and Liu, 1986). For liquid filtration applications, membrane filters are usually tested with bacteria or polystyrene latex(PSL) spheres (Grant and Liu, 1991; Pall et al., 1980). Although bacterial retention tests can provide realistic particulate challenge at levels up to 10^{13} organisms/liter, it is difficult to characterize the true physical process involved because the size of the organism is not verifiable during testing and it is not a real time test. Latex sphere retention tests with particles of a known size have been shown to be more convenient than bacterial challenge tests in elucidating the particle capture mechanisms in liquid filtration and the performance characteristics of the filter during particle loading. The latex sphere test can be done in real time and can be performed using on-line equipment that is commonly available, and with spheres that have well-controlled particle size characteristics.

The purpose of this study was to investigate experimentally the particle removal efficiency of microporous membranes using monodisperse and polydisperse latex spheres. Test methods have been developed for investigating the characteristics of the membrane filter for particle retention and loading effect in filters. Retention testing was done by measuring particle concentrations upstream and downstream of the test filter using an automatic liquid-borne laser particle counter(LPC).

2. Experimental Appratus and Test Procedure

2.1 Test Apparatus

Figure 1 is a schematic diagram of the filter test system developed for particle retention studies. It consists of a pump-driven water recirculating system to provide clean, near particle free deionized(DI) water for the tests, a particle injection system, a test filter housing, the LPC, a dilution system, and pressure measuring system. DI water contained in the tank is continuously recirculated by the pump and transported to a prefilter housing for the removal of unwanted contaminants. The particles are introduced using a syringe pump. The test filter holder is designed

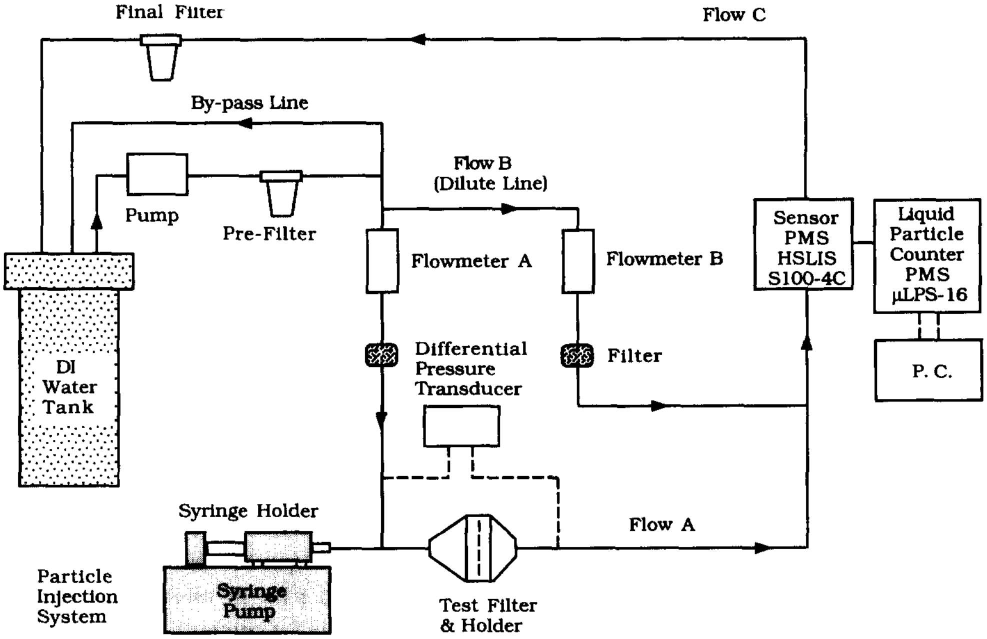

Fig. 1 Schematic diagram of the experimental system for particle retention testing

for 47 mm disc filters, but filters of other diameters can readily be used by using a different size filter holder. The differential pressure transducer in the system monitors the pressure drop across the test filter, while the laser particle counter measures the concentration of test particles, both upstream and downstream of the test filter. A final filter is used to collect particles downstream of the test filter. The prefilter and final filter contain Millipore filter cartridges with 0.1 μm rated polyvinylidence difluoride(PVDF) membrane in a stacked disc configuration. A dilution system is used to obtain the proper flow rate and particle concentration for the LPC. The test system is constructed of a fluorocarbon material to minimize particle shedding and the addition of unwanted contaminants from the material.

The system fluid is DI water containing 0.1% non-ionic surfactant(Triton X-100), the critical micelle concentration for that surfactant. This system fluid has a surface tension of 32.3 dyne/cm and a pH of 7.1. Since surfactant influences the filter efficiency by lessening the probability of particle adhesion to the filter surface by "depth filtration," its use will reduce particle retention to that by sieving alone and provide test data that would represent the "worst case" scenario in terms of particle retention characteristics for the specific filter(Lee, 1992).

The LPC used in this study is a Particle Measuring Systems High Sensitivity Liquid In-Situ(HSLIS S100-4C) sensor coupled with a μ LPS-16 spectrometer. This instrument incorporates an in-situ type sensor which samples a small portion of the total volume passing through the sensor. This sensor uses a He-Ne laser light source and can detect particles from 0.1 μm to 1.0 μm in diameter. The particle sensing occurs in a 1 cc/min stream flowing through the sensor for total sensor liquid flow rate of 300 cc/min. The total flow of 300 cc/min through the sensor is monitored by rotameters A and B placed upstream of the LPC.

The pressure drop across the test filter is measured using a differential pressure transducer(Setra Model 228-1) and a pressure readout(Setra, Model 300D). The accuracy of the pressure transducer is $\pm$0.15%. A personal computer is used to collect and record data from the transducer as well as receiving the output data from the LPC. The flow rate through a test filter is monitored by Rotameter A placed upstream of the filter. The tests are usually performed with filter face velocities of 2.7 cm/min which represents the typical face velocity in many industrial processes.

2.2 Test Filters

Microporous membranes of PVDF from Millipore Corporation were used in this study. Table 1 shows the specification of the various membrane filters used in this study.

The PVDF filter media used were 0.1, 0.22, 0.45, 0.65 μm rated microporous membranes. These hydrophilic media, 47 mm disc filters, have a typical filter thickness of 110 μm, a porosity of 70-75%, and a negatively charged zeta potential of 25.2 mV(Lee, 1992). The isopropyl alcohol bubble points using porosimetry testing for the 0.1, 0.22, 0.45, and 0.65 μm rated filters were 33.5, 20.9, 11.7, and 6.7 psig, respectively(Lee, 1992).

Table 1 Specifications of Membrane Media Used for Study.

Filter Type	Polyvinylidene Difluoride (PVDF)			
Mean Pore Size (μm)	0.1	0.22	0.45	0.65
IPA* Bubble Point (psig)	33.5	20.9	11.7	6.7
Water Pressure Drop (psig)**	10.3	3.1	1.1	0.5
Zeta Potential in DI Water	−25.2 mV			

Note :

* IPA : Isopropyl alcohol($\gamma_{IPA}=21.7$ dyne/cm).

**Pressure drop across a clean filter at 2.7 cm/min face velocity. Typical filter thickness : 110 μm, Porosity : 70~75%. All test filters were obtained from Millipore Corporation.

2.3 Test Particles

Particle suspensions used in these tests were monodisperse polystyrene latex(PSL) spheres obtained from Seradyn Inc. and Interfacial Dynamics Corp. The particle diameter ranged from 0.1 to 2.0 μm. The zeta potentials of these latex spheres were measured with a Model 500 Laser Zee Meter and found to be -40.5 mV and the corresponding surface conductance was found to be 430 μohm^{-1}cm^{-1}(Lee, 1992). The latex sphere concentration used in the tests were very high, and typically at the level 3.0×10^{12} particles/liter. To keep the spheres from agglomerating at these high concentrations, they were singly dispersed in 0.1% non-ionic surfactant(Triton X-100) and DI water. In addition, polydisperse particle suspensions were prepared by mixing monodisperse latex spheres of different sizes to simulate a typical industrial feed having a cumulative particle size distribution in which the log-log slope of particle concentration versus particle diameter was between -2.0 and -3.0.

2.4 Test Procedure

The test procedure used in each test includes the following three basic steps: (1) background particle check, (2) filter and filter holder flush, and (3) filter testing. The background check was performed by measuring the particle concentration of the system fluid without the test filter in place to ensure that the system contained a minimum of unwanted particles. The background particle concentration for particles larger than 0.1 μm in diameter was less than 10 particles/ml. Once a suitable background was obtained, the test filter was inserted into the filter holder. The system was flushed to remove any contaminants on the filter and to allow the pressure drop across the filter to stabilize, i.e., to ensure that the internal filter pores and filter holder were all free of gas bubbles. Once the particle background level was achieved and pressure drop became stable, the needle of a 10 ml syringe(Hamilton Co.) containing the test particle suspension was then inserted into the injection port and the system allowed to stabilize until the background level was reestablished. The particle challenge was then initiated.

The particle concentration downstream of the filter and the pressure drop across a filter were both monitored continuously. The output from the LPC and the pressure transducer output were both recorded into the memory of an IBM-compatible computer through an interface board. At the end of each particle retention experiment, the incoming particle concentration was measured. This was achieved by removing the test filter and injecting the test particles which were diluted to eliminate LPC counting error due to particle coincidence. Typical incoming particle concentration was between 1.8×10^{8} and 1.4×10^{10} particles/liter. This corresponds to a particle concentration which is 1,000-10,000 times the levels typically found in process chemicals. Particle retention was determined by calculating the filter efficiency as a function of particle size and loading. Table 2 shows the summary of test condi-

Table 2 Summary of Test Conditions for Particle Retention Test

System Fluid	DI Water with 0.1% Triton X-100[1] (Surface Tension[2] = 32.3 dyne/cm) pH[3] = 7.1
Test Particles	PSL spheres Zeta Potential in DI water = -40.5 mV Dispersed in 0.1% Triton X-100 Surface Conductance[4] = 430 μohm^{-1}cm^{-1}
Incoming Particle Concentration	1.8×10^{8} to 1.4×10^{10} particles/liter
Filter face velocity	2.7 cm/min
Filter face area	13.38 cm^2
Room temperature	25℃

Notes:

1. non-ionic surfactant, surface tension: 30 dyne/cm.
2. measured by KSV5000(Wilhelmy plate method).
3. measured by pH meter: Orion Model 611.
4. measured by Laser Zee Meter 500.

tions for the particle retention test.

3. Results and Discussion

3.1 Monodisperse Particle Retention

The efficiency of a filter is usually expressed as a log reduction value(LRV), which is defined as

$$LRV = Log\frac{C_i}{C_o} \tag{1}$$

where C_i is the inlet(upstream) particle challenge concentration, and C_o is the outlet(downstream) particle concentration. LRV of 1, 2, 3, and 4 correspond to retention efficiencies of 90, 99, 99.9 and 99.99%, respectively.

The LRV is expected to change during loading as particles are collected by the filter. The particulate loading level of the filter can be expressed as the dimensionless ratio of the total volume of particles collected by the filter to the total pore volume in the filter, or as the percent of pore volume of particles collected. For instance, a single layer of particles of 0.453 μm in diameter deposited on the filter surface will give a total particle volume that is 0.0037=0.37% of the total pore volume in the filter. For 0.741 μm particles the pore volume of particles collected would be 0.006=0.6% for the same single particle layer.

Figure 2 shows the experimental efficiency of the 0.45 μm rated hydrophilic PVDF filter as a function of particle size and particle loading when DI water containing 0.1% non-ionic surfactant is used. The filter efficiency is found to be strongly dependent upon the test particle size. An increase in particle size will lead to an increase in LRV. For the 0.741 μm particle size, the initial LRV is in excess of 5, or >99.999% in terms of efficiency for particle removal. The LRV initially decreases rapidly, and then more gradually, as the filter is partially loaded with particles. With heavier particle loading, the LRV eventually increases with particle loading. Similar results have been obtained for other particle sizes.

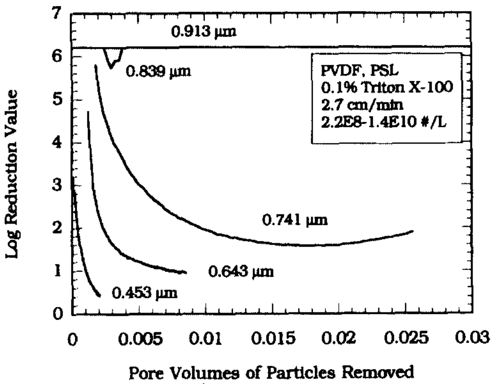

Fig. 2 Experimental filter efficiency of 0.45 μm rated PVDF filters

The above filtration and loading characteristics of the membrane filter provides strong evidence of a filtration regime initially dominated by sieving, followed by a transition regime and eventually a cake filtration dominated regime. The decrease in initial particle retention with loading is caused by some of the smaller pores in the filter becoming plugged by the particles, thus forcing more fluid through the larger pores. As a result, the filter efficiency and LRV both drop. As this proceeds, a cake is built up on the upstream face of filter surface. This surface cake layer provides additional filtration which partially compensates for the drop in filter efficiency caused by the plugging of the small pores. Eventually, the surface cake layer builds up to such a level as to cause increased filter efficiency and LRV for further loading. Similar loading characteristics have been obtained for the 0.22 μm rated PVDF membrane filter.

The efficiency of the 0.45 μm rated filter for 0.913 μm particle was found to be >99.9999999%, the upper limit of detection of the filter test system. Therefore, the data suggest that the 0.45 μm rated filter has achieved absolute particle retention characteristics for the 0.913 μm PSL spheres. Similarly for the 0.22 μm rated filter, absolute retention has been achieved for the 0.48 μm particles.

Figure 3 shows the initial filter efficiency as a function of particle size for various PVDF filters. For particle diameters equal to the rated pore size of the filter, the initial filter efficiencies are 97%, 99.8%, 99.9%, and 99.8% respectively for the 0.1, 0.22, 0.45, and 0.65 μm rated filters. Absolute retention(>99.9999999%) for 0.1, 0.22, 0.45, and 0.65 μm rated filters can be obtained by extrapo-

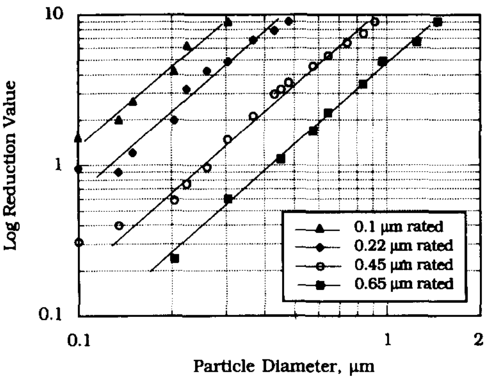

Fig. 3 Initial retention of various PVDF filters

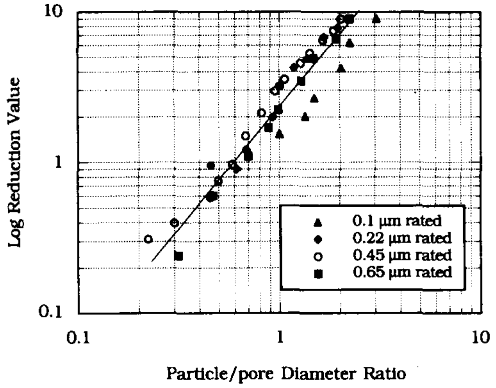

Fig. 4 Initial retention as a function of particle/pore diameter ratio

lation of the well-defined log-log relationship between particle diameter and LRV. This leads to monodisperse particle sizes of 0.3, 0.48, 0.913, and 1.46 μm for absolute retention by the 0.1, 0.22, 0.45, and 0.65 μm rated filters. The data indicate that to achieve absolute retention, the particle diameter must be equal to 2 to 3 times the rated pore size of the filter.

The results shown in Fig. 3 are replotted in Fig. 4 using a normalized particle/pore diameter ratio(PPR), the ratio of the test particle diameter to the filter pore size rating. Figure 4 shows the initial LRV as a function of PPR for various PVDF filters. The mean initial LRV is 2 when the PPR is 1, and 7 when the PPR is 2. The PPR for complete retention is between 2 to 3 for various PVDF filters.

3.2 Polydisperse Particle Retention

To study the influence of the size distribution of polydisperse suspensions on the filtration characteristics of membranes, several mixtures of monodisperse suspensions were prepared and used as the particle challenge for filter testing. Two polydisperse suspensions were prepared for the tests. Suspension I is a mixture of 0.741, 0.576, 0.453, and 0.305 μm PSL particles, and suspension II is the same mixture as suspension I with the addition of 0.913 μm PSL spheres. Figure 5 shows the measured size distributions of these two suspensions on a log-log plot. The slopes of the log-log distribution is found to be between -2.0 and -3.0.

The results of tests for a 0.45 μm rated PVDF filter are shown in Figs. 6 and 7. The different LRV curves are obtained by means of particle count data in discrete particle size channels of the

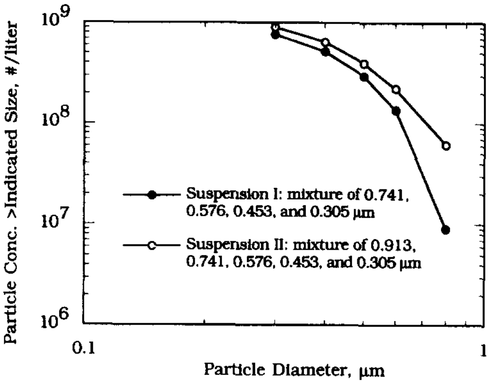

Fig. 5 Measured size distribution of polydisperse particle suspensions

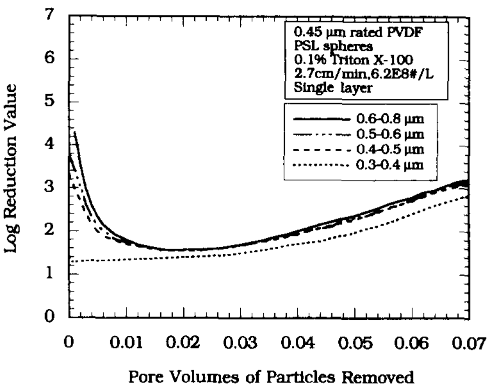

Fig. 6 Filter performance during polydisperse PSL challenge (Mixture of 0.741, 0.576, 0.453, and 0.305 μm)

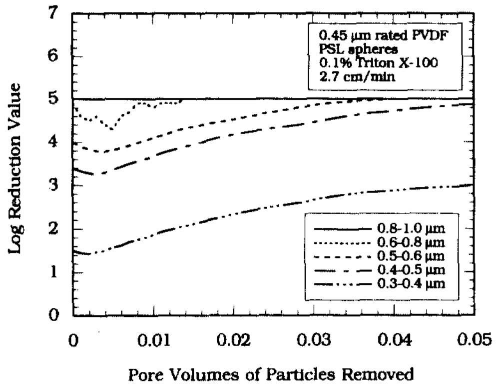

Fig. 7 Filter performance during polydisperse PSL challenge (Mixture of 0.913, 0.741, 0.576, 0. 453, and 0.305 μm)

LPC. The result in Fig. 6 for Suspension I shows that, for the three size channels between 0.4 and 0. 8 μm, there is only a slight difference between the LRV curves during the initial period of filtration. Beyond the minimum in the LRV curves, the three curves become almost indistinguishable. However, the data for the particle size channel of 0.3 – 0.4 μm show a continual increase in the LRV value throughout the filtration regimes. This can be attributed to the small size of particles in this channel, and the ability of the particles to penetrate through both the filter membrane and the cake throughout the filtration period. The increase in LRV can therefore be attributed to the increasing thickness and effectiveness of the filter cake to remove particles of this small size. The data also show that filtration of a polydisperse suspension is quite similar to that for a monodisperse suspension and the three important filtration regimes of sieving, partial cake formation and full cake filtration are also the same.

The retention characteristics of the membrane filter for Suspension II are shown in Fig. 7. The dramatic influence of the addition of the 0.913 μ m particles to Suspension I in altering the shape of the LRV curves can be clearly seen for particles in some of the size channels. The addition of the large 0.913 μm particles to the suspension is seen to cause a significant increase in the LRV values for particles in the 0.4-0.8 m range. The lowering of the LRV values with light and moderate particle loadings seen previously for suspension I is significantly curtailed. The only exception is the LRV for particles in the 0.3 – 0.4 μm range, the shape of the LRV curve being essentially the same as for Suspension I. The effect of the large 0.913 μm particles, for which the 0.45 μm rated membrane has absolute retention characteristics, is believe to cause an early plugging of the pores and the formation of the particle cake on the filter surface leading to the increasing retention of the 0.4 – 0.8 μm diameter particles. For particles in the 0.3 – 0.4 μm range the particles are sufficiently small and the equivalent pore openings of the cake is sufficiently large, so that the basic shape of the LRV curve is relatively unaffected both by the addition of the large particles and the formation of the particle cake on the filter surface.

The above results can be explained in detail as follows. Figure 8 shows a pictorial representation of a cross-sectional view of a tortuous pore membrane. In this representation, the shaded particles are retained by direct sieving and the unshaded particles are retained by cake filtration and by previously retained particles. The structure of the membrane used in this study resembles a sponge with an inter-connected tortuous pore structure. The tortuous pore membrane appears to have some very large pore openings on the surface, which are not indicative of straight-through

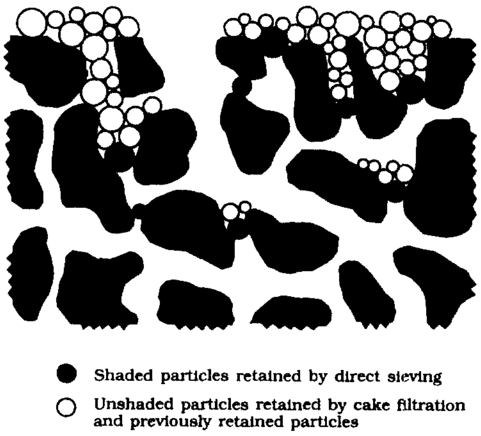

Fig. 8 Cross-sectional view through a tortuous pore membrane filter adjacent to the upstream face under heavy particle loading

pores in the filter structure. They are part of the normal pore size distribution, where smaller pores exist below the large pore opening on the surface. The possible maximum neck size in a tortuous flow path through the tortuous pore membrane is believed to be from 0.741 to 0.913 μm in diameter for a 0.45 μm rated filter, because the particle size complete retention(> 99.9999999%) is found by monodisperse particle challenge to be 0.913 μm. It is very difficult to clog pores of the maximum neck size in a tortuous flow path during the challenge of Suspension I which does not contain particles of 0.913 μm. Particle penetration through the unclogged pores can therefore be expected for Suspension I. On the other hand, with the addition of the large 0.913 μm particles in Suspension II, these pores are clogged, leading to increase filter efficiency and LRV.

3.3 Pressure Drop Measurement

The increase in pressure drop with increasing particle loading is shown in Fig. 9 for the 0.45 μm rated PVDF membrane for various loading particle sizes. The pressure drop data are normalized by taking the ratio of $\Delta P/(\Delta P)_o$ where ΔP is the pressure drop at a specific loading level, and $(\Delta P)_o$ is the initial pressure drop across a clean filter. The normalized pressure drop is seen to be proportional to the pore volumes of particles removed. It is not greatly affected by particle size for monodisperse particle challenge within the range of particle size studied. However, for the polydisperse challenge the pressure drop increases more rapidly with increasing particle loading as a result of the formation of a more dense particle cake during the polydisperse challenge tests.

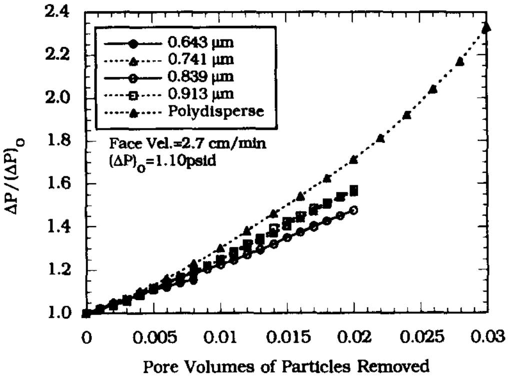

Fig. 9 Pressure drop across 0.45 μm rated PVDF filters as a function of particle loading

4. Summary and Conclusions

Particle removal by microporous membrane filters has been investigated experimentally with a continuous challenge of monodisperse and polydisperse particles. Test methods have been developed for investigating the characteristics of the membrane filter for particle retention and loading effect in filters. A filter test system has been developed that includes a pump-driven water recirculating system, a laser particle counter, a pressure transducer, a particle injection system and a computerized data acquisition system.

The filtration regimes during particle loading tests begin with a sieving dominant regime, followed by a transition regime characterized by the formation of a partial particle cake on the filter surface, and to a cake dominated filtration regime where a complete surface particle cake is formed. Retention by sieving is found to decrease with increased particle loading on the filter, due to the partial plugging of the smaller pores in the membrane. After substantial particle loading, a particle cake will begin to form on the filter surface. The filter efficiency will then decrease more slowly with increasing particle loading because the additional filtration effect of the particle cake. Finally, when a complete cake layer is formed, further increase in loading will lead to an increase in efficiency.

The efficiency of a membrane filter during the beginning stage of filtration when the filter is clean has been found to range between 97 to 99.9% for particle sizes that are equal to the rated pore size of the filter. Filters with rated pore sizes of 0.1, 0.22, 0.45, and 0.65 μm have been used in these experiments. Complete retention(> 99.9999999%) is achieved for a range of particle diameters that are approximately 2 to 3 times the nominal rated pore size of the filter.

Particle retention during polydisperse PSL challenge has been found to be dependent on the size distribution of the particles used in the loading tests. In the absence of particles larger than the particle size needed for absolute particle retention, a polydisperse suspension will give rise to lower filter efficiency. The breakthrough for smaller particles is found to occur more slowly when the challenge suspension is polydisperse, while the breakthrough for larger particles is more rapid.

References

Brock, T. D., 1983, *Membrane Filtration : A User's Guide and Reference Manual,* Science Technology, Madison, WI.

Grant, D. C. and Liu, B. Y. H., 1991, "Sieving Capture of Particles by Microporous Membrane Filtration Media," Part. Syst. Charact. 8, pp. 142 ~150.

Lee, J. K., 1992, "Particulate Retention by Microporous Membrane Filters in Liquid Filtration," Ph.D. Thesis, Mechanical Engineering Department, University of Minnesota, Minneapolis, Minnesota.

Pall, D. B., Kirnbauer, E. A. and Allen, B. T., 1980, "Particulate Retention by Bacteria Retentive Membrane Filters," Colloids and Surfaces, 1 : 235~256.

Rubow, K. L. and Liu, B. Y. H., 1986, Fluid Filtration : Gas, Volume I, ASTM STP 975, R. R. Raber, Ed., American Society for Testing and Materials, pp. 74~94.