THE DEFOULING OF MEMBRANES USING POLYMER BEADS CONTAINING MAGNETIC MICRO PARTICLES

Report to the

Water Research Commission

by

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EXECUTIVE SUMMARY

Background and Motivation

The cleaning of membranes is necessitated by fouling and is the main cost factor in water treatment using membrane processes, whether for desalination, removing contaminants, removing colour or removing bacteria and viruses, as in sterilization.

In practice most membranes are cleaned using chemicals. This method has the disadvantage that the plant must be shut down during cleaning and the chemicals add to the cost. Also the waste water containing the chemicals must be disposed of in an environmentally acceptable way. Physical cleaning methods eliminate the final two problems and in some cases it may not be necessary to shut down the plant while cleaning.

Physical antifouling techniques include faster flow rates of the feed, pulsed flow rates, reversing flow direction, sponged balls and adding particulate carbon black particles into the feed. Air bubbles can also be introduced into the stream to increase turbulence. More recently, back pulsing, infrasound and in the case of desalinization, applying electromagnetic pulses, have also been tested as antifouling methods.

For this project it was proposed that an electromagnetic method for the defouling of membranes should be thoroughly investigated, using both established and new expertise at the Polymer Science Institute. The leader of the team was Professor David McLachlan, who had newly arrived at the Institute and was a very experienced experimentalist in the field of electromagnetic measurements, having researched the electromagnetic properties of solids for over 40 years. Considerable experience in making nanomagnetite was already available at the Institute. All this, together with the vast existing polymer know-how available at the Institute, created the expertise necessary for making nanomagnet-polymer beads and manipulating them across the membrane and fouling layer of a filtration system using external magnetic fields.

A very interesting addition to the proposal was to investigate the potential of these scouring beads to disturb the concentration polarization layer right on the surface of a Reverse Osmosis (RO) membrane in seawater or brackish water. This may give rise to better fouling control and to the improvement of the flux over long periods.

Part of the motivation for this programme was that, if successful, it would produce cheaper clean and desalinized water for the benefit of the peoples of South Africa and elsewhere. This would be due to the development of a technology (technologies) which would enable the cost of cleaning membranes to be reduced. The benefit of this would be a lowering of both the operating costs and the number of filters needed for a given output (capital cost reduction).

Objectives and Aims

The overall objective was to see whether the magnetic bead system to be developed in this project could be used to clean membranes in commercial plants without the use of chemicals.

Aim 1

Exploit an existing technique for producing granular magnetite nanoparticles. Ferromagnetic nanoparticles (granular or needles) would probably be bought but could be made in SA.

1.1 Although beads which incorporated nanomagnetite were made, they turned out not to be suitable.

1.2 All the beads used in this project contained μm sized hematite powder as hematite has a higher residual magnetization.

Aim 2

Embed these nanoparticles in suitable sized and shaped magnetic beads.

2.1 Nanomagnetite was successfully blended into polystyrene but the fraction that formed spheres was low and the magnetic moment of the spheres was very low. It proved more difficult to blend the μm sized hematite particles into polystyrene and this was abandoned.

2.2 The hematite was blended into polyethylene from which irregular granules were made. These were used in some experiments not reported here.

2.3 Most of the experiments were made using Hematite-Poly Acryl Nitride spherical beads, made by a spraying process.

Aim 3

Develop a method of aligning the nanomagnets inside the beads to make them into strong permanent dipole magnets. (Note that magnetic nanoparticles, also known as super paramagnets, are themselves permanent magnets.).

3.1 As reported above the beads used contained hematite, which is a hard magnetic material (i.e. holds a large permanent magnetic moment).

3.2 Magnetic hystersis loops showed that a field of 7000 Gauss (0.7 Tesla) was necessary to fully magnetize the hematite. Therefore all beads were magnetized at this field at the University of Cape Town.

Aim 4

Design and construct a flat membrane cell, where the build up of the fouling layer and motion of the beads can be monitored, both visually and by ultrasound.

4.1 The flat membrane cell used in most of the cleaning experiments was based on the design used by Reineke *et al*. (2008: WRC Project K5/1441, Membrane Fouling and Visualization Studies). A high pressure cell based on this design was made from polycarbonate and used in the RO studies.

4.2. As no cleaning, from monitoring the flux, was observed with positive Trans Membrane Pressures (TMPs) and flowing beads, no monitoring using ultra sound was carried out.

4.3 A cylindrical flat bed cell was constructed using polycarbonate. This fitted into a pump cavity where a very high AC field (1200 Gauss) was generated from the 220V mains.

Aim 5

Develop a technique to photographically monitor and record the movement of the beads and to see where the fouling layer builds up (if at all).

5.1 This technique was developed in a commercial dead end filter with a flat base, and pictures of the moving particles were obtained on the flat surface of the filter. No cleaning was observed from visually assessing the permeate. It was later found that no cleaning took place when using a positive TMP.

5.2 A short movie clip of the beads moving under the influence of an AC magnetic field was made and submitted in an early report.

Aim 6

Monitor the filtration of coloured water with natural organic matter in it, and synthetically fouled waters to quantify the effect of the scouring beads on the quality of the water and the time needed before the membrane should be cleaned.

6.1 Due to the fact that it was almost impossible to obtain reproducible natural organic water it was decided to use other foulants. These were dextrin and three alumina powders, with very narrow size distributions. Cleaned yeast was used in a limited number of experiments.

6.2 It was not possible to observe any cleaning action of the beads when they were passing across the membrane with positive TMPs.

6.3 The only experiments which showed cleaning involved switching off the pump, flooding the feed chamber with beads at zero TMP, and then turning on the AC magnetic field. After this the clean water fluxes were re-measured and a considerable increase in the flux was observed. These experiments are reported here at some length.

Aim 7

To see if the magnetic bead system developed here can be used to increase the sustained throughput of a RO membrane in seawater desalinization.

Because of the results obtained using micro membranes, the only experiments made involved fouling the RO membranes with a quick fouling solution and then cleaning the membrane at zero TMP. It was found that the flux using lightly fouled membranes did not increase but that for more heavily fouled membranes, the flux improved but never to more than for the lightly fouled ones. Scanning Electron Microscope (SEM) images showed that the heavily fouled membranes had some coarse calcium carbonate ($CaCO_3$) deposits, which were removed by the scouring beads.

Aim 8

To put forward proposals to convert this technology to existing spiral wrap filters.

A possible use of this technique is chemical free cleaning at very low TMPs, which will unfortunately necessitate shutting down the plant. Another major problem here will be to introduce a high enough density of beads into the feed space to get a cleaning action. The

experiments already performed showed that a Root Mean Square field of 80 Gauss is usually sufficient to clean the membranes at zero TMP, but that in some cases a field of 24 Gauss is sufficient. These fields can be generated either using pairs of open coils or a U shaped magnetic yoke with the element between the tips of the U.

Results and Conclusions

A description of the preparation of the magnetic beads and the various experimental systems used in this project are given in the main report. The report also shows some of the flux-time results from which the ability of the magnetic beads to clean various foulants off the membrane was gauged. Also given are the flux-time results obtained from the RO experiments. A brief summary of the results is given in this section and some conclusions are drawn.

Soon after the project began it became apparent that a bead with a strong permanent moment was needed and the best material to use was found to be hematite. The beads were magnetized in a field of 7000 Gauss to get the maximum permanent magnetic moment possible.

Several methods of preparation were tested. The first was to polymerize magnetite and then hematite in polystyrene, which was generally unsuccessful. The second was to blend the hematite into polyethylene and to grind the resultant material down to suitable sized granules. However, it was not possible to form these irregularly shaped granules into spherical particles or to even blunt the sharp edges of the granules. Cleaning action at zero TMP was observed with the polyethylene beads, but as it was thought that the sharper edges would more easily give rise to membrane damage, most of the work was conducted using spherical Poly Acryl Nitride (PAN) beads. As described in the text the PAN beads were produced using a spraying process.

The membranes used were one micro polysulphone and two nylon membranes, with nominal pore sizes of 0.2 and 0.45 μm. The foulants used were dextrin (organic and sticky) and 1 μm alumina (inorganic and inert).

The principal aim of these experiments was not achieved as it did not prove possible to keep the membrane from fouling (i.e. an equilibrium flux value considerably above the saturation value) by continually passing rotating beads over it. The reason for this was that the cake layers that formed were, under the TMP, too well bonded to the membrane for the beads to be removed. Under some circumstances, even rotating beads could become embedded in the cake layer.

The principal positive result of the project was the observation that the beads could clean off the cake layer when the TMP was zero, which could possibly be used for (partial) chemical free cleaning. The report gives several flux-time plots which show how successfully the membranes had been cleaned.

The report concludes that chemical free cleaning of a filtration element is possible but not practical. One reason is that the feed space (which includes a spacer cloth) would have to be reasonably well filled with beads for the cleaning process to work and that, after the cleaning the beads would have to be removed. While it is quite possible to generate large enough AC

magnetic fields to clean membranes at zero TMP, no cost effective studies were made due to the difficulty of inserting sufficient beads into the feed space and subsequently removing them.

Experiments also showed that an enhanced flux for a badly fouled RO membrane cleaned by rotating beads, at zero TMP, could be obtained. Unfortunately, no enhanced flux was observed for a lightly fouled membrane. Scanning Electric Microscope images allow one to conclude that while the beads will remove thick flaky layers, they are incapable of removing the well bonded initial fouling layers.

Future Developments

It has been shown that the rotating beads did not have sufficient scouring action (except under zero TMP) to remove a cake layer that is strongly bonded (chemically or by the TMP) to the membrane. It has also been shown that the beads were incapable of removing the strongly bonded remnant fouling material that remains after cleaning at zero TMP, as well as any material lodged in the pores. Therefore the approach used in this work to clean membranes is not worth pursuing at this time. Some other possible uses of the magnetic beads are discussed at the end of the main report.

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1. INTRODUCTION

Membrane filtration of aqueous effluents is a widely used technique in water purification in the food industry, to clean industrial effluents prior to discharge or re-use and to obtain potable water from various sources (Porter, 1990). The fouling of membrane filters during the filtration process of all aqueous effluents is a well known phenomenon. Fouling of the membranes causes a decrease in permeate flux and eventually the filtration process becomes so inefficient that a cleaning procedure must be initiated.

The fouling of the membranes is characterized by a rapid initial decrease of flux followed by a medium or slow decrease in the permeate flux (Song, 2000; Czekaj *et al*., 2001). It is mainly the sub-µm proteins and polyphenols, i.e. smaller than the membrane pores, which are considered to be the cause of the initial rapid membrane fouling (Czekaj *et al*., 2001). After this the flux decreases due to the formation of a caking layer. When necessary, in order to restore permeate flux, the filtration process normally has to be interrupted to clean or to replace the membrane filters. For economic reasons a membrane cleaning procedure which does not seriously interrupt the process or use hard to dispose of chemicals is preferable. Cleaning by the use of scouring magnetic beads offers either one or both of the above advantages.

At the start of this project a detailed literature search was made on the Internet using Google and the relevant key words. The only reference that corresponded closely to this work was one project on the Water Research Commission (WRC) site. There were numerous references to magnetic beds used in drug delivery and to the ability of magnetic fields to prevent fouling. As this search showed no other work in this field there is, almost certainly, no previous work in the literature on the use of magnetic beads to clean membranes. Therefore only other physical methods for cleaning membranes will be discussed in the introduction.

A number of physical membrane cleaning techniques have already been investigated, which include back flushing, cross flushing, and back pulsing (or back shocking) (Redcar and Davies, 1995; Tanaka *et al*., 1995; Wetten, 1995; Kuruzonovich and Piergiovanni, 1996; Parnam and Davies, 1996; Redkar *et al*., 1996; Kuberkar *et al*., 1998). Although these techniques, applied in a non-continuous way, could be successfully used to clean membranes and partially or completely restore the original flux, they seem to be inefficient in the removal of adhesive foulants (Czekaj *et al*., 2000). In (Czekaj *et al*., 2000; 2001) rapid continuous back pulsing from the permeate space into the feed space was found to be very effective. In order to avoid contamination of the membrane on the permeate side, a clean feed (the permeate itself or reverse osmosis (RO) water) had to be used for the back pulsing. Czekaj *et al*. (2000; 2001) used infrasonic back pulsing at frequencies of 5-10 Hz for such a purpose. They filtered 0.66 g/L washed yeast and 0.5 g/L talc suspensions through flat-sheet filters of polyvinylidene difluoride (PVDF) membranes. Compared to the "steady state" fluxes achieved with standard cross-flow filtration, the permeate fluxes, with continuous back pulsing, were four times higher for the talc suspension and three times higher for the yeast suspension (Czekaj *et al*., 2001). Therefore infrasonic back pulsing from the permeate space shows considerable potential for flux enhancement.

As there is no appropriate theory for this process, the experimental apparatus is described in the next section. The procedures used will be given in Section 3 and the results and discussion will be presented in Section 4. A summary of the results and the conclusions is made in Section 5 and suggestions for future work in Section 6.

2. THE EXPERIMENTAL SYSTEMS

2.1 Magnetic Materials Used in the Beads

Initially nanoparticles of magnetite were produced using a well established method. However, early experiments on magnetite incorporated into 3 mm epoxy putty beads soon showed that, although magnetic, the particles in this bead could not be poled into permanent magnets. It is known that strong permanent magnetic particles would give stronger torques in a uniform field and stronger forces in an inhomogeneous field than on soft magnetic particles. Magnetically hard hematite is used in permanent ferrite magnets but no established method for producing nanohematite was found in the literature. However, experiments using locally mined hematite powder (approximately 1-2 μm), showed that it retained a more than adequate permanent moment. Therefore, the beads and particles produced and tested in this report all contain South African hematite powder.

While searching for a permanent magnetic material the possibility of using nanoparticles of iron was investigated. The cost of this material was found to be prohibitive ($2000/100 g). It was realized that an alternative was the met-glass flakes of NdFeB, which are sintered into the strongest known permanent magnets. One kilogramme of these was obtained on special order from China, at the more reasonable price of R2000/kg, and compounded into polyethylene. This compounded material produced satisfactory beads but as it is much more expensive than hematite no further investigations on beads containing NdFeB were made. Therefore, as the SA hematite proved to be a very satisfactory magnetic filler, it was used in most of the work described in this report.

2.2 Preparation of Magnetic Beads and Particles

Nanomagnetite was successfully polymerized into polystyrene spheres using established procedures. However, the yield of spheres, as opposed to irregular shaped large and small particles, was small. This coupled with the fact that the beads would not hold a permanent moment led to this method being dropped. Using the same procedure an attempt was made to polymerize SA hematite into spheres without success.

A new method for polymerizing μm sized magnetite was found in the literature and, with some modification, was used to produce hematite-polystyrene spheres. After some development this proved to be reasonably successful, with yields of spheres exceeding 50%. Unfortunately, all the runs yielded spheres; nearly all were over 50 μm and were too large to pass through the spacer cloth in a spiral wrap membrane element, so this method of producing beads was discontinued.

Commercial hematite powder and NdFeB powder (obtained from China and ground down to about 2 μm), were successfully compounded with and without surface coatings, into polyethylene by Dr. Breeksting from Tshwane University of Technology. The volume percentages of hematite powder needed to give beads which rotated, but did not clump

together in a magnetic field, was determined experimentally using 3 mm epoxy beads which became the target volume fractions. The volume percentage for the two extruded hematite/polyethylene materials was 8.15 and 8.16% (for the NdFeB/polyethylene it was 5.58% and 10.19%). As the compounded materials were almost spongy, due to having been quenched in water, sheets of the materials (about 0.1 mm thick) were prepared in a hot press. These sheets were cut into small sections, which were then reduced in size by cryogenic milling and separated into 38-75, 75-150 and 150-218 μm batches of granular particles. It was then attempted, without success, to make these irregularly shaped particles more spherical. As this was not successful and it was felt that the sharp edges may damage the membranes, only a limited number of experiments were carried out using these magnetic particles.

The last and most successful method of bead preparation was to encapsulate the SA hematite into Poly Acryl Nitrile (PAN) beads. All the successful experimental results reported here were obtained using PAN beads. The method of preparation is summarized below.

A spraying procedure was developed for creating magnetic micro spheres from a dissolved polymer solution. The method used was to spray a PAN-Dimethyl Formamide solution, into which hematite was mixed, into a bath of a non-solvent liquid phase. This solution was placed in a glass tube with a fine (± 2 mm) point and a ± 1 mm orifice at the bottom. This tube was surrounded by another annular glass tube, which also had a reduced diameter at the bottom, to match the tip of the previously mentioned (interior) tube. Nitrogen flowed in the annular space between the two tubes. A fine spray was created by the fast flowing stream of nitrogen over the point, where the solution exited the inner tube. (The shape of the tip, combined with the fast flowing stream of nitrogen over it, produced an aerosol effect.) The small droplets that formed were allowed enough "falling" time from the tip for the surface tension to form spherical droplets before they fell into the bath containing a non-solvent phase. The time needed for this sphere formation necessitated the tip of the spraying device to be one metre above the surface of the non-solvent phase, which was usually a 75% acetone: 25% water mixture.

Beads with diameters ranging from 5 μm up to 600 μm were produced. Wet sieving was used to separate out the various fractions. Most of the beads were between a 100 μm and 300 μm in size. In the initial experiments the size range used was 50 to 100 μm, but only a small fraction of the product lay in this range. In later experiments the size range used was 100 to 180 μm as at this stage, the proof of concept, using flat test cells was more important than the necessity for the beads to pass through the spiral wrap membrane element feed space cloth.

Scanning Electron Micrographs (SEM) micrographs (Figure 1) showed the beads to be almost perfectly round. Cross-sections of the beads (Figure 2) showed the beads to be inhomogeneous and to contain a large fraction of water. Figure 3 shows a collection of beads produced by this process.

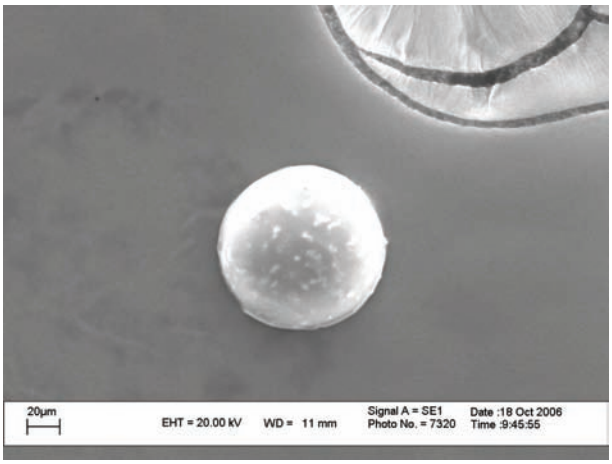


Figure 1: A PAN bead with a diameter of approximately 100 µm

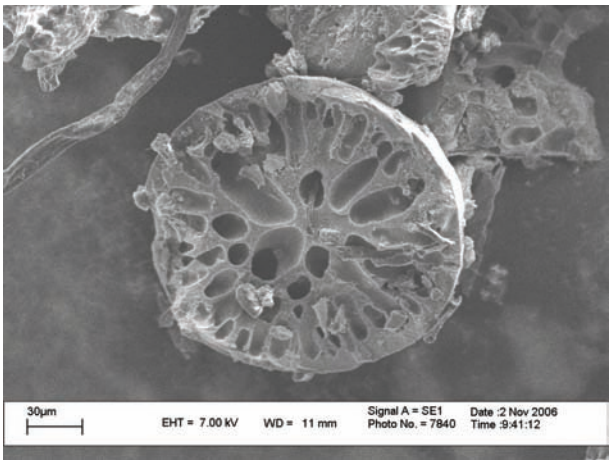


Figure 2: Cross-section of a PAN bead showing the internal structure (note the cavities and wall thickness)

After preparation, the beads had to be poled in a high magnetic field. A M-H loop of some of the beads was conducted using a vibrating sAmple magnetometer, by Professor Doyle of the University of KwaZulu-Natal, showed that a field (4000 Gauss) available from our permanent magnet was insufficient to fully magnetize the hematite (and NdFeB). Therefore the beads and particles were poled in an electromagnet giving in excess of 8000 Gauss, at the Physics Department of the University of Cape Town. The remnant magnetization in the hematite after this was 2.5×10^5 Amp/m. Poled hematite loaded beads could be easily activated by the magnetic fields described in Section 2.2.

2.3 The Magnetic Field Configurations

Initially the AC magnetic fields were provided by a pair of Helmholz coils, which gave 57 Gauss per Amp. The maximum continuous current was found to be 3 Amps (170 Gauss), but 5 Amps (285 Gauss) could be used for short periods. (In preliminary tests on a flat sheet in air and in water, all the magnetic spheres and particles started to move in a Root Mean Squared (RMS) AC field of less than 57 Gauss.) The current for the AC field was obtained from a function generator and an audio hi-fi power Amplifier and the DC current came from a power supply.

In order to increase the AC magnetic field and to create a downwards inhomogeneous field (force on the particles) "transformer" cores were used.

The E core field magnet: A transformer coil consists of an E and an I section which, when placed together (EI) provide a closed magnetic circuit. A single winding was wound around the central section of the E piece, which had a cross section of 55 mm × 45 mm, and the centre of the membrane placed 11 mm directly and above this section. For a current of 1 Amp, the field at the centre of the membrane was found to be close to 80 Gauss and to drop to 60 Gauss at the corners. The vertical gradient at the centre was found to be 0.75/Gauss/mm or 0.75 T/m. Most of the experiments performed in this project used this E field magnetic configuration.

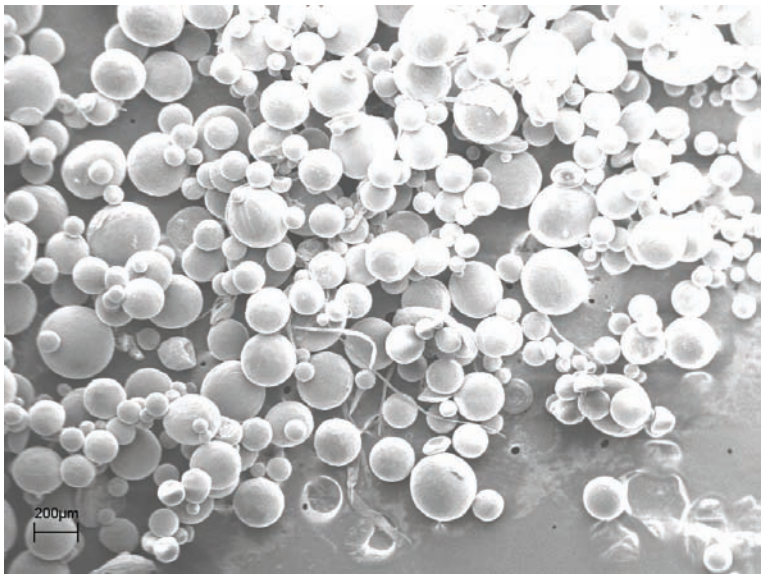


Figure 3: A typical collection of beads produced by spraying the PAN solution containing hematite into a 25/75 solution of water and acetone

The block magnets: Before the E core field magnet was obtained, the magnetic field was enlarged by (a) placing a block of transformer steel into the Helmholtz coil, with the top of the block flush with the top of the upper of the two windings (C1). The cell was placed on the upper end of the block. (b) Copper wire was wound directly onto the transformer steel block and the cell place at the upper end (C2). For the same current the maximum AC fields obtained this way were about one third of that obtained in the E field magnet. All the data reported result from experiments in which the C2 block magnet was used.

The rotating magnet: The calculations given below show that there is a possibility that the beads were flipping too rapidly (changing direction (spinning) in a very small fraction of the period of the AC field) to effectively clean the membrane, when using the E field magnet described above. In order to overcome this, a rotating field system was constructed. This consisted of two pairs of strong permanent magnets mounted at the tips of a rectangular aluminium "U", the field at the centre was found to be just over 500 Gauss. The "U" was rotated by a variable speed stirrer motor and the r.p.m. measured, using an adapted bicycle speedometer. The highest rotational speed used was 126 r.p.m., as above this value the apparatus became unstable. The inputs and outputs of the cell (described below) were adapted so that all the tubes entered and exited through the upper section of the flat cell (see below) and the open section of the "U". This enabled the cell to be placed horizontally on the axis of the "U" and for the beads to be rotated about the central axis of the "U" and along the direction of the feed flow. The nature of this field was such that the beads had to rotate with the field so that there was no spinning. The field provided by this system was in effect an AC one. However, in all the other field configurations used the magnetic field was always perpendicular to the membrane.

The pump magnet: In the hopes of achieving a stronger rotating field the following system was used. Small garden feature pumps have permanent magnetic dipoles attached to their impeller shafts, which are rotated at 50 Hz by the applied magnetic fields, generated by AC current from the mains, in the "dipole" cavity. The largest model "Waterfall" garden pump was bought to test the magnetic field and a smaller one was cut up to see how the AC

magnetic field was generated. Unfortunately, it turned out that the field (where the magnetic dipole attached to the impeller shaft) was between the ends of a transformer Si-Iron U shaped section, with the windings around the bottom ends of the "U". Therefore the AC magnetic field between the ends of the "U" section did not rotate. However, this did show that a rotating field was not necessary to rotate the pump impeller and that, with the correct rotational inertia and dAmping, many dipoles will rotate in an alternating field.

The alternating field inside the cavity, where the magnetic dipole which drove the impeller was housed, was measured and found to have a RMS value of 1200 Gauss when 220 V was applied to the "motor". Using a Variac, 70 V (380 G) and 20 V (110 G) were applied in order to get lower fields. Because of the very high AC fields obtainable in this system some experiments were carried out with this magnetic field system.

[Note that the garden pump configuration shows that under the right conditions a magnetic bead may rotate rather than spin rapidly through 180° in a non rotating magnetic field as the calculations given below imply. In any event the motion was always rotational (the beads move through 360° every cycle) even if it is a very jerky one. The rotational motion (angular velocity) should become more uniform as the field is reduced and must eventually cease when the applied torque no longer overcomes the frictional forces].

2.4 Calculations of the Torques and Forces Exerted on the Beads

The calculations will be made for a 200 μm spherical bead, which is bit larger than the ideal size, but the radius of 100 μm, can be easily be scaled. All calculations are in SI units.

Density of bead (20 mass % hematite) ≈ 2000 kg/m^3

Volume of bead (5 volume % hematite) ≈ 4×10^{-12} m^3

Mass of bead ≈ 8 x 10-9 kg

Saturation magnetization of hematite ≈ 5×10^5 A/m

Remnant magnetization of hematite ≈ 2.5×10^5 A/m

Remnant magnetization (M_R) of above bead = 12.5×10^3 A/m

Magnetic Moment ($M_R V$) ≈ 5×10^{-8} A/m^2

Force on a dipole particle in a magnetic field: $F = \mu_0 (M_R V) (dB/dL)$ (N)

For an inhomogeneous field of 1 Gauss/1 mm or 10^{-1} T/m:

$F \approx 5 \times 10^{-9}$ N

Acceleration (F/M) ≈ 40N or 4 × Gravitational acceleration (≈ 10 m/s^2)

(≈ 3 G was measured using an inhomogeneous field and an electronic balance)

Torque on bead $\tau = (MRV)B \approx 5 \times 10^{-10}$ Nm for B = 0.01 T (100 Gauss).

Moment of Inertia of bead $I = 2Mr^2/5 \approx 3.2 \times$ 10-16 kg/m^2

Angular acceleration of bead $\tau/I \approx 1.6 \times 10^6$ Radians/s^2

After 1/100 second angular velocity $\omega \approx 1.6 \times 10^4$ Radians/s

Speed on surface = $\omega r \approx 1.6$ m/s

Conclusions: With most of the fields used in this report, the beads were spun through 180° very shortly after the applied field changed sign and remained aligned with the new direction of the magnetic field for the rest of the half cycle, after which the bead spun through 180° again. This shows that the beads may have been slipping over the foulant rather than cleaning it. The calculations also show that a rotating field of 100 Gauss was more than sufficient to rotate the bead at 126 r.p.m.

2.5 The Flat Cells Used in the Project

The rectangular test cells, which had the same design as those described by Reineke *et al*. (2008), were constructed in the Physics Department workshop. However, a small modification to the input manifold was made in order to get the feed and beads to flow uniformly over the membrane at high flow rates. The cylindrical cell was of an original design and was also constructed in the Physics Department workshop.

A rectangular, flat-bed micro filtration module of 100 mm length, 32 mm width and 2 × 19 mm height, was used in all the flat-cell experiments. The modules were made of polymethyl methylacrylate (Perspex) for the low pressure experiments and polycarbonate for the RO studies. Each consisted of two plates (each 19 mm thick, 200 mm long and 94 mm wide). The feed space cavity in the top plate (2 mm deep, 88 mm long and 30 mm wide) had three 2 mm pipes at each end which, through separate manifolds, were connected to the input and output feed lines. The membrane rested on a sintered brass plate, set in the lower Perspex plate, and below this was another cavity (13 mm deep, 88 mm long and 30 mm wide) to collect the permeate. The effective membrane area was 0.0032 m^2 (100 mm × 32 mm), which was the area of the brass sintered plate. The membrane was placed on the sintered plate and the two halves were clamped together by a system of 12 nuts and bolts and sealed with an O ring.

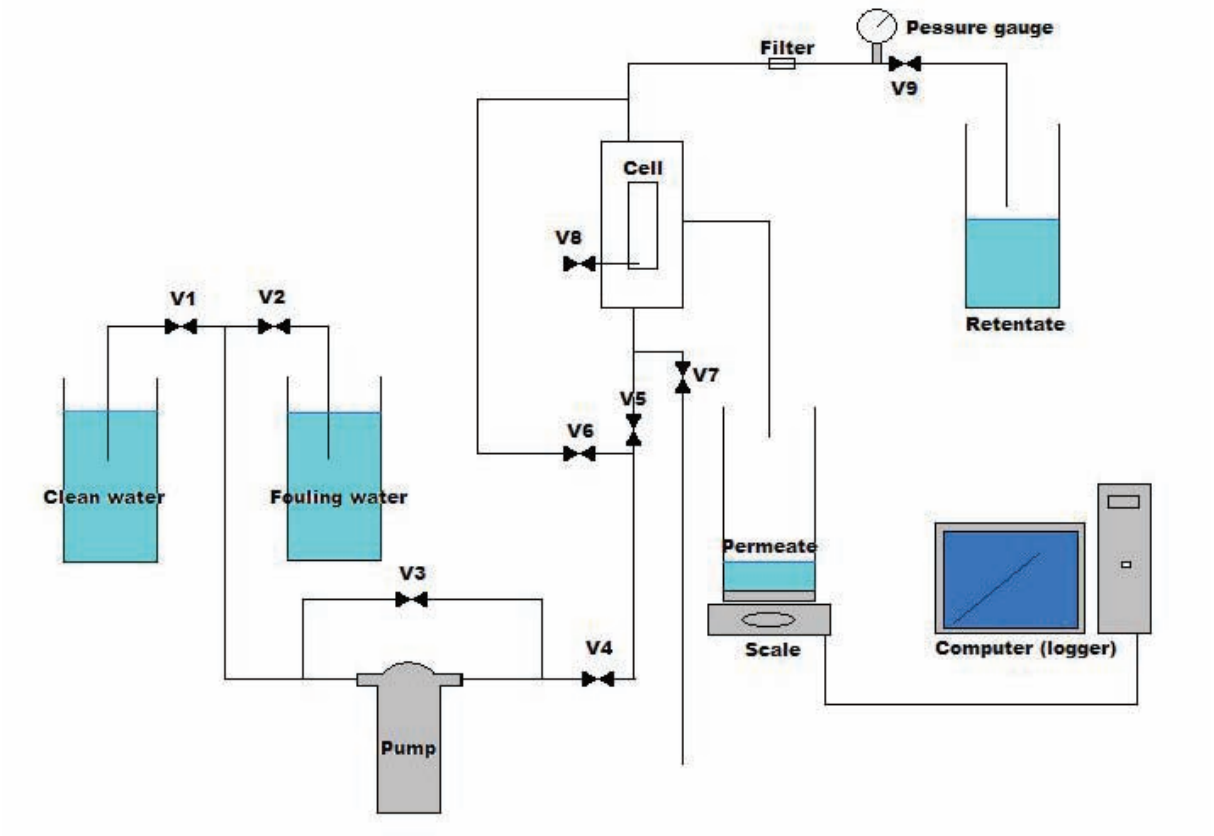


Figure 4: Layout of the filtration plant

2.6 The Low Pressure Flat Cell Filtration Plant

A schematic diagram of the plant used is given in Figure 4. Either the clean RO water or the fouling solution (for the alumina powders the reservoir was placed on a magnetic stirrer) was used to feed to the pump by the appropriate choice of valves (V1 or V2). The flow rate and applied pressure were controlled by the bypass (V3) and exit valve (V4) from the pump in conjunction with the cell exit valve (V9). The feed entered the cell through V5. The Trans Membrane Pressure (TMP) in the cell, which was largely determined by V9, was read on a pressure meter. The permeate flowed into a beaker on an electronic balance and the mass was measured and recorded by a PC connected to the balance. Valves 5 to 8 were used to introduce beads for cleaning at zero TMP, as will be described below.

Valve 7 was used to introduce the beads when it was attempted to use a continuous flow of beads over the membranes to obtain cleaning at non zero TMPs and V6 was a seldom used bypass valve.

2.7 The RO Flat Cell Filtration Plant

An existing RO plant was modified to carry out this project. The layout of this plant was very similar to the layout given in Figure 4, but the piping was all from stainless steel, rated at over 50 Bar. The pump could give a maximum pressure of 50 Bar and also had an excessively high flow rate. Therefore the pressure and flow rate were controlled using valves 3 and 9 (see Figure 4). To readily access the cell inside the available magnetic fields, it was decided to link the high pressure stainless steel part of the plant to the cell using 10 Bar flexible pipes and very convenient snap-in connections. When running the plant initially, it

was found that the feed pressure tended to oscillate. Therefore to dAmp this oscillation an 8 Bar ballast tank was installed. The presence of the ballast tank meant that it took up to 20 minutes to adjust the feed flow and pressure to the desired values. This system limited the testing to low pressure membranes, designed for brackish water. In this plant the pressure was measured at the input of the cell and the flow rate after the throttling valve (V9). The beads used to clean at zero TMP were introduced into the polycarbonate cell through V8. For a continuous flow of beads a small fraction of the feed (using constrictions and a flow valve (not shown)) was tapped off after V4 and led through a transparent reservoir. From this reservoir, which had been filled with beads at 0 kPa, the flow went through V7 where the, now bead-containing, RO water combined with the main flow and entered the cell. The beads were held in position and released from the reservoir using horse shoe magnets. After passing over the membrane the beads were collected in a small magnetic trap in the position of the filter shown in Figure 4.

Unfortunately, due to the high pressures, a simple continuous flow system was not practical and the one shot system meant that there was limited time to see the effect of the beads on the fouling of the RO membrane.

2.8 The Membranes and Foulants Used in the Cleaning of Foulant Layers

Membranes:

1. PALL Biodyne 0.20 μm pore size nylon membranes (Pall Corporation).
2. PALL Biodyne 0.45 μm pore size nylon membranes (Pall Corporation).
3. Polysulphone membrane (PSM) made in the laboratory.

The surface pore size of the PSM was examined in a SEM image and the pores were found to be much less than 1 μm. Also, as its clean water flux lay between that of the two nylon membranes, it was obviously also a micro membrane.

Foulants:

Dextrin (0.5 g/L).

Alumina powder (1 g/L), 0.3, 0.5 and 1.0 μm diameters with small size spreads.

Washed commercial yeast - this was only used in early experiments where the magnetic spheres were circulated.

2.9 The Membranes and Foulants Used in the Cleaning of RO Membranes

The membranes used in this work were cut from a small, commercial low pressure brackish water RO element. This was a FILMTEC RO Element XLE-2521, designed to operate at 6.9 Bar, with a maximum salt concentration of 500 ppm.

As the feasibility of this cleaning method had to be established fairly quickly, initial trials were conducted using a Rapid Fouling Solution (RFS), as used by Lisitsin *et al*. (2005). When using this foulant solution the pH and temperature were important and so had to be kept within the bounds for rapid fouling specified in the paper. The standard RFS was made up using 22 g $CaCl_2$, 1 g $MnSO_4$ and 14 g $NaHCO_3$ in 100 L of RO water.

3. PROCEDURES FOR LOW PRESSURE FOULING LAYER AND RO FILTRATION CLEANING EXPERIMENTS

3.1 The Procedure Used for Cleaning Fouling Layers Using Flowing Beads and a Finite TMP

Note that in the flowing bead experiments, even the peak density of the beads over the membrane was never very high – probably much less than 5% volume. This necessitated that the beads be forced into contact with the membrane. As the beads had a density of a little over 1 kg/L, the E magnetic field configuration used had a field gradient over the membrane which tended to pull the beads towards the surface. Section 2.4 showed that a field gradient of 1 Gauss/mm gave a downward acceleration of about 4 G (40 m/s^2).

Initially the beads were introduced as a suspension, through a Y shaped connector, using a large syringe. About 2 to 3 mL of the suspension were introduced in this manner whenever needed. Initially, for slow flow rates, most of the beads tended to remain over the active membrane area, being held there by field gradients in the AC magnetic field. The beads that escaped the magnetic field, as well as those that left the cell after the field had been switched off, were all caught in a sieve/filter placed just before the throttling valve (V9). Several experiments were performed using this procedure and the C2 core magnet configuration.

The above method did not work at high flow rates as the beads were rapidly swept out of the cell and off the membrane and it was not possible to have the beads flow slowly enough over the membrane to have a reasonable chance of cleaning it. Therefore, continuous circulation of the beads was introduced. Initially the exiting beads were caught in the cell at the far end of the membrane by a large magnet. The beads "attached" to the magnet were then mechanically moved back over the surface of the cell, so as to return the beads to the input side of the cell. This was not a permanent solution, especially when it was realized that the magnet was partially lifting the beads off the membranes, during the return "stroke" and hence lowering the efficiency of the process.

A continuous circulation system, which needed a second pump and a bead/water separator, was subsequently tried. The flow diagram of the separator is a T. The bead suspension enters at the top of the T (port 1) on the left and exits with some of the water removed at the right (port 2). At the junction a sieve is placed which prevents the beads from flowing down the T and out of port 3. The water, foulant and beads (retentate) exiting the cell, enters the separator at port 1, from where some of the water, carrying the excess beads, flowed directly over the sieve and, in a somewhat diluted suspension, out of port 2. The exit (retentate) pressure from the cell caused the beads to form a layer on the sieve, the top of which was continually removed by the cross flow (port 1 to port 2). Some of the water passes through the sieve and exits the separator at port 3 towards Valve 9 in Figure 4 and the flow monitoring electronic balance. This fraction of the water was the net retentate. When this system is operating satisfactorily the beads only built up to a certain thickness before they were picked up by the water flowing between ports 1 and 2. The bead suspension exiting port 2 was mixed with the incoming feed water and flows over the membrane again.

To provide the circulation needed to move the water between ports 1 and 2 (mentioned in the previous paragraph), which washed off the outer layer of beads of the sieve, a pump was

needed. A Venturi pump, where a net suction was created by the flow of the incoming feed water past a narrow constriction in the pipe where the bead suspension and feed water meet was originally used. Unfortunately, especially with granular hematite/PE particles, the system tended to clog rather easily and a more robust circulation system was needed. Therefore a small "Waterfall" brand garden pump was installed to circulate the beads between ports 1 and 2. This operated moderately well, but the system still tended to clog. The initial sieve was a 20 μm filter cloth but a fine stainless steel mesh coated with Teflon proved to be superior.

The main foulant used for these circulating bead experiments was an organic "sticky" commercial yeast, which had a diameter in the 30 μm range, and alumina polishing powders, an inorganic foulant with narrow size distributions and mean diameters of 0.1, 0.3 and 1.0 μm and low chemical binding properties. The membranes used were 0.2 and 0.45 μm pore size nylon membranes and the polyethersulphone, which were discussed in Section 2.7.

A number of cleaning experiments were carried out using the above circulating beads system. The TMP in all these experiments was positive (0.4 or 0.5 Bar), but no significant cleaning action was observed.

3.2 The Procedure Used for the Cleaning of Fouling Layers at Zero TMP

This procedure or routine was used in all the experiments on cleaning performed at zero TMP. The experiments themselves are reported on in Section 4 of this report.

To introduce the beads for zero TMP experiments, a large syringe was used to inject a suspension of beads into the cell cavity through an aperture (V8 in Figure 4) in the top plate, directly into the feed space. The water (and beads) contained in the large syringe flushed the feed space during the introduction of the beads. The beads were kept from moving off the membrane by a sieve that was inserted to cover the exit pipes. As the feed side valves (V5, V6 and V7 in Figure 4) were closed during this procedure, virtually no beads moved towards the feed pipes. After cleaning, the beads were flushed off the membrane using RO introduced by syringe via the entry port, which was not covered by a sieve. After this the beads could be spread using a small permanent magnet until a fairly uniformly layer of dispersed beads fully covered the active area of the membrane and also filled the feed space. The 2 mm deep feed space had a reasonable three dimensional density of beads in it (estimated to be about 50% volume). With this high a density, the motion of the beads, and the continuous collisions with each other and the walls of the cell in the confined space, meant that some of the spinning beads were always in contact with the fouled membrane. The "best" procedure/sequence given below was the result of many trials and variations that will not be mentioned in this document.

The plant filtration system was operated as follows (a typical flux-time plot, given in Figure 5 illustrates this procedure). First the membrane was mounted in the cell and the cell connected to the system. The clean water value was then measured for five minutes using RO water at 50 kPa (A in Figure 5). The retentate flow rate was found to be about 70 mL/min. at the bottom end of the membrane and about 70 mL/min, plus the permeate flow, at the top (input end) of the membrane. The cross flow velocity at the exit end of the membrane was approximately 0.0233 m/sec. The feed to the pump was then changed to the fouling solution/suspension and the membrane was fouled (B) until the permeate flow rate was less

than 10% of the clean water value or for five minutes, which ever occurred first. Reverse Osmosis water was then passed over the membrane to remove any loose foulant from the system (C). After this period the pump was switched off and a valve in the feed line was closed. The beads were introduced (D) into the cell at zero feed pressure using a syringe, through the entry port into the feed space of the cell. The excess water flowed out through the retentate ports, which were covered by a fine sieve. After the surface of the membrane had been covered with beads the entry port was closed and the bead density on the surface of the membrane was made more uniform using a small permanent magnet. The E field electromagnet (or in some cases the rotating magnet) was then re-activated (E) for five minutes. This was the period during which the cleaning took place. After five minutes the electromagnet (or rotating magnet) was deactivated and the beads were withdrawn from the system using the previously mentioned syringe. This also resulted in all or most of the foulant that had been cleaned off by the beads being removed from the feed cavity. Reverse Osmosis water at 50 kPa was then reintroduced (F) for five minutes to measure the new RO flow rate. After this period the beads were reintroduced (G) using the same procedure as before, and the magnetic field reactivated for five minutes to further clean the membrane. After this five minute period, the field was again turned off (H) and the beads and any foulant in suspension were removed. Finally the flow was again measure using RO water (I) for five more minutes.

It must be emphasized that it was no trivial exercise to introduce the beads onto the membrane so that they covered the membrane completely and contained no air pockets. Repeatability was further hindered by the beads moving their physical position as a result of the AC magnetic fields. This gave rise to what was initially a reasonably uniformly covered membrane, having less densely covered regions during the cleaning cycle.

A computer was connected to the electronic scale – upon which a beaker had been placed to collect the permeate – which logged the mass registered on the scale every 30, 60 or 120 seconds. The permeate flow and then the flux were calculated from these results and plotted as a function of time, to create the figures given in this report (see Figure 5).

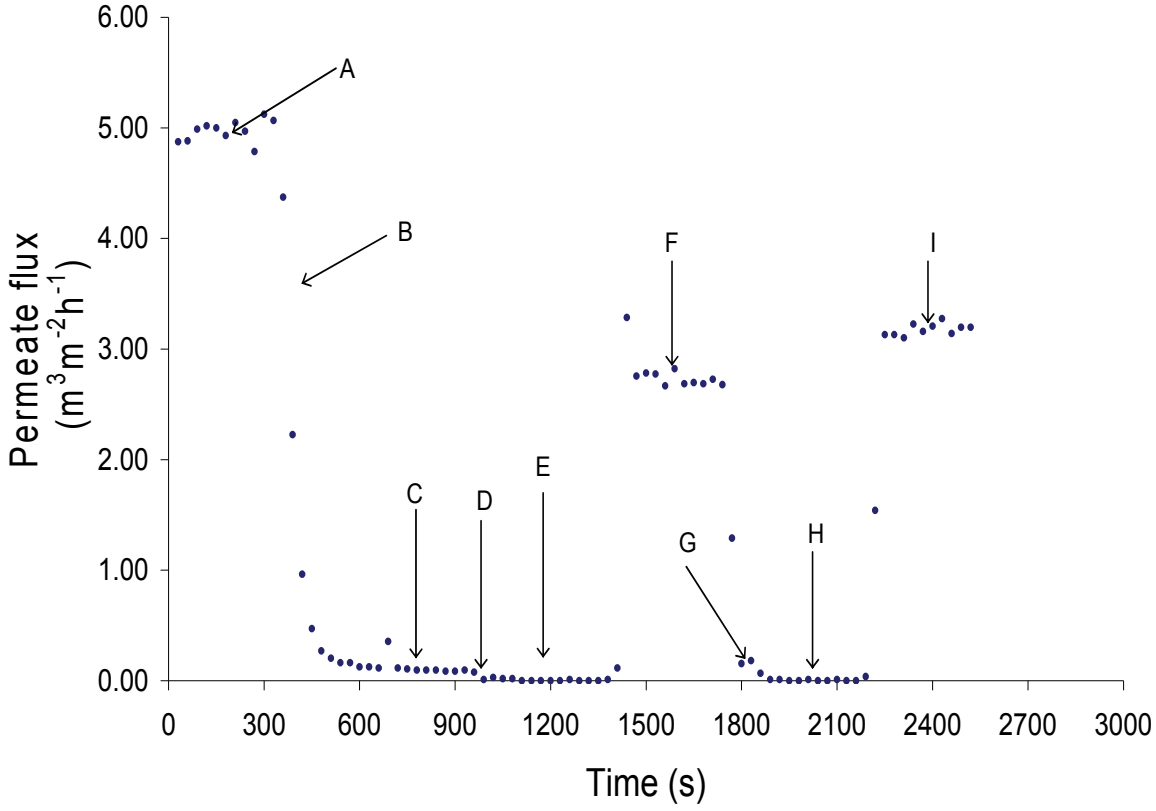


Figure 5: Results for an experiment using Dextrin as a foulant and a 0.2 µm pore space nylon membrane

3.3 The Procedure Used for Conducting the RO Cleaning Experiments at Zero TMP

As these tests involved introducing the beads onto the active area of the membrane after it had been fouled, a port (V8 in Figure 4) was placed in the top plate of the cell over the input side of the active membrane area (sintered bronze support area). For these tests, sufficient beads were then introduced through this port, using a modified syringe, to cover the active area of the membrane. In order to confine the beads to this area, a vertical sieve (made of fine stainless steel mesh and anchored to the polycarbonate top of the feed space) was placed at the exit of the flat cell.

The procedure was to first measure the clean water or RO flow rate. A RFS (Lisitsin *et al*., 2005) concentrate was then rapidly added to the feed tank which was continually being stirred. After this the fouling was monitored until no further drop in the permeate flow rate was observed. In order to add the beads after fouling, the pump was stopped and the water in the feed tank replaced with pure RO water. The system was then briefly flushed with RO water at a low pressure. With the pump off the beads were then added as described above and then the magnetic field was switched on, with the desired Amplitude and for the selected period. Note that the membrane was cleaned at zero TMP. The beads were then withdrawn using the same syringe through port V8. This port was then closed, the pump started and a new RO flow rate measured. The flow rate (converted to flux) for these studies was initially measured using the same electronic balance (0.1 g resolution) connected to a PC as used in the cleaning of the fouling layer experiments. This PC logged the data and calculated the

flow rate and flux. However, when using RO membranes it was found that the flow rate was much slower and in order to get good resolution in a 2 minute period, a balance with a resolution of 0.01 g was required. In order to solve this problem a 0.01 g resolution balance, operated using a LABview program, which logs both the time and mass and calculates the flow rate, was then used (to avoid "noisy" drips from the permeate pipe, the exit was placed under water).

When this procedure was used with even a very low feed flow and a positive TMP, the beads were all swept up against the exit sieve where, being soft, they distorted and blocked the feed flow.

4. RESULTS AND DISCUSSION

4.1 Early Studies of the Motion and Properties of the Beads

During the first year the motion of a large number of particles was monitored in a dry cell. This early work was vital to determine the nature and amount of magnetic material that had to be incorporated into the beads and particles in order that they move in a field of 100 Gauss or less. The (relative) magnetization of the different batches of beads was measured and the amount of magnetic material determined by Thermo Gravimetric Analysis.

At this stage the most important parameter measured for each type of bead was the initial AC field at which all the beads started to rotate in air. For most beads and particles, a field of more than twice this "rotation" field caused them to bounce. It was also found that if the magnetic moment of the beads was too high they tended to aggregate, and often it was these aggregates which were the units that moved in the magnetic field. A flood light, lens and ground glass screen were built into the fame holding the Helmholtz coil. This enabled the motion to be monitored at five times magnification on the screen. Short movie pictures of this magnified image were taken of some of the beads in motion and presented as part of a deliverable report. When the polystyrene beads were immersed in water some of them tended to float, which complicated the experiment. However, the fields where the rotation started appeared to be unaltered.

For the original polymerized polystyrene spheres the first rotational field was 34 Gauss. The compounded hematite-polyethylene particles (beads) were sorted into batches of 38-75, 75-150 and 150-212 μm. The first rotational fields for these are 51, 28 and 28 Gauss respectively. All these early experiments used the Helmholtz coil.

4.2 Experiments at Low Cross Flow Rates

Using a low flow rate (4 cm/sec), clean water was passed through a polysulphone membrane in the flat cell for 20 minutes, with a TMP of 0.4 Bar. At the end of this period the permeate flow rate was 54 mL/min. A yeast suspension (1 g/L) was then introduced under cross flow filtration conditions at 0.4 Bar. After 10 minutes the flow rate had dropped to 6.8 mL/min and became constant at 5.2 mL/min after 30 minutes. The feed was then switched back to clean water and after 15 minutes it was observed that there had been a negligible change in the permeate flow rate. Magnetic balls were then introduced into the feed water, with the magnetic fields already running. The sweeper magnetic circulation system, described earlier, was used to circulate the beads. A low surface density of balls was observed to cover the

entire membrane. By eye the balls appeared to execute a more bouncing than spinning motion and none of the balls were sticking in the foulant layer. After five minutes it was observed that the fouling layer of yeast had been removed from the membrane and during this period the water in the beaker which had caught the feed flow had become milky. However, the flow rate remained at 5.2 mL/min. The permeate flow rate increased very slightly when the cleaning was carried on for a further 15 minutes. The clogged membrane was later examined under a SEM and the pores of the filter were found to be clogged with a substance which could not be resolved in the SEM. It was hypothesised that the pores had become blocked by a protein or other material that had come from the live yeast cell walls. These could have included smaller fragments and proteins, which were able to penetrate and deposit in the pores. As they were below the surface of the membrane and the scrubbing action of the beads, they could not be removed.

Note that the block magnet was used for the above experiment and the beads were circulated using the previous described magnetic sweep, which would only operate at low cross flow rates.

It was then decided that the system might improve if it operated continuously, as would be required in practice. For this, new (hopefully non pore filling) foulants were tried. These were alumina powders (1 g/L) with diameters of 0.1, 0.3 and 1.0 μm and narrow size distributions. In these experiments, the beads were activated before switching from clean to foulant water and remained activated during the entire experiment. Unfortunately, this flux enhancement procedure was found to be ineffective. For instance with the 0.3 μm alumina powder, the flow rate fell from 66 mL/min to 4 mL/min over a period of 15 minutes. The flow did not improve even when a cross flow of clean feed water was reintroduced with the magnetic field still on. However, the liquid in the feed space turned a milky colour for the first few minutes, indicating some of the alumina was being removed. After 15 minutes with this cross flow of clean water, the flow rate had still not improved and some of the foulant layer was seen to have remained on the membrane. It was later observed, using the SEM, that some of the beads had become trapped in the foulant layer which was still on the membrane. Therefore, as the spinning beads could not break free of the alumina surface layer, they certainly could not keep it clean.

4.3 Experiments with Beads Moving Across the Membrane with a Positive TMP

In these experiments the beads were circulated using the sieve separator and a small circulation pump. The flow rate across the membrane was 20 cm/s at 40 kPa TMP and 6 cm/s at 10 kPa. The inhomogeneous AC magnetic field for the experiments described here was produced by the block field magnet. Later experiments were conducted with the E field magnet.

The following results were obtained when the beads were activated before the changeover from clean to foulant water, i.e. a continual enhancement of the permeate flux was being investigated. All experiments were carried out using the polysulphone membrane, as it was believed that this was the easiest to clean.

For washed yeast (2 g/L) at a low 10 kPa TMP the flow dropped from 29 mL/min to 12 mL/min in 15 minutes, but recovered to 17 mL/min after clean water was introduced. After a short period of the clean water flow no more yeast was observed through the top of

the cell on the membrane. It was therefore concluded that the low flux rate was due to foulant material embedded in the pores. A repeat run gave a drop from 30 mL/min to 15 mL/min and a recovery to 20 mL/min.

The permeate flow rates for washed yeast with a 40 kPa TMP and a higher flow rate decreased from 50 mL/min to 15 mL/min after 15 minutes, but only recovered to 18 mL/min after the clean water (with activated beads) was introduced. In both (10 and 40 kPa) cases, a close visual examination showed that some of the beads had became embedded in the foulant layer.

In a similar experiment, using the 1 μm alumina as a foulant, with a 40 kPa TMP, the flow rate dropped from 64 mL/min to 15 mL/min in 15 minutes, but unlike with the washed yeast, did not recover at all when clean water was introduced. Similar results were obtained using a 0.1 μm alumina powder at 40 kPa TMP.

In some of the above cases several beads remained embedded in the alumina foulant layer, which showed that insufficient torque was being applied to the beads to prevent them from being trapped. Therefore it was decided to increase the magnetic field and the E field magnet was introduced.

At this stage it should be noted that if the beads flowed across the membrane in zero inhomogeneous field (Helmholtz system), they did not become imbedded in the foulant. However, when a strong static inhomogeneous field (permanent magnets) was applied the beads again became embedded in the foulant.

These medium flow rate experiments were repeated using the previously described E core magnetic field, where the field was five times stronger than in the above experiments using the block magnet. The cell was now also placed in both horizontal and upright positions. In these higher cleaning field experiments, washed yeast, 0.1 μm, and 0.3 μm alumina were used as foulants. Cleaning was attempted with flowing beads at TMP of 0 kPa, 10 kPa, 40 kPa and 60 kPa. Basically, except at 0 kPa, the cleaning was marginal. For instance, with the cell in the horizontal position and using washed yeast at 40kPa, when the foulant was introduced the flow dropped from its clean water value of 30 mL/min to 15 mL/min in 6.7 minutes and when the clean water was reintroduced it rose to 18 mL/min after 6.7 minutes. Under similar conditions, with 1.0 μm alumina and the cell in the vertical position the flow decreased from 25 mL/min to 9 mL/min and increased again to 12 mL/min with clean water. In neither of these cases was any significant cleaning action observed.

One new feature observed was that with the cell in the horizontal position, some of the beads remained imbedded in the alumina foulant, while in the vertical position they did not. It would therefore appear that, using the E field magnet, a linear combination of an inhomogeneous field and gravity were needed to imbed beads in the alumina fouling layer.

4.4 Cleaning of the Membranes at Zero TMP

The foulant/membrane combinations for all the experiments performed are listed in Table 1 and some of the results are given in Figures 5 to 10. The experimental results reported are for those using the E field magnet (1a to 5b in Table 1) and the rotating magnet (7a to 7e). Note that during the cleaning period the foulant was mixed back into the water in the feed space,

but most of this was washed out using a syringe, before the TMP was reapplied. The results given are for the E magnet, where the field at the centre of the membrane was 80 Gauss. This field may was what was most often used when attempting to clean membranes with flowing beads and a positive TMP.

Figures 6 and 7 (p. 20) show fouling curves for alumina, which was a fine, chemically inert, particulate foulant, using both the nylon membranes and the PSMs discussed above. The decline in the permeate flow rate during initial clean water periods for the nylon membranes was attributed to conditioning of the membrane. Figures 8, 9 and 10 (p. 21-22, and also Figure 5, p. 14) show fouling curves for dextrin, which was a far more "sticky" foulant, using both nylon membranes and the PSM discussed above. Table 1 summarizes the results. From Table 1 it can be seen that the results were not very reproducible especially when using the two nylon filters.

Figures 9 and 10 (and also Figure 5) show fouling curves for dextrin, which was a far more "sticky" foulant, using both nylon membranes and the PSM discussed above. Table 1 summarises all the results.

Table 1: Summary of results obtained using different membranes and foulants. (The flux in experiments 1-6 is in m^3/hr; in experiments 7a-e the flow in mL/min is given instead of the flux.

	Exp	Membrane	Field Gauss	Fouling	Beads	Clean water flux[1]	After fouling flux	After 1st cleaning flux	After 2nd cleaning flux	% of clean water value[2]
1a	7	PSM	80	1 µm Al	Y	4.141	1.059	2.504	2.889	70
1b	3	PSM	80	1 µm Al	Y	4.622	1.107	2.167	4.334	94
1c	5	PSM	80	1 µm Al	Y	4.671	1.252	1.926	3.274	70
2a	8	Nylon 0.45 µm	80	1 µm Al	Y	7.704	1.541	1.926	4.334	56
2b	10	Nylon 0.45 µm	80	1 µm Al	Y	7.223	1.252	3.659	4.526	63
2c	6	Nylon 0.45 µm	80	1 µm Al	Y	6.548	0.963	1.445	2.985	46
3a	9	Nylon 0.2 µm	80	1 µm Al	Y	3.467	1.059	2.793	3.274	95
3b	1	Nylon 0.2 µm	80	1 µm Al	Y	1.637	0.674	0.963	1.204	74
3c	2	Nylon 0.2 µm	80	1 µm Al	Y	1.637	0.482	0.626	1.107	68
4a	11	Nylon 0.2 µm	80	Dextrin	Y	3.948	0.241	1.541	2.504	63
4b	12	Nylon 0.2 µm	80	Dextrin	Y	4.045	0.193	1.926	2.215	55
4c	13	Nylon 0.2 µm	80	Dextrin	Y	4.334	0.289	1.445	2.215	51
5a	14	PSM	80	Dextrin	Y	5.393	0.144	3.563	3.659	68
5b	15	PSM	80	Dextrin	Y	4.719	0.096	2.408	2.600	55
6a	20	PSM	0	Dextrin	N	2.504	0.193	0.241		10
6b	21	PSM	0	Dextrin	N	3.563	0.193	0.193		5
6c	22	PSM	0	Dextrin	N	2.985	0.144	0.144		5
7a	A	PSM	500 Rotating	1 µm Al	Y	1.6	0.4	1.6	1.6	100
7b	B	Nylon 0.45 µm	500 Rotating	1 µm Al	Y	15.5	1.1	11.5	11.5	74
7c	C	Nylon 0.2 µm	500 Rotating	Dextrin	Y	15.0	6.5	11.0	11.0	87
7d	D	Nylon 0.2 µm	500 Rotating	Dextrin	Y	15.0	6.5	11.5-12.5	11.5-12.5	77-81
7e	E	PSM	500 Rotating	Dextrin	Y	1.6	0.4	1.5		94

[1] Represents the value of the flux just before the foulant is added
[2] After 2nd cleaning value × 100/ clean water value

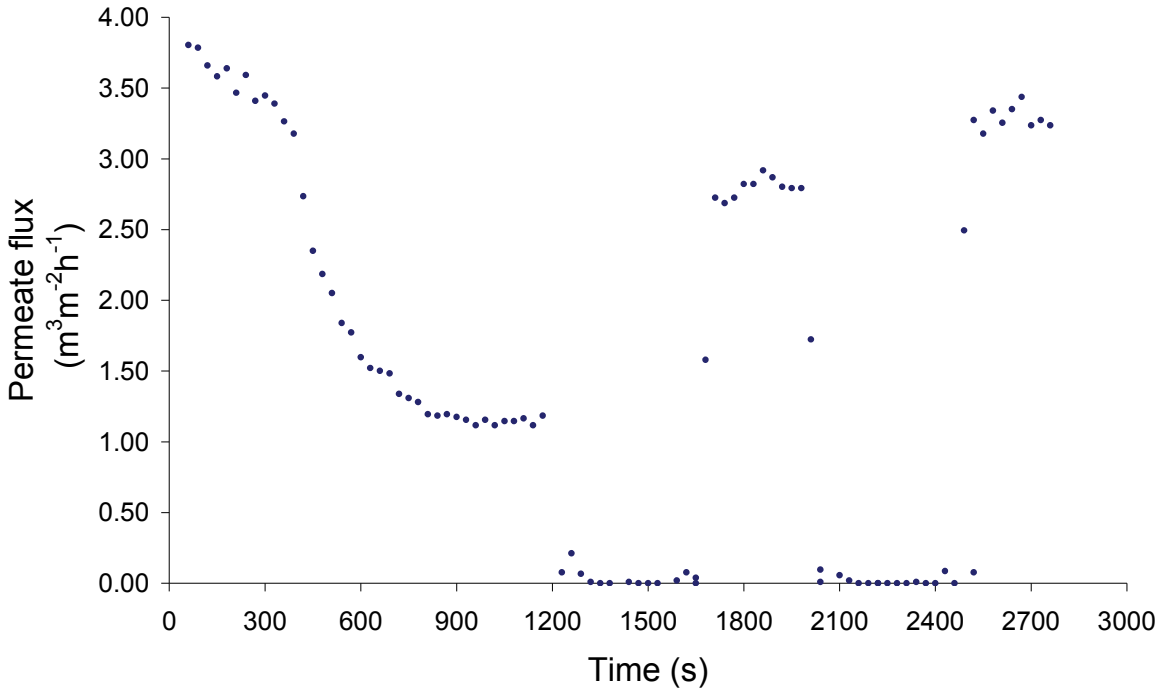


Figure 6: Permeate flux-time results for fouling with 1 µm alumina on a 0.2 µm nylon membrane

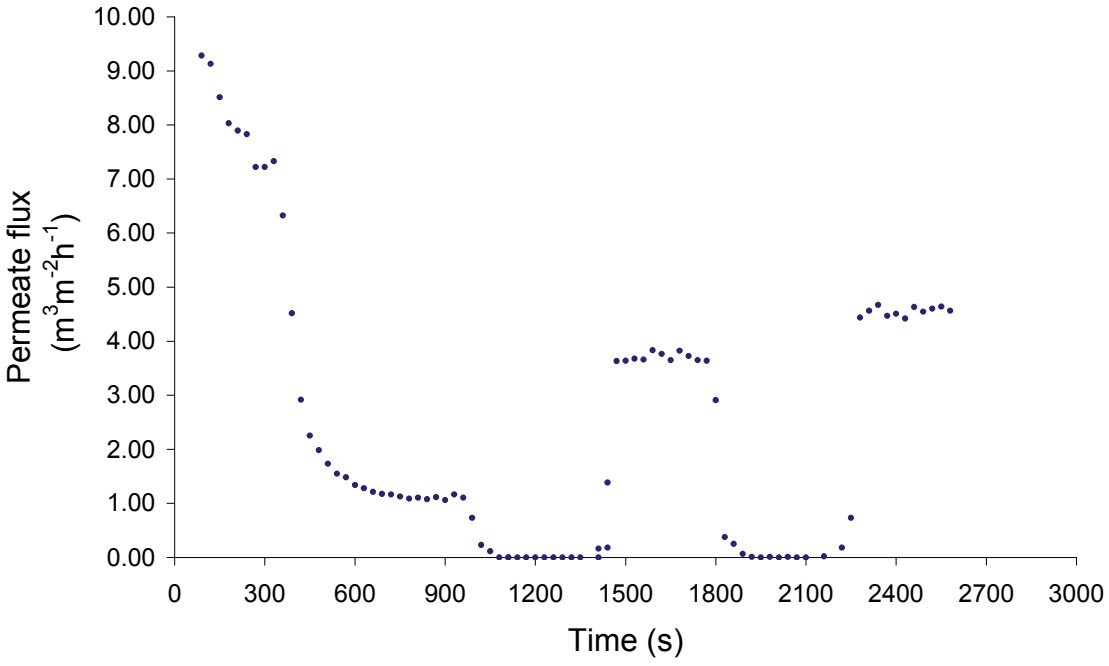


Figure 7: Permeate flux-time results for fouling with 1 µm alumina on a 0.45 µm nylon membrane

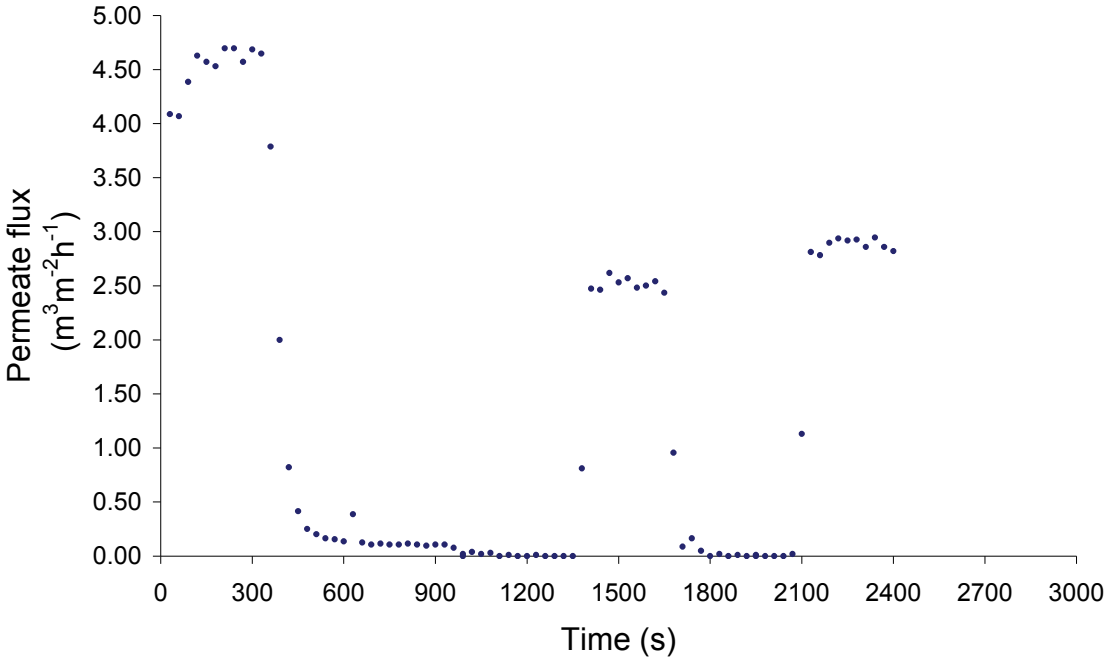


Figure 8: Permeate flux-time results for fouling with dextrin on the PSM membrane

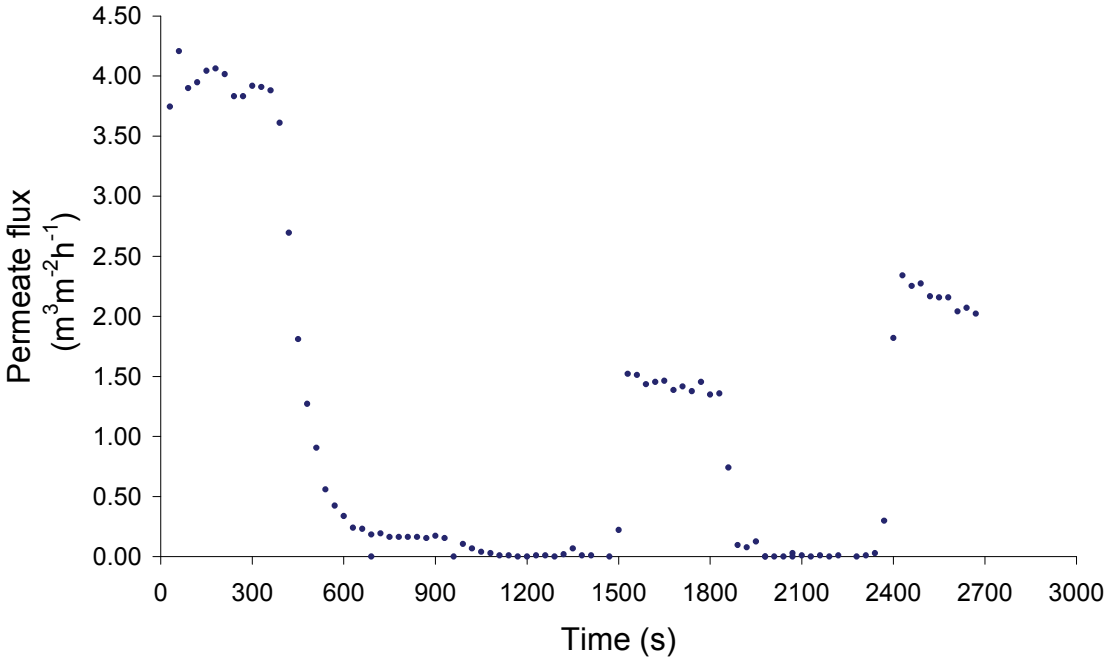


Figure 9: Permeate flux-time results for fouling with dextrin on a 0.2 µm nylon membrane

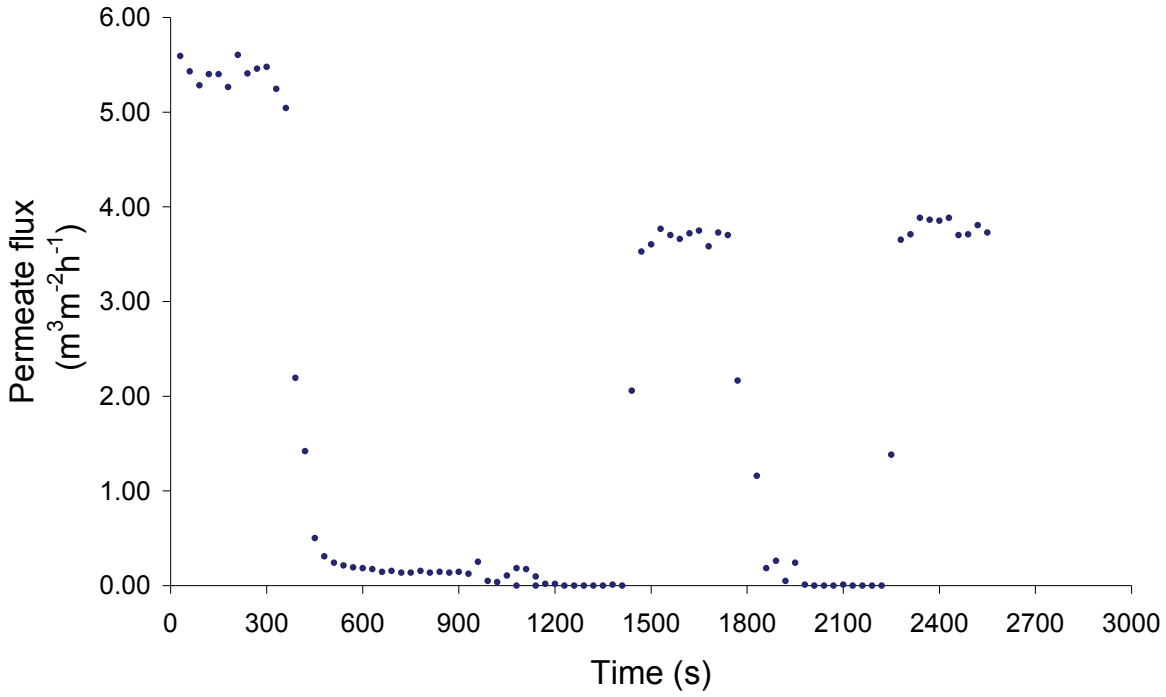


Figure 10: Permeate flux-time results for fouling with dextrin on the PSM membrane

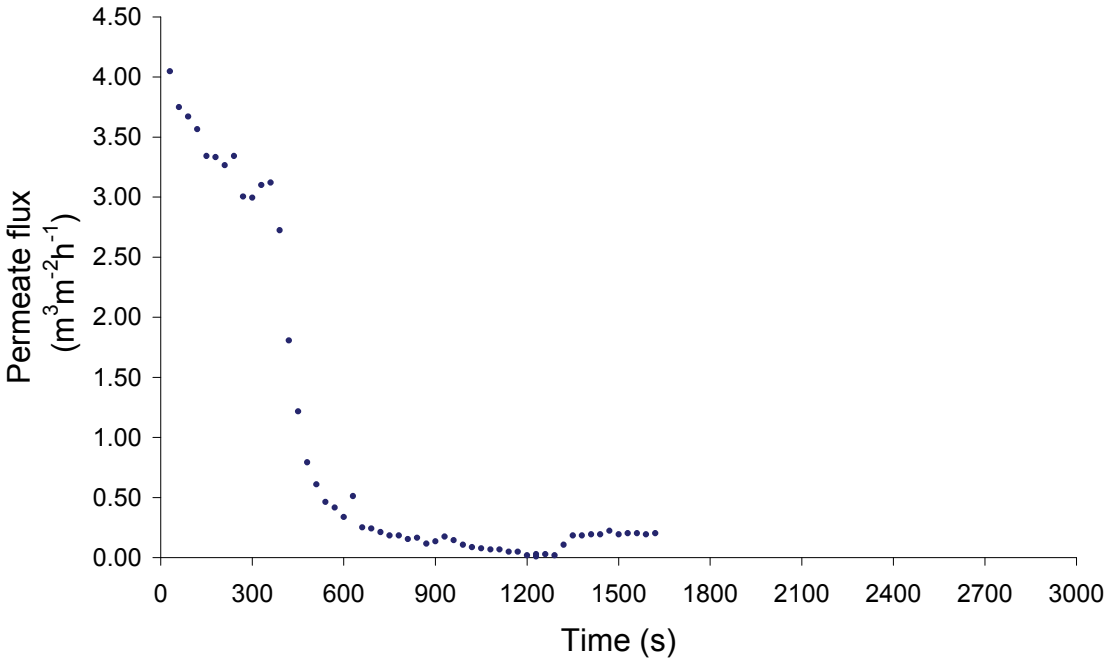


Figure 11: Permeate flux-time results for a PSM membrane fouled with dextrin and used as a control experiment

A control experiment (see Figure 11) was carried out to see if flushing RO water in and out of the cell had a cleaning effect. In this experiment the membrane was first fouled, after which RO water was added to the cell above the membrane where it was left for five minutes at zero TMP. The water was then removed as in the previous experiments. After this RO water, at 100 kPa, was passed over the membrane and the flow rate re-measured. The results for this experiment are shown in Figure 11, where it can be seen that no improvement in the

RO flux was observed, so introducing and removing the RO water had no cleaning effect. It should also be noted that, unlike observations in the previous cases presented in this section, no foulant was seen in the water flushed from the system, indicating that the fouling layer was still intact.

Results for cleaning the membrane using the rotating magnetic system are given in Figure 12 (alumina/nylon 0.2 µm) and Figure 13 (dextrin/PSM). The results for these experiments are given at the bottom of Table 1. The flux values for the nylon membranes showed a preliminary spike after cleaning. The values given in Table 1 are the equilibrium values reached after 10 minutes. It would appear that the cleaning obtained using the rotating field was better than for the fields obtained using the E field magnet.

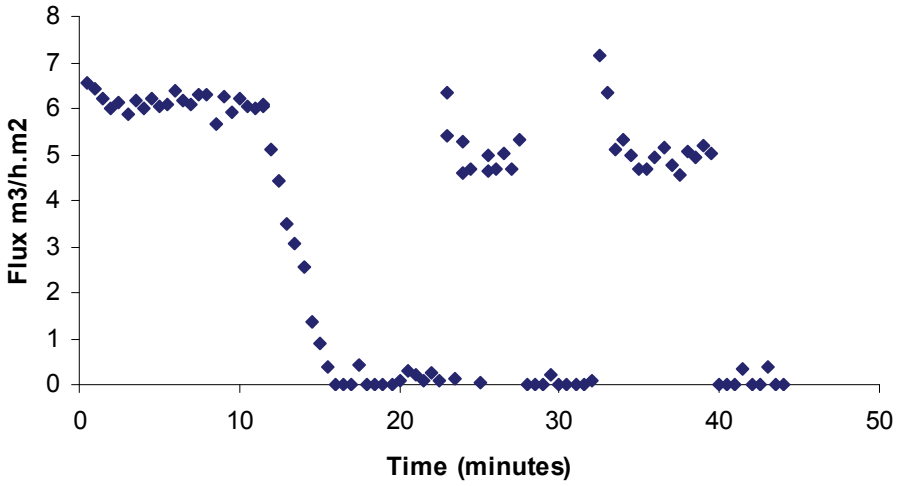


Figure 12: Flow rate for fouling with alumina on the nylon 0.45 µm membrane

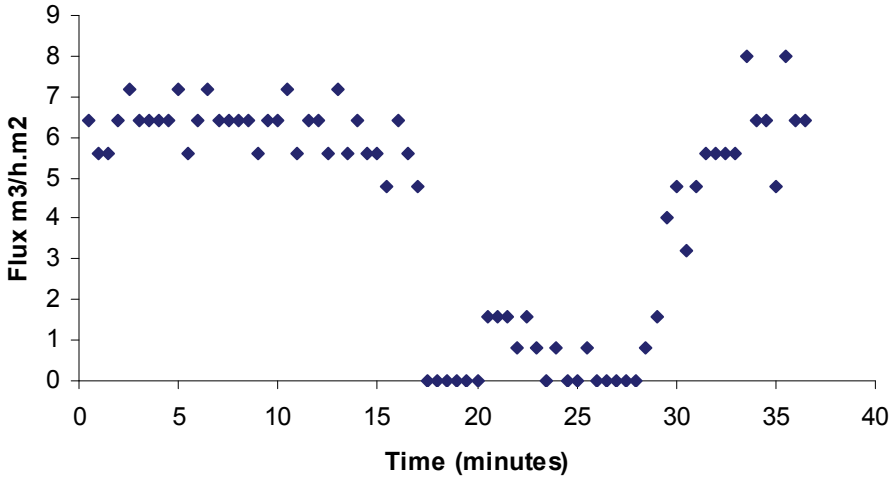


Figure 13: Flow rate for fouling with dextrin on the PSM membrane

All the results showed an increase in the flux or flow rate after an initial bead cleaning treatment and sometimes an additional improvement in the permeate flux or flow rate after a secondary treatment. Table 2 summarizes and compares the average results.

Table 2: A comparison of the experimental results (percentage of the clean water flux from Table 1) obtained using the E field and rotating magnets. The first result is obtained using the E field and the value in brackets is that obtained when using the rotating magnet.

Membrane	PSM (U)	Nylon 0.45 µm	Nylon 0.2 µm
Alumina	78 (100)	55 (74)	69 (X)
Dextrin	61 (94)	X	56 (83)

Two conclusions may be drawn from Table 2, although the statistics were not very reliable:

1. The cleaning action of the beads is better on the PSMs.

2. The cleaning action is better when using the rotating magnet rather than the E field systems.

From the experiments reported here, it can be seen that the permeate flow rate can be significantly improved by the cleaning action of the PAN beads at zero pressure, either in the alternating field of the E magnet or the rotating field. However, the rotating field appeared to be more efficient.

4.5 Cleaning RO Membranes at Zero TMP

Figure 14 gives a plot of the permeate flux versus time, showing the initial conditioning of the membrane and then the change in the permeate flux when a 500 ppm salt solution is filtered, and found to have a conductivity of 198 µS. Note in this and subsequent plots that, due to the ballast tank, it took about 20 minutes for the system to reach a steady state.

For the RO cleaning experiments (Figures 15 and 16), after conditioning the membrane was fouled using the RFS mentioned earlier. When the RFS was used at the initial recommended concentration, rapid fouling was not observed, so the cleaning experiments reported here were all carried out using two or three times the recommended RFS concentration and for periods of ± 90 minutes. Note that all measurements were taken at 6.9 ± 0.1 Bar, with a feed cross flow of 1 ± 0.05 L/min.

Bearing in mind the fact that magnetic beads have been found to be effective in cleaning a fouling layer, but only when the TMP was close to zero, it was decided as a first step to see if the beads could remove a scaling layer at zero TMP so as to give an improved permeate flow. This necessitated, as described in Section 3.3, the introduction of a large number of beads onto a scaled membrane and setting them in motion for ten minutes, at a frequency of 10 Hz using the E field magnet. The cleaning of the membranes and all subsequent measurements were conducted using RO water. Only results for membranes cleaned at zero TMP, using this procedure, are given in this report. In all these experiments the membranes are cleaned twice, after which 500 ppm salt water solution was reintroduced and the permeate flux logged for a further ±90 minutes.

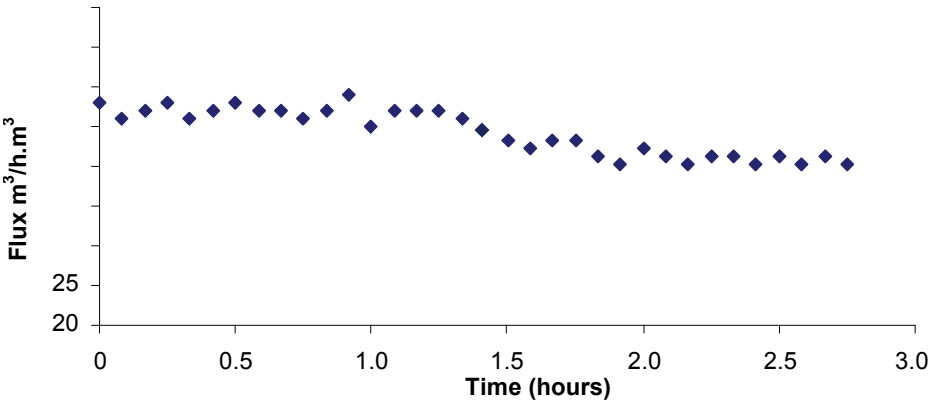


Figure 14: Plot of the permeate flux versus time when a 500 ppm salt solution is filtered

Figures 15 and 16 show the conditioning of the membrane and the RO or clean water flux for the first hour. After this the feed to the pump was changed to a double concentration RFS solution in the experiment shown in Figure 15 and three times the RFS solution in Figure 16, and the permeate flux as a function of time is shown over the next 90 minutes. After this the beads were introduced, the cleaning procedure described above was performed and the new RO value recorded. The cleaning procedure was repeated and a second "cleaned" RO value recorded. After this the feed to the pump was changed to a 500 ppm salt solution and the permeate flux was monitored for a further 90 minutes. These membranes were all stored for subsequent SEM measurements and the conductivity of the permeate was measured to see if the cleaning procedure had damaged the rejection value for the membrane.

Figure 15 gives a plot of the permeate flux versus time and shows the initial conditioning of the membrane and then the change in flux when a 2 × RFS fouling solution was introduced. After this the figure records where the first cleaning (zero flux) was made and the subsequent measurement of the RO flux. The figure then shows a repetition of the cleaning procedure and RO flux measurement. Finally the figure records the effect of introducing a 500 ppm salt solution. The RMS field was 80 Gauss from the E field magnet. In this figure one observes that the cleaning procedure actually decreased the flux.

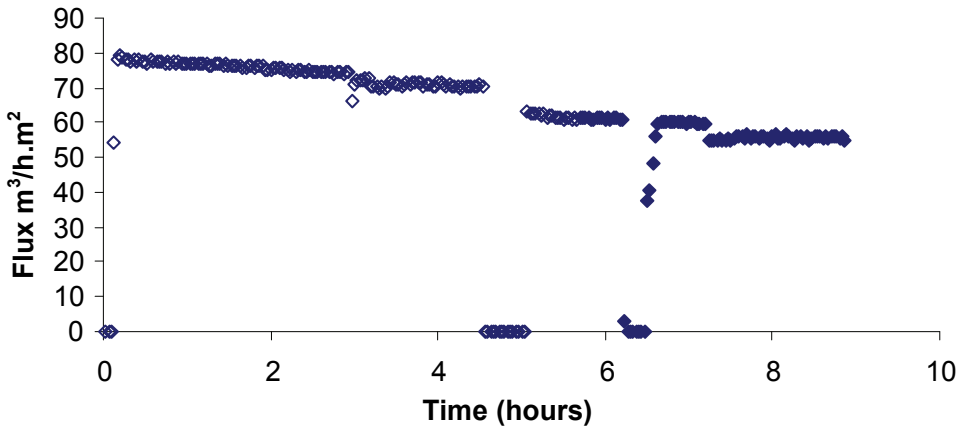


Figure 15: Plot of the permeate flux versus time when a 2 × RFS fouling solution is introduced

Figure 16 shows the initial conditioning of the membrane and then the change in flux when a 3 × RFS fouling solution was introduced. After this the figure records where the first cleaning (zero flux) was made and the subsequent measurement of the RO flux. The figure then shows a repetition of the cleaning procedure and RO flux measurement. Finally the figure records the effect of introducing a 500 ppm salt solution. Note the drop in the flux upon adding the 3 × RFS foulant was considerably larger than in the case where 2 × RFS concentration was used. This figure shows that the cleaning procedure improved the flux slightly after the first clean and that it returned to the last fouled value after the second clean. The results were obtained using an AC field of 80 Gauss. The results (not shown) obtained when using a 3 × RFS concentration and a RMS field of 48 Gauss in the E field magnet, were that the cleaning procedure improved the flux very slightly after the first clean but that the flux decreased very slightly after the second clean. Similar results were also observed for a field of 24 Gauss.

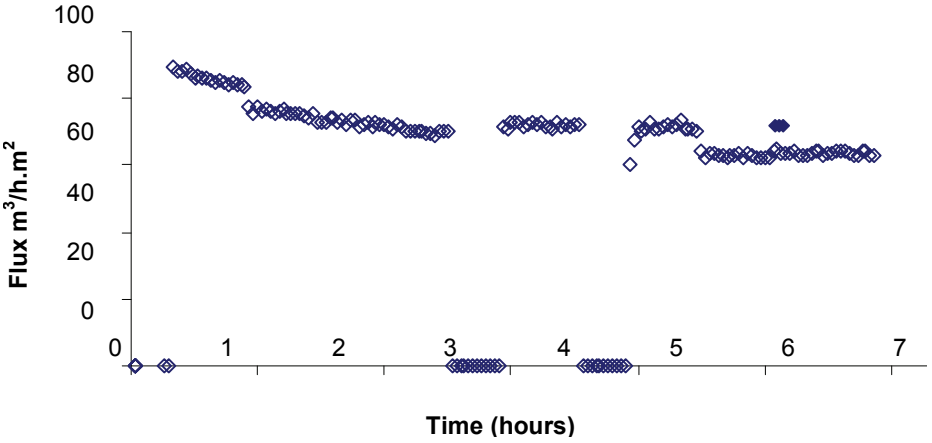
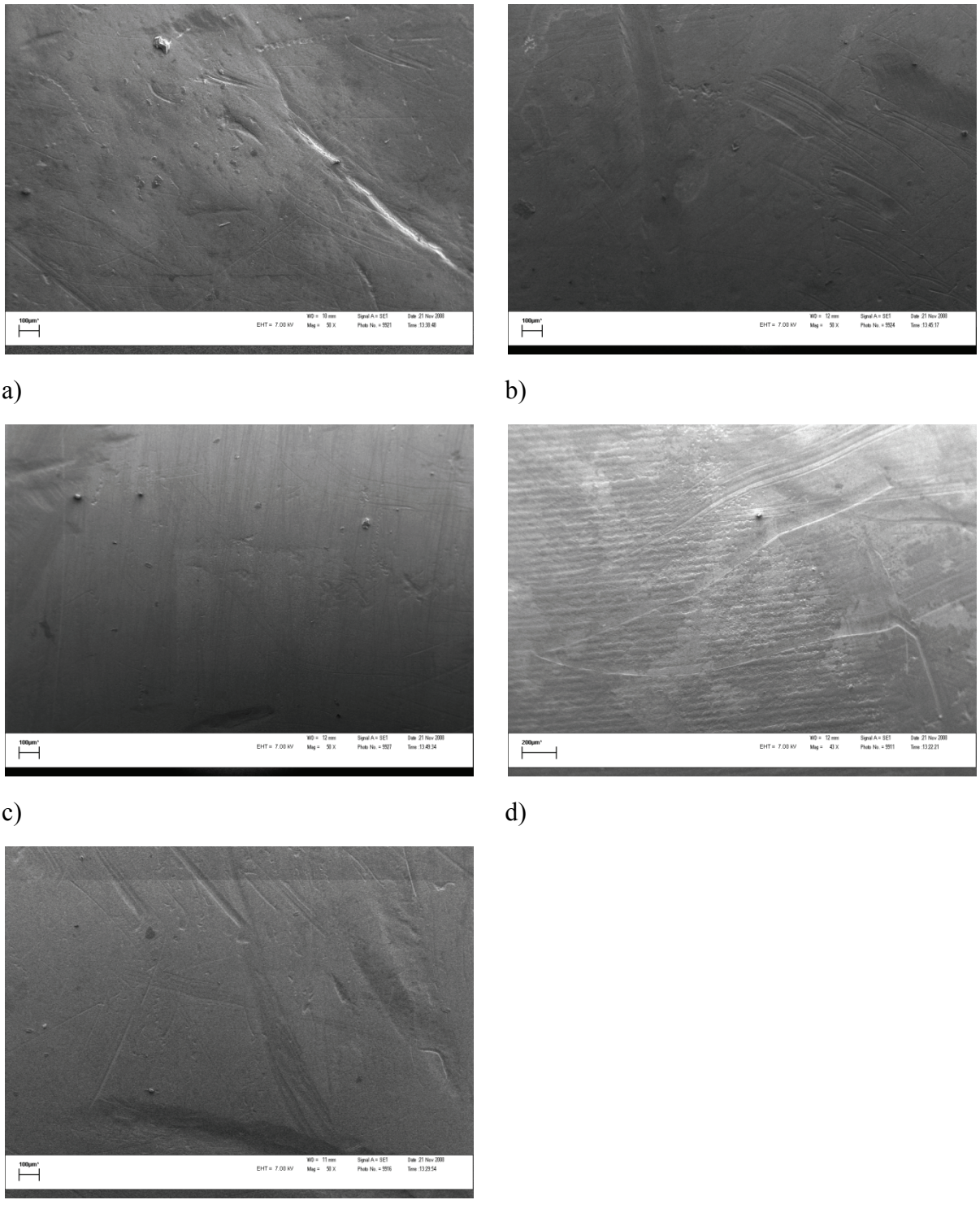


Figure 16: Plot of the permeate flux versus time when a 3 × RFS fouling solution is introduced

In order to try to understand what is happening, the images obtained from a series of SEM micrographs are presented and discussed. Figures 17 a - e all show images at a magnification of 50. Number 17a is an image of a conditioned membrane, number 17b is after 2 × RFS fouling and number 17c is after cleaning the 2 × RFS membrane. Note that these images are all very similar and it has to be assumed that 2 × RFS fouling is mainly in the nanopores. Figure 17d shows that a cloud like pattern of light on dark areas was obtained after 3 × RFS fouling and Figure 17e shows the light cloud-like areas to have gone after cleaning. It would appear that the "clouds" indicated a thicker, flakier fouling layer, which could not be cleaned by the beads.



a) b)

c) d)

e)

Figure 17: Scanning electron micrographs at a magnification of 50×

Figure 18a is an image of a conditioned membrane and Figures 18b and 18c were taken from a 2 × RFS fouled and cleaned membrane respectively. There may just be a discernable difference between these three images but it must be concluded that 2 × RFS fouling did not

produce a fouling/scaling layer which could clearly be seen using even high magnification SEM micrographs.

Figure 18d shows an enlargement of a light "cloudlike" area in figure 17d, which clearly shows a heavy scaling layer. Figure 18e is an enlargement made from a dark area in Figure 17d and shows that less fouling had occurred here than was observed in Figures 17d and 18e.

Figure 18f and 18g show images as seen at 500 magnification, after a 3 × RFS fouling and bead cleaning. Figures 18f and 18g are from the more heavily and more lightly scaled areas, respectively. The remnant scaling is seen to be somewhat heavier in Figure 18f than in Figure 18g and both are similar to what is observed for Figures 18b and 18c. Note that no thick fouling layers, as seen in Figure. 18d, were observed on any of the cleaned membranes.

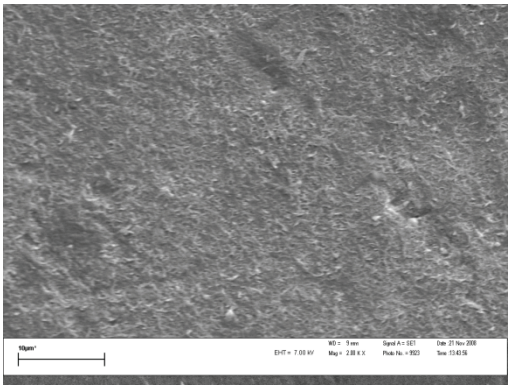
These images (Figures 18d to 18g), allow the conclusion to be made that the beads are capable of cleaning off heavy, probably flake-like, scaling layers but do not remove the finer scaling layers/particles, which are more firmly bonded to the membrane and embedded in the membrane pores.

Table 3 shows the conductivities of the permeate obtained using a 500 ppm salt solution, with and without cleaning. This table clearly shows that the rejection of salt water is not too badly affected by a double cleaning of a 2 × RFS fouled membrane, but that cleaning had a noticeable negative effect on 3 × RFS cleaned membranes. It can be postulated that when the heavy flakes that occur on 3 × RFS membranes are removed that some damage is done to the membrane.

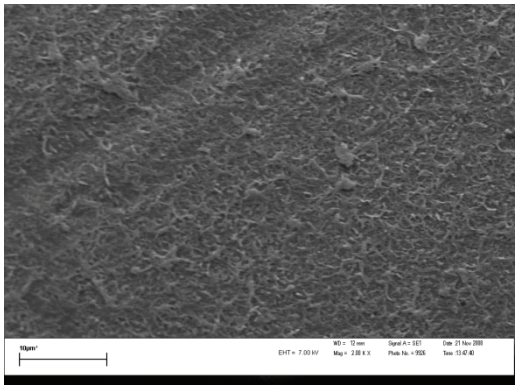
Table 3: The conductivities of the permeate obtained using a 500 ppm salt solution, with and without cleaning

Conductivity Readings (µS):	Permeate	Feed	Rejection %
3 times fouling, 2 times cleaning, 500 ppm salt @ end	274	1489	81.5
3 times fouling, 2 times cleaning, 500 ppm salt @ end	269	1390	80.6
2 times fouling, 2 times cleaning, 500 ppm salt @ end	203	1408	85.5
2 times fouling, 2 times cleaning, 500 ppm salt @ end	199	1456	86.3
Control 1 (membrane conditioning and 500 ppm NaCl addition)	198	1460	86.4
Control 2 (membrane conditioning and 500 ppm NaCl addition)	181	1401	87.0

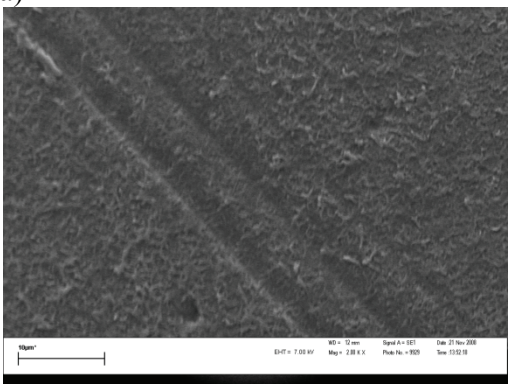
From the above, it must be concluded that the cleaning of fouled RO membranes with magnetic beads is not practical as only the flux through heavily fouled membranes can be somewhat improved.



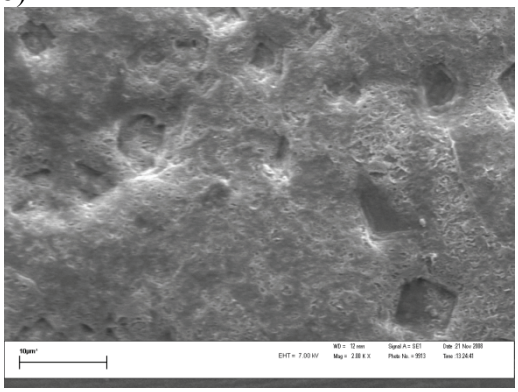
a)



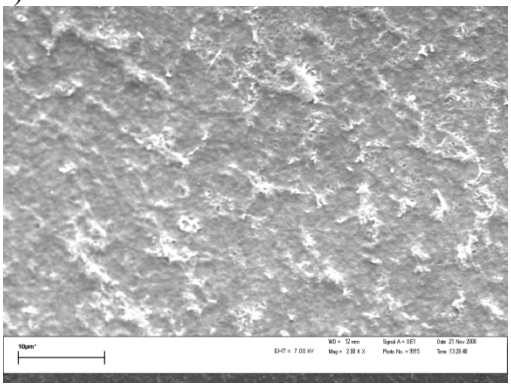
b)



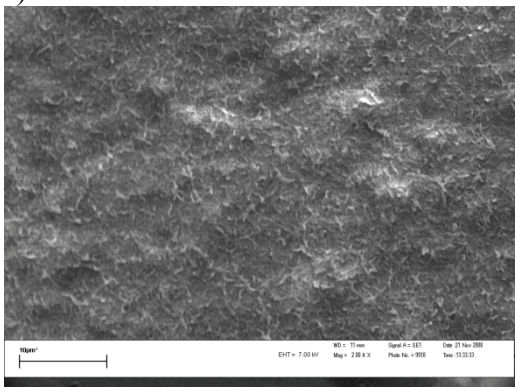
c)



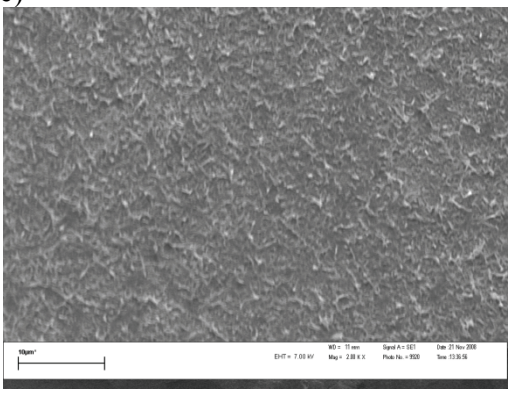
d)



e)



f)



g)

Figure 18: Images obtained using a SEM, from a) to e) at a magnification of 2000×. Figures 18 f) and g) are magnified 500×.

5. CONCLUSIONS

This report showed that satisfactory beads could be made by blending the hematite into polyethylene and PAN. However, as the polyethylene beads are not spherical, all the reported work was conducted with PAN beads. From experiments carried out on a dry or wet flat surface the motion of the poled beads appeared to be sufficient for cleaning purposes.

As the experiments all showed that cleaning could only be conducted at zero TMP it had to be concluded that beads could not continuously keep membranes from fouling and that the plant would have to be shut down in order to have the beads clean the membrane. From the flux-time curves and SEM micrographs it was concluded that the magnetic beads could only partially clean the membranes and that material in the pores and firmly bonded to the surface was not removed.

The report also concludes that chemical free cleaning of a filtration element, using beads, is possible but not practical in a spiral wrap membrane. One reason is that the feed space (which includes a spacer cloth) would have to be reasonably well filled with beads for the cleaning process to work and that, after the cleaning, the beads would have to be removed. While it is quite possible to generate large enough AC magnetic fields to clean membranes at zero TMP, no cost effective studies were made due to the difficulty of getting sufficient beads into the narrow feed space and subsequently removing them. It is probable that the process would be easier to implement in a capillary element where the internal diameter is sufficient to allow free passage of the beads.

Unfortunately no enhanced flux is observed for a lightly fouled RO membrane. Experiments also showed that an enhanced flux for a badly fouled RO membrane cleaned by rotating beads was obtainable but that the resulting flux was similar to that obtained for a lightly fouled membrane. This plus the SEM images allow one to conclude that while the beads are able to remove thick flaky layers, they are incapable of removing the well bonded initial scaling layers.

6. RECOMMENDATIONS FOR FUTURE WORK

Unfortunately this project showed that it was not possible to obtain a continuous enhanced flux flow (with a positive TMP) by using magnetic beads. Therefore no further work along these lines is recommended. However, as the beads can *partially clean* the membrane at zero TMP without using chemicals, this could be further explored where the use of chemicals is not desirable or possible; for example in the food and pharmaceutical industries.

It may also be worthwhile examining the use of magnetic beads in *partially cleaning* capillary membranes and elements. The beads are recoverable in a magnetic trap and the cleaning method does not use any chemicals. The beads are also confined on all sides by the membrane material and will therefore strike the membrane more often. Note that the size of the beads available determines the inner diameter of the capillaries that can be used as the beads must be able to be flushed in and out of the system without clogging. First experiments could use larger beads and capillaries to establish proof of concept. With the confined geometry in a capillary, it may even be possible to keep the membrane partially clean while passing the beads continually over it, with a low TMP.

Most filtration elements have a significant drop in flux during the first few minutes and then the fouling proceeds more slowly. Therefore, if the element can be *partially cleaned* so that the initial flux is equal to that which occurs after the rapid initial drop, it has been cleaned sufficiently for long term operation.

Due to the porous nature of the PAN beads they could be impregnated with reagents or even drugs. The beads could then be manipulated magnetically to where they are needed. Experiments are underway to see if such chemically impregnated beads can be used to help eliminate boron fouling problems that occur in some RO plants.

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