

**REAL-TIME OBSERVATION OF FOULING IN
MEMBRANE FILTRATION BY NON-INVASIVE
ULTRASONIC TECHNIQUES**

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WRC Report No. 1166/1/04



Water Research Commission



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Report to the
WATER RESEARCH COMMISSION

by

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WRC Report No 1166/1/04
ISBN No 1-77005-140-6

MARCH 2004

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EXECUTIVE SUMMARY

Introduction

Membrane fouling is universally accepted as one of the most critical problems limiting the wider application of membranes in liquid separations. The development and utilisation of a suitable non-invasive technique for the on-line monitoring of fouling in industrial and laboratory applications may enable the effectiveness of fouling remediation and cleaning strategies to be quantified.

The present research project was born from the words of Dr Irwing Murdoch, editor of *Water Desalination and Re-use* and chairman of a task group on membranes who, in 1999, stated that there was a need to revisit problems that limit the reverse osmosis (RO) field. In the project reported on here this was approached by using the tremendous recent gains made in available analytical equipment, including high-frequency digital and computer techniques. This was encouraged and supported by Professors Kranz and Greenberg, then of the Separation Centre, University of Colorado, USA, who had already two or three years experience in ultrasonic techniques. In this research project (#1166) we investigated the use of ultrasonics to detect and monitor in different membrane systems and in different configurations.

Through an initial programme funded by the WRC (#930) in which the use of ultrasonic waves was investigated it was proved that, using ultrasonics, fouling on RO membranes could be seen. This opened a number of doors to this investigation and gave rise to many of the aims.

Objectives

The overall objective of this research is to develop ultrasonic time-domain reflectometry (UTDR) for its use as an analytical tool for the real-time study of inorganic, organic and protein fouling of various types of membranes, including nylon, polysulfone (PSU) and polyethersulfone (PESU), and modules, including flat-sheet and tubular types. Different separation systems including microfiltration (MF), ultrafiltration (UF) and reverse osmosis (RO), flat-sheet and tubular modules, and suitable ultrasonic probes were used in this study.

Specific objectives were subsequently the following:

- In-situ measurement of particle deposition and removal in microfiltration
- Cleaning of microfiltration membranes by ultrasonics
- Determining cake layer deposition, its growth and compressibility, and removal during microfiltration

- Direct monitoring of membrane fouling and cleaning during ultrafiltration
- Measurement of protein fouling in tubular ultrafiltration membranes
- Visualisation and monitoring of inorganic fouling and cleaning of reverse osmosis membranes
- Generation of sufficient data to be able to propose and patent a modified plugging index meter.

Methodology

The overall aim of this project was to develop ultrasonic time-domain (UTD) and amplitude-domain reflectometry (UTDR) as a real-time visualisation technique for monitoring fouling in various pressure-driven membrane separations.

This was approached in the following way:

Consideration was first to be given to various designs for the development of the UTDR technique and suitable test cells. The latter should allow the simultaneous pressure-driven separation and monitoring of fouling. Systems for UTDR measurements and ultrasonic cleaning were set up and used. Flat-sheet and tubular membrane cells were designed and used. A mathematical model was to be developed and used to describe the process of ultrasonic testing, as related to the deposition of fouling in complex membrane environments.

UTDR was first to be used for the non-invasive, *in situ* measurement of particle deposition during microfiltration and, pending successful detection, particle removal, using flat-sheet nylon membranes. Scanning electron microscopy was to be used to confirm UTDR results. Further investigations into the cake-layer deposition, its growth on a membrane surface, and its compressibility were to be considered. This was then to be followed by similar investigations with polysulphone (PS) ultrafiltration membranes. Protein fouling of tubular polyethersulphone membranes (PES) was also to be considered. Finally, UTDR was to be used to monitor fouling and cleaning of reverse osmosis membranes

Results and Conclusions

This report describes the developments and successes achieved in both proving and understanding ultrasonic monitoring of membrane fouling. The overall achievement of this investigation was the development of ultrasonic time-domain (UTD) and amplitude-domain reflectometry (UTDR) as a real-time visualisation technique for fouling monitoring in various pressure-driven membrane separations. It was determined that UTDR can be used successfully

to monitor membrane fouling in MF, UF and RO with different membranes, foulants and configuration modules.

Specific results and conclusions, in the following areas, were as follows.

Microfiltration (MF)

- Ultrasonic response signals were obtained for kaolin particle deposition and subsequent cake layer formation on a nylon membrane surface during microfiltration (MF). A cake layer echo appeared, increased in amplitude, and moved in time due to layer thickening as fouling proceeded in MF.
- An ultrasonic cleaning technique was successfully used for cleaning membrane fouling in MF. It was established that ultrasound associated with forward flushing is a new and effective method for cleaning fouled MF membranes. Analysis by scanning electron microscopy (SEM) indicated that ultrasound with flushing was able to remove fouling layers from a membrane surface and restore the original structure of the membrane surface. The cleaning efficiency obtained by ultrasound with forward flushing was as high as 97.8%.
- UTDR was successfully used to measure the rate of cake layer formation at different flow rates. UTDR was also capable of detecting subtle changes such as the stop and restart operation.
- UTDR was successfully used for monitoring membrane cleaning and evaluating the cleaning effectiveness of various cleaning methods, namely: forward flushing, ultrasonic cleaning and ultrasound with flushing. Results showed that a cake-layer echo decreased after flushing and disappeared after ultrasonic irradiation in MF. UTDR results showed that ultrasound associated with flushing was the most effective cleaning method for cleaning membranes fouled by paper mill effluent.
- UTDR proved to be very useful method for the investigation of fouling mechanisms. The compressibility of the cake layer contributed to the flux decline during fouling. UTDR proved that increasing the flow rate during actual operation could not reduce fouling in MF carried out with paper mill effluent because a denser cake layer formed on the membrane surface at a high flow rate than it did at a low flow rate. An increase in flux could be seen when fouling operation was stopped and restarted. This is because interrupting the fouling experiment resulted in flow destabilisation and relaxation of the fouling layer. UTDR showed an increase in the thickness of the fouling layer and a decrease in the density of the cake layer.

Ultrafiltration (UF)

- In ultrafiltration (UF), an asymmetric polysulphone (PSU) membrane and its compaction could be detected by UTDR. Results showed a good correspondence between the UTDR signal response and the development of the fouling layer on the membrane surface in UF.
- The dynamic processes of deposition and growth of a fouling layer was confirmed by *in-situ* ultrasonic response signals. The sensitivity of ultrasonic responses revealed the coverage of a membrane surface with a fouling layer. UTDR results corroborated the flux measurements and SEM analyses.
- UTDR could also distinguish and recognise various response signals from ultrasonic measurements in a tubular cell. Protein fouling was successfully detected by UTDR in a tubular PESU UF membrane. Changes in the amplitude and time domain of the observed signals provided useful quantitative information about adsorption, deposition and gelation of BSA on the membrane. The thickness of the BSA gel layer was obtained. UTDR can provide an approach to understand protein-fouling behavior related to flux decline.

Reverse Osmosis (RO)

- UTDR was successfully used for the RO of saline water, calcium sulphate streams (such as in mining), real pulp and paper effluent and, more recently, biological systems, and for flat sheets and tubular membranes.
- The application of the UTDR technique is feasible for the non-destructive, in-situ visualisation of membrane fouling and cleaning in reverse osmosis (RO) modules. Results showed that the UTDR technique could effectively detect fouling-layer initiation, its growth on the membrane and its removal, in real-time. The acoustic signal response corresponded well with the membrane's flux-decline behaviour. The UTDR technique was capable of detecting subtle changes on a membrane surface and distinguishing between dead-end and cross-flow modes of fouling growth. This could assist in understanding the mechanism of membrane fouling.

A secondary fouling echo was obtained (the primary echo comes from the membrane). The second echo amplitude should be seen as an indication on the state of the fouling layer. The denser the fouling layer, the better the reflection, and thus the larger amplitude that is seen. The fact that the UTDR technique can monitor the removal of a fouling layer and membrane cleaning makes it a very suitable tool for studying the effectiveness of various cleaning techniques.

- The ultrasonic unit that evolved comprises a suitably programmed microprocessor and display panel, and can be used to compare reference and test signals to produce a differential signal (a fouling layer echo). A differential signal indicates the state and progress of a fouling layer on a membrane surface during actual operations. Both amplitude and arrival time of differential signals as a function of operation time provide useful quantitative information, i.e. changes in thickness and density of a fouling layer on the fouling processes. The resolution exceeds the theoretical limit by a considerable margin when using the differential signals.
- A predictive modelling program - ultrasonic reflection modelling (URM) - was developed to understand the processes of ultrasonic testing related to the deposition of fouling layers on membrane surfaces. The mathematical modelling could substantiate changes in the density and thickness of the cake layer. Deposit resistance is not only related to the layer thickness but also the cake density (compressibility). The predicted results of fouling layer deposition were in good agreement with the actual measurements obtained in MF and UF.
- Sufficient data were created to be able to propose and patent a modified plugging index (PI) meter. (PI meters are the basis of knowing the fouling potential of any feed water, and of studying the efficiency of any pretreatment stream. Therefore a PI meter that can visualise, in addition to its normal functions, has an as yet unexplored market need. Coupled to the fact that the PI meter can be used as a slave unit attached to any bank of membranes, and using equivalent membranes in the slave unit, direct monitoring of the bank is a capability. Further, since it gives an electronic signal it can be used for control of the process and defouling.)

Recommendations

The research has clearly shown that UTDR can indeed be successfully used to monitor membrane fouling in MF, UF and RO, with different membranes, module configurations and foulants.

An unsatisfied market need for a modified plugging index meter, based on ultrasonics, has been determined.

Hence, the following recommendations for further investigations in this area are made:

- The production of a modified plugging index meter based on technology developed in this project should be pursued and a world-patent registered. It should be created at reasonable cost.

- This technology should be applied 'real membrane situations', for example, to improve the production of drinking water that is high in colourants (e.g. natural organic matter).
- Investigations into the use of infrasound for cleaning membranes and for the prevention of fouling of membranes is further strongly recommended.
- The use of ultrasonics as an in-situ, non-invasive monitoring technique, to further investigate a new area of minimising fouling in membranes, i.e. the use of infrasound (low-frequency sound) as opposed to ultrasound (high-frequency sound), warrants consideration.
- The most urgent of these recommendations is what we need to do in the short term, namely the necessary purchase of the latest ultrasonics hardware and then to determine what further improvements can be obtained in terms of resolution, data transforms, speed of data recovery, etc. Specifically, improvements with using LabVIEW technology should be determined.

ACKNOWLEDGEMENTS

The research in this report emanated from a project funded by the Water Research Commission. It is entitled:

REAL-TIME OBSERVATION OF FOULING IN MEMBRANE FILTRATION BY NON-INVASIVE ULTRASONIC TECHNIQUES

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The financing of the project by the Water Research Commission and the contributions of the members of the Steering Committee are gratefully acknowledged.

This project was only possible with the co-operation of many individuals and institutions. The authors therefore wish to record their sincere thanks to the following:

- Dr EP Jacobs for his most generous assistance and useful advice throughout.
- Mr LJ Koen for his initial work on ultrasonic measurements.
- Professor G Chai, Central Research Institute of China Chemical Science and Technology, for her assistance and advice, especially during her visit to Stellenbosch (Jan – April 2002).
- Mrs Miranda Waldron, Department of Physics, University of Cape Town, for her patient recording of many SEM images.
- All the staff at the Institute for Polymer Science. A special word of thanks goes to Mrs Aneli Fourie, Mrs Erinda Cooper, Mr Johan Bonthuys and Mr Deon J Koen for their assistance.

LIST OF ABBREVIATIONS

BSA	Bovine serum albumin
CP	Concentration polarization
C_r	Coefficient/amplitude of reflected wave
C_t	Coefficient/amplitude of transmitted wave
E_c	Cleaning efficiency (%)
ED	Electrodialysis
MF	Microfiltration
NDT	Non-destructive technique
NF	Nanofiltration
Nylon	Dupont trade name for polyamide 6,6
J	Permeate flux
I	Intensity of sound wave (W/m^2)
ΔP	Transmembrane pressure difference (kPa)
P_0	Amplitude of pulse (N/m^2)
PA	Polyamide
PESU	Polyethersulfone
P_i	The sound pressure of the incident wave (N/m^2)
P_r	The sound pressure of the reflected wave (N/m^2)
P_t	The sound pressure of the transmitted wave (N/m^2)
PSU	Polysulfone
P_t	The sound pressure of the transmitted wave (N/m^2)

R	Distance between the sources (transducer) (m)
R_c	The resistance of residual fouling layer (m^{-1})
R_f	Fouling resistance (m^{-1})
R_g	Gel resistance (m^{-1})
R_m	Membrane resistance (m^{-1})
R_r	Reversible resistance (m^{-1})
R_t	Total resistance (m^{-1})
RF	Radio frequency
r_0	Unit of the vector, directed to the radius
RO	Reverse osmosis
dt	Difference in arrival times (s)
dS	Thickness of material (m)
SEM	Scanning electron microscope/microscopy
U	Particle velocity in sound wave (m/s)
UF	Ultrafiltration
URM	Ultrasonic reflection modelling
UTDR	Ultrasonic time-domain reflectometry
V	Velocity of sound wave in a medium (m/s)
W_1	The acoustic impedance of material 1 (kg/m^2s)
W_2	The acoustic impedance of material 2 (kg/m^2s)

Greek letters

a_p	Coefficient of the attenuation of the source (transducer)
ρ	Density of the material (kg/m^3)
t_1	Time of wave's arriving (s)
μ	Viscosity of solution (Pa.s)
ω	Frequency (Hz)
ω_0	$2 \pi/T$
ω_{op}	Frequency of the self-oscillation of source (transducer) (radian per second)

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1. INTRODUCTION

1.1 BACKGROUND

Membrane fouling is the single most critical problem limiting the wider application of separation by membrane filtration. The flux decline that accompanies fouling affects the operational efficiency and economics of many membrane separation processes such as microfiltration (MF), ultrafiltration (UF), nanofiltration (NF), electrodialysis (ED), and reverse osmosis (RO). In efforts to develop methods by which to reduce or prevent fouling, much research has been conducted. The development of a non-invasive and non-destructive technique (NDT) to monitor the presence and growth of a fouling layer in real time, under realistic operating conditions, is potentially of great importance - to optimize plant operation and minimize operating costs. The development and utilisation of a suitable NDT technique for the on-line monitoring of fouling in industrial and laboratory applications could go a long way to enable the fouling, the effectiveness of fouling remediation and cleaning strategies to be quantified.

The cleaning of fouled membranes by ultrasound is a relatively new approach. There are several patents and publications that deal with the application of ultrasound to water treatment processes [Harvey, 1965; Shimichi, 1995; Kost 1988; Lenard, 1980; Li et al., 1995]. An initial literature overview has revealed that ultrasound has an enhancing effect on the diffusion of solutes (electrolytes) through polymeric membranes [Brand, 1997; Chai et al., 1999; Greenberg et al., 1999]. There is however relatively little known about the effect of on-line ultrasound treatment on the cleaning of polymeric membranes fouled by inorganic mater such as calcium sulphate and other large molecules, without interrupting the filtration operation. Furthermore, not much is known about the influence of ultrasonic frequency, intensity and time on the permeate flux and rejection of membranes, and their life span.

In WRC project no 930 (Title: "Water clarification and desalination by electronically enhanced membrane defouling") an ultrasonic time-domain reflectometry (UTDR) technique was considered as a potential new, non-invasive technique (and NDT) to investigate fouling layer formation and growth on membrane surfaces in MF, NF, UF and RO. It was found that the ultrasonic testing technique indeed provided a method for the early detection and monitoring of fouling in progress. Results of this preliminary investigation formed the basis for this, a second, project (WRC No 1166) on the visualisation of the effects of electro-magnetic turbulence defouling techniques in membrane units, the results of which are reported on here.

1.2 MOTIVATION

In the NAMS, Membrane Quarterly, 14/1, January 1999, Dr Irwing Murdoch (Editor of Desalination and Water Reuse) states: "challenge the fundamental research community to revisit problems that limit the RO field, such as insufficient membrane rejection, fouling an durability. Bill Koros, world renowned expert in the field of membrane separation agrees: " Fresh looks at difficult problems can be very useful - as long as one avoids 'reinventing the wheel' "

In order to strengthen the local SA membrane industry we need to provide the industry with tools to understand plant operation and install improvement measures. Following on from this, we aims to provide a visualisation process so that plant operation can be optimised and capital cost minimised. For this it is important to understand, by measurement, the fouling of membranes by any specific waters to be treated.

1.3 OBJECTIVES

The overall objective of this project was the development and application of visualisation tools to study fouling and defouling of separation membranes and to apply the visualisation acoustic technique to optimizing cleaning techniques in UF systems developed at the Institute for Polymer Science, University of Stellenbosch.

The research product would be a visualisation method with which to study the fouling and defouling of membranes during operation, and an electronic anti-fouling technique that could be applied to UF and NF membranes (flat-sheet or tubular form).

Specific objectives were the following:

- 1 In-situ measurement of particle deposition and its removal in MF
- 2 Monitoring of ultrasonic cleaning of Nylon MF membranes
- 3 Cake layer deposition, growth, compressibility and its removal during MF
- 4 Direct monitoring of membrane fouling and cleaning during UF
- 5 Measurement of protein fouling in tubular UF membranes
- 6 Visualisation and monitoring of inorganic fouling and cleaning of RO membranes
- 7 Development of commercial products: A plugging index meter was to be made outside the program, in collaboration with a German group.

1.4 EXPERIMENTAL APPROACH

Rectangular flat-sheet cells and tubular membrane cells were designed and used in this study. Systems for UTDR measurements and ultrasonic cleaning were set up and used. Various liquid separation systems such as MF, UF and RO were set up. Different types of foulants were used: paper mill effluent, calcium carbonate, calcium sulphate and bovine serum albumin (BSA). Various cleaning techniques such as forward flushing, ultrasonic cleaning and ultrasound with flushing were used and evaluated by UTDR in this study.

Ultrasonic reflection modeling was also developed, in an effort to understand the signal reflection of a fouling layer on the membrane surface.

1.5 LAYOUT OF THIS REPORT

This report will be presented as follows:

Chapter 1	Introduction, including background, motivation, and objectives
Chapter 2	Historical and theoretical background, to include mention of membrane processes, concentration polarisation and fouling, and ultrasonic techniques
Chapter 3	Experimental
Chapter 4	Ultrasonic reflection modelling
Chapter 5	In-situ measurement of particle deposition and its removal in MF
Chapter 6	Monitoring of ultrasonic cleaning of nylon MF membranes
Chapter 7	Cake-layer deposition, its growth and compressibility, and its removal during MF
Chapter 8	Direct monitoring of membrane fouling and cleaning during UF
Chapter 9	Measurement of protein fouling in tubular UF
Chapter 10	UTDR as a non-destructive instrumental visualization technique for the monitoring of fouling and cleaning of RO membranes
Chapter 11	Plugging index meter - patent
Chapter 12	Conclusions and recommendations for future research

2. HISTORICAL AND THEORETICAL BACKGROUND

2.1 SCOPE OF THIS CHAPTER

In the past ten years the literature has shown that ultrasonic testing, as a non-destructive, real-time visualization technique, may be useful to monitor fouling phenomena in actual operations in membrane processes. [Kools et al, 1998; Reinsch et al, 2000; Petersen et al, 1998; Mairal et al, 1999; Mairal et al, 2000.] Such an investigation was launched in WRC project 1166.

There are four major areas relevant to the research that was to be carried out during this project, namely:

- pressure-driven membrane processes,
- concentration polarization,
- membrane fouling, and
- ultrasonic techniques.

Brief mention of the above will be made in the sections that follow:

Section 2.2: The main pressure-driven membrane processes: microfiltration (MF), ultrafiltration (UF), nanofiltration (NF) and reverse osmosis (RO), and their characteristics;

Section 2.3: Concentration polarization and membrane fouling, and consideration of the various methods and techniques available for the use of the prediction and measurement of fouling, and strategies for fouling control;

Section 2.4: The ultrasonic techniques, including a description of the working of ultrasonics and various applications of ultrasonic techniques.

A more detailed description of all the above has been given elsewhere by Li [Li, 2002].

2.2 MEMBRANE PROCESSES

2.2.1 Microfiltration

Microfiltration (MF) is the membrane process that most closely resembles conventional coarse filtration. The pore sizes of MF membranes range from 10 to 0.05 μm . MF typically operates at low trans-membrane pressures to minimise build-up of the suspended solids at the membrane surface. Pressures of 0.03-0.3 MPa and cross-flow velocities of up to 3-6 m/s in tubular modules are common. MF can separate 0.1 to 10 μm -sized particles from a liquid or gaseous feed stream. As a consequence of the large pore size of MF membranes, MF is used primarily for particle and microbial removal. MF separates macro-materials and suspended solids like starch, bacteria, moulds, yeast and emulsified oils. It is finding increased applications as a pre-treatment to other membrane processes, in bioreactors for sludge concentration, recovery of backwash waters and for the replacement of conventional clarification and filtration technologies [Porter, 1986; Eykamp, 1995; Cheryan, 1998].

2.2.2 Ultrafiltration

Ultrafiltration (UF) is a membrane process whose nature lies between that of NF and MF. The pore sizes of UF membranes range from 0.05 μm to 1 nm. UF separates dissolved solutes of 0.005 to 0.1 microns. This corresponds to a molecular weight cut-off of about 1,000 to 500,000 [Cheryan, 1998]. Depending on the molecular weight cut-off selected, the membrane will concentrate high molecular weight species while allowing dissolved salts and lower molecular weight materials to pass through the membrane. UF membranes are used in numerous industries, for the concentration and clarification of large process streams such as in the food and dairy industry, pharmaceutical industry, textile industry, metallurgy, paper industry and leather industry [Jönsson and Trägårdh, 1990; Cheryan, 1998;]. It is also widely used as a pre-treatment process for downstream membrane systems.

2.2.3 Nanofiltration

Nanofiltration (NF) is similar to RO and is applied in the area between the separation capabilities of RO and UF. NF is a relatively new process that uses charged membranes with pores that are larger than RO membranes, but too small to allow permeation of some organic compounds such as sugars [Wadley et al, 1995]. The NF membrane displays excellent rejection of divalent ions while allowing the majority of mono-valent ions to pass. Organic molecules in the 200-300 molecular weight range are also highly rejected. NF systems typically operate at lower pressures than required for RO (e.g. 1.0 - 1.5 MPa), but yield higher flow-rates of water, albeit of a different quality to RO permeate.

The unique separation capability of NF provides the opportunity to selectively concentrate either valuable or undesirable substance from a process stream with great effectiveness, consistency, reliability and economy. In most water sources there will be single-charged ions, such as sodium ions (Na^+) and chloride ions (Cl^-), and double charged ions, such as calcium ions (Ca^{2+}) and sulphate ions (SO_4^{2-}). The single-charged cations do not generally participate in scale formation, so they may be considered as soft ions. The double-charged cations such as calcium and magnesium, in conjunction with certain anions, can form hard scale in water treatment equipment and piping and are called hard ions. Depending upon the membrane, water chemistry, and operating conditions, NF membranes can remove more than 90% of feed water's hardness ions. NF membranes also remove large colour molecules and many of the trihalomethane (THM) precursors. Nanofiltration can treat the same amount of water, or more, than RO at half the pressure. Since NF membranes can remove the double-charged scaling ions like calcium and magnesium ions, another term for NF is membrane softening. The largest users of NF technology are municipal drinking water plants.

2.2.4 Reverse Osmosis

Reverse osmosis (RO) is the most complex technique in membrane separation. RO membranes concentrate low molecular weight organic materials and salts while allowing water and solvents to pass. High pressures of about 3.5-10 MPa are required in order to overcome the high osmotic pressures across the membrane. This permits water to flow from the concentrated feed stream to the dilute permeates - a direction that is just the reverse of what occurs naturally during osmosis. The pore sizes of RO membranes are < 2 nm. Most RO membranes are prepared from polymeric materials such as cellulose triacetate, aromatic polyamides, poly (ether urea) [Mulder, 1996]. RO has been the most widely used technology for desalinating seawater and reclaiming brackish well water [Porter, 1986; Eykamp, 1995; Mulder, 1996]. A RO membrane will typically reject all of the organic molecules over 150 molecular weight and a percentage of those between 25 and 150 MW.

2.3 CONCENTRATION POLARIZATION AND FOULING

In order to achieve a particular separation via a membrane process, the first step is to develop a suitable membrane. However, during an actual separation, the membrane performance can vary greatly over time; often typical flux-time behaviour is observed: the flux through the membrane decreases over time. Especially in MF and UF, the flux decline is very severe; the process flux is often less than 5% that of pure water. This is mainly due to concentration polarization (CP) and fouling, although membrane compaction and physical transformation of the membrane structure also occur during operation [Anderson et al., 1981; Fane and Fell, 1987; Eisold et al., 1990; Brinkert et al., 1993].

2.3.1 Concentration Polarization

In membrane-based liquid separation processes, one or more components in the feed solution are preferentially retained on the membrane surface. Generally, the convective transport of these components to the surface is greater than the diffusive and convective transport away from the membrane [Mulder, 1999]. CP is caused by the accumulation of retained solutes or particles on the membrane or in the boundary layer adjacent to the membrane surface. This concentration is highest at the membrane surface, and decreases exponentially toward the solution. In the case of higher molecular weight (or inorganic) substances, the solubility limit is often reached at the membrane surface. The precipitated layer then acts as a secondary membrane, referred to as the 'gel layer'. Formation of the gel layer decreases the flux considerably. The gel layer may also have a higher retention than the membrane itself, which increases the actual retention of the membrane as the filtration process proceeds.

The effects of CP include: a decline in permeate flux as a result of a reduced driving force for separation, a decline in product quality due to the increased diffusion of undesirable components through the membrane, and the increased risk of deposition of these components on the membrane surface. CP is considered to be reversible and can be reduced by diluting the process solution, stirring, tangential flow of the solution across the membrane surface or by means of pulsation, ultrasound and an electric or magnetic fields [Gupta et al, 1992; Howell et al., 1993; Lin and Nativ, 1988; Wakeman and Tarleton, 1991].

2.3.2 Fouling

Fouling may be defined as the irreversible deposition of retained particles, colloids, macromolecules, salts, etc., at the membrane surface or inside the membrane at the pore wall, which causes a continuous flux decline. Membrane fouling is complicated in that it is considered as a group of physical, chemical, and biological effects leading to irreversible loss of membrane permeability. Attempts to analyse the fouling phenomenon have shown that the main factors that cause it are: adsorption of feed components, clogging of pores, deposition of solids on the membrane surface accompanied by crystallization and compaction of the membrane structure, chemical interaction between membrane material and components of the feed solution, gel coacervation (coacervation: the separation into two liquid phases in colloidal systems) [IUPAC Compendium of Chemical Technology (1997)], and bacterial growth [Potts et al, 1981; Fane and Fell 1987; Belfort et al, 1994; Mulder, 1996].

Membrane fouling is universally accepted as the most critical problem in several membrane processes including microfiltration (MF), ultrafiltration (UF), nanofiltration (NF), reverse osmosis (RO), and electrodialysis (ED) [Belfort, 1984; Rautenbach and Albrecht, 1989; Mulder, 1996;

Davis, 1992]. An extensive body of literature exists on the various aspects of membrane fouling due to the importance of this problem. Some excellent reviews on various aspects of membrane fouling are given by Potts et al. [1981], Belfort and Altena [1983], Fane and Fell [1987], Belfort [1989], Nilsson [1990], Marshall et al. [1993], Belfort et al. [1994], and Mulder [1998].

2.3.3 Membrane fouling studies

2.3.3.1 Experimental Investigations

Membrane fouling has been observed in nearly all of liquid separation applications [Strathmann, 1981; Lonsdale, 1982]. The experimental investigations of membrane fouling can be classified into three broad categories – inorganic fouling, colloidal fouling, and fouling due to dissolved organics and biological constituents in the feed.

Inorganic fouling occurs in separations where the solubility of a dissolved salt is exceeded. It is typically encountered in RO and ED but has also been observed in MF and UF. Colloidal fouling is a very common phenomenon in almost all membrane processes, and occurs when colloidal organic constituents in the feed are deposited on the membrane surface due to hydrodynamic and physical-chemical characteristics of the separation system. Biological and organic fouling is observed in separations where the feed solution exhibits substantial biological growth and dissolved organic content.

2.3.3.2 Theoretical Investigations

Membrane fouling is widely acknowledged to be the most important economic determinant of most membrane processes. A number of mathematical models of CP and fouling have been developed to understand this complicated phenomenon. The following mathematical models are available:

1. Empirical models [Sheppard et al., 1972]
2. Gel polarisation models [Michaels, 1968; Belfort and Altena, 1983; Kimura and Nakao, 1975]
3. Osmotic pressure models [Vilker et al., 1981; Jonsson, 1984; Wijmans et al., 1985]
4. Particle trajectory models [Hung and Tien, 1976; Bacchin et al., 1995]
5. Differential rate models [Carter and Hoyland, 1976]

6. Resistance models [Belfort and Marx, 1979; Schippers et al., 1981; Fane and Fell, 1987]
7. Surface reaction models [Gilon and Hasson, 1987; Borden et al., 1987]
8. Compressible cake filtration models [Shirato et al., 1969; Tiller, 1975; Murase et al., 1995; Tiller and Kwon, 1998; Tiller and Li, 2001].

Gel polarization model

The gel polarisation model [Michaels, 1968] was proposed to explain the effects of concentration polarisation in UF. The solute concentration at the membrane surface reaches a very high value and a maximum concentration, the gel concentration (c_g), may be reached for a number of macromolecular solutes. The two phenomena, concentration polarisation and gel formation, are shown in Fig. 2.1.

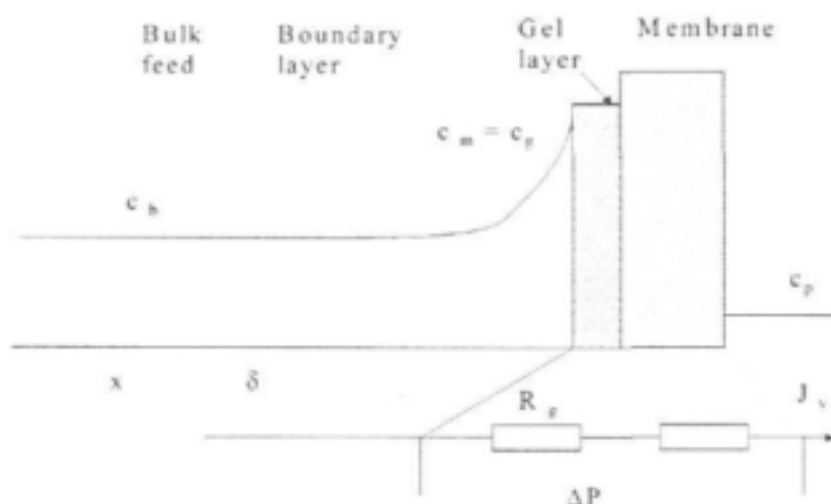


Figure 2.1: Concentration polarisation and gel layer formation [Mulder, 1996].

Osmotic pressure model

The limiting flux in the osmotic pressure model is regarded as being due to the increased osmotic counter-pressure produced by the high concentration of the rejected solute near the membrane surface [Denisov, 1994].

Resistance model

By analogy to the standard Darcy's-law filtration model, flux can be considered to be controlled by several resistances. The resistance models constitute one of the most common approaches for analyzing flux-decline behavior via visualization of the system as resistances-in-series [Belfort and Marx, 1979; Schippers et al., 1981; Fane and Fell, 1987]. These phenomenological models allow for the evaluation of the resistance due to individual components and factors such as membrane compaction, internal and external fouling, osmotic effects, and the back-diffusion of the solute using the experimental data.

2.3.4 PREDICTION AND MEASUREMENT OF FOULING

The phenomenon of fouling is very complex and difficult to describe theoretically. A number of studies have been carried out to understand fouling before the start of the separation process, during the process, or after the process. The ability to accurately measure fouling is essential for the development of fouling control strategies, which is the ultimate goal of membrane fouling research.

2.3.4.1 Prediction of Fouling

For the design of RO facilities, it would be most desirable to have an analytical procedure available to quantitatively predict how rapidly or severely a given feed will foul a membrane. Many parameters have been used to describe fouling, for example: the plugging index (PI), the fouling index (FI) [Lipp et al., 1990] or silt-density index (SDI) [Potts et al., 1981], the modified fouling index or the membrane filtration index (MFI) [Schippers and Verdouw, et al., 1980] and the Langelier saturation index [Du Pont, 1977].

The silt density index [Potts et al., 1981] is, to date, the only widely accepted test for fouling prediction in the RO industry. Shippers and Verdouw [1980] applied a filtration theory to the SDI test and derived a formula for a modified fouling index (MFI). With the SDI no linear relationship exists between the index and the colloid or suspended matter concentration, while the MFI is directly proportional to colloidal concentration in the feed, as confirmed experimentally [Schippers et al., 1981]. Thus, the MFI can be used to predict the fouling tendency of one feed solution relative to another. Fouling is, however, too complex to be described by a single parameter.

2.3.4.2 Membrane Autopsy

The term autopsy is used to describe a series of observations made of and scientific tests carried out on, a used membrane element. Chemical, physical and microbiological analyses determine the type of foulant present and its effect on membrane performance. Other techniques used to investigate membrane fouling are: scanning electron microscopy (SEM), X-ray fluorescence (XRF), X-ray diffractometry (XRD), inductively coupled plasma (ICP) spectrometry, ion chromatography (IC), energy-dispersive X-ray spectroscopy (EDS), atomic absorption spectroscopy (AAS), prompt ion X-ray excitation (PIXE) and biocide sensitivity tests [Butt et al, 1995; Dudley and Darton, 1996; van Hoof et al., 2002].

Van Hoof et al. [2002] investigated 150 eight-inch (200 mm) polyamide elements, received within the last two years from around the world, by various autopsy methods. Results from so many systems have been helpful in developing improved anti-scalants and anti-foulants, more effective cleaners and improved cleaning programmes. A better understanding of membrane fouling has also helped many equipment manufactures predict problem areas and take remedial actions at the system design stage. Although these analytical methods can supply some information on the fouling mechanism, they have provided little information regarding the actual and dynamic build-up of foulant on a membrane surface. Furthermore, an autopsy is a destructive procedure and the membrane cannot be returned to service once the autopsy is completed.

2.3.4.3 *In situ* Measurements

Numerous indirect and direct real-time measurements have been conducted to study membrane fouling. Traditionally, real-time fouling investigations have involved the analysis of flux-decline data for inference of fouling [Mashiko et al., 1983; Bhattacharjee and Bhattacharya, 1992; Herrero et al., 1997]. Other methods of fouling analysis include the monitoring of permeate concentration change, increase in the pressure drop along the membrane, and sudden change in retentate concentration [Fárková, 1991; Karode and Kumar, 2001]. These indirect methods however provide little information regarding direct observation of the fouling deposition process.

Non-invasive techniques have been developed to overcome the limitations of the above-mentioned methods in providing direct information about CP and fouling. These are described elsewhere by Li [Li, 2002].

2.3.5 FOULING: PREVENTION AND REDUCTION

The ultimate objective of the numerous fouling studies is the prevention and reduction of fouling. The methods used to date to mitigate fouling include:

- pre-treatment of the feed solution,
- modification of membrane properties,
- optimisation of the module and process conditions, including flow manipulation and application of external fields (including an ultrasonic field ,and
- frequent cleaning of the fouled membranes by chemical, biological and physical (electric, magnetic, ultrasonic) methods [Mulder, 1991].

These methods have been discussed in great detail by Mathiasson and Sivik [1980], Potts et al. [1981], Belfort and Altena [1983], Fane and Fell [1987], Howell et al. [1993]; Belfort et al. [1994]; Cheryan [1998]; and Wakeman and Williams [2002]. A review and some illustrative examples have also been given by Li [Li, 2002].

2.3.5.1 Ultrasonic fields

Several articles [Hurvey, 1965; Wakeman and Tarleton, 1991; Shimichi, 1995; Li et al. 1995; Band, 1997; Kobayashi et al. 1999] deal with the application of ultrasound in water treatment. Hurvey [1965] used an acoustic liquid whistle or transducer to produce cavitation on membranes. It is believed that the formation of air bubbles during cavitation suppresses fouling. When a cavitating air bubble is oscillating near a solid surface, it generates micro-jets of very high velocities that can effectively decrease the boundary layer thickness. In effect, mass transfer is enhanced.

Lenart and Auslander [1980] studied the effect of ultrasound on the diffusion of some electrolytes – sodium, potassium and calcium chlorides – through cellophane membranes. The intensity of the ultrasound field in their experiment varied from 1.2 to 6 Wcm⁻² at 1 MHz frequency. The results obtained demonstrated intensification of the diffusion process by the ultrasound. The authors considered the main cause of acceleration of diffusion with ultrasound to be the appearance of acoustic microcurrents on the liquid. Radiation pressure, gravitation, cavitation and acoustic pressure also play a role.

Li et al. [1995] described the results of investigations of the influence of ultrasound on the diffusion of electrolytes through a cellophane membrane. It was found that the diffusion velocity of electrolyte through the membrane with ultrasound irradiation is higher than that without ultrasonic and the amount of solvent permeated increases with acoustic pressure. Band [1997] studied the influence of specially mounted ultrasound signals on water desalination through special polymeric ion-exchange hollow fibres. Both Na^+ and H^+ ion exchange were enhanced under ultrasound.

Wakeman and Tarleton [1987] reported that the filtrate flux could be markedly increased by the simultaneous addition of electric and ultrasound fields. Kobayashi et al. [1999] used on-line ultrasound to enhance permeation in UF. Ultrasound effects at frequencies of 28, 45 and 100 kHz and at a power intensity in the range of 2.5-3.3 W/cm^2 on a permeate flux of dextran solution through polyacrylonitrile UF membranes were examined. Although ultrasound with a low frequency (28 kHz) and a high intensity (3.3 W/cm^2) was beneficial to permeation through the membrane, ultrasonic waves have to be used with care, as the polymeric material itself is sensitive to the ultrasonic waves at the chosen frequency and intensity [Masselin et al., 2001].

2.3.5.2 Membrane Cleaning

Physical cleaning

The physical removal of a fouling layer utilizes hydraulic cleaning and mechanical cleaning. Hydraulic cleaning methods include backflushing, backshock treatment, alternate pressurising and depressurising and by reversing the flow direction at a given frequency [Potts et al., 1981; Strathmann, 1981; Leger and Hawker, 1987; Redkar and Davis, 1995; Pontie et al., 1997; Kennedy et al., 1998]. Mechanical cleaning includes sponge-ball cleaning in tubular membranes [Burch, 2001], electrically-induced vibrations [Bowen et al., 1989], and ultrasonically-induced vibrations [Wakeman and Tarleton, 1991; Ebrahim, 1994; Chai et al., 1999; Czekaj et al., 2000].

Kost and Langer's patent [1988] proposes a method for enhancing or controlling the permeability of small and large molecular weight molecules in a membrane system which is exposed to ultrasound of selected intensity of 0.05 to 30 W/cm^2 and frequency between 10 kHz and 20 MHz for most polymeric membranes and an intensity of 0.05-3 W/cm^2 and a frequency of 1-3 MHz for biological membranes.

Leger and Hawker [1987] investigated turbulent flushing, flow reversal, sponge-ball cleaning, and alkali cleaning for the removal of complex fouling layers containing organics, colloid clays, quartz, and iron and zinc compounds. Their results suggested that a combination of the tested techniques was necessary to completely clean the RO membranes.

Ebrahim [1994] presented a comprehensive review of various cleaning strategies employed in RO desalination and wastewater applications. He cited ultrasonic cavitation as an effective physical cleaning method for RO and UF membranes.

Chai et al [1999] used an ultrasonic technique to clean polymeric UF and MF membranes fouled by peptone. Ultrasound generated by a sonicator bath was employed to examine the effect of ultrasound on the cleaning of fouled membranes in a cross-flow cell under various filtration-operating conditions. It is suggested that the cleaning of fouled membranes by ultrasound in association with water cleaning is an effective method.

Czekaj et al. [2000] used an infrasonic pulsing technique to remove foulant cake and improve flux through MF membranes. The technique consists of applying pressure pulses with frequencies on the order of 1-10 Hz on the permeate side. It is proposed that the infrasonic pulses cause rapid vibrations of the membrane, which lift a portion of the foulant cake off its surface.

Note: ultrasound with low frequencies (kHz) and high power outputs was used as a cleaning method [Mason and Lorimer, 1989]. Frequencies in the order of 20 - 100 kHz showed the best cleaning abilities. In contrast to this, the visualisation technique needs good spatial resolution, and thus a shorter wavelength is required. Ultrasound with higher frequencies (> 1 MHz) is therefore needed. At this high frequency it has no cleaning ability (ultrasound of frequency 5 - 7.5 MHz is used for visualisation in the human body) and is therefore suitable to study membrane fouling.

2.3.6 OVERVIEW OF THE FOULING LITERATURE

Numerous fouling studies have been carried out worldwide to better understand the complexity of fouling. The efforts to develop means of fouling mitigation have been only partially successful. Fouling remains problematic in most membrane processes because of an incomplete understanding of the dynamics of fouling and its relationship to membrane performance decline.

Although membrane autopsy or destructive analytical methods can supply some information on the fouling mechanism [Butt et al, 1995; Dudley and Darton, 1996; van Hoof et al., 2002], they have provided little information regarding the actual and dynamic build-up of foulant on a membrane surface. Furthermore, an autopsy is a destructive procedure and the membrane cannot be returned to service once it is completed.

A number of non-invasive observations using microelectrode measurements, laser interferometry and light reflectometry have been applied to the measurement of CP [Hendricks

and Williams, 1971; Mahlab et al., 1978; Ethier and Lin, 1992]. Although these measurements were limited by the spatial resolution of the various techniques very close to the membrane surface, they have provided significant insights into CP development in membrane systems. Over the last ten years, other non-invasive techniques such as radioisotope, micro-array of semiconductor photosets, optical methods and photography have been developed to study CP and fouling on a membrane surface in real time [McDonogh et al., 1990 and 1995; Mores and Davis, 2001; Lu et al., 2002; Macklay and Shereman, 1992; Wakeman, 1994 et al.]. Although these studies have provided valuable information on polarisation profiles and fouling layer, these measurements are limited.

In conclusion:

A non-invasive ultrasonic technique is a relatively inexpensive and versatile technique. It can successfully measure the membrane compaction, and growth of fouling layers. Additionally, it can be extended to visualize the fouling layer in real time under realistic operating conditions [Peterson et al. 1998; Mairal et al. 1999 and 2000; Koen, 2000].

In the light of what has been stated above, it is clear that membrane fouling continues to be a significant problem in membrane-based liquid separations. The development and utilisation of a suitable non-invasive technique for the on-line monitoring of fouling in industrial and laboratory applications would enable the effectiveness of fouling remediation and cleaning strategies to be more quantified. Ultrasonic testing appears to be most useful for the on-line monitoring of fouling under realistic operating conditions. The focus of the present study is hence the development and application of this ultrasonic technique to provide quantitative information regarding deposition and growth of a fouling layer on a membrane surface in real-time. The following sections discuss topics relevant to the further development of this technique.

2.4 ULTRASONIC TECHNIQUES

2.4.1 SOUND RANGES

Acoustics, the science of sound, describes the phenomenon of mechanical vibrations and their propagation in solid, liquid or gaseous materials. The sound is audible if it reaches the ear either through the air or through the body. The range of human hearing is from about 16 Hz to 16 kHz [hertz = cycles per second (c/s)] (with middle C at 261 Hz and the meadow grasshopper at around 7 kHz), as shown Figure 2.2 [Mason and Lorimer, 1989]. Sound below 10 Hz and above 16,000 to 20,000 Hz is inaudible to the human ear. The sound waves below 10 Hz are called subsonics [Krautkrämer et al., 1969]. The sound waves above 20,000 Hz (20 kHz) are referred to as ultrasound or ultrasonics. The upper limit of ultrasonic frequency is not defined, but is

usually taken to be 5 MHz for gases and 500 MHz for liquids and solids. Completely different demarcations apply in the case of their generating and detecting methods.

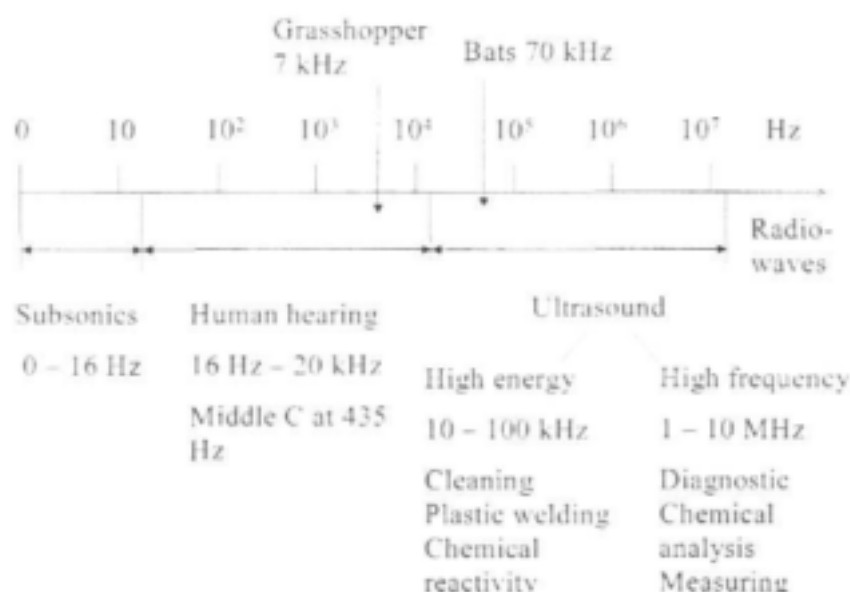


Figure 2.2: Sound frequencies [Mason and Lorimer, 1989].

The uses of ultrasound within a large frequency range may be divided broadly into two areas. The first area involves high frequency (low amplitude), which is concerned with the effect of the medium on the wave, is commonly referred to as low power or high frequency ultrasound. Typically, high frequency waves are used to measure the velocity and absorption coefficient of the wave in a medium in the 2 to 10 MHz range. The high frequency waves are used in medical scanning, chemical analysis, testing materials for flaws and the study of relaxation phenomena. The second area involves high energy (low frequency) waves between 20 and 100 kHz, known as power ultrasound, which is used for cleaning, plastic welding and, more recently, to effect chemical reactivity [Mason and Lorimer, 1989].

2.4.2 ULTRASONICS

The whole study of ultrasonics is primarily concerned with the generation, transmission and reception of energy in the form of longitudinal waves in matter. The following topics have been discussed by Li [Li, 2002]: Generation of Ultrasonic Waves, Propagation of Ultrasonic Waves, Types of Waves: Longitudinal waves, Shear waves, Surface or Rayleigh Waves, Reflection and Transmission.

2.4.2.1 Some applications of ultrasound

The ultrasonic technique has been used in a wide range of applications in industry, military and medicine. The following table [Mason and Lorimer, 1989] summarises this.

Table 2.1: Some industrial uses of ultrasound [Mason and Lorimer, 1989]

Field	Application
Biology, biochemistry	Homogenisation and cell disruption: Power ultrasound is used to rupture cell walls in order to release contents for further studies.
Engineering	Ultrasound has been used in drilling, grinding and cutting. It is particularly useful for processing hard, brittle materials, e.g. glass, ceramics. Other uses of power ultrasound are welding (both plastics and metals) and metal tube drawing. High-frequency (MHz) ultrasound is used in the non-destructive testing of materials and flaw detection.
Dentistry	For both the cleaning and drilling of teeth
Geography, geology	Pulse/echo techniques are used in the location of mineral and oil deposits and in depth gauges for seas and oceans. Echo ranging at sea has been used for many years (SONAR).
Industrial	Pigments and solids can be easily dispersed in paints, inks and resins. Engineering articles are often cleaned and degreased by immersion in ultrasonic baths.
Medicine	Ultrasound imaging (2-10 MHz) is used, particularly in obstetrics, for observing the foetus and for guiding subcutaneous surgical implements. In physiotherapy, lower frequencies (20-50 kHz) are used in the treatment of muscle strains.
Plastics and polymers	The welding of thermoplastics is effectively achieved using power ultrasound. The initiation of polymerisation and polymer degradation is also affected.

	Cure rates of resins and their composition can be measured with high-frequency ultrasound. Recently the mechanical rheological parameters of polymers can be determined [Alig, 1997 and 1998].
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2.4.2.2 Power ultrasound in membrane processes

Ultrasound with low frequencies (20 - 100 kHz) has high power outputs and shows the best cleaning abilities. Ultrasonic cleaning basically consists of immersing the article to be cleaned in a suitable solvent, which is then ultrasonically irradiated as follows. High-frequency electrical oscillations produced by an electronic generator are fed to a transducer, which converts them to mechanical vibrations. By suitably coupling the transducer to the cleaning solvent (or medium/water), the ultrasonic vibrations thus produced are propagated in the solvent (or water). Provided the energy and frequency of the ultrasonic waves are suitable, their propagation through the liquid initiates cavitation. Shock waves produced during cavitation impinge on any solid surfaces present in the liquid and very effectively scour the surface. The effect is similar to mechanical scrubbing but acts much more efficiently, rapidly penetrating to every hole and corner of an assembly immersed in the liquid.

The range of useful frequencies is from about 13 kHz to about 1 MHz and the type of transducer used varies with the frequency. The production of low-frequency (power) ultrasonic waves for cleaning purposes is accomplished by the use of various types of magneto-strictive and piezoelectric transducers made of quartz or barium titanate. The electronic generator is normally fairly simple in design supplying electrical oscillations at a fixed frequency and power output.

Power ultrasound has been widely used as a method for cleaning materials [Mason and Lorimer, 1989; Price, 1992]. Furthermore, this power ultrasound can enhance permeate flux and clean membranes in membrane processes [Hurvey, 1965; Lenart and Auslander 1980; Wakeman and Tarleton, 1991; Ebrahim, 1994; Shimichi, 1995; Chai et al., 1999].

3. EXPERIMENTAL

3.1 ABSTRACT

This chapter covers five sections.

Section 3.2 describes the various design considerations for the experimental development of the UTDR technique. These considerations provide the rationale for choosing an appropriate membrane separation system.

Section 3.3 presents the measurement principle of UTDR as it applies to the membrane separation system used in this work.

Section 3.5 describes the test cells that were used in this study. The test cells allow for simultaneous monitoring and separation were designed and employed in this study.

An ultrasonic measurement system including all the hardware i.e. pulser-receiver, oscilloscope, transducers etc. was designed and implemented to monitor membrane compaction and fouling. These components are briefly discussed in Section 3.6.

3.2 DESIGN CONSIDERATIONS

The overall objective of this study was to develop UTDR for the real-time measurement of fouling. In developing an experimental methodology for achieving this, important design considerations regarding the selection and development of a suitable membrane separation system and the ultrasonic measurement system had to be addressed.

The selection of an appropriate membrane separation system involves the choice of a separation process, a feed solution containing one or more potential foulants, a membrane, a separation module, and an associated flow system. The design of the ultrasonic measurement system involves selection of appropriate hardware including ultrasonic transducers, a pulser-receiver, and an oscilloscope, as well as the development of suitable software for the generation and post-processing of the ultrasonic signals.

The separation process should be industrially relevant and should be significantly affected by fouling during operation. The feed solution is also predicated by the commercial importance; in particular, the potential foulant chosen should occur frequently in industry. The membrane chosen to effect the separation must also be readily available and widely employed. The module should allow a safe and continuous operation under existing process conditions. The associated

flow system should ensure constant operating conditions and permit automated, and quantitative, monitoring and control of systemic parameters.

The ultrasonic measurement system should provide sensitive and continuous measurements of fouling. The ultrasonic transducers should have a frequency that allows for sufficiently sensitive detection of the fouling layer while providing a strong signal response. The pulser-receiver employed to generate and receive signals should have a wide range of signal modification capabilities including signal gain, attenuation and filtering. The oscilloscope should have a digitizing capability for real-time processing and display of the ultrasonic signals as well as appropriate time-domain and amplitude-domain resolution, and sensitivity for accurate measurement of fouling layer growth.

3.3 PRINCIPAL OF ULTRASONIC MEASUREMENT OF FOULING

Ultrasonic measurements are based upon the propagation of mechanical waves. The velocity of the waves is dictated by the medium through which they travel. When an ultrasonic wave encounters an interface between two media, energy will generally be partitioned such that a reflected wave occurs. The energy partition is controlled by the ultrasonic impedance contrast (W_1/W_2), where $W = \rho V$ (ρ is the mass density of the medium and V is the velocity of sound wave in the medium), as shown in Equation 3.1.

$$W = V_p \rho \quad (3.1)$$

where: V_p is the sound velocity (m/s); ρ is the material density (kg/m^3).

Figure 3.1 is a cross-sectional view of the typical flat-sheet cell that was used in our UTDR experiments. A membrane was placed between two polymethyl methacrylate (Perspex) plates. A transducer was externally mounted, in contact with the top plate. The feed solution flowed over the top of the membrane. The permeate was withdrawn from the bottom side. Now, suppose a fouling layer with thickness d_S is present on the membrane surface and the reflected echoes A, B and C are generated from the various interfaces within the cell. The corresponding time-domain response is shown in Figure 3.2. The top plate/feed solution interface is represented by echo A and the initial feed solution/membrane interface by echo B. Note: The transducer produces one pulse each time. The pulse is reflected when it encounters an interface, then continuously goes through the following mediums and interfaces.

Generally, once fouling is initiated on the membrane surface, the acoustic impedance difference and the topographical characteristics at the feed solution/membrane interface will change, resulting in a change in the amplitude of echo B, this is echo B'. Further, if the fouling layer is

thick enough to be measured by an ultrasonic signal, i.e., it falls within the spatial resolution capabilities of the system, a new echo C will be formed as a consequence of the new feed/fouling interface. If the difference in arrival times, dt , between echoes B and C is measured, the thickness of the fouling layer, dS , can be determined from the following equation [Birks, 1991]:

$$dS = 0.5 V \quad (3.2)$$

where V is the velocity of the ultrasonic wave in the medium.

Thus, the detection of the interface echoes allows fouling to be monitored in real-time. Two basic quantities are measured in ultrasonic testing: the time of flight, or the amount of time taken for the sound to travel through the sample, and the amplitude of the received signal.

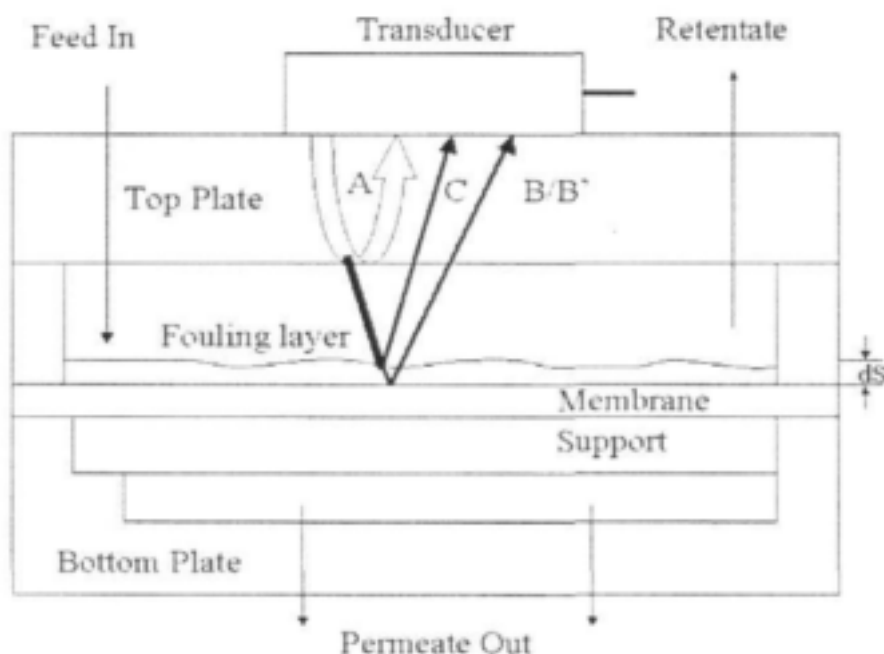


Figure 3.1: Schematic representation of the principle of UTDR measurement in a flat-sheet membrane module.

Note: The monitored incident and reflected acoustic waves (A, C, B/B') are perpendicular to the transducer and the membrane surface. The angle display is used for clarity of explanation.

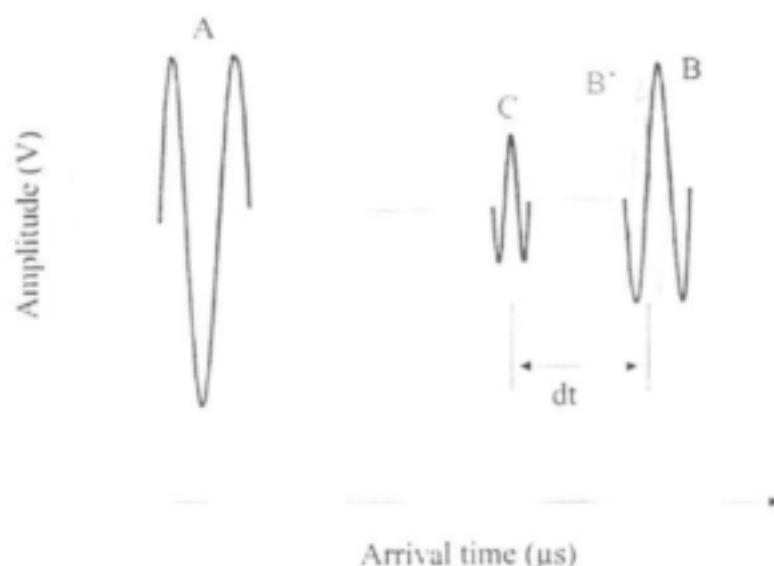


Figure 3.2: Corresponding time-domain response for the set-up in Figure 3.1.

Note: At the interface from a denser material (top plate: Perspex) to material of lesser density (water) an inversion of the reflected signal (A) occurs.

3.4 EXPERIMENTAL SYSTEM

Different experiments were carried out with different foulants, membranes and flow systems (see Table 3.1), details of which will be described in Chapters 5 - 10.

Table 3.1: Use of UTDR with various types of membranes, foulants and modules

Foulant	Membrane	Test cell	Separation system	Chapter
Kaolin	Nylon	Flat-sheet	MF	5
Paper effluent	Nylon	Flat-sheet	MF	7
Paper effluent from MF products	PSU	Flat-sheet	UF	8
Bovine Serum Albumin	PESU	Tubular	UF	9
Calcium carbonate	Polyamide	Flat-sheet	RO	10

Kaolin was used as it occurs frequently in the mining and paper industries, especially in the mining-wastewater treatment in South Africa. Fouling experiments were carried out with 0.5 g/l kaolin. Paper effluent was from taken from a wastewater treatment plant at the Mondi Kraft mill at Piet Relief, SA. It contained breakdown products of lignin and lignosulphate. The wastewater treatment plant comprised the following processes: pre-treatment, dissolved air flotation (DAF), MF and UF. (See also Table 6.1.)

3.5 TEST CELLS

3.5.1 FLAT-SHEET CELL

The characteristic properties of the material selected for construction of the test cell are very important, as the ultrasonic signal must be able to penetrate the material. Figure 3.3 is a schematic representation of the test cell used in the MF and UF separation systems, with all dimensions. The cell was made from polymethyl methacrylate (Perspex).

The topside of the top part of the cell had a 90 mm × 45 mm × 16 mm flat recess. It was filled with a coupling agent, which connects the transducer with the cell. The membrane with a support-plate/spacer combination was positioned on the bottom plate (Figure 3.4) and the unit was sealed with a dual o-ring combination. The complete module assembly was clamped together with fourteen 6 mm-diameter bolts. A rectangular channel 100 mm × 20 mm × 2.5 mm formed the actual flow channel.

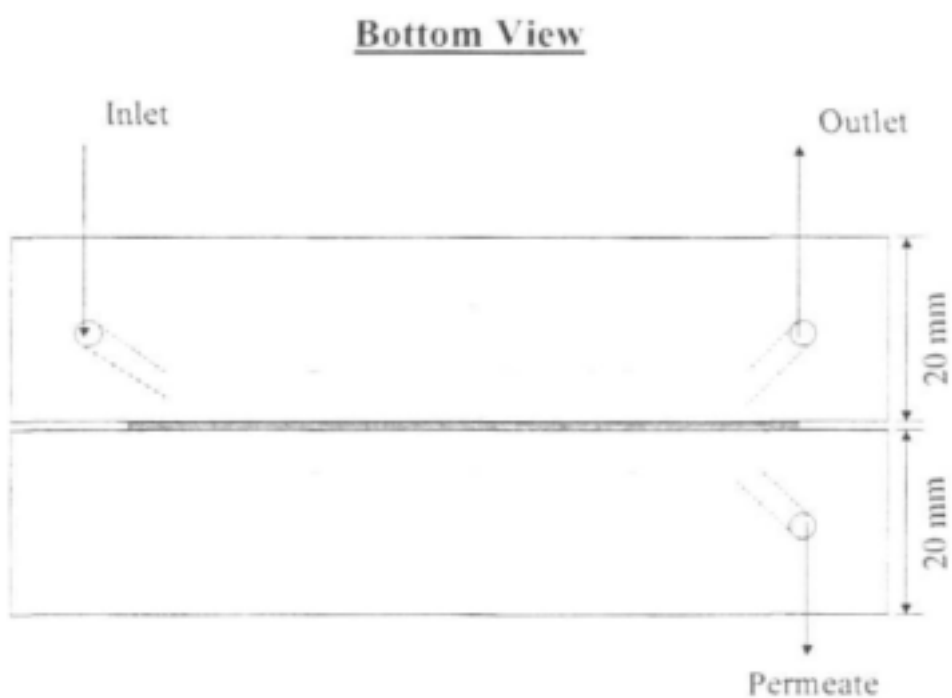
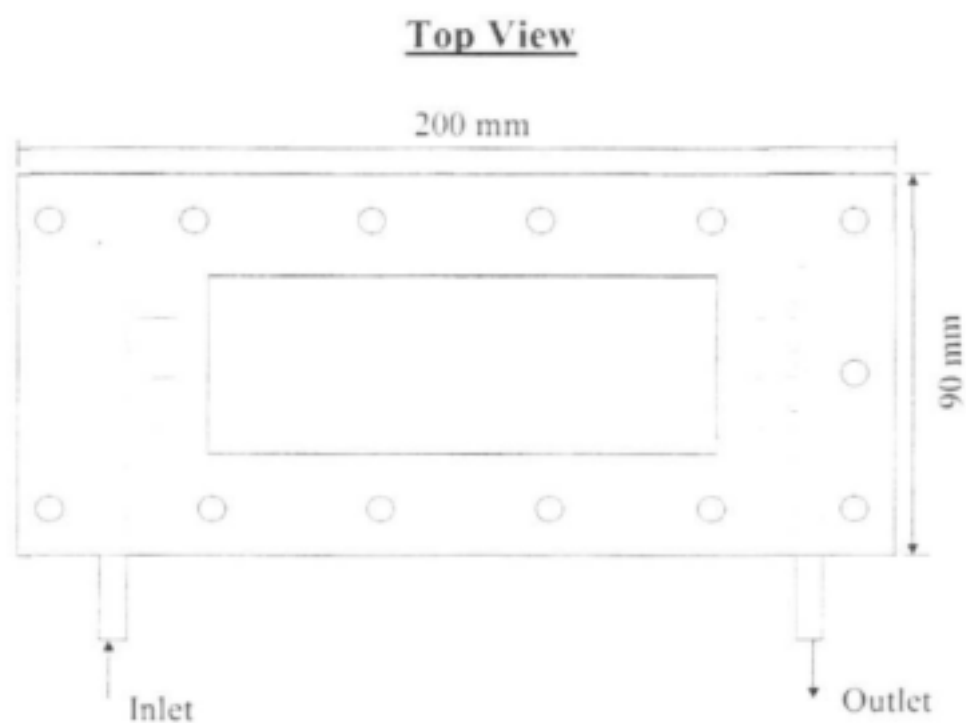


Figure 3.3: Schematic representations of the flat test cell used in MF and UF separations.

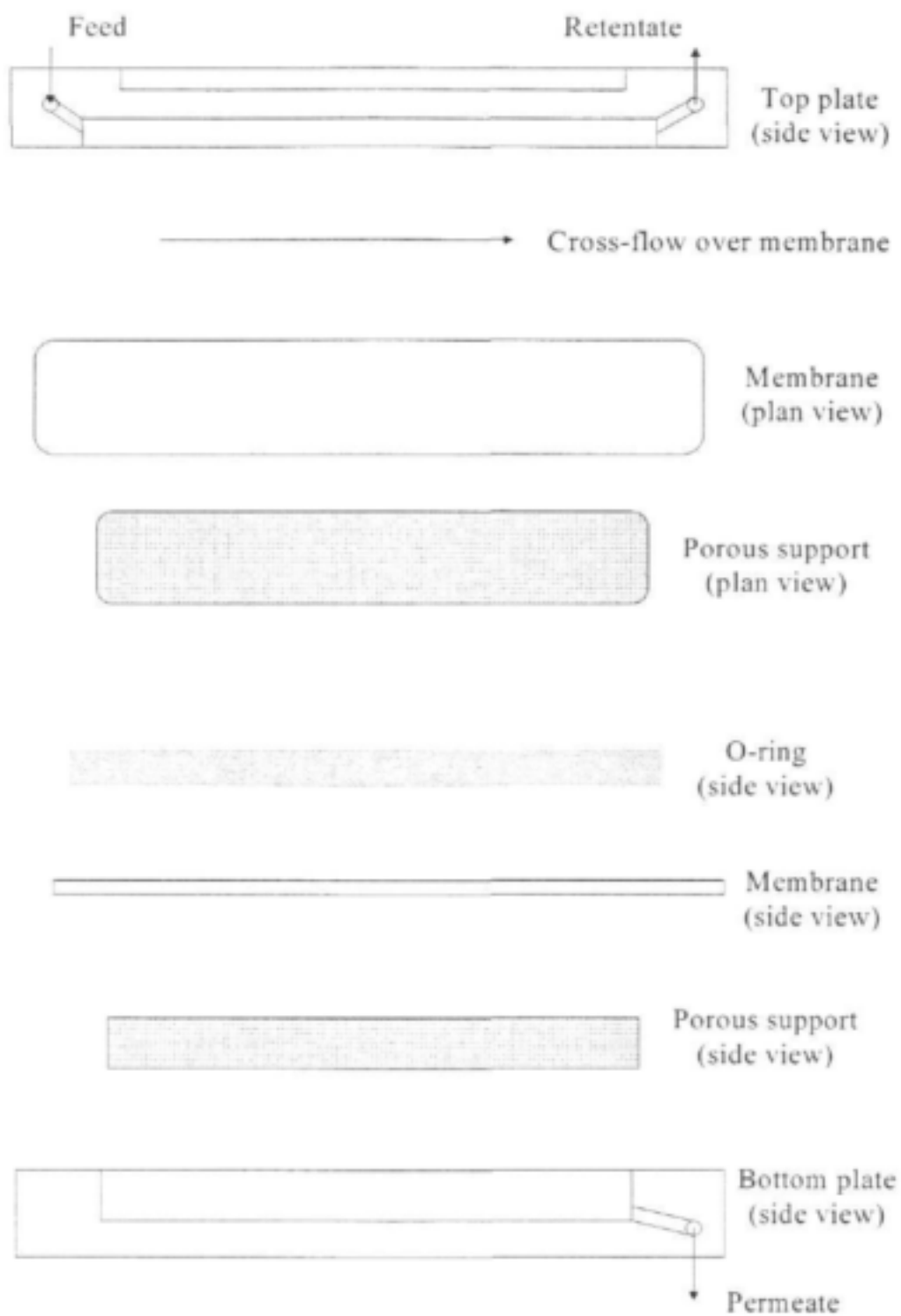
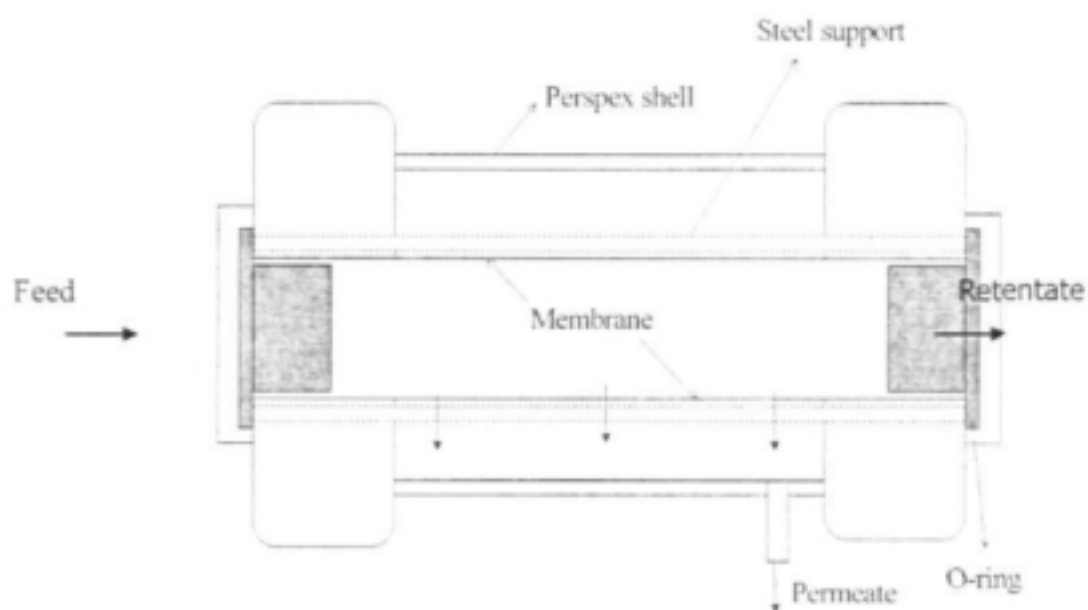


Figure 3.4: Placement of membrane in a flat-cell.

3.5.2 TUBULAR CELL

Figure 3.5 shows a drawing of the tubular test cell for UF. The shell was made of Perspex. The membrane, with a steel support was set up in the center of the cell. The dimensions of the membrane were: internal diameter 14×180 mm. The unit was sealed with two O-rings at each side. Feed flows in the inside of the membrane. The permeate was drawn from the inside to the outside of the tubular membrane and entered the channel between the steel support and Perspex shell.



Tubular membrane: diameter 14mm, length 180mm

Perspex shell: diameter 32mm, length 210mm

Figure 3.5: Schematic representation of tubular test cell used in UF.

3.6 ULTRASONIC TESTING SYSTEM

3.6.1 ULTRASONIC SET-UP

Figure 3.6 is a simplified drawing of all the hardware in a typical ultrasonic set-up. A pulser/receiver generates the voltage signal that triggers the transducer to send out an ultrasonic wave. The oscilloscope that is connected to the pulser/receiver captures and displays the data as amplitude changes on its front panel. These data can be stored on a computer's hard drive.

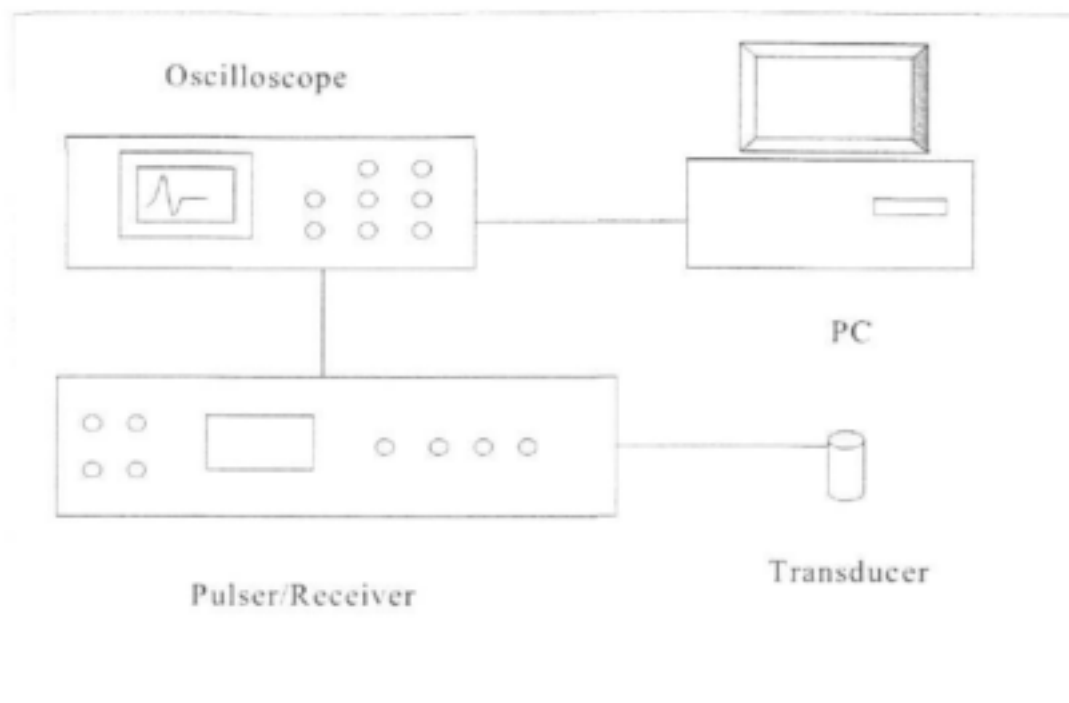


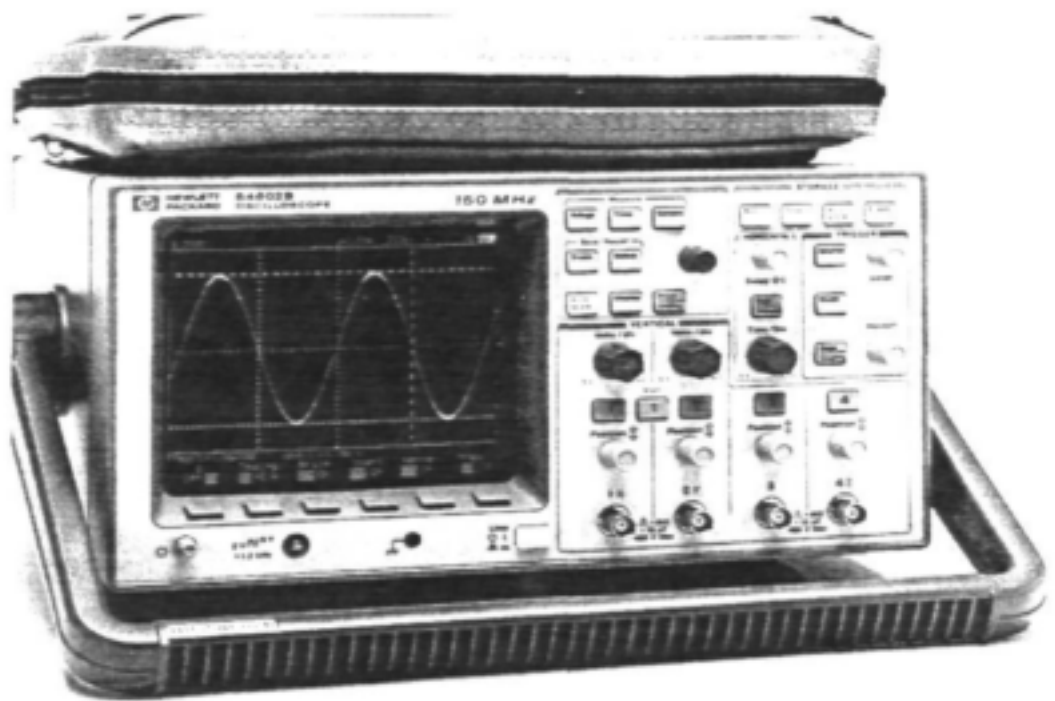
Figure 3.6: Ultrasonic set-up for UTDR pulse-echo operation.

3.6.2 PULSER/RECEIVER

A Panametrics Model 5058PR High Voltage Pulser-Receiver was used. It was designed especially for ultrasonic testing and measurement applications that require a high material penetration capability. The pulser section of the Model 5058PR can deliver up to 900 volts in an impulse-type excitation pulse to appropriate low frequency transducers. The receiver section provides 60 dB RF gain, with an additional 30 dB available from an integral auxiliary preamplifier. A full range of front panel controls permits either discrete, calibrated settings or continuous adjustments for all important instrument functions. Pulse voltage is continuously adjustable by four values from 100 to 900 volts with a front panel meter displaying the available voltage to the transducer. Receiver gain is selectable as 40 or 60 dB, while receiver attenuation is adjustable from 0 to 80 dB in 1dB steps, with a ± 1 dB vernier for precise setting. The Model 5058PR includes an internal preamplifier that can be used to create an additional 30 dB gain. Echo pulses can be selected as either normal or inverted 180° for peak detection applications. The 5058PR can be internally triggered at any of seven preamplifier radio frequency (PRF) rates from 20 Hz to 2 kHz, or externally triggered at any frequency up to 2 kHz. Pulse damping is continuously adjustable over a range of 50 to 333 Ω , or in stepped values of 50, 100, 200, or 500 Ω . All transducer and radio frequency (RF) output connectors are front-panel mounted for easy access.

3.6.3 OSCILLOSCOPE

The choice of the correct oscilloscope is very important, as real-time signal changes are displayed on it. The oscilloscope should have a digitising capability for real-time processing and display of the ultrasonic signals as well as appropriate time-domain resolution and sensitivity for accurate measurement of fouling layer growth. A 150 MHz Hewlett Packard oscilloscope of 150 MHz bandwidth was used. Figure 3.7 shows a schematic representation of the Hewlett Packard Oscilloscope Model 54602B. Figure 3.8 shows the pulser/receiver – oscilloscope set-up for pulse-echo operation.



IP 54602B (2+2) Channel 150 MHz Oscilloscope

Figure 3.7: Hewlett Packard Oscilloscope Model 54602B

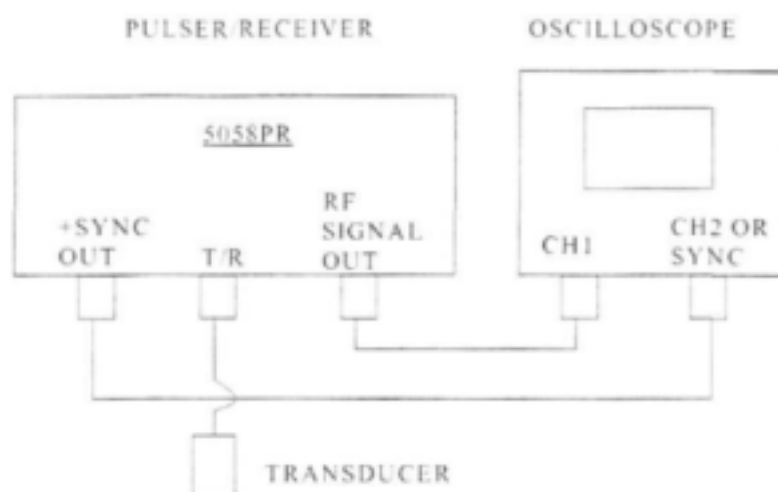


Figure 3.8: Pulsar/Receiver – oscilloscope set-up for pulse-echo operation.

3.6.4 TRANSDUCER

The transducer is one of the most critical components of any ultrasonic test system. Careful attention was given to selecting the most suitable transducer for the application. Variation in instrument characteristics and settings as well as material properties and coupling conditions play a major role in system performance.

In this study the following Panametrics Videoscan transducers were investigated: V106-RB, 2.25 MHz; V182-RB, 3.5 MHz; V109-RB, 5 MHz; V120-RB, 7.5 MHz and V111-RB, 10 MHz. Videoscan transducers are untuned transducers, which provide heavily damped broadband performance. They are the best choice in many applications where good axial or distance resolution is necessary or in tests that require improved signal-to-noise in attenuating or scattering materials.

In Figure 3.9 the typical signal waveform and frequency spectrum for a 5 MHz transducer (Panametrics V109-RB) is shown, having a central frequency of 5 MHz [Panametrics, 2000]. It has a relatively broad frequency band and is thus useful in this context. Other transducers used have central frequencies of 7.5 and 10 MHz, respectively. After numerous experiments it was found that the 7.5 MHz and 10 MHz transducers gave the best response for the system under investigation. 10 MHz transducers were thus used in all the flat-sheet experiments. A 7.5 MHz focal transducer was designed and used to measure fouling in tubular UF.

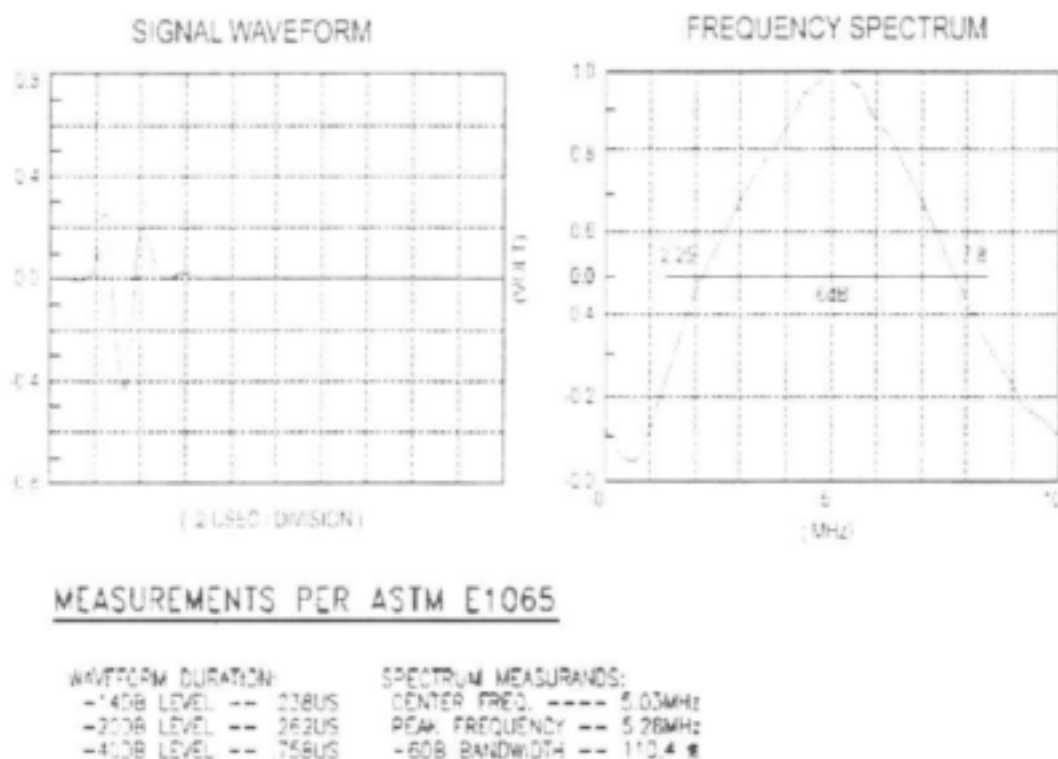


Figure 3.9: Typical signal waveform and frequency spectrum for a 5 MHz transducer [Panametrics, 2000].

3.6.5 THEORETICAL RESOLUTION

The theoretical resolution of a specific frequency transducer can be calculated if the speed of the sound wave in the medium that is under investigation is known.

The wavelength can be calculated from the well-known Equation 3.3:

$$\lambda = v/f \quad (3.3)$$

where: λ - wavelength [m];

v - speed of sound wave [m/s];

f - frequency [Hz].

The smallest detail that the transducer will pick up is that which is 0.25 of the sound wave's wavelength (explained in Figure 3.10). The theoretical resolution can thus be calculated with Equation 3.4, where:

$$\text{resolution} = 0.25 \lambda$$

(3.4)

The possible theoretical resolution (in water) of the range of transducers that were used during this study is tabulated in Table 3.2.

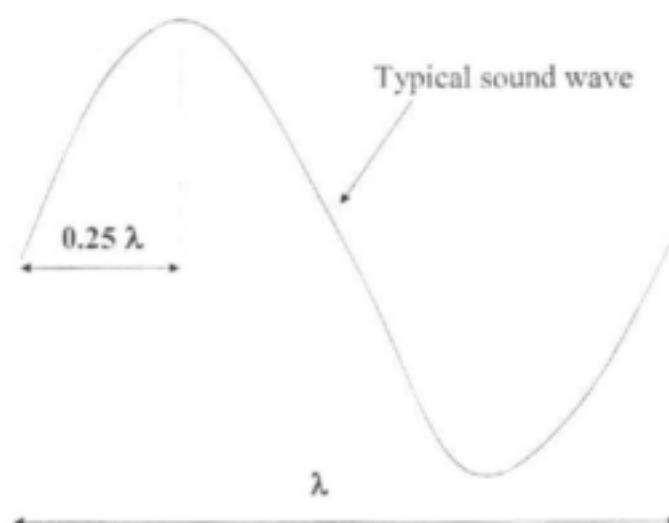


Figure 3.10: Typical sound wave.

Table 3.2: Theoretical resolution of the range of transducers used in this study [Koen, 2000]

Transducer	Frequency (MHz)	Resolution (μm)
V106-RB	2.25	159
V182-RB	3.5	102
V109-RB	5	72
V120-RB	7.45	48
V111-RB	10	36

3.7 MORPHOLOGICAL CHARACTERISATION OF THE FOULING LAYER

Morphological studies of the fouled and cleaned membrane samples were carried out to establish a correlation between the measurement of UR and the coverage of the membranes. A LEO S440 scanning electron microscope (SEM) was used and samples were viewed at 10 kV and 20 mm working distance. Optical microscopy was also used to investigate the membrane surfaces.

4. ULTRASONIC REFLECTOMETRY MODELLING

4.1 ABSTRACT

Mathematical modelling is used to describe the process of ultrasonic testing related to the deposition of fouling in complex membrane environments. It was developed as part of this research project. Section 4.2 summarises the program development of software for ultrasonic reflectometry. The program "ultrasonic reflectometry" modelling (URM) can handle an environment of 11 layers and uses as input parameters the sonic velocities, thickness and densities of these layers. The modelling is based on some actual ultrasonic records. The modelling procedure is described in Section 4.3. The chapter is concluded with a few representative simulation results to demonstrate some actual ultrasonic records and the accuracy of this program. Section 4.4 gives examples of modelling applications.

4.2 PROGRAM DEVELOPMENT OF SOFTWARE FOR ULTRASONIC REFLECTOMETRY

Process simulation and modelling have become increasingly important approaches of the research and development environments as tools to improve the effectiveness of the research and development process. In order to gain more insight into the process of ultrasonic testing of membranes and membrane fouling, and to better understand the processes related to the deposition of fouling layers, a predictive program, ultrasonic reflection modelling (URM) was developed [Hallbauer-Zadorozhnaya, 2001].

It is a well-known principle that acoustic waves are generated if a spherical source of pressure $D(t)$ with a radius r_1 is applied to a medium at time t [Gurvich, 1960]. The acoustic waves thus generated propagate in the medium away from the source by displacing small volumes of the material they pass through. Such a displacement of material at each point of the model can be given as:

where: r_0 - unit of the vector, directed to the radius,

$$U_p(R, t) = \left[\frac{f_s(\tau_1)}{R^2} + \frac{f_s'(\tau_1)}{V_p R} \right] \frac{r_0}{\rho} \quad (4.1)$$

V_p - longitudinal velocity of acoustic wave [m/s],

ρ - density of the material [kg/m³],

R - distance between the sources (transducer) [m].

$$f_s(\tau_1) = \frac{1}{2\pi} \int_{-\infty}^{+\infty} \frac{D(\omega) \exp i\omega\tau d\omega}{\omega_{0p}^2 - \omega^2 + 2i\omega\alpha_p} \quad (4.2)$$

At the receiver, values of $f_s(\tau)$ can be given as a function of the pressure spectrum $D(\omega)$ as:

where: $\tau = t - (R-r_1)/V_p$ - time of wave's arriving [s],

$\omega_{0p} = 2V_S/r_1$ - angular frequency of the self-oscillation of source (transducer)

[radian per second],

$\alpha_p = 2V_S^2/RV_p$ - coefficient of the attenuation the source (transducer),

$D(\omega)$ represents the spectrum of the pressure, and

V_S is the shear wave velocity (we assume $V_S \sim 2V_p/3$).

The systematic change of pressure or a sound wave is an oscillation and, for modelling purposes, we assume in first-order approximation a 3/2 sine function. (See also Fig 7.24.)

The spectrum of that pressure transmission can be given as:

$$D(\omega) = P_0 \cdot \frac{\omega_0 \left[1 + \exp\left(-i\omega \frac{3T}{2}\right) \right]}{\omega^2 - \omega_0^2} = D_S(\omega) \cdot P_0, \quad (4.3)$$

where: P_0 - amplitude of pulse [N/m²],

T - period of sinus function (i.e. $3/2 = .1T$ - duration of the pulse),

$$\omega_0 = 2\pi/T,$$

ω - angular frequency [rad per second].

For the analysis of sound waves in an assembly of membranes a number of material boundaries or free boundaries at which the propagation of a wave is disturbed have to be considered, i.e. at which a signal is reflected. We consider a case where the sound signal strikes planes and smooth boundaries at right angles. For reasons of symmetry only plane waves can then be propagated at right angles from the boundary. Reflected waves and transmitted waves are in opposite directions.

In order to apply the above formulae (Equations 4.1 – 4.3) and to calculate or predict the behaviour of a sound signal in the layered medium of a membrane assembly, the sound pressures and acoustic impedances of the materials contained in the assembly have to be considered. The acoustic impedances of two adjacent materials, W_1 and W_2 , depend on their specific sound velocities and densities, as described by Equation 3.1.

Considering the sound pressures of the incident wave, P_i , the reflected wave, P_r , and the transmitted wave, P_t , we can form two ratios; also known as the coefficient of reflection and the coefficient of transmission. C_r is the amplitude of the reflected wave and C_t is the amplitude of the transmitted wave.

The transmission coefficients are as follows:

$$C_r = \frac{W_2 - W_1}{W_2 + W_1} = \frac{\rho_2 V_2 - \rho_1 V_1}{\rho_2 V_2 + \rho_1 V_1} \quad (4.4)$$

$$= \frac{2W_2}{W_2 + W_1} = \frac{2\rho_2 V_2}{\rho_2 V_2 + \rho_1 V_1} \quad (4.5)$$

The program URM combines the above mathematical considerations and, from input parameters, produces a text file-type output, which can be used to produce a graphical presentation of the problem, using Microsoft EXCEL, Sigma Plot or similar commercially available software. In its present form, URM can handle an environment of 11 layers and uses as input parameters the sonic velocities, thickness and densities of these layers. The output contains data on the individual pulses as well as a combined signal, as would be observed on an oscilloscope screen.

At present the program is only available as a FORTRAN version. A WINDOWS version is currently being developed in collaboration with an overseas company.

4.3 MODELLING APPLICATIONS

The current model of fouling predicts that during ultrasonic testing of a fouling process an extra echo or reflection would develop in front of the membrane echo and grow according to the progress of fouling. It is also known that the physical and elastic parameters of the system have an influence on the reflection pattern. Input parameters for modelling based on theoretical considerations would thus be:

- acoustic velocities in the participating components
- densities of the components
- thickness of individual layers.

A number of modelling exercises was carried out and good agreement obtained with the above model. However, observations that depart from that model have also been made. The ultrasonic records of such an experiment are shown in Figure 4.1, where the individual records have been stacked according to the fouling progress. In this experiment a polysulfone (PSU) membrane was tested with paper mill effluent as feed in a flat-sheet test cell test.

Three principal echoes were recognised for the clean membrane (bottom of Figure 4.1) i.e. from left to right: PSU membrane, polyester support and the porous metal support for the membrane. While the latter two echoes remain stationary during progressing fouling, the first echo moves forward and a stationary, additional echo develops in front of the polyester support. In a first hypothesis this behaviour was explained as:

- The PSU membrane consists of three physically different parts: top layer, intermediate layer and polyester backing;
- The fouling layer has properties similar to the top layer and, during fouling, obscures the PSU echo.

This hypothesis was tested by mathematical modelling and repeated variation of the parameters. The final input parameters used for the flat cell configuration are given in Table 4.1.

The results of the modelling are presented in Figure 4.2. It shows the modelled echoes up to and including the polyester layer. It is a reasonable likeness of the echo records shown in

Figure 4.1 and appears to confirm the above hypothesis. However, according to the nature of a hypothesis it is not proof but a good indication that layers can 'fuse' as far as their echoes are concerned, if the acoustic parameters are close enough. It would, in such a case, not be possible to calculate the thickness of a fouling layer directly from the ultrasonic record in the conventional way. Modelling would be a support in finding the correct approach. Mathematical modelling could therefore play an important role in the handling and understanding of ultrasonic test records. Detailed applications of URM are presented in Chapters 7 and 8.

Table 4.1: Input parameters used for modelling PSU membrane fouled by paper mill effluent

Layers\Parameters	Velocity [m/s]	Thickness [m]	Density [g/cm ³]
Perspex	2762	0.00569	1.18
Water/feed	1483	0.002	1.0
Fouling	2300	0, 50, 100, 150 μm	1.05
PSU ₁	2500	0.00001	1.13
PSU ₂	2450	0.00015	1.1
Polyester	3100	0.00002	1.53
Metal backing	4590	0.003	3.2

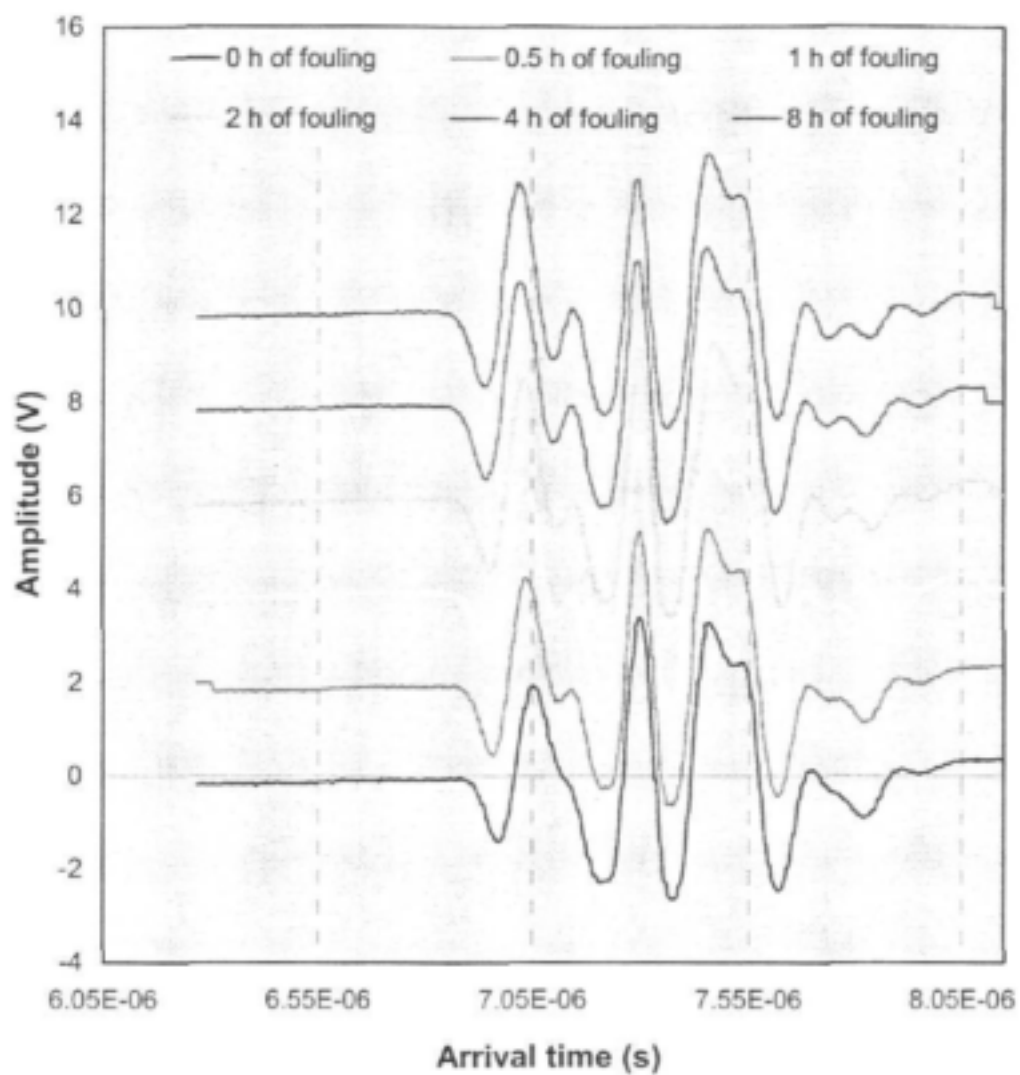


Figure 4.1: Ultrasonic reflectometry during filtration of paper mill effluent by PSU membranes.

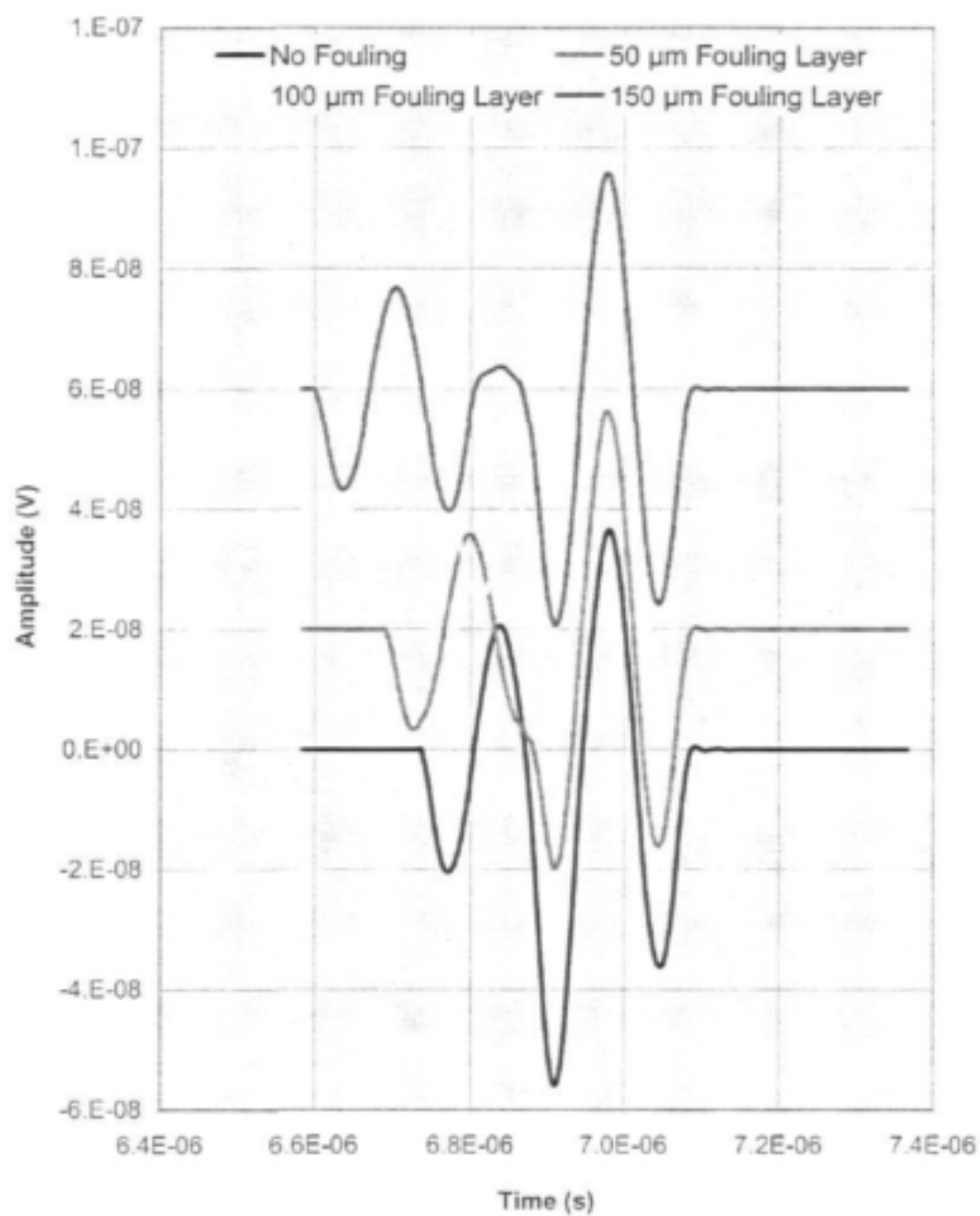


Figure 4.2: Modelling of fouling layers on PSU membranes.

5. IN-SITU MEASUREMENT OF PARTICLE DEPOSITION AND ITS REMOVAL IN MICROFILTRATION

5.1 ABSTRACT

This chapter describes the use of the ultrasonic time-domain reflectometry (UTDR) technique for the non-invasive, *in situ* measurement of particle deposition and its removal during cross-flow microfiltration (MF) with nylon membranes. The study was carried out with 0.5 g/l kaolin (average particle size 2 μm). Ultrasonic response signals were obtained upon particle deposition and subsequent cake layer formation on the membrane surface. A cake layer echo appeared in the time domain. The UTDR technique was also used to quantify the thickness of a fouling layer on the membrane surface. Moreover, UTDR was applied to monitor membrane cleaning and evaluate the effectiveness of different cleaning methods in MF. The UTDR results corroborated flux measurements and SEM analyses.

5.2 INTRODUCTION

One of the major problems associated with the more widespread use MF separation is the significant flux decline during operation. This is because of particle deposition and the build-up of a filter cake on the surface of a MF membrane. The development of a non-invasive visualization technique that is sensitive to changes in the condition of a membrane surface is therefore of considerable interest and was investigated. The application of the non-destructive, *in situ*, UTDR technique to investigate particle deposition and its removal in a MF system is described here. Ultrasonic response signals obtained provide quantitative information on the occurrence of kaolin fouling on MF membranes.

5.3 EXPERIMENTAL

5.3.1 MF SYSTEM AND ULTRASONIC SET-UP

Figure 5.1 is a schematic representation of MF separation system used. The assembly consisted of the following: a 10-litre feed tank for storage and supply of the fouling solution, a peristaltic pump (WATSON-MARLOW 313S, Watson-Marlow Limited, England) for pressurisation of the feed solution, a rectangular test module (see Figures 3.3 and 3.4), a temperature-control system for the feed tank, pressure gages, valves and a flow meter.

The ultrasonic measurement system consisted of a 10 MHz ultrasonic transducer (Panametrics V111-RB), a pulser-receiver (Panametrics 5058PR) and a digital oscilloscope (HP Model 54602B) (Figure 5.1). The oscilloscope connected to the pulser-receiver captures and displays

the data as amplitude changes on its front panel. Each set of ultrasonic data generated consisted of 500 data points. This data can be stored on a computer's hard drive. Commercially available salad oil was used to couple the transducer to the top plate surface.

Nylon MF membranes (disc Φ 290 mm) made by Pall Ltd., England, with a nominal pore size of 0.2 μm , were used in all of the fouling experiments. Kaolin was chosen as a potential foulant because kaolin occurs frequently in the mining and paper industries, especially in the mining wastewater treatment in South Africa. Fouling experiments were carried out with 0.5 g/l kaolin (average particle size 2 μm).

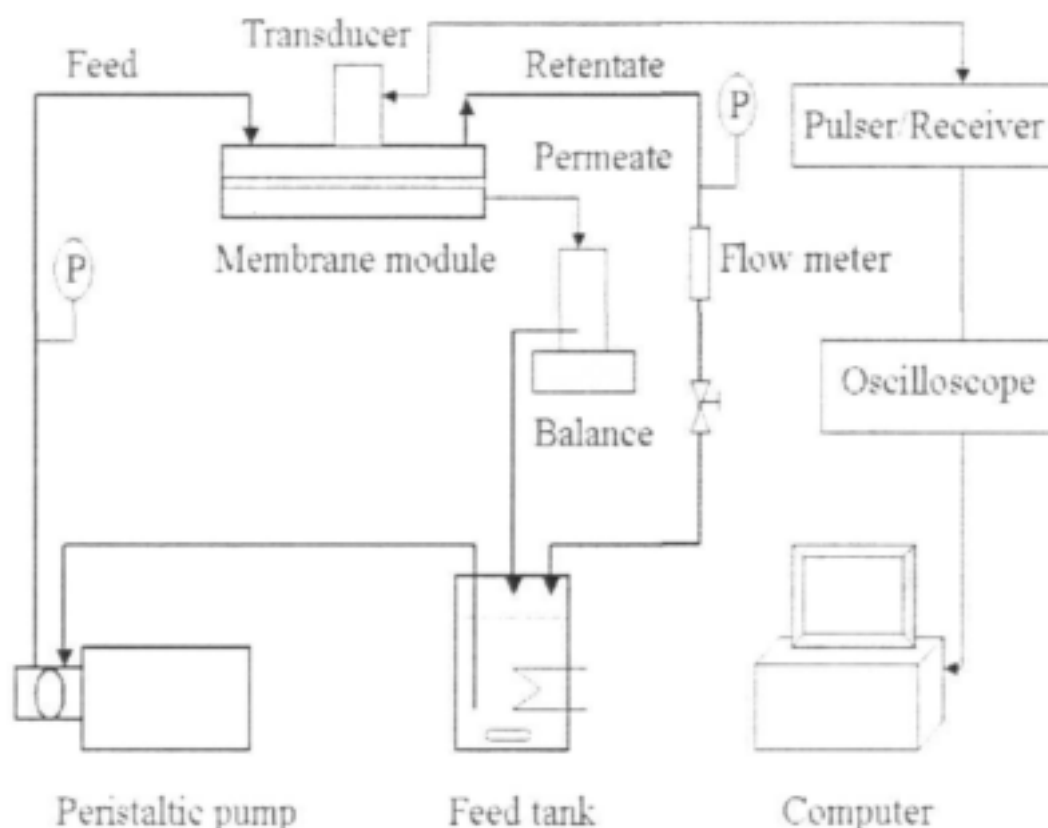


Figure 5.1: Schematic representation of MF separation system and ultrasonic measurement.

5.3.2 EXPERIMENTAL PROCEDURE AND FOULING

Each experiment commenced with pure water being circulated through the system at the desired flow rate and applied pressure for 1 h to compress the membrane and to build up a stable flow field. Once steady state was attained, the feed was switched to the kaolin solution to initiate the fouling phase. The fouling experiment was carried out at a flow rate of 6.97 ± 0.07

cm/s ($Re = 253 \pm 2.5$), applied pressure 100 ± 5 kPa and temperature $24 \pm 1^\circ\text{C}$. This phase was allowed to continue until the ultrasonic response and permeate flux had stabilized.

5.3.3 CLEANING EXPERIMENT

After the membranes were fouled with kaolin, they were cleaned by two methods, consecutively, namely: reverse flushing (at a flow rate of 50 cm/s) and ultrasonic cleaning, for cleaning times of 5 min each. The feed solution was changed from effluent to water under the same operating conditions as used in the fouling phase in order to compare the cleaning efficiencies of these three methods. The cross-flow filtration cell was immersed in a water bath at temperature $24 \pm 1^\circ\text{C}$ during ultrasonic cleaning. The cell was irradiated with a horn ultrasonic cleaner (Model W-375, Ultrasonics), frequency 20 kHz and power 375 W.

To investigate the cleaning efficiency of each cleaning method, the cleaned membrane was used to filter pure water under the same operating condition as used in the fouling phase. The UR measuring system captured the changes in ultrasonic signal responses after the different cleaning methods. These data were stored on a computer's hard drive.

5.4 RESULTS AND DISCUSSION

Prior to discussing the detection of fouling by UTDR, it is necessary to understand the basic principle of ultrasonic measurements and distinguish or recognise various response signals from ultrasonic records in the flat-sheet cell (refer to Figures 3.3 and 3.4).

5.4.1 PRINCIPLE OF ULTRASONIC REFLECTOMETRY IN CELL

A representative waveform obtained during pure water operation with a clean nylon membrane is shown in Figure 5.2.

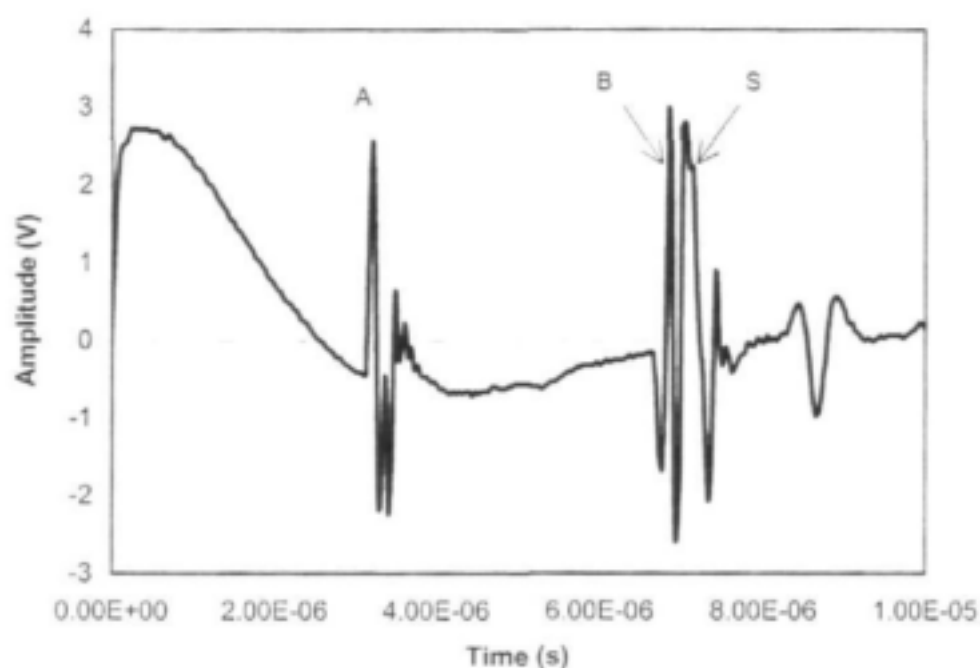


Figure 5.2: Ultrasonic signals from the flat-sheet cell during pure water filtration at an operation pressure of 100 kPa.

Figure 5.2 plots the ultrasonic signal amplitude in volts (V) vs. the time in seconds (s). Each peak corresponds to a reflected acoustic wave from one of the multiple interfaces in the flat cell. Peaks A, B and S were generated from the following interfaces: Perspex plate/feed (water), water/nylon membrane and membrane/porous metal support. Peak B is a single echo that exhibits the structure of the nylon membrane - a symmetric layer. The UTDR measurement was focused on the front of Peak B (as an observed peak), which indicates the membrane surface.

In order to prove the above observation, a mathematical model of the reflections inside the flat-sheet cell was designed and the results were compared to the actual cell and nylon membrane dimensions measured by vernier. Figure 5.3 is a cross-sectional view of the cell with the received reflections supposed from the various interfaces where:

A: echo between top plate of the cell and water interface;

B: echo between water and nylon membrane interface;

S: echo between nylon membrane and porous metal support.

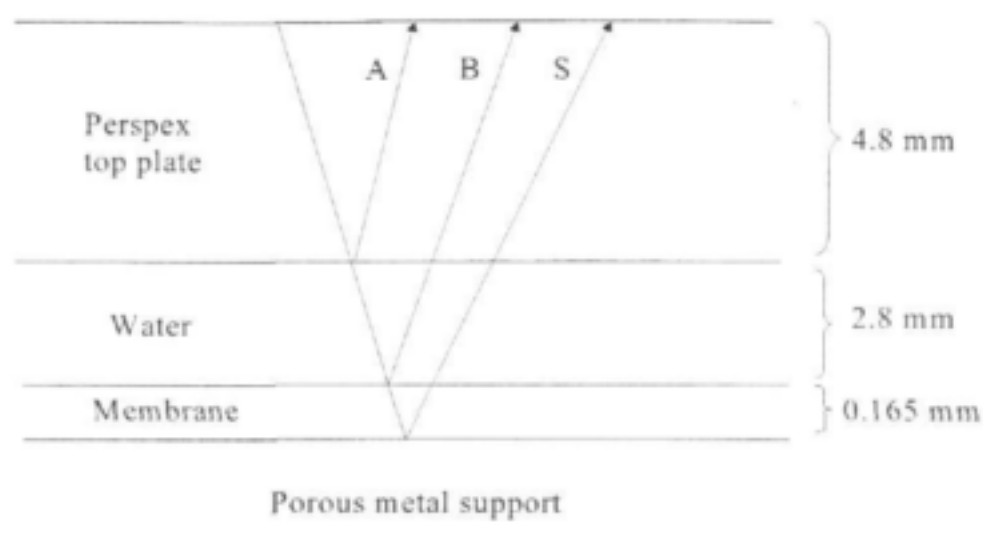


Figure 5.3: Mathematical model in a flat-sheet cell.

The arrival times of the response signals as measured by UTDR (Figure 5.2) were:

$$t_A = 3.40 \mu\text{s}$$

$$t_B = 6.84 \mu\text{s}$$

$$t_S = 7.00 \mu\text{s}$$

If the speed of sound in Perspex, water and a nylon membrane is known, then the thickness of each layer can be mathematically correlated, by using the received echo time and Equation 3.1, with:

$$V_{\text{perspex}} = 2730 \text{ m/s};$$

$$V_{\text{water}} = 1438 \text{ m/s}$$

$$P_{\text{polyamide (nylon)}} = 2200 \text{ m/s [Krautkrämer, 1969]}.$$

$$dS_{\text{perspex}} = 0.5 \times V_{\text{perspex}} \times t_A$$

$$= 0.5 \times 2730 \times 3.40$$

$$= 4.64 \times 10^{-3} \text{ m}$$

$$= 4.64 \text{ mm}$$

$$dS_{\text{water}} = 0.5 \times V_{\text{water}} \times (t_B - t_A)$$

$$= 0.5 \times 1438 \times (6.84 - 3.40)$$

$$= 2.47 \times 10^{-3} \text{ m}$$

$$= 2.47 \text{ mm}$$

$$dS_{\text{nylon}} = 0.5 \times P_{\text{polyamide (nylon)}} \times (t_B - t_A)$$

$$= 0.5 \times 2200 \times (7.00 - 6.84)$$

$$= 0.176 \times 10^{-3} \text{ m}$$

$$= 0.176 \text{ mm}$$

The calculated thickness of the Perspex plate is 4.64 mm, which is very close to the measured value of 4.80 mm by vernier. The calculated value of the water (feed channel) thickness of 2.47 mm is smaller than the measured value of 2.8 mm because of the compaction of the rubber O-ring. The thickness of the nylon membrane was measured by vernier under dry conditions, hence the measured value of 0.165 mm is thinner than the calculated value of 0.176 mm (probably due to compaction). Overall, the model showed excellent correlation between the echoes received and the measured cell dimensions.

5.4.2 FOULING EXPERIMENT AND ULTRASONIC MEASUREMENT

As shown in Figure 5.4, the permeate flux declines rapidly after commencement of fouling and then reaches a near steady-state flux. The rapid flux decline to 34.2% of its initial value after 60 min of operation implies that significant membrane fouling occurs.

The UTDR echo signals recorded during the fouling experiments are shown in Figure 5.5. Generally, once foulants (particles) are deposited on the membrane surface, the acoustic impedance difference and the topographical characteristics at the feed solution/membrane interface will change, resulting in a change in the amplitude of the membrane echo, as shown

after 5 min of fouling operation in Figure 5.5b. Further, if a cake layer builds up on the membrane surface, a new echo signal (Peak C) will be seen, as seen after 10 min of fouling operation in Figure 5.5c. An increase in the amplitude of Peak C and its movement in the time-domain can be observed at 0.5, 2 and 7 h of operation in Figure 5.5 d–f. Peaks B' and C were generated from the interfaces: the kaolin layer/ nylon membrane and the feed/kaolin layer. The formation of an additional reflex (shoulder to the right of peak C) is interpreted at this stage as an echo from a dense fouling layer that formed directly on the membrane.

Figure 5.4 also shows the amplitude of Peak C as a function of operation time during kaolin fouling. At the beginning of the fouling experiment there is an instantaneous and rapid increase in the amplitude, followed by a more gradual increase after 1 h operation. The former increase results primarily from particle deposition and the formation of a dense kaolin layer. The gradual amplitude increase is presumed to occur as result of the effective density of the fouling deposit, which does not change significantly once the fouling layer becomes reasonably dense and thick. Indeed, the flux decline corresponds to the changes in the amplitude of peak C.

The decline in the amplitude of peak B with operating time is related to the growth of the echo signal of the bottom of the kaolin layer. This has an effect on the reflection signal of the membrane as a result of the build up and consolidation of the fouling layer on the membrane surface.

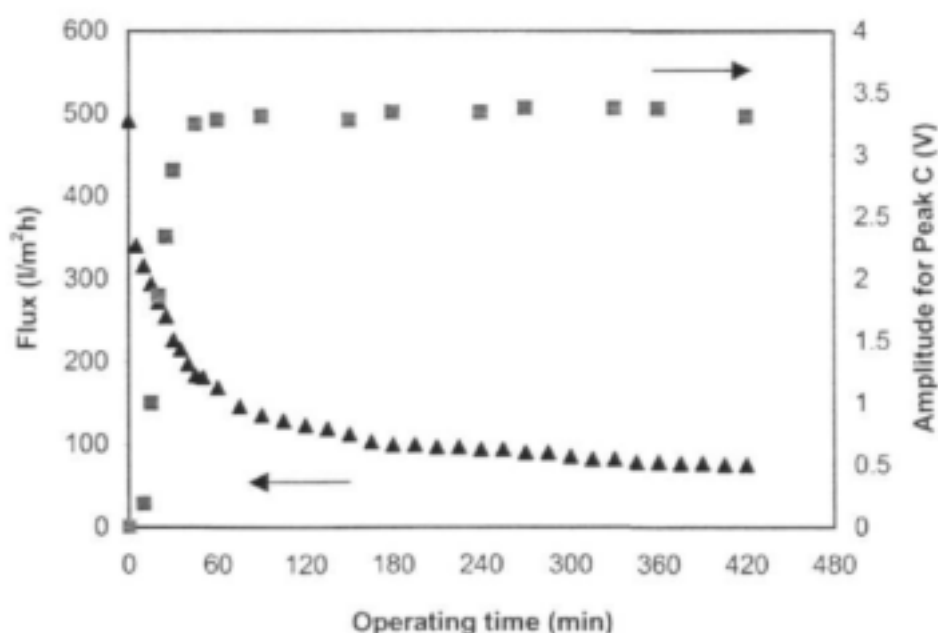


Figure 5.4: Effect of kaolin fouling on permeate flux decline and amplitude of Peak C (echo of fouling layer) with operating time, at pressure 100 kPa and flow rate 6.97 cm/s in MF.

Ultrasonic responses:

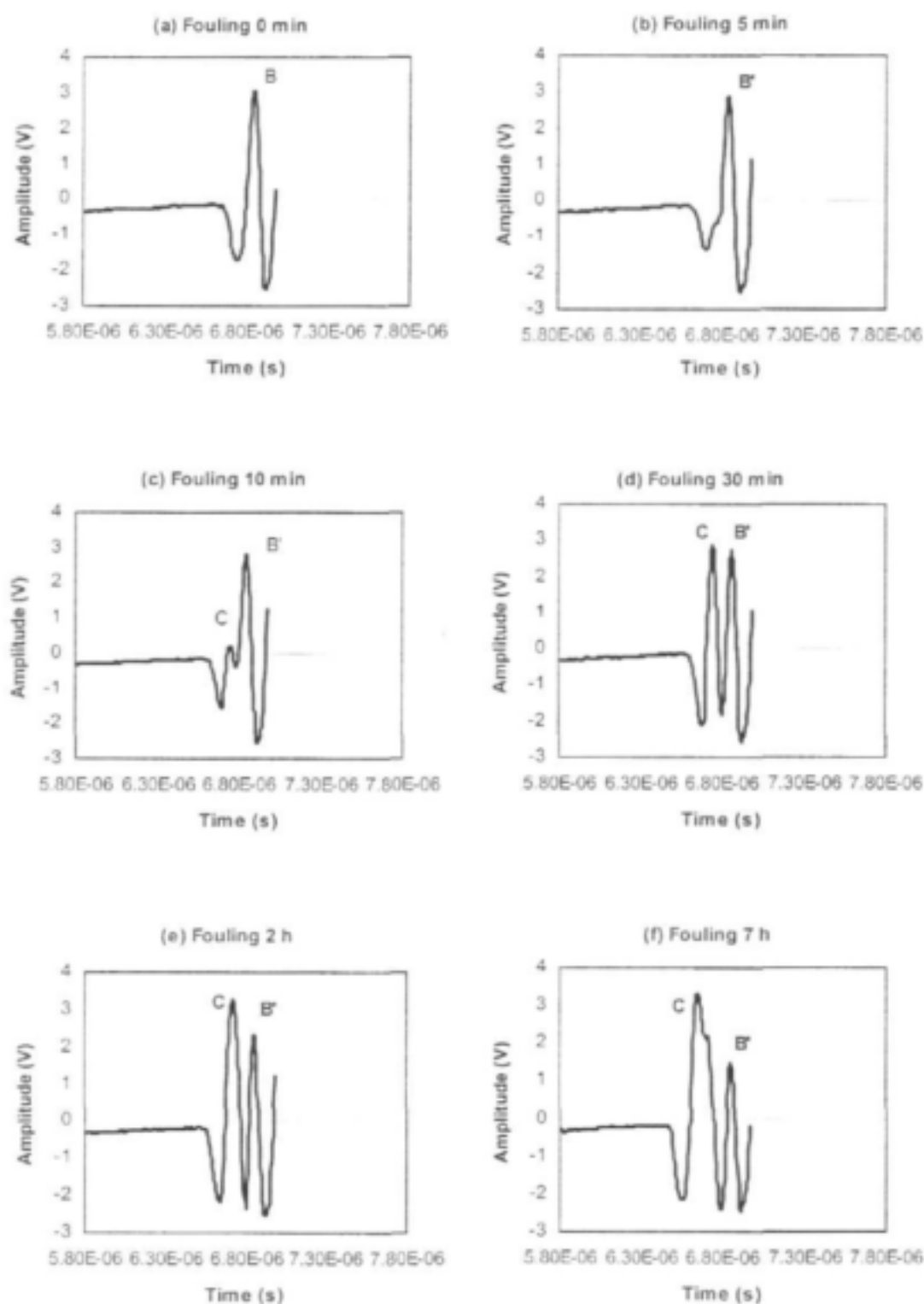


Figure 5.5: Ultrasonic response signals after (a) 0 min (start), (b) 5 min, (c) 10 min, (d) 30 min, (e) 2 h and (f) 7 h of operation in the fouling experiment carried out with kaolin (0,5 g/l in MF).

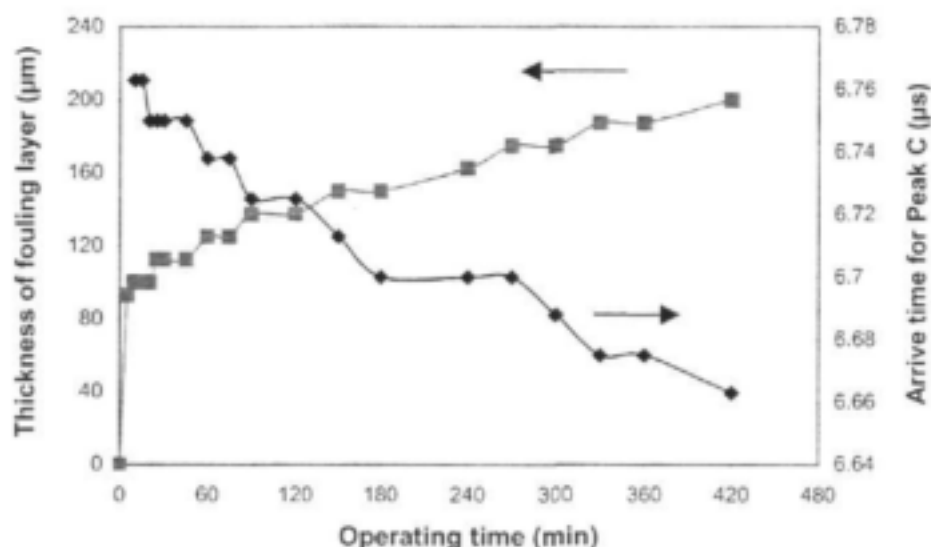


Figure 5.6: Plots the thickness of fouling layer and arrival time of peak C during kaolin fouling in MF.

Figure 5.6 plots the arrival time of peak C during the fouling process. According to the difference in arrival times, dt , between echoes B and C, the thickness of the kaolin layer on the membrane surface can be calculated from Equation 3.1 ($V = 2000$ m/s), as shown in Figure 5.6. Although there is an obvious change (with time) in the thickness of the kaolin layer, there is little change in flux. This implies that the pore size of the top kaolin layer is bigger than that of the bottom layer.

In order to study the correlation between the measurement of UTDR and membrane coverage by the fouling layer, membrane samples were taken for SEM analysis. Results are shown in Figure 5.7. Morphological characterization of the membrane surface after 5 min of fouling operation revealed particle deposits on the membrane surface (Figure 5.7a). Complete membrane coverage with aggregate kaolin particles and layers was observed after 30 min and 2 h of operating (Figure 7b and c). After 7 h of fouling operation, there was a dense kaolin layer covering on the membrane surface (Figure 5.7d).

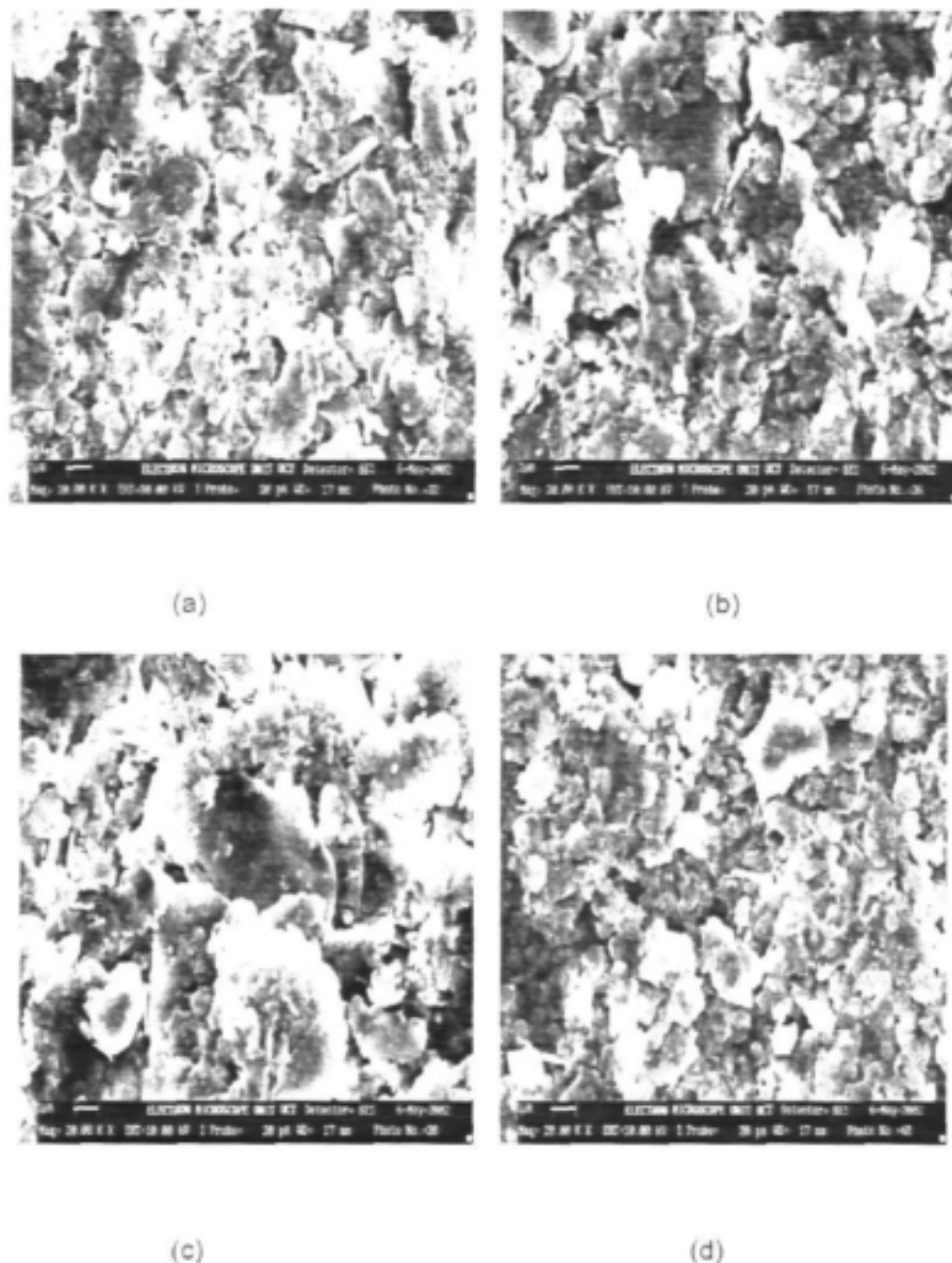


Figure 5.7: SEM images of a fouled Nylon membrane after (a) 5 min, (b) 30 min, (c) 2 h and (d) 7 h of fouling operation in MF.

5.4.3 CLEANING EXPERIMENT

To investigate the possibility of using the UTDR technique for monitoring fouling removal in real time, cleaning experiments were carried out by reverse flushing and ultrasonic cleaning, consecutively. The results of the UTDR response signals and permeate fluxes after the cleaning processes are shown in Figures 5.8 and 5.9.

Reverse flushing can reduce the cake layer covering on the membrane surface and enhance the permeate flux, although not to the original value (Figure 5.8). The UTDR response signal in Figure 5.9a shows that a fouling layer still covered the membrane. The disappearance of peak C (fouling echo after ultrasonic irradiation) indicates that the fouled membrane was cleaned by ultrasonic irradiation, as shown in Figure 5.9b. The recovery of flux after ultrasonic cleaning confirms this observation (see Figure 5.8). The amplitude of peak B for ultrasonic cleaning (Figure 9b) is, however, only 84.2% of that of peak B for fouling start (Figure 5.5a). This suggests that there are still some particles that remain on the membrane surface after ultrasonic cleaning. The microscope image of the membrane surface cleaned by ultrasonic cleaning proves the above observation (Figure 5.10 b). These results therefore demonstrate that the UTDR technique can indeed monitor removal of the fouling layer and membrane cleaning.



Figure 5.8: Change in flux during fouling and cleaning processes (at pressure 100 kPa and flow rate 6.07 cm/s).

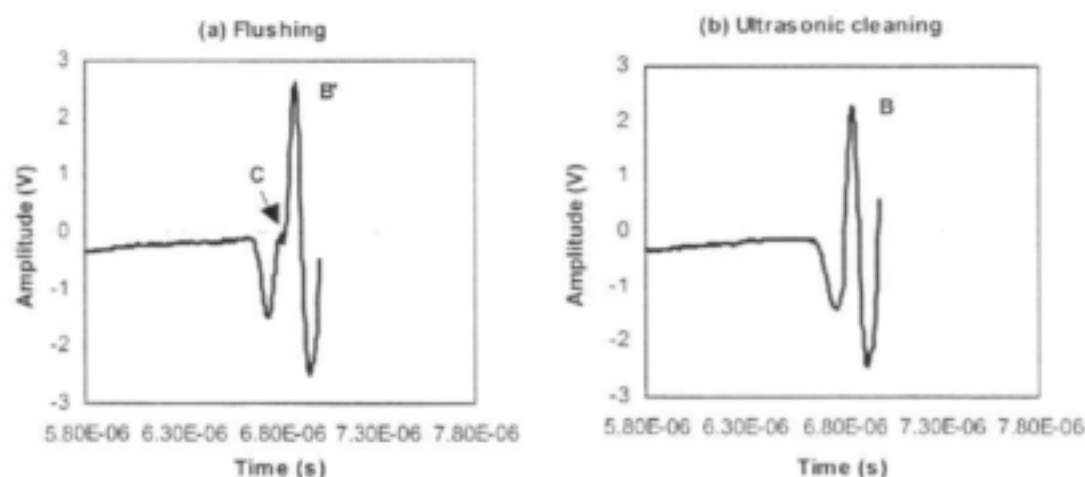
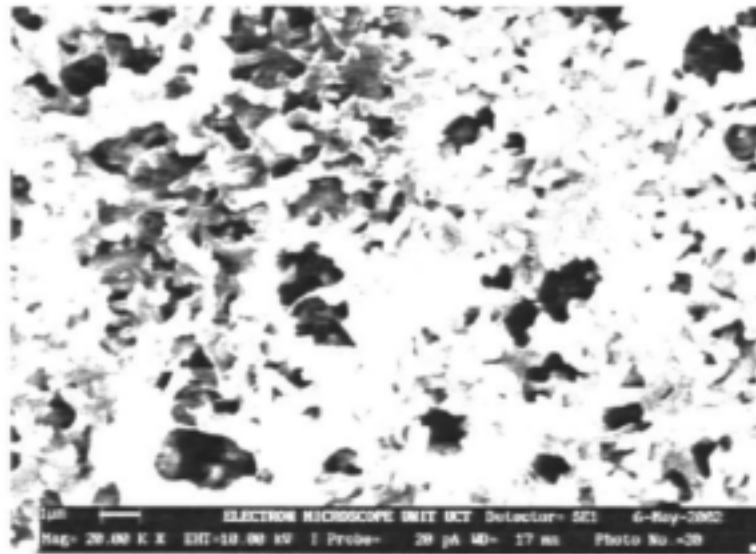
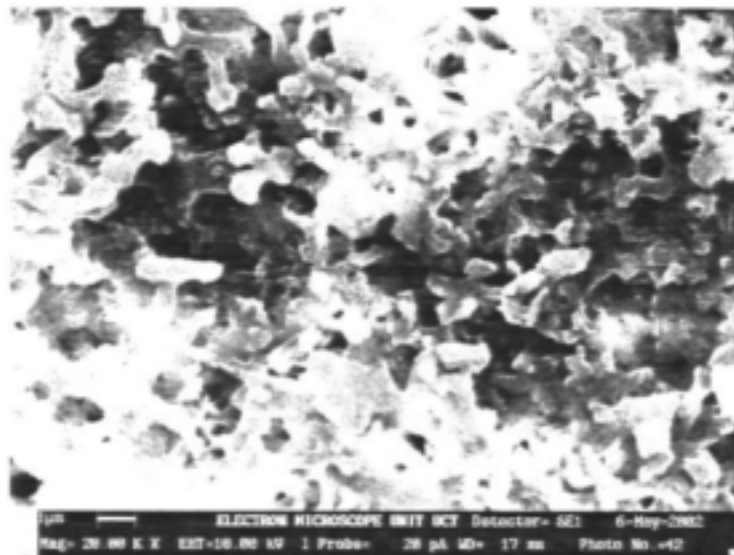


Figure 5.9: Ultrasonic echo signals in the cleaning processes: reverse flushing and ultrasonic cleaning.



(a)



(b)

Figure 5.10: SEM images of: (a) a clean nylon membrane surface; (b) the membrane surface cleaned by ultrasonic treatment.

5.5 CONCLUSIONS

The mathematical model analysis revealed good correlation between the echoes received and the measured cell dimensions.

Both the UTDR signal amplitude and arrival time of a fouling peak as a function of operating time provide usefully quantitative information on the fouling processes. Results show that UTDR

can monitor particle deposition, and the build up and consolidation of a fouling layer on a MF membrane surface in real time.

A dense cake layer formed in a short time, with a corresponding flux decline. Although there is an obvious change (with time) in the thickness of the kaolin layer after the formation of a dense layer, there is little change in flux. This implies that the pore size of the top kaolin layer is larger than that of the bottom layer.

UTDR can also be used to monitor membrane cleaning. Ultrasonic cleaning is an effective cleaning method. The UTDR results corroborate the flux measurements and SEM analyses.

6. ULTRASONIC CLEANING OF NYLON MICROFILTRATION MEMBRANES

6.1 ABSTRACT

An ultrasonic technique was successfully used to remove fouling and recover the permeate flux of flat-sheet MF membranes. Three kinds of cleaning methods were used to clean MF membranes: forward flushing, ultrasonic cleaning and ultrasound with forward flushing, and their cleaning efficiencies compared. It was found that ultrasound associated with forward flushing was a new effective method for the recovery of permeate flux. Scanning electron microscopy (SEM) analysis indicated that this method was able to remove fouling layers from a membrane surface and restore the original structure of the membrane surface. The operating conditions during cleaning were investigated. In general, a high forward-flushing velocity and low cleaning solution (water) temperature, under the same ultrasonic conditions, gave higher cleaning efficiency. Moreover, online ultrasound reduced membrane fouling and enhanced permeate flux. The horn sonicator that was used had a frequency of 20 kHz and a power of 375 w. Fouling and cleaning experiments were performed with nylon membranes with 0.2 μm average pore diameter. The membranes were fouled by Kraft paper mill effluent.

6.2 INTRODUCTION

Wastewater reclamation in the pulp and paper industry is important because of the large volume of water used in this field [Ahn et al. 1998]. Increasing attention has been given to it, as the regulations on the effluent become more stringent. Many technologies, including: adsorption, chemical oxidation, ion exchange, evaporation and membrane processes have been used to purify wastewater from the paper industry. Of these technologies, membrane processes can be tailored according to the required degree of purification [Nourtila-Jokinen and Nyström, 1996]. One of the limiting aspects in applying MF and UF for wastewater treatment is, however, that of problems with membrane fouling and consequent flux reduction.

Most of the literature that has appeared over the past two decades has focused on fouling rather than cleaning, even though what appears to be a fouling problem may really be a cleaning problem. Considerable progress has been made in understanding the interactions between the foulants, the membrane and the operating conditions [Potts et al, 1981; Fane and Fell, 1987; Robertson and Zydney, 1990; Belfort et al., 1994]. However, although many techniques have been developed to overcome fouling, membrane-cleaning techniques still need to be improved.

In the past few years, ultrasound has been widely used as a method for cleaning materials because of the cavitation phenomenon [Price, 1992]. Cavitation is defined as the formation, growth and collapse of bubbles, which are formed when a large negative pressure is applied to a liquid medium. When ultrasound is transmitted through a liquid medium, such as the feed solution, alternate compression and expansion cycles of the medium occur. The compression cycle can cause micro bubbles to collapse, with a release of energy, which causes cleaning of the membrane surface. The collapse of the cavities has sufficient energy to overcome the interaction between the foulant and the membrane and remove the foulant from the membrane surface.

Many studies have been carried out to enhance the solvent permeate flux and clean the membrane using ultrasound treatment [Harvey, 1965; Lenart and Auslander, 1980; Kost and Langer, 1988; Li et al., 1995; Chai et al., 1999] (see Chapter 2). The above studies provided valuable information on flux enhancement by ultrasonic irradiation, but use of the ultrasonic method and its effectiveness is limited. Online ultrasonic irradiation has low efficiency and high cost. An ultrasonic bath is only useful in laboratory studies because there is a high waste of acoustic energy in the bath during the cleaning process that cannot be tolerated in industrial process.

In the present study, a horn ultrasonic cleaner was used. Research was focused on the effect of ultrasound on the cleaning of fouled membranes and a comparison of results obtained from cleaning by forward flushing, ultrasonic cleaning and ultrasound associated with forward flushing. The operating conditions during cleaning and the effect of online ultrasound on permeate flux were also investigated.

6.3 EXPERIMENTAL

6.3.1 MF AND ULTRASONIC CLEANING SYSTEMS

Nylon MF membranes (disc Φ 290 mm) made by Pall Ltd., England, with a nominal pore size of 0.2 μm , were used in all of the fouling experiments. The feed solution selected was Mondi paper mill effluent (Kraft fluid) (refer to section 3.4). This plant has looked for ways for further reduce membrane fouling. The characteristics of the effluent are summarised in Table 6.1.

Table 6.1: Characteristics of paper mill effluent feed^a

ITEMS	VALUE	ITEMS	VALUE
pH	4.96	Conductivity, $\mu\text{S}/\text{cm}$	5550
Aluminium as Al, mg/l	16	Boron as B, mg/l	2
Calcium as Ca, mg/l	353	Iron as Fe, mg/l	3
Magnesium as Mg, mg/l	27	Sodium as Na, mg/l	908
Potassium as K, mg/l	30	Sulphur as S, mg/l	1075
Bicarbonate as HCO_3 , mg/l	98	Nitrate as NO_3 , mg/l	50
Chloride as Cl, mg/l	10	M-Alkalinity as CaCO_3 , mg/l	27.2
Turbidity, NTU	64	Suspended solids (SS), mg/l	6636

^a Data supplied by Mondi Piet Retief, Mondi Ltd, South Africa.

The flat-sheet MF experimental set-up, shown in Figure 6.1, allows for the accurate control of inlet pressure, retentate flow rate and temperature. In each MF experiment, continuous stirring in the feed tank was provided. Permeate flux was measured by an electrical balance. During the experiments both the retentate and permeate were recycled to the feed tank after flux measurements. Figure 6.1 is also a schematic representation of the ultrasonic cleaning system used. A horn ultrasonic cleaner (Model W-375, Ultrasonics INC.), with a frequency of 20 kHz and a power density of $82.9 \text{ W}/\text{cm}^2$, was used in this study. The cross-flow filtration cell was immersed in a water bath during ultrasonic cleaning. The cell was irradiated with the sonicator.

The flat cell had the following specifics: the thickness of the top plate 20 mm, a recess with $90 \times 35 \times 14 \text{ mm}$ on the top plate, and the height of feed channel 2.5-3.0 mm (See Figure 3.3). The horn transducer was fixed by a rack to clamp so as to maintain the same distance between transducer and cell in each experiment.

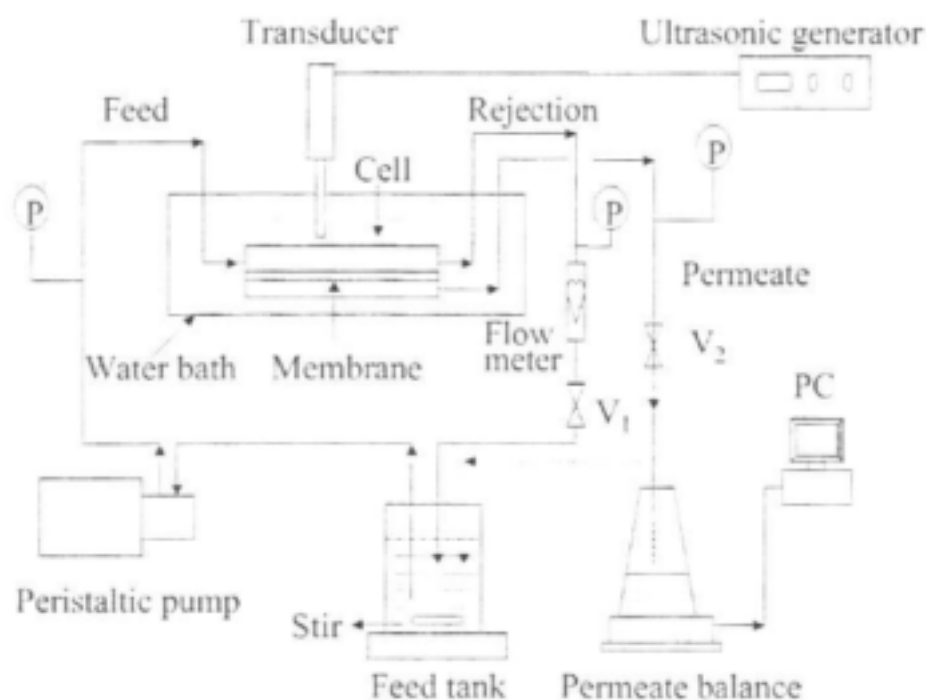


Figure 6.1: Experimental set-up for cross-flow MF and ultrasonic cleaning.

6.3.2 MF FOULING EXPERIMENTS

6.3.2.1 Fouling Experiments

Each experiment commenced with pure water being circulated through the system at a fixed flow rate and applied pressure for about half an hour to compress the membrane and to build up a stable flow field. The flux values for a new, clean membrane, referred to as J_w , were recorded after 30 min of pure water filtration. The pure water was then replaced by effluent. The flow rate of the feed and the operating pressure were fixed at 0.125 m/s and 50 kPa, respectively, for the duration of the filtration experiments. The turbidity of the feed and permeate solutions were 64 and 1, respectively.

6.3.2.2 On-line Ultrasound

The following experiment was conducted in order to investigate the effect of on-line ultrasound on the permeate flux during the fouling. The fouling experiment was carried out with a feed of paper mill effluent at 0.125 m/s axial velocity and 50 kPa, after an initial 30-min period of pure water filtration. The sonicator was turned on after fouling filtration for 90 min.

6.3.3 CLEANING EXPERIMENTS

After the membranes were fouled with paper mill effluent, the feed solution was changed from effluent to pure water. The fouled membranes were cleaned by three methods, namely: forward flushing, ultrasonic cleaning, and ultrasound associated with forward flushing. The duration was 10 min. Forward flushing was performed with valve V2 closed. Valve V1 was opened only after the trans-membrane pressure differential over the membrane subsided and reached zero, under the pre-determined flushing velocity. Ultrasound associated with forward flushing was performed with intermittent flushing under a pre-determined flushing velocity during ultrasonic irradiation. To investigate the cleaning efficiency of each cleaning method, the cleaned membrane was used to filter pure water under the same operating condition as used during the fouling phase (section 6.3.2).

6.4 RESULTS AND DISCUSSION

6.4.1 EFFECT OF ON-LINE ULTRASOUND ON THE FLUX DURING FOULING

Figure 6.2 shows the influence of on-line ultrasound on the permeate flux. A rapid decline in permeate flux is observed because of the presence and formation of a fouling layer on the nylon membrane surface. A final permeate flux value of $21.5 \text{ l/m}^2\text{h}$ was reached after 90 min of fouling operation. The flux increased to $28.8 \text{ l/m}^2\text{h}$ when the sonicator was turned on for 5 min, then slightly decreased from $28.8 \text{ l/m}^2\text{h}$ to $26.0 \text{ l/m}^2\text{h}$ after ultrasonic irradiation for 30 min. Figure 6.2 also shows the results of on-line ultrasonic cleaning for 20 min, after 90 min of fouling operation. Online ultrasonic irradiation can enhance the permeate flux from 21.5 to $29.0 \text{ l/m}^2\text{h}$. But the flux also slightly decreased from $29.4 \text{ l/m}^2\text{h}$ to $23.0 \text{ l/m}^2\text{h}$ after 30 min of fouling operation under ultrasonic irradiation.

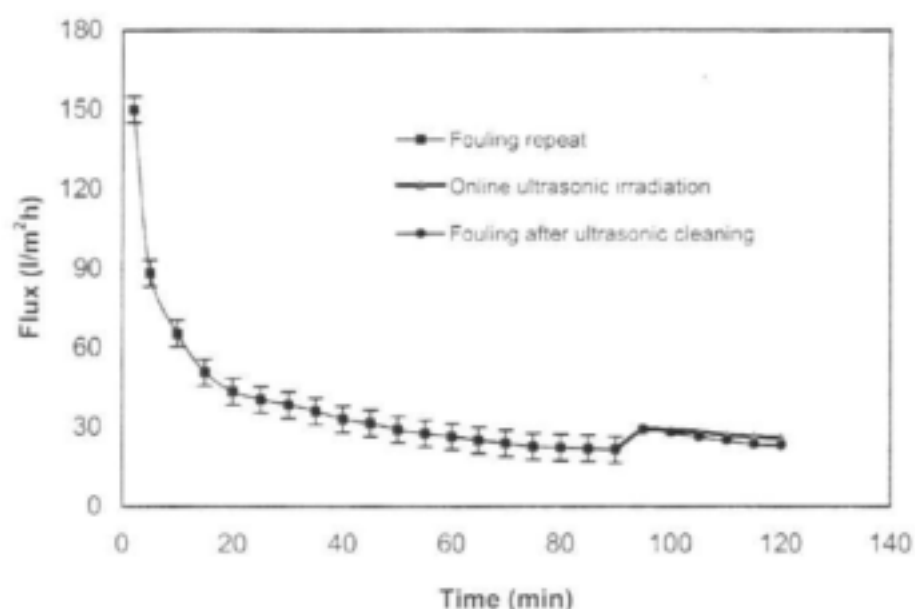


Figure 6.2: Permeate flux change with filtration time during paper effluent fouling experiment in the absence and presence of ultrasound (20 kHz), and fouling again after on-line ultrasonic cleaning for 20 min, after fouling time of 90 min.

Further experiments were carried out with and without ultrasonic irradiation during the paper-mill effluent fouling experiment. Figure 6.3 shows the changes in the permeate flux with and without ultrasonic irradiation. Without ultrasonic irradiation, the flux value declined from an initial 172 l/m²h to 66 l/m²h and 40 l/m²h at 10 and 30 min. On the other hand, when ultrasonic irradiation was used at the beginning of fouling, the flux decline was slower and the flux values obtained were 81 l/m²h and 51 l/m²h at 10 and 30 min. Results of this experiment suggest that ultrasonic irradiation can enhance the flux during MF. However, no flux difference was found between membrane treated with and without ultrasonic irradiation after 50 min of fouling operation. There may be two reasons why the flux enhancement cannot be obtained over long periods of on-line ultrasonic treatment. First, the sound energy will decrease because of the increase temperature of the transducer during operation. Second, the agitation due to the ultrasonic irradiation is likely to be complicated by the substantial increase in the number of cavitation nucleation sites generated on the new particle surface. When larger particles exist in the feed (average particle size: 0.947 μ m in the paper mill effluent), ultrasound can lead to a reduced flux rate. Presumably the momentum needed to re-suspend these particles is more than that which can be supplied by the application of the ultrasound, and the motion that is imparted to the particles in the fouling layers cause them to 'jostle' and pack more densely [Tarleton and Wakeman, 1992].

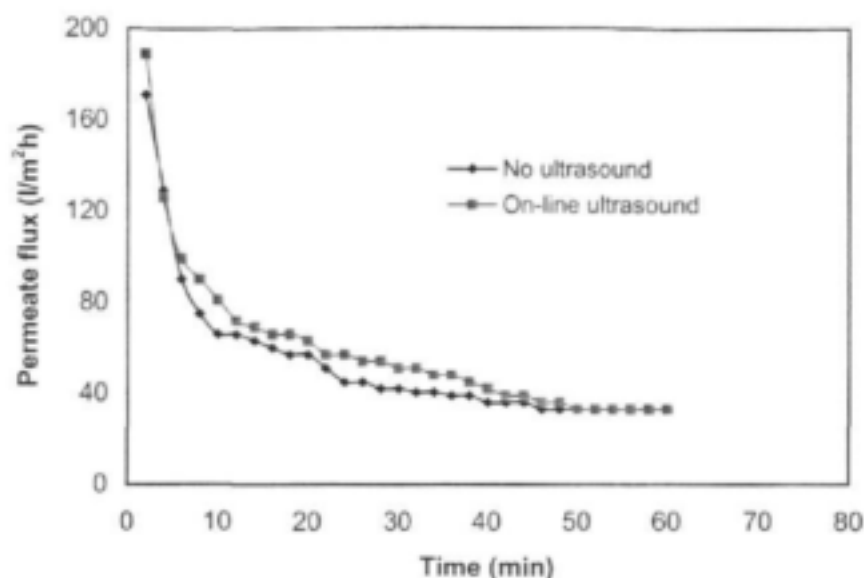


Figure 6.3: Changes in the permeate flux with and without ultrasonic irradiation during paper effluent fouling experiment at 50 kPa and 0.125 m/s.

6.4.2 RECOVERY OF FLUX BY DIFFERENT CLEANING METHODS

The effect of membrane cleaning by three different cleaning methods was investigated: forward-flushing, ultrasonic cleaning and ultrasound associated with forward flushing. To compare the efficiencies of these methods, nylon membranes were fouled, under the same conditions, with effluent fouled by the DAF product from the paper industry, after pure water filtration. Each cleaning process was then applied, individually, for 10 min, after 80 min of fouling operation. These nylon membranes were used to filter pure water, under the same conditions and their permeate fluxes determined. A graphical representation of permeate flux versus time is shown in Figure 6.4.

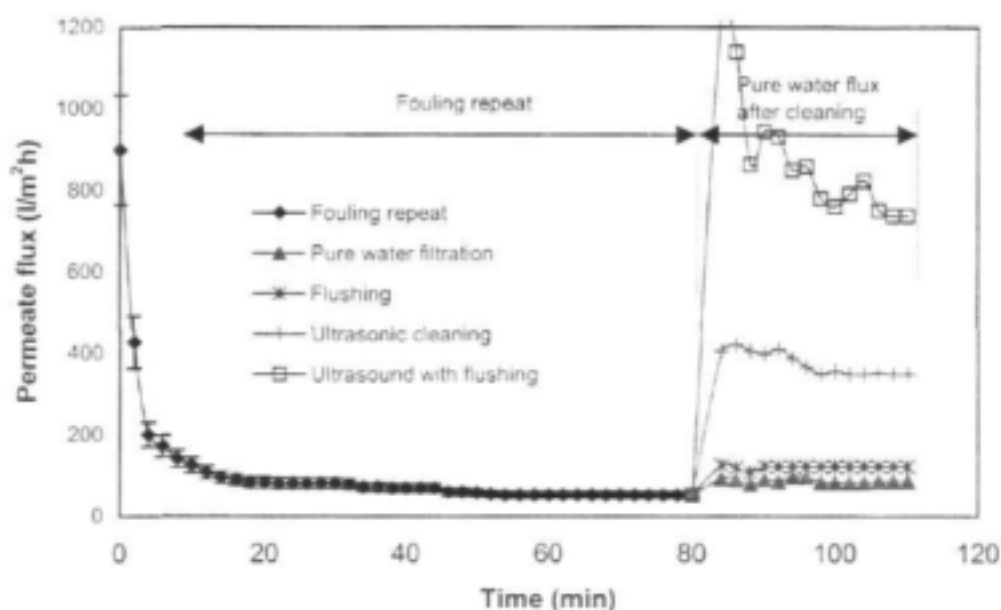


Figure 6.4: Effect of different cleaning methods on the water flux through a membrane after 80 min of fouling operation by paper-mill effluent: water filtering, forward-flushing, ultrasonic cleaning and ultrasound with forward-flushing.

At the beginning of fouling operation the permeate flux declined rapidly, followed by a more gradual decline after 20 min fouling (Figure 6.4). The permeate flux was 52.8 l/m²h after an 80-min fouling period. When the feed was changed from the effluent to pure water, the permeate flux increased to 86.4 l/m²h after 30 min of pure water filtration, because of a reduction in concentration polarisation. Forward flushing increased the water permeate flux from 86.4 l/m²h to 122.4 l/m²h after 110 min of operation. An increase in the water permeate flux was observed after ultrasound cleaning. It is suggested that ultrasonic irradiation can effectively clean membrane fouling in MF. The value of 350 l/m²h at 30 min of pure water operation obtained after ultrasonic cleaning was however still lower than the original water flux of 900 l/m²h. Hence, ultrasound associated with forward flushing was applied in an effort to restore the permeate flux of the membrane. The water permeate flux of the membrane cleaned by ultrasound with forward flushing was 738 l/m²h at 30 min of pure water operation. In this case results showed that ultrasound associated with flushing was the most effective of the cleaning methods investigated.

In an effort to obtain a better understanding of the fouling and cleaning processes we calculated the various resistances of the membrane during the fouling and cleaning procedures. The permeate flux during MF is usually written in terms of trans-membrane pressure difference (ΔP) and a total resistance, according to the resistance model [Jiraratannon and Chanachai, 1996; Mulder, 1991]:

$$J = \Delta P / (\mu R_t) \quad (6.1)$$

where: J is the permeate flux of solution (m/s), ΔP is the trans-membrane pressure difference [kPa], R_t is the total resistance [m^{-1}] and μ is the viscosity of the permeate solution [Pa.s]. The viscosity of the paper effluent in the experiments was measured to be 1.02×10^{-3} Pa.s at 20 °C. In this study, the total resistance R_t is defined as

$$R_t = R_m + R_r + R_f \quad (6.2)$$

where: R_m , the resistance of new or clean membranes, can be calculated from Equation 6.1, written for pure water, i.e.

$$J_w = \Delta P / (\mu_w R_m) \quad (6.3)$$

where: J_w is the pure-water permeate flux for a new membrane [m/s] (as at 30 min of pure water operation); μ_w is the viscosity of pure water [Pa.s]; R_r is a reversible resistance i.e. particle polarisation, cake layer, and R_f is a fouling resistance, an irreversibly adsorbed layer which cannot be removed by water cleaning. R_r is removed by cleaning the membrane with water at a low flow rate (<12.5 cm/s). The water flux measured after different cleaning methods is J_w . Therefore,

$$R_m + R_t = \Delta P / (\mu_w J_w) \quad (6.4)$$

Each resistance can be calculated using the experimental data and Equations 6.1 - 6.4.

Table 6.2: Various resistances R ($\times 10^{12} \text{ m}^{-1}$) and their percentages during fouling

Resistances	R ($\times 10^9 \text{ m}^{-1}$)	%
R_m	0.4	6
R_r	2.33	34.9
R_f	3.95	59.1
R_t	6.68	100

Note: R_m , the resistance of new or clean membranes; R_r , a reversible resistance; R_f , fouling resistance; R_t , total resistance.

Table 6.2 shows various resistances and their percentages during fouling. The membrane resistance was 6 % of the total resistance. Therefore, the main resistances of the fouled membrane were R_c and R_f . This is because concentration polarisation and fouling layers appeared on the membrane surface during fouling. The reversible resistance, R_r , is 34.9% of the total resistance. It is known that changing operating conditions or using flow destabilisation can reduce reversible resistance, enhance the mass transfer coefficient and increase permeate flux. Fouling resistance, R_f , is 59.1 % of the total resistance. R_f was 1.7 R_r , meaning that fouling was the main cause of the decrease in permeates flux in MF.

To compare the effectiveness of these cleaning methods, the cleaning efficiency E_c was defined as follows:

$$E_c (\%) = (R_f - R_c) / R_f \times 100 \quad (6.5)$$

where: R_f and R_c represent the resistance (m^{-1}) of fouling layer and residual fouling layer, respectively. (This allows R_c to be zero for a perfect clean and gives $E_c = 100\%$.) R_c was calculated from Equation 6.4. Table 6.3 shows R_c and E_c for each cleaning method. It is seen that flushing can decrease the fouling resistance by only 8.8%. It is suggested that paper effluent fouling is difficult to clean using only water cleaning or flushing. In this case, membrane fouling is caused by the adsorption of foulant both on and inside the membrane. This membrane fouling is irreversible and additional cleaning methods are needed.

Ultrasonic cleaning is an effective method to decrease membrane fouling in MF. It was determined that ultrasonic irradiation can reduce the fouling resistance by 84%. Under similar conditions, the cleaning efficiency of ultrasound associated with flushing was 97.8%. This suggests that both procedures are necessary to completely remove the foulant from a membrane. It is known that in many liquids high-energy ultrasound (a horn transducer with a frequency of 20 kHz and a power density of 82.9 W/cm² in this study) produces observable effects such as cavitation, the rapid movement of fluid caused by variations of sonic pressure, and micro-streaming [Wakeman and Tarleton, 1991].

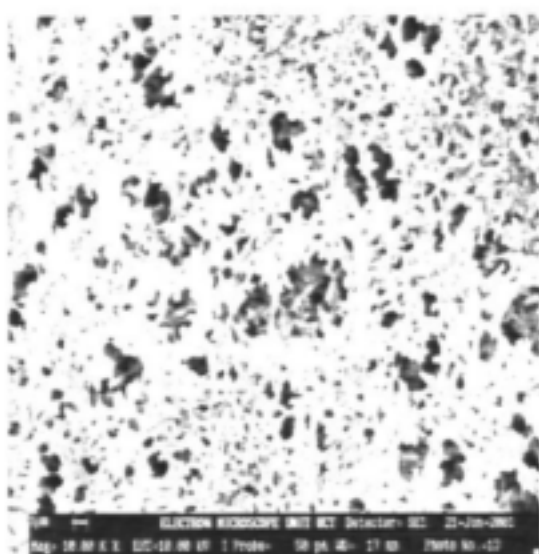
Table 6.3: The resistance of the residual fouling layer R_c ($\times 10^{11} \text{ m}^{-1}$) and cleaning efficiency E_c (%) of different cleaning methods

Cleaning methods	R_c ($\times 10^{11} \text{ m}^{-1}$)	E_c (%)
Flushing	36	8.8
Ultrasound	6.3	84
Ultrasonic flushing	0.88	97.8

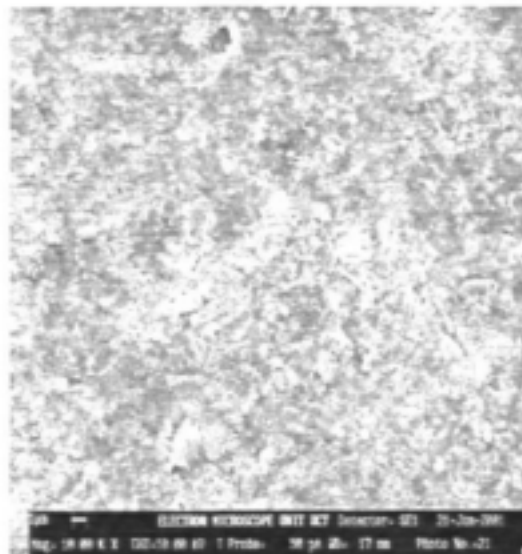
6.4.3 SCANNING ELECTRON MICROSCOPY

To further investigate the effect of different cleaning methods on the fouling layer of a nylon membrane, Figure 6.5 shows SEM micrographs of new, fouled and cleaned MF membranes. The image of a new membrane surface (Figure 6.5a) shows the typical membrane surface structure, including the membrane pores. Figure 6.5b shows that after 80 min of operation, only some larger pores remained partially unblocked. Inductively coupled plasma analysis showed that the main chemical composition of the fouling layer is breakdown products of lignin or lignosulphonate [Domingo, 2001].

The surface of the fouled membrane appeared to have more pores after forward flushing (Figure 6.6 a). This indicated that forward flushing could partly reduce fouling resistance. It was, however, difficult to remove all fouling matter by flushing alone. Ultrasonic irradiation can loosen, break and disperse the fouling layer because of ultrasonic cavitation and acoustic streaming (Figure 6.6 b). Hence, the permeate flux increased after ultrasonic cleaning although some fouling still remained on the membrane surface. The clear pore structure of the cleaned membrane (Figure 6.5) was seen again after ultrasound with forward flushing because this cleaning method can completely remove the fouling from the membrane surface.

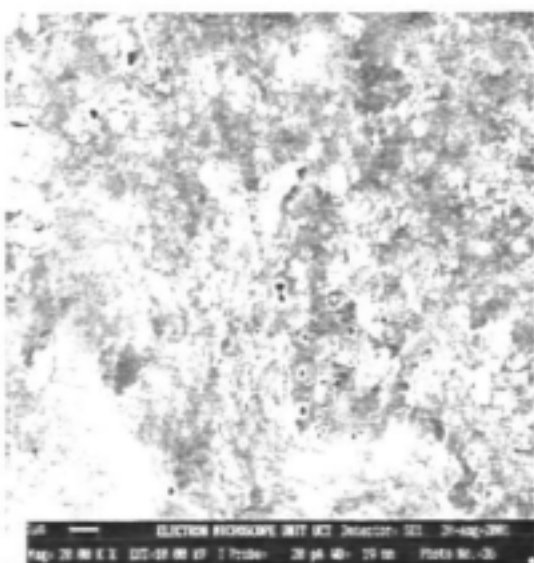


(a)

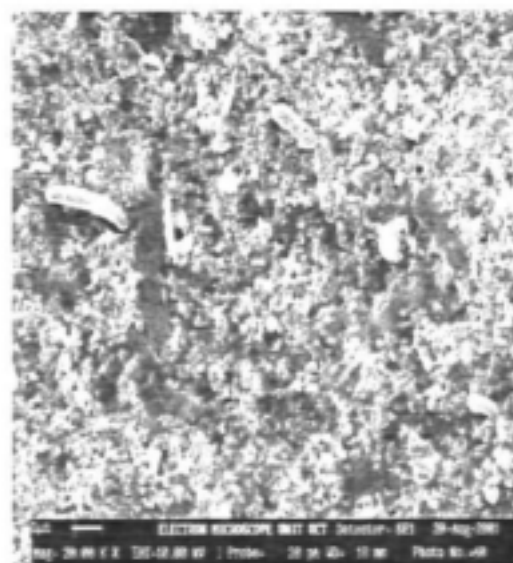


(b)

Figure 6.5: SEM micrographs of nylon membranes: (a) new membrane; (b) fouled membrane.



(a)



(b)

Figure 6.6: SEM micrographs of nylon membranes cleaned by (a) forward flushing; (b) ultrasonic irradiation.

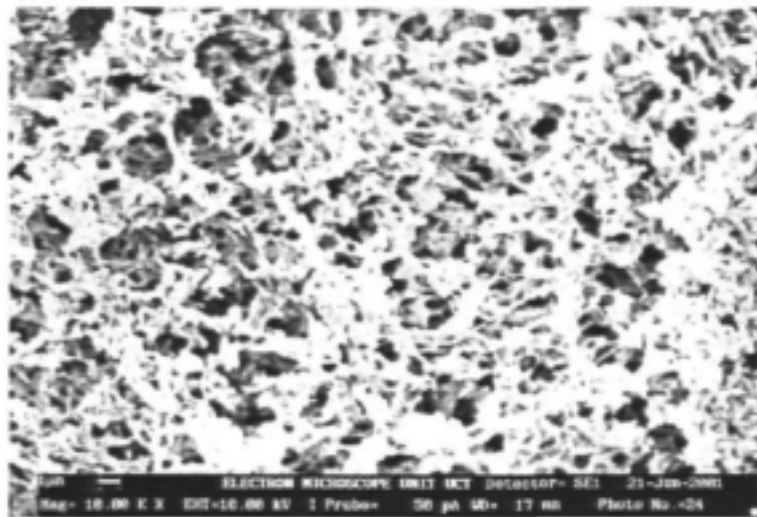


Figure 6.7: SEM micrographs of nylon membrane cleaned by ultrasonic forward flushing.

6.4.4 EFFECT OF DIFFERENT CROSSFLOW RATES DURING ULTRASONIC IRRADIATION

Fouling involves the accumulation and compaction of retained material at a membrane surface, while the solvent (water) passes through the pores. The deposited fouling layer is expected to become re-suspended and swept away by tangential- or cross-flow [Perusich and Alkire, 1991]. So, the different forward-flushing velocities resulted in different cleaning efficiencies.

The effect of different forward flushing velocities with ultrasonic irradiation is shown in Figure 6.8. Forward flushing slightly increased the water permeate flux (compared with water flow) even when the velocity was increased from 0.21 to 0.56 m/s. This indicated that a fouling layer accumulated and compacted on/within the membrane surface and that it was difficult to clean it and sweep it away by the forward flushing method only. Figure 6.8 also shows that ultrasound with forward flushing can apparently enhance water permeate flux, as the forward flushing velocity increased from 0.21 to 0.56 m/s under ultrasonic irradiation. This is because of the effectiveness of ultrasound and forward flushing. The forward flushing produces a high tangential or cross-flow rate on fouling layers as the forward flushing velocity increases.

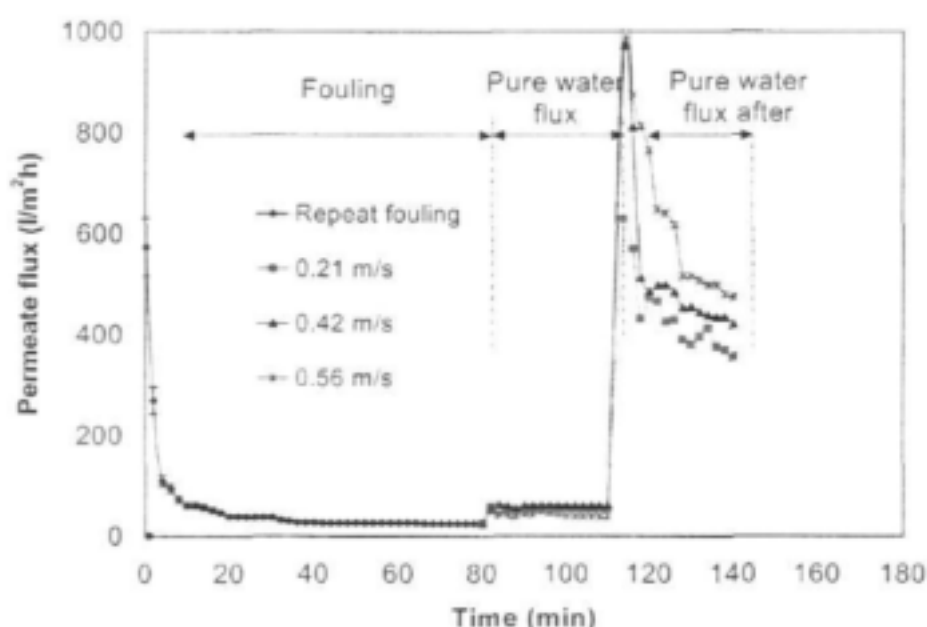


Figure 6.8: Effects of different forward flushing velocities on the recovery of permeate flux.

Note: The water filtration is used for cleaning and examining the recovery of permeate flux after an 80 min fouling period at the same pressure and flow rate as used in the fouling phase.

6.4.5 EFFECT OF DIFFERENT CLEANING TEMPERATURES ON FLUX

Since temperature influences the cleaning efficiency of ultrasound [Zhu and Liu, 2000], the cleaning performance of flushing under ultrasound was examined at different cleaning temperatures. Nylon membranes were again fouled for 80 min, then cleaned by ultrasound associated with forward flushing (velocity: 0.4 - 0.5 m/s) at temperatures of 23, 30 and 40°C, for 10 min. The pure water fluxes of the cleaned membranes were determined under the same operating conditions.

Figure 6.9 shows the changes in permeate fluxes during fouling and after cleaning. It is seen that the water permeate flux of the nylon membrane decreases as the cleaning temperature increases from 23 to 40°C. Firstly, this is due to a change in the ultrasonic cavitation intensity as the temperature decreases [Zhu and Liu, 2000]. Ultrasonic cleaning of the MF membrane is mainly caused by ultrasonic cavitation and the acoustically excited bubble break-ups on the membrane surface. An increase in solution temperature gives rise to an increase in the vapour saturation pressure in the bubble so that the shock-wave intensity during the bubble break-up is reduced. In other words, the cavitation effectiveness decreases. Secondly, the fluid viscosity also changes with temperature and could have caused the change in ultrasonic effectiveness. An increase in the viscosity of a liquid will result in an increase in the threshold of cavitation

[Mason, 1989]. There will probably be several different types of cavity in the liquid: (a) an empty cavity (true cavitation), (b) a vapour-filled cavity, (c) a gas-filled cavity, and (d) a combination of vapour and gas filled cavities. A lower temperature favours the formation of empty cavities.

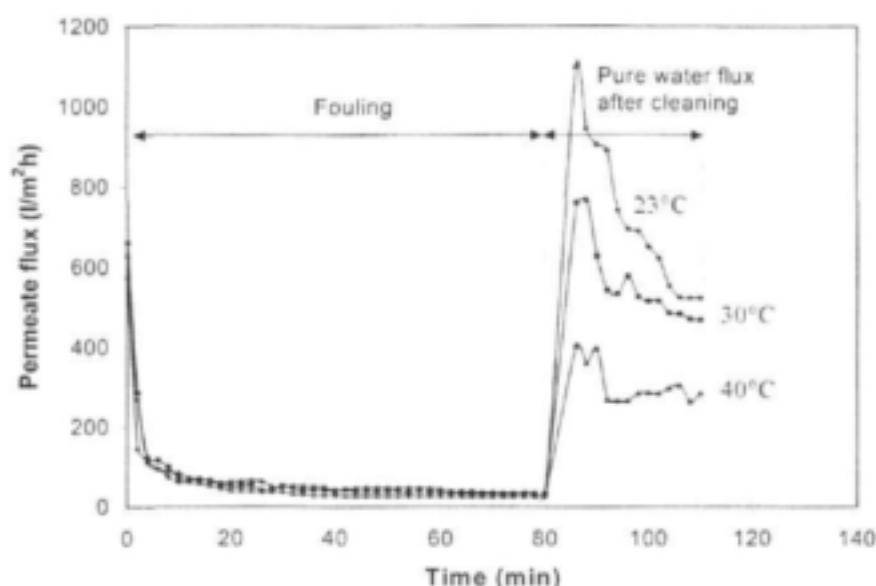


Figure 6.9: Effects of different temperatures of ultrasound on the recovery of permeate flux.

6.5 CONCLUSIONS

This study described the effect of ultrasound on the cleaning of nylon MF membranes. Nylon membrane were fouled by pulp paper effluent and cleaned by the methods of forward flushing, ultrasonic cleaning and ultrasound associated with forward flushing. The cleaning efficiencies were determined by pure water flux comparisons.

Experimental results showed that ultrasound associated with flushing was the most effective of these cleaning methods. Cleaning by this method cleaned fouled membranes and restored the original membrane morphology. Resistance analysis indicated that the cleaning efficiencies of ultrasonic cleaning and ultrasound with forward flushing were 87% and 97.8%, respectively. It was also found that high forward flushing velocity combined with ultrasound was also beneficial for cleaning.

To be effective, the flushing velocity should be greater than the normal operating velocity. At different cleaning temperatures, under ultrasonic irradiation, the pure water flux increased as the cleaning temperature decreased from 40 to 23°C.

7. MEASUREMENT OF CAKE-LAYER DEPOSITION, GROWTH, COMPRESSIBILITY AND ITS REMOVAL IN MICROFILTRATION

7.1 ABSTRACT

Further investigation of cake-layer deposition, its growth and compressibility in MF by UTDR was required. Ultrasonic response signals were recorded as particles deposited and a cake layer formed on a nylon membrane surface. The ultrasonic testing technique can measure the cake thickness as a function of time. Results also showed that the ultrasonic unit is a suitably programmed microprocessor, and can be used to compare reference and test waveforms. It produced a separated signal (from reference and test waveforms), indicating the state and progress of the cake layer on the membrane surface under operating conditions.

A predictive modelling program - ultrasonic reflection modelling (URM) - was developed, to better understand the processes related to the deposition of cake layers on the membrane surface. The modelling program can predict the shape of the curve of the ultrasonic wave at the beginning of the signals, indicating the cake compressibility. In MF, the flux decline is related to not only the layer thickness but also the cake density (compressibility). Changes in the densities of cake layers as well as their thickness can be substantiated by the modelling. The predicted results were in good agreement with the actual measurements.

7.2 INTRODUCTION

The significant flux decline during microfiltration is as a result of particle deposition and the build-up of a filter cake on the surface of a septum or the membrane.

A variety of theoretical models quantitatively describing the fouling phenomenon during microfiltration have been developed [Vyas et al. 2001]. These can be classified mainly into: (1) resistance models, including the standard blocking model [Hermia, 1982]; the cake filtration model [Persson and Nilsson, 1991]; blocking law [Persson and Nilsson, 1991] and the resistance in series model [Persson et al, 1993]; (2) particle back-transport models, including Brownian diffusion [Green and Belfort, 1980]; shear-induced diffusion [Zydney and Colton, 1986] and inertial lift [Altena and Belfort, 1984]; (3) flowing cake and surface transport models [Vyas et al. 2001].

The compressible cake filtration model describing the filtration behaviour of particulate suspensions is applicable to cross-flow microfiltration [Shirato et al. 1969, Tiller, 1975; Murase et al. 1995; Tiller and Kwon, 1998; Tiller and Li, 2001]. From practical experience, it is acknowledged that flow through compressible cakes composed of deformable particles results

in a highly non-uniform structure, with a tight skin layer of very low porosity next to the supporting medium. This skin layer often has adverse effects; such that, increasing the filter pressure has little effect on the flow rate or average porosity. This usually results in an erroneous prediction of the filtration rate if a rigid particle cake is assumed when using the conventional cake filtration theory. Therefore, various theoretical models to describe concentration polarisation and to predict the filtration rate during cross-flow filtration are based upon the assumption of the incompressibility of the fouling layer and the rigidity of suspensions [Altena and Belfort, 1981; Zydney and Colton, 1986; Davis and Leighton, 1987; Romero and Davis, 1990; Blake et al. 1992]. Although these models are able to quantitatively predict the steady-state flux for some types of particles, they provide no detailed information about how the skin layer is formed on the filter septum/membrane because of the unavailability of a suitable non-destructive measurement technique to measure fouling build-up in real-time.

Most cross-flow microfiltration studies have typically been limited to measurements of filtrate flux alone because cake thickness information was not available. Over the last ten years, however, numerous experimental methods have been used to study cake deposition and characterisation so as to infer the possible mechanisms. The methods used to measure cake layer thickness can be classified into two broad categories: destructive [Al-Malack and Anderson, 1996; Schmidt and Löffeler, 1990; Vyas et al. 2000] and non-destructive measuring methods [Tiller et al. 1995; Wakeman, 1994; McDonogh et al. 1995; Li and Fane, 1998; Mores and Davis, 2001]. Although these destructive measuring methods can measure cake thickness and porosity, they provide little information regarding the actual and dynamic build-up of the cake on the membrane surface.

The work described here aims to contribute to a further understanding of the ultrasonic response signals including differential signals obtained and the deposition, growth and compressibility of a cake layer on the membrane surface. A predictive modelling program - ultrasonic reflection modelling (URM) was developed, to better understand the processes related to the deposition of cake layers.

7.3 EXPERIMENTAL

7.3.1 MF SYSTEM AND ULTRASONIC MEASUREMENT

The investigations carried out here were done with the MF separation system described in Section 5.3.1 (see Figure 5.1). The ultrasonic measurement system, flat-sheet module and nylon MF membrane used were also as described in Section 5.3.1. Again the feed was taken from the wastewater treatment plant of Mondi Kraft Mills, Mondi Ltd, South Africa (see Table 6).

7.3.2 EXPERIMENTAL PROCEDURE AND FOULING

The MF experimental set-up (Figure 5.1) allows for the accurate control of inlet pressure, retentate flow rate and temperature. Each experiment commenced with pure water being circulated through the system at the desired flow rate and applied pressure, for 2 h, to compress the membrane and to build up a stable flow field. Once steady state was attained, the feed was switched to the effluent solution to initiate the fouling phase in which fouling occurred. This phase was allowed to continue until the ultrasonic response and permeate flux had stabilised. The fouling experiment was carried out at flow rates of 1.83 ± 0.02 cm/s ($Re = 65 \pm 0.7$) and 6.97 ± 0.07 cm/s ($Re = 253 \pm 2.5$), applied pressure 150 ± 5 kPa and temperature $24 \pm 1^\circ\text{C}$. All runs were made in the laminar flow regime with $Re < 400$. The total operating time for the fouling experiments was about 7-18 h, depending upon the specific axial velocity employed.

7.3.3 CLEANING EXPERIMENT

To investigate the suitability of the UTDR technique for fouling removal strategies, the following fouling and cleaning experiments were carried out. First, a new fouling experiment was carried out with paper mill effluent at a flow rate of 4.2 ± 0.05 cm/s ($Re=150 \pm 1.5$), applied pressure 100 ± 5 kPa and temperature $24 \pm 1^\circ\text{C}$. The total operating time for the fouling experiments was 16 h. After the membranes were fouled with paper effluent they were cleaned by three methods, in turn, namely: forward flushing, ultrasonic cleaning and ultrasound together with forward flushing for cleaning times of 20 min each. The feed solution was changed from effluent to pure water filtration at the same operating conditions as used in the fouling phase in order to compare the cleaning efficiencies of these three methods.

In Figure 6.1, forward flushing was performed with valve V1 opened and V2 closed. The cross-flow filtration cell was immersed in a water bath at temperature $24 \pm 1^\circ\text{C}$ during ultrasonic cleaning. The cell was irradiated with a horn ultrasonic cleaner (Medal W-375, Ultrasonics INC.) with a frequency of 20 kHz and a power of 375 w. Ultrasound associated with forward flushing was performed with intermittent forward flushing with a flow rate (40-50 cm/s) during ultrasonic irradiation. To investigate the cleaning efficiency of each cleaning method, the cleaned membrane was used to filter pure water under the same operating condition as used in the fouling phase. The UR measuring system captures the changes in ultrasonic signal responses after different cleaning methods. These data can be stored on a computer's hard drive.

7.4 RESULTS

7.4.1 CROSSFLOW MF AND ULTRASONIC MEASUREMENTS

The pure water filtration was carried to investigate the resolution capabilities of the UR technique and obtain pure water flux of the membrane and reference waveform inside the cell during the steady state. Figure 7.1 plots the ultrasonic signal amplitude in volts (V) vs. the arrival time in seconds (s) inside the cell. Each peak corresponds to a reflected acoustic wave from one of the multiple interfaces in the flat cell. Note: Peak A is a reverse signal because the sound wave travels from high impedance Perspex ($W_{\text{perspex}} = 2.4 \text{ kg/m}^2\text{s}$) to low impedance water ($W_{\text{water}} = 1.0 \text{ kg/m}^2\text{s}$). The UR measurement was focused on at the front of Peak B, which indicates the membrane surface. Changes in flux with operation time at velocities of 1.83 and 6.97 cm/s are summarized in Figure 7.2.

The UTDR echo signals during the fouling experiments at 1.83 cm/s are shown in Figures 7.3 and 7.4. Peaks B, B' and C were generated from the interfaces: water/nylon membrane, cake layer/nylon membrane and feed/cake layer. Morphological characterisation of the fouled membrane is shown in Figure 7.5.

Results of the UTDR responses during the fouling experiments at 6.97 cm/s are shown in Figures 7.6 - 7.8. A new echo (Peak C) appeared after 5 h of fouling operation at 6.97 cm/s (see Figure 7.7a). As fouling layer growth progressed, an increase in echo amplitude was observed in Figures 7.7 and 7.8. SEM analysis showed complete membrane coverage with the cake layer in Figure 7.9. The cross-section showed the dry fouling layer and membrane thickness to be 40 μm and 90 μm (Figure 7.9d).

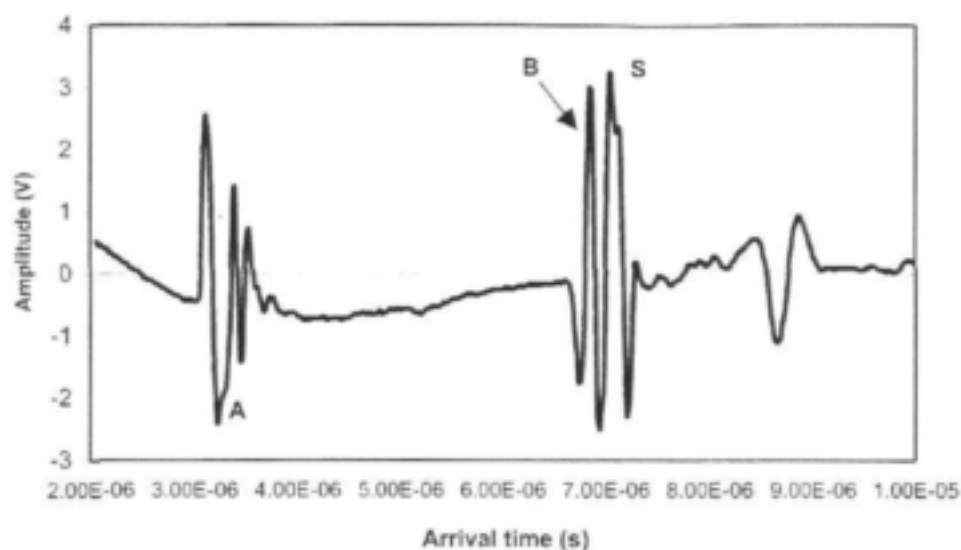


Figure 7.1: Ultrasonic spectrum inside the flat sheet cell during pure water filtration at operating pressure of 150 kPa.

Note: Peaks A, B and S were generated from the following interfaces: perspex plate/feed (water), water/nylon membrane and membrane/porous metal support.

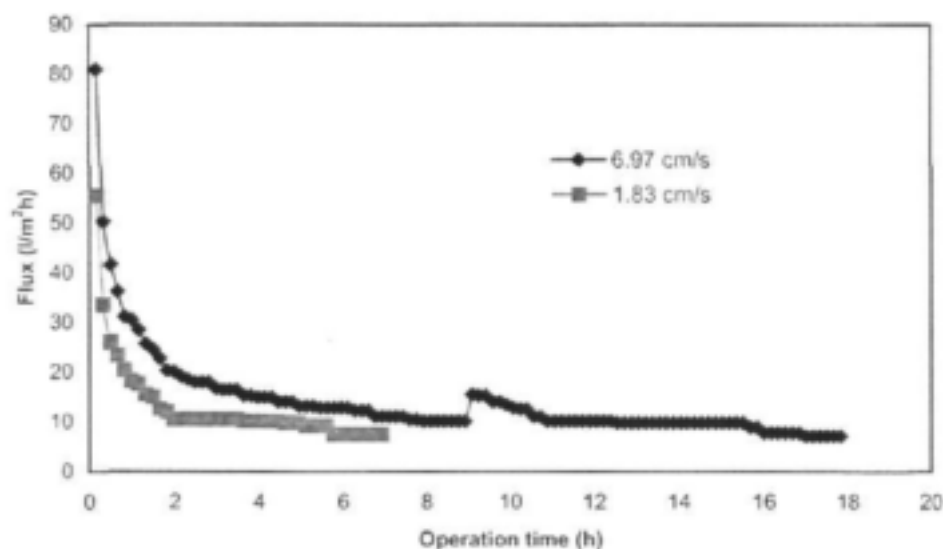


Figure 7.2: Flux decline with time in the paper mill effluent fouling experiment at flow rates of 1.83 and 6.97cm/s (stop & restart of the fouling operation at 9 h).

Ultrasonic responses:

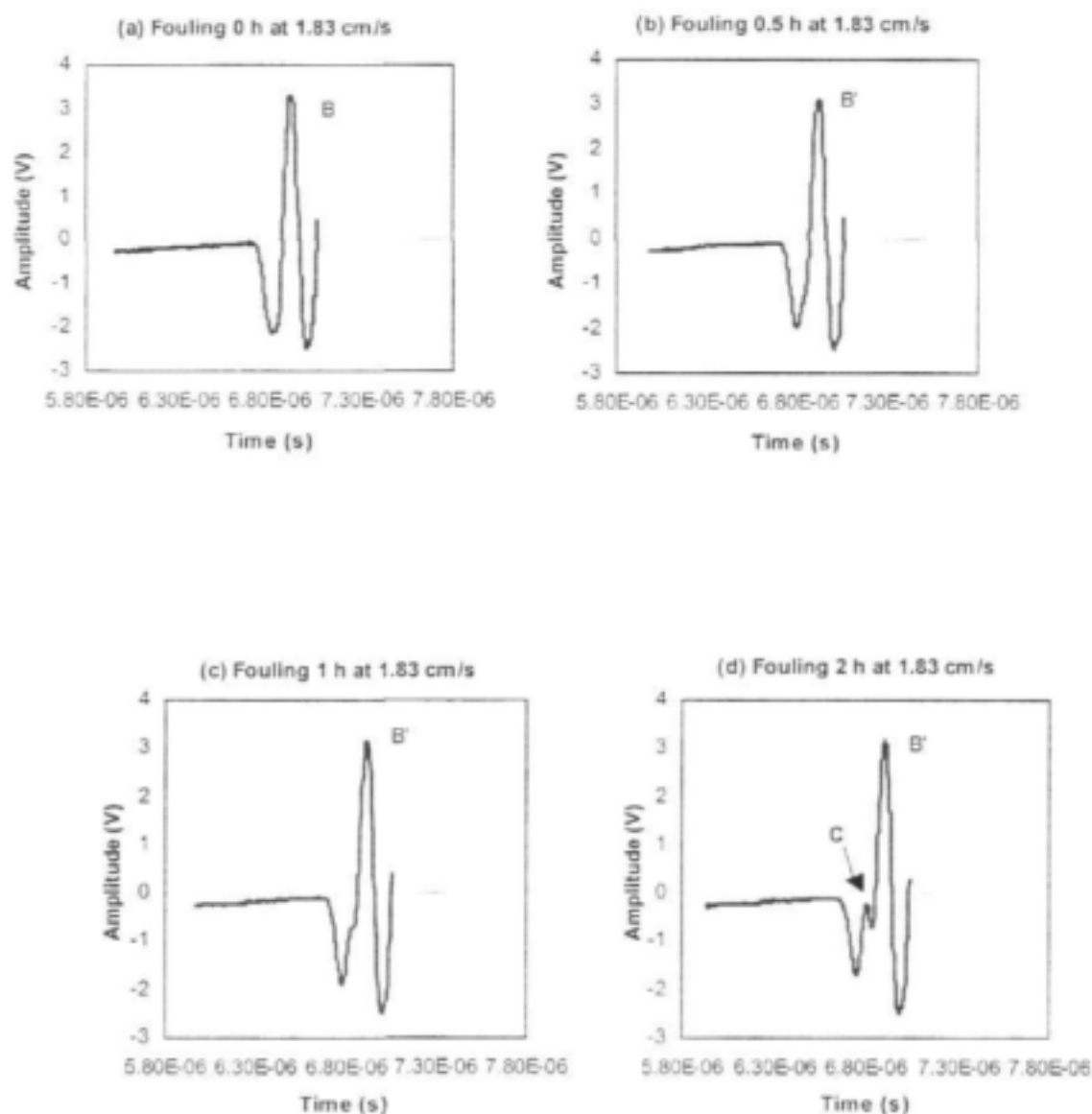


Figure 7.3: Ultrasonic responses (a) at 0 h (start), (b) after 0.5 h, (c) 1 h and (d) 2 h of operation in the fouling experiment carried out with paper mill effluent at a flow rate of 1.83 cm/s.

Note: Peaks B, B' and C were generated from the interfaces: water/nylon membrane, cake layer/nylon membrane and feed/cake layer.

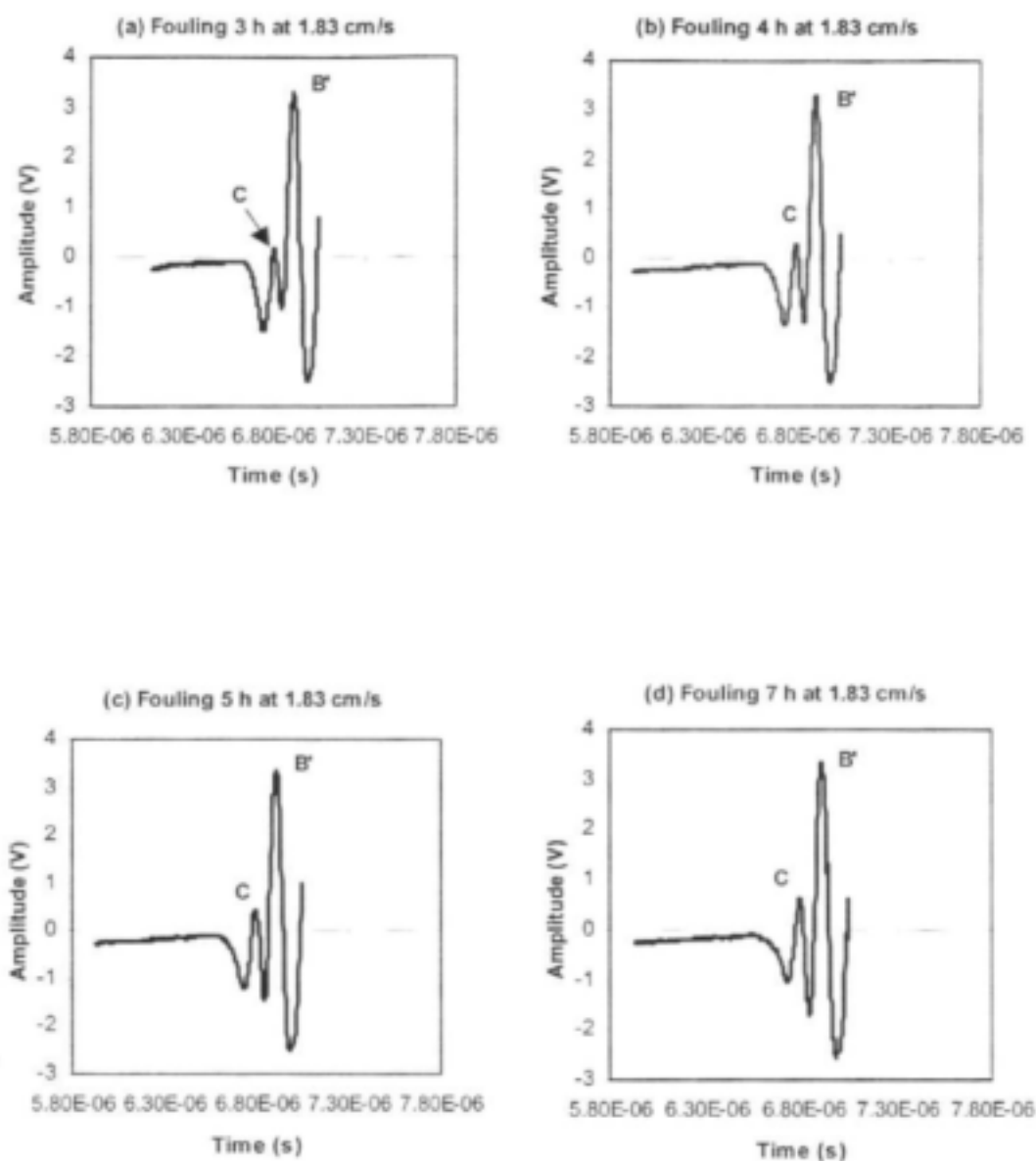
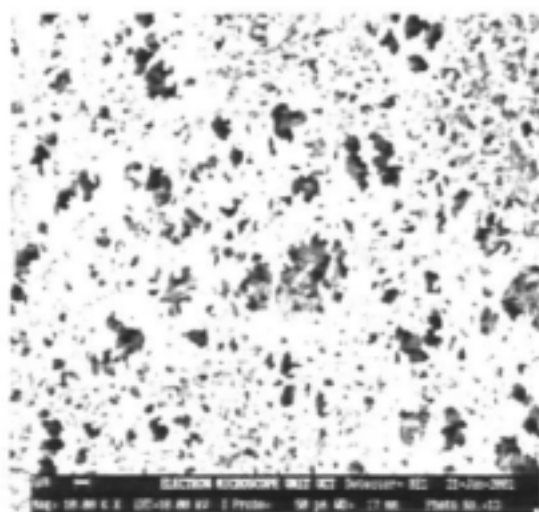
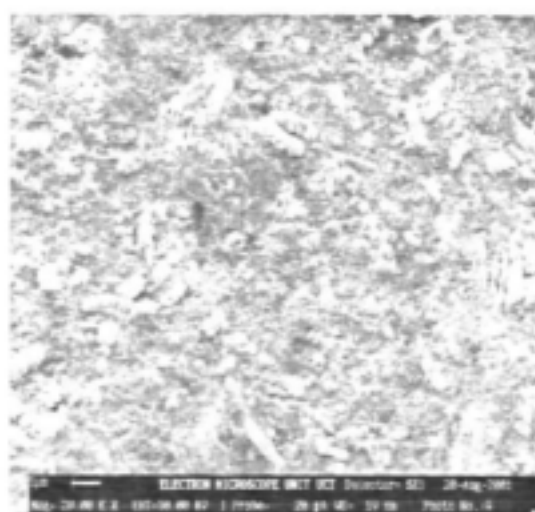


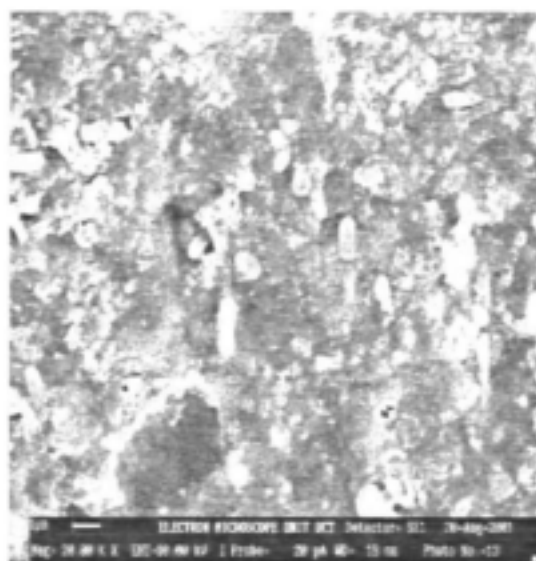
Figure 7.4: Ultrasonic responses after (a) 5 h and (b) 7 h of operation in the fouling experiment carried out with paper mill effluent at a flow rate of 1.83 cm/s.



(a)



(b)



(c)



(d)

Figure 7.5: SEM micrographs of the nylon membrane surfaces: (a) clean nylon membrane; fouled membranes after (b) 2 h and (c) 7 h of fouling operation; (d) optical micrograph: cross-section of nylon membrane fouled by paper mill effluent (1.83 cm/s, 150 kPa).

Total membrane thickness: 168 μm .

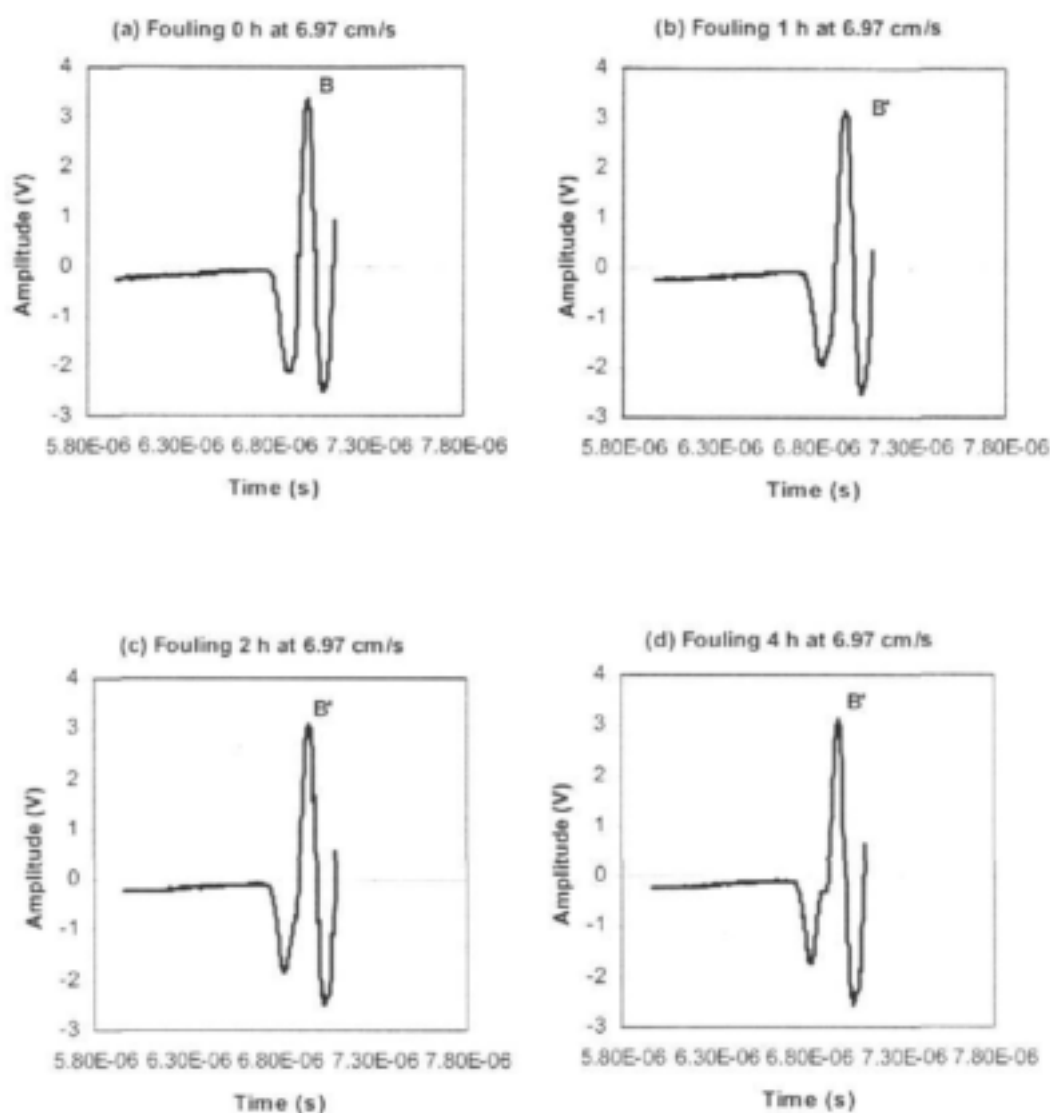


Figure 7.6: Ultrasonic responses at (a) 0 h, after (b) 1 h, (c) 2 h and (d) 4 h of operation in the fouling experiment carried out with paper mill effluent at a flow rate of 6.97 cm/s.

Note: Peaks B and B' were generated from the interfaces: feed (water)/nylon membrane and fouling/nylon membrane, respectively.

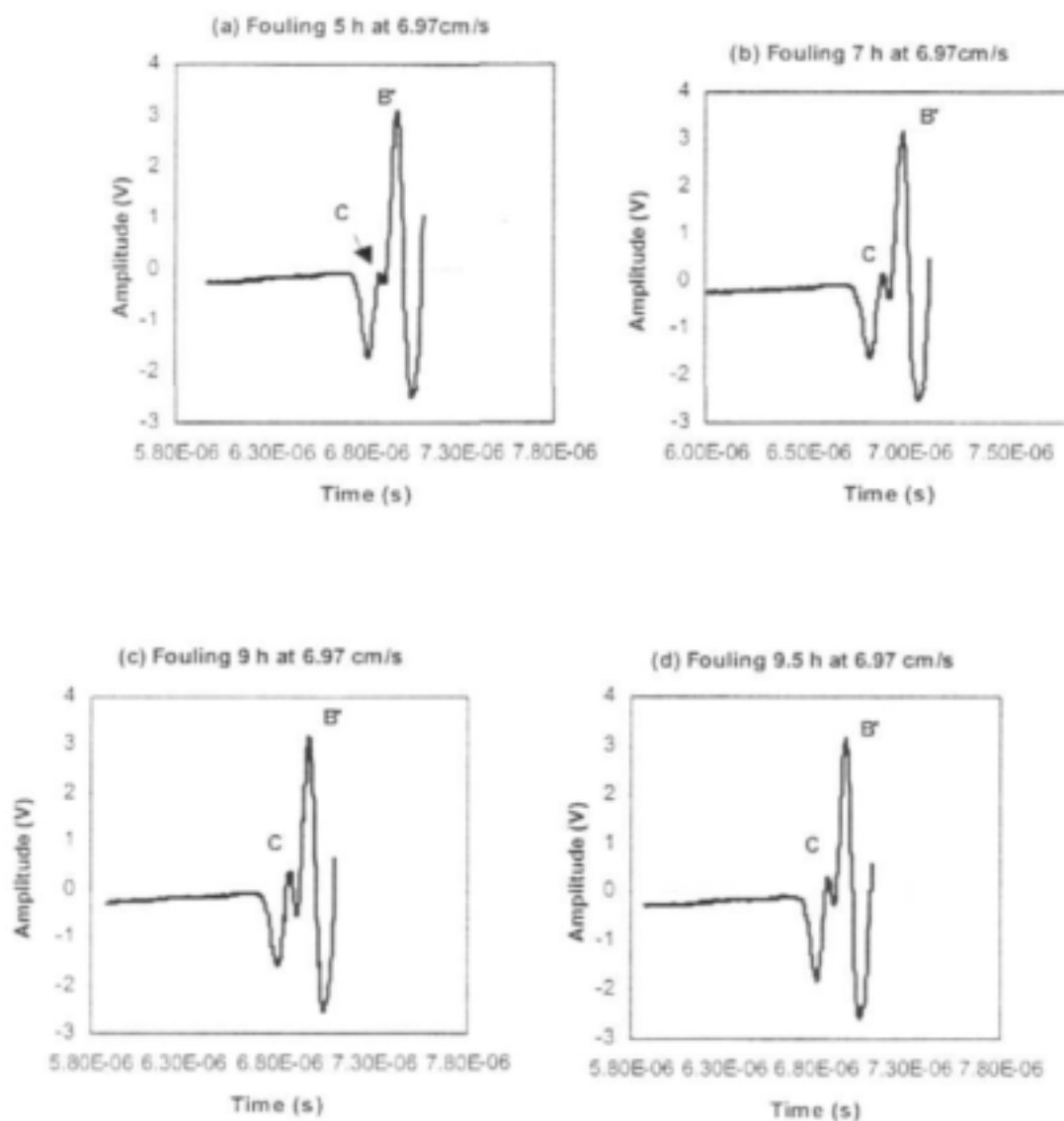


Figure 7.7: Ultrasonic responses after (a) 5 h, (b) 7 h, (c) 9 h and (d) 9.5 h of operation in the fouling experiment carried out with paper mill effluent at a flow rate of 6.97 cm/s.

Note: Peaks B, B' and C were generated from the interfaces: water/nylon membrane, cake layer/nylon membrane and feed/cake layer, respectively

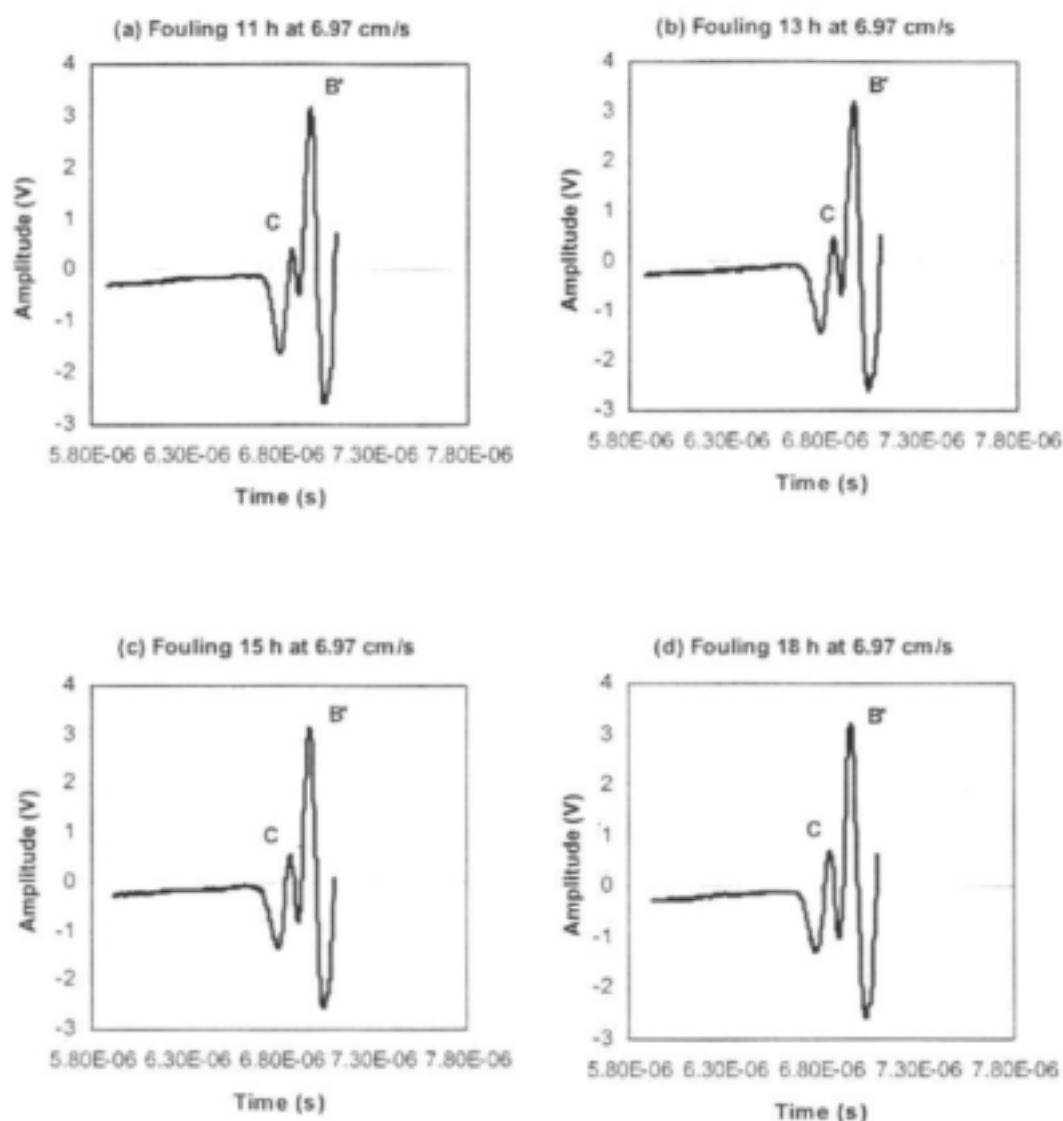


Figure 7.8: Ultrasonic responses after (a) 11 h, (b) 13 h, (c) 15 h and (d) 18 h of operation in the fouling experiment carried out with paper mill effluent at a flow rate of 6.97 cm/s.

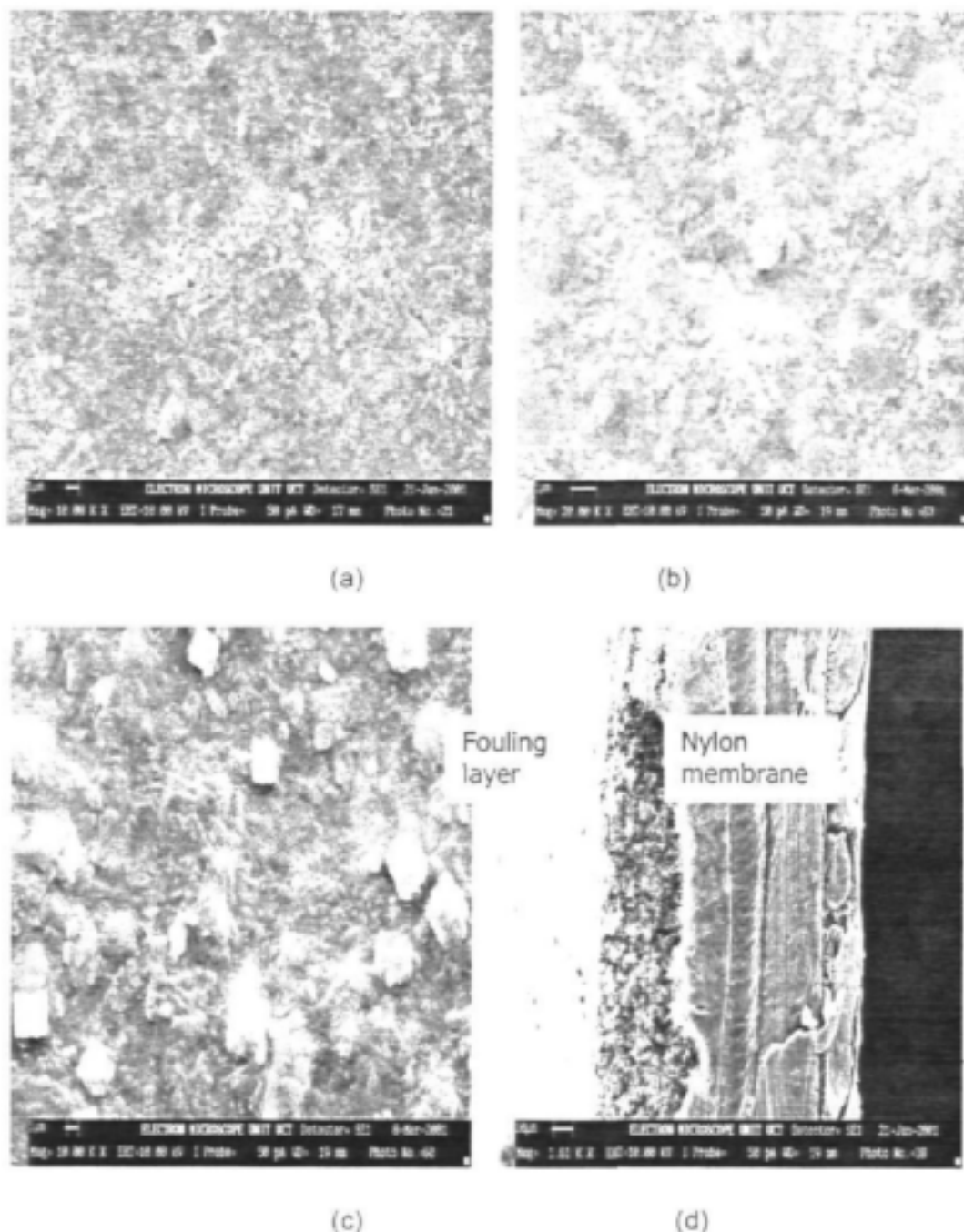


Figure 7.9: Representative SEM micrographs of the membrane surface after (a) 2 h, (b) 4 h, (c) 18 h of fouling operation (6.97 cm/s, 150 kPa) and (d) cross-sectional view of the fouled membrane after 4 h (fouled with paper mill effluent).

7.4.2 DIFFERENTIAL SIGNALS

Further studies were carried out to investigate the build-up of a cake layer and its physical state on a membrane surface so as to interpret the results observed in the above experiments. This study showed that the UTDR technique provides a means of producing a differential signal, i.e. the signal remaining after subtraction of a reference signal (clean membrane) from that obtained

from a fouled membrane. A clean membrane waveform obtained upon pure-water filtration or at fouling start (0 h) is used as the reference waveform for later use during fouling and cleaning process. A fouled membrane waveform obtained during the fouling processes can be used as a test waveform. Hence, a differential signal equals the difference between test waveform and reference waveform and the differential signal represents an echo signal of a cake layer on a membrane surface. This technique can be used to observe minor differences in a signal shape, far below the resolution limit that the wavelength imposes.

Results of differential signals during the fouling experiments carried out with the paper mill effluent at flow rates of 1.83 and 6.97 cm/s are shown in Figures 7.10 – 7.14. Note: Peak B is an echo of a clean nylon membrane (white line); Peak C' is an echo of a cake layer on the membrane surface. The growth and movement of Peak C' can be seen in Figures 7.10 – 7.14.

Changes in time- and amplitude-domain of Peak C with operation time during fouling are summarised in Figure 7.15. According to the difference in arrival times, dT , between echoes B and C', the thickness of the cake layer on the membrane surface can be calculated from Equation 3.1, as shown in Figure 7.16. The calculation is based on the parameter: $v = 1500$ m/s in the cake layer and a frequency of 7.5 MHz. Quantitative information about the cake layer during fouling processes was obtained. For instance, a cake layer thickness of down to 15 μm was determined. This was better than predicted by the theoretical resolution. As yet, there is however no known lower limit.

Differential signals:

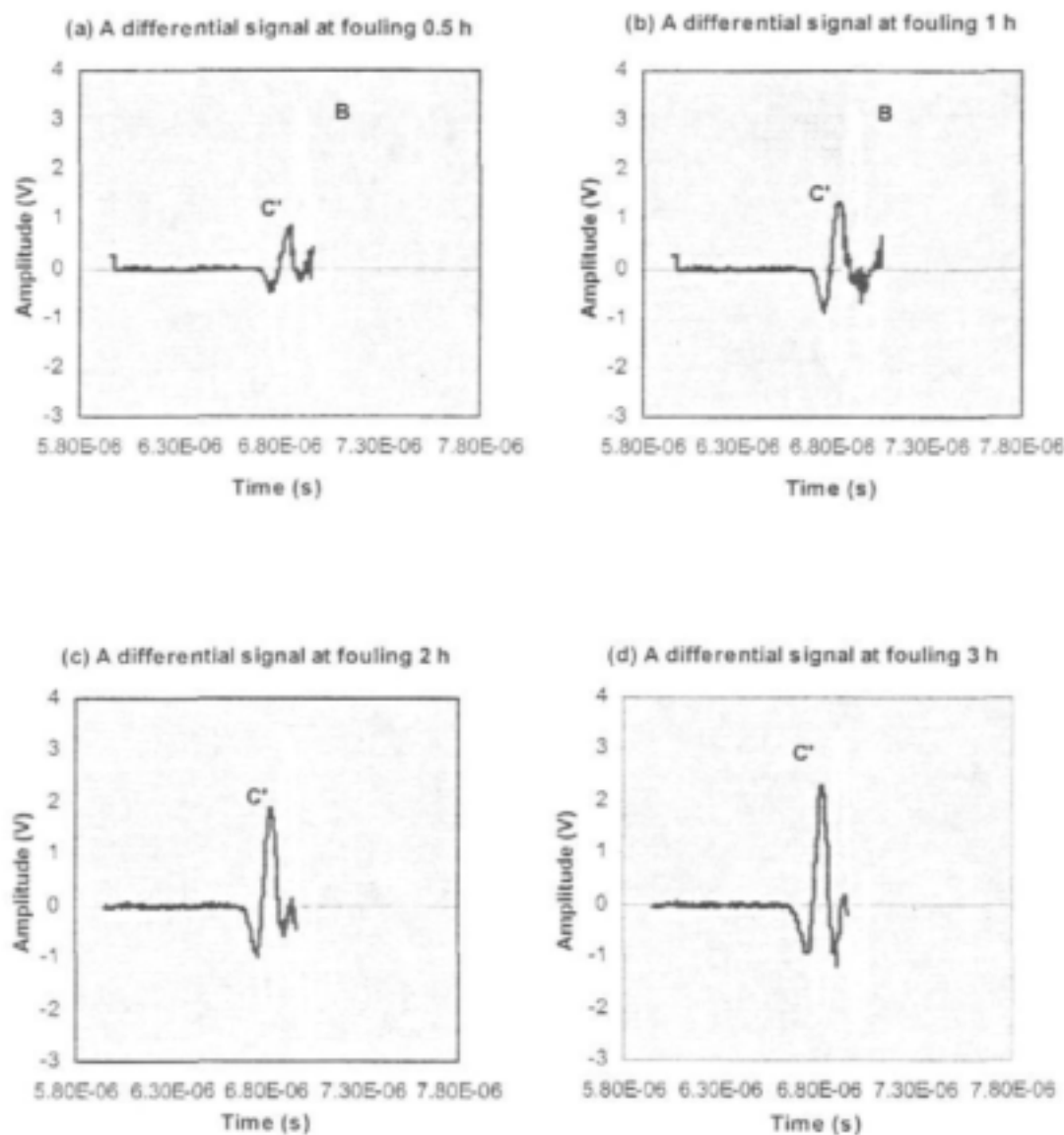


Figure 7.10: Differential signals after (a) 0.5 h, (b) 1 h, (c) 2 h and (d) 3 h of operation in the fouling experiment carried out with paper mill effluent at a flow rate of 1.83 cm/s.

Note: Peak B – echo of clean Nylon membrane (white line), Peak C' – echo of a cake layer.

Differential signals:

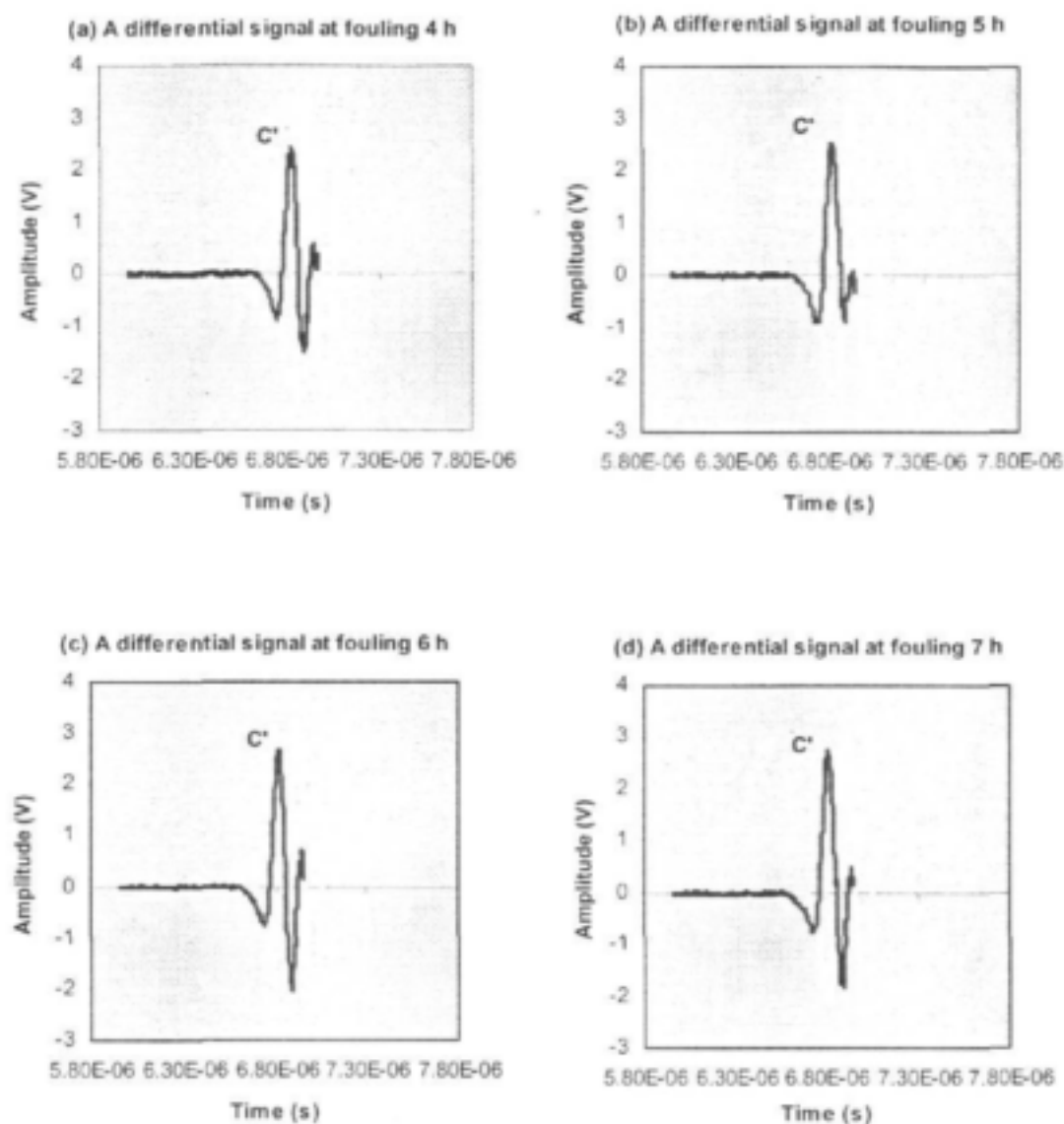


Figure 7.11: Differential signals after (a) 4 h, (b) 5 h, (c) 6 h and (d) 7 h of operation in the fouling experiment carried out with paper mill effluent at a flow rate of 1.83 cm/s.

Note: Peak B – echo of clean Nylon membrane (white line), Peak C' - echo of a cake layer.

Differential signals:

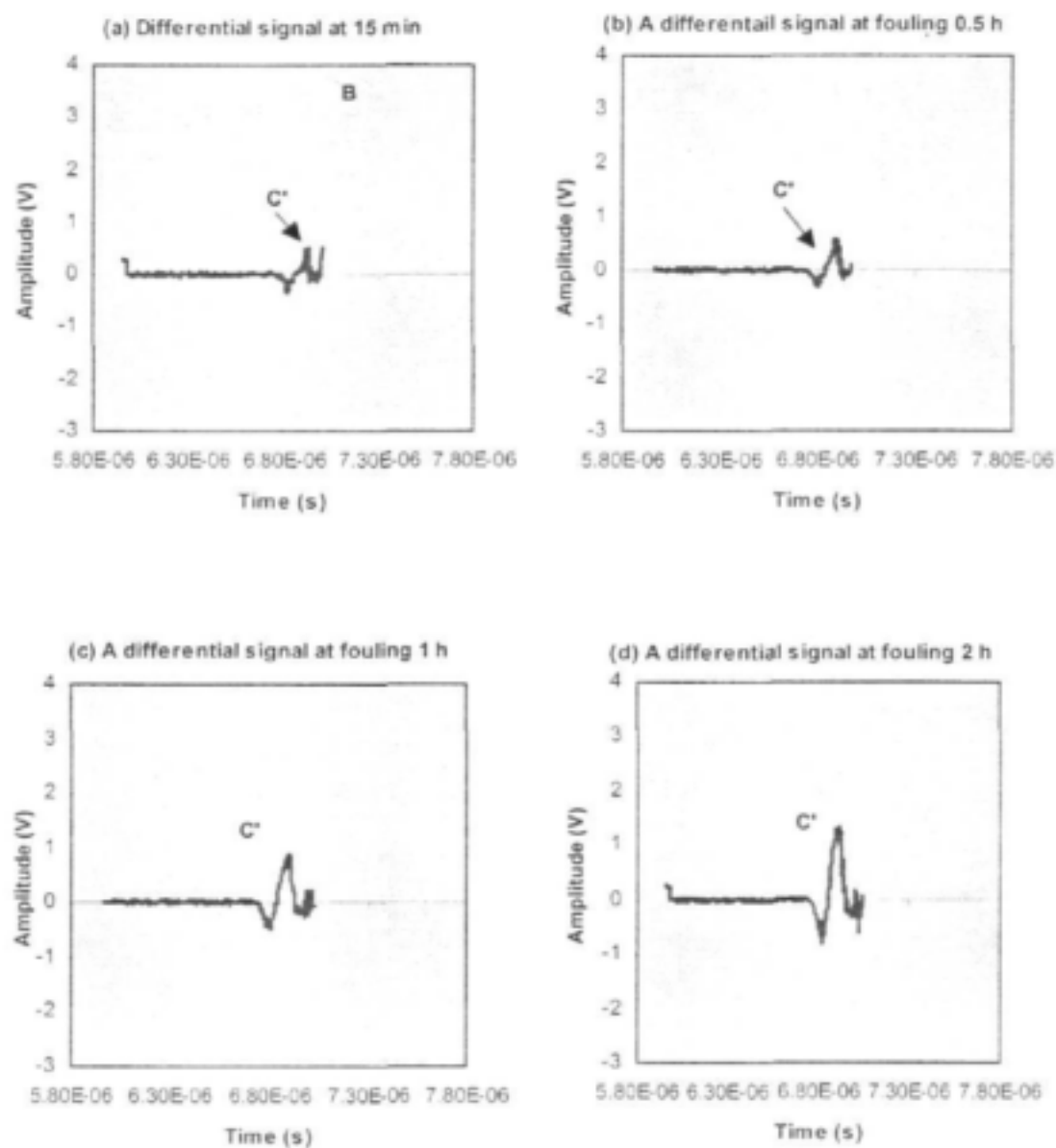


Figure 7.12: Differential signals after (a) 15 min, (b) 0.5 h, (c) 1 h and (d) 2 h of operation in the fouling experiment carried out with paper mill effluent at a flow rate of 6.97 cm/s.

Differential signals:

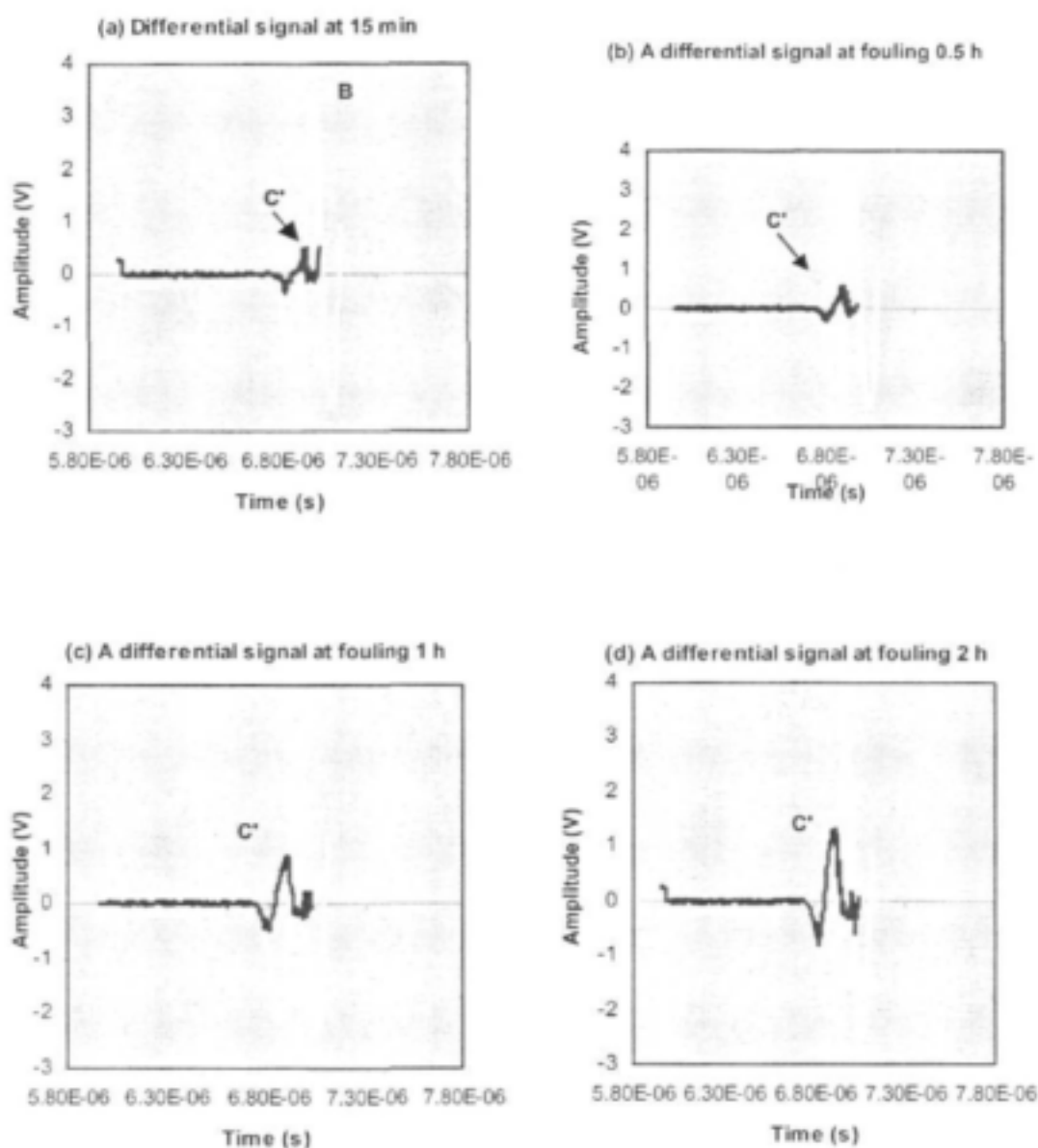


Figure 7.13: Differential signals after (a) 4 h, (b) 6 h, (c) 8 h and (d) 9 h of operation in the fouling experiment carried out with paper mill effluent at a flow rate of 6.97 cm/s.

Differential signals:

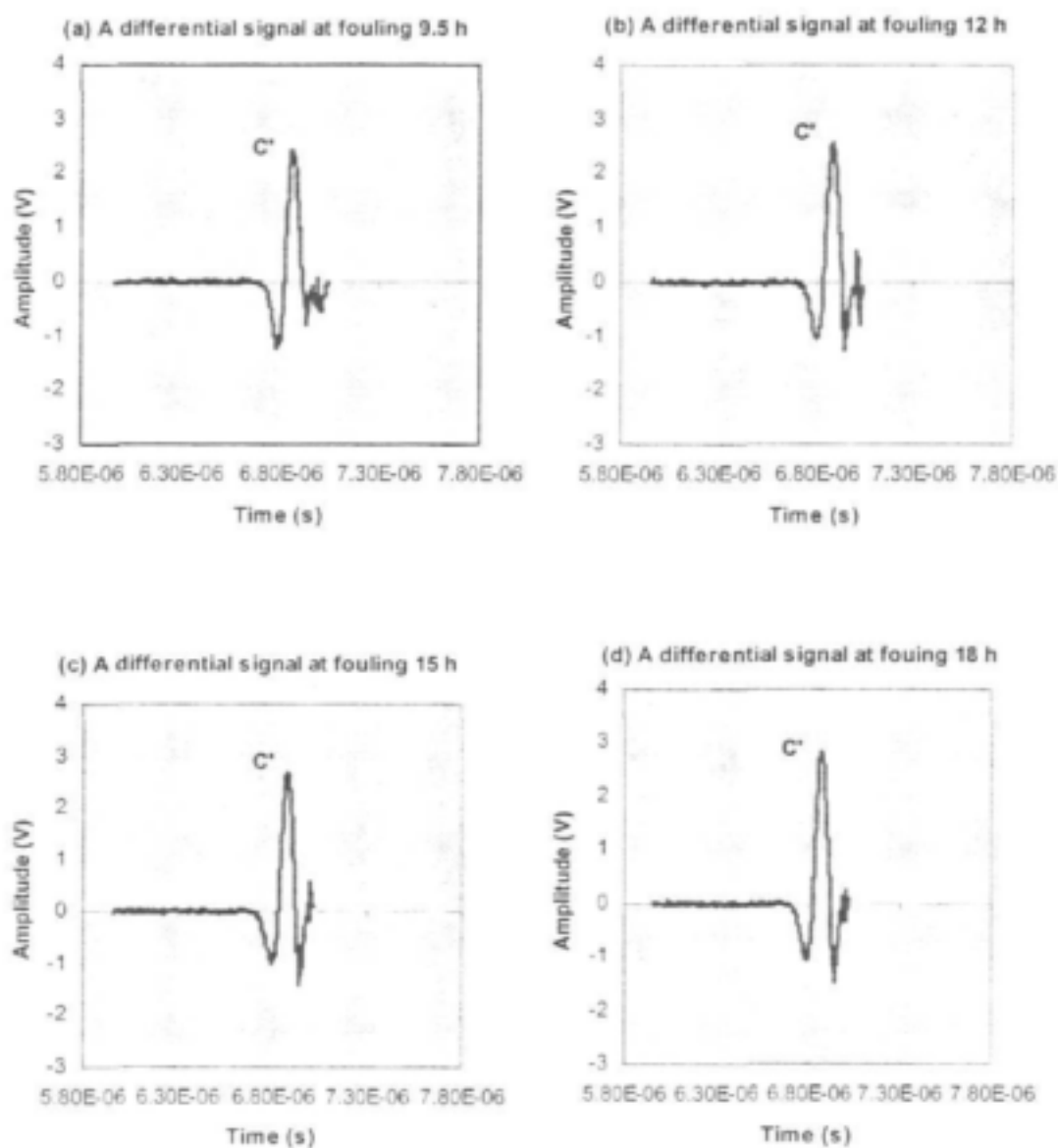


Figure 7.14: Differential signals after (a) 9.5 h, (b) 12 h, (c) 15 h and (d) 18 h of operation in the fouling experiment carried out with paper mill effluent at a flow rate of 6.97 cm/s.

Note: Stop and restart at fouling 9 h of operation.

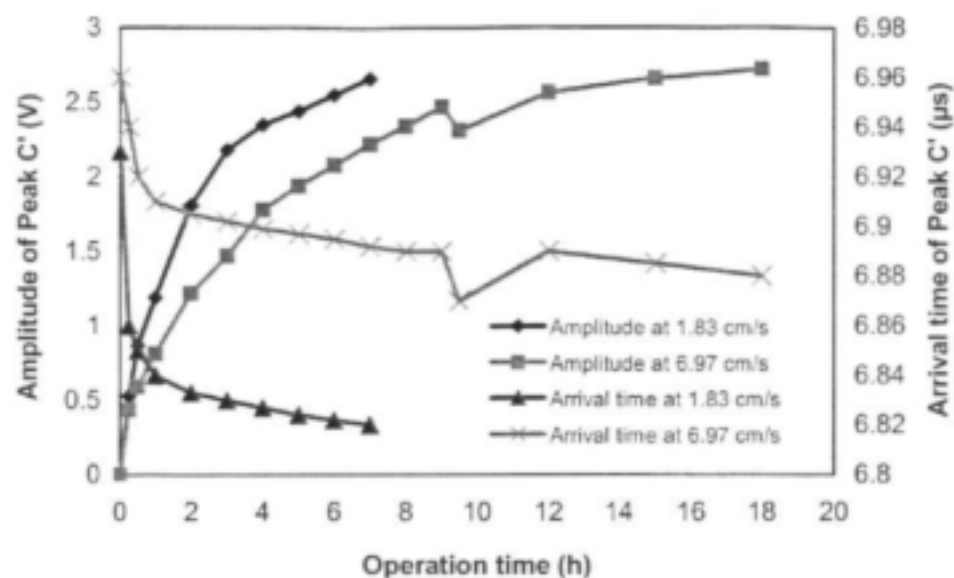


Figure 7.15: Amplitude and arrival time of differential signal (Peak C') versus operation time during the fouling experiments with paper mill effluent at flow rates of 1.83 and 6.97 cm/s (stop and restart of the fouling operation at 9 h).

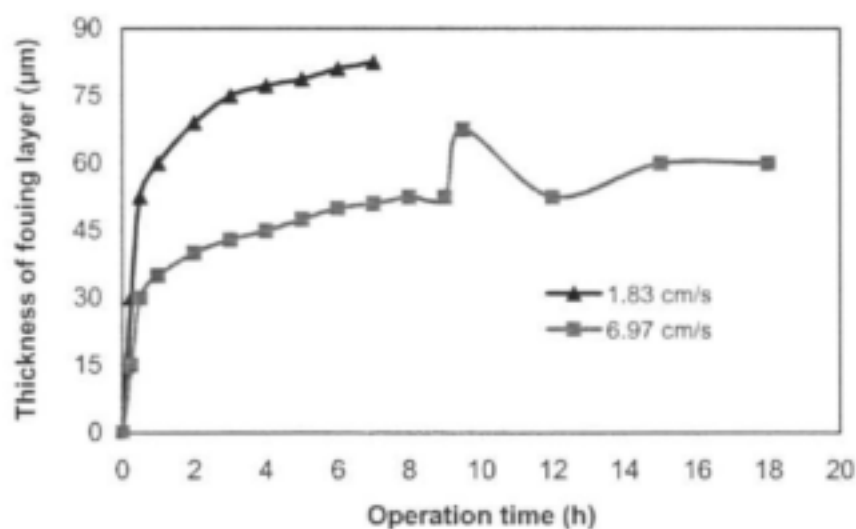


Figure 7.16: Thickness of fouling layer vs. operation time at flow rates of 1.83 and 6.97 cm/s (stop and restart of the fouling operation at 9 h).

7.4.3 CLEANING EXPERIMENTS AND ULTRASONIC MEASUREMENTS

Results of ultrasonic reflections in the fouling experiment carried out with paper mill effluent at a flow rate of 4.2 cm/s and applied pressure 100 kPa (section 7.3.3) are shown Figure 7.17. SEM analysis of the fouled membrane is shown in Figure 7.18.

Figure 7.19 shows the results of ultrasonic response signals during the cleaning experiments. Results of differential signals during the cleaning processes are shown in Figures 7.20 and 7.21. Figure 7.22 displays changes in the amplitude of differential signal - Peak C' during cleaning. Pure water flux recovery of the cleaned membrane obtained by different cleaning methods is shown in Figure 7.23.

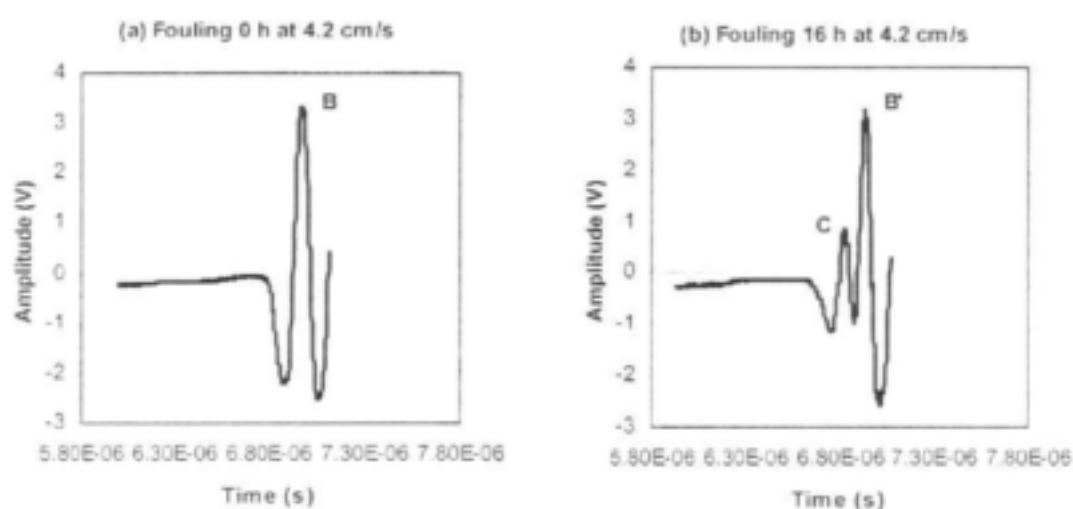
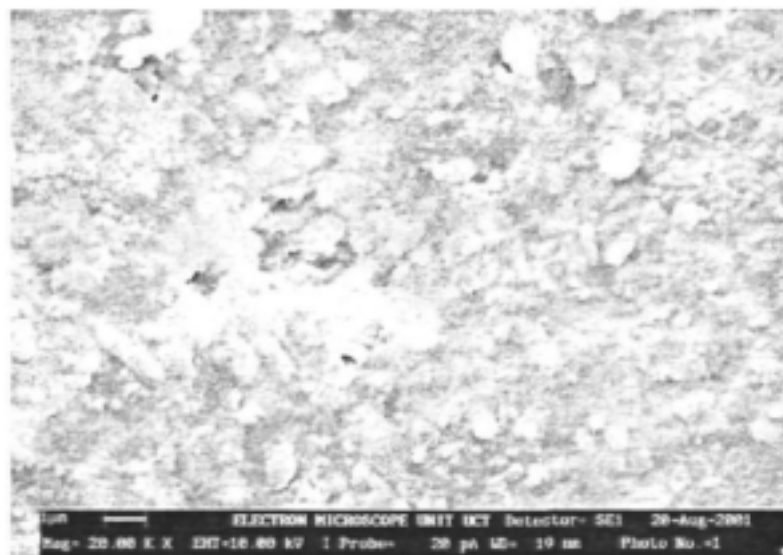
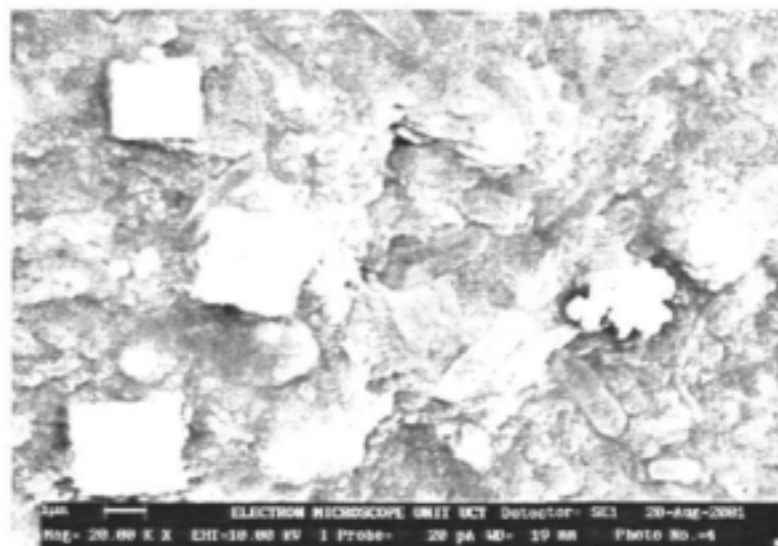


Figure 7.17: Ultrasonic responses (a) at the start, (b) after 16 h of operation in the fouling experiment carried out with paper mill effluent at a flow rate of 4.2 cm/s and applied pressure 100 kPa.



(a)



(b)

Figure 7.18: Microscope images of the Nylon membrane surface during paper mill effluent fouling experiments: after (a) 4 h and (b) 16 h of operation (4.2 cm/s and 100 kPa).

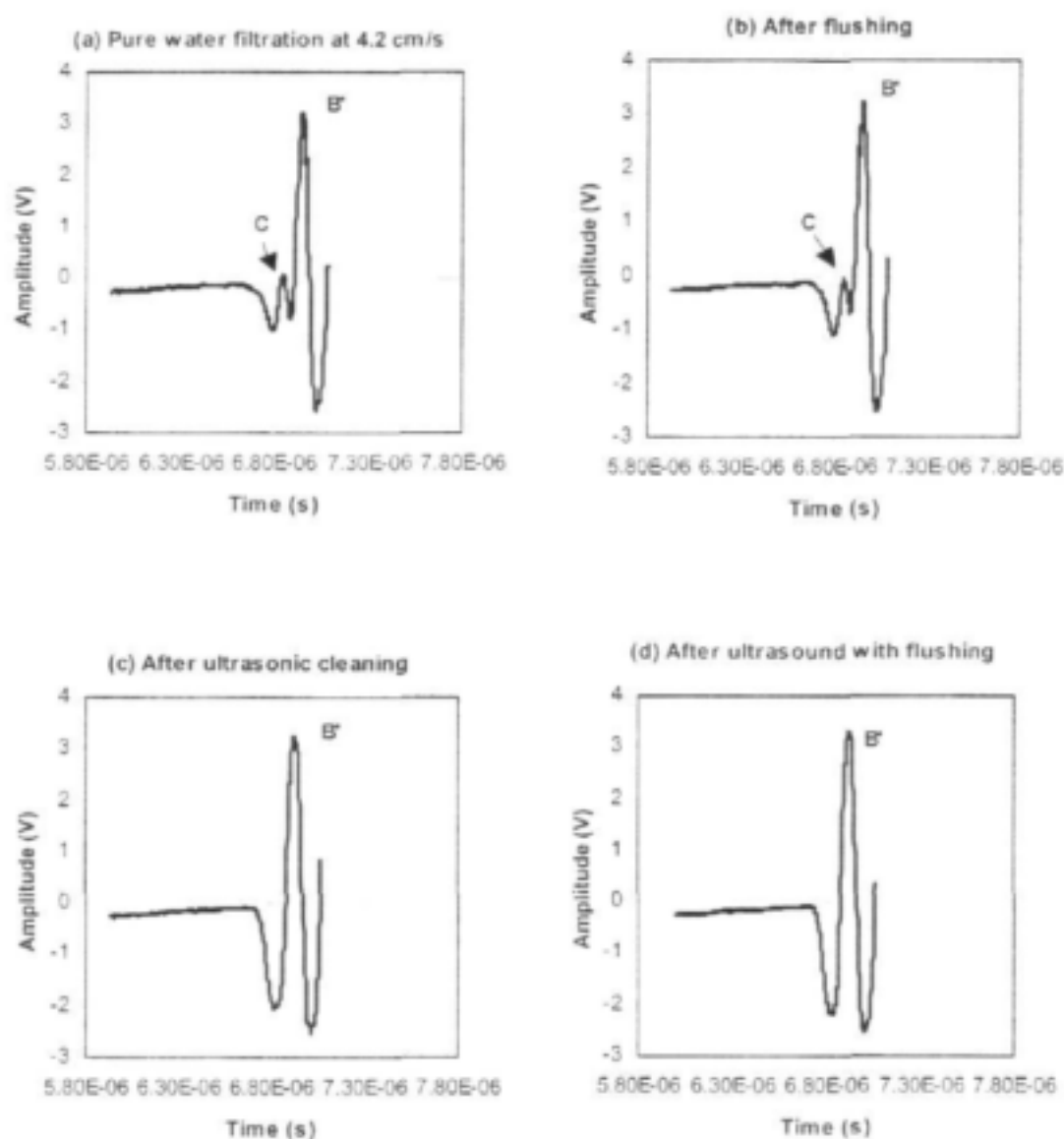


Figure 7.19: Ultrasonic responses during the cleaning experiments: pure water filtration After 16 h of fouling operation, (b) flushing, (c) ultrasonic cleaning and (d) ultrasound associated with flushing.

Note: Peaks B, B' and C were generated from the interfaces: water/nylon membrane, cake layer/nylon membrane and feed/cake layer.

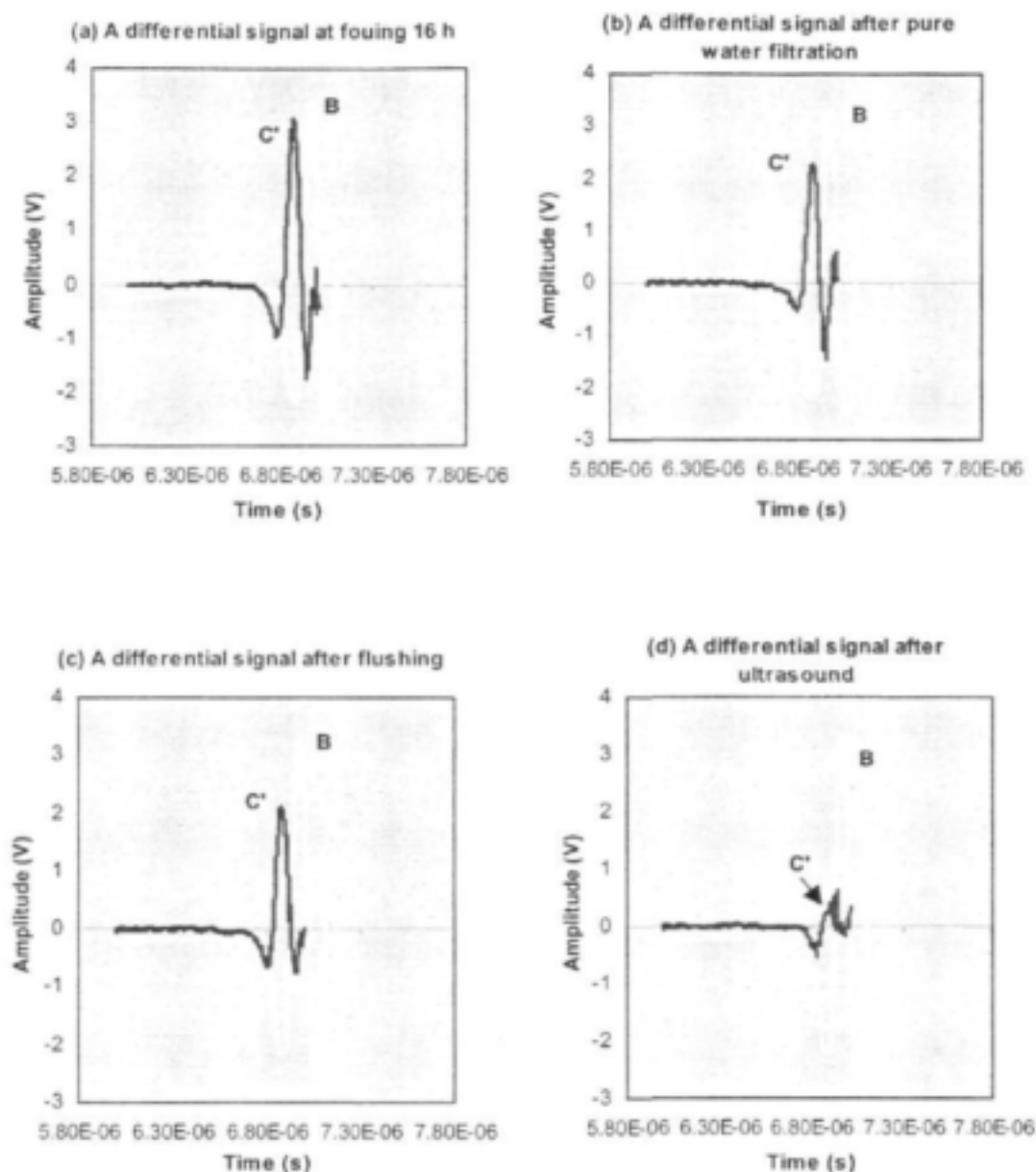


Figure 7.20: Differential signals after (a) 16 h of fouling operation, (b) pure water filtration after fouling, (c) flushing and (d) ultrasonic cleaning.

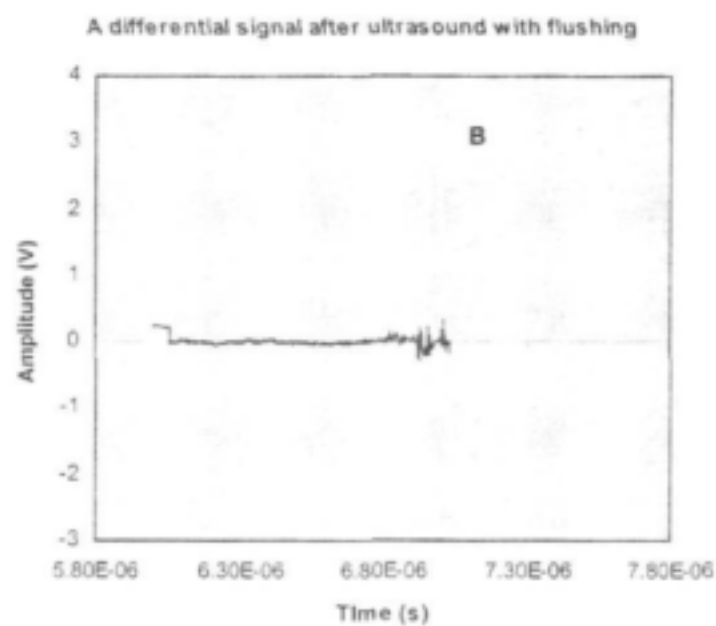


Figure 7.21: Differential signals after ultrasound with flushing.

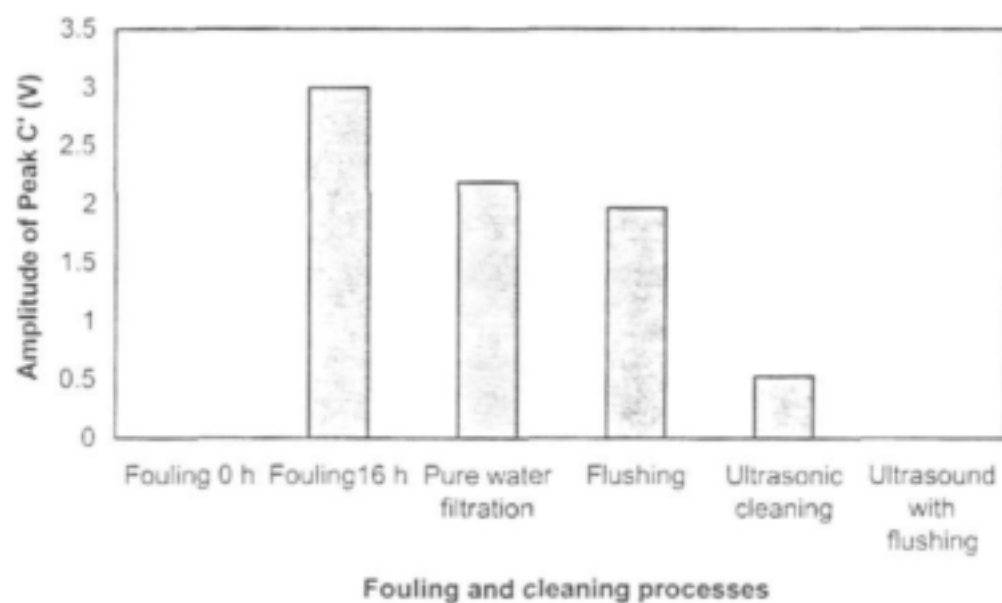


Figure 7.22: Changes in the amplitude of differential signal - Peak C' during cleaning.

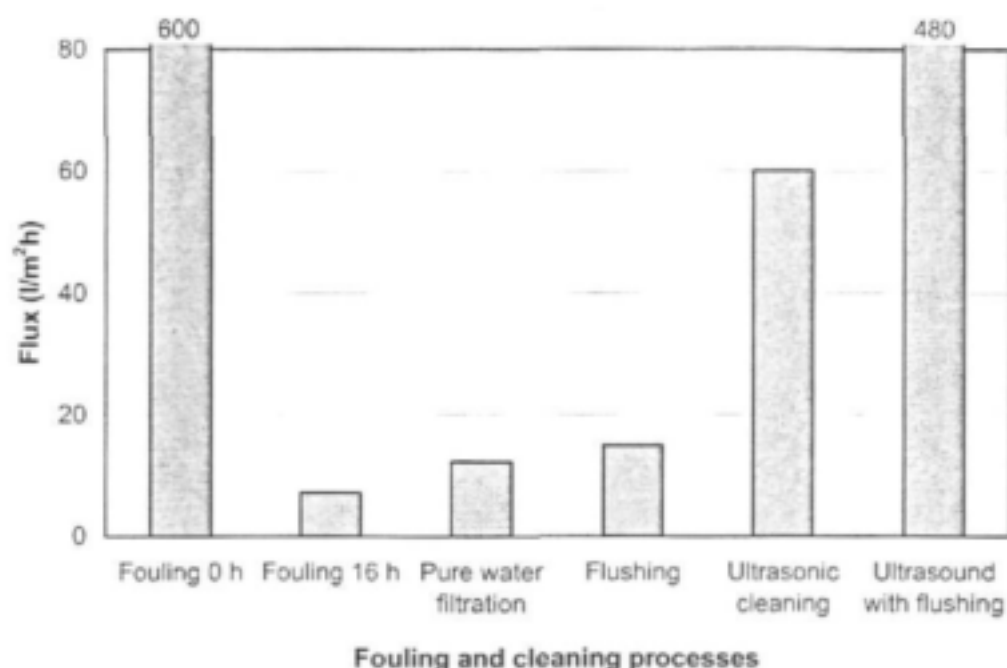


Figure 7.23: Changes in flux during fouling and cleaning processes.

7.5 INTERPRETATION OF RESULTS

7.5.1 FOULING AND ULTRASONIC MEASUREMENT

Figure 7.2 shows that at the beginning of the fouling experiment an instantaneous and rapid decline in the flux was observed, followed by a more gradual decline after 2 h of operation. The instantaneous flux-decline results primarily from particle deposition and the formation of a cake layer on the membrane surface, whereas the gradual decline is presumed to occur as a result of the slow growth of the cake layer and consolidation the cake layer. Figure 7.2 also shows that the decrease in flux was faster at the flow rate of 1.83 cm/s than at 6.97 cm/s. It may be that high shear rates generated at the membrane surface tend to shear off deposited material and thus reduce the hydraulic resistance of the cake layer. Both fluxes had similar values. This suggests that the high flow rate does not mitigate the fouling.

Consistent with above observation, the corresponding ultrasonic measurements exhibit relatively rapid changes in ultrasonic response signals. The peak B represents the clean nylon membrane echo in Figure 7.3a. Generally, once foulants are deposited on the membrane surface, the acoustic impedance difference and the topographical characteristics at the feed solution/membrane interface will change, resulting in a change from echo B to echo B', as shown in Figure 7.3b and c, after 0.5 and 1 h of fouling operation at 1.83 cm/s. The formation of a very thin cake layer (compared with the nylon membrane layer) on the membrane surface

generated an echo signal of the cake layer, which combined with the echo signal of the clean nylon membrane layer to form a new waveform B' (although the echo signal of the cake layer could not be seen at this moment). Inductively coupled plasma analysis showed that the main chemical composition of the fouling layer is breakdown products of lignin or lignosulphonate [Domingo, 2001].

Further, if the cake layer is thick enough as the cake layer grows, the echo signal (peak C) of the cake layer will be seen (Figure 7.3d). If still more particles or fouling covers the membrane surface, a denser fouling layer is formed and a greater acoustic impedance change between the bulk solution and the membrane is expected. This would be detected as a sharper reflection. Thus, an echo signal (peak C) with greater amplitude is observed at 3 – 7 h of fouling operation in Figure 7.4. This is because of the gradual increase in the density and thickness of the cake layer (the amplitude of the reflected wave related to material density). However, it is also important to note that the initial slope of the echo signal changed significantly during the experiment, from a steep slope (Figure 7.3a or b) to a shallow slope (Figure 7. 4b - d). This implies that the lower layers resemble bound aggregates and the upper layers have a more loosely flocculated structure. This observation will be discussed on the basis of URM (section 7.6).

In order to study the correlation between the measurement of UTDR and membrane coverage by the fouling layer, membrane samples were taken for SEM analysis. Results are shown in Figure 7.5a-d. The SEM micrograph of a clean membrane with a clear pore structure is shown in Figure 7.5a. Morphological characterisation of the fouled membrane surface after 2 h of fouling operation revealed complete membrane coverage with the cake layer (Figure 7.5b). There are more and bigger particles on the membrane surface after 7 h than 2 h of fouling operation (Figure 7.5c). A cross-sectional view of a fouled membrane displayed a cake layer covering on the membrane surface. This suggests that morphological observations of the fouling layer corroborate the ultrasonic signal response of the fouling layer.

Similar results of ultrasonic responses in the fouling experiment at the 6.97 cm/s flow rate can be seen in Figures 7.6 – 7.8. Peak B (Figure 7.6a) was changed into peak B' when fouling initiated on the membrane surface (Figure 7.3b – c). By comparison with results recorded at a flow rate of 1.83 cm/s (Figure 7.3), it was found that the fouling echo peak C at 6.97 cm/s appeared later than that at 1.83 cm/s. A new echo (peak C) appeared at the front of the membrane echo peak B' after 5 h of fouling operation at 6.97 cm/s (Figure 7.7a). The growth of peak C can be seen in Figure 7.7 as fouling proceeded. A sharp reflection peak C (cake layer echo) emerged after 13 – 18 h of fouling operation at 6.97 cm/s in Figure 7.8. However, a large peak C arose only after 3 h of operation at 1.83 cm/s. The fouling echo appeared and grew

quickly at a low flow rate because of the low shear rate. This indicates that the UTDR technique is able to detect the fouling rates under different operation conditions.

Morphological characterisation of the membrane surface after 2, 4 and 18 h of fouling operation revealed complete membrane coverage with the fouling layer (Figure 7.9). There were more and bigger particles on the membrane surface after 18 h of fouling operation. A SEM cross-sectional view of the fouled membrane revealed that the thickness of the fouling layer was about 40 μm after 4 h of fouling (Figure 7.9d).

7.5.2 DIFFERENTIAL SIGNAL ANALYSIS

In the case of a very thin fouling layer, it is not possible to calculate the thickness of the fouling layer directly from the ultrasonic record in the conventional way. Differential signal analysis (the difference between test waveform and reference waveform) would be a correct approach to track the real echo of a cake layer. It is shown in Figures 7.10 and 7.11 that a differential signal (peak C') appeared within 0.5 h of fouling operation at 1.83 cm/s, and grew over the period 1, 2, 3, 4, 5 and 6 h as fouling proceeded. A sharp signal emerged after 7 h of fouling due to a denser cake layer on the membrane surface (Figure 7.11d). Time-domain movement was also observed and obtained by the ultrasonic digital device as a result of an increase in the thickness of the fouling layer.

Differential signals obtained in the fouling experiment by paper mill effluent at a flow rate of 6.97 cm/s are shown in Figures 7.12 – 7.14. Results also reveal the echo of cake layer appeared in a very short time measurement, namely, 15 min after start of fouling (Figure 7.12a). The growth of peak C' was observed as the fouling proceeded. It is as a result of the build up of cake layer. A sharp peak C' also emerged after 18 h of fouling operation at 6.97 cm/s (Figure 7.14), though the peak C' arose slower at 6.97 cm/s than at 1.83 cm/s.

The changes in amplitude and arrival time of the differential signals (peak C') with operating time of cross-flow filtration are summarised in Figure 7.15. These indicated that the amplitude of the differential signals increased as fouling proceeded. The cake build-up and growth results from increases in the acoustic impedance of the cake layer ($W = V\rho$), meaning that the density of the cake covering on the membrane surface increased due to particle deposition and compressibility as fouling proceeded. In the early stages of cross-flow filtration, the filtration flux dominates the fluid mechanism and particles are advected directly onto the membrane and cake layer. Hence a rapid increase in amplitude of differential signal (the density of the cake layer) was observed in the early stages. In the later stages, the gradual amplitude increase is presumed to occur as result of the effective density of the cake deposit, which does not change significantly once the cake layer becomes reasonably dense and thick. At this stage, the cross-

flow velocity dominated the fluid mechanics. The particles are highly selective as to where they finally reside and packing efficiency will be increased [Mackley et al. 1992]. Indeed, the flux decline corresponds to the changes in amplitude of the differential signal (peak C').

Another basic quantity measured in non-destructive ultrasonic testing is the time of flight, or the amount of time taken for the sound to travel through the sample. Figure 7.15 illustrates changes in the amplitude and arrival time of the differential signal (peak C') with operation time in the paper mill effluent experiments. The arrival time of peak C' declines with time as a result of an increase in the thickness of the fouling layer. Figure 7.16 illustrates an increase in the thickness of the fouling layer with time.

The thickness of the cake layer increased rapidly at the beginning of fouling because of particle deposition and cake layer formation, followed by a slow increase because of gradual growth and compressibility of the cake layer (Figure 7.16). Although the thickness (82.5 μm) of the fouling layer obtained after 7 h of operation at cross-flow 1.83 cm/s is thinner than the thickness (60 μm) obtained after 18 h of operation at 6.97 cm/s, the flux of 7.5 $\text{l/m}^2\text{h}$ obtained after 7 h of operation at 1.83 cm/s is higher than the flux of 7.2 $\text{l/m}^2\text{h}$ obtained after 18 h of operation at 6.97 cm/s. The amplitudes of differential signals are 2.66 and 2.72 V, after 7 h of operation at 1.83 cm/s and 18 h of operation at 6.97 cm/s, respectively. This indicates that the 60- μm cake layer (obtained after 18 h of operation at 6.97 cm/s) is denser than the 82.5- μm cake layer (obtained after 7 h of operation at 1.83 cm/s). The compressibility of cake layer contributes the flux decline.

Something particularly interesting is seen to occur at 9 h of operation at 6.97 cm/s, in Figure 7.15. At this point the amplitudes show a decrease for a period longer than 30 min, followed by an increase. These changes in amplitude coincided with a stop and restart of the fouling operation (at 9 h). Interrupting the fouling experiment resulted in flow destabilisation and relaxation of the fouling layer. An increase in the thickness of the fouling layer from 52.5 to 67.5 μm and a decrease in amplitude of the cake layer from 2.47 to 2.31 V (density reduction) are seen in Figures 7.15 and 7.16.

Changes in flow-rates and shear-rates upon re-commencement of the fouling experiment resulted in a decrease in the fouling layer thickness or partial dissolution of the fouling layer and. These factors resulted in a rapid increase in the ultrasonic amplitude as the fouling layer conformation on membrane surface was altered. Indeed, the flux increase observed (Figure 7.2) corresponded to the substantial amplitude change. The results obtained from this study suggest that the combination of flux determination and UTDR measurements can provide a much clearer view of the fouling behaviour than the flux measurement alone.

An important distinction should be noted between the flux-decline behaviour and the ultrasonic response in Figure 7.2. While there is no change in the flux-decline curve after operating for 11h at 6.97 cm/s, there are significant differences in the ultrasonic measurements logged. This may indicate that the UTDR technique is more sensitive to fouling layer growth than the flux-decline behaviour is towards transport resistance.

7.5.3 CLEANING EXPERIMENT

Results of the fouling experiment (4.2 cm/s and 100 kPa) show the appearance of a cake layer echo and coverage of the cake layer on the membrane surface in Figures 7.17 and 7.18, indicating that membrane fouling occurs. When the feed was changed from the effluent to pure water, flux increased from 7.2 to 12.3 l/m²h and amplitude of peak C' decreased from 3 to 2.19 V (Figures 7.20, 7.22 and 7.23). It is because of a reduction in concentration polarisation.

Ultrasonic responses and differential signals revealed a change in the fouling echo after flushing (Figures 7.19 and 7.20). The amplitude of peak C', the fouling echo, decreased from 2.19 to 1.97 V after flushing because fouling was reduced (Figure 7.20). Indeed, forward flushing slightly increased the water permeate flux from 12.3 to 15 l/m²h (Figure 7.23). This suggests that forward flushing can reduce the reversible fouling cake layer by reversing the pressure differential across the membrane. The deposited cake layer on the membrane is expected to become re-suspended and swept away by tangential- or cross-flow [Redkar and Davis, 1995]. Therefore, the UR technique is able to explore the presence and the removal of the cake layer in real-time. In addition, it was found that the paper effluent fouling on the nylon membrane is difficult to clean using only flushing (see SEM image in Figure 6.6a). Additional cleaning methods are required.

Figures 7.22 and 7.23 show that the pure water flux increased from 15 to 60 l/m²h and the amplitude of differential signal - peak C' decreased from 1.97 to 0.53 V after ultrasonic cleaning. This suggested that ultrasonic treatment could effectively disperse the fouling layer on the membrane because of the cavitation phenomenon and acoustic steaming [Zhu and Liu, 2000]. Collapse of the cavities has sufficient energy to remove the foulants from the membrane. The disappearance of peak C in Figure 7.19 indicated the fouling layer was removed. However, the amplitude of peak C' is 0.53 V, signifying that there is still some fouling on the membrane. Hence, ultrasound associated with flushing was applied in an effort to remove the membrane fouling.

Results in Figure 7.23 also show that the pure water flux was enhanced from 60 to 480 l/m²h, after ultrasound associated with flushing, although it is still lower than the original pure water flux of 600 l/m²h. The disappearance of peak C' (Figure 7.21) after ultrasound with flushing

indicated that the fouling on the membrane was removed. This is because ultrasonic cavitation results in hydraulic pressure impulses on the deposited fouling layer by impinging actions, similar to the water-hammer effect [Perusich and Alkire, 1991]. Acoustic streaming jets give rise to an enhanced convection and mixing, in terms of a series of micro-vortices, near the membrane surface. The cross flushing produces a high tangential or cross-flow rate (40-50 cm/s) on fouling layers.

Thus, ultrasound associated with flushing was the most effective of the cleaning methods used; this method cleaned the fouled membranes (refer a SEM image of cleaned membrane in Figure 6.7). These results demonstrate that the UTDR technique can monitor removal of the fouling layer and membrane cleaning. It is suitable to study the effectiveness of various cleaning techniques.

7.5.4 APPLICATION OF MODELLING TO UNDERSTANDING CAKE-LAYER DEPOSITION AND GROWTH

In order to aid in the interpretation of the results and to gain an understanding of the formation of fouling, a series of mathematical models based on the physical parameters of the above actual experiments were conducted. A full wave recording (near 1 sine signals) was produced in the mathematical modelling. The physical parameters used for modelling were closely related to actual parameters, although some assumptions had to be made. In particular, no or little information was available on the acoustic velocities of membrane materials. Some published information on the properties of polymers had to be adopted and adjusted in order to produce echo patterns similar to the measured ones. For example, the sound (longitudinal) velocity of nylon 6-6 is 2620 m/s [Lawrence, 1962]. However, there was no information on the sound velocity of a porous nylon membrane. We adjusted the sound velocity of a porous nylon membrane to 2200 m/s according to our results obtained from Section 7.4. We also adjusted the sound velocity of PSU membrane with dense layer PSU_1 , porous layer PSU_2 and polyester support, and the velocity and density of the cake layer (in paper mill effluent experiments) as shown in Table 4.1.

Nylon membrane was modelled on the basis of an actual membrane. Figure 7.24 shows the modelling echo response for a nylon membrane, in response to its reflecting properties and position in the cell based on internal velocities, thickness and densities. A signal frequency of 10 MHz was used in the actual experiments. To produce a smooth signal curve, points were calculated at intervals of 3×10^{-9} s.

A further model was based on the assumption that a cake layer consisting of lignin and lignosulphonate ($\rho = 1.05 \text{ g/cm}^3$), with a thickness of 20 μm , had been deposited on the

membrane. Results of modelling are presented in Figure 7.25. A response very similar to the signal obtained during actual measurements (Figure 7.10a) was obtained. A small echo peak formed in front of the membrane peak. The arrival time for the fouling peak is $6.92 \mu\text{s}$ (Figure 7.25). A further increase in the thickness of the fouling layer to $40 \mu\text{m}$ led to a small movement ahead in the time domain (the arrival time for the fouling peak: $6.89 \mu\text{s}$ in Figure 7.26). However, maintaining the density and increasing the thickness of the layer to $80 \mu\text{m}$ resulted in a further movement ahead in the time domain (the arrival time for the fouling peak: $6.84 \mu\text{s}$ in Figure 7.27), without significantly changing the shape and peak height of the 'fouling peak'.

In Figures 7.3 and 7.4 the initial slope of the echo signal, recorded at a flow rate of 1.83 cm/s , became shallower with increasing thickness of the fouling layer. However, in the fouling experiment in which the flow rate was 6.97 cm/s , no obvious changes in the slope of the echo were observed with increasing thickness of the fouling cake (Figures 7.6 – 7.8). This indicates that the cake layer obtained in paper mill effluent experiments is composed of compressible materials. The cake layer obtained at 6.97 cm/s is more compressible than that obtained at 1.83 cm/s . This is because a high shear force under a high flow rate (6.97 cm/s) affected to the cake layer. A similar phenomenon was observed in experiments where dispersed clay (kaolin) was used as fouling agent (Figure 5.5). The kaolin used was the moderately compressible material [Tiller and Kwon, 1998].

If, in the case of the Kraft fluid (paper mill effluent), the initial fouling layer has a high density, the ultrasonic response signal will be as shown in Figure 7.3b-c. Decreasing density (in the upper layers) in the subsequent fouling deposit would, however, produce a different response, resulting in a shallow slope of the echo signal in Figures 7.4. Such a case was modelled and, in the following model, the density of a $30 \mu\text{m}$ - fouling layer was increased from 1.005 to 1.400 g/cm^3 . An increase in peak height of the fouling echo was obtained as the density of the fouling layer increased (Figure 7.28). A concomitant change of the initial slope with changing density is apparent, supporting the earlier interpretation that foulants such as Kraft fluids produce a non-uniform fouling layer of decreasing density towards its top. This also suggests that changes in the densities of the fouling layer can be predicted by the shape of the curves. In addition, maintaining the thickness and increasing the density of the fouling layer to 1.4 g/cm^3 resulted in a further increase in peak height and a slight change in slope at the beginning of the signal, without changing the position of the fouling echo.

In order to understand the process of the cake formation and the character of the cake layer, results of differential signals (from 0.5 to 7 h) during the fouling operation at 1.83 cm/s are summarised in Figure 7.29. Firstly, the movement of the differential signals in the time-domain were observed (Figure 7.29) as the fouling time increased from 0.5 hours to 7 h as a result of an

increase in the thickness of the cake layer (as shown in Figure 7.15). Secondly, it is seen that the amplitude of the differential signal increases with operating time due to the compressibility of cakes or an increase in the density of the cake layer. Thirdly, the initial slope of the differential signal became shallower with an increase in the thickness of the cake layer or operating time. It implies that the cake layer covering on the membrane surface is a non-uniform layer. Its density decreases from the lower layers to the upper layers. However, results of differential signals during the fouling operation at 6.97 cm/s show in Figure 7.30 that a uniform cake layer was obtained under a high shear force. It implies that the operation at a high flow rate could not reduce fouling. These results indicate that growth of the cake layer in thickness and density results in an increase in the deposit resistance.

For a given thickness of deposit, the resistance grows with pressure, and this growth becomes all the more significant with increasing thickness of a cake layer. At the same time, stress applied to the cake decreases porosity and increases resistance to flow. The observed increase in deposit resistance is mainly due to the compressibility [Tiller and Kwon, 1998; Tiller and Li, 2001].

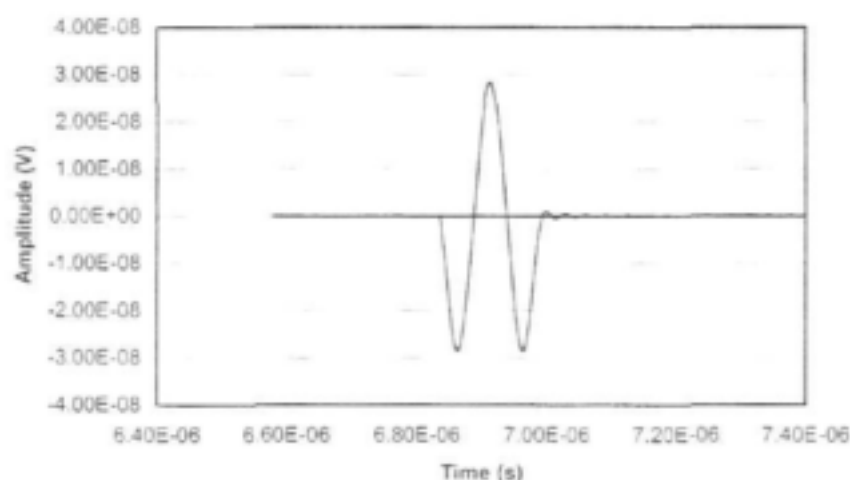


Figure 7.24: Mathematical model of the arrival times and echo for a clean nylon membrane (using a 10-MHz signal input), using a 3/2 sine signal in first approximation of the actual transducer signal.

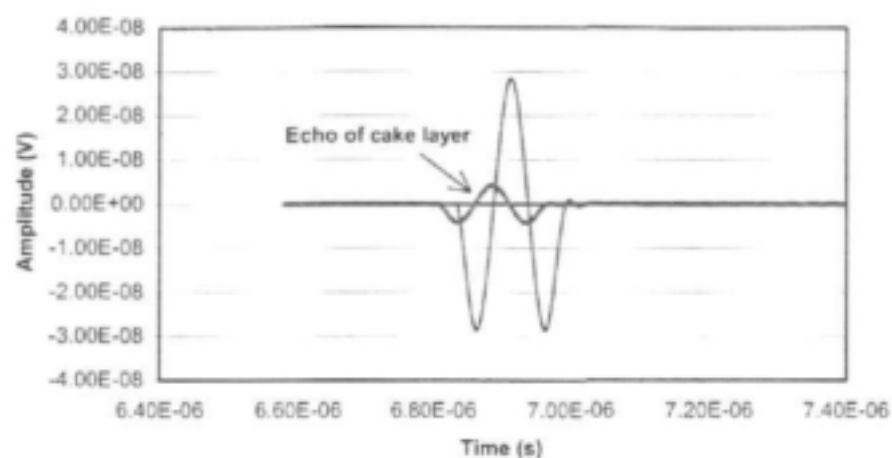


Figure 7.25: Model of a 20 μm thick cake layer ($\rho = 1.05 \text{ g/cm}^3$) on a nylon membrane.

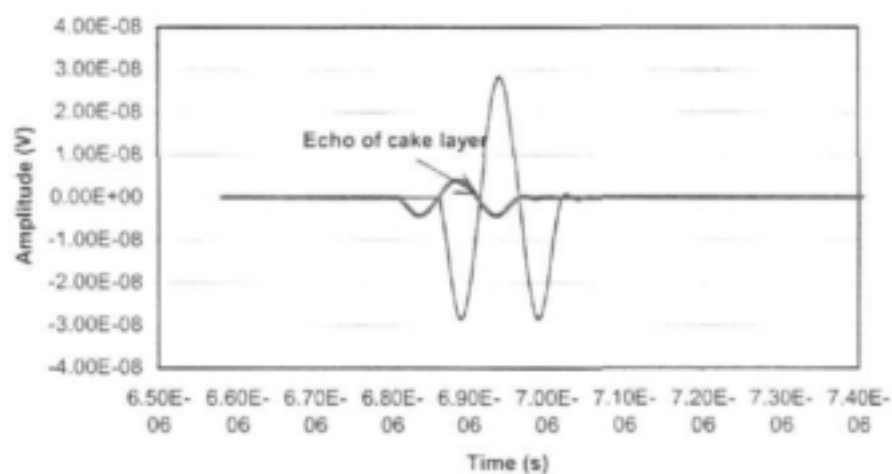


Figure 7.26: Model of a 40 μm thick cake layer ($\rho = 1.05 \text{ g/cm}^3$) on a nylon membrane.

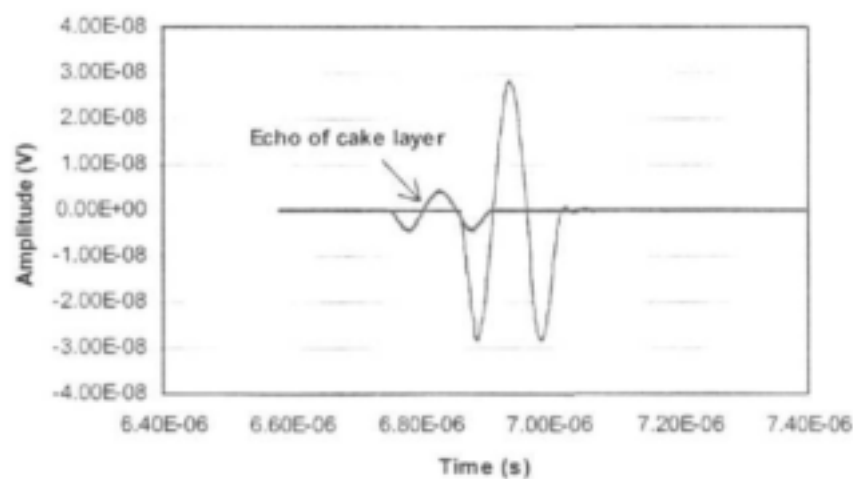


Figure 7.27: Model of an 80 μm thick cake layer ($\rho = 1.05 \text{ g/cm}^3$) on a nylon membrane.

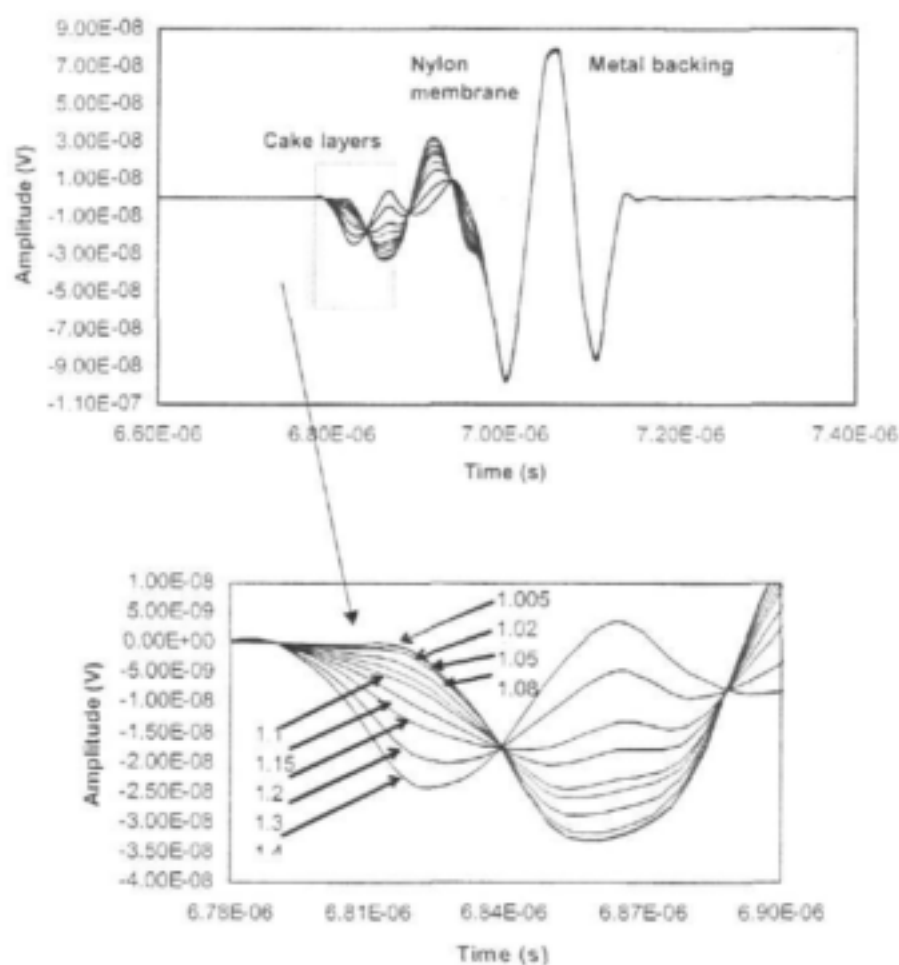


Figure 7.28: Mathematical model of density increases in a cake layer ($\rho = 1.005 - 1.4 \text{ g/cm}^3$).

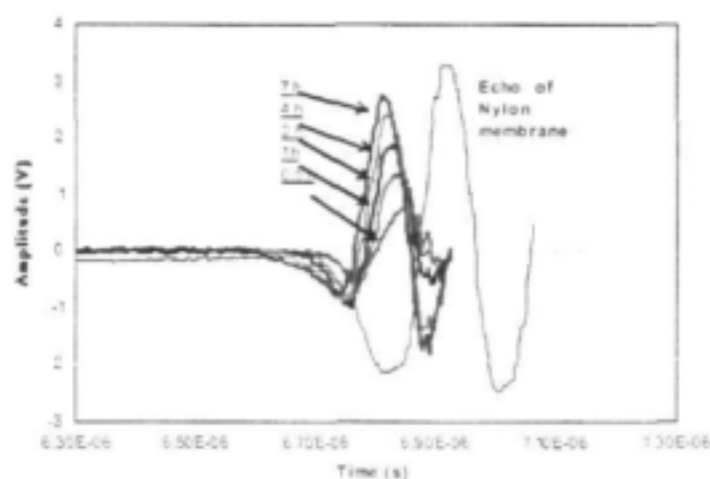


Figure 7.29: Actual ultrasonic response signal of a clean nylon membrane and differential signals after 0.5 - 7 h of operation in a fouling experiment (150 kPa, 1.83 cm/s) carried out with paper mill effluent.

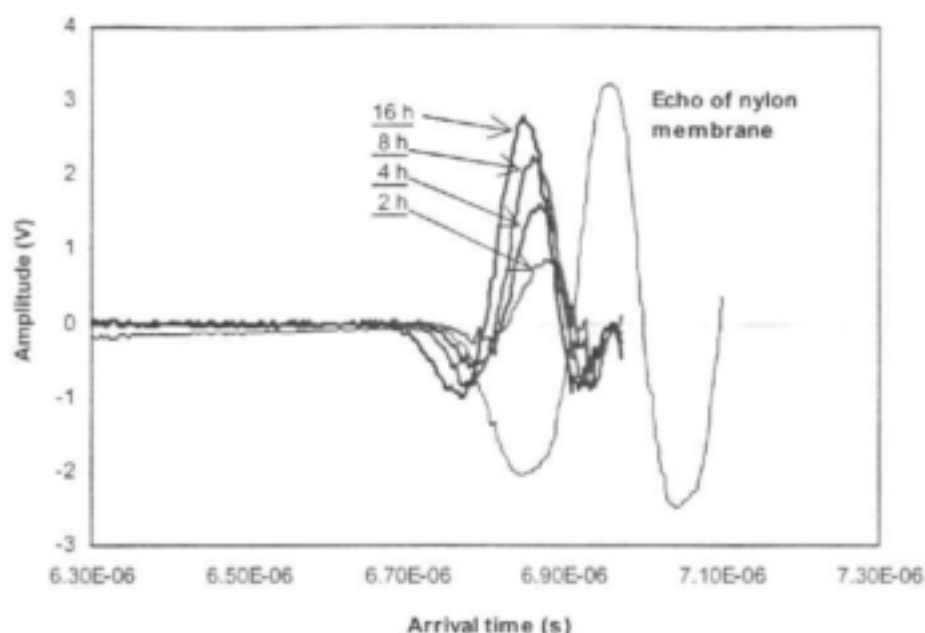


Figure 7.30: Actual ultrasonic response signal of a clean nylon membrane and differential signals after 0.5 - 18 h of operation in a fouling experiment (150 kPa, 6.97 cm/s) carried out with paper mill effluent.

7.6 CONCLUSIONS

In cross-flow microfiltration, cake formation, growth and compressibility were observed by an ultrasonic testing method. Results showed that the ultrasonic testing technique could monitor the particle deposition, and the formation and growth of a cake layer on the membrane surface. The ultrasonic technique could measure the rate of cake layer formation at different flow rates.

The UTDR technique was also capable of detecting subtle changes such as stop and restart operation. In cleaning experiments, results showed that a cake-layer echo decreased after flushing and disappeared after ultrasonic irradiation. UTDR results consolidated the results obtained and reported in Chapter 5, namely that ultrasound associated with flushing is the most effective cleaning method for membranes fouled with paper mill effluent. The fact that the UTDR technique monitors changes on the membrane surface makes it very suitable to study membrane cleaning and determine effectiveness of various cleaning techniques.

Results further showed that the differential signal of a fouling layer echo was obtained, indicating the state and progress of a cake layer on the membrane surface in actual operations. Both amplitude and arrival time of differential signals as a function of operation time provided useful quantitative information on the fouling processes. The UTDR technique could overcome

the conventional way to quantify the thickness of a very thin cake layer on a membrane surface, using a differential signal. UTDR results corroborated the flux measurements and SEM analyses.

A predictive modelling program - ultrasonic reflection modelling (URM) was developed to better understand the processes related to the deposition of cake layers on membrane surfaces. Changes in both the densities and the thickness of the cake layer can be substantiated by the mathematical modelling. In microfiltration the deposit resistance is not only related to the layer thickness but also the cake density (compressibility). The cake layer covering on the membrane surface is a non-uniform layer in the fouling experiment at a flow rate of 1.83 cm/s, and a uniform layer in at 6.97 cm/s. UTDR proved that increasing flow rate in the actual operation could not reduce fouling. The predictive results were in good agreement with the actual measurements.

In conclusion, the echo signal of the cake layer can indicate the density state and progress of the cake layer on the membrane surface in real time and provide an early warning to adjust system-operating parameters, often faster than observable flux reduction.

8. DIRECT MONITORING OF MEMBRANE FOULING AND CLEANING DURING ULTRAFILTRATION

8.1 ABSTRACT

UTDR was used as a non-destructive, real-time, *in situ* measuring technique for the non-invasive study of fouling and cleaning during UF with polysulphone (PSU) membranes. Paper-mill effluent from a wastewater treatment plant was used as feed solution. First, the structure and compaction of an asymmetric PSU membrane, its compaction and fouling were detected by UTDR. Experimental results showed a good correspondence between the UTDR signal response and the development of the fouling layer on the membrane surface. Second, the UTDR technique was successfully used to monitor membrane cleaning and evaluate the cleaning effectiveness of various cleaning methods in UF. A differential signal obtained indicated the state and progress of the fouling layer on a membrane surface. Such a signal gives warning of advanced fouling during realistic operation. Results showed the nature and thickness of the fouling layer as a function of operating time. Ultrasonic reflection modelling (URM) was used to model the density and thickness of a fouling layer on a membrane surface, so as to predict the fouling behaviour. Overall, UTDR is a most useful technique for the non-destructive investigation of fouling and cleaning in membrane applications.

8.2 INTRODUCTION

UF has become an increasingly important separation process. It is used for product recovery and pollution control in industrial effluents, oil emulsions, wastewater, ultra-pure water, biological macromolecules, colloidal paint suspensions and medical therapeutics [Lonsdale, 1982; Jönsson and Trägårdh, 1990; Cheryan, 1998]. The main problem related to UF however is the flux decrease caused by concentration polarisation and fouling.

An *in-situ* visualisation technique can not only characterise and distinguish between the various phenomena causing the flux decline, but also aid in elucidating the exact mechanism and nature of the fouling layer growth. The development and utilisation of a suitable non-invasive technique for on-line monitoring of fouling in industrial and laboratory applications would also enable the effectiveness of fouling remediation and cleaning strategies to be quantified.

In Chapters 5 and 7 we described the use of an ultrasonic reflectometry technique for the *in-situ*, non-invasive observation of fouling deposition and growth on MF membranes. The work described here aimed to further understand the UTDR technique for the real-time, non-invasive investigation of organic fouling deposition and removal during UF, to further evaluate the capabilities of the UTDR technique and its applicability in different membrane separation systems. The multi-layer structure and compactness of an asymmetric PSU membrane was detected by UTDR. The different signals obtained and ultrasonic reflection modelling provided correct approaches to gain an understanding of the processes of ultrasonic testing related to fouling deposition.

8.3 EXPERIMENTAL

8.3.1 UF SYSTEM AND ULTRASONIC MEASUREMENT

Again, the effluent from a wastewater treatment plant of Mondi Kraft Mills, Mondi Ltd, South Africa, was used as the feed solution. The wastewater treatment plant comprised the following processes: pre-treatment, dissolved air flotation, MF and UF. Samples were taken from the MF product. The characteristics of the effluent were summarised in Table 8.1.

Flat-sheet polysulphone membranes with a molecular weight cut-off (MWCO) of about 35 kD were prepared and used in all the fouling experiments. In order to monitor and determine the onset and advancement of fouling on a membrane surface, a flatbed filter cell was designed and used (Figure 3.3). A PSU membrane was placed between two Perspex plates.

Investigations were carried out with the UF separation system described in Section 5.3.1 (Figure 5.1). The ultrasonic measurement system used was the same as that described in Section 5.3.1.

Table 8.1: Characteristics of paper mill effluent from MF products^a

ITEM	VALUE	ITEM	VALUE
pH	5.33	Sulphate, SO ₄ , mg/l	1232
Conductivity, µS/cm	315	Fluoride, F, mg/l	0.2
Suspended solids (SS), mg/l	720	Silica as Si, mg/l	5.8
Total Dissolved Solids, mg/l	4545	Chloride, Cl, mg/l	103
Chemical Oxygen Demand, mg/l	4090	Soap, oil & grease, mg/l	2.8
Biochemical Oxygen Demand, mg/l	900	Potassium, K, mg/l	24
Aluminium as Al, mg/l	12.6	Iron as Fe, mg/l	3
Calcium, Ca, mg/l	122	Sodium, Na, mg/l	1270
Total Iron, Fe, mg/l	3.3	Magnesium, Mg, mg/l	16.2
Total Dissolved Iron, mg/l	3.3	Potassium as K, mg/l	30

^aData supplied by Mondi Piet Retief, Mondi Ltd, South Africa.

8.3.2 EXPERIMENTAL PROCEDURE AND FOULING EXPERIMENTS

In each UF experiment, continuous stirring in the feed tank was provided. Each experiment commenced with pure water being circulated through the system at the desired flow rate and applied pressure, for 0.5 h, to compress the membrane and to build up a stable flow field. Once steady state was attained, the feed was switched to the effluent solution to initiate the fouling phase in which concentration polarisation and fouling occurred. This was allowed to continue until the ultrasonic response and permeate flux had stabilised.

Both cross-flow and dead-end filtrations were investigated. The fouling experiment was carried out at flow rates of 0 and 12.5 ± 0.12 cm/s ($Re = 454 \pm 4.5$), applied pressure 175 ± 5 kPa and temperature $20 \pm 1^\circ\text{C}$. The total operating time for the fouling experiments was 8.5 h.

8.3.3 UF CLEANING EXPERIMENT

Further fouling experiments were carried out at flow rates of 2.1 ± 0.02 cm/s ($Re=532 \pm 5.3$), applied pressure 185 ± 5 kPa and temperature $20 \pm 1^\circ\text{C}$. The total operating time for the fouling experiments was 20 h. Before commencing with the cleaning experiments, the feed solution was changed from effluent to pure water at 185 kPa and an axial velocity of 2.1 cm/s, in order to obtain pure water flux (PWF) of a fouled membrane. The fouled membrane was cleaned with pure water by three methods, in turn, namely: forward flushing, ultrasonic cleaning and ultrasound together with forward flushing, for cleaning times of 20 min each. The cross-flow filtration cell was immersed in a water bath during ultrasonic cleaning. The cell was irradiated with a horn ultrasonic cleaner (Medal W-375, Ultrasonics INC.) with a frequency of 20 kHz and a power of 375 w.

Ultrasound associated with forward flushing was performed with intermittent forward flushing at a flow rate of 40-50 cm/s during ultrasonic irradiation. To investigate the cleaning efficiency of each cleaning method, the cleaned membrane was used to filter pure water under the same operating condition as used in the fouling phase. The UTDR measuring system captured the changes in ultrasonic signal responses after the different cleaning methods. These data can be stored on a computer's hard drive.

8.4 RESULTS

8.4.1 ULTRASONIC REFLECTIONS AND HYDROSTATIC PRESSURE EXPERIMENT

Ultrasonic reflections in a flat cell are shown in Figure 8.1. The representative waveform plots the ultrasonic signal amplitude in volts (V) versus the arrival time in second (s). Each peak

corresponds to a reflected acoustic wave from one of the multiple interfaces in the flat cell. Peaks A, B, C and D are generated from the following interfaces: Perspex plate/feed (water), water/PSU layer, PSU layer/polyester backing layer and polyester backing layer/metallic porous support.

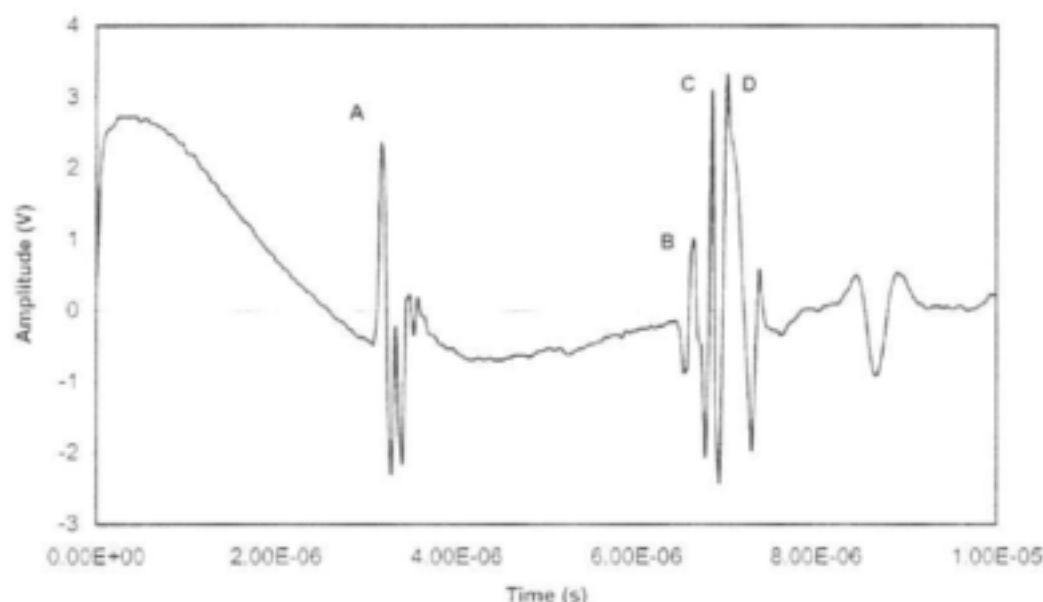


Figure 8.1: Ultrasonic reflections in a flat cell.

Note: Peaks A, B, C and D are generated from the following interfaces: Perspex plate/water, water/PSU layer, PSU layer/polyester backing, polyester backing/porous metal support.

A hydrostatic pressure experiment with pure water was first carried out to investigate the resolution capabilities of the UTDR technique. Figure 8.2 shows ultrasonic response signals of a clean PSU membrane at hydrostatic pressures of 0 and 160 kPa during the hydrostatic pressure experiment.

Figure 8.3 shows the changes in the arrival time and shift distance of peak B (as a reference/observed signal) with hydrostatic pressure. The hydrostatic pressures ranged from 0 to 220 kPa.

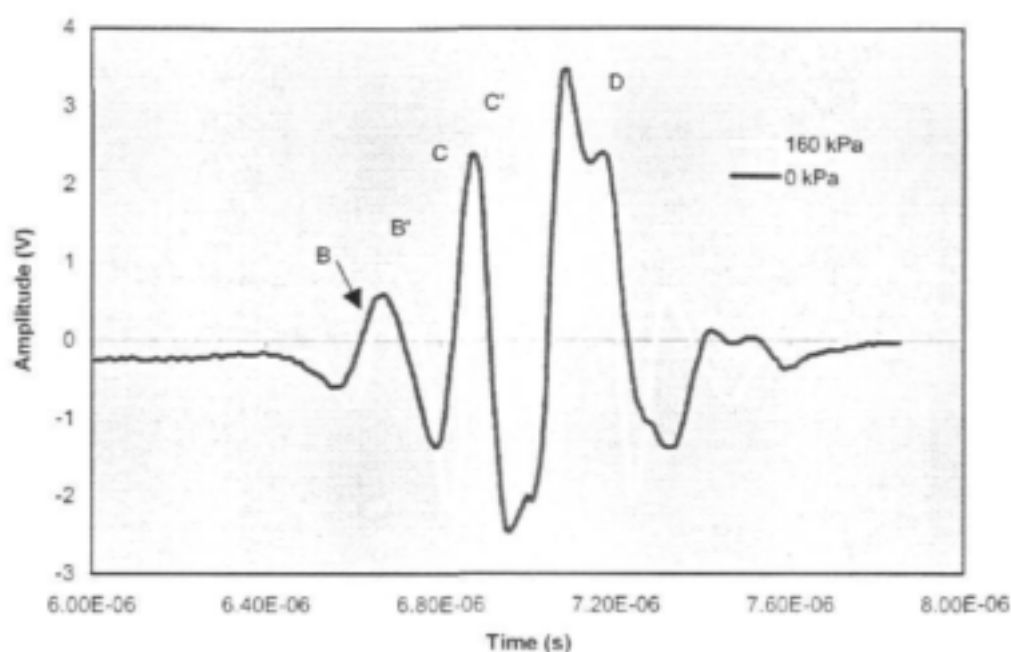


Figure 8.2: Ultrasonic response signals of a composite PSU membrane at hydrostatic pressures of 0 and 160 kPa during a hydrostatic pressure experiment with pure-water.

Note: the changes in slope and amplitude of peak B' while show density changes with hydrostatic pressure.

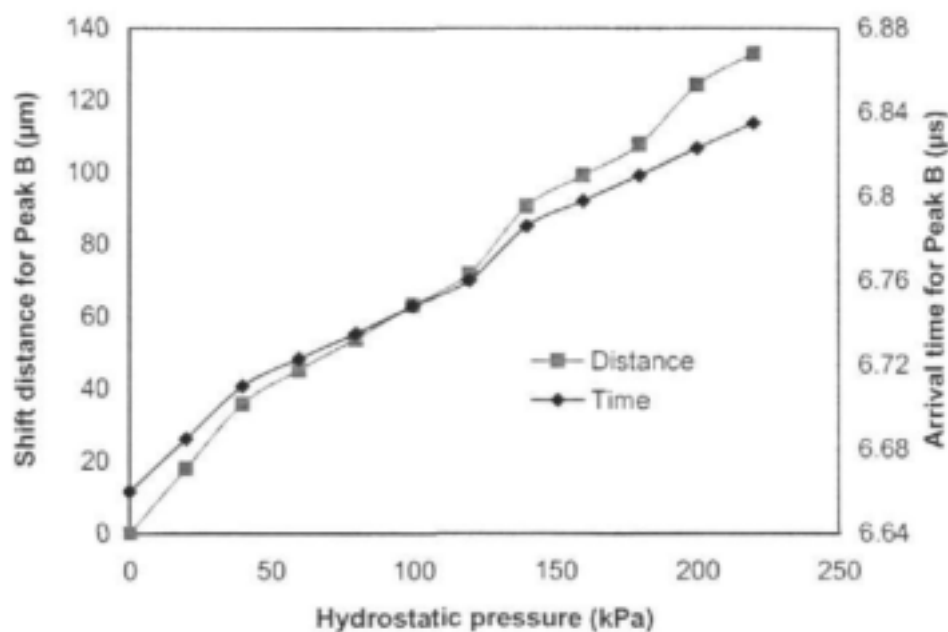


Figure 8.3: Time delay and shift distance of Peak B versus hydrostatic pressure.

8.4.2 FOULING EXPERIMENT AND UTR MEASUREMENT

Figure 8.4 shows changes in the permeate flux with operating time during the fouling experiments carried out with paper mill effluent in dead-end and cross-flow (12.5 cm/s) filtration.

Results of ultrasonic response signals during dead-end fouling experiments are shown in Figures 8.5 and 8.6. Figure 8.7 shows a scanning electronic microscope (SEM) cross-sectional view of a clean PSU membrane and an optical microscope cross-sectional view of a PSU membrane fouled by paper mill effluent during dead-end filtration. Further experiments were carried out with paper mill effluent at a cross-flow rate 12.5 cm/s and pressure 175 kPa. Results of ultrasonic response signals during cross-flow fouling experiments are shown in Figures 8.8 and 8.9.

Figure 8.10 shows the microscopic images of PSU membranes fouled by paper mill effluent after 8 h of fouling operation at (a) dead-end and (b) 12.5 cm/s cross-flow rate.

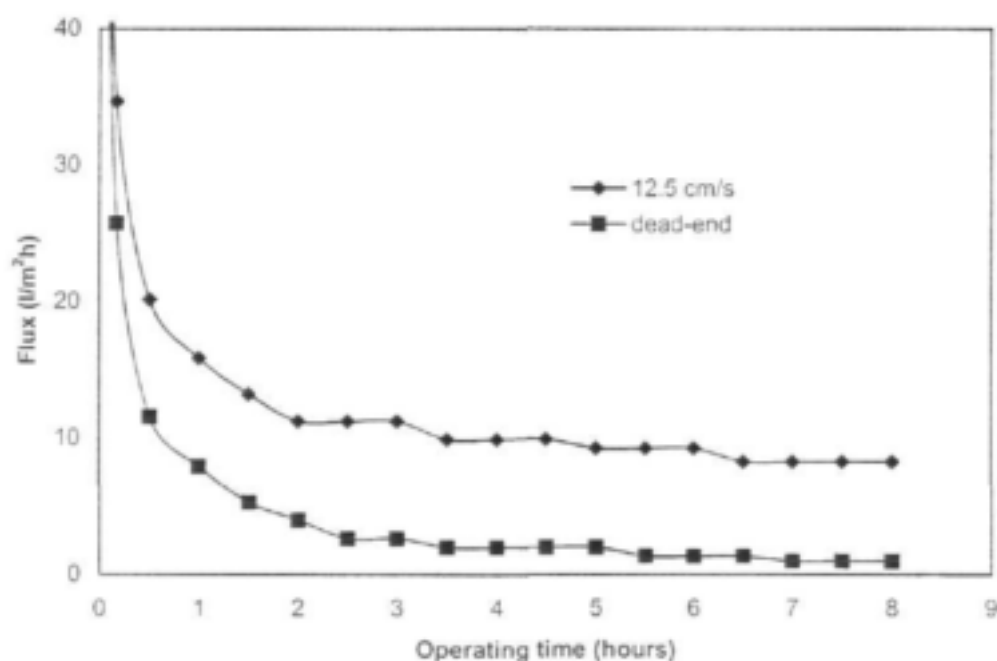


Figure 8.4: Permeate-flux vs. operation time in the fouling experiment carried out with paper mill effluent at flow rates: dead-end and 12.5 cm/s, and pressure 175 kPa.

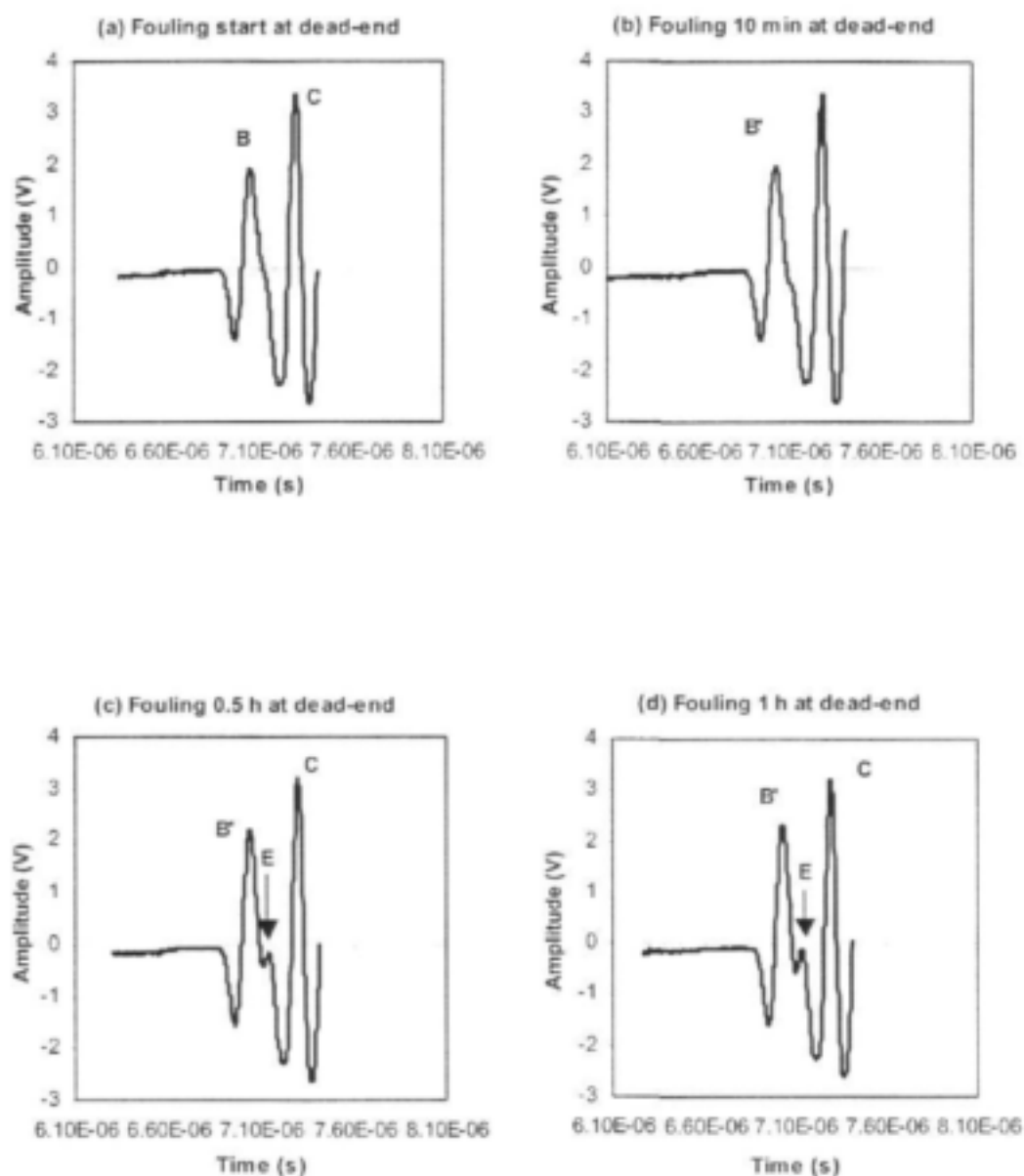


Figure 8.5: Ultrasonic signal responses after 0 (start), 10 min, 0.5 and 1 h of operation in the fouling experiment (175 kPa, dead-end) carried out with paper mill effluent.

Note: The reflection signals B, B', C and E are generated from the interfaces: water/PSU₁ layer, feed/fouling layer (combined PSU₁), PSU₂ layer/polyester backing, PSU₁ layer/ PSU₂ layer.

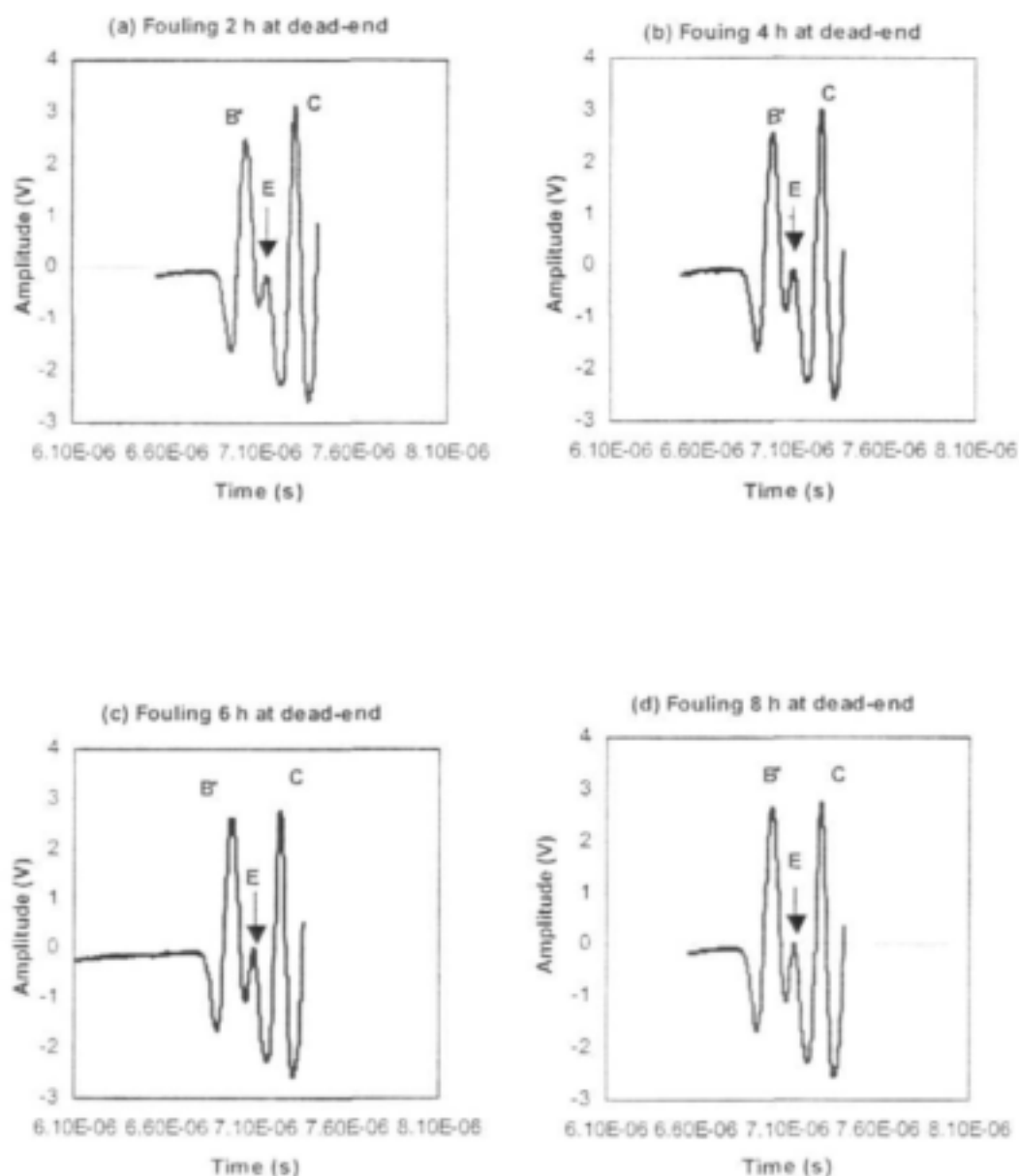
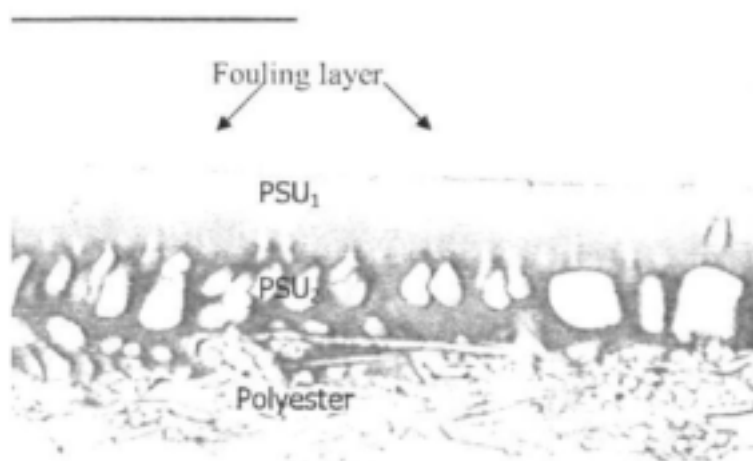


Figure 8.6: Ultrasonic signal responses after 2, 4, 6 and 8 h of operation in the fouling experiment (175 kPa, dead-end) carried out with paper mill effluent.

Microscopic images:



(a)



(b)

Figure 8.7 (a) SEM micrograph: cross-sectional view of a clean PSU membrane, magnification 1250 $\times$; (b) micrograph of cross-sectional view of PSU membrane fouled by paper effluent, magnification 250 $\times$. PSU₁ – a dense PSU layer, PSU₂ – a porous PSU layer, polyester (a non-woven polyester backing).

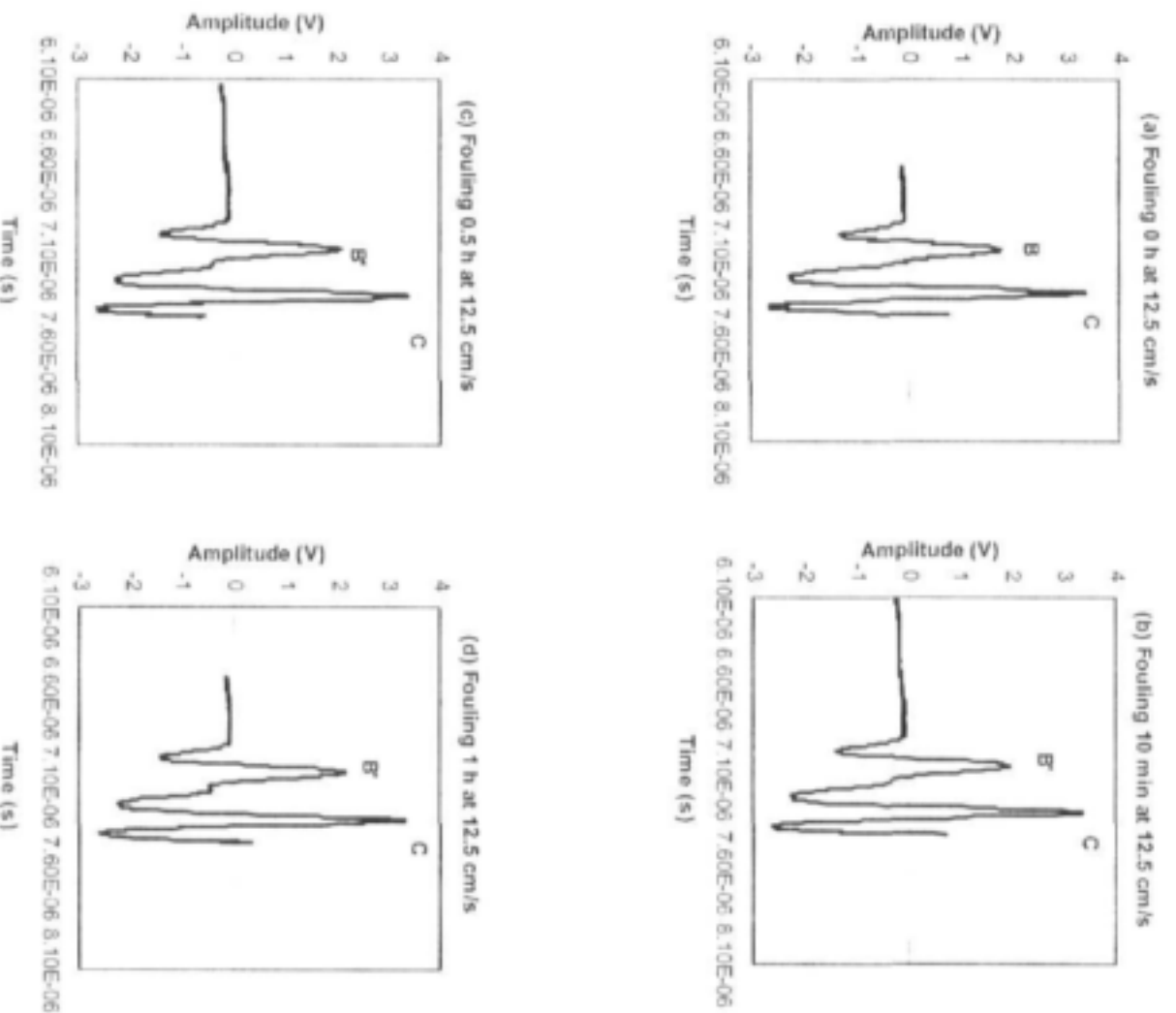


Figure 8.8: Ultrasonic signal responses after 0 (start), 10 min, 0.5 and 1 h of operation in the fouling experiment (175 kPa, 12.5 cm/s) carried out with paper mill effluent.

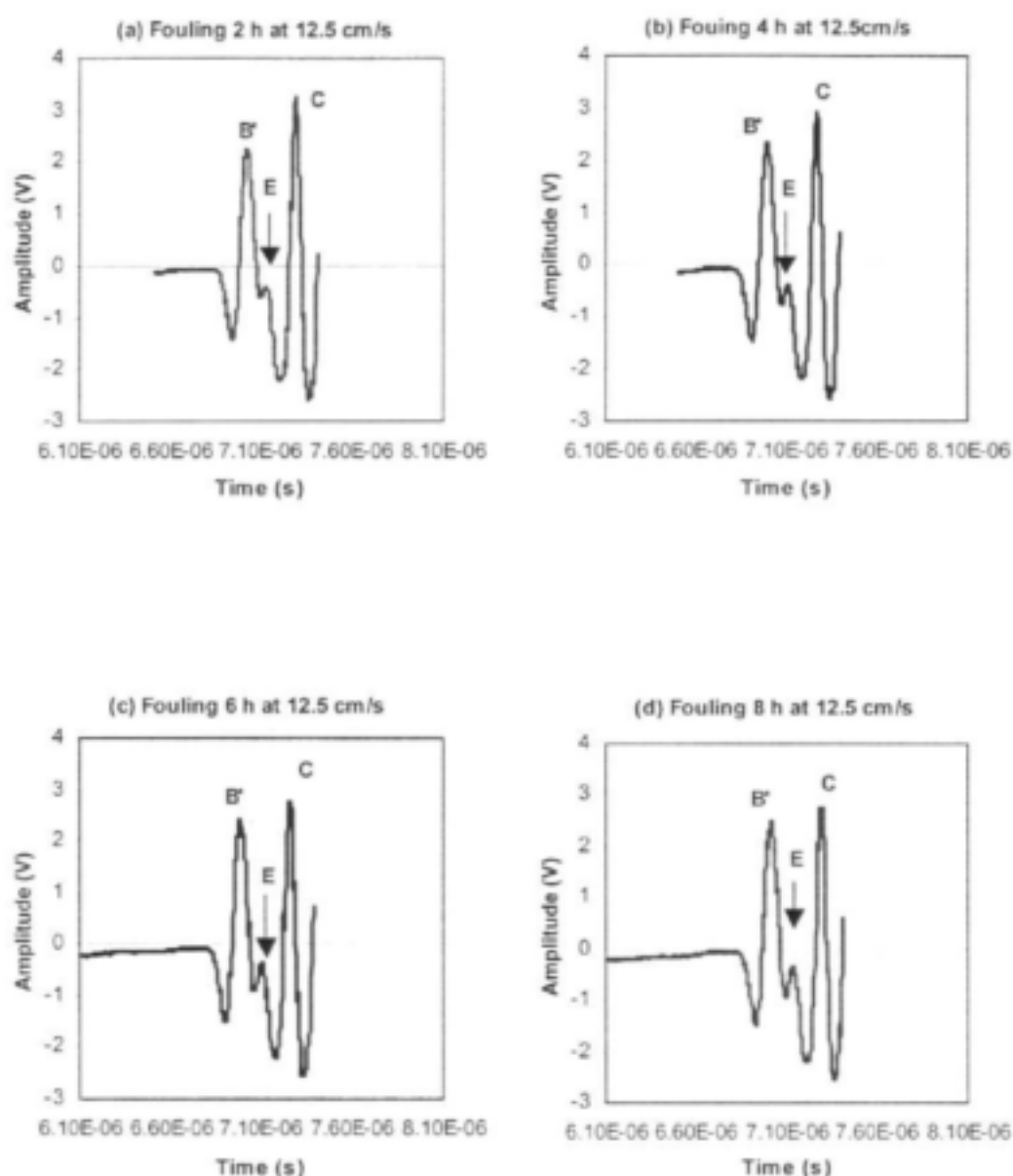
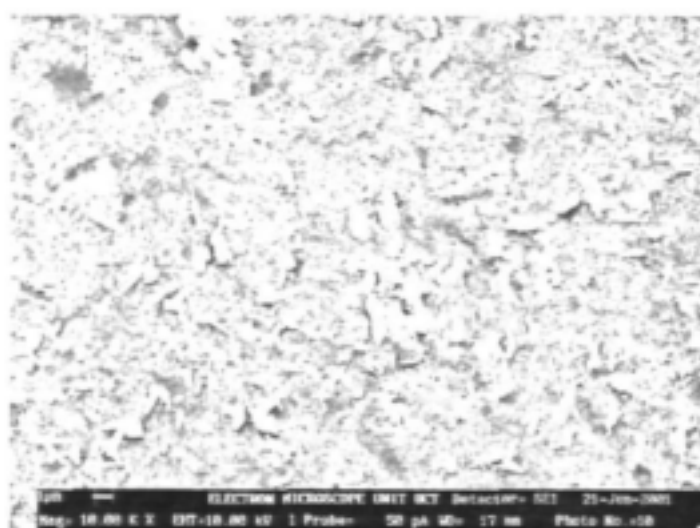
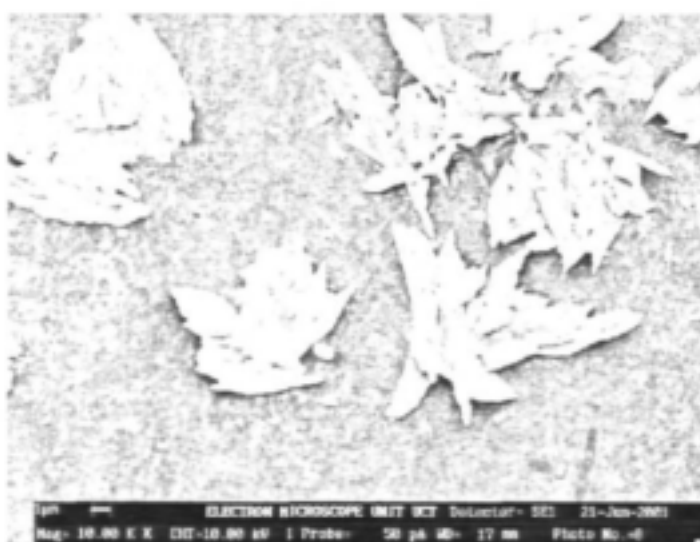


Figure 8.9: Ultrasonic signal responses after 2, 4, 6 and 8 h of operation in the fouling experiment (175 kPa, 12.5 cm/s) carried out with paper mill effluent.

Note: The reflection signals B, B', C and E are generated from the interfaces: water/PSU₁ layer, feed/fouling layer (combined PSU₁), PSU₂ layer/polyester backing, PSU₁ layer/ PSU₂ layer.



(a)



(b)

Figure 8.10: Microscopic images of PSU membranes fouled by paper mill effluent after 8 h of fouling operation at flow rates (a) dead-end and (b) 12.5 cm/s.

8.4.3 DATA ANALYSIS – DIFFERENTIAL SIGNALS

Further studies were carried out to investigate build-up of a fouling layer and its physical state on a membrane surface so as to interpret the results observed in the above experiments. It was

found from this study that the UTDR technique provides a means of producing a differential signal (an echo signal of a fouling layer) by comparing a reference waveform and a test waveform according to wave superimposition principles [Bland, 1988]. A clean membrane waveform obtained upon pure-water filtration or at fouling start is used as a reference waveform for later use during fouling (or cleaning) processes. A fouled membrane waveform obtained during fouling process can be used as a test waveform.

Results of differential signals during dead-end and cross-flow (12.5 cm/s) experiments are shown in Figures 8.11 and 8.12.

Changes in amplitude of the differential signals during dead-end and cross-flow (12.5 cm/s) filtration are shown in Figure 8.13.

Figure 8.14 illustrates the thickness of the fouling layer as a function of operation time during fouling experiments with paper mill effluent at flow rates of dead-end and 12.5 cm/s.

Differential signals at dead-end:

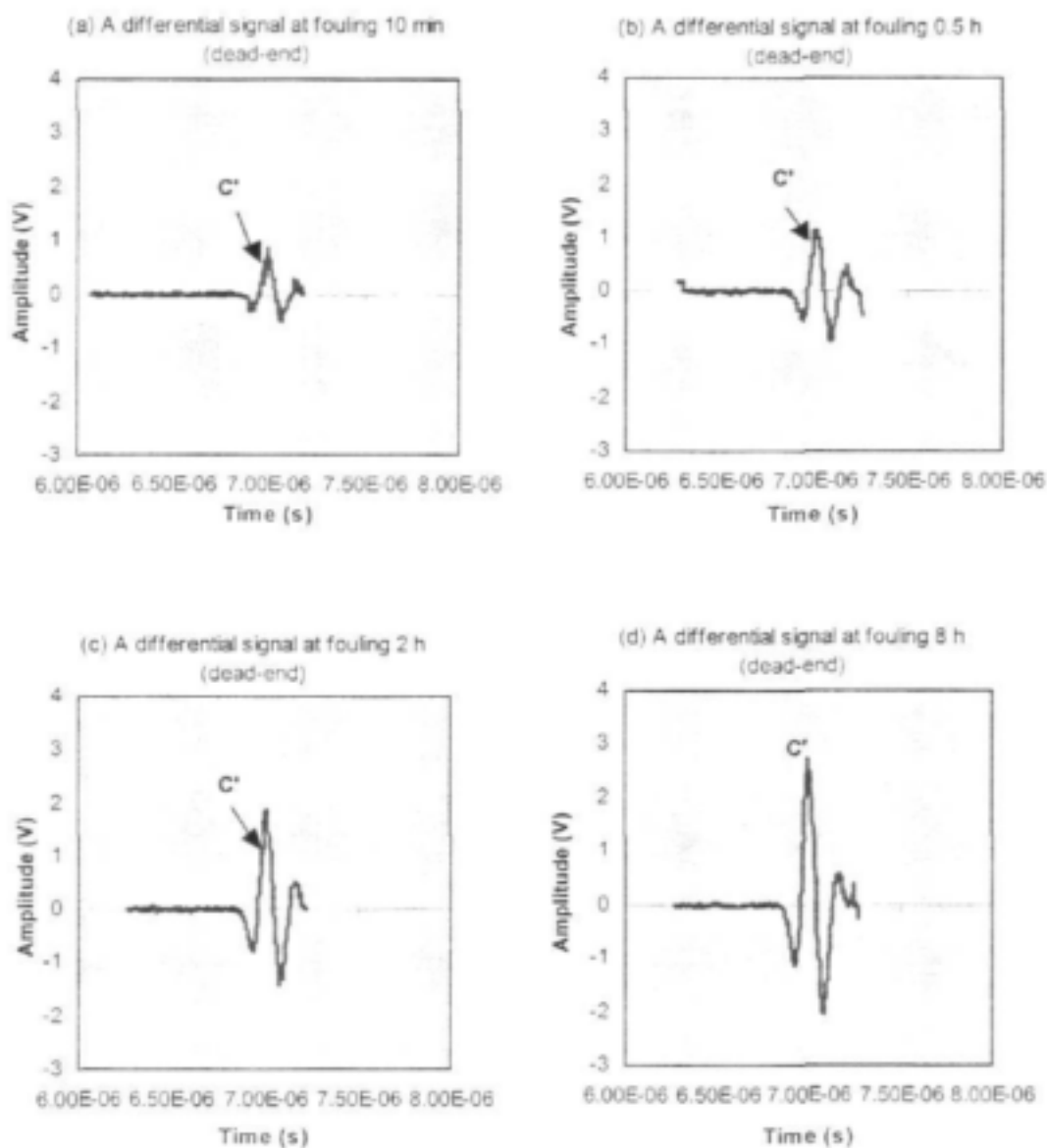


Figure 8.11: Differential signals (peak C') after 10 min, 0.5, 2 and 8 h of operation in the fouling experiment carried out with paper mill effluent at pressure 175 kPa and dead-end filtration.

Note: the white line represents ultrasonic signal responses of a clean PSU membrane.

Differential signals at cross-flow:

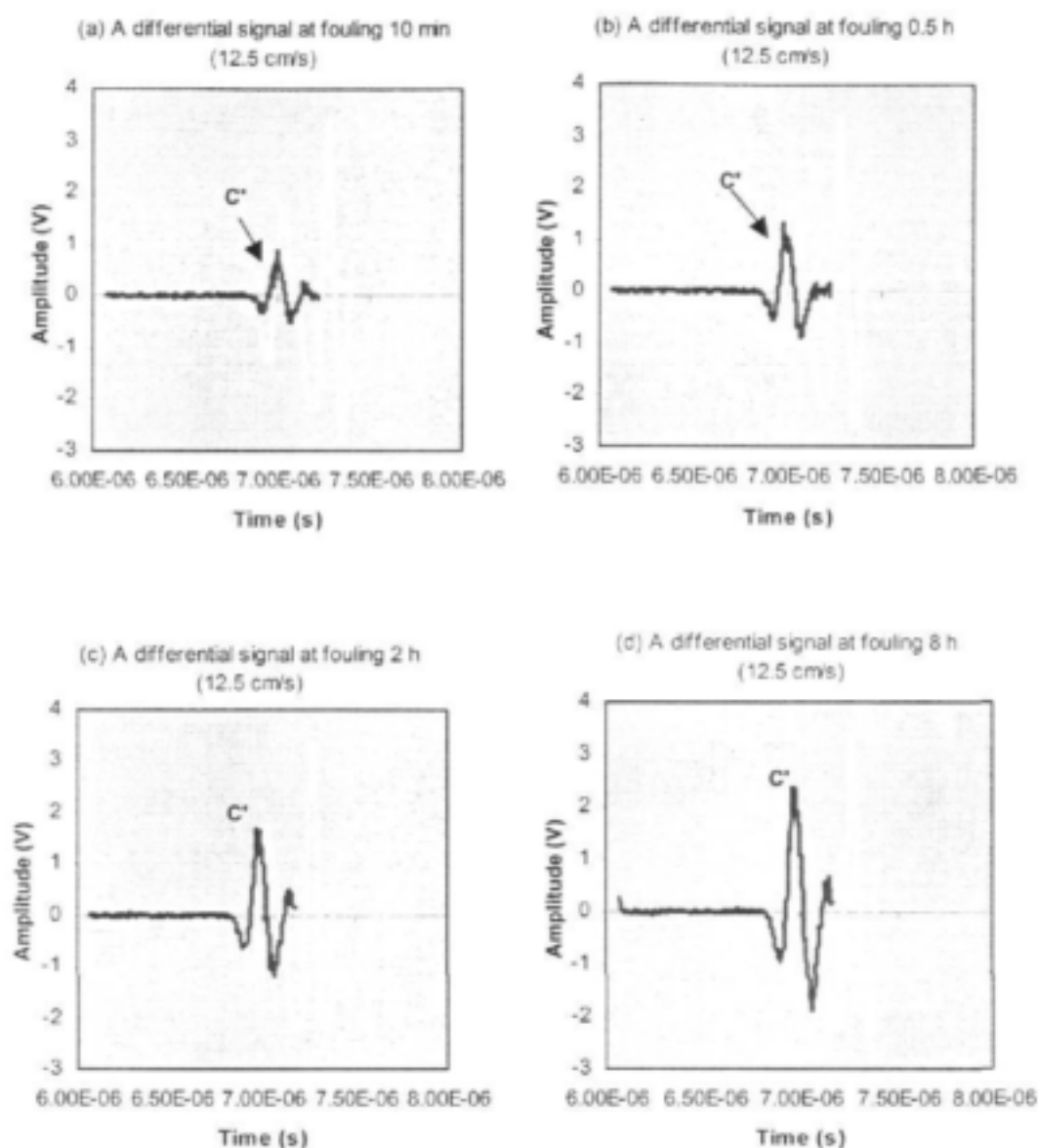


Figure 8.12: Differential signals (peak C') after 10 min, 0.5, 2 and 8 hours of operation in the fouling experiment carried out with paper mill effluent at pressure 175 kPa and cross-flow rate 12.5 cm/s.

Note: The white line represents ultrasonic signal responses of a clean PSU membrane.

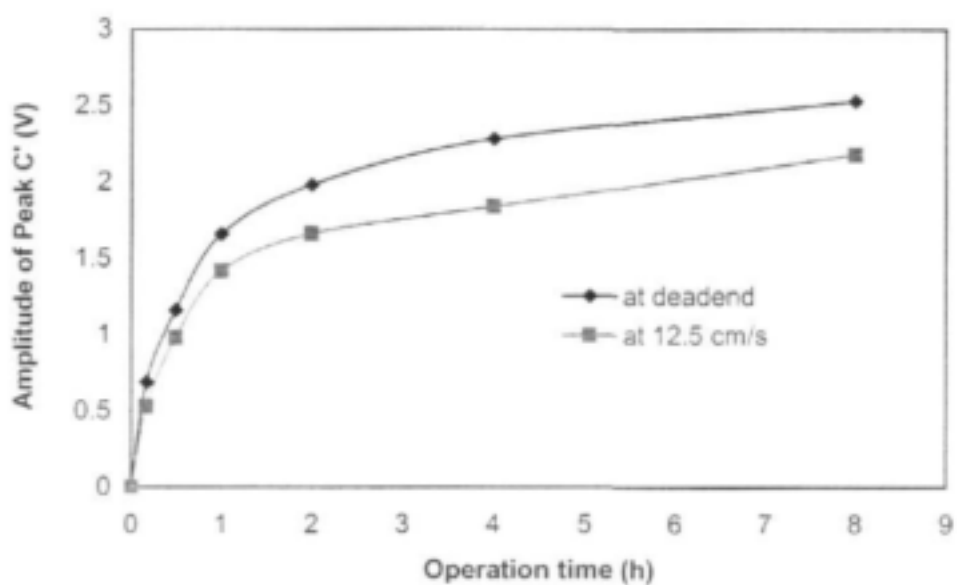


Figure 8.13: Amplitude of differential signal (peak C') versus operation time during fouling experiments carried out with paper effluent at flow rates of dead-end and 12.5 cm/s.

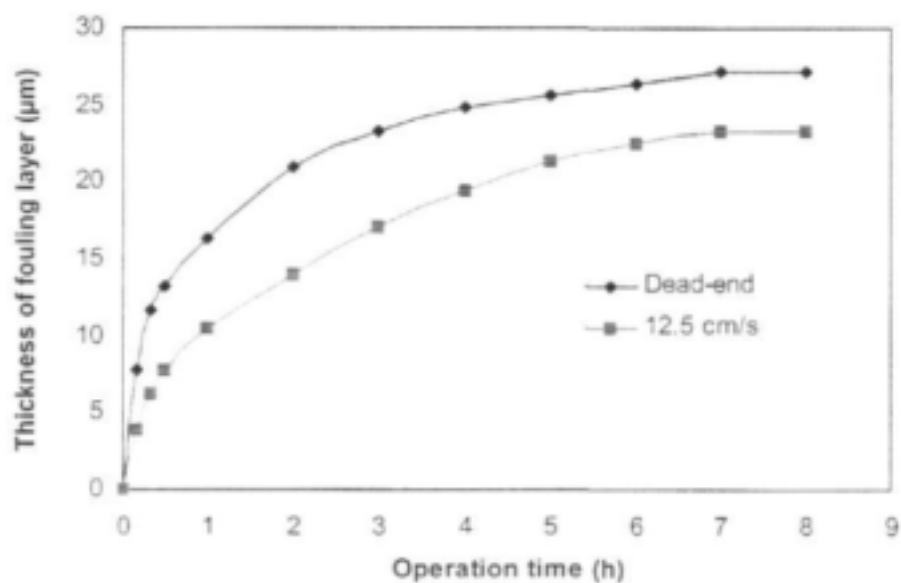


Figure 8.14: The thickness of fouling layer as a function of operation time during fouling experiments at flow rates of dead-end and 12.5 cm/s.

8.4.4 CLEANING EXPERIMENT AND UTDR MEASUREMENT

To investigate the suitability of the UTDR technique for fouling removal strategies, the following fouling and cleaning experiments were carried out. A further fouling experiment was carried out with paper mill effluent at a flow rate of 2.1 cm/s and applied pressure 185 kPa. The total operating time for the fouling experiments were 20 h. Results of ultrasonic reflections in the fouling experiment are shown Figure 8.15. Figure 8.16 displays SEM analysis of clean and fouled membranes.

Figure 8.17 shows the results of ultrasonic response signals during the cleaning experiments. Pure water flux recovery of the cleaned membrane obtained by different cleaning methods is illustrated in Figure 8.18. SEM micrographs of the cleaned samples were also recorded (Figures 8.19 and 8.20). Results of differential signals recorded during cleaning processes are shown in Figure 8.21.

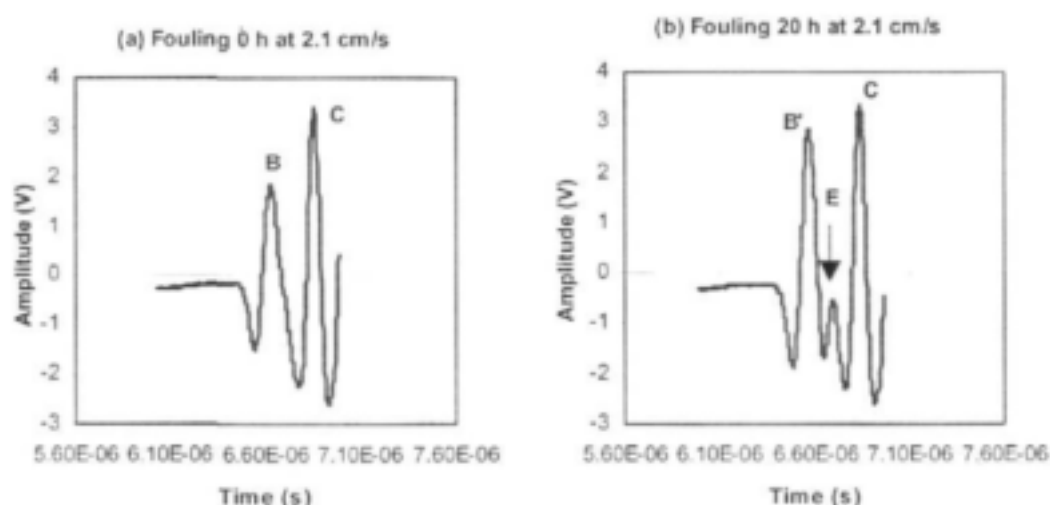
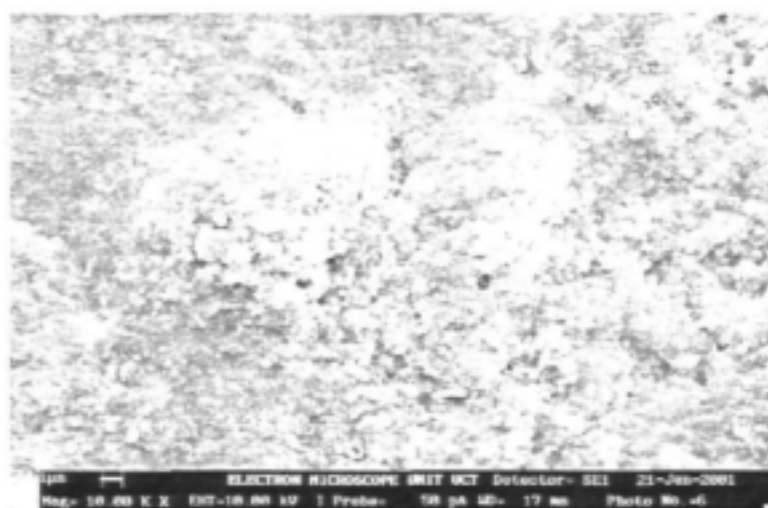


Figure 8.15: Ultrasonic signal responses after 0 (start) and 20 h of operation in the fouling experiment carried out with paper mill effluent at pressure 185 kPa and flow rate 2.1 cm/s.

Microscopic images:



(a)



(b)

Figure 8.16: SEM images of (a) a clean PSU membrane and (b) a PSU membrane fouled by paper mill effluent after 20 h of operation.

Ultrasonic responses:

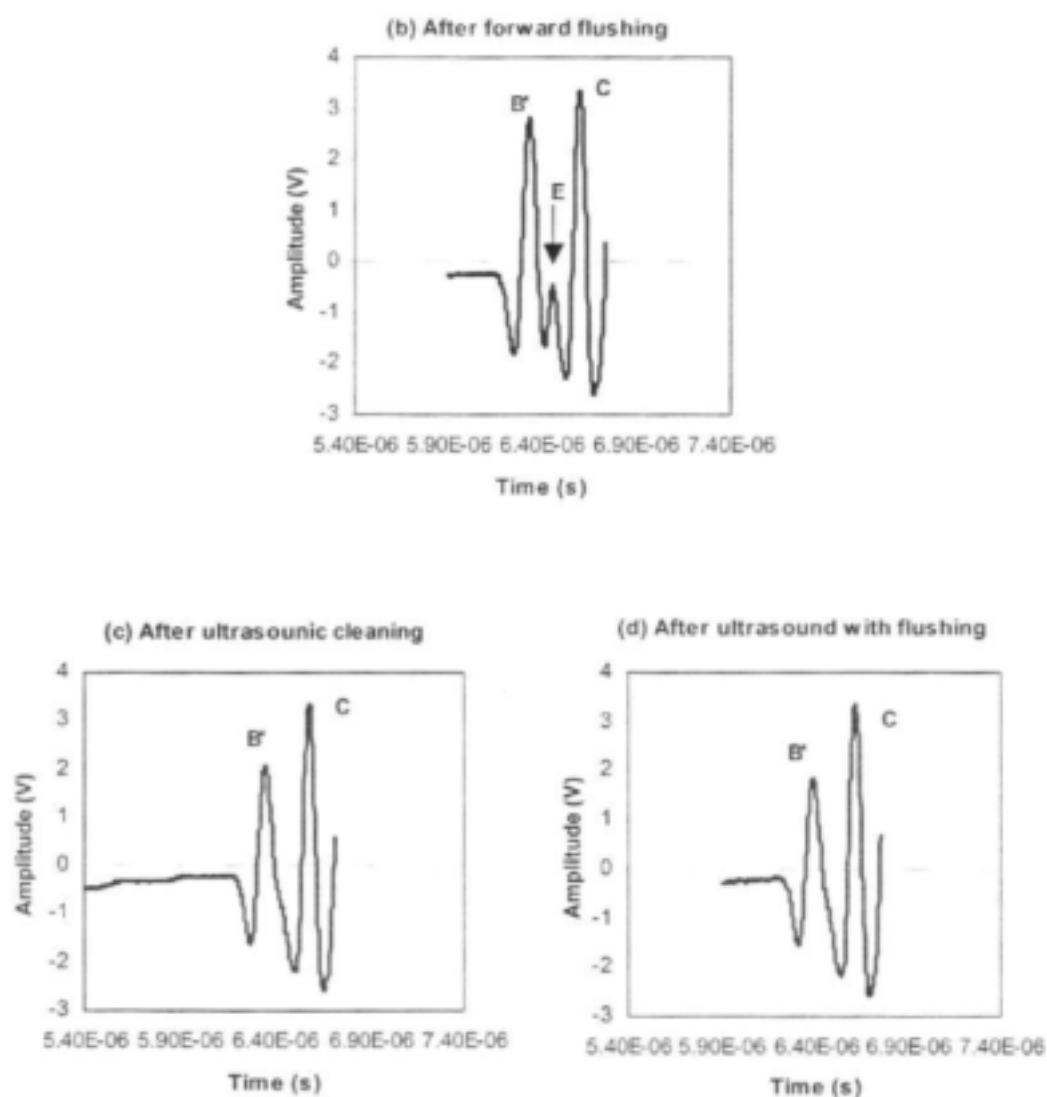


Figure 8.17: Ultrasonic signal responses during pure water experiments after different cleaning methods: forward flushing, ultrasonic irradiation and ultrasound with forward flushing.

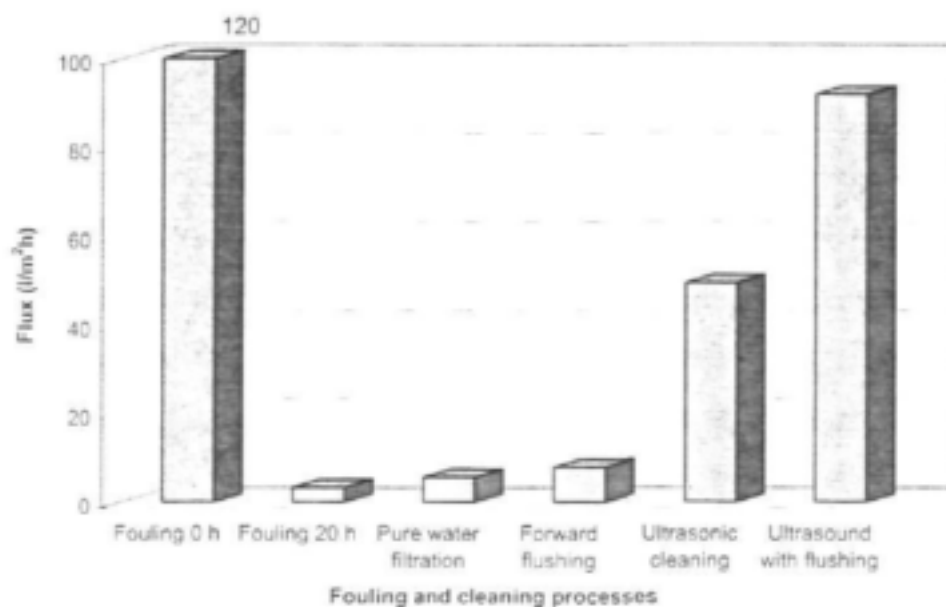


Figure 8.18: Changes of permeate flux during fouling and cleaning processes (at 2.1 cm/s and 185 kPa): fouling 20 h; pure water filtration; forward flushing; ultrasonic cleaning and ultrasound associated with flushing.

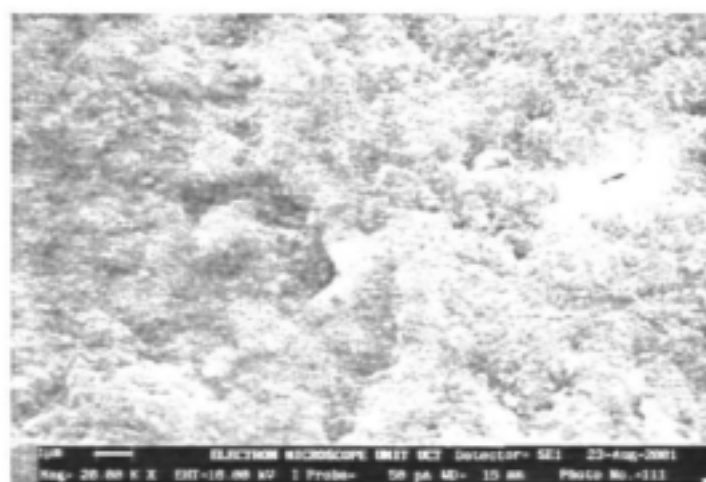
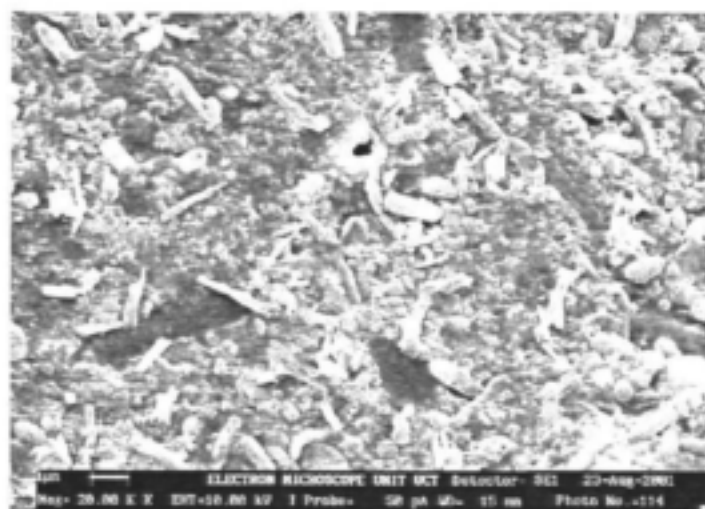
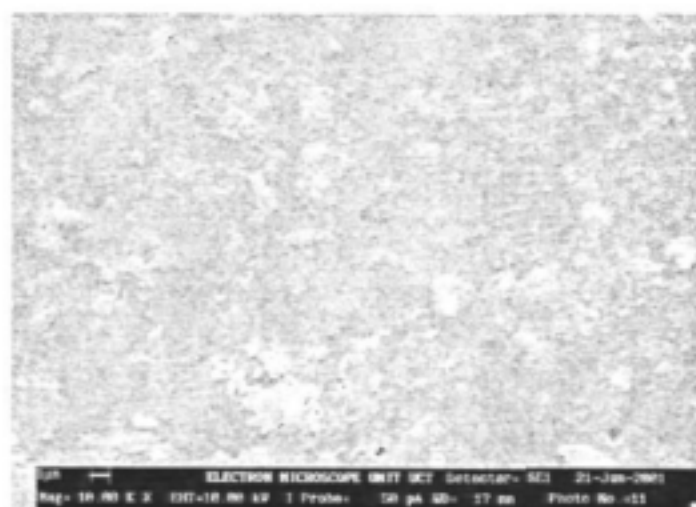


Figure 8.19: SEM image of the PSU membrane surface cleaned by forward flushing.

Microscopic images:



(a)



(b)

Figure 8.20: SEM images of the cleaned PSU membrane surface: after cleaning by: (a) ultrasonic cleaning; (b) ultrasound with forward flushing.

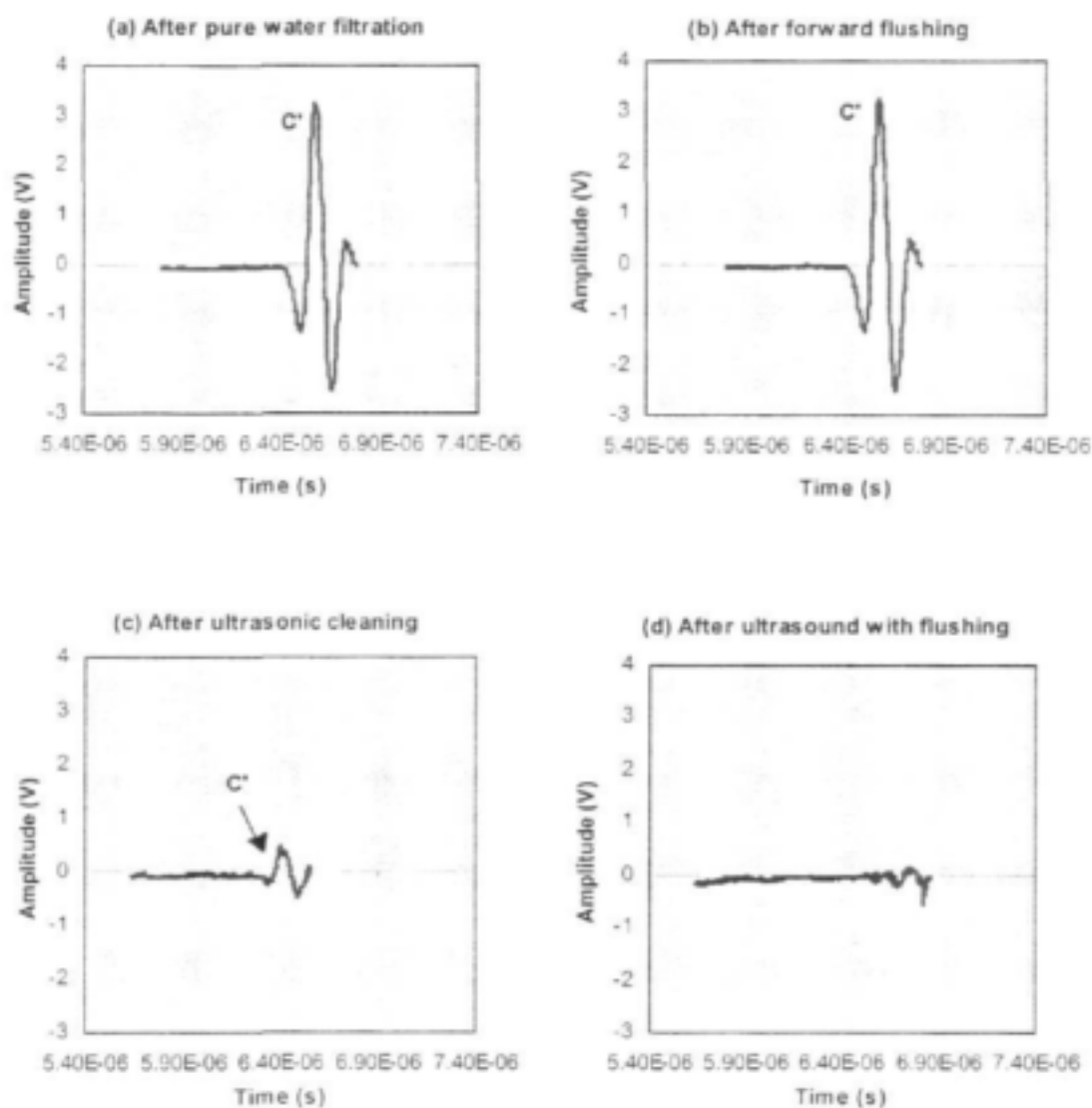


Figure 8.21: Differential signals after (a) pure water filtration after 20 h of fouling operation; cleaning by (b) forward flushing; (c) ultrasonic cleaning; (d) ultrasound with flushing.

Note: The white line represents ultrasonic signal responses of a clean PSU membrane.

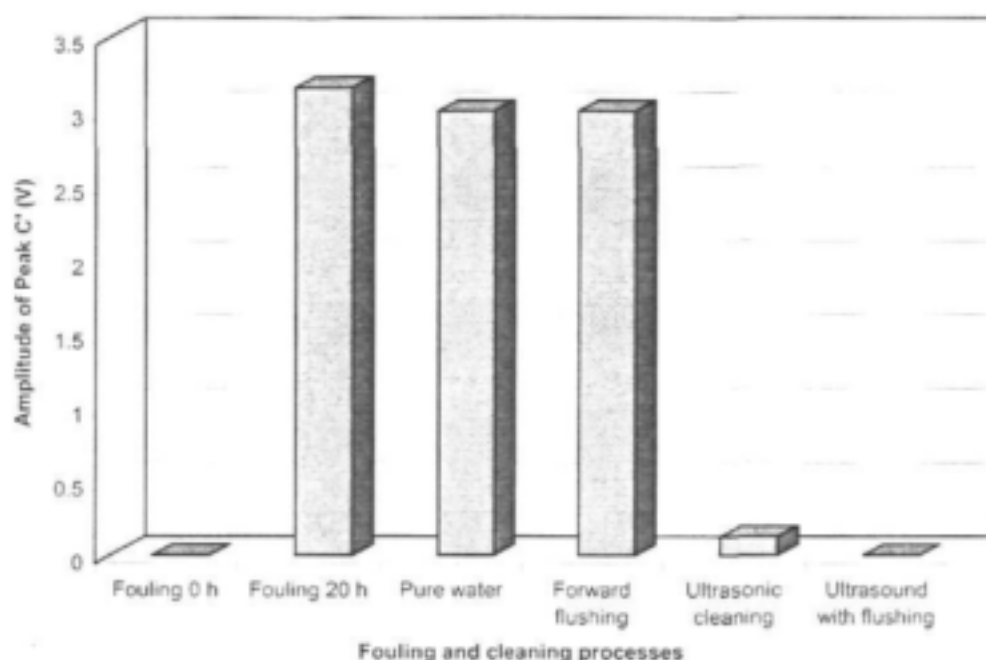


Figure 8.22: Differential signals during fouling and cleaning processes.

8.5 INTERPRETATION OF RESULTS

8.5.1 HYDROSTATIC PRESSURE EXPERIMENT

The ultrasonic response signals revealed a PSU composite membrane that is composed of a PSU layer and a polyester backing layer. The UTDR measurement was focused on Peak B, which indicates the membrane surface (Figure 8.1).

The membrane echo signals B and C shifted to signals B' and C' when the hydrostatic pressure increased from 0 to 160 kPa (Figure 8.2). Figure 8.2 also shows that reflection signals B' and C' are sharper at a hydrostatic pressure of 160 kPa than at 0 kPa. This suggests that the PSU membrane is compacting, causing changes in acoustic impedance under a higher hydrostatic pressure, and becomes denser.

As the hydrostatic pressure increased, the membrane moved farther from the transducer. A near linear relationship exists between the hydrostatic pressure and the arrival time of the reflected signal from membrane signal B (Figure 8.3). The shift distance of peak B with the hydrostatic pressure can be calculated by Equation 3.1 (the sound velocity in pure water is 1438 m/s) as shown in Figure 8.3. This corresponds to a change in spacing between the top plate and the membrane. The shift distance from peak B to peak B' is 133 μm as the hydrostatic

pressure increased from 0 to 220 kPa. The distance also includes the shift because of the membrane compaction. As shown in Figure 8.3, the difference in the arrival times between peaks B and C is 0.22 μ s and the difference in the arrival times between peaks B' and C' is 0.2 μ s. The thickness of PSU membrane decreases by 24 μ m with an increase in pressure from 0 to 160 kPa (the average sound velocity in a PSU membrane: 2400 m/s). Results of the hydrostatic pressure experiments proved the membrane compaction.

8.5.2 FOULING EXPERIMENT AND UTDR MEASUREMENT

As shown in Figure 8.4, the value of the flux declined rapidly at the beginning and then reached a near steady-state flux after 2 h of operation. Further, the decline in the permeate flux was faster at dead-end filtration (0 cm/s) than in cross-flow (12.5cm/s). It implies that significant membrane fouling occurred.

Consistent with the above observation, the corresponding ultrasonic signal responses exhibited rapid changes in amplitude as fouling proceeded (Figure 8.5). Peak B (Figure 8.5a) represents the PSU layer(s). Peak B has a shoulder, showing that the PSU membrane has two layers, a thin and dense layer (PSU₁) and a porous layer (PSU₂, small shoulder, later a peak). In general, once fouling is initiated on the membrane surface, the acoustic impedance difference at the feed solution/membrane interface will change, resulting in a change in the amplitude of echo B. As shown in Figure 8.5c, an increase in the amplitude from peak B (1.687 V) to B' (2.06 V) can be seen after 0.5 h of fouling, as a result of the deposition and growth of a fouling layer on the membrane surface. The ultrasonic response of the fouling layer combined with that of PSU₁ formed Peak B'. The difference in arrival times, dT, between peaks B and B' is 20 ns, due to an increase in the thickness of the fouling layer. Simultaneously a 'new' peak E appeared. It was generated from the interface between PSU₁ and PSU₂. The PSU membrane has two layers: PSU₁ and PSU₂. PSU₁ is so thin compared to PSU₂ that the two traces appear merged (following from waves superimposition principles) before fouling has taken place. After fouling, the fouling layer with PSU₁ becomes thick enough, relative to the PSU₂ layer, to form a distinct echo. The ultrasonic response models that are related to fouling deposition processes are illustrated in Figure 8.23.

As the chemical composition of the fouling layer is mainly lignin or lignosulphonate [Domingo, 2001], both of which have densities similar to the PSU₁ layer, the fouling layer and PSU₁ give a single peak in the UTDR. Hence the reflected signals B, B', C and E were generated from the interfaces: water/PSU₁, feed solution/fouling layer (combined PSU₁), PSU₂ layer/polyester backing and PSU₁/PSU₂. SEM and optical microscope cross-sectional views of a PSU membrane revealed a composite PSU membrane structure - a denser skin layer PSU₁, a porous

layer PSU₂ and a non-woven polyester backing as shown in Figure 8.7. These observed results are consistent with real-time ultrasonic measurements.

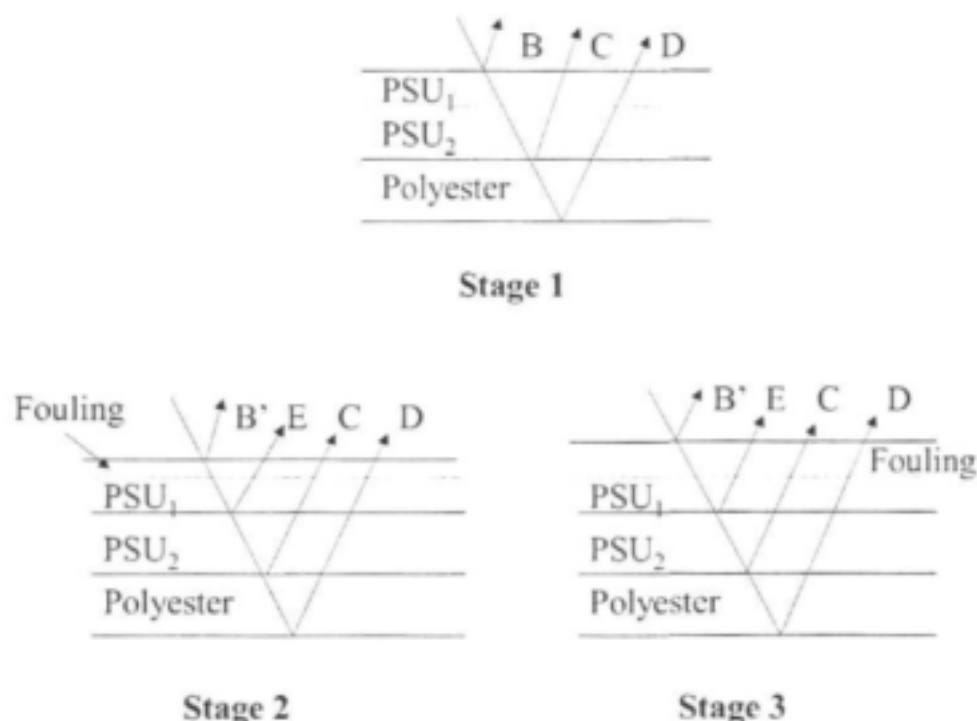


Figure 8.23: Ultrasonic reflection models in the fouling processes. Stage 1: a clean two-layer PS membrane with polyester backing; Stage 2: deposition of a fouling layer on the membrane surface; Stage 3: growth of a fouling layer.

As fouling layer growth progressed, more fouling covers the membrane surface, a denser fouling layer is formed and a greater acoustic impedance change between the bulk solution and the membrane is expected. This will be detected as a sharper reflection. Thus, an echo with greater amplitude was observed at 1, 2, 4, 6 and 8 h of fouling operation in Figure 8.5 and 8.6. The time-domain movement (ahead) of the fouling echo signal (B') was observed as a result of an increase in the fouling layer thickness. The arrival time of peak B was 7.07 μ s. After 8 h of fouling operation, the amplitude and arrival time of peak B' were 2.468 V and 7.028 μ s, respectively.

Similar results of ultrasonic responses can be observed in Figures 8.8 and 8.9 as further experiments were carried out with paper mill effluent at a cross-flow rate 12.5 cm/s and pressure 175 kPa. It was found that the amplitude of peak B' at cross-flow 12.5 cm/s increased at a slower rate than that at dead-end. An apparent peak E at 12.5 cm/s appeared after 2 h of operation (Figure 8.9a). However, after 0.5 h of operation peak E was already present in dead-

end (Figure 8.5c). The fouling layer on the membrane surface appeared and grew fast at lower axial velocity because of the lower shear rates. This indicates that the ultrasonic testing technique is able to distinguish between the growth rates of a fouling layer on a membrane surface in dead-end and cross-flow operations. In order to study membrane coverage, the fouled membranes were taken for SEM analysis to confirm the ultrasonic measurement and membrane coverage in Figure 8.10. The micrographs of the membrane surface after 8 h of fouling operation under dead-end and cross-flow (12.5 cm/s) revealed complete membrane coverage with a fouling layer. A number of particles arrived simultaneously at the deposit layer so that a disordering arrangement of particles was seen on the membrane surface in dead-end filtration (Figure 8.10a). This is because the particles deposited approach the membrane directly at right angles, giving a compact cake that can resist deformation under pressure [Xu-Jiang et al., 1995]. This suggests that the sharper echo peak is reflected from the fouled membrane surface with a denser fouling layer (Figure 8.6d). In cross-flow filtration, the particles that are found in the cake approach the membrane at an acute angle. The surfaces of these cakes are also subject to shear forces by the cross-flow of the suspension, which tends to remove the larger particles from the surface, so giving a preferential capture of finer particles [Xu-Jiang et al., 1995; Lu and Ju, 1989]. At same time, there are more large particles reaching the membrane in cross-flow filtration than dead-end. According to a force balance mechanism [Vyas et al., 2001], if the drag forces are less than the joint forces including gravitational adhesive force and friction forces, the larger particles will be retained on the membrane surface. Note the flow rate of 12.5 cm/s is much lower than flow rates in UF. So Figure 8.10b shows the fine particles covered and some larger ones interspersed on the surface of the fouling layer in the cross-flow filtration. A rough/sparse fouling layer surface covering on the membrane surface resulted in some sound distribution. Hence, reflection signals during cross-flow operation are weaker than that during dead-end operation. It is concluded that the flux decline and morphological observations of membrane coverage corroborated the *in situ* ultrasonic measurements.

8.5.3 DIFFERENTIAL SIGNALS

It is shown in Figure 8.11 that a differential signal was observed within a short time, namely 10 min of fouling operation, and grew at 0.5, 2 and 8 h as fouling proceeded. A sharper differential signal emerged due to a denser fouling layer on the membrane surface after 8 h of fouling operation at dead-end. Time-domain movement from peaks B to B' can be also observed as a result of an increase in the thickness of fouling layer. Figure 8.12 shows similar results achieved at 10 min, 0.5, 2 and 8 h of fouling operation during cross-flow filtration.

Changes in amplitude of the differential signals during dead-end and cross-flow (12.5 cm/s) filtration are shown in Figure 8.13. These indicated that the amplitude of the differential signals increased as fouling proceeded. Furthermore, the increase in the ultrasonic amplitude became

slower as the axial velocities increased. This suggests that the rate of fouling was lower at a higher axial velocity.

Another basic quantity measured in non-destructive ultrasonic testing is the time of flight or the amount of time required for the sound to travel through the sample. That is to say that the ultrasonic technique can quantify the thickness of a fouling layer (on a membrane surface) by comparing ultrasonic response signals. The thickness of a fouling layer on a membrane surface can be calculated by Equation 3.1 (the sound velocity in the fouling layer is 1550 m/s). The thickness of the fouling layer increased rapidly at the beginning of fouling because of concentration polarisation and fouling layer formation, followed by a slow increase due to gradual growth of the fouling layer (Figure 8.14). Moreover, an increase in the thickness of the fouling layer grew faster during dead-end filtration than during cross-flow (12.5 cm/s). The thickness of the fouling layer after 8 h of fouling operation was 27.1 μm at dead-end filtration, and 23.2 μm at cross-flow (12.5 cm/s), respectively.

8.5.4 CLEANING EXPERIMENT

Results of a further fouling experiment showed an increase in amplitude-domain and movement in time-domain from Peaks B to B' after 20 h of fouling operation in Figure 8.15. Peak E also appeared after 20 h of fouling operation. It indicated that a dense fouling layer was formed on the membrane surface. SEM analysis of the fouled membrane (Figure 8.16) corroborated this observation.

An increase in permeate flux and a decrease in the amplitude of the ultrasonic response signal of the fouling layer, in comparison with the 20 h fouling echo signal, were observed (Figures 8.18 and 8.22) because of changing the bulk solution from effluent to pure water. The change in the bulk solution from effluent to pure water resulted in the reduction of concentration polarisation on the membrane surface. This again suggests that the UTDR technique is able to detect subtle changes on the membrane surface.

Flushing slightly increased the pure water flux (Figure 8.18) and decreased the amplitude of the ultrasonic response signal of the fouling layer (Figures 8.21b and 8.22). This again suggests that forward flushing can reduce the rate of membrane fouling. The deposited fouling layer on the membrane surface is expected to become re-suspended and swept away by tangential- or cross-flow [Redkar and Davis, 1995]. The peak of the fouling echo signal decreased because the density of fouling layer was reduced after forward flushing. Therefore, the UTDR technique is able to explore the presence and the removal of the fouling layer in real-time.

In addition, it was found that the paper effluent fouling on the PSU membrane is difficult to clean using only forward flushing. SEM analysis revealed that there is still a dense fouling layer on the membrane surface after forward flushing, although many pores produced by forward flushing appeared on the fouling layer (Figure 8.19). Hence, membrane fouling is caused by the adsorption of foulants both on and inside the membrane. Additional cleaning methods are needed.

Figure 8.18 shows that the pure water flux increased from 8 l/m²h after forward flushing to 50 l/m²h after ultrasonic cleaning. The disappearance of the echo signal E showed that the fouling layer was destroyed by ultrasonic irradiation (Figure 8.17c). There is a significant decrease in ultrasonic amplitude of the differential signal, from 3.0 volts after forward flushing to 0.125 volts after ultrasonic irradiation (Figures 8.22c and 8.23). This suggests that ultrasonic treatment can effectively break the fouling layer on the membrane. However, Figure 8.21c shows that the amplitude after ultrasonic cleaning is 0.125 volts, signifying that there is still some fouling on the membrane as shown in Figure 8.21a. Furthermore, the permeate flux of 49.5 l/m²h obtained after ultrasonic cleaning is still lower than the original pure water flux of 190 l/m²h.

After ultrasound associated with flushing, the pure water flux was 92 l/m²h (Figure 8.18). Although it is still lower than the original water flux of 120 l/m²h, the ultrasonic signal response shows that the differential signal disappeared after ultrasound with forward flushing (Figure 8.21). Hence, the fouled membrane was cleaned by ultrasound associated with flushing. Morphological analysis of the cleaned membrane showed that there is almost no fouling layer on the membrane surface (Figure 8.20b). This is because forward flushing produces a high tangential or cross-flow rate (40-50 cm/s) on fouling layers. These results demonstrate that the UTDR technique can monitor the removal of the fouling layer and membrane cleaning. It is suitable to study the effectiveness of various cleaning techniques.

8.6 APPLICATION OF MODELLING

The PSU composite membrane was modeled on the basis of an actual membrane. Figure 8.24 shows the modelled individual and combined response signals of a clean two-layer PSU membrane with polyester backing. The modeling for an asymmetric PSU membrane in response to its reflecting properties was based on internal velocities, thickness and densities of multi-layers made of the PSU. A signal frequency of 10 MHz was used in the actual experiments. In order to produce a smooth signal curve, points were calculated at intervals of 3×10^{-9} s. Results of this mathematical modeling display a composite PSU membrane, which is composed of two layers (PSU₁ and PSU₂) and polyester backing.

The next model was based on the assumption that a fouling layer consisting of lignin and lignosulphonate (density 1.05 g/cm^3), with a thickness of $20 \text{ }\mu\text{m}$, had been deposited on the membrane. The results of modeling a $20\text{-}\mu\text{m}$ fouling layer on a PSU membrane are presented in Figure 8.25. A response very similar to the signal obtained during actual measurements of fouling deposition carried out with paper mill effluent in Figures 8.11b or 8.12b was obtained. A small echo peak formed in front of the membrane peak. Further, maintaining the density and increasing the thickness of the layer to $80 \text{ }\mu\text{m}$ resulted in a movement ahead in the time domain (Figure 8.26), without any significant change in the shape and peak height of the "fouling peak".

In the following model the density of a $50 \text{ }\mu\text{m}$ fouling layer was increased from $1.03\text{--}1.4 \text{ g/cm}^3$. An increase in peak height of the fouling echo was obtained as the density of the fouling layer increased (Figure 8.27). In addition, maintaining the thickness and increasing the density of the fouling layer to 1.4 g/cm^3 resulted in a further increase in peak height and a slight change in slope at the beginning of the signal, without changing the position of the fouling echo. The differential signals obtained in Figures 8.28 and 8.29 corroborate the modelling results. Results of the UTDR indicate that growth of a fouling layer in thickness and density results in flux decline.

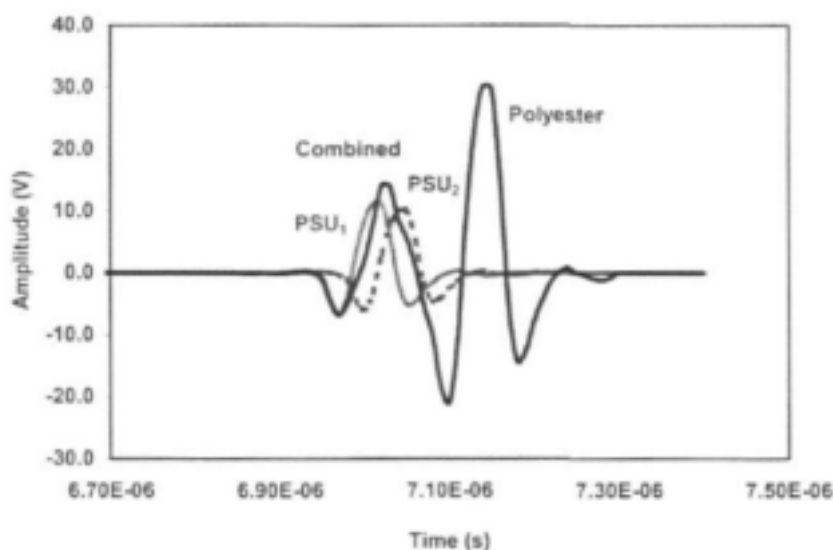


Figure 8.24: Modelling individual and combined response signals of a clean two-layer PSU membrane with a polyester backing.

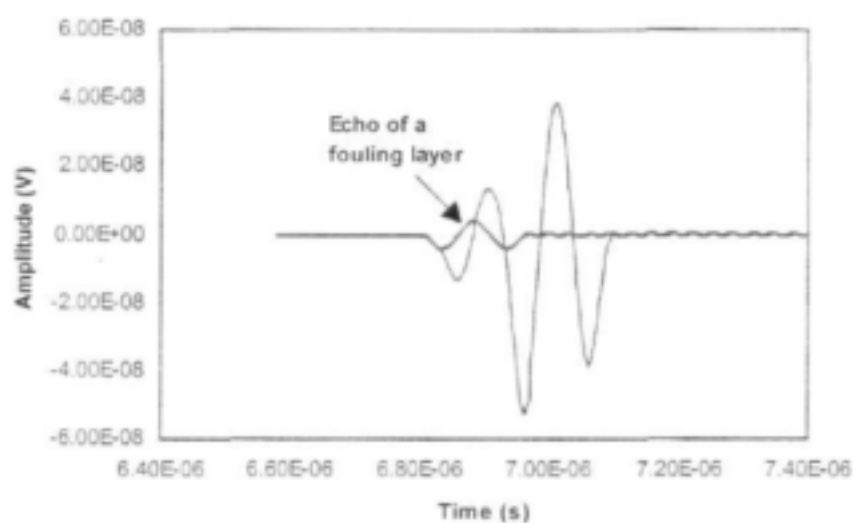


Figure 8.25: Model of a 20 μm thick fouling layer ($\rho = 1.05 \text{ g/cm}^3$) on a PSU membrane.

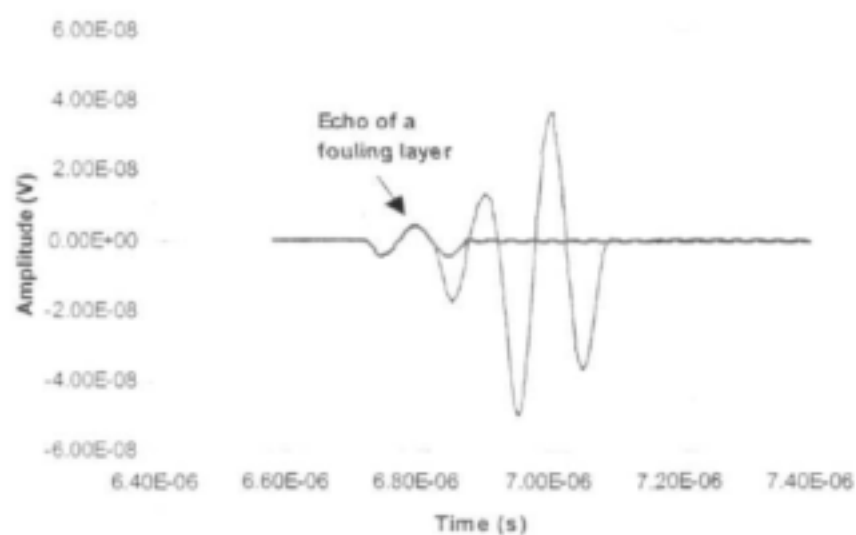


Figure 8.26: Model of an 80 μm thick fouling layer ($\rho = 1.05 \text{ g/cm}^3$) on a PSU membrane.

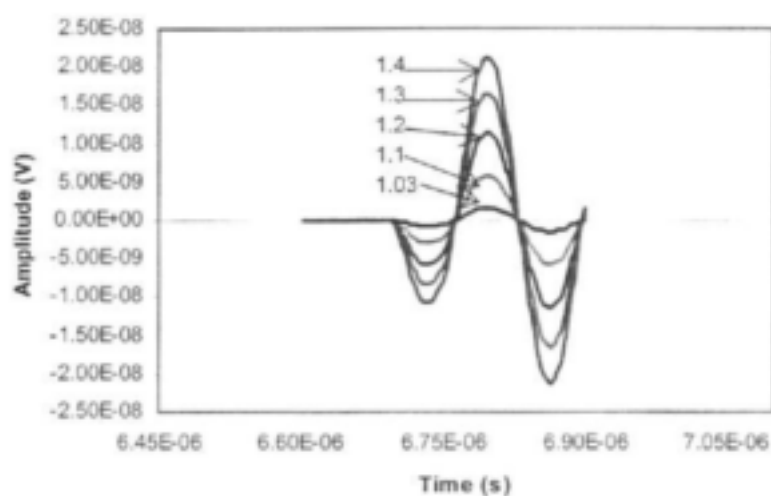


Figure 8.27: Mathematical model of density increases from 1.03 to 1.40 g/cm³ in a 50 μm fouling layer.

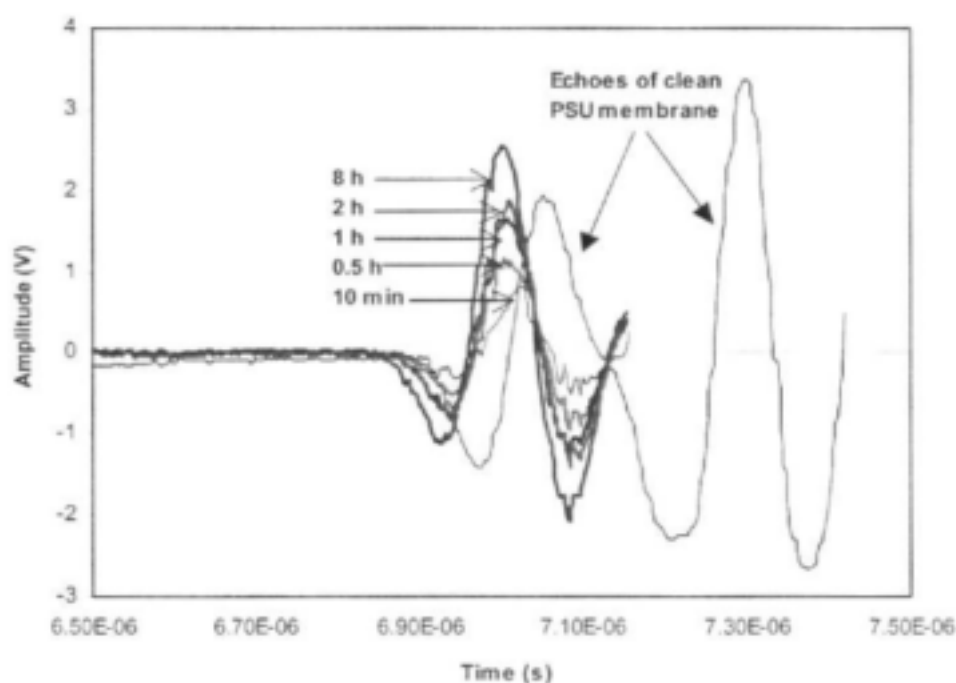


Figure 8.28: Actual ultrasonic response signal of a clean PSU membrane and differential signals after 10 min - 8 h of operation in the fouling experiment carried out with paper mill effluent at applied pressure 175 kPa and dead-end.

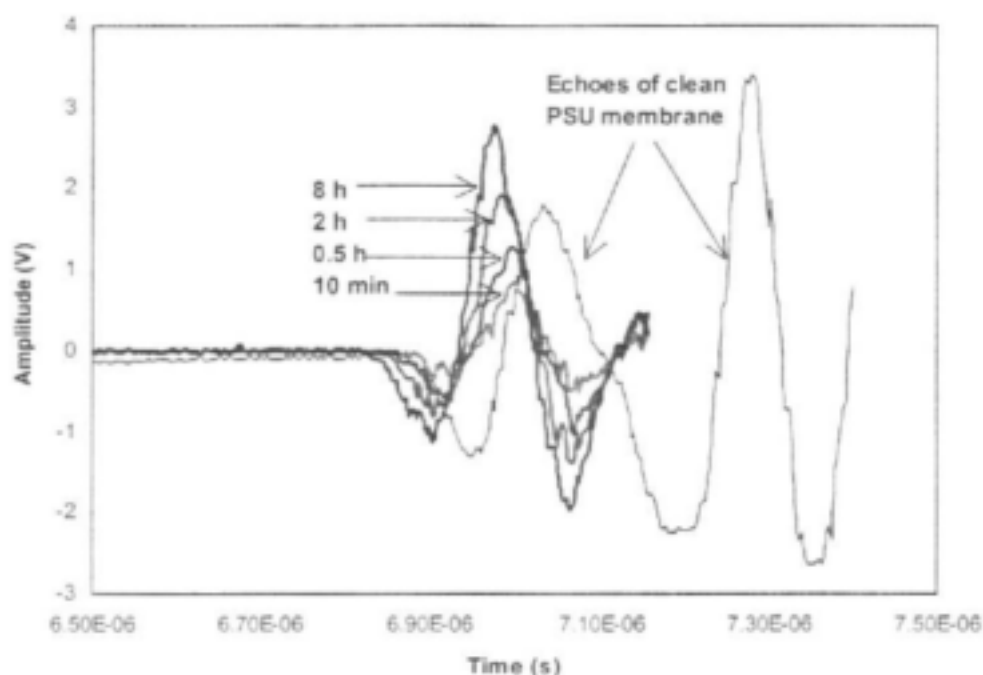


Figure 8.29: Actual ultrasonic response signal of a clean PSU membrane and differential signals after 10 min - 8 h of operation in the fouling experiment carried out with paper mill effluent at applied pressure 175 kPa and a flow rate of 12.5 cm/s.

8.7 CONCLUSIONS

This chapter describes the UTDR technique as a non-destructive method by which to monitor and measure organic fouling and cleaning in real time in UF. An asymmetric, composite PSU membrane and its compaction can be detected by UTDR. Results show a good correspondence between the UTDR signal response and the development of the fouling layer on the membrane surface. The ultrasonic technique can measure the rate of fouling layer formation at the different operating conditions: dead-end and cross-flow filtrations.

The most important finding is the differential signal obtained. Both amplitude and arrival time of differential signals as a function of operation time provide useful quantitative information such as the thickness of a fouling layer and its density changes in the fouling processes.

The UTDR technique can effectively not only detect deposition and growth of a fouling-layer on a membrane in real-time, but also monitor the progress of membrane cleaning and evaluate the cleaning effectiveness of various cleaning methods. The UTDR results corroborated traditional flux measurements and analysis of the membrane surface by microscopy.

Ultrasonic reflection modelling (URM) was applied to model the density and thickness of a fouling layer on a membrane surface so as to predict the fouling behaviour. The growth of a fouling layer in thickness and density results in flux decline. The modelling results are consistent with the actual observations. All indicate that the URM program is a useful tool with which to gain an understanding of the processes of ultrasonic testing related to fouling deposition and density changes of the cake layer.

9. MEASUREMENT OF PROTEIN FOULING IN TUBULAR ULTRAFILTRATION

9.1 ABSTRACT

Membrane filtration is an attractive process for the concentration and separation of bioproducts. Protein fouling is however a phenomenon affecting filtration operation and membrane performance. A great challenge is the development of non-invasive methods that allow for the early, *in-situ* protein fouling detection, especially in tubular membrane modules.

A new non-invasive ultrasonic technique was used for the *in-situ* monitoring of protein fouling in UF. A focal transducer with a frequency of 7.5 MHz was designed and used in this study. A tubular UF module was used to investigate the capabilities of the ultrasonic technique and its applicability for different configuration modules. The tubular membrane was a polyethersulphone (PES) UF membrane with MWCO 40 kDa. The feed used was 0.08 and 3 g/l bovine serum albumin (BSA) solution. The experiments were conducted at a flow rate of 0.04 cm/s and applied pressure 150 kPa.

Protein fouling was successfully detected in tubular UF by the ultrasonic technique. The ultrasonic technique can distinguish and recognise various response signals from ultrasonic measurements in a tubular cell. The degree of the observed signal amplitude change correlated well with BSA fouling behaviour, such as adsorption, deposition and gelation on the membrane. The ultrasonic technique can provide an approach to understanding the nature and severity of protein fouling related to flux decline. Permeate flux through the membrane will decline due to the adsorption and concentration polarisation, and then as retentate concentration increases. Moreover, the ultrasonic technique is capable of detecting membrane cleaning. Flux measurements and UV analysis corroborate the ultrasonic testing. Ultrasonic frequency spectra obtained may be useful as an additional tool for fouling detection.

9.2 INTRODUCTION

The most serious operation restraint in UF is the flux decline [Cheryan, 1998]. Such flux decline is mainly ascribed to concentration polarization [Kimura and Sourirajan, 1967], adsorption and

deposition of small particles and proteins or other macromolecules [Robertson and Zydney, 1990; Opong and Zydney, 1991], pore constriction and/or pore blockage [Iritani et al. 1992; Tracey and Davis, 1994], the build-up of a filter cake of macromolecular solutes on the top surface of the membrane [Iritani et al., 2002] or a combination of these factors.

Understanding protein fouling behavior would greatly assist in developing strategies that may prevent this phenomenon from occurring, or minimizing its impact. Although a significant amount of research has been conducted to better understand the dynamics of UF, the real mechanism of separation remains incompletely understood. This is because there was no method that allows for *in-situ*, real time detection of protein fouling in membrane processes, and practical counter measures are only initiated when significant flux decline has occurred. Detecting the earliest stages of protein fouling formation is critical to the efficient and cost-effective management of membrane separations, and real-time protein fouling monitoring could be used to initiate appropriate counter measures against the maturation of protein fouling and help avoid the detrimental effects associated with their irreversible attachments.

This section focuses on the development of a new ultrasonic technique to detect in situ protein fouling and cleaning in UF, and further investigate the capabilities of the ultrasonic technique and its applicability for different membrane module configurations. A focal transducer with a frequency of 7.5 MHz was used. Ultrasonic frequency spectra and differential signal were applied to describe the sensitivity of ultrasonic testing.

9.3 ULTRASONIC FREQUENCY SPECTRA

Ultrasonic resonance spectroscopy or ultrasonic absorption/attenuation spectroscopy is a well-known physical method of analysis having a variety of applications [Ford, 1970; Bhatia, 1985; Migliori et al. 1993 and 1996; Darling et al. 1997]. Ultrasonic frequency spectra are defined as the distribution of the frequency components of ultrasonic signals used in the non-destructive testing of materials [Lavrentyev and Rokhlin, 2001]. They are obtained by using the well-known Fast Fourier Transform procedure (FFT) and applied to ultrasonic measurements.

Ultrasonic testing uses short pulses of vibration energy, which have characteristics similar to white light. According to Fourier's theorem such short pulses can be regarded as arrays of various radiation frequencies and can be called frequency spectra. Figure 9.1 shows a typical signal waveform and frequency spectrum for a focal transducer used, having a central frequency of 7.5 MHz.

A spectrum analysis of these short pulses, carried out after they have passed through and interfered with materials to be tested, can be expected to yield information related to the

physical properties of the materials. Ultrasonic sound waves represent elastic waves. An ultrasonic frequency spectrum thus contains information on the elastic behaviour and properties of the material.

Most metals show low attenuation or absorption of ultrasonic waves, whereas many polymers and organic materials exhibit strong absorption [Ford, 1970]. At present, little information is available on the interpretation of ultrasonic spectra and the causes for absorption/dissipation in certain materials. Ultrasonic frequency spectra were used here to further study the processes of fouling deposition related to ultrasonic responses in membrane separations.

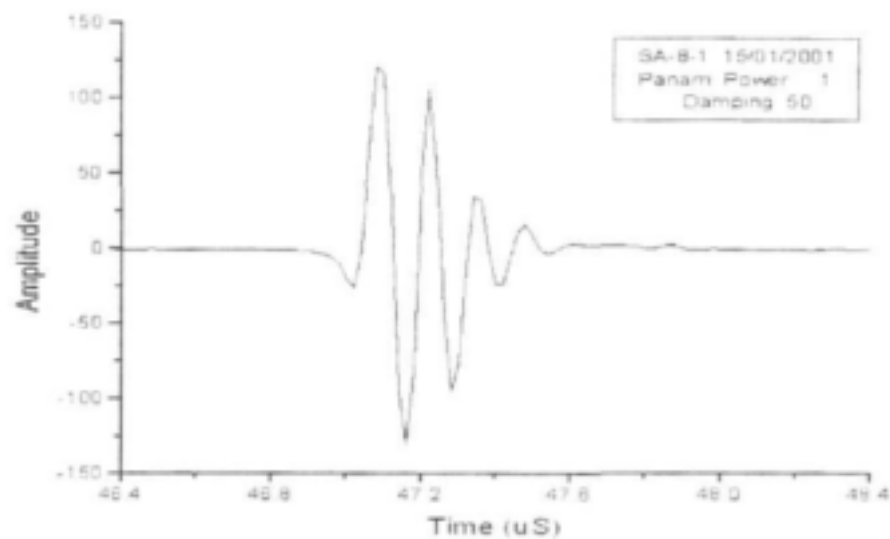
9.4 EXPERIMENTAL

9.4.1 MATERIALS AND APPARATUS

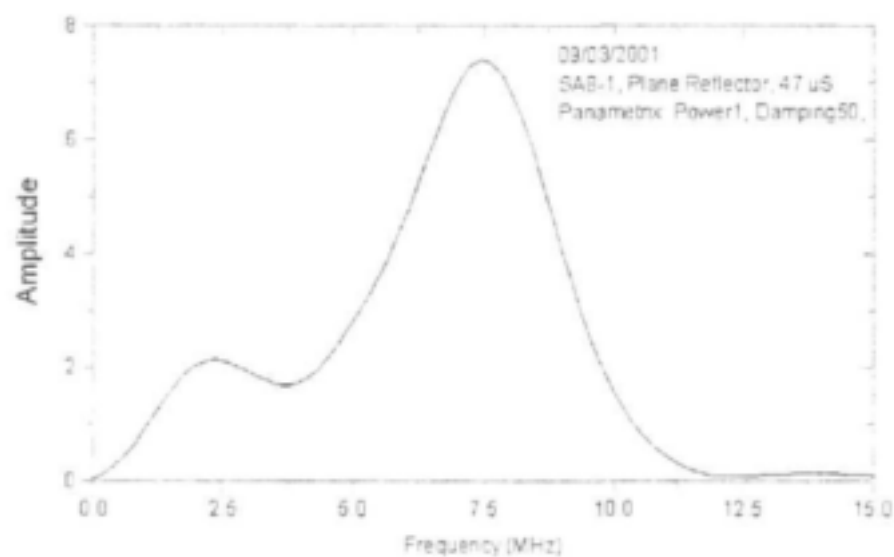
Bovine serum albumin (BSA) (Fraction V, Boehringer Mannheim GmbH, Germany) with molecular weight of 67 kDa was used in this study. Powdered BSA was dissolved in distilled water. Feed concentrations of BSA solution investigated were 0.08 g/l (pH = 6.9) and 3 g/l (pH = 6.2). The BSA concentration was measured with a UV spectrophotometer (Model Lambda 20 UV/VIS, Perkin-Elmer Ltd.) at 280 nm.

The tubular membrane was a polyethersulphone (PES) UF membrane (Weir-Envig Ltd. South Africa) with a molecular weight cut-off (MWCO) of 40 kDa. The dimensions of the membrane were $\Phi 14 \times 21$ mm. A tubular test cell was designed, as shown in Figure 3.5, and used in this study.

The ultrasonic measurement system consisted of a 7.5 MHz focal ultrasonic transducer, a pulser-receiver (Panametrics 5058PR) and a digital oscilloscope (HP Model 54602B) with sweep speeds of 2 μ s/div and 1mv/div sensitivity. The focal transducer emitting signals to and receiving them from the various layers within the tubular cell was externally mounted, in contact with the tubular test cell. The couplant used to couple the transducer was salad oil.



(a)



(b)

Figure 9.1: Typical signal waveform in (a) time domain and (b) frequency domain for a focused transducer with a frequency of 7.5 MHz.

9.4.2 EXPERIMENTAL PROCEDURE

Figure 9.2 is a schematic representation of a UF experimental system and an ultrasonic measurement system. The UF system allows for the accurate control of inlet pressure, retentate flow rate and temperature. In each UF experiment, continuous stirring in the feed tank was

provided. Each experiment commenced with pure water being circulated through the system at the desired flow rate and applied pressure, for 2 h, to compress the membrane and to build up a stable flow field. Ultrasonic spectra inside the tubular test cell and echoes of a tubular membrane during the pure water phase were obtained. Once steady state was attained, the feed was switched to the BSA solution to initiate the fouling phase. This phase was allowed to continue until the ultrasonic response and permeate flux had stabilised.

The fouling experiment was carried out at a flow rate of 0.04 cm/s, applied pressure of 150 kPa and a temperature of 25 °C. Note: The fouling experiment was carried out at a very low flow rate in order to observe the adsorption and deposition of BSA with increases in retentate concentration and get the retentate samples for UV analysis. The fouled membrane was cleaned with 0.1 g/l enzyme solution (from Terg-A-Zyme enzyme detergent power – Alconox INC., New York, USA) after the fouling experiment with 3 g/l BSA. Before commencing with the cleaning experiments, the feed solution was changed from BSA solution to pure water at 150 kPa and an axial velocity of 0.04 cm/s, in order to obtain the pure water flux of a fouled membrane.

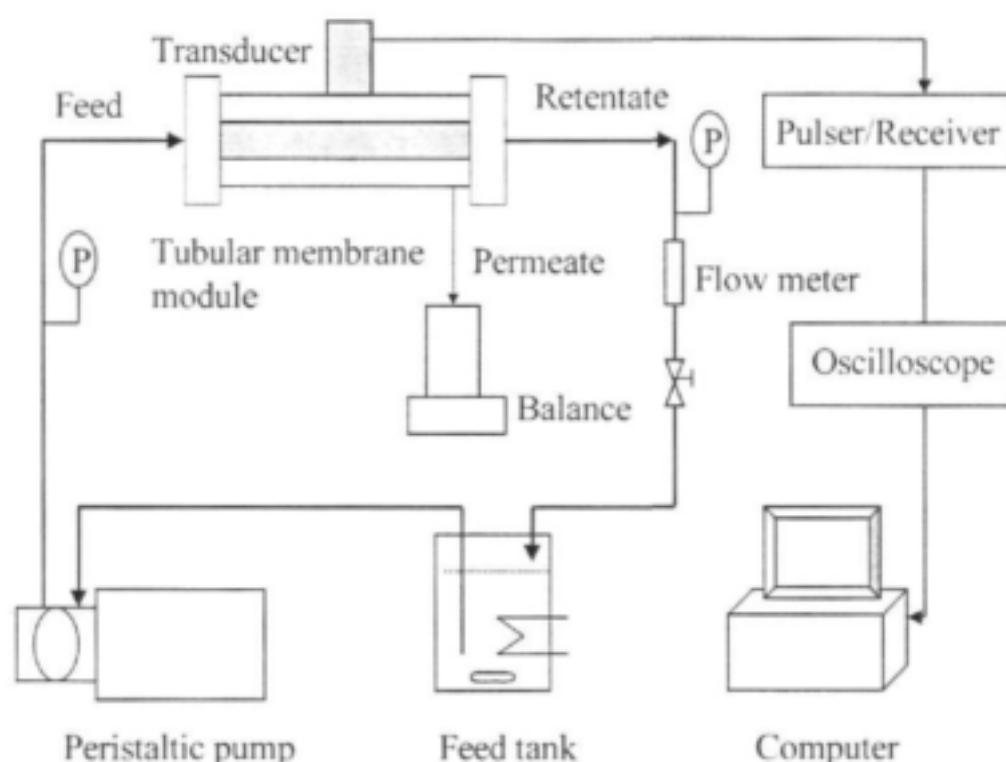


Figure 9.2: Schematic representation of the tubular UF separation system and the ultrasonic measurement system.

9.5 RESULTS AND DISCUSSION

9.5.1 ULTRASONIC SPECTROMETRY IN A TUBULAR CELL

The pure water filtration was carried to investigate the resolution capabilities of the UTDR technique and distinguish or recognise various response signals from ultrasonic records in the tubular cell

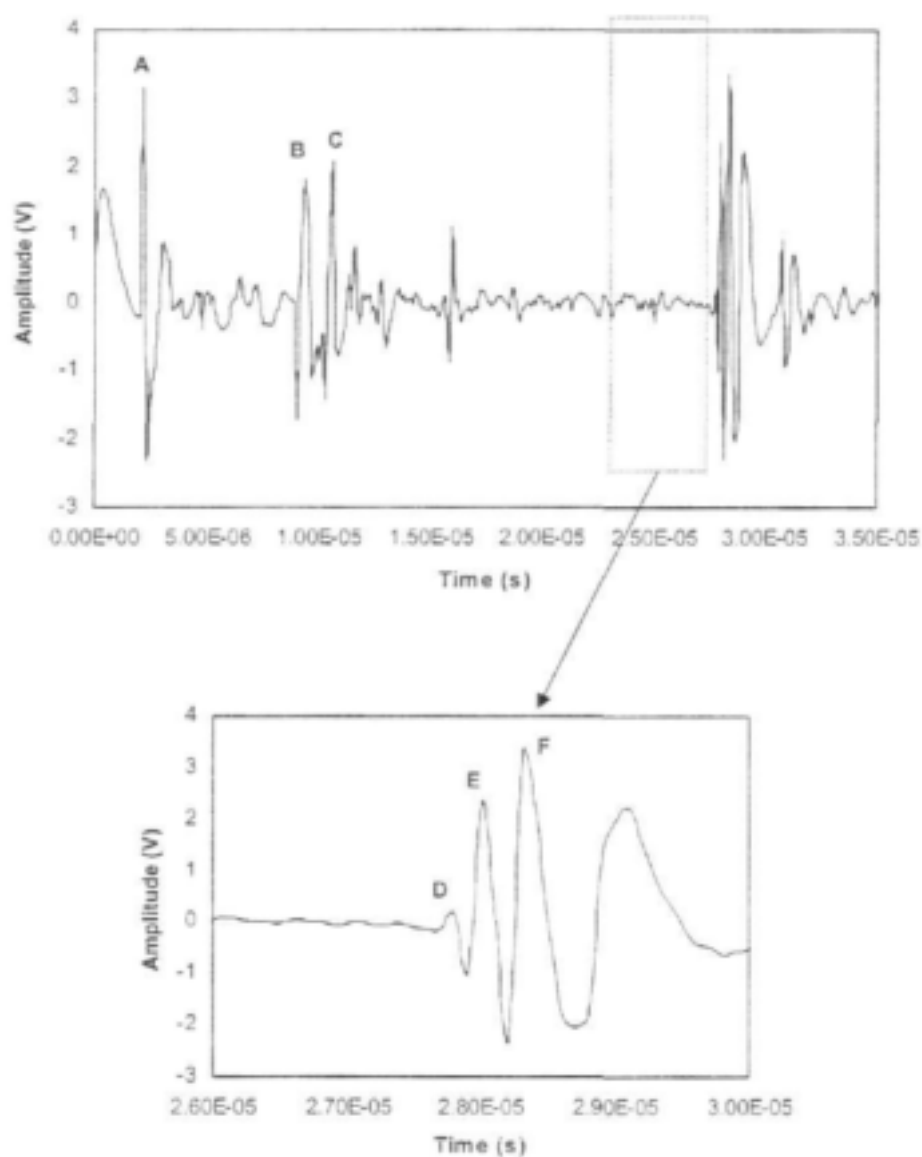


Figure 9.3: Ultrasonic signal recorded from the inside of a tubular UF cell.

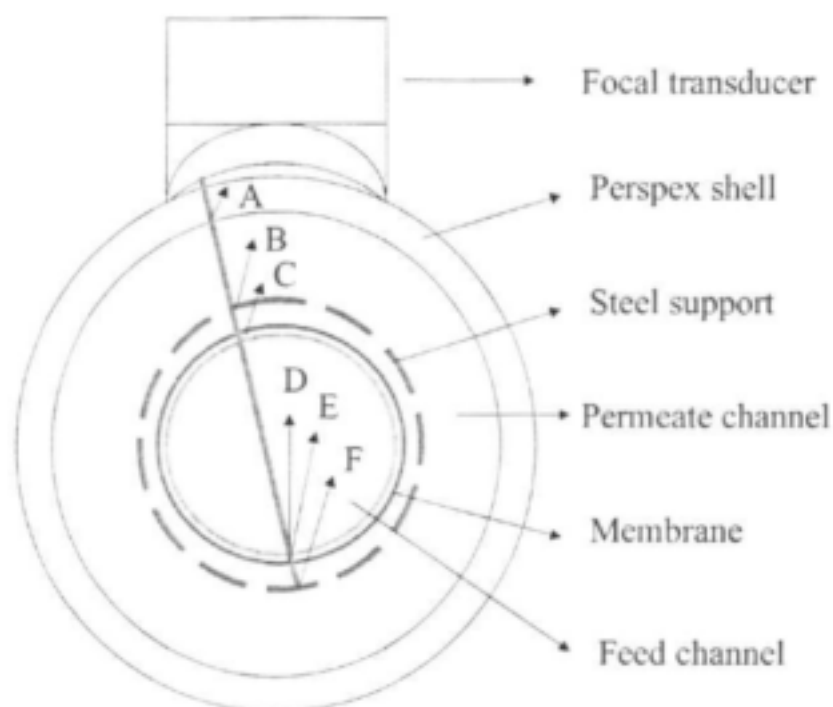


Figure 9.4: Cross-sectional view of tubular UF cell and ultrasonic reflections for set-up in Figure 9.3.

Figure 9.3 plots the ultrasonic signal amplitude in volts (V) vs. the time in seconds (s) inside the tubular cell. Each peak corresponds to a reflected acoustic wave from one of the multiple interfaces inside the tubular cell. Peaks A, B, C, D, E and F were generated from the following interfaces: Perspex shell/water, water/steel support, PES membrane/water, water/PES membrane, PES membrane/polyester backing, polyester backing/steel support. The ultrasonic responses show the structure of the tubular cell as shown in Figure 9.4.

The ultrasonic response signals revealed a PES membrane that is composed of a PES layer and a polyester backing. The UTDR measurement was focused on the front of Peak D, which indicates the membrane surface. The pure water flux and echoes of the clean PES membrane as reference waveform were also obtained during the pure water phase.

9.5.2 BSA FOULING EXPERIMENT AND ULTRASONIC MEASUREMENT

Figure 9.5 shows changes in the permeate flux with operation time during the fouling experiments carried out with 0.08 and 3 g/l BSA. Flux, first decreased rapidly to 26.2 % and 35.4 % of the pure water flux in 10 min of fouling operation with 0.08 and 3 g/l BSA respectively, followed by a gradual decline. The BSA rejection was > 99.5 % and 92.4 % in the fouling experiments with 0.08 and 3 g/l BSA respectively (Table 9.1). The immediate flux-decline results

primarily from the adsorption and concentration polarization of BSA on the PES membrane [Aimar et al., 1986; Mulder, 1991]. The flux gradually declined due to the formation of gel layer and then as retentate concentration increased (such as 0.08 to 0.22 g/l after 4 h of fouling operation with 0.08 g/l BSA solution in Table 9.1). This is because the diffusivity of the BSA macromolecules is rather low and the retention is normally very high. This implies that the solute concentration at the membrane surface reaches a very high value, and the gel concentration of a number of macromolecular solutes may be reached.

The corresponding ultrasonic responses at 0 and 4 h of fouling operation carried out with 0.08 and 3 g/l BSA are shown in Figures. 9.6 and 9.7. Peaks D and E combined together represent the clean PESU membrane. Once BSA foulants are initiated on the membrane surface, the acoustic impedance difference and the topographical characteristics at the feed solution/membrane interface will change, resulting in a change in the amplitude of echo D. The echo of BSA gel layer combined with peak D to form a new echo D'. Figure 9.8 shows changes in amplitude and time domain movement of peaks D' with operation time. An amplitude decline of the observed Peak D' and an increase in the arrival time difference between peaks D' and E with operation time were observed by UTDR. This is relative to the deposition and formation of a gel layer [Noble and Stern, 1995]. However, the gel layer is so thin that two successive echoes cannot be separated. Further observation is limited by the interference of ultrasonic signals reflected from the BSA thin layer and membrane.

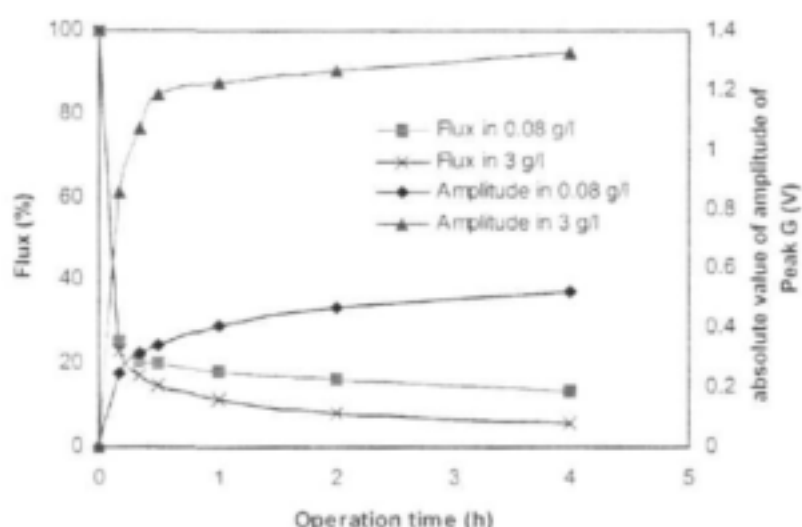


Figure 9.5: Permeate flux and amplitude of differential signal (Peak G) as a function of operation time during the fouling experiments carried out with BSA 0.08 and 3g/l.

Table 9.1: BSA concentration in retentate and rejection during fouling experiments carried out with 0.08 and 3 g/l BSA

Operation time (h)	0.08 g/l BSA solution		3 g/l BSA solution	
	BSA concentration in retentate (g/l)	BSA rejection (%)	BSA concentration in retentate (g/l)	BSA rejection (%)
0	0.08		3.00	
0.25	0.09	99.70	4.00	
0.50	0.12	99.70	4.80	
1			5.20	92.50
2.50	0.14	99.50		
4			7.20	92.70
5	0.22	99.50		

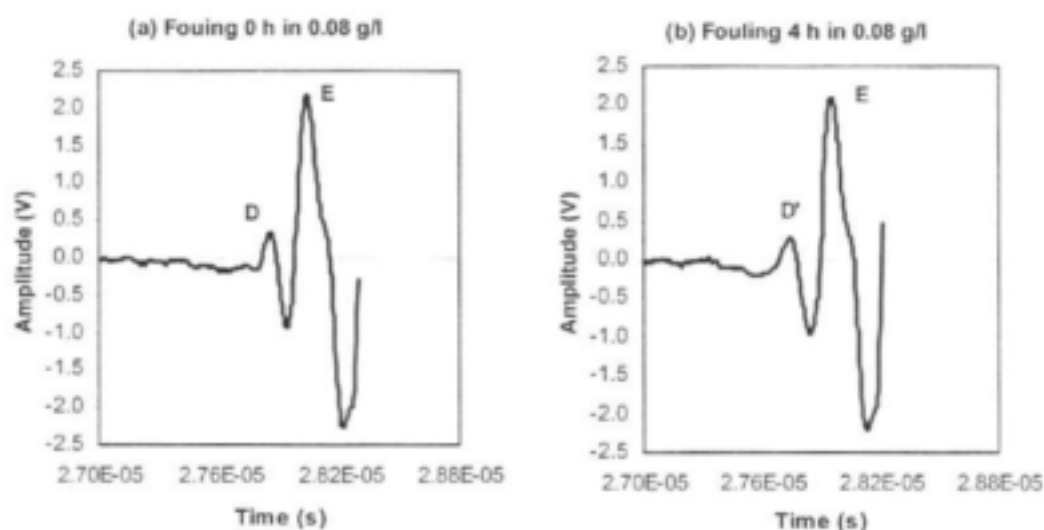


Figure 9.6: Ultrasonic signal responses after 0 (start) and 4 h of operation in the fouling experiment carried out with 0.08 g/l BSA at flow rate 0.04 cm/s and applied pressure 150 kPa.

Note: Peaks D, D' and E are generated from the following interfaces: water/PES layer, BSA solution/BSA gel layer combined PES layer, PES layer/polyester backing.

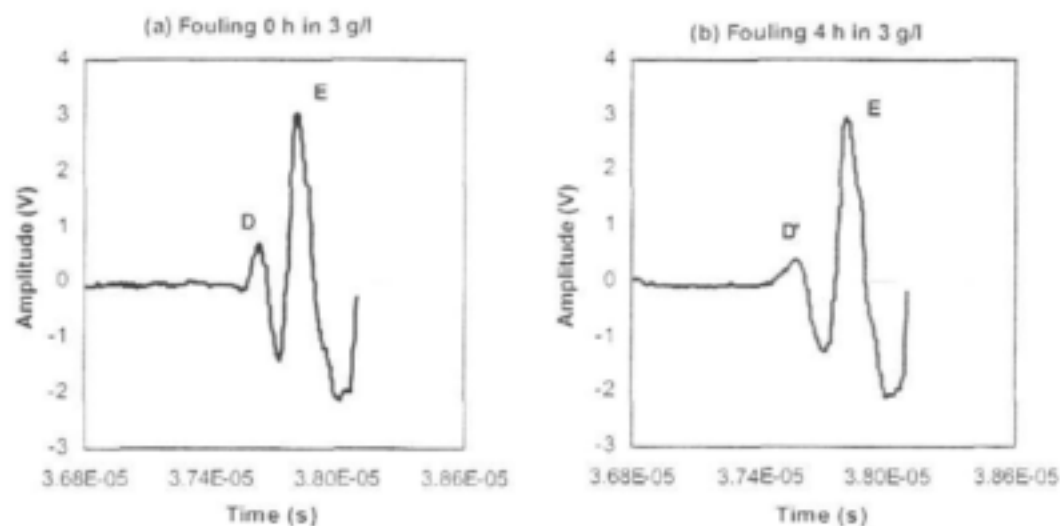


Figure 9.7: Ultrasonic signal responses after 0 (start) and 4 h of operation in the fouling experiment carried out with 3 g/l BSA at flow rate 0.04 cm/s and applied pressure 150 kPa.

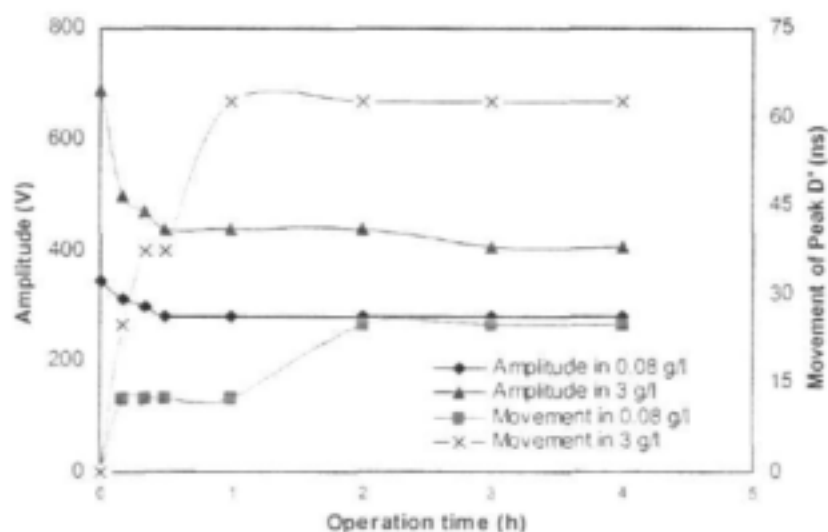


Figure 9.8: Changes in amplitude and time domain movement of Peaks D' with operation time in the fouling experiments with 0.08 and 3 g/l BSA.

9.5.3 DIFFERENTIAL SIGNALS

Results of differential signals during BSA fouling experiments are shown in Figures 9.9 and 9.10. Figure 9.5 also plots the amplitude of the differential signal (fouling echo G) as a function of operation time during BSA fouling experiments.

It is shown in Figure 9.9 that a clear differential signal had appeared within a short time (as was measured at 10 min of fouling operation) due to the adsorption of BSA on the PES membrane. The BSA adsorbed quite strongly in or on the membrane surface, resulting in 65 % flux decline, even at a low BSA solution concentration (0.08 g/l). The growth of differential signals also can be seen at 0.5, 2 and 4 h as fouling proceeded (Figures 9.5 and 9.9). Note: the differential signals are reverse signals. It might indicate that the impedance of the BSA gel layer is lower than that of water. A differential signal with 0.524 V emerged after 4 h of fouling operation with 0.08 g/l BSA. Figure 9.10 shows similar results achieved at 10 min, 0.5 h, 2 h and 4 h of fouling operation with 3 g/l BSA. But the rate at which the ultrasonic amplitude increased became faster at fouling operation with 3 g/l BSA than with 0.08 g/l BSA. (Figures 9.5 and 9.10). An increase from 3 to 7.2 g/l in retentate concentration can be seen as fouling proceeded (Table 9.1). The high BSA concentration might result in a low rejection (92.7 %). A sharp differential signal with 1.327 V appeared after 4 h of fouling operation with 3 g/l BSA. This is because aggregation and deposition of BSA formed a dense gel layer as a second barrier on the membrane surface. Further flux decline resulted from the formation of a dense gel layer on the membrane surface.

According to the resistance model [Mulder, 1991], the gel layer resistance can be calculated by Equations 6.1, 6.3 and 9.1.

$$R_t = R_g + R_m \quad (9.1)$$

where: R_g = gel resistance, including reversible or irreversible resistance.

As shown in Figure 9.11, a linear relationship between absolute value of amplitude of differential signals and fouling-resistance exists in the fouling experiment with 0.08 g/l BSA. It suggests that fouling resistance increase with operation time results from the protein adsorption, aggregation and gelation. The ultrasonic technique is capable of detecting and quantifying these changes on the membrane surface.

The thickness (dS) of the BSA gel layer was calculated by Equation 3.1. As shown in Figure 9.12 (assume a sound velocity of 1480 m/s in BSA gel), the thickness of the gel layer was 3.7 and 5.18 μm after 10 min of fouling operation with 0.08 and 3 g/l. The thickness increased very

slowly as fouling proceeded. A very thin layer with high gel concentration results in the continuous flux decline.

Differential signals:

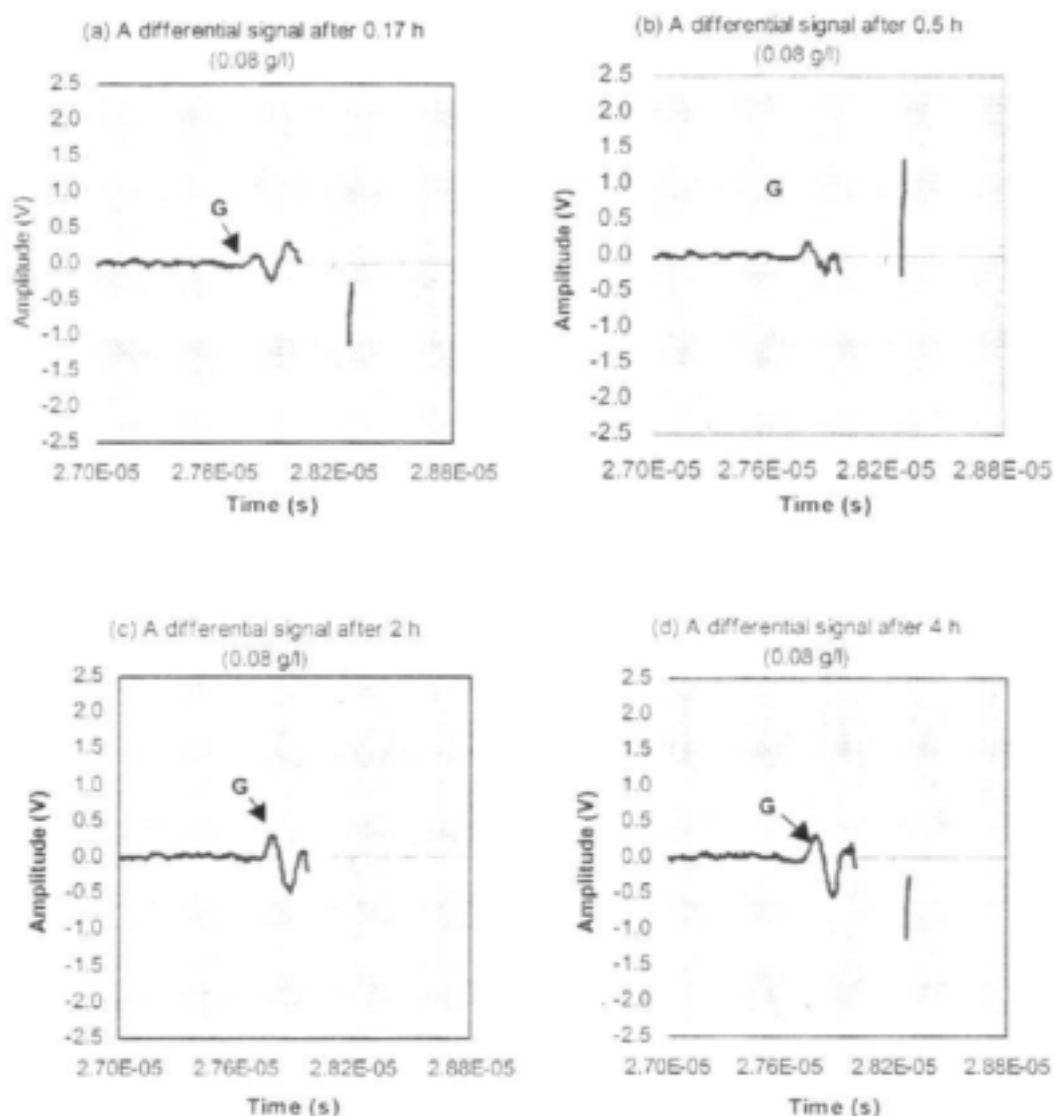


Figure 9.9: Differential signals (Peak G) after 10 min, 0.5 h, 2 h and 4 h of operation in the fouling experiment carried out with 0.08 g/l BSA.

Note: the white line represents ultrasonic signal responses of a clean tubular PES membrane.

Differential signals:

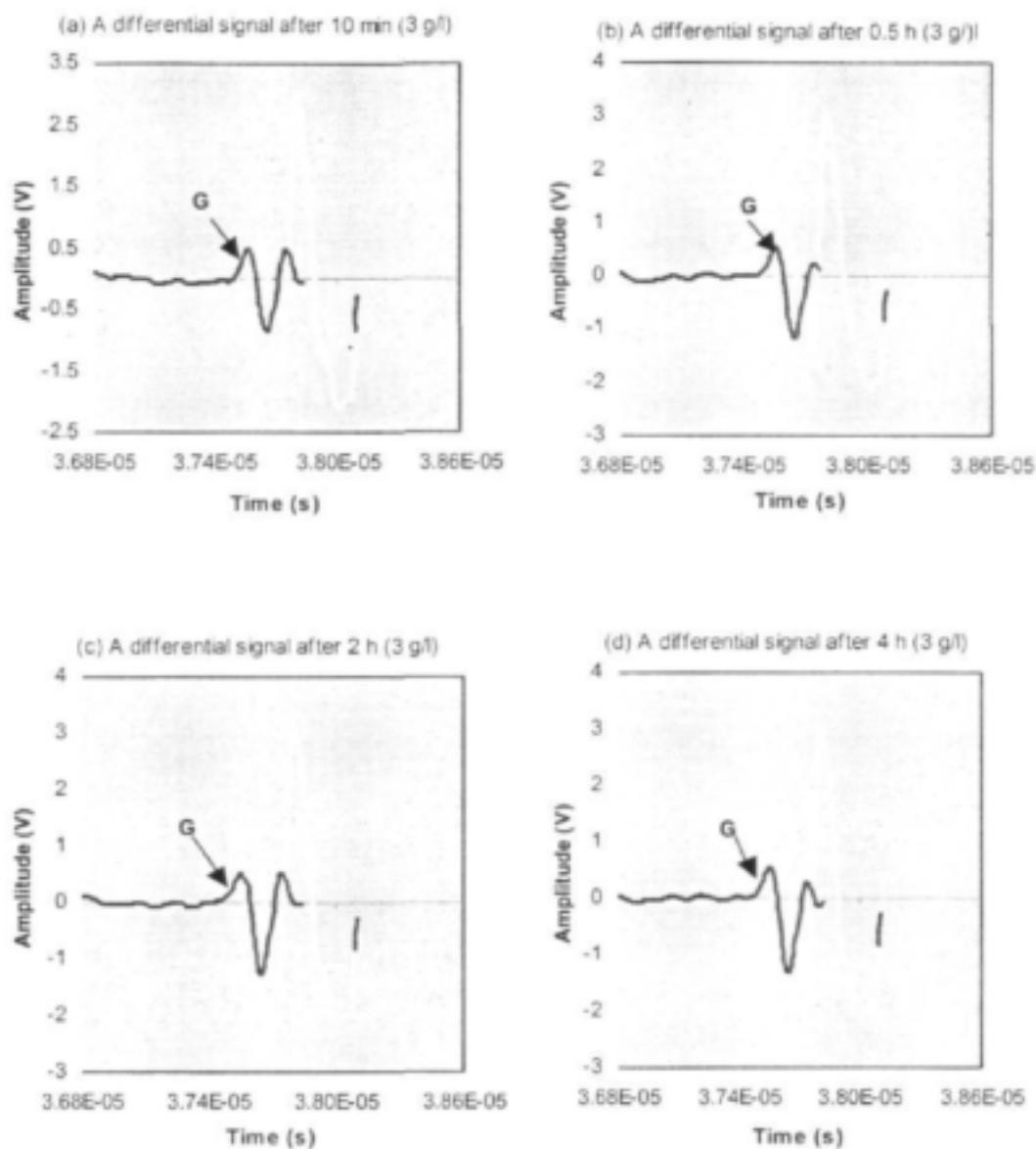


Figure 9.10: Differential signals (Peak G) after 10 min, 0.5 h, 2 h and 4 h of operation in the fouling experiment carried out with 3 g/l BSA.

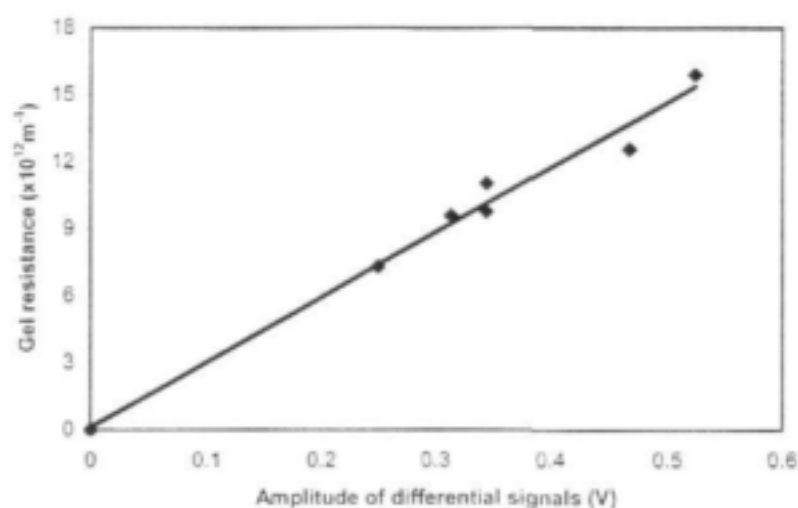


Figure 9.11: Relationship between the absolute value of amplitude of peak G and gel resistance in the fouling experiments carried out with 0.08 g/l BSA.

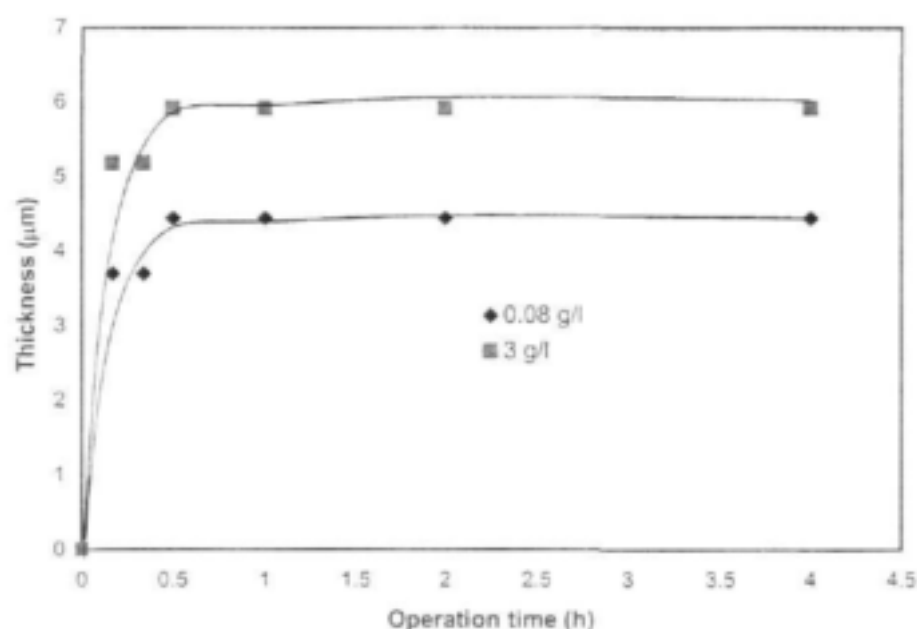


Figure 9.12: Thickness of BSA gel layer as a function of operation time in the BSA fouling experiments with 0.08 and 3 g/l BSA.

9.5.4 CLEANING EXPERIMENTS AND ULTRASONIC TESTING

Before commencing with the cleaning experiments, the feed solution was changed from 3 g/l BSA solution to pure water at 150 kPa and an axial velocity of 0.04 cm/s, in order to obtain the pure water flux of a fouled membrane. The fouled membrane was cleaned with 0.1g/l enzyme

solution for 30 min. Pure-water flux recovery of the cleaned membrane is shown in Figure 9.13. Figure 9.14 shows the results of ultrasonic differential signals during the cleaning experiments.

An increase in flux from 5.68 to 20.36 % and a decrease in absolute value of the amplitude of differential signal from 1.32 to 0.08 V were observed (Figures 9.13 and 14a) after pure water filtration because of changing the bulk solution from BSA to pure water. The change in bulk solution from BSA to pure water resulted in the reduction of concentration polarisation. Figure 9.13 shows that the pure water flux increased from 20.36 to 68.38 % after enzymatic cleaning. The disappearance of the differential signal G showed the gel layer was removed by enzymatic cleaning (Figure 9.14b). However, the recovery flux recorded by enzymatic cleaning is still lower than the original flux. Protein pore plug or protein-membrane interactions results in the irreversible fouling on or in the membrane [Robertson and Zydney, 1990; Huisman et al., 2000].

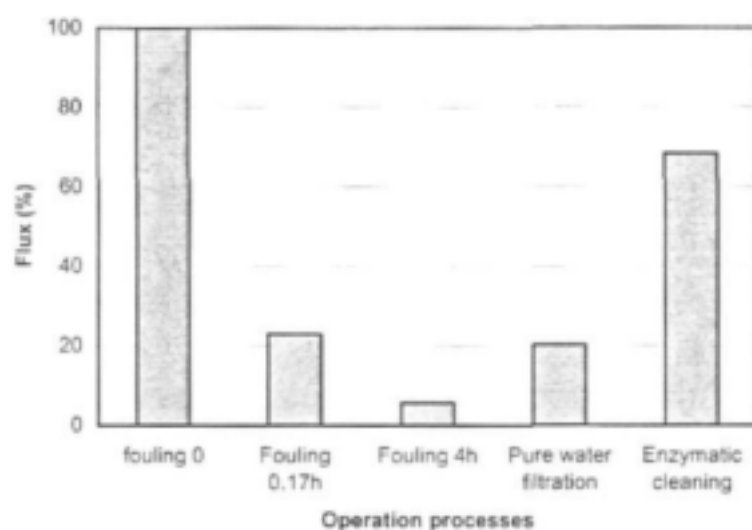


Figure 9.13: Changes in flux with operation processes during the fouling experiment with 3 g/l BSA.

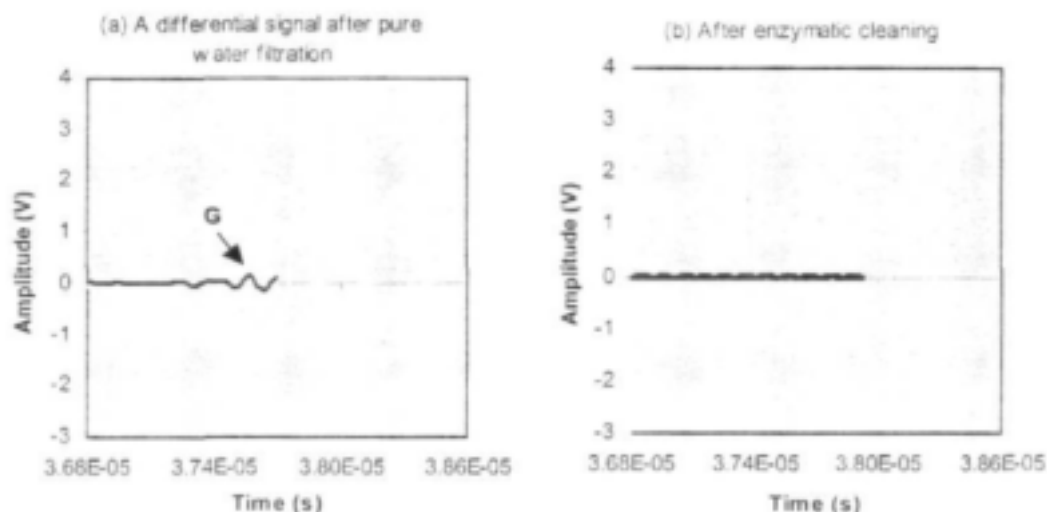


Figure 9.14: Differential signals (black line) after pure water filtration and enzymatic cleaning in the fouling experiment with 3 g/l BSA.

9.5.5 ULTRASONIC FREQUENCY SPECTRA

Figure 9.15 shows ultrasonic frequency spectra obtained from ultrasonic measurements by Fast Fourier Transform (FFT) during fouling (carried out by 0.08 g/l BSA). Each frequency spectrum contains a frequency band from 0 to 11 MHz. As seen in Figure 9.15, the frequency spectra show obvious changes in ultrasonic resonance in the 9 MHz range. There is increasing resonance (increasing negative peaks) with fouling operation with 0.08 g/l BSA. Figure 9.16 shows the appearance and growth of differential signals of ultrasonic resonance minima with BSA fouling time. The broad resonance minima correspond to the properties of the fouling layer such as density and thickness etc. because the foulants were imbedded in or deposited on the membrane surface to form a smooth surface. The foulants with the membrane caused a stronger resonance than membrane self [Migliori et al., 1993, Pierce, 1996]. Further attempts will be made to interpret the results in terms of physical behavior, i.e. elastic properties of the membranes and foulants involved and reported in future publications.

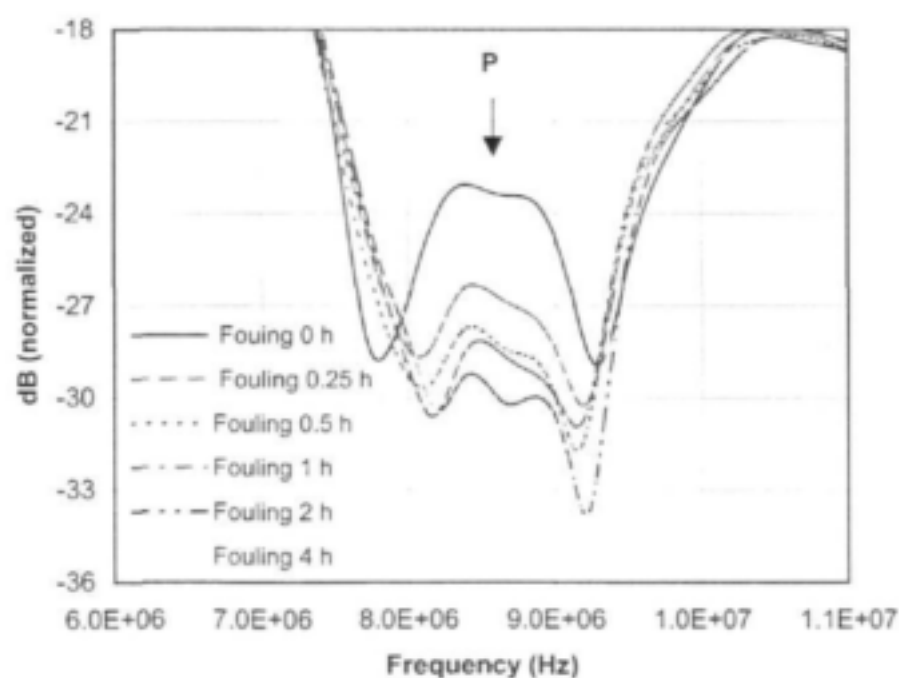
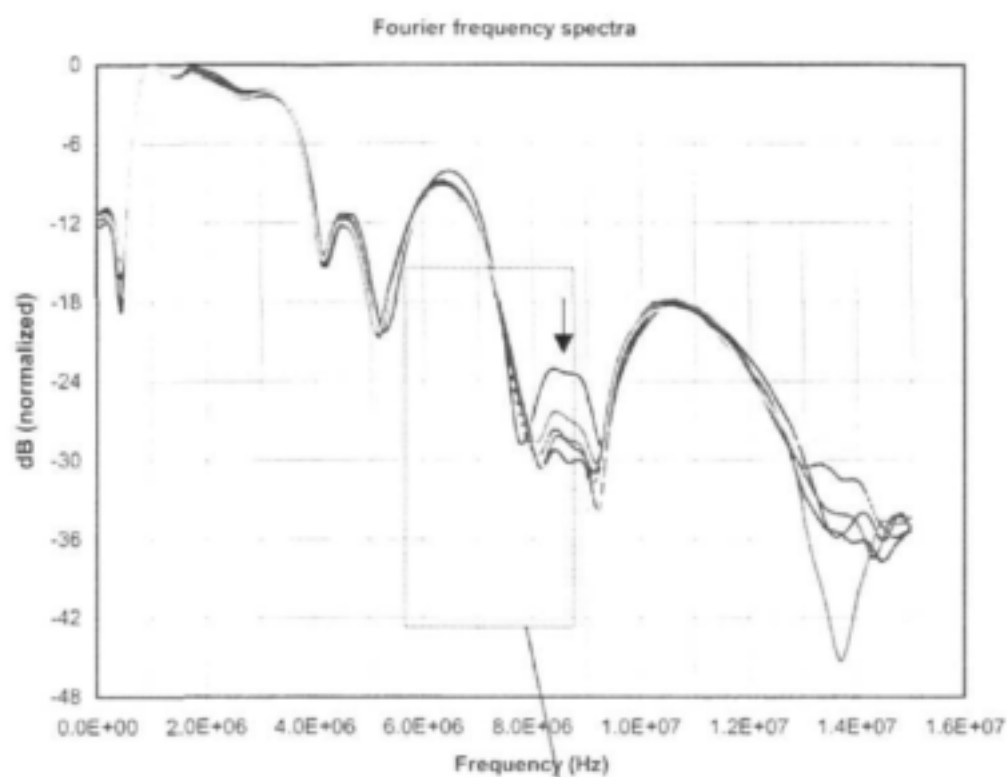


Figure 9.15: Ultrasonic frequency spectra from 0 to 4 h of fouling operation carried out with 0.08 g/l BSA in tubular UF.

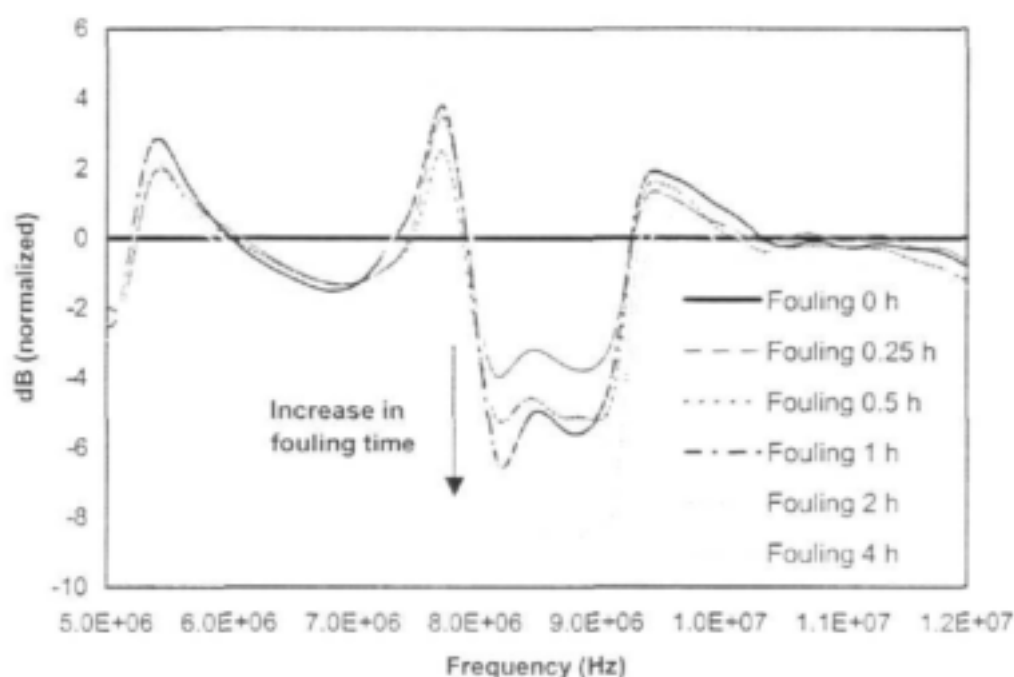


Figure 9.16: Spectra of differential signals of ultrasonic amplitude (dB) with operation time during the fouling experiment with 0.08 g/l BSA in tubular UF.

9.6 CONCLUSIONS

The use of a new ultrasonic technique to monitor, *in-situ*, protein fouling in tubular UF membranes has been described here. It shows show that the ultrasonic technique can distinguish and recognise various response signals from ultrasonic measurements in a tubular cell.

Protein fouling was successfully detected in tubular UF by the ultrasonic technique. Changes in the amplitude of the differential signals obtained provide useful quantitative information about adsorption, deposition and gelation of BSA on the membrane. A linear relationship between the absolute value of amplitude of differential signals and fouling resistance exists in the fouling experiment with 0.08 g/l BSA. The ultrasonic technique can provide an approach to understand protein-fouling behavior related to membrane flux decline. Flux will decline due to the adsorption, concentration polarisation and then as retentate concentration increases.

The ultrasonic technique is capable of detecting membrane cleaning. Flux measurements and UV analysis corroborate the ultrasonic testing. Furthermore ultrasonic frequency spectra were developed and may be useful as an additional tool for detection of fouling.

10. UTDR AS A NON-DESTRUCTIVE VISUALIZATION TECHNIQUE TO MONITOR FOULING AND CLEANING OF RO MEMBRANES

10.1 ABSTRACT

Ultrasonic-time-domain-reflectometry (UTDR) was used as a visualization technique for the real-time characterisation of a fouling layer on a membrane. Experimental results confirmed that there is a correspondence between the flux-decline behaviour and the UTDR response from membranes in reverse osmosis (RO) modules. The ultrasonic technique could effectively detect fouling layer initiation and growth on the membrane in real-time, at different axial velocities. In addition to the measurement of fouling, the ultrasonic technique was also successfully used for monitoring membrane cleaning.

10.2 INTRODUCTION

This study was conducted to determine the usefulness of UTDR for the visualisation of membrane fouling in RO modules. This study describes that the UTDR technique is able to detect the appearance of a fouling echo signal, its growth on the membrane, and its disappearance with cleaning.

Fig. 10.1 is a cross-sectional view of a typical flat-sheet cell with a membrane placed between two aluminium plates and an externally mounted transducer in contact with the top plate. The high-pressure feed solution flows on the top of the membrane and permeate is withdrawn from the bottom side. Suppose a fouling layer with thickness dS is present on the surface of the membrane, and the reflected echoes A, B and C are generated from the various interfaces within the cell.

The corresponding time-domain response is shown in Fig. 10.2. The top plate/feed solution interface is represented by echo A, and the initial feed solution/membrane interface by B. If the fouling layer is thick enough to be measured by the ultrasonic signal i.e. it falls within the spatial resolution capabilities of the system, a new echo C will be formed as a consequence of the new feed/fouling interface. Further, if the difference in arrival times between echoes B and C, dT , is measured, the thickness of the fouling layer, dS , can be determined by the following equation:

$$ds = 0.5Vdt \quad (10.1)$$

(see also 3.2)

where: V is the velocity of the ultrasonic wave in the medium.

Thus, the detection of the interface echoes allows fouling to be monitored in real-time.

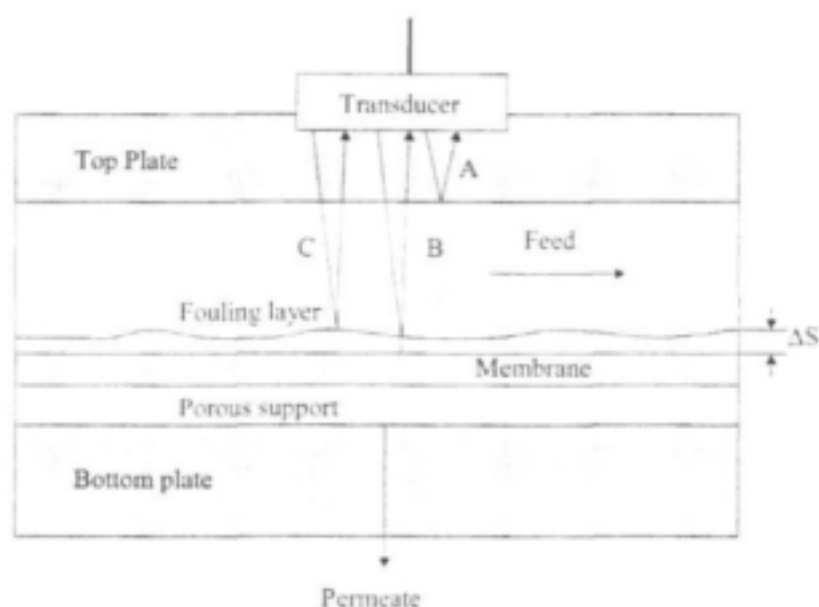


Fig. 10.1: Cross-sectional view of flat-sheet cell.

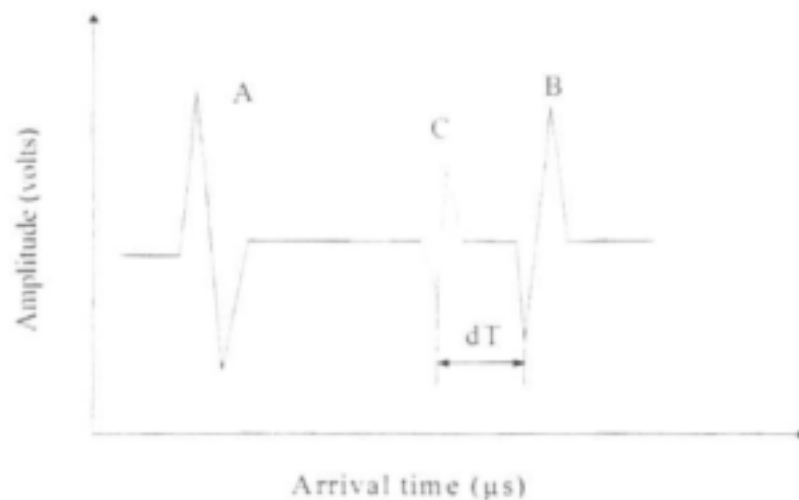


Fig. 10.2: Amplitude vs. time curve for set-up in Fig. 10.1.

10.3 EXPERIMENTAL

10.3.1 DESALINATION SYSTEM AND EXPERIMENTAL DESIGN

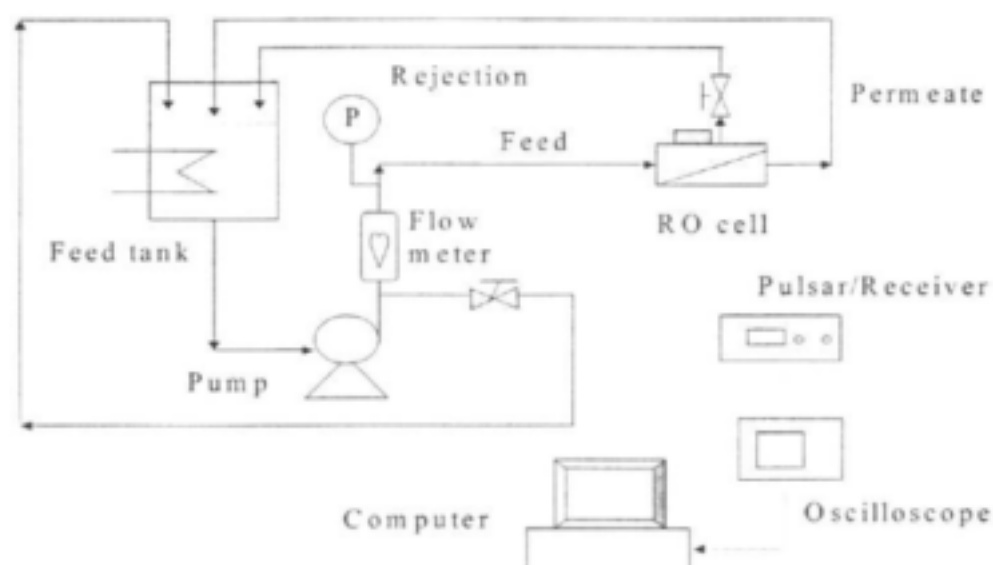


Fig. 10.3: RO experimental set-up and UTDR measurement system.

Fig. 10.3 is a schematic representation of the RO desalination system and UTDR measuring system. The assembly consisted of: a 40-liter feed tank for storage and supply of the fouling solution, a high-pressure positive displacement pump for pressurisation of the feed solution, a rectangular test module, a cooling system on the feed tank, analogue pressure gauges and valves, and a by-pass line parallel to the test module. The by-pass line is necessary in order to vary both the flow rate and the pressure inside the cell, separately. Pressure was controlled by means of the backpressure valve on the outlet line of the cell. The cross-flow membrane system had one feed stream entering the system, one rejection stream (brine) and one permeate stream (purified water) leaving the system. These three streams are circulated back to the feed tank in the experimental set-up. Feed flow to the cell was measured with a flow meter and manually controlled with a valve. Permeate was measured manually with a stopwatch.

Hydranautics ESPA3 Polyamide membranes were used in all of the fouling experiments. Membranes were cut from manufacturer-supplied long rolls, 1 m wide and several meters long. All experiments were carried out in the pressure range of 2 - 2.5 MPa (20 - 25 bar) with flow-rates varying between 0 - 100 ml/min. Feed concentrations varied between 0.5 - 2 g/l while the temperature was controlled at $25 \pm 1^\circ\text{C}$.

The ultrasonic measurement system consisted of a 7.5 MHz ultrasonic transducer (Panametrics V111), a pulser-receiver (Panametrics 5058PR) and a 150 MHz digital oscilloscope (HP Model 54602B) with sweep speeds from 5s/div to 2ns/div and 1mv/div sensitivity. The oscilloscope that was connected to the pulser-receiver captured and displayed the data as amplitude changes on its front panel. Each set of ultrasonic data generated consisted of 500 data points. Instead of a full-wave, radio-frequency (RF)-type record, a rectified record was chosen. The waveforms displayed in the Figs. 10.5 – 10.14 thus only show the upper parts of the RF signals. This data can be stored on a computer's hard drive. Commercially available, food-grade honey was used to couple the transducer to the top plate surface.

10.3.2 FOULING EXPERIMENTS

The fouling experiments were carried out using chemically pure calcium carbonate. Cross-flow as well as dead-end situations were investigated. All cross-flow experiments were carried out in the laminar area range with axial velocities between 0 - 5 cm/s. Each experiment consisted of three phases. First, the membrane was soaked in pure water for at least 24 h prior to the start of the experiment. Then the membrane was placed inside the cell and exposed to clean water at the desired operating conditions of the experiment. Once steady state with respect to the permeate flux and the ultrasonic signal was achieved, the feed was switched to the fouling solution to initiate the third phase, in which changes in the measured variables occurred due to concentration polarisation and fouling. The pure water phase ensured that processes such as membrane compaction and adsorption of trace organic ions on the membrane surface stabilised before initiation of the fouling phase, thereby facilitating an unambiguous interpretation of UTDR and flux behaviour. The experiments were allowed to continue until the ultrasonic response and permeate flux had stabilised. The module was then opened and fouled membrane samples were collected for morphological analyses.

10.3.3 CLEANING EXPERIMENTS

The potential ability of the UTDR technique to detect the presence of a fouling layer may also make it suitable for monitoring the removal of a fouling layer. Cleaning experiments were therefore carried out to demonstrate the potential of the UTDR technique for such an application. The membranes were first fouled to steady-state levels, as described in the previous section, after which clean water was introduced to clean the membranes. Experiments were carried out at the same operating pressures as those used in the fouling phase. At the end of the cleaning experiments, membrane samples were removed for morphological characterisation.

10.3.4 Morphological characterisation of the fouling layer

The purpose of the morphological study of the fouled membrane samples, using scanning electron microscopy (SEM), was deemed necessary in order to establish a correlation between the measurement of UTDR and the fouling layer.

10.4 RESULTS AND DISCUSSION

10.4.1 CROSS-FLOW EXPERIMENT

As mentioned, once steady state was attained after pure water filtration, the feed was switched to 2 g/l calcium carbonate (CaCO_3) solution, to initiate the fouling experiment in which concentration polarisation and fouling occurred. Cross-flow fouling experiments were carried out at 22 ± 0.5 bar and a cross-flow velocity of 50 ± 15 ml/min (1.1 cm/s). The permeate flux of a 7 h fouling experiment is summarised in Fig. 10.4.

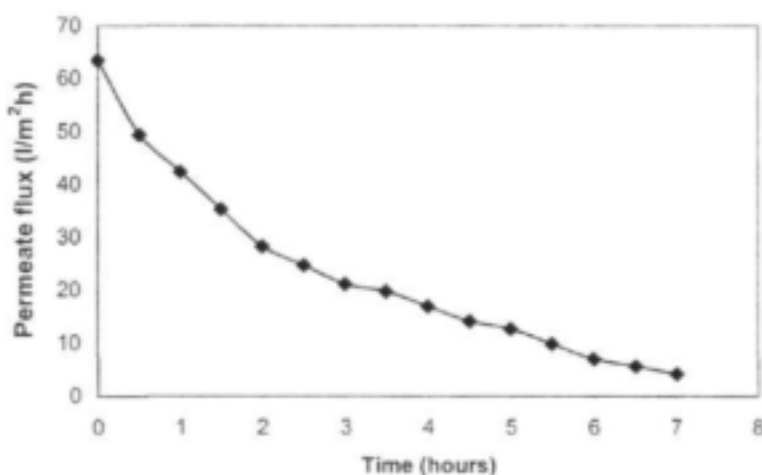


Fig. 10.4: Permeate flow data for calcium carbonate fouling experiment with 1.1 cm/s cross-flow.

Fig. 10.4 indicates that the permeate flux declines as fouling proceeds. The flux decline results primarily from concentration polarisation and the slow growth of the fouling layer. Consistent with this observation, the corresponding ultrasonic signal responses exhibit rapid amplitude changes as fouling proceeds (Figs. 10.5 and 10.6). The large peak represents the membrane. The broadness of the peak could be a function of the composite structure of the desalination membrane, having a denser face and a more porous and compressible substrate. The formation of the second echo representing a response signal of a fouling layer in Fig. 10.5 was observed

within the first hour of operation. The fouling layer on the membrane surface has different acoustic impedance to that of the bulk solution. The cause of appearance of the second echo is as a result of the changes in acoustic impedance between the bulk solution and the membrane.

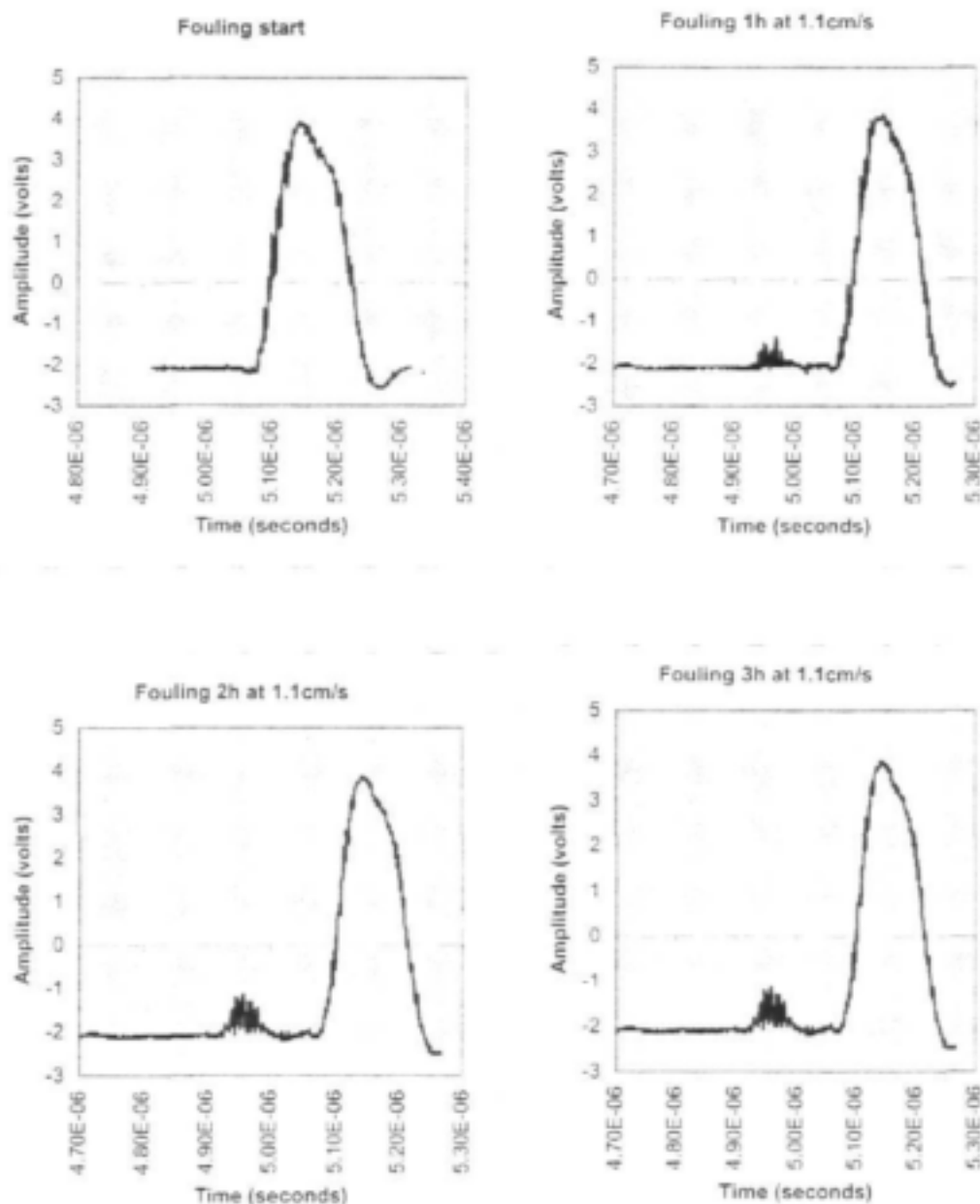


Fig. 10.5: Ultrasonic responses at the start and after 1, 2 and 3 h of operation with 2 g/l CaCO_3 fouling experiments at 1.1 cm/s cross-flow.

Note: No high frequency filters have been used to smoothe the waveforms

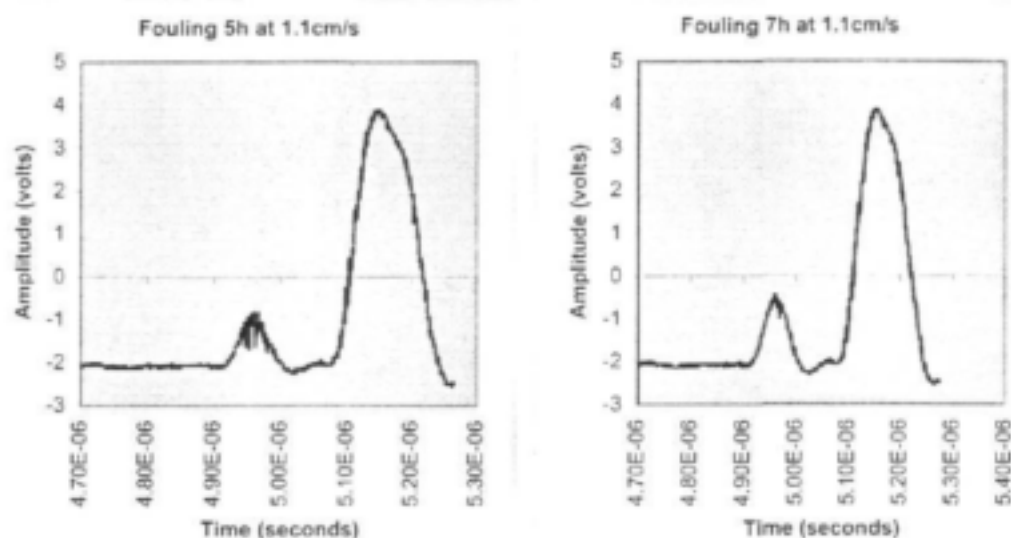


Fig. 10.6: Ultrasonic responses after 5 and 7 h of operation for the cross-flow fouling experiment with 2 g/l CaCO_3 at 1.1 cm/s cross-flow.

If the fouling layer is thick enough to be measured by the ultrasonic signal, that is, it falls within the spatial resolution capabilities of the system, a new echo will be formed as a consequence of the bulk solution/fouling interface.

As fouling layer growth progressed, more fouling layers formed, until the entire membrane was covered with a uniform fouling layer. If more fouling covers the membrane surface, a denser fouling layer is formed and a larger acoustic impedance change between the bulk solution and the membrane is expected. This would be detected as a sharper reflection. Thus, an echo with greater amplitude is observed at 2, 3, 5 and 7 h of fouling operation in Figs. 10.5 and 10.6. The time-domain movement (ahead) of the second/fouling echo was observed as a result of an increase in the fouling layer thickness.

In order to study membrane coverage, four experiments were carried out under exactly the same fouling conditions, and stopped after specific times. Membrane samples were taken for SEM analysis after 1 h, 2 h, 3 h and 7 h of operation. Results are shown in Figs. 10.7 and 10.8. Morphological characterisation of the membrane after 7 h revealed complete membrane coverage with calcium carbonate. Deposits of the calcium carbonate may be transformed into the more stable calcite form from a meta-stable form after 7 h of fouling operation due to unstable ambient temperatures and pressure (Kronenberg, 1998).

At this stage it was not possible to determine which type of crystals they were.

The UTDR technique was in fact used for measuring fouling layer thickness, which could be calculated by Eq. 10.1. The thickness of the fouling layer was about 153 μm after 7 h of fouling (the velocity of the ultrasonic wave in the fouling layer was 1530 m/s). Measurement of fouling layer thickness by UTDR is not an accurate indication of the fouling layer thickness, but the echo signal of the fouling layer can indicate the state and progress of the fouling layer on the membrane surface and provide early warning to adjust system-operating parameters.

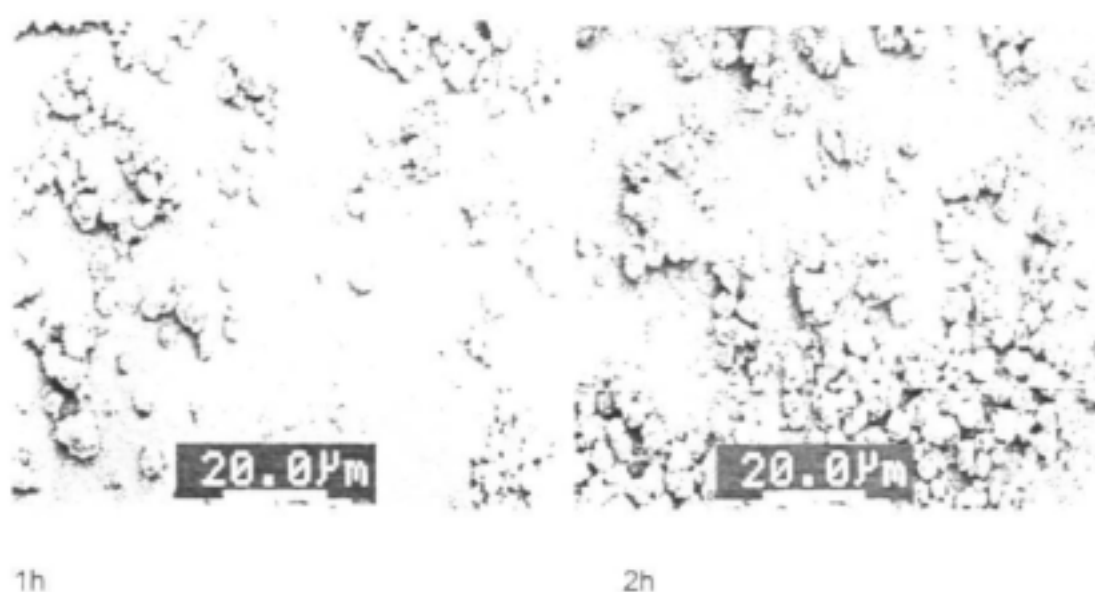


Fig. 10.7: Representative SEM images: the membrane surfaces after 1 h and 2 h of operation with 2 g/l CaCO_3 feed solution at flow rate 1.1 cm/s and pressure 22 bars.

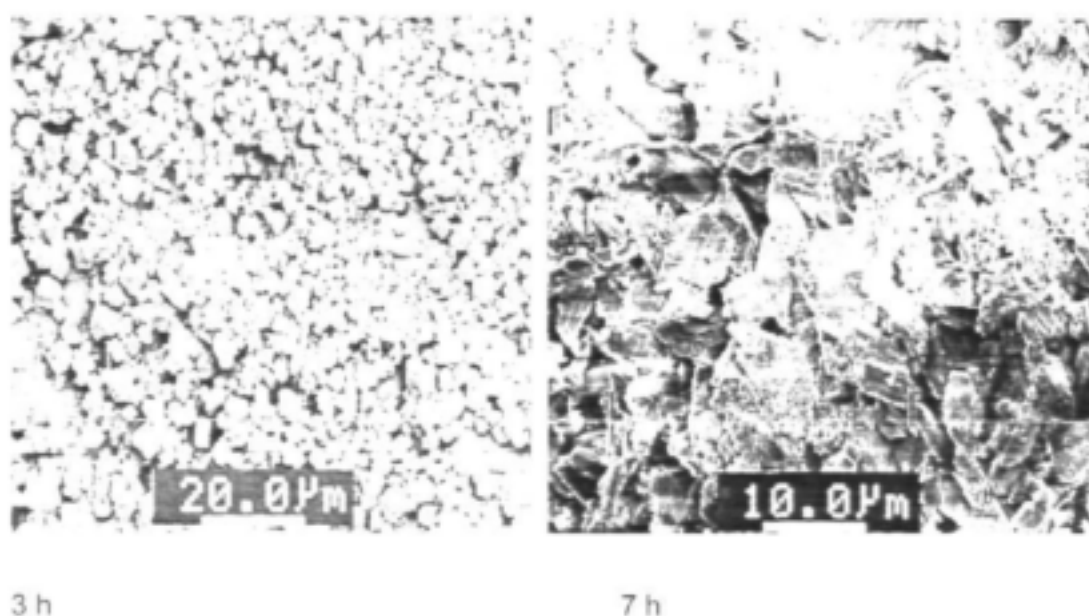


Fig. 10.8: Representative SEM images: the membrane surfaces after 3 h and 7 h of operation with 2 g/l CaCO_3 feed solution at flow rate 1.1 cm/s and pressure 22 bar.

10.4.2 DEAD-END EXPERIMENT

Dead-end experiments were carried out with 2 g/l calcium carbonate at 22 bar. Results showed that the most significant changes took place within a very short time. Permeation-rate values dropped to very low levels within 20 minutes and permeate measurements could no longer be performed accurately. The formation of a second echo in the time domain was almost immediately noticeable in the ultrasonic response (Fig. 10.9). This is because there is lack of turbulence and flow rate during dead-end experiments. Turbulence, whether produced by stirring, pumping the fluid, or moving the membrane, has a great effect on flux in the mass transfer-controlled region. Agitation and mixing of the fluid near the membrane surface can control the effects of concentration polarisation and reduce the hydraulic resistance and thickness of fouling layer (Cheryan, 1998). Morphological analysis of the fouled membranes revealed complete coverage of the surfaces in 30 min of dead-end operation (Fig. 10.10). The UTDR fouling layer thickness was calculated as 135 μm after 30 min of fouling operation in the dead-end experiment.

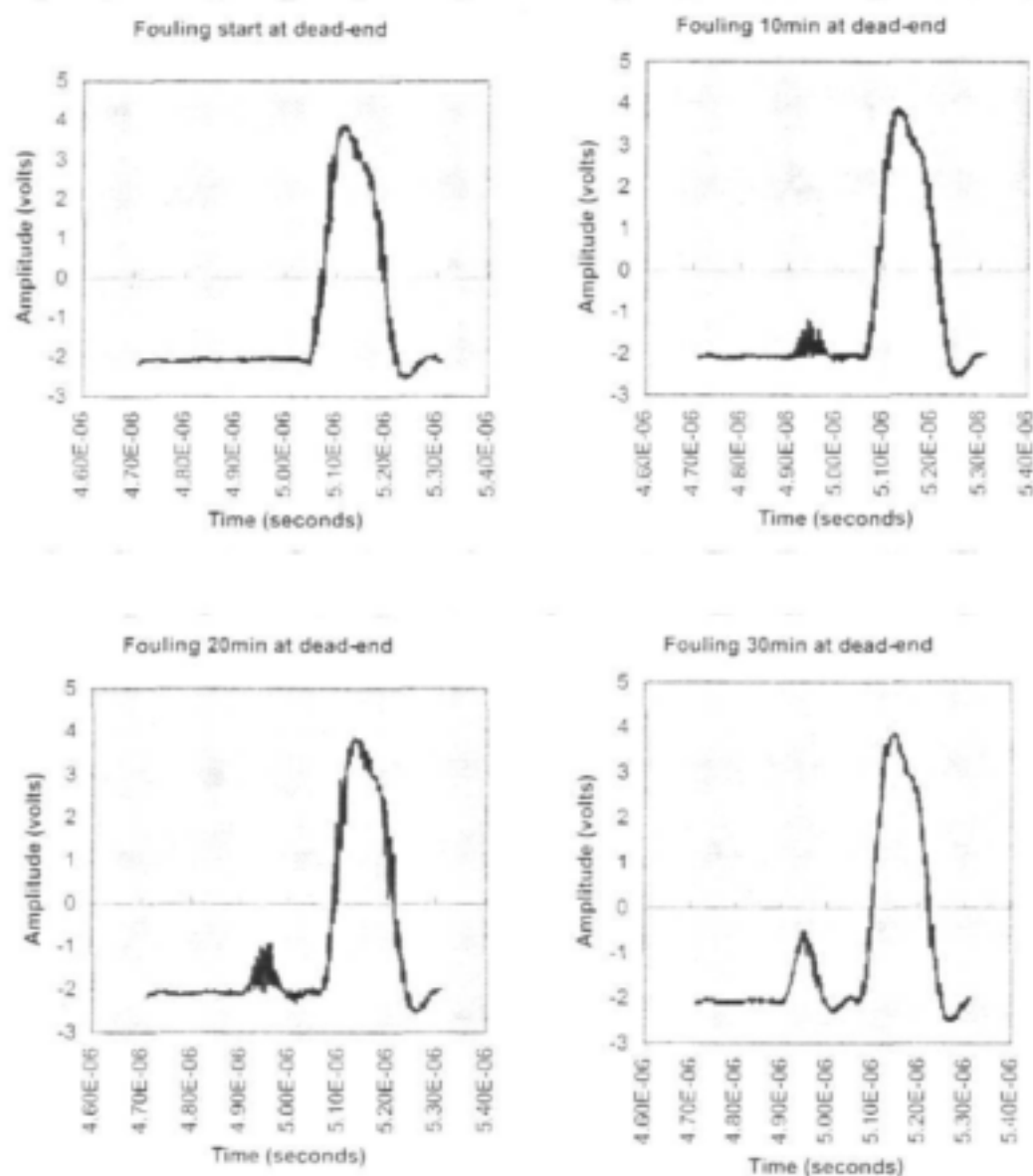


Fig. 10.9: Ultrasonic responses at the start and after 10, 20 and 30 min of operation with 2 g/l CaCO_3 in a dead-end experiment.

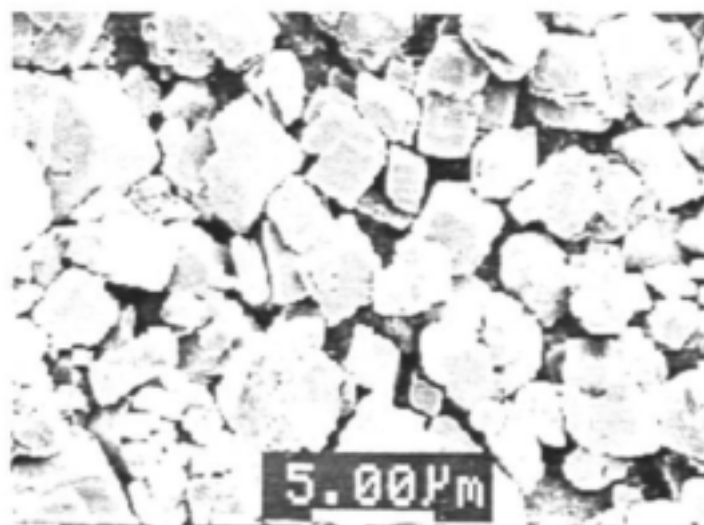


Fig. 10.10: Representative SEM images: the membrane surfaces after 30 min of operation with 2 g/l CaCO_3 in dead-end experiments.

10.4.3 CLEANING EXPERIMENT

Several experiments were carried out to investigate the possibility of using the UTDR technique for monitoring fouling removal in real time. The experimental procedure was to foul a membrane to steady state levels, after which it was cleaned with pure water. Both the fouling and cleaning phases were carried out at the same pressure of 20 ± 0.5 bar and cross-flow velocity of 50 ± 15 ml/min (1.1 cm/s). After a membrane was fouled with 2g/l calcium carbonate, it was cleaned again with water. Fig. 10.11 shows the fouling results. The second/fouling echo with a sharp reflection, before the main membrane echo, appeared after 9 h of fouling operation. It also indicated that a denser fouling layer was formed on the membrane surface.

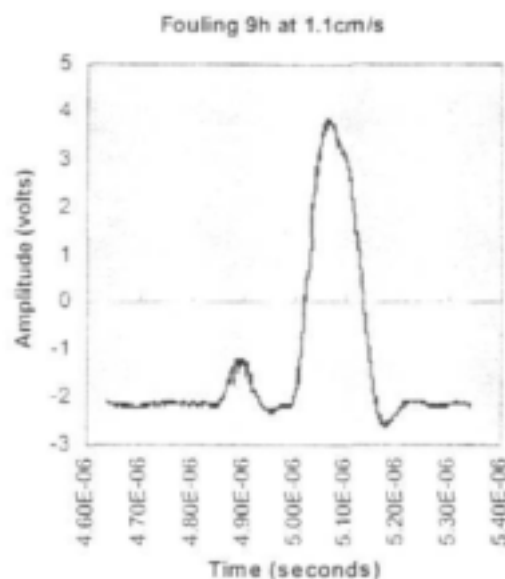


Fig. 10.11: Ultrasonic response of membrane after 9 hours of fouling with CaCO_3 at pressure 20 bar and flow rate 1.1 cm/s.

The cleaning process was done under the same pressure and cross-flow conditions as the fouling process. Fig. 10.12 shows changes in permeate flux during the cleaning process. Although permeate flow increased during the 3 h cleaning experiment, because of reduction of the concentration polarisation and partial dissolution of the fouling layer and reduction of its density, the original flux of a clean membrane was never obtained. It indicated that there was still some fouling on the membrane.

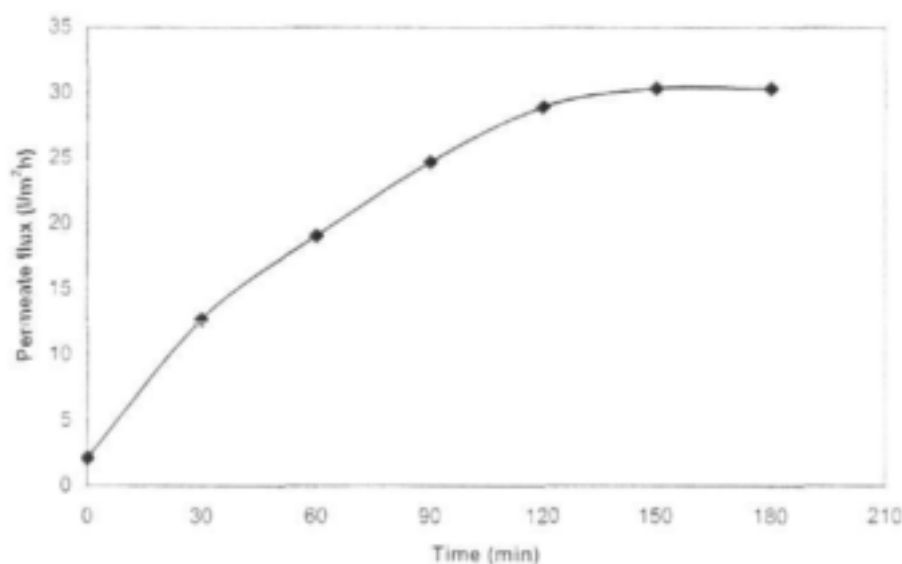


Fig 10.12: Permeate flow vs. time for the cleaning phase of the cleaning experiment.

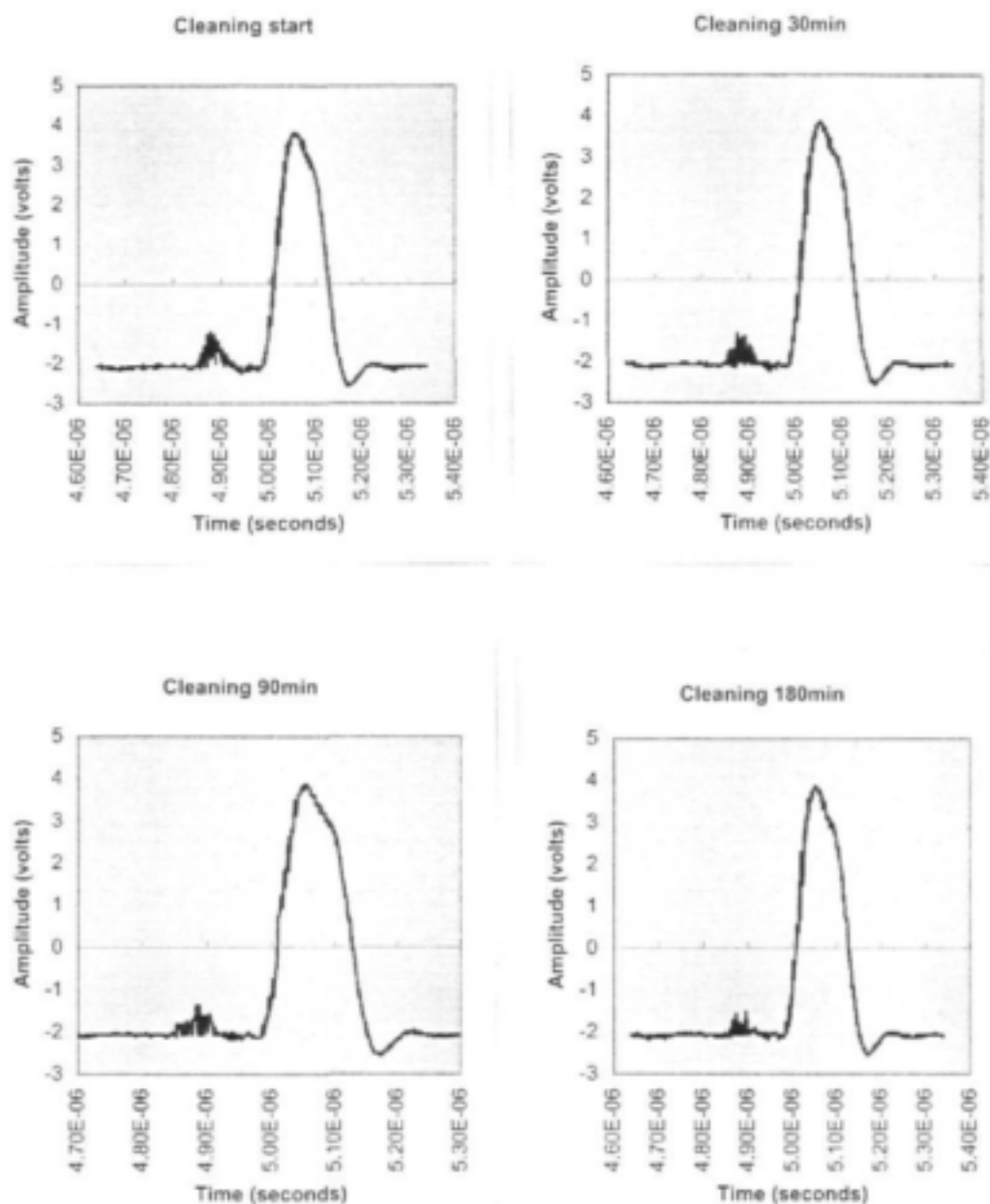


Fig. 10.13: Ultrasonic responses at the start and after 30, 90 and 180 min of operation for the cleaning phase of the cleaning experiment.

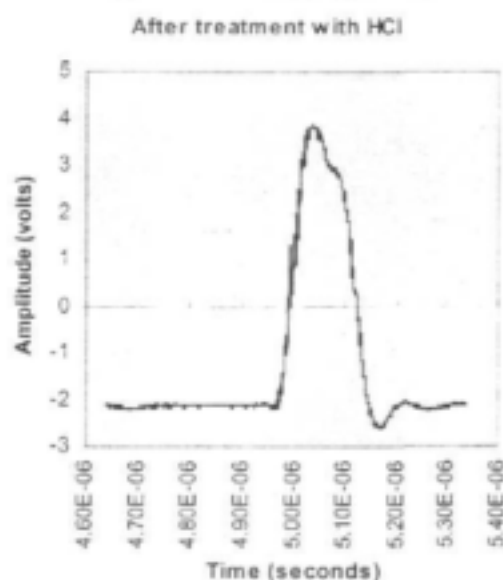


Fig. 10.14: Ultrasonic responses after treatment with hydrochloric acid, for the cleaning phase of the cleaning experiment.

Corresponding ultrasonic responses during the cleaning phase are presented in Figs. 10.13 and 10.14. The absolute signal amplitude of the fouling layer with time is illustrated in Fig 10.12. In Fig. 10.13 it was found that the peak of the second (fouling) echo decreased at the start of the cleaning phase, in comparison to the ultrasonic signal response after 9 hours of fouling with calcium carbonate (Fig. 10.11). This is because the change in the bulk solution from calcium carbonate solution to pure water resulted in a decrease in the fouling layer density. This suggests that the UTDR technique is able to detect subtle changes on the membrane surface. In Fig. 10.13, the peak of the second echo gradually declined as cleaning proceeded, because of partial dissolution of the fouling layer and reduction of its thickness. The absolute signal amplitude of the fouling echo is 0.81 and 0.63 V after 1.5 h and 1.5 h cleaning, respectively (Fig. 10.12).

Fig 10.13 shows that the peak after 1.5 h cleaning is gentler than after 0.5 h cleaning. This suggests that the density of the fouling layer after 1.5 h is lower than after 0.5 h cleaning.

After 3 h cleaning operation, the second echo was still observed (the absolute amplitude of the fouling layer is 0.44 V in Fig 10.12). This demonstrated it is difficult to clean the fouled membrane with water alone. In fact, morphological analysis of the membrane after the cleaning phase with pure water revealed that some fouling was still visible on the membrane (Fig. 10.15a). Additional cleaning methods are needed. Results of ultrasonic responses after treatment with hydrochloric acid during the cleaning experiment are shown in Fig. 10.14. The

disappearance of the second echo clearly indicated the removal of fouling layer from the membrane. Morphological analysis of the membrane by SEM showed the same results. After treatment with diluted HCl, the membrane was almost clean (Fig. 10.15b).

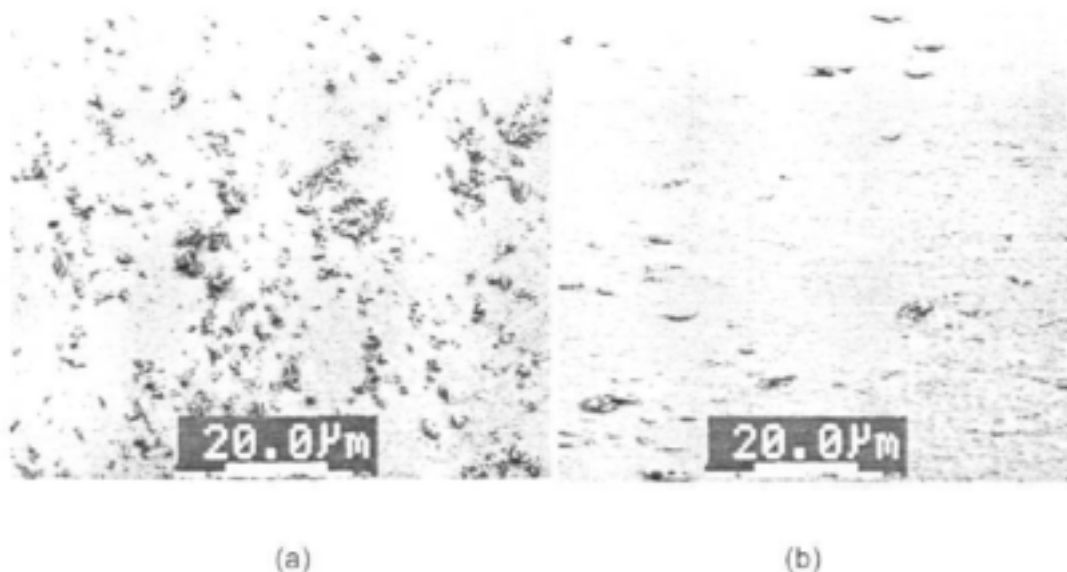


Fig. 10.15: SEM images of a membrane surface: (a) after 180 minutes of cleaning with water; (b) after 30 min treatment with dilute HCl.

10.5 CONCLUSIONS

This study describes the application of the UTDR technique for the non-destructive, in-situ visualisation of membrane fouling and cleaning in RO modules. Results show that the UTDR technique can effectively detect fouling-layer initiation, its growth on the membrane and its removal, in real-time. The acoustic signal response corresponds well with the membrane's flux-decline behaviour. The UTDR technique is also capable of detecting subtle changes on a membrane surface, and distinguishing between dead-end and cross-flow modes of fouling growth. It should therefore assist in understanding the mechanism of membrane fouling.

Furthermore, an important finding of this study is that a second/fouling echo was obtained in the time domain. The second (fouling) echo's amplitude should be seen more as an indication on the state of the fouling layer. The denser the fouling layer, the better the reflection, and, thus, the larger the amplitude that is seen. Moreover, the fact that the UTDR technique can monitor the removal of a fouling layer and membrane cleaning makes it a very suitable tool for studying the effectiveness of various cleaning techniques.

11. FLAT-BED-TYPE SLAVE UNIT FOR THE DETECTION AND MONITORING OF FOULING OF MEMBRANES USED IN LIQUID SEPARATION PROCESSES

Background to the invention

During the course of the project, enough data was generated to patent a monitoring device, described as a plugging index meter, for monitoring fouling on a membrane. The monitoring for the fouling process in a membrane facility is important to determine the state of fouling which has a detrimental effect on the filtration process. Furthermore, when the membrane is being cleaned, it is also desirable to know the state of cleaning of such a membrane.

An apparatus for monitoring the fouling of a membrane is proposed. Specifically, an apparatus for the monitoring, at the initial start of filtration, the fouling of any membrane assembly, as well as other aspects of the fouling layer, eg. thickness, density, UV/Vis spectra and ultrasonic absorption spectra. Furthermore, the apparatus will measure, on a once-off or continuous basis, the suitability of the pre-treatment and the quality of the feed waters and feed-back signals to improve pre-treatment steps.

Summary of the invention

The monitoring apparatus, a surveillance plugging-index meter, for monitoring fouling on a membrane comprises:

- a secondary fluid line connected in parallel to at least one primary fluid line containing a membrane or membrane assembly,
- a housing in fluid connection with the secondary fluid line
- a secondary membrane situated in the housing, the secondary membrane being of substantially the same filtration type as the primary membrane,
- monitoring means for monitoring the fouling on the secondary membrane as well as permeate flux, thereby giving an indication of the fouling on the primary membrane.

The monitoring means is preferably an ultrasonic time-domain relectometry transducer of a central frequency between 0.5 Hz and 50 MHz.

The monitoring means may be a broadband ultrasonic spectroscopy transducer.

The housing may have a window so that the secondary membrane situated in the housing can be viewed and analysed from outside the housing.

The window is preferably made from quartz or silica.

According to the invention a further method for the detection of fouling is provided; it comprises the following steps:

- Taking sample ultrasonic measurements when the membrane is substantially clean and storing these in a memory means
- Taking further ultrasonic measurements when the membrane has been used for filtration
- Calculating a differential signal by comparing the further measurements with the stored measurements, and
- Displaying the differential signal to a user via a display means.

The ultrasonic measurements may be ultrasonic time-domain reflectometry measurements in combination with differential signal processing.

Alternatively, the ultrasonic measurements may be ultrasonic absorption spectroscopy measurements.

Details of the invention

These are contained in the provisional patent (SA 2002/4753), and will not be repeated here.

12. CONCLUSIONS AND RECOMMENDATIONS

12.1 CONCLUSIONS

The overall achievement of this investigation was in the development of ultrasonic time-domain (UTD) and amplitude-domain reflectometry (UTDR) as a real-time visualization technique for fouling monitoring in various pressure-driven membrane separations. The major conclusions of this study can be summarized as follows:

Microfiltration (MF):

1. Ultrasonic response signals were obtained for kaolin particle deposition and subsequent cake layer formation on a nylon membrane surface during microfiltration (MF). A cake layer echo appeared, increased in the amplitude domain and moved in the time domain as fouling proceeded in MF.

2. An ultrasonic cleaning technique was successfully used for cleaning membrane fouling in MF. From experimental results it could be concluded that ultrasound associated with forward flushing was a new and effective method for cleaning fouled MF membranes. Analysis by scanning electron microscopy indicated that ultrasound with flushing was able to remove fouling layers from a membrane surface and restore the original structure of the membrane surface. The cleaning efficiency obtained by ultrasound with forward flushing was as high as 97.8%. High forward-flushing velocity combined with ultrasound was also beneficial for cleaning. In general, a high forward-flushing velocity and low cleaning solution (water) temperature, under the same ultrasonic conditions, gave higher cleaning efficiency.
3. In MF, cake formation, its growth and compressibility were observed by an ultrasonic testing method. UTDR can measure the rate of cake layer formation at different flow rates. UTDR is also capable of detecting subtle changes such as the stop and restart operation.
4. UTDR was also successfully used for monitoring membrane cleaning and evaluating the cleaning effectiveness of various cleaning methods, namely: forward flushing, ultrasonic cleaning and ultrasound with flushing. Results showed that a cake-layer echo decreased after flushing and disappeared after ultrasonic irradiation in MF. UTDR results showed that ultrasound associated with flushing was the most effective cleaning method for cleaning membranes fouled by paper mill effluent.
5. UTDR is very useful for the investigation of fouling mechanisms. An increase in flux could be seen when fouling operation was stopped and restarted. This is because interrupting the fouling experiment resulted in flow destabilisation and relaxation of the fouling layer. UTDR showed an increase in the thickness of the fouling layer and a decrease in the density of the cake layer. As illustration the following data are quoted. Although the thickness (82.5 μm) of the fouling layer obtained after 7 h of operation at cross-flow 1.83 cm/s was thicker than the thickness (60 μm) obtained after 18 h of operation at 6.97 cm/s in MF, the flux of 7.5 $\text{l/m}^2\text{h}$ obtained after 7 h of operation at 1.83 cm/s was higher than the flux of 7.2 $\text{l/m}^2\text{h}$ obtained after 18 h of operation at 6.97 cm/s. UTDR showed that the 60- μm cake layer (obtained after 18 h of operation at 6.97 cm/s) was denser than the 82.5- μm cake layer (obtained after 7 h of operation at 1.83 cm/s). The compressibility of the cake layer contributed to the flux decline. UTDR proved that increasing the flow rate during actual operation could not reduce fouling in MF carried out with paper mill effluent because a denser cake layer formed on the membrane surface at a high flow rate than it did at a low flow rate.

Ultrafiltration (UF):

6. In ultrafiltration (UF), an asymmetric polysulphone (PSU) membrane and its compaction could be detected by UTDR. Results showed a good correspondence between the UTDR signal response and the development of the fouling layer on the membrane surface in UF.
7. Fouling of a membrane leads to flux decline. The dynamic processes of deposition and growth of a fouling layer was confirmed by *in-situ* ultrasonic response signals. The sensitivity of ultrasonic responses revealed the coverage of a membrane surface with a fouling layer. UTDR results corroborated the flux measurements and SEM analyses.
8. UTDR could also distinguish and recognise various response signals from ultrasonic measurements in a tubular cell. Protein fouling was successfully detected by UTDR in a tubular PESU UF membrane. Changes in the amplitude and time domain of the observed signals provided useful quantitative information about adsorption, deposition and gelation of BSA on the membrane. The thickness of the BSA gel layer was obtained. UTDR can provide an approach to understand protein-fouling behavior related to flux decline. Ultrasonic frequency spectra could be useful as an additional tool for fouling detection.

Reverse Osmosis (RO):

9. It was determined that the application of the UTDR technique is feasible for the non-destructive, *in-situ* visualisation of membrane fouling and cleaning in reverse osmosis (RO) modules. Results showed that the UTDR technique could effectively detect fouling-layer initiation, its growth on the membrane and its removal, in real-time. The acoustic signal response corresponded well with the membrane's flux-decline behaviour. The UTDR technique was capable of detecting subtle changes on a membrane surface and distinguishing between dead-end and cross-flow modes of fouling growth. This could assist in understanding the mechanism of membrane fouling.

A secondary fouling echo was obtained (the primary echo comes from the membrane). The second echo amplitude should be seen as an indication on the state of the fouling layer. The denser the fouling layer, the better the reflection, and thus the larger amplitude that is seen. The fact that the UTDR technique can monitor the removal of a fouling layer and membrane cleaning makes it a very suitable tool for studying the effectiveness of various cleaning techniques.

10. The ultrasonic unit contains a suitably programmed microprocessor, and can be used to compare reference and test signals to produce a differential signal (a fouling layer echo).

A differential signal indicated the state and progress of a fouling layer on a membrane surface during actual operations. Both amplitude and arrival time of differential signals as a function of operation time provide useful quantitative information, i.e. changes in thickness and density of a fouling layer on the fouling processes. The resolution exceeds the theoretical limit by a considerable margin when using the differential signals.

11. A predictive modelling program - ultrasonic reflection modelling (URM) was developed to understand the processes of ultrasonic testing related to the deposition of fouling layers on membrane surfaces. Changes in the densities of the cake layer as well as the thickness could be substantiated by the mathematical modelling. Deposit resistance is not only related to the layer thickness but also the cake density (compressibility). The predicted results of fouling layer deposition were in good agreement with the actual measurements obtained in MF and UF.
12. Sufficient data were created to be able to propose and patent a modified plugging index meter.

12.2 RECOMMENDATIONS

The research has clearly shown that UTDR can indeed be successfully used to monitor membrane fouling in MF, UF and RO, with different membranes, module configurations and foulants.

An unsatisfied market need for a modified plugging index meter, based on ultrasonics, has been determined.

Hence, the following recommendations for further investigations in this area are made:

- The production of a modified plugging index meter based on technology developed in this project should be pursued and a world-patent registered. It should be created at reasonable cost.
- This technology should be applied 'real membrane situations', for example, to improve the production of drinking water that is high in colourants (e.g. natural organic matter).
- Investigations into the use of infrasound for cleaning membranes and for the prevention of fouling of membranes is further strongly recommended.
- The use of ultrasonics as an in-situ, non-invasive monitoring technique, to further investigate a new area of minimising fouling in membranes, i.e. the use of infrasound (low-frequency sound) as opposed to ultrasound (high-frequency sound), warrants consideration.
- The most urgent of these recommendations is what we need to do in the short term, namely the necessary purchase of the latest ultrasonics hardware, and then to determine what

further improvements can be obtained in terms of resolution, data transforms, speed of data recovery, etc. Specifically, improvements with using LabVIEW technology should be determined.

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14. PUBLICATIONS AND PRESENTATIONS EMANATING FROM THIS STUDY

14.1. PUBLICATIONS AND PATENT

1. Jianxin Li, RD Sanderson, EP Jacobs, Ultrasonic cleaning of nylon microfiltration membranes fouled by Kraft paper mill effluent, *J. Membr. Sci.* 205 (2002) 247-257.
2. Jianxin Li, RD Sanderson, EP Jacobs, Non-invasive visualization of the fouling of microfiltration membranes by ultrasonic time-domain reflectometry, *J. Membr. Sci.* 201 (2002) 17-29.
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14.2 PAPERS AND POSTERS PRESENTED

1. R.D. Sanderson*, Jianxin Li, EP Jacobs, The use of ultrasonics in membrane visualization and fouling, paper presented at 4th WISA-MTD Symposium-Membranes: Science & Engineering, Stellenbosch, South Africa, March 26-27, 2001.
2. Jianxin Li, R.D. Sanderson*, D.K. Hallbauer, E.P. Jacobs, Visualization of membrane fouling and cleaning in microfiltration and ultrafiltration by ultrasonic time-domain reflectometry, paper presented at 2001 International Conference – Membrane Technology, Shanghai, China, Sept. 17-21, 2001. (Invited keynote plenary)
3. Jianxin Li*, RD Sanderson, EP Jacobs, Noninvasive in-situ visualization of fouling and cleaning in flat-sheet microfiltration membranes by ultrasonic time-domain reflectometry, paper presented at WISA 2002, Durban, South Africa, 19-23 May, 2002.
4. Jianxin Li*, R.D. Sanderson, EP Jacobs, Ultrasonic cleaning of membrane fouling in MF fouled by paper mill effluent, poster presented at 4th WISA-MTD Symposium-Membranes: Science & Engineering, Stellenbosch, South Africa, March 26-27, 2001.
5. Jianxin Li*, R.D. Sanderson, Visualization of membrane fouling and its removal during microfiltration and ultrafiltration by ultrasonic time-domain reflectometry, poster presented at the International Congress on Membranes and Membrane Processes (ICOM2002), Toulouse, France, July 7-12, 2002.
6. Jianxin Li*, D.K. Hallbauer, R.D. Sanderson, V Yu Hallbauer-Zadorozhnaya, Modelling of ultrasonic reflections during the testing of membrane fouling by ultrasonic signal reflections, poster presented at the International Congress on Membranes and Membrane Processes (ICOM2002), Toulouse, France, July 7-12, 2002.

14.3 DISSERTATION

Jianxin Li, Real-time investigation of fouling in membrane filtrations by a non-invasive ultrasonic technique, PhD dissertation, University of Stellenbosch, December 2002.

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