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Erratum

Page 1	paragraph 5	line 4	"were" should be "was"
Page 25	paragraph 5	line 4	"arising" should be "carried"
Page 28	paragraph 1	line 1	"periodical" should be periodic"
Page 29	paragraph 2	lines 1-3	should be "An alternative method of hydraulic cleaning is back-pulsing; short bursts of backpressure, alternative pressurising and depressurising and reversing the feed flow direction with the permeate exit closed (Scott, 1995)."
Page 31	paragraph 2	lines 4-5	should be "Only a few are actually compatible with membranes (Krack, 1995)."
Page 35	paragraph 1	line 5	"avoid" should be "prevent"
Page 85	paragraph 3	line 2	"decreased" should be "increased"
Page 86	paragraph 3	lines 1-8	should be "This work also assisted in highlighting that further work needs to be conducted to evaluate the performance of enzyme cleaners on a commercial scale. These are probably capable of removing foulants not easily removed by other cleaners and have the advantage of being gentle to membranes and of possibly increasing membrane lifespan. They also present fewer chemical disposal problems compared with caustic/acidic based cleaners. However, better performance must be achieved with these in order to realise their benefits."

Evaluation and Development of Chemical Solutions for Membrane Cleaning in the Dairy Industry

A thesis presented in partial fulfilment of the requirements for the degree of Master of Technology in Food Science at Massey University, Albany, New Zealand

Nisha Maria D'Souza
1999

Abstract

Membranes must be cleaned regularly to remove organic material deposited on the surface from the food or biological fluids processed. Cleaning is a compulsory step in maintaining the permeability and selectivity of the membrane and is also necessary to return the plant to its original capacity, to avoid bacteriological contamination, and to produce products with a long shelf-life. Without cleaning, the flux of solution through the membrane would decline to uneconomic levels.

Caustic, acidic and enzymatic based cleaners may be used for membrane cleaning. Such cleaners affect the lifetime and performance of a membrane and should thus be surface-active, soluble, rinsable, non-corrosive, safe, effective and easy to use. The primary objective of work carried out was to evaluate a range of cleaning chemicals and cleaning regimes on a pilot-scale.

Cleaning regimes employing conventional caustic and acidic cleaners, and enzymatic detergents have been evaluated for a Desal ultrafiltration membrane. The membrane was reproducibly fouled during the processing of skim milk and skim milk concentrate on a pilot-scale plant supplied by Tuchenhagen (N.Z.) Limited and compared favourably with an industrial plant. A spiral wound membrane of polyethersulfone with an active area of 7.4 m^2 and a 10,000 molecular weight cut-off was selected. A transmembrane pressure of 2.5 bar, a retentate flow rate of 60%, a temperature of 18.5°C, and a recirculation flow rate of 7 m^3h^{-1} was kept constant during filtration. A combination of flux recovery after cleaning and solute resistance removal was used to assess cleaning performance.

Higher flux recoveries (87.3-93.6%) were achieved with surfactant based formulations compared with enzymatic detergents. This was attributed to the wetting action of surfactants which when used in conjunction with a high strength blended alkali solution, aided the convective cleaning solution flow through the membrane pores.

Enzymatic cleaning was found to be milder to the membrane. While the enzyme-sanitiser regime yielded good flux recoveries (68.4-87.3%), the enzyme-acid and acid-enzyme regimes were not capable of restoring membrane permeability, resulting in low flux recoveries 64.2-78.9%. The acid in these regimes caused the membrane pores to shrink, restricting the ability of the enzymatic detergent or rinse water to penetrate the foulant and remove it. Based on these results, a new formulation (DR292) with more surfactant action was developed and evaluated. Flux recovery using this new formulation increased by 3.5%.

Regimes incorporating non-ionic surfactants and high strength alkali solutions were found to successfully restore membrane permeability because a higher level of surfactant was obtained from the mixture. Further experiments using enzyme-acid and acid-enzyme regimes, and the new formulation need to be trialed on new membranes to determine their long-term effect on membrane permeability and selectivity.

Acknowledgments

I wish to express my deepest thanks to God for blessing me with the health, patience, motivation and skill required to successfully complete this project.

My sincere thanks to my supervisors Dr. John Mawson at Massey University and Mr. Paul Hofland and Dr. Terry Smith at Orica (N.Z.) Limited, for their guidance, advice and encouragement throughout this project. They have enabled me to gain an understanding of the principles of membrane technology as well as helped me improve my research skills which will aid me in future work.

I also wish to thank The Foundation for Research, Science and Technology (FRST), for funding this project and to Tuchenhagen (N.Z.) Limited for supplying the pilot plant.

I would like to thank all those who helped me access information regarding this project and to all those at Anchor Products, Lichfield, for their invaluable assistance during the period of my research.

A big thankyou to Ms. Marian Holdaway and her family who opened their hearts and home to me while conducting research at Anchor Products, Lichfield.

Last but not least, I am honoured to have a loving family who have constantly supported and encouraged me to carry on when things got difficult. I am deeply grateful to them for everything and God bless them always.

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1.0 Introduction

Pressure driven membrane processes like ultrafiltration and microfiltration have been widely adopted by food processing industries over the past two decades and the New Zealand Dairy industry has been at the forefront of this development. Approximately 100,000 m^2 of membranes are installed in New Zealand, with over 80% of this area installed in the last five years (Bennett, 1997). A greater part of this area is in the form of polymeric membranes made of polysulfone or polyethersulfone materials in a spiral wound configuration.

Processing of dairy fluids causes the formation of both organic and inorganic (fats, proteins, mineral salts) fouling deposits on the membranes. Apart from surface fouling, internal fouling also presents a serious problem as degraded soil may enter the membrane during the cleaning process. Hence, regular and effective cleaning of membranes is an integral part of membrane separations.

Cleaning of membranes is a legal requirement and is necessary to avoid bacteriological contamination, and to produce products with a long shelf-life without using preservatives. Without cleaning, the flux of solution through the membrane would also decline to uneconomic levels and reduce the throughput and selection characteristics of the membranes. Hence cleaning acts to return the plant to its original capacity.

Cleaning a membrane is more complex than cleaning a stainless steel surface. A membrane's surface is rough and requires the cleaning of the surface, pores and also the permeate side or chamber.

Caustic, acidic and enzyme based cleaners may be used for membrane cleaning. As the membranes are susceptible to damage by the cleaning chemicals, these must be formulated specifically for each type of cleaning application. The development of improved membrane cleaning methods were to some extent neglected in the past and abrasive chemical cleaning agents like hydrochloric or sulphuric acid, were mainly used to restore transmembrane flux. While these cleaning chemicals were effective, they were also toxic and corrosive. The cleaning agents used should be surface-active, soluble, rinsable, non-corrosive, safe, effective and easy to use. The choice of cleaning agent depends on the chemical and thermal resistance of the membrane, the nature of the foulant, and the severity of the fouling.

The primary objective of work carried out was to evaluate a range of cleaning chemicals and cleaning regimes on a pilot-scale, and more specifically to:

- develop reproducible methods for fouling a membrane with skim milk, and skim milk concentrate (SMC) to provide soil properties matching those found on fouled industrial membranes,

- develop suitable methods for measuring membrane performance of fouled membranes, and establish that the required membrane performance is attained and maintained with repeated fouling and cleaning,

- optimise the cleaning conditions required for the above and recommend appropriate operating regimes for full scale trials with the cleaning chemicals, and

- evaluate the results obtained for conventional cleaners and trial new cleaning formulations for potential commercial applications.

2.0 Literature Review

2.1 Introduction

Membrane separation technology has been of interest in the process industries since the early 1960s as it provides a unique opportunity for both the fractionation and concentration of components in liquid systems without phase change, whilst retaining desirable physical and chemical structures of components (Bennett, 1997).

For the major operations employed in the food industries, namely reverse osmosis (RO), nanofiltration (NF), ultrafiltration (UF) and microfiltration (MF), separation is based primarily on component size. The membrane acts as a selective barrier permitting the passage of certain components while retaining certain other components of a mixture (Cheryan, 1986). The driving force for such a process is a differential pressure across the membrane (Bennett, 1997; Rosenberg, 1995) and the key to the successful operation of these membranes is the maintenance of a high cross-flow or transverse flow in which the feed flow is parallel to the membrane surface (Bennett, 1997). The alternative to cross-flow is dead-end flow, which is perpendicular to the membrane, and so is only suitable for dilute suspensions (Shorrock & Bird, 1998), for example, sterile filtration of fruit juices, wine, beer and pharmaceutical liquids.

In addition to pressure gradients, other driving forces are also used in conjunction with membrane separation processes in experimental or large scale industrial applications. Concentration gradients are used in dialysis, while electrodialysis is based on the electrical potential gradient as the driving force for separation of differently charged particles.

RO achieves the "tightest" separation of the pressure-driven membrane processes as used in liquid separation. The solvent (water) along with some low molecular weight salts passes through the membrane, but essentially all dissolved and suspended material (molecular weight > 100; molecular size > 1 nm) are retained by this process. RO operates typically at pressures greater than 20 bar and is used in dairy processing for concentrating the permeate produced by ultrafiltration of skim milk in the manufacture of milk protein concentrates (MPCs), and in the concentration of the permeate from cheese or rennet whey ultrafiltration prior to evaporation for crystalline lactose manufacture.

NF is similar to RO, but the membranes are slightly more open. Small ions, organic molecules and water pass through the membrane while larger molecules and macromolecules such as protein and fat are retained (molecular weight > 300-400; molecular size > 2 nm). Operating pressures range from 15 to 30 bar. NF is used in the preconcentration of lactic whey permeate prior to evaporation; this partial demineralisation achieved reduces evaporator scaling.

UF retains only macromolecules of molecular size larger than about 1-20nm. It is a process where high molecular weight compounds (HMWCs) like proteins, lipids or complex polysaccharides and suspended solids are rejected by the membrane. Water, salts, and low molecular weight compounds (LMWCs) pass the membrane freely. UF operates within a range of 2 to 10 bar.

UF is still the major application of membrane technology in the New Zealand Dairy Industry and is used in the production of whey protein concentrates (WPCs), soft cheese, MPCs, high calcium milks and cheese milk standardisation.

MF separates particles and suspended material of sizes in the order of 10-10,000nm. Therefore, it can effect the separation of bacteria and fat globules from milk or whey. Water, salts, and selected macromolecules pass through the membrane and operating pressures are very low, typically from 0.1 to 2 bar.

MF can be used to reduce fat and bacterial loadings, for example, in whey being used for whey protein concentrate production. MF also offers the potential to separate larger protein particles (casein micelles) from smaller components (whey proteins) thus producing products with novel properties and compositions.

The major processes are outlined in Table 2.1. The mechanisms governing mass transport in these processes varies as a function of membrane type, process conditions such as temperature and pH, and equipment configuration (Rosenberg, 1995). Relevant aspects are developed further in later sections of this review.

Table 2.1 Comparison of major pressure-driven membrane processes (Wagner, 1996)

	RO	NF	UF	MF
membrane	assymetrical	assymetrical	assymetrical	symmetrical assymetrical
size of solutes retained	>1nm	>2nm	1-20nm	10-10,000nm
rejection of	HMWCs, LMWCs, NaCl, glucose, aminoacids	HMWCs, monosaccharides, disaccharides and oligosaccharides, polyvalent negative ions	macromolecules, proteins, polysaccharides	particles, bacteria, clay
membrane materials	Cellulose acetate, thin film	Cellulose acetate, thin film	Ceramic, Polysulfone, Polyvinylidenefl-uoride, Cellulose acetate, thin film	Ceramic, Polysulfone, Polyvinylidenefl-uoride
membrane module	Tubular, Spiral wound, Plate and Frame	Tubular, Spiral wound, Plate and Frame	Tubular, Spiral wound, Plate and Frame, Hollow fibre	Tubular, Hollow fibre

According to Kessler (1981), membranes should be:

- stable over a wide range of pH values,
- capable of being cleaned effectively, and
- unaffected by temperatures.

Having outlined the four major pressure-driven membrane processes, this review will discuss the different membrane materials available today and the kinds of configurations they can be assembled into. In particular, emphasis will be placed on the UF of whey and milk as these are the major food applications of membrane processes in the dairy industry and the conditions which cause flux decline, as cleaning aims to remove foulants. In certain circumstances, it is possible to delay the onset and reduce the amount of fouling by feed pretreatments or other steps and these measures will also be outlined. However, it is highly unlikely that the fouling will be completely eliminated, hence the need for regular cleaning. The two processes (fouling and cleaning) are thus intrinsically linked.

The optimisation of membrane cleaning protocols requires in-depth understanding of the complex interactions between the foulant and the membrane. Cleaning is a costly operation in time, energy, chemicals and water, but is an essential step in maintaining the permeability and selectivity of membrane processes which will be the primary focus of this review, and the integrity (especially microbial) of the product.

2.2 Ultrafiltration

The evolution and expansion of UF on an industrial scale became possible after the development of asymmetric membranes by Loeb and Sourirajan in 1960 (Cheryan, 1986). Since then, UF has been widely used for concentration, recovery, fractionation, and purification in food processing and bioprocessing.

Operationally, UF is a simple process. A solution flows under pressure over the surface of a suitable supported membrane (Figure 2.1). As a result of the applied pressure gradient across the membrane, the solvent passes through the membrane and is collected as permeate or ultrafiltrate (Renner & El-Salam, 1991). Depending on the characteristics of the membrane used, the suspended material and some of the dissolved components of the feed solution are retained by the membrane and concentrated. The exit stream is known as retentate or concentrate and will also contain some of the permeable solutes.

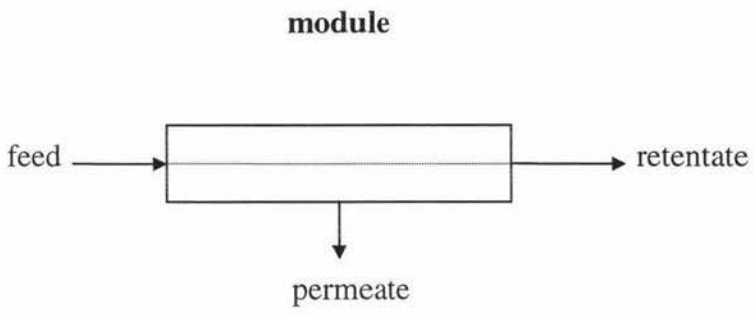

Figure 2.1 Schematic drawing of a single module design (Mulder, 1991)

The dynamic forces of the circulating fluids continuously remove part of the retained materials into the stream, thus minimising the accumulation of the retained molecules on the membrane surface.

UF is an important process in the food industry, particularly for dairy applications such as concentration and dewatering of milk and whey (Clarke and Heath, 1997). Other applications include production of protein enriched milk, yoghurt, quark (curd cheese), soft cheese, feta cheese, protein powder, ice-cream, and products for infant foods and special diets.

According to Rosenberg (1995), the use of membrane processes such as UF in the manufacture of fermented dairy products improves control of quality attributes such as consistency, post processing acidification and extent of syneresis.

2.2.1 Ultrafiltration of whey

Whey is a by-product of cheese or casein production, a precipitation process in which a casein-rich fraction is obtained as a result of adding rennet or increasing the acid concentration of the milk. Apart from water, whey contains almost all of the lactose, 20% of the milk proteins (that is, the whey proteins), and most of the water soluble vitamins and minerals present in whole milk.

The UF membranes used for whey processing should retain the proteins while LMWCs such as lactose and minerals largely permeate, although limited retention may be observed at high solids concentrations. The optimum membrane cut-off should be at molecular weights of 10,000-25,000 (Rautenbach and Albrecht, 1991).

Depending on the precipitation agent, either sweet or sour whey will be obtained. Sweet whey is a by-produce of cheese and rennet casein manufacture. Acid whey can be sub-divided into three classes (Nielsen, 1988):

- lactic acid whey produced from fresh cultured cheese or lactic casein,
- hydrochloric acid whey produced from casein, and
- sulphuric acid whey also produced from casein.

The actual composition of the whey depends on the composition of the milk, the variety of cheese or the type of casein, and the processing conditions.

The whey proteins, that part of the milk proteins which remains dissolved when casein is precipitated, is the most valuable component of whey. Whey comprises of a number of proteins such as β-lactoglobulin, α-lactalbumin, serum albumin, immunoglobulins, and proteose-peptones (Nielsen, 1988).

Whey protein concentrates are defined as a whey product containing a minimum of 25% protein on a dry product basis, and are obtained by removing lactose and minerals from the whey protein. A wide range of whey protein concentrates have been prepared by cross-flow UF, with a protein/total solids ratio between 0.25 and 0.80. Higher levels of protein purity create a significantly higher value product. These possess excellent functional properties such as emulsifying, water binding, foaming and gelling characteristics making them useful ingredients in dairy and food products. According to Gesan *et al.* (1993), their high nutritional value is attributed to their balanced content of essential amino acids. Whey protein concentrates have been used in the following applications as listed in Table 2.2.

Table 2.2 Applications of Whey protein concentrates (Nielsen, 1988)

Application	Examples
Nutritional products	infant formulas, dietetic and health foods
Meat products	minced, ground, and cured meat products
Fish products	
Beverages	
Confectionery products	bakery products, chocolates and candy bars
Emulsified products	mayonnaise and salad dressings; soups, gravies, and coffee whiteners; low-calorie spreads
Dairy products	ice-cream, yoghurt, desserts and milkshakes, and a variety of cheeses
Miscellaneous products	texturised proteins, non-dairy ice-cream, pasta products, and potato products

UF of whey is generally accepted as a gel-layer controlled process, that is, flux through the membrane is limited by the protein concentration. Almost any desired protein:lactose:minerals ratio in a product can be obtained by simple UF provided that:

- a suitable membrane (rejecting protein and not lactose and minerals) is used, and
- the protein gel-layer is unselective with respect to the minerals.

As a result the concentration of the LMWCs will remain constant while protein concentration increases during the UF process (Rautenbach & Albrecht, 1991). In practice, this process is limited since permeate flux decreases significantly with increasing protein concentration and retention of other components increases (Figure 2.4). This problem can be solved by washing the retained solids, a procedure known as diafiltration (DF), which involves the addition of water to the

feed material at the same rate as permeate is being removed. This enables permeable components of a mixture like lactose in a protein-lactose stream to be separated from retained components to the degree required (Beaton, 1979).

The percentage of protein in the total solids can be improved when combining DF in processing whey with UF. The permeate from this treatment can be further concentrated in a RO plant to remove lactose, salts, amino acids and other components from the permeate and so reduce the biochemical oxygen demand (BOD) of the permeate, making it easier to dispose off. Limited recycle of RO permeate for use in cleaning is also possible.

2.2.2 *Ultrafiltration of milk*

The early development of UF was directed towards the productions of whey protein concentrates, but has now moved into a variety of products derived from milk (Bennett, 1997). The compositions of milk and whey streams are shown in Table 2.3.

Table 2.3 Compositions of typical liquid dairy streams (%w/v) (Cheryan, 1986)

Component	Milk	Skim Milk	Sweet Whey	Acid Whey
Total solids	12-13	9-10	6.0-7.0	6.0-6.5
Fat	3.5-4.0	0.1-0.2	0.1-0.5	0.1
Protein (Total Nitrogen x 6.38)	3.2-3.3	3.2-3.4	0.7-0.9	0.7-0.8
Lactose	4.5-5.0	4.6-5.0	4.2-5.0	4.2-4.9
Ash	0.6-0.8	0.6-0.8	0.5-0.6	0.5-0.7
Calcium	0.12	0.12	0.047	0.103
Potassium	0.15	0.17	0.161	0.143
Sodium	0.05	0.05	0.054	0.048
Magnesium	0.013	0.011	0.008	0.01
pH	6.6-6.7	6.6-6.7	5.6-6.3	4.4-4.7

During UF of milk, the retentate contains proteins, fat and colloidal minerals while the permeate contains water, soluble minerals, lactose, non-protein nitrogen compounds and water soluble vitamins.

The major application of UF of milk in the dairy industry is for standardisation of the protein content for continuous mechanised cheesemaking, or to reduce storage milk space and to improve the organoleptic quality of the cheese (Daufin & Merin, 1995). Ultrafiltration also offers the potential to produce soft cheeses, cheesemilk of standard protein level, and milk protein concentrates (Bennett, 1997).

According to Bennett (1997), the protein level in milk protein concentrates range from 56% to 85%. These are used in the production of cheeses and cultured foods by recombination, without the need for subsequent whey removal. UF also helps elevate total solids levels in milks being used for cultured products such as yoghurts, without the need for milk powder addition (Bennett, 1997). According

to Russell (1994), special high protein, low lactose liquid milk products can also be produced.

The objective of UF of skim milk is to remove water, some lactose, and some minerals to produce a retentate in which all the protein (casein and whey) is contained.

Concentration of skim milk by UF not only elevates the protein level, but also the calcium level, as much of the calcium is associated with the casein. As a result, a range of products with high calcium contents are produced.

2.3 Membrane materials

Several polymers and other materials are used for the manufacture of permselective membranes. The choice of membrane material is important with respect to the chemical and thermal stability and sensitivity to fouling. The type of membrane material does have a significant influence on cleaning formulation composition. Over the years, three generations of membrane materials have been developed (Table 2.1).

First generation products were based on cellulose acetate (CA) and were used primarily for RO. Cellulose acetate was the original material used to form asymmetric skinned membranes. These membranes exhibit higher fluxes because of the thinness of the skin, and better resistance to plugging. They also have a good retention capacity. However, in spite of a more open structure, their limited tolerance of pH beyond the range of 3-7, temperatures above 35°C and chemicals (such as chlorine) used for cleaning and sanitising, made them unsuitable for processing most biological materials (Hobman, 1992), although they are still used in some biotechnology applications as they are low binding with respect to proteins.

Second generation membranes are based on engineering polymers like polysulfone (PS), polyacrylonitrile (PAN), polyvinylidene-fluoride (PVDF), polyethersulfone (PES), polyamide (PA), and polyethyleneimide (PEI). Of these materials, PS and PES are in general use today.

A third generation of membranes of inert mineral alumina or other ceramic materials (for example, ZrO_2, TiO_2), have now been developed. These are more expensive than most other membrane materials but do find food applications in some countries - notably France and Germany.

Nearly all UF membranes are anisotropic or asymmetric in morphology, that is, they have a dense 'skin' layer on top which defines the degree of separation effected, and a spongy support layer underneath. Other non-asymmetric membranes structures available include symmetrical types (Table 2.1), in which the membrane is of the same material and structure throughout, and composite

asymmetric membranes, which incorporate a very thin polymer membrane on a highly porous substructure (Hobman, 1992).

2.3.1 Polymeric membranes

The greater part of the membrane area currently installed is in the form of polymeric membranes in spiral wound configuration. Polymeric UF membranes are generally regarded as having low fluxes and low cost prices, whereas ceramic membranes show high fluxes and probably have a longer lifetime, but are more expensive. This longitivity is one of the reasons why ceramic membranes are sometimes preferred.

PS and PES membranes are most widely used in UF applications and are similar to each other. PS membranes have in their structure repeating diphenylene sulfone units as shown in Figure 2.2, and these are responsible for their chemical resistance.

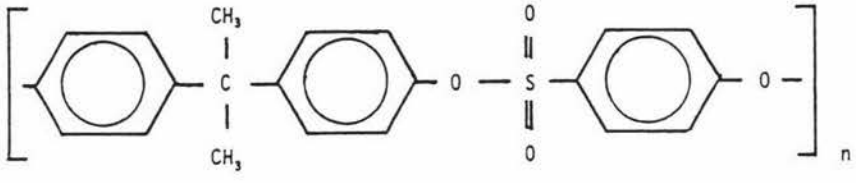

Figure 2.2 Structure of polysulfone (Leslie *et al.*, 1974)

PS has been considered an important breakthrough for UF applications due to its wide temperature limit (up to 75°C) and wide pH tolerances (pH 1-13), both providing advantages for cleaning purposes. They are quite resistant to oxidising agents such as hypochlorite. They have a wide range of pore sizes for UF applications ranging in molecular weight cut-offs from 1000 up to 500,000 in commercial size modules, and can easily be fabricated into a wide variety of configurations (Tragardh, 1989).

Unfortunately, these membranes exhibit very hydrophobic properties which are undesirable in membrane filtration. Molecules such as proteins contain both hydrophobic and hydrophilic regions. If the protein interacts hydrophobically with the membrane surface it tends to be denatured unfolding on the membrane surface. In its unfolded state it exposes more hydrophobic regions and the process cascades resulting in quite thick fouled layers appearing on the surface (Howell, 1996). Additionally, Wallwork (1994) recommends that such membranes should never be allowed to dry out because of the difficulty of overcoming the surface tension to wet the pores again.

2.3.2 *Mineral or ceramic membranes*

Membranes comprising only inorganic mineral materials are commonly referred to as mineral or ceramic membranes. Inorganic membranes are asymmetric and are composed of a thick sintered porous structure which serves as a mechanical support for the thin filtering layer. This layer may be made of the same material as the support or from a different material (composite material). Today, all the industrial inorganic membranes are of tubular configuration with pore sizes usually in the UF and MF range, but are now capable of NF or even pervaporation.

The first inorganic membrane was produced under the trade name Carbosep®. The filtering skin layer was made of ZrO_2 powder which formed a membrane of various pore sizes on a porous carbon support (Daufin and Merin, 1995). Zirconium oxide remains a commonly used solute, while porous carbon tubes and porous metal (stainless steel) tubes of about 6.35×10^{-3} metres in diameter are most common as base supports.

Aluminium oxide is another material used to prepare a strong and durable porous support. It serves as a microfilter with a range of pore sizes. Tradenames of two common alumina membranes are Membralox® and Kerasep® (Daufin & Merin, 1995).

From the presence of hydroxyl-groups on these oxide materials, the membranes are hydrophilic. This is especially important in high value (biotechnology) applications, but not so important in lower value (dairy) applications. Pure hydrophilic membranes are rather difficult to use as they tend to be biodegradable or alternatively difficult to construct so that they resist a wide enough range of cleaners and chemicals (Howell, 1996).

Mineral or ceramic membranes are extremely versatile. The membrane composition, the sintering process and the tubular design render inorganic membranes highly resistant to organic and inorganic solvents in the entire pH range, high pressures and temperatures. Inorganic membranes do have some disadvantages compared to polymeric ones, especially with respect to the cost associated with pumping and, the large floor area and high price per square metre of membranes (Daufin and Merin, 1995).

2.4 Membrane configurations

Membranes can be assembled into various module designs for commercial applications. Different combinations of configuration and material are suitable for different applications (Table 2.1). There are four basic designs of equipment, arising from the fact that membranes can be manufactured in two configurations: (i) a flat configuration giving rise to pleated sheets, spiral wound and plate and frame units and (ii) a tubular configuration giving capillaries, tubes and hollow fibres.

2.4.1 Tubular

Tubular membranes are usually not self-supporting and so are often made by coating the inside of a porous support tube with membrane material. The feed solution flows through the centre of the tubes, and the permeate is collected in the module housing after flowing through the porous support. The packing density is less than 300 m^2/m^3. Such membranes typically range from $6x10^{-3}$ to $2.5x10^{-2}$ metres inside diameter (Mulder, 1991).

2.4.2 Hollow fibre and Capillary

Hollow fibre and capillary membranes consist of a bundle of thin membrane tubes, bonded around the outsides at the ends, and cased in a larger tube. The two types differ only in the diameter of the membrane tubes; capillaries are larger than hollow fibres. Hollow fibres have internal diameters in the range of $5x10^{-4}$ to $1x10^{-3}$ metres and also the highest packing density, which can attain values up to 30,000 m^2/m^3 for RO modules used with very clean feeds (Mulder, 1991).

2.4.3 Plate and Frame

In these designs, membranes are made up from sets of a sandwich of two flat sheet membranes mounted on porous or grooved support plates. In each of the feed and permeate compartments thus obtained, a suitable spacer is placed. The plate and frame stack is built up to the required membrane area by hanging the number of sets necessary on a frame between two end plates. The packing density of these modules is about 100-400 m^2/m^3 (Mulder, 1991).

2.4.4 Spiral wound

These membranes are formed from a 'sandwich' comprising two flat sheets of membrane which are separated by a layer of highly porous material and laid on a plastic mesh. The edges and one end of the membrane is sealed with adhesive and the remaining open end is fastened and sealed to a permeate collection tube, around which the 'sandwich' is rolled into a spiral (Figure 2.3). The membrane assembly is completed by insertion of the roll into a suitable cylindrical housing. (Hobman, 1992). These modules have a good packing density at 300-1000 m^2/m^3 (Mulder, 1991). Overall these have become the standard against which other food applications are compared.

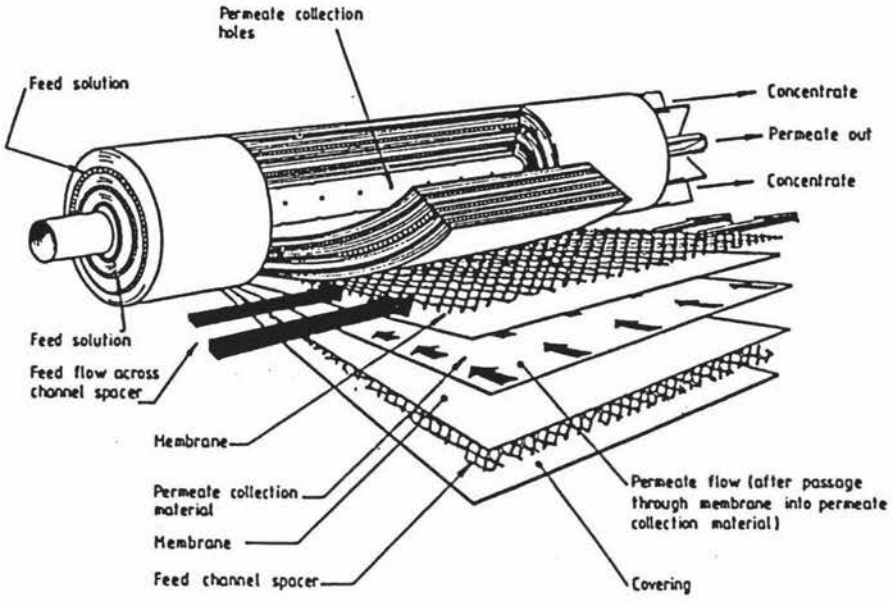

Figure 2.3 Construction of a spiral wound module (Courtesy of Koch Membrane Systems)

Individual membrane elements or cartridges are usually incorporated into a single pressure vessel to form a membrane assembly (or module). Modules can be connected together either in parallel or in series, depending on the type of process whether these operate in continuous or batch, and the size of plant. Complete UF plants are assembled by connecting the modules to suitable pumps and other ancillary components such as feed and balance tanks, control valves, heat exchangers and instrumentation. A qualitative comparison of the above configurations proposed by Mulder (1991) is shown in Table 2.4.

Table 2.4 Qualitative comparison of four membrane configurations (Mulder, 1991)

	Tubular	Plate-and-Frame	Spiral wound	Hollow fibre
Packing density	low	→	→	very high
Investment	high	→	→	low
Fouling tendency	low	→	→	very high
Cleaning	good	→	→	poor
Operation cost	high	→	→	low
Membrane replacement	yes/no	yes	no	no

Tubular membranes are used for processing materials with large suspended particles. They are easier to clean because of a low packing density, but are more expensive per m^2 of membrane area and are relatively high in energy usage. The tubular design provides superior performance at high concentrations of solids. Plugging is minimised and high product recovery is achievable (Koch Membrane Systems, 1998).

Hollow fibres (as used for MF and UF) are comparatively inexpensive but are limited in terms of their suspended solids handling abilities. The hollow fibre geometry allows a high membrane surface area to be contained in compact

modules providing high capacity while utilising minimal space (Koch Membrane Systems, 1998). Hollow fibre membrane plants must be run at low flow rates to prevent concentration polarisation and a clean feed is essential to prevent clogging of the fibres (Mulder, 1991).

Plate and frame membranes come in a wide range of membrane types and are able to deal with high viscosity fluids. They permit the use of easily cast flat membranes but have a limited membrane area per stage. The plate and frame construction is also high in equipment costs and skilled labour, required for membrane assembly and replacement. There is a high probability of leaks or membrane failures because of the complexity of membrane handling. Also, the flow patterns across the filter surface are difficult to control, leading to insufficient liquid flow patterns (Brock, 1983).

As noted above, spiral wound membranes have revolutionised the application of membrane technology in the food industry in recent years. They are compact in design and can be operated at elevated pressures and temperatures, resulting in greater throughput. They have a limited capability in handling suspended solids and a low relative cost per unit membrane area (Russell, 1994). They are more difficult to clean than tubular configurations, but more economic both in purchase price and energy use due to reduced pumping requirements and higher packing density. They have an advantage over flat sheet membranes, because they can maximise the amount of membrane surface that can be placed in a given space (Brock, 1983). The ease of replacement has greatly increased the attractiveness of this technology (Bennett, 1997).

2.5 Theoretical Aspects

Flux and solute rejection are two key parameters used to describe mass transport across UF membranes (Hobman, 1992).

The flux, J, is a measure of the permeate (solvent) flow rate through the membrane per unit area. The appropriate SI unit is metres per second ($m^3/m^2s = ms^{-1}$) but other commonly used units are LMH (litres per metre squared per hour) or GFD (U.S. gallons per foot squared per day). The flux of the membrane is a key design parameter, as it is independent of the size of a plant and so can be used for scale-up and comparison of plants with differing membrane areas. For a given application (feed, membrane, operating conditions), the flux determines the area required, and hence capital cost, for a given throughput.

Solute rejection, or rejection, R (expressed either as a fraction or as a percentage), is defined as:

$$R = 1 - \frac{C_p}{C_f} = \frac{(C_f - C_p)}{C_f} \qquad (1)$$

where C_f = solute concentration in the feed (gL^{-1})
C_p = solute concentration in the permeate (gL^{-1})

J and R are functions of operating pressure, temperature, solute concentration, time and boundary layer concentration. Typical behaviour for the flux is shown in Figure 2.4.

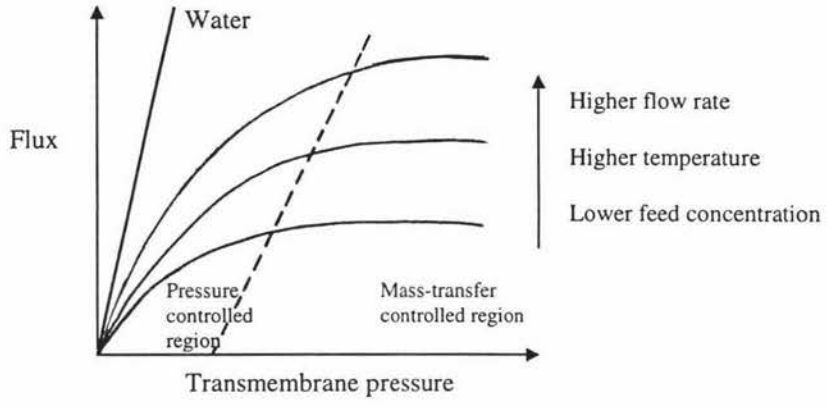

Figure 2.4 Generalised correlation between operating parameters and flux, indicating the areas of pressure control and mass transfer control (Cheryan, 1986).

For RO and UF of process fluids, permeate flux increases less than linearly with transmembrane pressure (ΔP_{TM}), and is generally always smaller that the pure water flux for the following reasons (Cheryan, 1986):

- change in membrane properties
- change in feed solution properties
- concentration polarisation
- membrane fouling

Changes in membrane properties can occur as a result of physical or chemical deterioration. Since membrane processing is a pressure-dependent process, it is possible that under high pressures, the membrane may undergo a "creep" or "compaction" phenomenon, which may change the permeability of the membrane. This is not of concern in UF applications where pressures are typically 2 to 10 bar. Chemical deterioration could occur if the pH, temperature and other environmental factors are incompatible with the particular membrane. Harsh cleaning regimes will decrease membrane lifetime and if pH is too extreme, permeate flux could be greater than the pure water flux (Cheryan, 1986).

Most importantly, the feed stream's viscosity and density increase and diffusivity decreases as solids levels increase. Hence, flux can be expected to be lower than that of water (Cheryan, 1986). This will be discussed in further sections.

Permeate flux exhibits two domains of behaviour: pressure-dependent and pressure-independent (Clarke & Heath, 1997). With totally rejecting membranes, pressure-dependent flux can be described by Equation (2):

$$J = \frac{\Delta P_{TM} - \Delta \Pi}{\mu_p \cdot R_m} \quad (2)$$

where J = permeate flux (ms^{-1})
ΔP_{TM} = transmembrane pressure (pressure difference between the upstream (retentate side) and downstream (permeate side) of the membrane) (kPa)
$\Delta \Pi$ = average osmotic pressure difference (kPa)
μ_p = viscosity of the permeate (Pa.s)
R_m = hydraulic resistance of a new membrane (m^{-1})
P_r = average pressure on the retentate side (kPa)
P_p = average pressure on the permeate side (kPa)

According to Cheryan (1986), the net driving force for an ideal membrane process should be $\Delta P_{TM} - \Delta \Pi$ where $\Delta P_{TM} = P_r - P_p$ and $\Delta \Pi = \Pi_r - \Pi_p$. In practice, for most UF applications, osmotic pressures of the retained solutes are negligible due to the HMWCs and using ΔP_{TM} alone in Equation (2) is quite adequate. However, Π_r can be quite high when concentration of HMWCs is high (for example, > 200 kgm^{-3}).

There exists a number of theoretical models that explain the kinetic and mass transport phenomena associated with UF membranes. One of the simplest and widely used theories for modelling flux in pressure-independent, mass transfer-controlled systems is the film theory shown schematically in Figure 2.5.

At steady state, the amount of solute carried towards the membrane as a result of permeate flux is equal to the amount of solute carried away by diffusion, resulting in a concentration boundary layer at the membrane surface.

$$J = \frac{D}{C} \cdot \frac{dC}{dx} \quad (3)$$

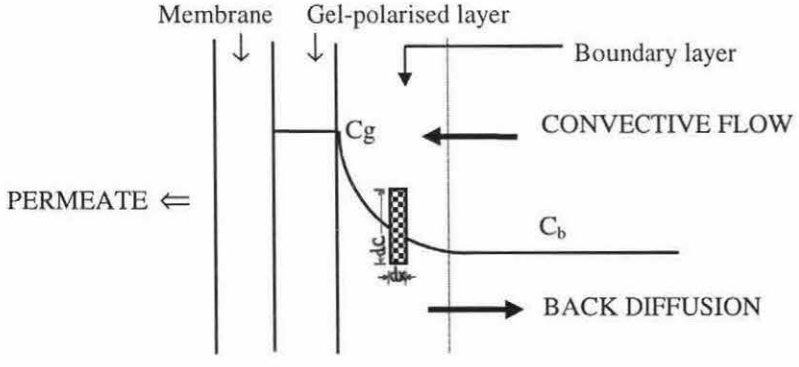

Figure 2.5 Schematic of concentration polarisation during ultrafiltration of colloidal and macromolecular solutes, showing built-up gel-polarised layer and associated boundary layer (Cheryan, 1986)

Integrating Equation (3) over the concentration boundary layer, assuming that mass diffusivity is constant , gives:

$$J = k \ln \frac{C_g}{C_b} \quad (4)$$

where dC/dx = concentration gradient over a differential element in the boundary layer
D = diffusion coefficient (m^2s^{-1})
k = mass transfer coefficient and $k = D/\delta$ (ms^{-1})
δ = thickness of the boundary layer over which the concentration gradient exists (m)
C_g = gel concentration at the membrane surface (gL^{-1})
C_b = bulk concentration (gL^{-1})

Equation (4) can be used to determine the flux if k and C_g are known. The final UF flux will be controlled by the rate at which solute is transferred back from the membrane surface into the bulk fluid. Since, in most operations, the values of C_g and C_b are fixed by physico-chemical properties of the feed, the flux can only be improved by enhancing k as much as possible, such as by reducing the thickness of the boundary layer. Any attempts to increase flux (such as increasing pressure) without providing a compensating mechanism to increase rate of back-transport will be self-defeating (Cheryan, 1986). This is not a perfect model but is adequate in many instances.

In general, the effect of pressure on flux can be summarised as follows (Figure 2.4): at low pressures, low feed concentrations, and high feed velocities, flux is influenced by the ΔP_{TM}. At high ΔP_{TM}, the permeate flux typically is no longer increased by increases in pressure and attains a constant value. This constant flux is called the "limiting flux". This pressure independent region occurs at lower ΔP_{TM} when the flow rate is lower or when the feed concentration is high. With constant mass-transfer conditions, only the feed concentration is an important variable and a linear relationship between the logarithm of the feed concentration and the limiting flux is often obtained, as in Equation (4) (Marshall and Daufin, 1995).

2.5.1 Fouling and Concentration polarisation

The processing of dairy fluids by RO, UF or MF is characterised by a progressive decline in flux with time (at constant pressure, feed concentration, flow rate and temperature). There are a number of phenomena that act simultaneously to reduce the permeate flux. With respect to UF, three separate phases of flux decline can be identified as shown in Figure 2.6.

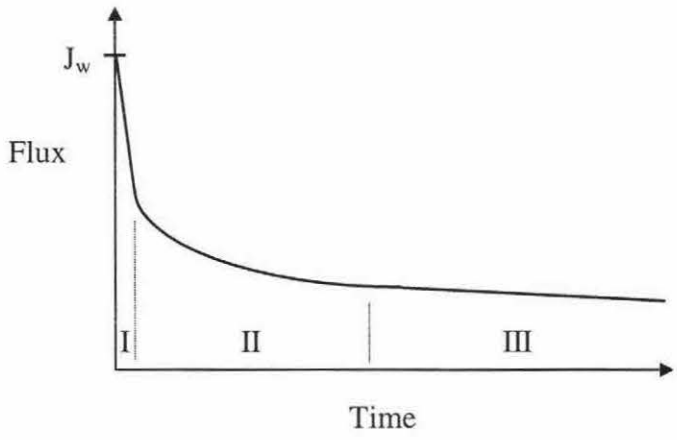

Figure 2.6 Conceptual stages of flux decline in ultrafiltration with constant pressure: stage I, concentration polarisation; stage II, membrane fouling (usually protein); stage III, further particle deposition or consolidation of the fouling layer (Marshall & Daufin, 1995).

In the first few minutes, the initial rapid drop in flux is due to concentration polarisation (CP). This describes the increased solute concentration adjacent to the membrane resulting from the balance between the different transport phenomena, that is, convective transport to the membrane and back diffusion (Figure 2.5).

CP is a function of the hydrodynamic conditions in the membrane system and is independent of the physical properties of the membrane.

The loss of flux due to CP can be attributed to a decrease in effective ΔP_{TM} or an increase in hydrodynamic resistance for transport and also promotes adsorption of proteins at the membrane surface and inside the pores. The first two effects are reversible, that is, upon flushing of the membrane with water, the portion of flux loss due to CP is restored and, where fouling is insignificant, the flux returns to its original value. The effects of CP can be reduced by decreasing the ΔP_{TM} or lowering the feed concentration (Cheryan, 1986).

After the initial drop in flux due to CP, the flux continues to decline due to membrane fouling (protein deposition). This decline in flux is rapid initially, then eventually stabilises to give a quasi-steady state flux, typically after 1-2 hours. This value is often used to characterise the membranes response to differing environmental and operating conditions, but decreases slowly with continued filtration. After several hours of operation, the final flux may be significantly lower than this initial quasi-steady state value.

Fouling comprises the matter that has left the liquid phase to form a deposit onto the membrane surface, or inside the porous structure, especially for UF or MF membranes which have a more "open" structure compared to a dense surface structure in RO membranes.

The effect of fouling is generally considered as an addition to the membrane resistance of another resistance (R_f), resulting from the deposition of material both on the membrane surface and in the membrane pores. Equation (2) can be modified to account for membrane fouling and concentration polarisation (and assuming negligible osmotic pressure effects):

$$J = \frac{\Delta P_{TM}}{\mu_p . (R_m + R_f)} \tag{5}$$

R_m can be determined from pure water flux data. R_f is often broken up into reversible fouling (R_{rf}), that is the fouling removed by flushing with water, and irreversible fouling (R_{if}), that which is only removed by chemical cleaning. R_f can be quantified easily from experiments but cannot be predicted a priori since it is a function of many variables including pressure, concentration, velocity and diffusivity. In the absence of fouling, permeate flux is measured at fixed temperature and pressure and Equation (5) gives:

$$J = \frac{\Delta P_{TM}}{\mu_p . R_m} \tag{6}$$

Membrane fouling is influenced by the (Doyen *et al.*, 1996; Marshall *et al.*, 1993):

- hydrodynamics of the filtration processes, and
- the surface interaction between the membrane and the foulants.

Its consequences are a modification of the transport properties of the membrane, that is, a reduction in both permeability and molecular weight cut-off.

Key phenomena in membrane fouling are protein adsorption and protein or particle deposition. According to Marshall *et al.* (1993), adsorption refers to molecules in direct contact with the membrane and usually describes all of the protein that accumulates on the membrane, while deposition refers to all material irreversibly deposited at the membrane surface due to convection, protein-protein interactions and further adsorption onto initial adsorption layers.

Protein adsorption occurs on the membrane surface and is mainly irreversible. This layer is tightly bound and can only be removed by cleaning.

Upon the application of ΔP_{TM}, further protein deposits on the membrane due to convective flow. This deposit, consisting of many protein multi-layers, is not as strongly bound as the protein adsorbed directly to the membrane. The degree of protein deposition is affected by both the membrane and the state of the protein. Increasing the charge of the protein, for example, by adjustment of the pH away from the iso-electric point (IEP), results in greater protein adsorption but, overall, less deposition of protein due to a reduction in the protein that is loosely bound (Marshall *et al.*, 1993). Protein deposits not only on the surface but also within the membrane. Particulate matter diffuses into the membrane blocking the pores. In

UF the amount of protein deposited within the membrane pores is small compared with that on the membrane surface. However, in MF there is a greater deposition within the pores, and internal fouling appears to dominate with large pores.

Often, some fraction of fouling may be non-permanent (or reversible), where part of the deposited material is swept away by the cross-flow just after the pressure difference has been released (Aimar *et al.*, 1994).

Overall, CP and fouling are serious problems which have limited the development of membrane technology. Methods to decrease flux decline due to these effects are aimed at process control and pretreatment of the feed.

Fouling and cleaning are related to each other, and since fouling must be removed by cleaning, there is a need to understand the nature of foulants, and possible mechanisms of fouling, to appreciate cleaning requirements. This coupling between fouling and cleaning is the subject of recent research and from this simple models for the cleaning process are being produced.

2.5.2 Fouling with dairy fluids

Milk and whey processing are two of the larger, more successful and challenging applications of membrane processing due to the complexity of the feed streams. Whey contains about half the solids in native milk, almost all the lactose and about one-third the nitrogenous compounds, most of it in the form of whey proteins. As shown in Table 2.3, milk contains much more solids, protein and calcium than whey. Eighty percent of the protein in milk is in the form of casein micelles which are so large that they simply "roll" off the membrane surface under high shear forces (Cheryan, 1986). Hence, membrane fouling by whey is far more a problem than by skimmed milk. In addition, most of the calcium in milk is tied up within the micelle, and thus is less available to form "bridges" between the protein and the membrane.

Most established UF plants for whey protein concentration operate at 50°C, but it is also possible to choose a lower operating temperature of 10-20°C which is becoming increasingly common. At this lower temperature, the solubility of calcium is much higher than at 50°C, and a larger amount of calcium will permeate the membrane without causing fouling problems. Further advantages of low-temperature UF is that the heat-and-hold treatment and pH adjustment otherwise used to stabilise or reduce calcium to minimise fouling becomes unnecessary and that the capacity of the UF plant becomes more stable. Also, less microbial activity occurs at such low temperatures. The key disadvantage is that, at 10-20°C, the flux is only approximately half of the flux at 50°C, which means that the membrane area has to be twice as large (Nielsen, 1988). However, the operation at 50°C may be more susceptible to microbiological contamination especially that of thermophilic micro-organisms.

Studies on membrane fouling during UF of whole and skim milk are rare in the open literature. Very little appears to have been done with respect to any specific fouling materials or mechanisms in these fluids.

Factories processing skim milk are able to hold the flux more steady through prolonged periods, and the average flux is kept more constant than in factories processing whole milk. Micellar casein was found to have no role in membrane fouling, while whey proteins and calcium phosphate were the major contributors in membrane fouling during UF of milk (Renner & El-Salam, 1991).

Almost every component in the feed stream can foul a membrane to some extent and each component reacts differently with the membrane. Contributions to fouling in dairy systems come from: proteins, lactose, peptides and minerals (especially calcium phosphate salts), fat or lipid material and micro-organisms. Fouling by some individual components will now be discussed.

2.5.3 Physico-chemical factors affecting fouling

Deposits on membranes arise from several key interactions: protein-protein, protein-mineral, and protein-lipid. These are influenced by the salts present, pH and heat effects, and the nature of the components.

2.5.3.1 Role of Calcium salts

Mineral salts have a profound influence on the fouling of UF membranes. On one hand, they can interact with the membrane directly or precipitate on the membrane and cause a reduction in flux. On the other hand, they contribute to the ionic strength of the solution, which in turn effects the conformation and dispersion of the protein and consequently the fouling of the membrane (Cheryan, 1986).

Calcium (Ca) is present in whey in two forms with reference to the UF membranes: a permeable and an impermeable fraction. The latter is present as colloidal calcium phosphate and attached to the β-lactoglobulin of whey.

The solubility of calcium is pH and temperature dependent, and decreases as both temperature and pH increase. Increasing the pH of whey or other calcium containing feed streams will increase the amount of insoluble calcium salts, which will precipitate out on the membrane and increase fouling. A lower pH increases the solubility of the salts, with less chance of their being deposited on the membrane and greater chance of their permeating through the membrane (Cheryan, 1986).

The pH dependency is reflected in the fact that cheese whey contains less than half the calcium of mineral acid whey. Increasing the calcium content of the cheese whey to a level of the mineral acid whey at pH values around 6 increases the fouling of membranes during UF. The severity of fouling was shown to be greater if the method of pH adjustment favoured precipitation of calcium phosphate in a gelatinous, apatite form (Muller and Harper, 1979).

Hayes *et al.* (1974) also noted that increasing the calcium content of hydrochloric acid casein whey at room temperature and adjusting pH to 6.7-6.9 gave a precipitate of protein and calcium salts. Removing the precipitate by centrifuging, resulted in a small improvement in flux.

The role of calcium in membrane fouling has been verified by Merin & Cheryan (1980) and Kessler & Gernedel (1982). Calcium was reported to produce considerable hardening of the deposited layer which was further enhanced by an increase in the pressure. A high calcium content and high pressure led to the formation of a layer on the membrane which adhered so strongly that it could hardly be removed by washing with water (Kessler & Gernedel, 1982).

Even soluble calcium salts can be a problem as they can interact with and bind to negatively charged groups on the membrane by electrostatic or charge effects. This could result in a "salt bridge" between the membrane and proteins, which will lead to faster protein fouling. Also, the permeate passing through the pores is a solution of lactose, mineral salts and non-protein nitrogen. Due to pore crowding and the frictional resistance or drag exerted by the walls of the pores, the solution becomes more concentrated and unstable within the pores, causing some of the salts to precipitate out or crystallise in the pores. Since the solubility of these calcium salts decreases as the temperature increases, higher temperatures should result in greater fouling. The salts are more stable in the bulk whey due to the stabilising effect of the whey proteins but become destabilised in the pores in the absence of the whey proteins (Cheryan, 1986).

The control of the soluble calcium phosphate is often essential. Decreasing pH will improve solubility of whey proteins and calcium phosphate whereas increasing pH will lower the level of ionic calcium. A similar control of ionic calcium can be achieved by addition of a sequestrant such as ethylenediaminetetra-acetic acid (EDTA), which will also improve the solubility of calcium phosphate salts. Alternatively, an increase in ionic strength of the feed, by addition of NaCl, will produce similar effects on the level of ionic calcium (Ca^{2+}) and on the solubility of calcium phosphate (Pouliot & Jelen, 1995).

Overall then, the control of ionic calcium and calcium phosphate can be achieved by pH adjustment, increase of ionic strength and addition of a sequestrant. Calcium phosphate is assumed to be present in a complex soluble-colloidal semi-equilibrium with the casein micelles as dicalcium phosphate salts, as shown by Equations (7) and (8):

$$CaHPO_4\ (ppt) \longleftrightarrow Ca^{2+} + HPO_4^{2-} \qquad (7)$$

$$H_2PO_4^- \xleftrightarrow{pK = 7.02} HPO_4^{2-} + H^+ \qquad (8)$$

Any physico-chemical condition favouring the decrease in Ca^{2+} or HPO_4^{2-} will favour the solubilisation of calcium phosphate. The decrease in pH will displace the equilibrium of phosphoric acid towards $H_2PO_4^-$ while decreasing the HPO_4^{2-} content, and therefore more $CaHPO_4$ will be solubilised in order to restore the

ionic conditions. When pH is slowly adjusted and time is given for equilibrium to be attained, the physical form and structure of the apatite formed is different and does not foul the membranes easily (Cheryan, 1986).

It must however be considered that the use of chemical pretreatments requires a very accurate control and monitoring of the physico-chemical parameters (pH, Ca^{2+}) of the feed. The extent of chemical modification (for example amounts of EDTA to be added) is often very limited, and therefore detrimental conditions can easily be reached, leading to other fouling problems associated with extreme pH values, excess of added chemicals, or even destabilisation of other components in the fluid being processed (Pouliot & Jelen, 1995).

2.5.3.2 pH and Heat Treatment

The effect of pH on membrane fouling has been discussed above as far as fouling by mineral salts is concerned. Flux is lowest at the iso-electric point (IEP) of the protein and is higher as the pH is moved away from the IEP. Changes in pH affect the solubility and conformation of proteins. The solubility of a protein is generally lowest at the IEP and increases as pH is adjusted away from it. The interaction between proteins and membranes also changes with pH. Thus these effects of pH on flux should not be unexpected, especially in the view of the effect on solubility of salts (Cheryan, 1986).

Maximum fouling from calcium salts occurs at pH 5.8. If pH was adjusted upwards rapidly, calcium phosphate would form apatites of a gelatinous nature which would readily foul membranes. However, as noted above, if pH was slowly adjusted, the apatite formed would be different and would not foul the membrane easily.

Flux values for whey are high below pH 3.0 and low at about pH 4.0-5.0. As the pH is increased further, permeation rates improve with sweet cheese whey but not usually with acid whey. This difference is related to changes in the nature of the deposit which forms on the membrane surface during UF. The pretreatment of acid whey is generally simplified because its native pH value (4.5-4.6) provides good solubility conditions for calcium phosphate; thus, no further precipitation pretreatment is required (Pouliot & Jelen, 1995).

Decreasing the pH of the milk, for example, from 6.8 to 6.4, causes a strong increase in fouling, mainly due to additional deposition of caseins. In the case of whole milk the deposition of both protein and fat is increased, but the deposition of minerals is reduced. The increased deposit formation from pH-reduced milk is mainly due to reduced stability of protein to heat (de Jong *et al.*, 1998). Milk is often preacidified to pH 5.9-6.1 before UF in making UF cheese. This pretreatment increases the amount of calcium entering into the permeate from the colloidal state. A low pH however, is always accompanied by an increase in the viscosity of milk, a factor of major importance for the flow properties of milk (Renner & El-Salam, 1991).

Heat treatment of whey is often combined with pH adjustment to maximise the flux. The most common treatment appears to be 72-85°C for 15 seconds and then adjustment of pH carefully to 5.6 for acid whey, or the heat treatment alone for sweet whey. The heat treatment apparently causes the formation of casein-β-lactoglobulin complexes which are "non-fouling" (Cheryan, 1986).

A combination of heating-holding and pH adjustment has been found to be particularly beneficial in the processing of whey. Increasing the pH and heat assists the removal of calcium for later addition to other streams as is done in the production of Alamin here in New Zealand. This helps to reduce fouling. The choice of the membrane module may also be dictated by its fouling tendencies, since a particular design may have better shear and turbulence characteristics, which has been found to affect particulate fouling rates (Cheryan, 1986).

2.5.3.3 Proteins

The behaviour of the membrane during the processing of protein streams is dominated by the protein multilayer that builds up on the membrane surface. Many researchers have found proteins to be a major foulant in UF of food and biological systems since they are rejected by the membrane, and have a high concentration at the membrane surface. The surface concentration is often high enough to cause the protein to form a "gel," depending on the temperature, shear rate and other environmental factors. The rate of fouling by proteins is significantly affected by their conformation, charge and other properties, which are in turn affected by pH, ionic strength and heat treatment, as discussed earlier. Any major change in protein structure affects the nature of protein deposition on the membrane.

Proteins and other macromolecules in whey have a greater influence on performance than smaller solute molecules. Fouling occurs when the large whey constituents including micro-organisms settle on the membrane in a lattice network which fills in and is coated over with small sheet-forming proteins such as β-lactoglobulin (Renner & El-Salam, 1991).

2.5.3.4 Lipids

Lipids are esters of fatty acids soluble in non-polar organic solvents and insoluble, or nearly so, in aqueous liquids. Skim milk and whole milk behave in a similar manner during UF, the permeate flux being only about 20% higher during the UF of skim milk even though skim milk has a lower viscosity and total solids. This indicates, at least with milk, that globular fat has little effect on fouling. Protein probably forms a fouling layer with a lower porosity because of the smaller size of the protein compared with the fat globules (Marshall & Daufin, 1995).

Lipids and fragments of milk-fat globule membranes associated with whey products adversely affect the functionality of whey proteins, impair the UF membrane flux during the manufacture of whey protein concentrates and promote the development of off-flavour in whey protein concentrate products (Rosenberg,

1995). These cannot effectively be removed by centrifugation hence it is necessary to remove or reduce the lipid content of whey prior to UF to improve the flux and certain functional properties, such as foaming. A thermocalcic aggregation of lipoproteins has been developed based on the tendency of lipoproteins to form aggregates through calcium bridging when subjected to moderate heat treatment (Fauquant *et al.*, 1985). The aggregation of lipoproteins by this method and the removal of the aggregates by MF (pore size 0.2 μm) in ceramic tubular membranes has proven efficient in producing lipid-free whey protein products.

2.5.3.5 Phosphate interactions

The concentration of phosphate is higher in acid whey and can bind to membranes and serve as a locus for binding other species (Lee and Harper, 1977). Addition of calcium increased the binding of phosphate on polyamide membranes.

In summary, simple procedures of whey pretreatment before UF, combining physical treatments (clarification, preheating, separation and pasteurisation) with chemical manipulations of pH can be used to modify fouling tendency and improve flux. Flux rates during UF can be improved by prefiltration and centrifugation of the whey. Centrifugation is often used to remove fines from whey. The advantage of such a technique lies in the fact that residual fat and even bacteria can sometimes be removed from the feed in the same unit operation (Pouliot & Jelen, 1995). It must be remembered that any pretreatment resulting in precipitation and separation of precipitated components will generate a number of by-products; in the case of whey pretreatment, there are casein fines and whey cream that will need further processing (Pouliot & Jelen, 1995).

2.5.4 Factors affecting flux: Operating parameters

In addition to the complicated physico-chemical interactions of feed components, operating parameters such as temperature, shear rate, pressure and feed concentration, as well as equipment design, have great influence on membrane fouling (Cheryan, 1986).

2.5.4.1 Temperature

Increasing temperature results in a decrease in the viscosity (Equation 6) of the processed fluid which reduces the resistance to flow and promotes turbulence and on the other hand, also increases diffusivity and hence the rate of transport of solutes arising from the membrane surface into the bulk stream. Increasing temperature should therefore result in higher flux, but may also result in a decrease in flux for certain feeds due to decreases in solubility of feed components at higher temperatures or changes in fouling.

The retention of protein can decrease with increasing temperature and can be attributed to increased CP as a result of higher membrane fluxes rather than to a reduction in membrane fouling. Prior heat treatments of the feed material can also have a beneficial effect on flux as previously shown. On the other hand, the removal of the fouling surface layer may lead to greater internal fouling. In solutions where protein denaturation or precipitation of calcium phosphate is likely the rate of fouling may increase, resulting in a final flux lower than that at a lower temperature (Marshall *et al.*, 1993). There is thus a balance between an increase in flux and therefore an increase in convection and backdiffusion, and possible changes in fouling or retention, but generally flux increases with temperature.

2.5.4.2 Shear rate

Higher shear rates at the membrane surface are an important factor in combating membrane fouling, as the deposited materials are continuously removed thus reducing the hydraulic resistance of the fouling layer.

High shear rates required to reduce the thickness of the fouling layer can be obtained by increasing the fluid velocity or recirculation rate, which requires higher pumping costs and more energy consumption per unit permeate removed, and/or decreasing the flow channel dimensions (Cheryan, 1986).

Alternatively, local turbulence can be increased by inserts of various kinds. In tubular modules one can insert rods with rings, glass beads, kenics mixers or moving balls to decrease the hold-up volume, increase velocity or to increase turbulence within the tubes. Mesh-like spacer material in spiral wound elements and some parallel-plate modules also cause considerable turbulence and can enhance flux, but at the expense of higher power consumption. Sometimes the spacer screens (such as those used in spiral wound units) can be more harmful for certain dairy feeds due to particle hang-up in the stagnant areas behind the spacer material (Cheryan, 1986).

Thus both the module design and the circulation velocity over the membrane surface are important. Too low a velocity leads to increased CP and fouling, resulting in rapid flux decrease and the need for frequent cleaning. Increasing the cross-flow velocity generally results in an improvement in permeate flux. However this can also produce some surprising effects. For in a study by Taddei *et al.* (1988), the retention of proteins β-lactoglobulin and α-lactalbumin was found to decrease with increasing velocity, contrary to the result expected from the CP theory. This is evidence that while membrane fouling decreases with increasing velocity, the effective pore size of the dynamic membrane system (rather than of the true membrane itself), increases. This is true for cases where retention of the protein was high and surface fouling was predominant. However, where internal fouling occurs the cross-flow velocity has limited effect which suggests that the effect of cross-flow velocity on membrane fouling is connected to CP and supports the concept that protein deposition is linked to the rate of accumulation of protein at the membrane surface.

In summary, various means of creating greater turbulence at the membrane surface generally result in an improvement in mass transfer and a higher membrane flux (Marshall *et al.*, 1993).

2.5.4.3 Pressure

According to the CP theory, flux increases with the increase of applied pressure until the gel formed reaches a concentration limit where flux becomes independent of pressure. Further increase in applied pressure results in a temporary increase in flux; however, this pressure increase raises the driving force for UF but does not affect transport of solutes back into the bulk stream. A thicker and denser gel layer is formed which reduces flux until it reaches its initial steady state. Increasing pressure over a critical point may also result in a lower flux due to compaction of the gel layer formed and the consequent increased hydraulic resistance (Renner & El-Salam, 1991; Cheryan, 1986).

Typical of these trends is the data of Taddei *et al.* (1988) who found that during UF of cheese whey with an M4 Carbosep (inorganic) membrane, increasing the ΔP_{TM} from 1 to 4 bar increased the permeate flux but also increased membrane fouling. Increasing the pressure further to 5.7 bar did not result in further increases in the permeate flux. For a range of concentrations, higher pressures and lower velocities resulted in increased resistance.

2.5.4.4 Feed concentration

As the concentration of solutes in the feed increases, its viscosity and density increase and the diffusivity of a given solute decreases. These changes in the physical properties acts to decrease the absolute value of flux and higher feed concentrations will also aggravate fouling (Cheryan, 1986).

Thus increasing the feed concentration generally results in a decrease in the permeate flux and has little effect on the membrane retention characteristics, except where the component size changes with concentration. Flux will decrease exponentially with increasing feed concentration (C_b) as stated by the film theory model (Equation 4, Figure 2.5). Where surface fouling occurs, increasing concentration has little effect on irreversible membrane fouling but causes an increase in reversible fouling (Daufin *et al.*, 1991; Taddei *et al.*, 1988). This suggests that membrane fouling does not increase but that the decrease in flux is due solely to CP. In addition, retentions do not generally vary with increasing concentration in spite of the decrease in permeate flux, suggesting that the "actual" membrane resistance has not changed (Taddei *et al.*, 1988). When internal membrane fouling dominates, increasing the concentration resulted in a more rapid loss of permeate flux with time. This may be due to the increased exposure of the membrane to solute with increasing concentration. However, at high concentrations, cake or surface fouling is likely to dominate (Marshall *et al.*, 1993).

2.6 Membrane Cleaning

2.6.1 *Introduction*

Periodical cleaning of membrane systems is a necessity to maintain the membrane performance at an acceptable level from process and economic viewpoints. The preceding sections have introduced the different types of membrane configurations, the range of different membrane materials, and the alternative separation techniques available. With such a large variety of possible combinations of membrane materials, configurations and feed materials, it is not surprising that each situation could require unique cleaning and sanitising procedures (Krack, 1995).

Cleaning can be defined, according to Tragardh (1989), as "a process where material is relieved of a substance which is not an integral part of the material". Disinfection on the other hand implies the destruction of all pathogenic micro-organisms and the reduction of the number of micro-organisms which degrade the product.

The aim of cleaning and disinfection procedures is to obtain a hygienically acceptable surface which must be physically clean (free from visible impurities), chemically clean (free from all impurities), and biologically clean (free from living micro-organisms).

Optimal operation is required and cleaning should be performed only when necessary due to its adverse effect on membrane life, due to the cost of purchasing and disposing of cleaning chemicals, and due to the volume of water used for cleaning (Wagner, 1996).

As Hall (1992) points out, a wrong approach to a cleaning problem can increase almost all other filtration costs:

- A too aggressive cleaning reagent will result in an increased frequency of membrane replacement and their irreversible deterioration.
- A cleaning reagent with low efficiency will increase cleaning time and therefore energy consumption and labour costs.

Poor cleaning protocols will result in loss of flux and lower throughput, and/or contamination of product.

There are four possible methods of membrane cleaning (or foulant removal): chemical cleaning and three alternatives to this cleaning: (hydraulic, mechanical and electrical cleaning). The suitability of these methods depends upon the separation process, the module configuration and the membrane material.

Hydraulic cleaning of the membrane is achieved with backflushing of the permeate through the membrane. The process is carried out by reversing the

direction of flow of the permeate, usually for a few minutes, at a pressure which can be as large as the filtration pressure. This dislodges the foulant from the membrane and restores the flux to a value close to the initial (or previous high) value. Backflushing is carried out repeatedly at regular intervals and leads to a saw-tooth type of flux behaviour as shown in Figure 2.7. The method is effective with many kinds of foulants, but particularly larger particles where surface fouling arises. Backflushing can only be used on certain membrane types like ceramic membranes for MF and UF because they are mechanically very strong.

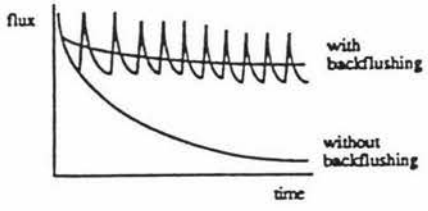

Figure 2.7 Effect of backflushing on membrane flux rate (Scott, 1995)

An alternative method of hydraulic cleaning is back-pulsing; short bursts of back pressure alternatively pressurising and depressurising the membrane and the permeate exit is rapidly opened and closed to induce back-pulsing (Scott, 1995).

Mechanical cleaning involves scouring the fouled surface with solid abrasive material and is generally limited due to the sensitivity to damage of the membrane surface. One method is the use of foam balls (polyurethane foam) for removing deposits from tubular membranes. These balls are slightly smaller than the bore of the tube, and are forced down the tubes at high velocity by the application of fluid pressure, which creates turbulence at the membrane surface as the ball passes, and helps to dislodge fouling matter (Scott, 1995).

Electrical methods of cleaning can utilise electrical pulsing which results in the movement of charged species (particles, molecules) away from the surface. The process is carried out while the membrane separation is in process, although special module designs are required to introduce the charge to the membrane surface, which is generally metal (Scott, 1995). In the case where electrolysis of water occurs, the formation of gas bubbles dislodges the foulants, in addition to the electrical repulsion effects.

Whilst these methods can be applied in certain situations, chemical cleaning remains the major method of restoring membrane performance.

2.6.2 *Chemical cleaning and cleaning agents*

The cleaning process must remove fouling deposits and restore the normal capacity and separation characteristics of the equipment. In practice this is achieved through a variety of chemical and physical interactions between the cleaning solution and the soil on the membrane surface. The chemicals used in the cleaning solution should:

- loosen and dissolve the fouling
- keep the foulant in dispersion and solution
- avoid new fouling
- not attack the membrane (and other parts of the system), and
- disinfect all wetted surfaces

A cleaning reaction is a heterogenous reaction between the detergent solution and the fouled layer and Luss (1984) summarised the following requirements that a cleaning compound should possess in order to clean membrane units:

- high active compound concentration,
- good solubility,
- moderate foam level,
- compatibility with internal unit components,
- good buffer system,
- good stability.

The major cleaning agents often used to clean membrane plants are shown in Table 2.5.

Table 2.5 Cleaning agents and their general properties (Shorrock & Bird, 1998; Tragardh, 1989)

Cleaning agents	Examples	General Properties
Alkalis	hydroxides, carbonates, and phosphates	hydroxides generally saponificate fats and solubilise proteins
Acids	nitric and phosphoric	dissolve inorganic salts or oxide films
Enzymes	proteases, lipases	compatible with sensitive membranes
Surfactants	Quaternary ammonium compounds (QACs)	increase wettability promoting contact with the detergent and hence removal
Sequestrants	Ethylenediaminetetra-acetic acid (EDTA)	prevention of re-deposition and/or removal of mineral deposits
Disinfectants	Hydrogen peroxide (H_2O_2), metabisulphite, and hypochlorite,	destruction of pathogenic micro-organisms

While individual components can be used (example Sodium hydroxide (NaOH)), most commonly several chemicals are incorporated into built or formulated cleaning solutions. Cleaning formulations must balance action against foulant with effect on the membrane. Formulated detergents consist of a mixture of alkalis,

phosphates, sequestering agents and wetting agents. Alkaline formulations sometimes contain free chlorine. Such detergents have a better cleaning effect than the alkali alone and also have a disinfectant effect. (Hypochlorite itself has some cleaning ability - one reason for this is thought to be the enlargement of the pores of the membrane).

Antifoaming agents are also added to most detergents to avoid foam formation arising from air contact in turns and high turbulence. However these can prove a problem in membrane cleaning as most antifoaming agents will block the membrane. Only a few are actually compatible with membranes, so concentration in selection is important (Krack, 1995).

2.6.2.1 Alkalis

Sodium hydroxide and potassium hydroxide (KOH) are highly alkaline inorganic substances which dissolve readily in water to release free hydroxide ions. The high alkalinity provides for efficient removal of fats, oils, and general food residues particularly at warm temperatures. Hydroxide solutions of about pH 12 are recommended with protein foulants (Cheryan, 1986).

Carbonates do not have a very good cleaning ability but they can aid cleaning through their pH-regulating properties. Mono-, di- and triphosphates have a limited cleaning effect as they are slightly alkaline. Polyphosphates or complex phosphates have a moderate cleaning effect. These act as dispersants, they solubilise carbonates, bind ion salts, regulate pH, emulsify fat and peptise proteins (Tragardh, 1989).

2.6.2.2 Acids

Acids are principally used to dissolve precipitates of inorganic salts or oxide films. Nitric acid or phosphoric acid are often used in the cleaning of membrane plants. However, citric acid is commonly used these days because of its mildness compared to nitric acid.

Usually $CaCO_3$ and $Ca_3(PO_4)_2$ precipitation can be removed easily with acid cleaners or with complexing agents. Solubility is dependent on time, temperature and concentration. Using only mild acids in too low concentrations or alkaline detergents with mild complexing agents, it is possible for $Ca_3(PO_4)_2$ to concentrate on the permeate side and this can lead to a reduction in capacity. Strong acids or higher concentrations of a mild acid detergent should be used at least once a week if not permitted daily (Krack, 1995).

2.6.2.3 Surfactants

The word surfactant comes from an abbreviation of surface-active agent, and is a substance that concentrates at an interface (surface). It consists of a hydrophilic

and a hydrophobic end (Figure 2.8). The incompatibility between the ends is the reason for a surfactant's unique properties.

Figure 2.8 A surfactant molecule with hydrophilic and hydrophobic ends

There are a variety of surfactant types, falling into four general classes - anionic, cationic, non-ionic and amphoteric.

1. Anionic surfactants are neutral, organic, foaming agents, for example, soap, alkyl sulphate, and alkyl sulphonate.

2. Cationic surfactants are quaternary ammonium compounds. They are less effective than anionic or non-ionic agents. Their use in the dairy industry is not recommended since very low concentrations can prohibit the growth of starter cultures used in cheese or yoghurt manufacture. These compounds can also decrease the capacity of membrane filtration plants.

3. Non-ionic surfactants can be used to significantly enhance the performance of anionics. They have a synergistic effect on both anionic and cationic wetting agents (von Bockelmann, 1986). They consist of condensation products of, for example, ethylene oxide (EO). Examples, are alkyl phenol ethoxylates, alcohol ethoxylates, and alkyl polysaccharides. They are low foaming, independent of pH, easy to rinse off but less effective than anionic agents.

   Non-ionic surfactants are also good fat removers but can decrease flux. Unfortunately the non-ionic surfactants with the best fat removing power also decrease membrane capacity the most. The frequently used surfactants are fatty alcohols which are hydrophilised with the addition of EO. The more EO added the more hydrophilic a surfactant becomes. For successful membrane cleaning it is necessary to choose the more hydrophilic surfactants which are not as effective in removing fat.

4. Amphoterics can carry both negative and positive charges and can vary their net charge in differing environments (for example, pH).

The surface properties of a phase of a solution will be very different from the bulk properties. The molecules in the bulk solution will experience no net force, whereas the surface molecules will have exerted on them a net downward force that tends to contract the surface. This in effect forms a "skin" and is known as

surface tension. It is a force acting at the surface of the liquid and pulling toward the bulk phase (or centre in a droplet). Surfactants tend to disrupt this layer, lowering the surface tension.

Surfactants are used for wetting, emulsification (removal of oil from the substrate) and dispersion (suspension and anti-redeposition of the soil) (Anonymous, 1997). Overall anionic surfactants were found to be the best for membrane cleaning (Krack, 1995). Many cationic and non-ionic agents are adsorbed onto membranes made from aromatic polyamides, resulting in a decrease in flux.

As a wetting agent, a surfactant has three main purposes:

- adhesion of liquids to solids,
- spreading of liquids over solids, and
- removal of air bubbles from pores.

Surfactants facilitate the wetting effect by adsorbing onto the solution and leaving hydrophobic ends "sticking out" where they may adhere to hydrophobic surfaces, and by adsorbing at the solid/liquid interface breaking down surface tension and causing spreading. Without an added wetter a droplet maintains its form due to surface energy (tension); with an added wetter there is reduced surface tension, the surface is more hydrophilic, and the liquid can be spread more effectively.

Detergency or emulsification of oils and other hydrophobic soils proceeds via the following mechanism: the hydrophobic ends of the surfactant embed in the oil droplets; as the surface becomes saturated, the surfactant molecules "roll-up" the oil eventually lifting it into the wash/rinse water (Anonymous, 1997).

A dispersion usually consists of solid particles suspended in a liquid medium, and a dispersant confers stability to the system. It can do this through two basic mechanisms after the surfactant adsorbs to the surface of the solid material:

- steric stabilisation - where the surfactant is relatively bulky and the layer it forms around each particle cushions it and prevents two particles from colliding and sticking, and

- electrostatic stabilisation - where a charged surfactant is attached, and the individual particles repel each other through charge repulsion (like charges repel).

Surfactants are used to wet the inorganic additives (like acids or alkalis) into the substrate or soil complex and therefore must be stable and functional in both the acting cleaning liquid and the concentrate.

2.6.2.4 Enzymes

Enzymatic cleaners are usually employed if the pH limitation is at or below 10 or if a high level of soil is present; they are usually necessary where proteins are

concentrated to a very high solid content leading to severe fouling. They play a vital role in scissioning specific points in the protein strands and are most effective when operated at a concentration that optimises the cutting of proteins (Munoz-Aguado *et al.*, 1996).

Enzymes are also found in detergents although not as pure enzyme (Krack, 1995). Traditionally enzyme detergents have especially been used on cellulose acetate membranes which cannot withstand high temperature and pH. Hence, cleaning agents with very good dispersion and emulsifying effects at low temperatures are required to remove fat and break down proteins and other high molecular weight compounds (Tragardh, 1989).

Enzymes hold an advantage over traditional caustic or acid regimes as they are biodegradable and do not cause additional pollution problems. They also have the advantage of being gentle to the membranes as they are highly substrate and reaction specific, and are thus believed to lengthen membrane lifespan. These advantages have promoted a resurgence of interest in their replacement of conventional chemical agents.

Enzyme detergents do however have the following disadvantages (Kane & Middlemiss, 1985):

- They are costly and formulating them into effective detergents is also expensive.
- Residual enzyme activity can affect cultures such as starters used in cheese making.
- They act slowly and longer cleaning times are thus needed, as they are applied at a lower pH range.

2.6.2.5 Disinfectants

Disinfection destroys all pathogenic micro-organisms and reduces the number of other micro-organisms present. Detergents do have a disinfecting ability. Their stand alone use is to ensure adequate reduction in microbial numbers. Hydrogen peroxide and hypochlorite are quite effective as disinfectants.

Hypochlorites are membrane-swelling agents, and are thus effective in flushing out material that may be lodged within the pores (Cheryan, 1986). Sodium hypochlorite is a powerful oxidising agent and is easily decomposed by common surfactants to give the hypochlorous acid (HOCl) or anion (OCl^-), or eventually oxygen (O_2). The available oxidising power of sodium hypochlorite will oxidise surfactants, often cleaving surfactant structure with an end result being the loss of available chlorine in the concentrate. Amine oxides are designed to be stable in sodium hypochlorite formulations where they contribute wetting and detergency properties. By improving the wetting efficiency of the system, the overall effectiveness of the product can be improved, through increased penetration, spreading and detergency (Anonymous, 1997).

Sodium bisulphite is also often used for disinfection of membrane plants. At pH 4.7, a bisulphite solution of 0.2% was shown to be ineffective in controlling micro-organisms while at pH 3.5, it was microstatic (Smith & Bradley, 1985). If a membrane plant is idle for some time, a diluted disinfectant solution is often left in the plant in order to avoid microbial growth (Tragardh, 1989).

2.6.3 Physical aspects of membrane cleaning

The main physical aspects affecting cleaning are temperature, concentration (that is, chemical activity), mechanical energy (encompassing appropriate combinations of pressure and flow rate), and time. These are necessary in developing effective cleaning procedures, and decreasing one or more of these elements can be compensated by an increase in one or more of the others.

For membrane cleaning design, the type of soil (deposit layer on the membrane), water quality, and membrane material must also be taken into consideration. These points are considered in the following sections.

2.6.3.1 Temperature

An increased temperature is a key influence on the cleaning process especially for removing fat residues. Increasing temperature improves diffusion and increases the chemical splitting of soil, it increases the solubility of different substances and also increases the reaction rate.

However the use of high temperatures in membrane cleaning is not very often possible. Nearly all polymeric membranes are sensitive to cleaning at high temperatures compared to mineral or ceramic membranes (Section 2.3). For example, heating a cellulose acetate membrane above the limit (35°C) can result in decomposition.

2.6.3.2 Mechanical Aspects

Increased flow leads to a higher turbulence of the cleaning solution, better dispersion and better soil carrying properties. However, pump capacity and mechanical forces limit the flow increase that is possible in practice.

For membrane processing plants it is necessary to ensure that the proportion of pressure parallel to and normal to the filter surface is correct for the clean. For cleaning RO and UF plants, the filtering capacity should be as low as possible, otherwise it is possible that a secondary membrane builds up during cleaning (Figure 2.9).

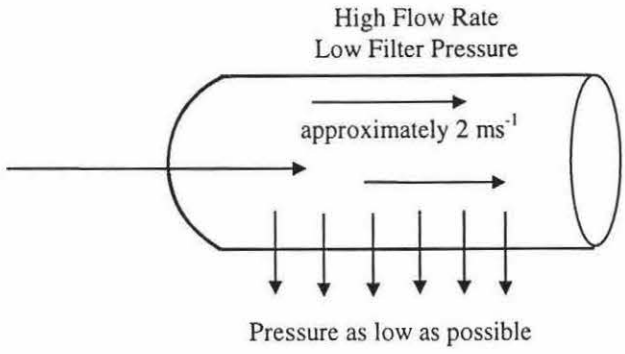

Figure 2.9 General recommendation for cleaning RO, NF and UF membrane equipment (Krack, 1995)

On a UF membrane, the soil lies predominantly on the surface but on a MF membrane the fouling deposits may also be present in the pores. In some cases fouling on the permeate side is also found. For cleaning MF plants, it is therefore best to clean first with a low pressure to take away the loose soil on the surface and then change to a higher filtration capacity to clean the pores of the membrane.

To obtain a good mechanical cleaning effect, the circulation flow rate should be higher and the pressure lower than those used during normal operation. Under these conditions, the compressible fouled layer is released and less able to withstand shear stresses (Tragardh, 1989).

2.6.3.3 Module design

The connection between module types and cleaning behaviour is complex. The effect of the flow pattern in the modules, that is whether turbulent or laminar, is important but not completely understood in every case. Some modules are inherently more difficult to clean than others. The flow is influenced by design as well as the type of support and spacer material used.

Tubular membranes are normally in stainless steel, polysulfone or PVC housings. Here the detergent must only be compatible with the membrane and possibly membrane seals. However, in plate and frame and spiral wound membranes the detergent comes into close contact with the often sensitive adhesive and the spacer material as well. The compatibility of the detergent with these materials must also be guaranteed as very often the permeate spacer is made of polypropylene or polyester and this limits the pH and temperature stability (Tragardh, 1989) and the use of many classical cleaning compounds, especially surfactants.

Spiral wound modules were originally of concern for hygienic operation but experience has now shown that they can be cleaned effectively.

2.6.4 Chemical aspects of membrane cleaning

2.6.4.1 Water Quality

Water used in membrane cleaning should be of good quality. Any impurities contained in the water can be filtered out during cleaning and may block the membranes rather than clean them. Consequently, suspended solids should be removed by prefilters and bacteriological contamination should be at a very low level to prevent biofouling.

Biofouling is the development of a biofilm layer on the surface of the membrane; biofilm is a general term that applies to microbial communities forming coherent layers on solid surfaces (Krack, 1995). Water hardness is not a problem as with both acidic or alkaline formulated detergents, hardness can be complexed or removed. Water quality can be tested by measuring the salt density index (SDI). This should not be higher than 5 for RO plants and should be less than 3 for UF and MF plants, and is the best available technique for determining the potential of colloidal fouling from the water (Krack, 1995).

The presence of iron, silica, calcium and other salts can lead to deposits which are difficult or occasionally impossible to remove. Several metals form salts which precipitate, especially iron and manganese, and together with silicates, form insoluble salts. Normal deposition of non-silicate salts of iron and manganese may be removed, but silicates can only be removed with hydrofluoric acid. This is not a viable proposition as, using this, most membranes and nearly every plant would be destroyed, not including any human risks. Hence the need for deionised water produced by ion-exchange or RO plants to be used in cleaning.

Overall, a summary of suggested guidelines for water quality is shown in Table 2.6.

Table 2.6 Recommended water quality guidelines for membrane cleaning and rinsing.

	Koch Membrane Systems*	Tragardh (1989)	Krack (1995)
Iron	< 0.3 ppm	< 0.05 ppm	≤ 0.5 ppm
Manganese	< 0.05 ppm	< 0.02 ppm	≤ 0.2 ppm
Silicates (SiO_2)	< 10 ppm	< 5 ppm	≤ 5 ppm
Aluminium	< 1 ppm		
Calcium	< 10 ppm		
Hardness as $CaCO_3$	300 mgL^{-1}		357 mgL^{-1}
Particle size	< 25 µm	< 25 µm	
Total plate count	< 1000 per mL	< 1000 per mL	1000 per mL
Coliform count	0 per 100 mL	0 per 100 mL	< 1 per mL
Turbidity	< 1 NTU		

* Source: Koch Membrane Systems cleaning in Place (CIP) water specifications

2.6.4.2 Influence of soil composition

The usual soil arising from dairy processing consists of proteins, fat, carbohydrates and minerals. Lactose and minerals are not normally a problem in membrane cleaning. Occasionally, some carbohydrates used for gelification or production of other special dairy products are more difficult to remove than lactose alone but overall, fat and protein residues are the most difficult to remove.

Removal of fat is more difficult on hydrophobic surfaces like organic polymers than on stainless steel or glass because of the hydrophobic character of the fat molecules, which adsorb at the membrane surface. Surfactants are normally used to emulsify and alkalis to saponify the fat into the cleaning solution which is then drained.

Proteins are removed well by alkaline detergents. The higher the pH, the faster the protein hydrolysis and better the solubility. Protein solubility is poor in the acid pH range; at a pH of 4-5 casein proteins are denatured and precipitated. The early use of pH-sensitive membranes like cellulose acetate led to the development of enzymatic detergents to remove proteins. Initially, only inorganic ceramic membranes were pH stable; later also organic polymers like polysulfone, polypropylene and polyvinylidenefluoride with high pH stability were developed.

However, the best cleaning process is not achieved by attaining the correct pH alone (Krack, 1995). A pH of 11-11.5 is very often the limit for membrane stability, but only a low concentration of caustic may be enough to reach this value, but may not be sufficient to clean well. In addition to alkalinity, there is a need for dispersants, emulsifiers, soil carrying agents, stabilisers for hardness promoting salts, buffering systems, and available chlorine or oxygen as cleaning boosters, to be incorporated in the detergent.

2.6.5 Sanitation

The sanitation of membrane plants should be carried out following a thorough clean. Sanitiser products based on available chlorine can be used on many organic polymer membranes, but often decrease the membrane's lifetime and should hence be used with caution.

Products based on quaternary ammonium compounds and iodophors are often adsorbed on to the membrane surface which leads to flux losses and irreversible damage to the membrane.

Peracetic acid based products are an ideal sanitiser, compatible with nearly all membranes and have the following advantages;

- fast reactive
- good rinsability
- can pass through RO membranes enabling sanitation of the permeate side.

For more sensitive membranes, sanitisers based on sodium metabisulphite should be used. Products based on this compound are not oxidising but a significant disadvantage is the very long reaction time (Krack, 1995). This increases the time required before the membrane can be returned to use.

Mildly acidic detergent sanitisers containing surfactants have recently been developed. These products show synergistic effects and good sanitation properties, and can only be used on cellulose acetate RO, UF and MF membranes.

2.6.6 Cleaning procedures

As discussed earlier, it is essential to know what components of the feed stream are causing the fouling so as to develop an effective cleaning strategy. It is also important to establish whether the cleansers being used solubilise or disperse the foulants. This is because some soluble components that are small enough to pass through the membrane pores during UF could precipitate in the pores during rinsing, depending on the water or cleanser used (Cheryan, 1986).

There are many different cleaning regimes, and the exact procedure for a given membrane system depends on the product treated, the membrane type and the system design (Wagner, 1996).

A typical cleaning cycle, as shown by Tragardh (1989), generally includes the following stages:

- product removal from the system
- rinsing with water
- cleaning in one or more steps
- rinsing with water
- disinfection

Table 2.7 provides an overview of the various types of cleaning regimes which are currently used in ultrafiltration equipment in the dairy industry.

The flush and rinse times are always dependent on the size of the plant, but usually the time is between 5 and 20 minutes. Plants with low membrane area can be flushed out within a very few minutes, while bigger plants need a longer time (Krack, 1995). The product should be rinsed out at the same temperature as that used in the process. This is important for products which tend to form gels at low temperatures. During rinsing, both the retentate and permeate should be discharged. The rinsing should continue until both the retentate and permeate are totally clear and neutral. At the end of the run, the process stream should be immediately followed by a water rinse of the entire UF plant, including the tanks, pipelines, pumps and other ancillary components, until the exit water appears clean (Cheryan, 1986).

Table 2.7 Cleaning regimes used in ultrafiltration equipment installed in the dairy industry (Luss, 1984)

Step	Time	Temperature	pH	Comments
Flush	10-15 min.	40-70°C[a]	Near neutral	Flush till neutral pH
Acid	30 min.	35-65°C[a]	About 2.0	Some manufacturers prefer nitric acid while others prefer phosphoric acid.
Alkaline	30 min - indefinite	40-70°C[a]	8.5-13.0 [a]	Alkaline washes on polysulfone membranes vary widely in alkalinity, chlorine content and other variables
Sanitation	15-30 min.	Ambient	Near neutral or acidic	Chlorine, iodine or peroxide

[a] Lower value for cellulose acetate, higher value for polysulfone membranes
Note: Flushes intervene between all ultrafiltration cleaning in place (CIP) steps

After cleaning, it is advisable to check the pH of the cleaning solution and the amount of hypochlorite or other cleaning boosters added. An incorrect pH value or a zero or too low a hypochlorite concentration probably indicates that the cleaning has not yet been sufficient.

Concentration, temperature, time and mechanical forces are not the only parameters responsible for successful cleaning. The amount of cleaning solution in comparison to the membrane surface is another factor (Krack, 1995). The amount of cleaning solution normally used in process plants today is between 4 and 5 litres per m^2 membrane surface, while lower amounts in most cases lead to unsatisfactory results.

2.6.7 Comparison of cleaning regimes

A number of researchers have used a variety of cleaning solutions (Table 2.8) to clean UF and MF membranes in food applications The cleaning method employed is always similar to that described in Table 2.7 involving acid and alkaline cleaning steps with intermittent water flushes, followed by disinfection.

2.6.7.1 Effect of cleaning concentration using conventional cleaners

Efficient cleaning was obtained by using NaOCl (with or without an HNO_3 step) or a NaOH based formula including complexing agents and surfactants (Daufin *et al.*, 1992). However, Daufin *et al.* (1991) found that NaOCl alone was not sufficient in trying to restore the permeability of severely fouled membranes because while NaOCl was responsible for the dissolution of organic material, HNO_3 was also required to remove inorganic deposits. This was similarly observed by Shorrock & Bird (1998). In their study, when 0.064M HNO_3 was applied to the membrane fouled with 1wt% baker's yeast suspension at 50°C, the

flux recovery was just 88%. However, when the membrane was first cleaned with 0.01 wt% NaOH for 2 minutes at 40°C, a subsequent clean with 0.064M HNO_3 completed flux recovery. Results suggest that the yeast deposit essentially comprised of both organic and inorganic species.

Tran-Ha and Wiley (1998), noticed that at higher acid concentrations (1 and 1.5 wt%), flux recoveries were found to be slightly reduced. The highest recovery was obtained when using 0.5 wt% citric acid at pH 2.3. This is because low pH causes membrane pores to shrink or the foulant layer to contract and hence the ability of the acid to enter the layer is restricted. This effect was similarly observed in a study by Bartlett *et al.* (1995), where increasing NaOH concentration, increased the maximum flux recovery up to an optimum value. For the sintered stainless steel membrane the use of 0.2 wt% NaOH resulted in a maximum flux recovery of 80% of the initial water flux. For the ceramic membrane an optimum concentration of 0.4 wt% NaOH resulted in a maximum flux recovery of 73%. For both membrane systems, increases in NaOH concentration above the optimum value did not aid the cleaning process but resulted in lower maximum flux recovery values. Kim *et al.* (1993) noted that for concentrations of NaOH above 0.4 wt%, there was reduced cleaning efficiency for milk deposit removal from ultrafiltration membranes. A study by Shorrock & Bird (1998) showed that an optimal NaOH concentration of 0.01 wt% produced a flux recovery of $93\pm3\%$ independent of cleaning temperature (30-60°C) and flow regime. This optimal concentration is rather low compared to studies by Kim *et al.* (1993) and Bartlett *et al.* (1995) and was attributed to the relatively thin deposit generated which required a relatively small amount of energy for removal.

2.6.7.2 Effect of cleaning concentration using formulated detergents

Greater the flux recovery and/or faster or more complete soil removal is possible in built detergents (Section 2.6.2.3) achieved by wetting, dispercency and emulsification.

The use of non-ionic surfactants (Triton X-100) below their critical micelle concentration (CMC) caused a small but significant decrease in water flux. This is because the surfactant exists as discrete molecules in solution, below the CMC. These surfactant molecules could then diffuse into membrane pores where they could form submicellar agglomerates which block the "pores" thereby reducing the water flux. Similarly, surfactants cetyl-trimethyl-ammonium bromide (CTAB) and sodium dodecyl sulfate (SDS) also decreased water flux at concentrations below their critical micelle concentrations because charge repulsion may have caused a decrease in the rate of submicellar aggregation (Chong *et al.*, 1985).

Traditional membrane cleaners like NaOH, a blend of nitric and phosphoric acids, a non-ionic surfactant (Ultraclean II) and NaOCl were found to effectively clean polysulfone membranes fouled with separated Cheddar cheese whey (Bohner & Bradley, 1992).

For those cleaners containing enzymes, higher concentrations of enzyme beyond an optimum value decreased the flux recovery. For one study (Tran-Ha & Wiley, 1998), at the optimum concentration (2 %v/v Enzyme L at 50°C for 30 minutes), the enzyme reached its maximum activity. Beyond this optimum concentration, the excess enzyme could possibly contribute to fouling of the membrane, thus slightly decreasing flux recovery. In addition, the presence of a detergent in an enzyme formulation, could attack the membrane itself when its concentration was beyond the optimum concentration for effective cleaning (Munoz-Aguado *et al.*, 1996).

2.6.7.3 Effect of cleaning order

For some products it is necessary to apply different chemicals in succession to obtain satisfactory cleaning. For milk, where protein deposits dominate, an alkaline formulation is used first, sometimes followed by an acid in order to remove mineral deposits. For polysulfone membranes, a final alkaline cleaning step is often carried out in order to improve flux. This opens up the membrane pores making it easier for the rinse water that follows to lift the soil and any traces of cleaning solution. For whey, where mineral deposits dominate, acid cleaning is often performed first, followed by alkaline cleaning (Tragardh, 1989). In all cases, cleaning and sanitising agents must contact both the retentate and the permeate side of the membrane to be effective.

It is often debated whether alkaline-acid-alkaline or acid-alkaline is best. The choice is to a large extent product related. If the mineral content in the product is high then acid may be used first. If there are reducing sugars and proteins in the product then acid may also be used first. This minimises the risk of a condensation reaction, similar to the Maillard reaction, taking place in the alkaline environment. The result of condensation is a red-brown sticky deposit (Wagner, 1996). Such products are difficult to get off the membranes. Oxidisers are the only fast remedy; alternatively, many cleaning cycles can gradually restore water flux.

Cleaning with an alkali followed by an acid achieved a higher final flux recovery than cleaning in the reverse order (Bartlett *et al.*, 1995).

Tran-Ha & Wiley (1998), observed that cleaning with citric acid and then the enzyme, gave a better flux recovery than cleaning in the reverse order. The role of citric acid is to dissolve minerals, while the enzyme removes fat and breaks down proteins. The acid probably opens up the foulant layer, making it easier for the enzyme and detergent to further penetrate the foulant and remove it. However, Munoz-Aguado *et al.* (1996) found that the enzymes worked best when followed by a detergent, which removes protein fragments reduced by the enzymatic reaction. No mention was made of the effect of acid.

2.6.7.4 Effect of cleaning frequency

There exists an optimum for the cleaning frequency but typically this needs to be established for each application and situation. Excessive cleaning or too infrequent cleaning results in lower productivity (or an overall lower flux). It was also found that UF performance slowly deteriorated for multiple cycles of usage and cleaning (Tran-Ha & Wiley, 1998; Kim *et al.*, 1993). Typically in dairy processing, plants are cleaned after 8-10 hours and again at 18-24 hours.

2.6.7.5 Effect of cleaning temperature

Bartlett *et al.* (1995), studied the effect of temperature in the range of 30-70°C was investigated at the optimum NaOH concentrations of 0.2 wt% for the sintered stainless steel membrane and 0.4 wt% for the ceramic membrane. An optimum temperature of 50°C was found for both systems. Further increases in temperature resulted in lower maximum flux values. The temperature must be above the melting points of fat for those systems where this predominates.

2.6.7.6 Effect of pH on cleaning

Greater the cleaner concentration, more extreme will be the pH and thus greater the cleaning effect (within constraints of optimum cleaning). The pH of solution is very important as mentioned in Section 2.5.3.2. One example of this behaviour was the study of Kim *et al.* (1993) who found that cleaning an ultrafiltration membrane used on a BSA solution with NaOH or HCl greatly improved if the ultrafiltration occurred at pH 5 (around the IEP) instead of pH 7 (natural pH). On the other hand, a surfactant such as CTAB proved to be effective at pH 7. It is assumed that NaOH, HCl and CTAB increase the charge on the BSA stuck on the membrane thus causing greater repulsion and solubility. Using membranes with high charge can improve cleaning with acidic or basic cleaners significantly. Raising the concentration or increasing cleaning velocity improved cleaning only marginally.

The PTTK membrane showed better cleaning at all pH values, since the internal deposits within the partially permeable membranes (PTHK and Memtec MPS) were difficult to flush out of the membrane even if they were loosened off the pore walls of the membranes. Water flux after cleaning was almost unaffected. In the case of permeable membranes (MPS), internal deposition occurred and the amount of deposit varied according to pH. Also, water flux after cleaning decreased with pressure because of the difficulty in removing the foulant from inside the pores (Kim *et al.*, 1993).

Table 2.8 Cleaning regimes used by different researchers

Ref	Membrane type	Fouling material and conditions	Cleaning materials	Method
1	Polyethersulfone flat sheet Supor 100 MF membrane	1 wt% Baker's yeast (*Saccharomyces cerevisiae)* suspension	*Acid*: Citric acid *Alkali*: NaOH *Formulated detergent*: P3 Ultrasil II	1) Cleaning with acid, alkali or formulated detergent. 2) Rinse with RO water at 23°C and 0.74 ms^{-1} for 1 minute with permeate side closed and retentate sent to drain.
2	Spiral wound polysulfone Koch HFK-131 UF membrane	0.5 wt% Reconstituted whey protein concentrate (RWPC) 80 at pH 6.7	*Acid*: 0.5 wt% citric acid *Alkali*: NaOH *Sanitiser*: 100 ppm NaOCl *Enzyme detergent*: 2% v/v Enzyme L-Builder 95	1) Citric acid for 30 min. at pH 2.3 and 50°C. 2) Rinse with filtered tap water for 5 min. at 20°C. 3) Enzyme L-Builder 95 for 30 min. at pH 9 and 50°C. 4) Rinse with filtered tap water for 5 min. at 20°C. 5) NaOCl with NaOH at pH 10.5 for 10 min. at 50°C. 6) Rinse with filtered tap water for 5 min. at 20°C. *Note*: All steps were carried out at 0 kPa ΔP_{TM} and a flow rate of 9 $Lmin^{-1}$.
3	A Millipore PTTK polysulfone UF membrane	1) Bovine serum albumin (BSA; fraction V) 2) RWPC	*Surfactants and enzymes*: CTAB (cetyl-trimethyl-ammonium bromide), TAZ (Terg-A-Zyme), and α-CT (α-chymotrypsin)	1) Flush with 100 mL of MilliQ water at 400rpm for 30 min. 2) Chemical cleaning with CTAB, α-CT, TAZ at 400rpm and no applied pressure.
4	Sintered stainless steel and ceramic MF membranes	20L of RWPC powder with 3.5 wt% protein at pH 6.4	*Acid*: 0.3 wt% HNO_3 *Alkali*: 0.2 wt% NaOH *Surfactant*: 0.5wt% Ultrasil 11	Three cleaning methods were used: 1) NaOH for 30min. followed by 30 min. rinse with distilled water 2) NaOH for 30 min, rinse with distilled water for 10min., HNO_3 for 30min., rinse with distilled water for 10min. 3) Ultrasil for 20min. at 10$Lmin^{-1}$ followed by a rinse with distilled water for 10min. *Note*: Distilled water and all cleaners were used at 50°C

Ref	Membrane type	Fouling material and conditions	Cleaning materials	Method
5	3 polysulfone UF membranes were used: 1) Millipore PTTK 2) Millipore PTHK 3) Memtec MPS	200 mL of 0.1 wt% aqueous bovine serum albumin (BSA; fraction V)	*Acid*: HCl *Alkali*: NaOH *Surfactants*: Sodium dodecyl sulfate (SDS) & CTAB	1) 100 mL distilled water at 400 rpm for 30 min. 2) 100 mL of cleaner at stirring speeds of 200, 400 and 600 rpm without applying pressure for 1 hour.
6	Spiral wound polysulfone UF membrane	Separated Cheddar cheese whey	*Acid*: 1:1(v/v) blend of HNO_3 and phosphoric acid *Alkali*: NaOH *Surfactant*: 0.05% (v/v) non-ionic surfactant Ultraclean II *Sanitisers*: dichloroisocyanurate, NaOCl, and chlorine dioxide. *Note:* NaOH with NaOCl containing 200 ppm of active Cl_2.	1) 200 L warm softened water at 54°C 2) NaOH with Ultraclean II at 54°C, pH 11 for 20 min. 3) 200 L warm softened water 4) Blend of HNO_3 and phosphoric acids at 54°C, pH 2 for 20 min. 5) warm water flush 6) NaOH with NaOCl at 54°C, pH 11 for 20 min. 7) warm softened water 8) 200 L of sanitiser solution for 20 min.
7	Inorganic UF membrane consisting of a single Carbosep tube and a ZrO_2 filtering layer	Milk with pH 6.4-6.7 at 50°C, protein 30.6-35.4gL^{-1}, total calcium 1.2 gL^{-1}.	*Acid:* 0.036 M HNO_3, *Alkali:* 0.036 M NaOCl with 1 gL^{-1} NaOH *Note:* nine cleaning formulations based on NaOH with the addition of surfactants and calcium complexants were also used	1) HNO_3 for 15 min. 2) NaOCl for 20 min. 3) one of the nine formulations for 30 min.
8	Inorganic UF membrane consisting of a single Carbosep tube and a ZrO_2 filtering layer	1) Skim milk with pH 6.4-6.8 at 50°C, protein 30.6-35.4 gkg^{-1}, total calcium 1.2 gL^{-1} 2) Rennet casein whey with pH 6.5 at 50°C, protein 11.3 gkg^{-1}, total calcium 0.4 gL^{-1}	*Acid*: 0.036 $molL^{-1}$ HNO_3, *Sanitiser*: NaOCl containing 1000 mgL^{-1} active Cl_2	1) HNO_3 for 15 min. at 50°C. 2) NaOCl for 20 min. at 50°C. 3) water for 15 min. at 50°C.

Ref	Membrane type	Fouling material and conditions	Cleaning materials	Method
9	Two Amicon PM-10 flat sheet UF membrane	200mL (0.1%) solution of α-lactalbumin.	*Acid*: 1M HNO_3 *Alkali:* 1.2M NaOH *Surfactants and enzymes*: 0.01M & 0.002M SDS, 0.002M & 0.0005M CTAB, 0.75% & 0.075% TAZ, 0.002M & 0.0001M Triton X-100, 0.1M EDTA	1) 300 mL of each chemical was stirred in contact with the membrane for 15min. 2) 2x100 mL water at 3.5 $kgcm^{-2}$ was used to flush the cell

Ref.1: Shorrock & Bird (1998)
Ref.2: Tran-Ha & Wiley (1998)
Ref.3: Munoz-Aguado *et al.* (1996)
Ref.4: Bartlett *et al.* (1995)
Ref.5: Kim *et al.*(1993)
Ref.6: Bohner & Bradley (1992)
Ref.7: Daufin *et al.*(1992)
Ref.8: Daufin *et al.* (1991)
Ref 9: Chong *et al.*(1985)

2.6.7.7 Effect of cleaning velocity

Cross-flow velocities were examined by Bartlett *et al.* (1995) to investigate the effect of changing the cleaning solution flow from laminar to turbulent conditions. The optimum concentration of 0.4 wt% NaOH and a temperature of 50°C were employed using a ceramic membrane. The results showed little improvement in flux recovery with increasing cross-flow velocity confirming the work of several previous researchers (Kim *et al.*, 1993; Daufin *et al.*, 1991; Daufin *et al.*, 1992). It appears that cleaning performance was not a strong function of the surface shear rate or cross-flow velocity although changes in cross-flow velocity may affect the removal of dissolved material.

2.6.8 Methods of checking the cleaning efficiency

The criteria for cleanliness are usually based on indirect indices such as appearance and smell of rinse water or flux and quality of the final product (Semerad, 1985). Visual inspection of the membranes can give an idea of the state of the membrane, but this is difficult in practice. Most membrane systems cannot be inspected and besides, some foulants such as surface-active agents, cannot be seen using a microscope (Tragardh, 1989).

Harper and Moody (1981) considered the degree of restoration of flux and level of dissolved solids in the permeate during cleaning to be effective indicators for assessing the efficacy of cleanliness. According to Tragardh (1989), the product

flux in the following run was considered to be a better indication of whether the membranes were cleaned satisfactorily.

A membrane system is considered clean when the original water flux has been restored. Cleaning is checked by measuring the water flux after cleaning at defined pressure, temperature and circulation velocity. Practical restoration of membrane flux is now accepted as an index for the cleanliness in UF plants (Renner & El-Salam, 1991; Tragardh, 1989). This is however not a reliable measure, since good water flux does not guarantee a good operational flux. However, a low water flux is an indication that the cleaning is not sufficient.

Membrane cleaning efficiency is therefore commonly assessed by comparison of the water flux before and after cleaning. Flux recovery based on the initial clean water flux is an assessment of the overall effectiveness of cleaning techniques.

Direct microbiological counts have been considered as more reliable indices for the cleanliness of UF equipment. These have their limitations as much time is needed before getting the results, but they can be used at least in testing the efficacy of the different cleaning systems and conditions before selecting the most efficient one for a newly established UF plant.

Scanning electron microscopy has been used (Smith & Bradley, 1987b, 1988) to verify the cleanliness of UF membranes and to examine the effect of different cleaners in removing micro-organisms from the membrane surface. Using this technique showed that an alkaline cleaner resolved both soil and bacterial linkages to the membrane surface, while an enzyme based cleaner could only remove soil, leaving bacteria attached to the membrane.

2.7 Conclusions

Fouling is an inevitable part of membrane operations and is a collective term for any mechanism that has a negative effect on permeate flux and/or membrane selectivity. Fouling causes an increase in protein retention in typical food applications involving filtration of proteins, for example, whey protein concentrate production or microfiltration of skim milk.

Fouling can be either reversible or irreversible. Reversible fouling is defined as being rinsable at zero transmembrane pressure and comprises a loose cake and concentration polarisation layer. Irreversible fouling is defined as not being removed by rinsing and includes strongly adhering cake and material lodged in pores or adsorbed to surfaces. This must be removed by cleaning.

An obvious consequence of fouling then is higher cleaning costs. In addition, depending on the nature and extent of fouling, restoring the flux may require some powerful cleaning agents which may damage the membrane.

The choice of cleaning method depends on the module configuration, the chemical and physical resistance of the membrane and ancillary equipment and the nature of

fouling. Standard procedures for cleaning membranes fouled with milk or whey involves cycles of alkaline and acid solutions circulated through the system. Most of the commonly used cleaners are sodium hydroxide, nitric acid, sodium hypochlorite, surfactant mixtures, and enzyme detergents.

Different types of compounds give different results. While individual components (like acids) can be used, most commonly several chemicals are incorporated into built or formulated cleaning solutions. Formulated detergents consist of a mixture of alkalis, phosphates, sequestering agents and wetting agents.

Further work is required to elucidate cleaning mechanisms and important factors influencing these. This is of particular importance for dairy systems, being the major user of membrane processes in the food industry, and includes the need to improve existing cleaners and develop new formulations. These must be tested and different regimes optimised. It is possible to do all this under controlled laboratory conditions but this is not necessarily representative and is therefore best done in systems approximating a production plant.

3.0 Methods And Materials

In this study, a polymeric ultrafiltration (UF) membrane was reproducibly fouled during the processing of skim milk and skim milk concentrate (SMC). This fouling layer was then chemically cleaned using various basic, acidic and enzymatic formulated detergents.

3.1 Materials

3.1.1 Membrane

A spiral wound Desal polyethersulfone UF membrane (supplied by Tuchenhagen (N.Z.) Limited) was used (Table 3.1). This element is very commonly used for food related processes requiring stringent sanitary procedures and key applications include whey concentration and protein recovery both in the food and dairy industries. The module features a Durasan™ outerwrap, polysulfone parts, and a selection of feed spacers (0.76-1.27 mm).

Table 3.1 Characteristics of the Desal polyethersulfone ultrafiltration membrane (Desalination Systems, 1998)

Element specifications	
Model	PW3838C-1098
Spacer thickness	3.8″ (0.097 m)
Active area	7.4 m^2
Operating and Design Parameters	
Rating	10,000 molecular weight cut-off
Typical operating pressure	555-931 kPa
Maximum pressure	1379 kPa
Maximum temperature	50°C
Recommended pH	Operating range 2.0-11.0 Cleaning range 2.0-11.5
Chlorine tolerance	5000+ ppm-days
Module dimensions	
Length	38.75″ (0.984 m)
Module outer diameter	3.785″ (0.096 m)
Permeate tube outer diameter	0.844″ (0.021 m)

3.1.2 Cleaning Agents

The properties and characteristics of cleaning agents used to clean the membrane pilot plant are detailed in Tables 3.2 and 3.3. Full information on the composition cannot be given as this information is proprietary. Table 3.2 gives the typical dosage rate and physical characteristics, while Table 3.3 indicates the chemical composition of each cleaning agent.

Table 3.2 Characteristics of cleaning agents used (Orica N.Z., 1997 & 1998)

Product Name	Type of cleaner	Appearance	Specific Gravity	Use directions
Reflux A230	UF membrane CIP additive	Clear colourless viscous liquid	1.02	Used in conjunction with Reflux B610. Concentration range 0.3-0.6 % v/v.
Reflux B610	UF, RO and NF membrane alkaline detergent	Clear liquid	1.33	Used in conjunction with other Reflux acid or enzyme based formulations. Concentration range 0.1-0.4 %v/v, pH 10.5-11 at 50°C.
Reflux B620	UF, RO and NF membrane alkaline detergent	Clear liquid	1.11 at 20°C	Used in conjunction with other Reflux acid or enzyme based formulations. Concentration range 0.3-1.5 %v/v, pH 10.5-11 at 50°C
DR292	UF membrane alkaline detergent	Clear liquid	-	Used in conjunction with other Reflux acid or enzyme based formulations. Concentration range 0.3-1.5 %v/v, pH 10.5-11 at 50°C
Reflux R400	UF, RO and NF membrane acidic detergent	Clear liquid	1.37 at 20°C	Used in conjunction with other Reflux alkali or enzyme based formulations. Concentration range 0.2-0.5 %v/v, pH 1.8-2.0 at 50°C
Reflux E1000	UF, NF and RO enzymatic membrane detergent	Clear amber liquid	1.10	Used in conjunction with other Reflux alkali or acid based formulations. Concentration range 0.1-0.2 %v/v
Reflux S800	UF membrane cleaner and sanitiser	Pale yellow liquid	1.24 at 20°C	Dosed in conjunction with Reflux alkaline detergents. Typical levels for cleaning cycles are 150-200 ppm, pH 10.5 at 50°C

Table 3.3 Properties of cleaning agents used (Orica N.Z., 1997 & 1998)

Product Name	Key Ingredients	Company Description
Reflux A230	Octylphenoxypolyethoxy-ethanol, water, sodium hydroxide	A non-ionic surfactant designed to provide excellent wetting of milk soils. Effective removal and dispersal of fat and protein deposits from UF membranes.
Reflux B610	Sodium hydroxide, Potassium hydroxide, water, surfactants, sequestrants	A high strength blended alkali solution. It contains a surfactant system which rapidly emulsifies soils composed of whey precipitates, milk proteins and fats.
Reflux B620	Water, Potassium hydroxide, surfactants, alkaline builders	A medium strength blended alkali solution. It contains a surfactant system which rapidly emulsifies whey precipitates, milk proteins and fat deposits.
DR292	Alkali, sequestrants, non-ionic surfactants, water	A medium strength blended alkali solution with more surfactants. It rapidly emulsifies whey precipitates, milk proteins and fat deposits.
Reflux R400	Nitric acid, Phosphoric acid, water	A is a blended acid solution formulated for the effective removal of calcium phosphate and hard scale mineral deposits from membrane systems.
Reflux E1000	Surfactants, Buffers, Protease enzyme, water	An enzyme based liquid detergent containing proteolytic enzymes, used to dissolve proteins and other organic impurities. It also contains a surfactant system that reduces surface tension and enhances the enzyme contact with stubborn soil deposits.
Reflux S800	Sodium hypochlorite, water	A buffered sodium hypochlorite solution with non selective highly effective bacterial killing properties.

3.1.3 Feed solutions

Un-pasteurised and non-heated skim milk from milk separators, and skim milk concentrate (SMC) collected from the retentate balance tank during the UF of standardised milk was supplied by Anchor Products, Lichfield. The SMC is rich in proteins, lipids and suspended solids and was collected and used immediately. If SMC could not be used immediately after collection, it would be kept in cool storage (< 7°C) until required. Storage time never exceeded 4 hours.

3.2 Method

3.2.1 Pilot plant setup

The pilot plant (Figure 3.2) supplied by Tuchenhagen (N.Z.) Limited has the following components as outlined in Table 3.4. A process and instrumentation diagram of the pilot plant (Figure 3.1) is also shown.

Prior to fouling of the UF membrane, the permeate (FI2) and retentate (FI3) flowmeters were calibrated at 25°C and 50°C, over a range of retentate flow rates and transmembrane pressures (Appendix 2), using demineralised water. A recirculation flow rate of $7x10^3$ Lh^{-1} (7 m^3h^{-1}), controlled by the recirculation flow regulating valve (V17), was maintained throughout calibration.

The initial membrane flux (J_{wi}) was then determined at 25°C and 2.1 bar ΔP_{TM} with the recirculation pump (P2) turned off.

Feed and cleaning solutions were prepared in a stainless steel cylindrical tank of 65L capacity. A feed pump, P1, (Wanner/Model D-10) of capacity ≈ 21 Lh^{-1} at 2-3 bar and 1420 rpm, and a recirculation pump, P2, (Corcoran/Model 2000) of capacity ≈ 6720 Lh^{-1} (112 $Lmin^{-1}$) at 1.5 bar and 2890 rpm delivered feed, demineralised water, and various cleaning solutions to the membrane module.

Temperatures and pH of the recycle fluid were measured during fouling and cleaning with a portable Microprocessor pH/mV meter (Model HI 9025). A Microprocessor Conductivity meter (Model LF 196) was also used to record the conductivities of the feed solution, the cleaning solutions, and that of clean water.

Permeate flux was measured using a variable rotameter, FI2, (Gemu/Model 05) with a flow range of 0-1600 Lh^{-1}. Retentate flow rate was also recorded using a similar rotameter (FI3), while the recirculation flow rate was maintained using a recirculation flowmeter, FI1, (Gemu/Model 07/--/73) with a flow range of 1-10,000 Lh^{-1}.

The desired feed temperature was achieved by recycling through a tubular heat exchanger and adjusting cold and hot water flows via the spent water flow regulating valve (V4).

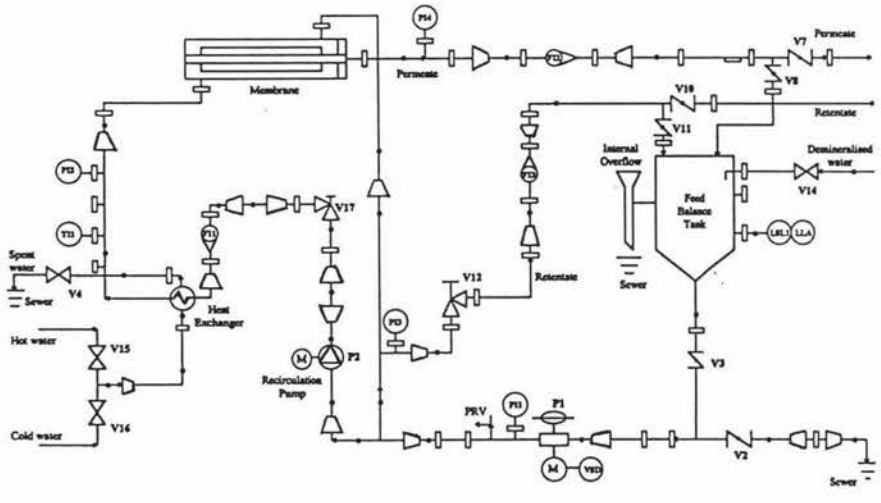

Figure 3.1 Process and Instrumentation diagram of the pilot plant

Table 3.4 Component list of the pilot plant

Component	Code (Figure 3.1)	Make/Model
Hardware		
Feed Pump	P1	Wanner/Model D-10
Recirculation Pump	P2	Corcoran/Series Model 2000
Feed balance tank		
Membrane module		Desal/ Model PW3838C-1098
Heat exchanger		
Valves		
Drain valve	V2	
Balance tank outlet valve	V3	
Spent water flow regulating valve	V4	
Permeate to drain valve	V7	
Permeate to balance tank valve	V8	
Retentate to drain valve	V10	
Retentate to balance tank valve	V11	
Retentate flow regulating valve	V12	
Demineralised water supply valve	V14	
Hot water inlet valve	V15	
Cold water inlet valve	V16	
Recirculation flow regulating valve	V17	Handet/Model 174744 VPR
Pressure release valve	V20	
Instruments-control & monitoring		
Recirculation flowmeter	FI1	Gemu/Model 07/--/73
Permeate flowmeter	FI2	Gemu/Model 05,15/-/-/62
Retentate flowmeter	FI3	Gemu/Model 05,15/-/-/62
Temperature gauge	TI1	Teltherm (0-100°C)
Feed pressure gauge	PI1	Wika (0-4 bar)
Membrane inlet pressure gauge	PI2	Wika (0-6 bar)
Pressure gauge on the retentate side	PI3	Wika (0-4 bar)
Pressure gauge on the permeate side	PI4	Wika (0-4 bar)
Instruments-Miscellaneous		
Variable speed drive		Microdrive/Model PDL UD3
Transformer		Model PX69
Low level float switch	LSL1	
Feed pump speed control knob		

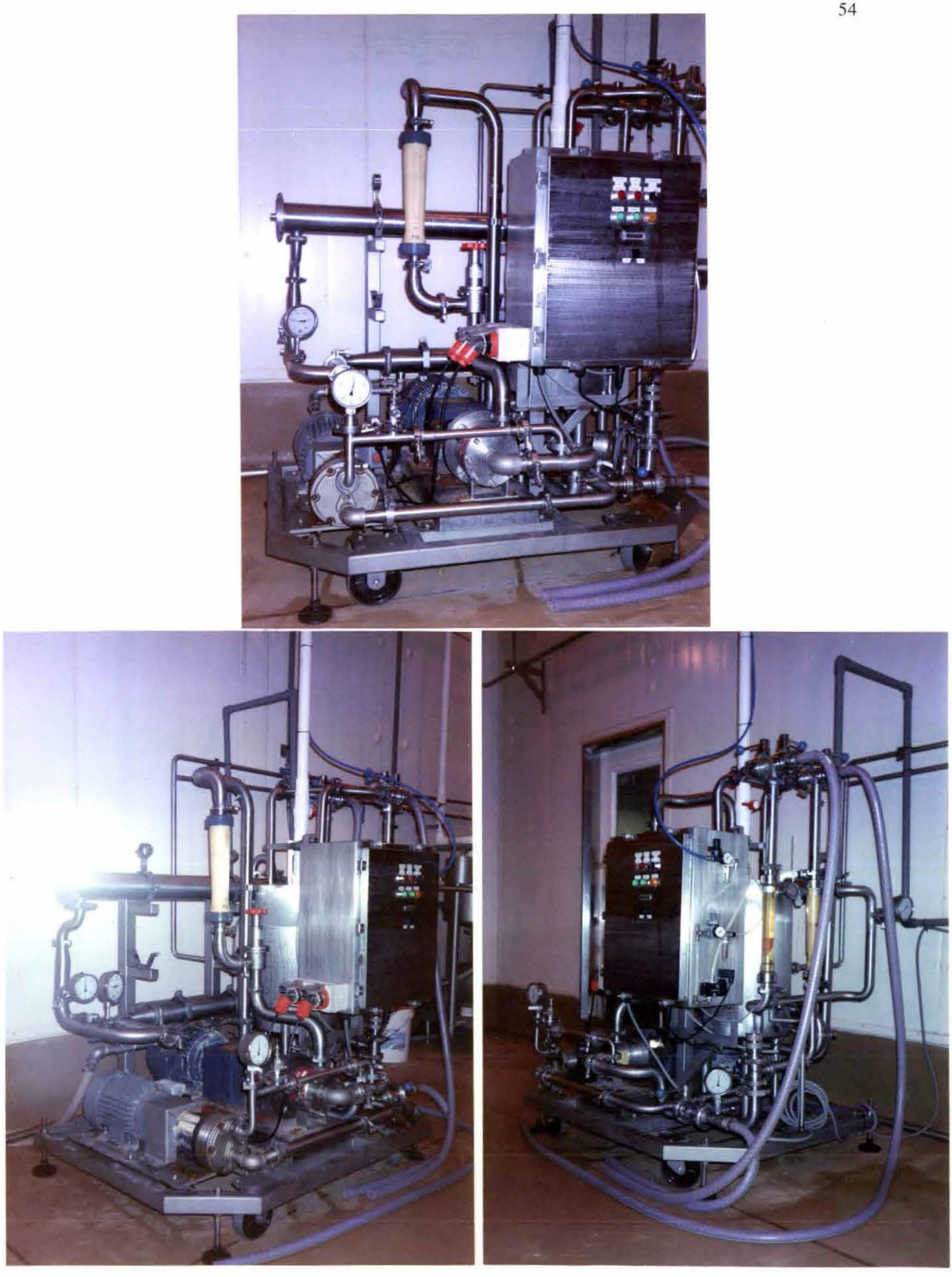

Figure 3.2 Front and side views of the pilot plant

3.2.2 Fouling and Cleaning experiments

Details of the operating procedure for the pilot plant can be found in Appendix 1. Each trial consisted of six stages: fouling, first water rinse, clean water flux, cleaning, second water rinse, and a final clean water flux. Demineralised water prepared by ion exchange was used for preparing all solutions and for rinsing.

3.2.2.1 Clean Water Flux

The clean water fluxes after fouling and cleaning (J_{wc}) were measured under recycle conditions at 25°C, with a retentate flow rate of 60%, 2.1 bar ΔP_{TM} and the recirculation pump turned off. The retentate flow rate varied with each run (as detailed in Appendices 8, 9, and 10) but was in the range 215.4 - 285.1 Lh^{-1}.

3.2.2.2 Fouling

Fouling cycles involved recycling skim milk or SMC at a constant temperature of 18.5°C for 3 hours and 4 hours, respectively. A retentate flow rate of 60%, a recirculation flow rate of 7 m^3h^{-1}, and a transmembrane pressure of 2.5 bar were kept constant during filtration. Fouling was performed for various conditions as described in Table 3.5.

Table 3.5 Fouling conditions for different experimental runs

Test	Feed material	Feed volume (L)	Temperature (°C)	Duration of fouling (h)	ΔP_{TM} (bar)
1	Skim milk	40-60	18.5	3	2.5
2	Skim milk	40-60	18.5	6	2.5
3	Skim milk	40-60	50.0	3	2.5
4	Skim milk	half feed	18.5	3	2.5
5	SMC	40-60	18.5	2	2.5
6	SMC	40-60	18.5	4	2.5
7	SMC	40-60	50.0	4	2.5
8	SMC	half feed	18.5	4	2.5

The concentrate (or retentate) and permeate was recycled back to the feed tank for all tests except 4 and 8, where the permeate was allowed to bleed (no recycle) while the retentate was recycled back into the tank, until the feed volume had reduced to half its original volume (that is, volume concentration factor (VCF) 2).

Permeate flux (J_{uf}) during fouling was monitored by recording the amount of permeate collected in a given time. This was done every five minutes for the first 20 minutes and every 20 minutes thereafter using a measuring cylinder and stopwatch.

The degree of fouling is given by the residual resistance of the solute, R_{sw} (due to several factors such as adsorption, gel layer formation and plugging of the pores) using:

$$R_{sw} = \frac{\Delta P_{TM}}{J} - R_m \tag{9}$$

where R_{sw} = residual solute resistance of the fouled membrane (m^{-1})
R_m = hydraulic resistance of a new membrane (m^{-1})

A sample of the feed before fouling, and samples of retentate and permeate after each fouling cycle, were analysed for protein, fat, lactose and total solids, using the FOSS NIRSystems LiquiFlow Analyser (NLA) (Model - 6500 Series) (discussed in Section 3.2.3.1)

3.2.2.3 Rinsing

After fouling, the membrane was given its first rinse to remove loose cake and to flush all traces of milk from the system. After chemical cleaning, a second rinse was required to remove any remaining debris and cleaning chemicals. In both cases, flushing was carried out at 45°C, a membrane inlet pressure of 2.5 bar, and a recirculation flow rate of 2.5 m^3h^{-1} until the pH of water in the balance tank was between 6.5 and 7.5.

3.2.2.4 Cleaning

Cleaning was performed under recycle conditions at a temperature of 50°C, a retentate flow rate of 60%, a recirculation flow rate of 7 m^3h^{-1}, and a transmembrane pressure of 2.5 bar. The variables examined included: type of cleaning agent, concentration, temperature, and run time. Table 3.6 lists the seven cleaning regimes tested on the pilot plant.

A flux recovery of 100% after cleaning is considered ideal. If it is greater than 100%, the membrane might have been corroded or damaged during operation or cleaning. A flux recovery of less than 50% signifies severe pore plugging or irreversible fouling (Tran-Ha & Wiley, 1998).

Membrane performance after cleaning, was expressed as water flux recovery and relative solute resistance removal (SRR). The flux recovery is defined as:

$$\text{flux recovery} = \frac{J_{wc}}{J_{wi}} \tag{10}$$

and the solute resistance removal (SRR) is defined as:

$$SRR = \frac{R_{sw} - R_{sc}}{R_{sw}} \quad (11)$$

where J_{wi} = initial pure water flux of the new membrane (ms^{-1})
J_{wc} = pure water flux after cleaning (ms^{-1})
R_{sc} = residual solute resistance of the cleaned membrane (m^{-1})

Flux recovery relates present membrane performance to initial new membrane performance; whereas SRR compares performance after a run to performance before that run.

Table 3.6 Cleaning regimes used to clean the pilot plant

Cleaning regime	Type of cleaner	Orica's cleaning reagents	Cleaning concentrations (%v/v)	Tempera-ture (°C)	pH	Cleaning time (min.)
A	Alkali	Reflux B610	0.1-0.4	50°C	10.5-11	15
	Acid	Reflux R400	0.2-0.5	50°C	1.8-2.0	15
	Sanitiser	Reflux B610	0.1-0.4	50°C	11.0	20
		Reflux S800	150-200 ppm		10.5	
B	Alkali	Reflux B620	0.3-1.5	50°C	10.5-11	15
	Acid	Reflux R400	0.2-0.5	50°C	1.8-2.0	15
	Sanitiser	Reflux B620	0.3-1.5	50°C	11.0	20
		Reflux S800	150-200 ppm		10.5	
C	Alkali	Reflux B610	0.1-0.4	50°C	10.5-11	15
		Reflux A230	0.1 or 0.2		11.0	
	Acid	Reflux R400	0.2-0.5	50°C	1.8-2.0	15
	Sanitiser	Reflux B610	0.1-0.4	50°C	11.0	20
		Reflux S800	150-200 ppm		10.5	
D	Enzymatic	Reflux E1000	0.2	50°C	9.0-9.5	15
	Sanitiser	Reflux B610	0.1-0.4	50°C	11.0	20
		Reflux S800	50-100 ppm		10.5	
E	Enzymatic	Reflux E1000	0.2	50°C	9.0-9.5	15
	Acid	Reflux R400	0.2-0.5	50°C	1.8-2.0	20
F	Acid	Reflux R400	0.2-0.5	50°C	1.8-2.0	20
	Enzymatic	Reflux E1000	0.2	50°C	9.0-9.5	15
G	Alkali	DR292	0.3-1.5	50°C	10.5-11	15
	Acid	Reflux R400	0.2-0.5	50°C	1.8-2.0	15
	Sanitiser	DR292	0.3-1.5	50°C	11.0	20
		Reflux S800	150-200 ppm		10.5	

The reason Reflux A230 was added to Reflux B610 and not to Reflux B620 was because Reflux B610 contains a large amount of caustic materials. As a result, the inclusion of sufficient surfactant to be active at the recommended dilution is impossible. An alternative is to add the surfactant separately. Reflux B620 has a lower caustic content which allows the inclusion of surfactant.

3.2.3 Miscellaneous methods

3.2.3.1 Standardisation of instruments

The pH meter was calibrated daily using pH buffers 4.01 and 7.00 supplied by BDH Chemicals (N.Z.) Limited. The procedure for calibration of the meter as outlined in the manual was followed.

The conductivity meter was used for comparison purposes only. Therefore, calibration of the meter was not carried out.

The FOSS NIRSystems LiquiFlow Analyser (NLA) supplied by Science and Technology (N.Z.) Limited, is a special liquid handling detector module. It analyses the fat, protein, lactose and total solids content in milk (whole and skim), cream and whey. When presented with a liquid in a vial, the LiquiFlow takes a sample of the liquid, preheats it, places an aliquot in a quartz cuvette and initiates the Near Infrared Radiation (NIR) analysis. After the analyser has completed the scan, the LiquiFlow then flushes the system with a wash solution, and returns to *standby* mode (FOSS NIRSystems & Science and Technology (N.Z.) Limited, 1998).

NIR (0.01-1 cm) is commonly used to analyse turbid liquids or solids. Light of different wavelengths is absorbed by different chemical bonds. Fats, proteins and other such species all have different absorption maximums and the NIR uses these and some form of calibration to determine the percentage of each.

Calibration of the LiquiFlow was performed using skim milk powder samples (Appendix 3) and was also carried out once a month by Control Room operators at Anchor Products, Lichfield.

3.2.3.2 Measurement of enzyme activity

One detergent trialed, Reflux E1000, contained a protease enzyme. Measurement of enzyme activity was performed as follows:

Preparation of Tris Buffer:

12.1 g Tris (supplied by BDH Chemicals (N.Z.) Limited) was dissolved in 800 mL distilled water. This was titrated with 1M HCl until the pH reached 9.00$\pm$0.05 and then made up to 1000 mL with distilled water.

Preparation of Azocasein solution:

0.2000$\pm$0.0005 g Azocasein (supplied by Sigma, Australia) was made up to 100 mL with Tris buffer solution.

Preparation of dilute enzyme solution:

100 µL 10% Reflux E1000 was added to 50 mL of Tris buffer.

Activity of enzymatic detergent Reflux E1000 was measured as follows:

1. 100 µL of the diluted enzyme solution was added to 900 µL of Azocasein solution in a test tube.
2. Test tube was placed in a 50°C water bath for 10 minutes.
3. 500 µL 15% Trichloroacetic acid was added to the test tube.
4. Test tube was again placed in a 50°C water bath for 5 minutes.
5. Sample was centrifuged at 3900 rpm for 5 minutes.
6. Solution was decanted into a cuvette and absorbance was measured at 420 nm.

All measurements were performed in triplicate.

3.2.3.3 Chlorine measurement

The concentration of chlorine present in a sanitiser solution during circulation through a membrane decreases as the chlorine reacts with organic matter in the system. Measurement of chlorine concentration was achieved using a Lamotte Chlorine test kit (Model PCT-DR Code 4497-DR, Lamotte Company, Maryland).

The test kit consists of three chlorine reagents (Table 3.7), a direct reading titrator (0-200 ppm) and a titration tube (10 mL). The titration tube is filled to the 10 mL mark with a chlorine containing sample. Five drops of chlorine reagent #1 and five drops of chlorine reagent #2 are added to the tube. The tube is capped and shaken. The titrator is then filled with chlorine reagent #3 and inserted into the centre hole of the titration tube cap. While the titration tube is slowly swirled, the plunger is pressed slowly to titrate until the solution turns colourless. The test result is directly read where the plunger meets the titrator scale and is recorded as ppm chlorine (Lamotte Company, 1996). Three measurements were performed for each experiment to ensure that the required chlorine levels were attained.

Table 3.7 Properties of chlorine reagents used in the chlorine test kit (Lamotte Company, 1996).

Product	Key Ingredients	Physical Appearance	pH
Chlorine reagent #1	Sodium hydroxide, soluble starch, 2-Furoic acid, Kathon® CG/ICP preservative, Potassium iodide, water	Clear, colourless liquid	7
Chlorine reagent #2	Lactic acid, water	Clear, colourless liquid	<2
Chlorine reagent #3	Sodium hydroxide, 2-Furoic acid, Sodium thiosulfate, water	Clear, slightly yellow liquid	12

3.2.3.4 Titration curves

Titration curves were developed for three Reflux cleaners: B610, B620 and R400 at 25°C, to determine their buffering capacity. Each cleaning agent was used in three ways:

1. cleaner was added dropwise to a beaker of demineralised water
2. cleaner was added dropwise to a beaker of demineralised water containing 0.1%w/v skim milk powder
3. cleaner was added dropwise to a beaker of demineralised water containing 1%w/v skim milk powder.

With every drop of cleaner added to a beaker, pH was measured until the concentration of the cleaner in solution was in the specified range for normal use (Table 3.2).

4.0 Results And Discussion

4.1 Calibration of the pilot plant

Calibration of the pilot plant (permeate and retentate flowmeters) was achieved at 25°C and 50°C over a range of transmembrane pressures and retentate flow rates using demineralised water. Calibration was performed on a new membrane. Plots of flux versus transmembrane pressure (Figures 4.1 and 4.2) using retentate flow rates of 10% and 40%, are shown below. These flow rates differ between individual runs and their ranges can be referred to in Appendix 2.

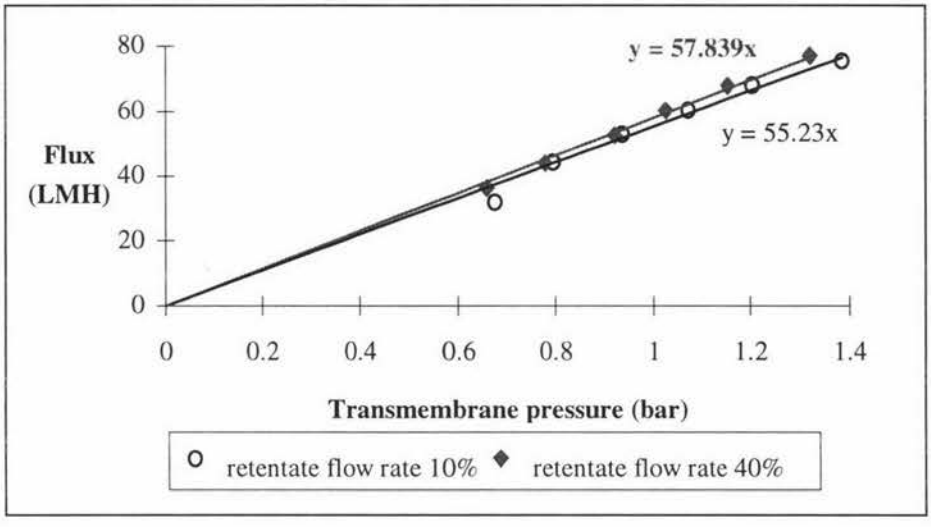

Figure 4.1 Effect of transmembrane pressure on flux behaviour during ultrafiltration (demineralised water, 25°C)

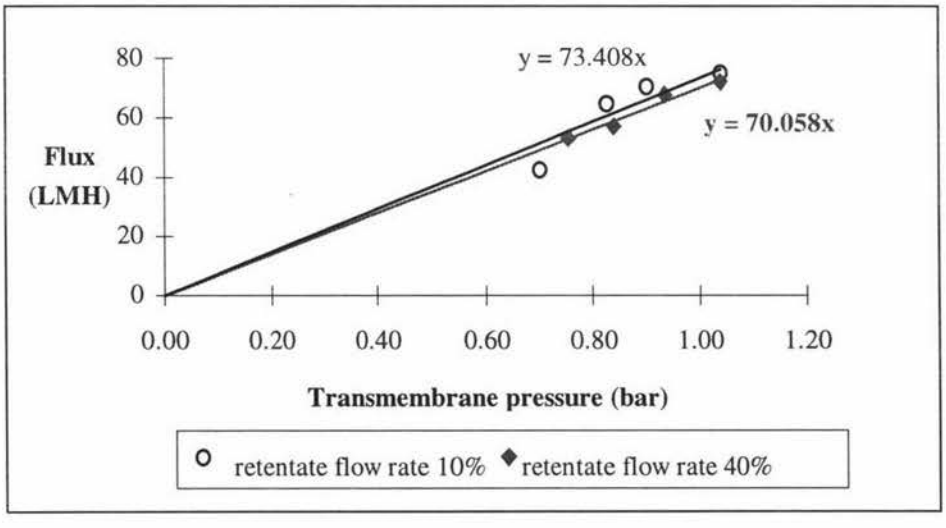

Figure 4.2 Effect of transmembrane pressure on flux behaviour during ultrafiltration (demineralised water, 50°C)

A linear response of flux versus transmembrane pressure passing through the origin resulted at a range of pressures indicating a calibrated system. Water flux was consistently higher at 50°C than at 25°C as indicated by the slopes of the two lines (55.2 LMH/bar at 10% and 25°C; 73.4 LMH/bar at 10% and 50°C).

With reference to Figure 4.1, flux at 1 bar and at a retentate flow rate of 10%, was 56 LMH. Using Equation (6), the hydraulic resistance of the new membrane, R_m, was calculated to be 7.2×10^{12} m^{-1} at 25°C. From Figure 4.2, flux at 1 bar and at a retentate flow rate of 10% was 74 LMH and R_m was calculated to be 8.9×10^{12} at 50°C. However, using the value of R_m calculated above at 25°C, the viscosity of demineralised water using Equation (6), was calculated to be 674 μPa.s, which corresponds to a temperature of 38.4°C (Cooper & Le Fevre, 1969) and not 50°C for which calibration data was obtained.

An increase in temperature causes a decrease in viscosity. If it were just a viscosity effect, Equation (6) would give the same R_m. One needs to assume that if R_m changes then temperature also affects the membrane. Hence, the same R_m cannot be used for different operating temperatures as it changes with temperature. However, it was considered important to have a reference R_m for comparison purposes. The membrane water flux (J_{wi}) on initial use was calculated to be 107 LMH at 25°C and 2.1 bar ΔP_{TM}, under no recirculation (Table A2.1). Using Equation (6), R_m for the new membrane was therefore calculated to be 7.9×10^{12} m^{-1}. This value was assumed to be independent of operating conditions (temperature) for the purpose of all experiments carried out. Another alternative, which could prove expensive on pilot-scale, would be the use of a new membrane for each experiment.

4.2 Experiments performed on the pilot plant

4.2.1 Fouling conditions

The purpose of a fouling step was to obtain a reproducible deposit on the membrane that was sufficiently severe as to be representative of fouling layers formed during commercial processes. The following figures were plotted using data detailed in Appendices 8, 9 and 10.

4.2.1.1 Effect of feed material

A comparison with ultrafiltration of demineralised water was made using skim milk, skim milk concentrate (SMC) and skim milk concentrated to volume concentration factor (VCF) 2. Figure 4.3 shows the effect of feed material on the ultrafiltration flux.

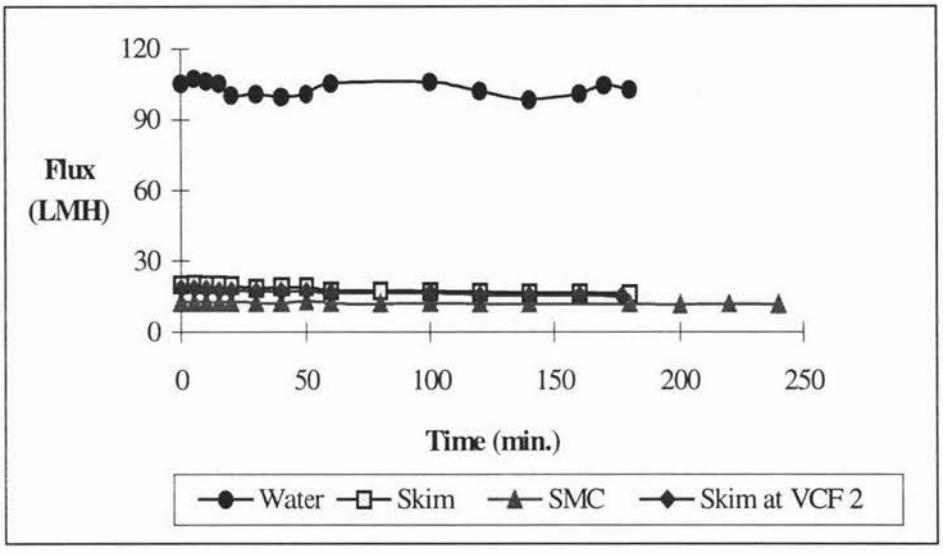

Figure 4.3 Effect of feed material on ultrafiltration flux (18.5°C, 2.5 bar ΔP_{TM}, recirculation flow rate $7 m^3 h^{-1}$)

The flux values for skim milk concentrated to VCF 2 (Appendix 10, Table A10.6, Run 35) were similar to those obtained using unconcentrated skim milk (Appendix 8, Table A8.12, Run 24) throughout the 3 hour operation although runs with concentrated skim milk started with slightly lower flux values (18.5 LMH compared to 20.3 LMH for unconcentrated skim milk). Flux decline during the processing of concentrated skim milk was 16.8% while that during the processing of unconcentrated skim milk was 19.7%.

Cheryan and Chiang (1984) also observed very little flux decline at 3-fold and 5-fold concentrations of skim milk compared to unconcentrated skim milk, although the absolute values of the flux were much lower with concentrated skim milk.

Skim milk concentrate (SMC) on the other hand, gave very much lower fluxes than skim milk, with a low initial flux (12.9 LMH). This stabilised quickly, without much further reduction in flux during the 4 hour operation (Appendix 9, Table A9.12, Run 22). These observations indicate that it is the concentration of protein (7.47% compared to 3.69% in unconcentrated skim milk and 3.83% in concentrated skim milk) that determines the extent of flux decline during membrane processing. At higher levels of protein, as in SMC, the formation of a concentration polarisation layer within a short period of commencing the operation brought the initial flux to lower levels.

As noted in Section 2.5.4.4, increasing the feed concentration results in a decrease in permeate flux during UF. Flux decreases exponentially with increasing feed concentration as shown in Figure 4.4 and indicated by Equation (4).

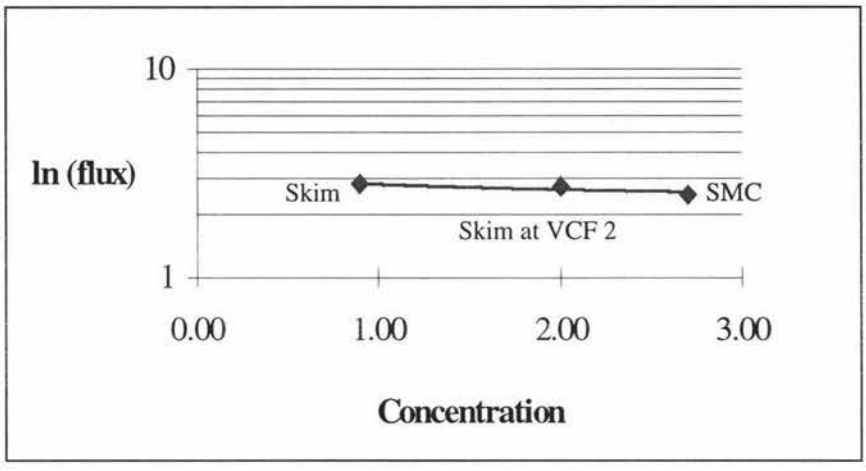

Figure 4.4 Effect of feed concentration on ultrafiltration flux (140 minutes, 18.5°C, 2.5 bar ΔP_{TM}, recirculation flow rate 7 m^3h^{-1})

Based on the residual solute resistances (R_{sw}) of the fouled membrane during the processing of skim milk ($R_{sw} = 2.6x10^{13}m^{-1}$), SMC ($R_{sw} = 2.48x10^{13}m^{-1}$) and skim milk concentrated to VCF 2 ($R_{sw} = 2.51x10^{13}m^{-1}$), it appears that the membrane was reproducibly fouled (Appendix 7, Tables A7.1-A7.8). This was confirmed by t-tests which accepted the null hypothesis that fouling was reproducible at the 1 and 5% probability levels, especially during the processing of concentrated and unconcentrated skim milk (Appendix 6).

4.2.1.2 Effect of fouling time

Run time was an important factor in determining the number of experiments that could be performed in the given period of time. Hence, it was desirable to foul the membrane for the shortest time possible whilst trying to achieve a reproducible and adequate degree of fouling. Figures 4.5 and 4.6 show the effect of time on flux behaviour for skim milk and SMC.

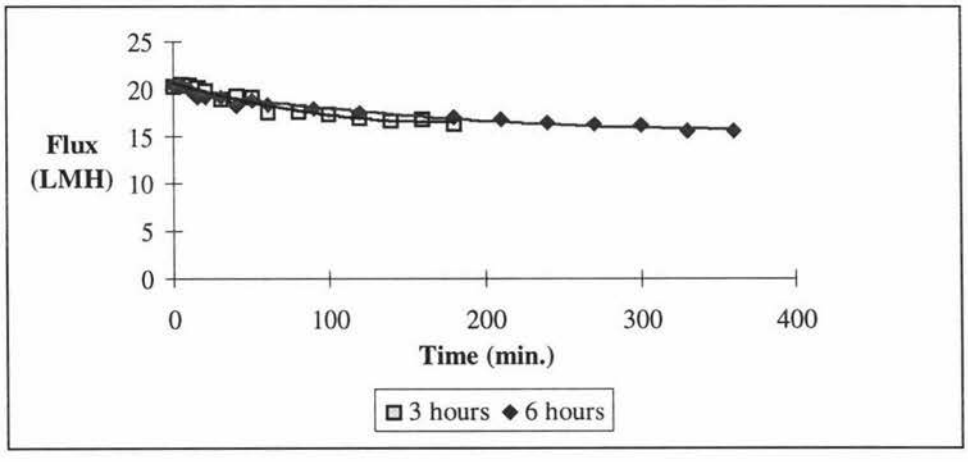

Figure 4.5 Flux behaviour during a 3 and 6 hour fouling with skim milk (18.5°C, 2.5 bar ΔP_{TM}, 7 m^3h^{-1})

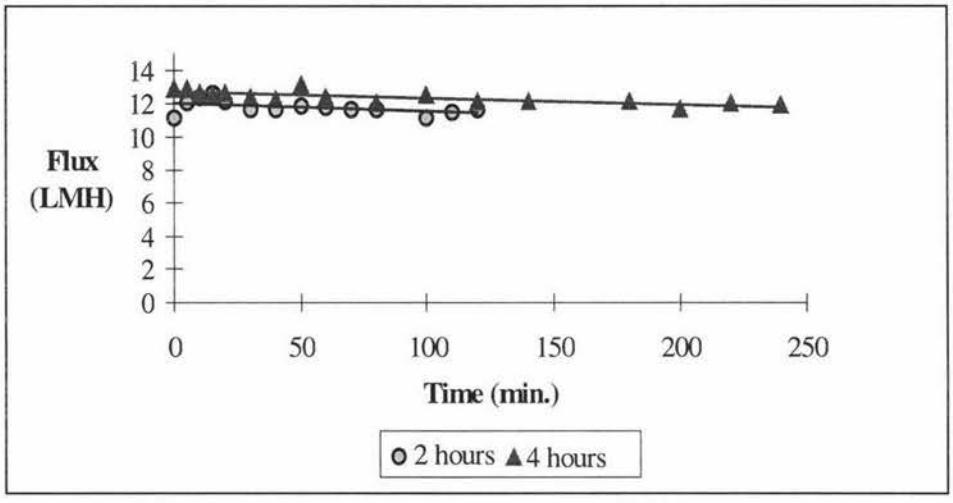

Figure 4.6 Flux behaviour during a 2 and 4 hour fouling with skim milk concentrate (SMC) (18.5°C, 2.5 bar ΔP_{TM}, 7 m^3h^{-1})

Figure 4.5 shows the result of a 3 hour (Appendix 8, Table A8.12, Run 24) and a 6 hour (Appendix 8, Table A8.13, Run 25) fouling test using skim milk at 18.5°C and 2.5 bar ΔP_{TM}. Flux progressed slowly during the 6 hour test and changed relatively little after the initial 3 hours (Run 25). Hence a fouling time of 3 hours seemed a reasonable choice for further experiments using skim milk as the feed material.

Figure 4.6 shows the result of a 2 hour (Appendix 9, Table A9.2, Run 2) and 4 hour (Appendix 9, Table A9.12, Run 22) fouling test using SMC at 18.5°C and 2.5 bar ΔP_{TM}. Not much fouling was observed during the 2 hour test. This was confirmed by a t-test which accepted the alternative hypothesis at the 1 and 5% probability levels that flux increases when fouling time increases (Appendix 6). A fouling time of 4 hours seemed a reasonable choice for further experiments using SMC as the feed material.

Trendlines were fitted to all curves in Figures 4.5 and 4.6. The effects of a lower fouling rate are seen later in a run while the greatest effect is seen early in a run. In both cases, the slope was higher for runs where the membrane was fouled for shorter periods of time than for runs where the membrane was fouled for longer periods of time (-0.72 LMH/h for 6 hours and -1.48 LMH/h for 3 hours using skim milk; -0.23 LMH/h for 4 hours and -0.3 LMH/h for 2 hours using SMC).

4.2.1.3 Effect of operating temperature

Two operating temperatures (18.5 and 50°C) were chosen during the processing of skim milk and SMC. Figures 4.7 and 4.8 show the effect of temperature on flux behaviour. Data used to plot these figures can be referred to in Tables A8.4 (Appendix 8, Run 12) and A8.12 (Appendix 8, Run 24) for skim milk and Tables A9.12 (Appendix 9, Run 22) and Table A9.13 (Appendix 9, Run 23) for SMC.

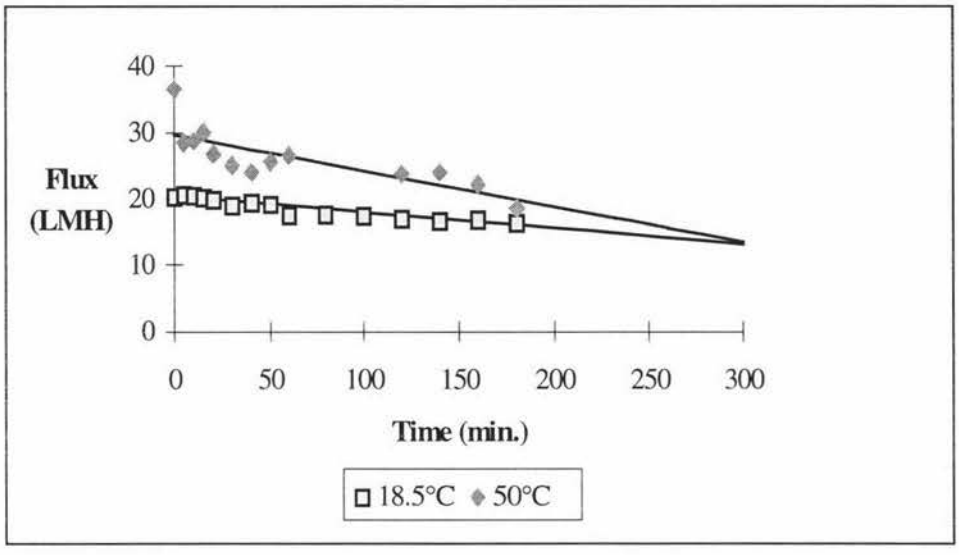

Figure 4.7 Effect of operating temperatures on flux behaviour during the ultrafiltration of skim milk (3 hours, 2.5 bar ΔP_{TM}, 7m^3h^{-1}).

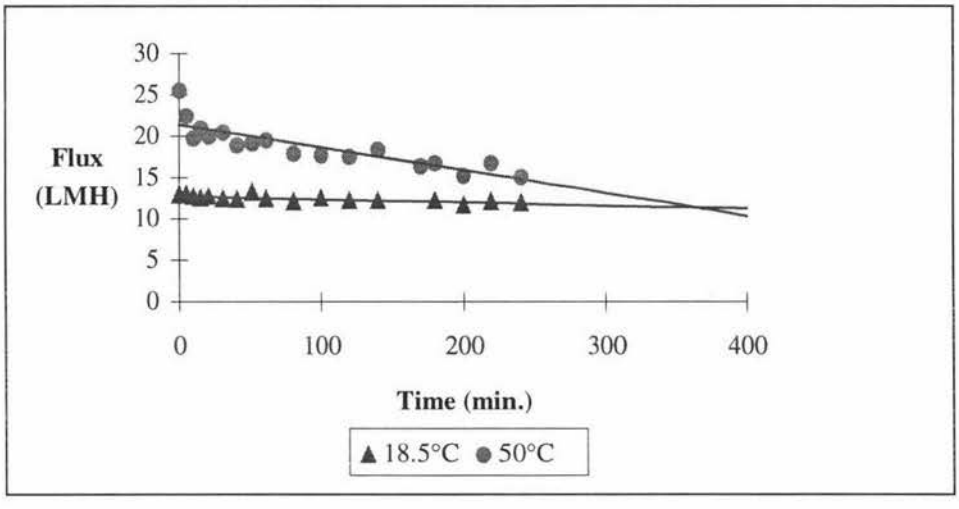

Figure 4.8 Effect of operating temperatures on flux behaviour during the ultrafiltration of skim milk concentrate (SMC) (4 hours, 2.5 bar ΔP_{TM}, 7 m^3h^{-1})

Higher operating temperatures generally increase the ultrafiltration flux. This is due to decreased solubility of some feed constituents as mentioned in Section 2.5.4.1 (minerals, proteins, fat) and the reduced viscosity at higher temperatures. Increasing temperature also increases diffusivity and possible effects on the membrane. Fluxes at lower temperatures are subject to less change, that is, fouling is established rapidly whereas fluxes at higher temperatures undergo a continuous decline for longer periods of time. This could eventually lead to lower average flux values but probably not in the 8-10 hours before the mid run clean.

Fitting linear trendlines to all curves in Figures 4.7 and 4.8 indicates that fluxes at higher temperatures would eventually decline to flux values obtained at lower

temperatures if fouling time was prolonged. For example, with reference to Figure 4.8, Run 23 (11.2 LMH) would meet Run 22 (11.31 LMH) at 370 minutes.

Comparing the flux relationship at 50°C (Run 12) with that of water at 18.5°C (Appendix 11, Table A11.1, Run 43) shows by way of a t-test (Appendix 6) that these two relationships are very different from each other and could likely indicate the role of temperature in changing the nature of fouling.

In the dairy industry, ultrafiltration has often been carried out at 50-60°C which limits microbial growth (including thermophiles) in the feed solutions. Very few plants now operate at such high temperatures and cold processing (below 10°C) is much preferred as it is suitable to kill thermophilic micro-organisms that cannot grow at 10°C compared with any other micro-organisms. Hence, a temperature of 18.5°C was chosen as the lowest operating temperature that could be achieved without chilled water for further cycles.

Referring to Table A7.2 (Appendix 7), Run 12 and 21 showed a 50% decline in ultrafiltration flux while Run 23 showed only a 33% decline in ultrafiltration flux. These differences are quite likely to be due to experimental errors which can be overcome if further experiments using an operating temperature of 50°C were conducted. Following fouling with SMC, Run 21 (71.6%) had a much lower flux recovery than Run 23 (77.1%) because chlorine concentration in the sanitising step was below the accepted range of 150-200 ppm.

4.2.2 Cleaning regimes

Tables A7.1 to A7.8 in Appendix 7 summarise the experiments performed on the pilot plant using cleaning regimes A to G. Data from these tables have been put together to plot the following figures.

4.2.2.1 Cleaning Efficiency

Figures 4.9 and 4.10 show the cleaning efficiency in terms of flux recoveries, final water fluxes and solute resistance removals (SRR) after cleaning for experiments using cleaning regimes A to F after fouling with skim milk and SMC.

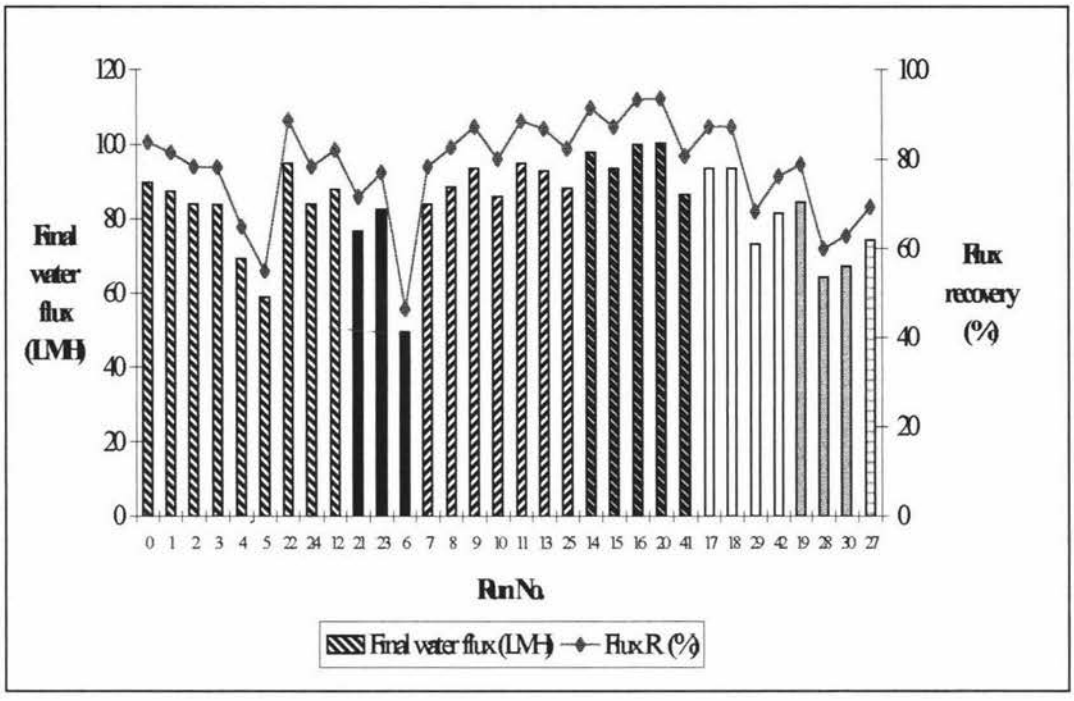

Figure 4.9 Cleaning effect of cleaning regimes A to F - final water flux and flux recovery after cleaning following fouling with skim milk and SMC (25°C, 2.1 bar ΔP_{TM})

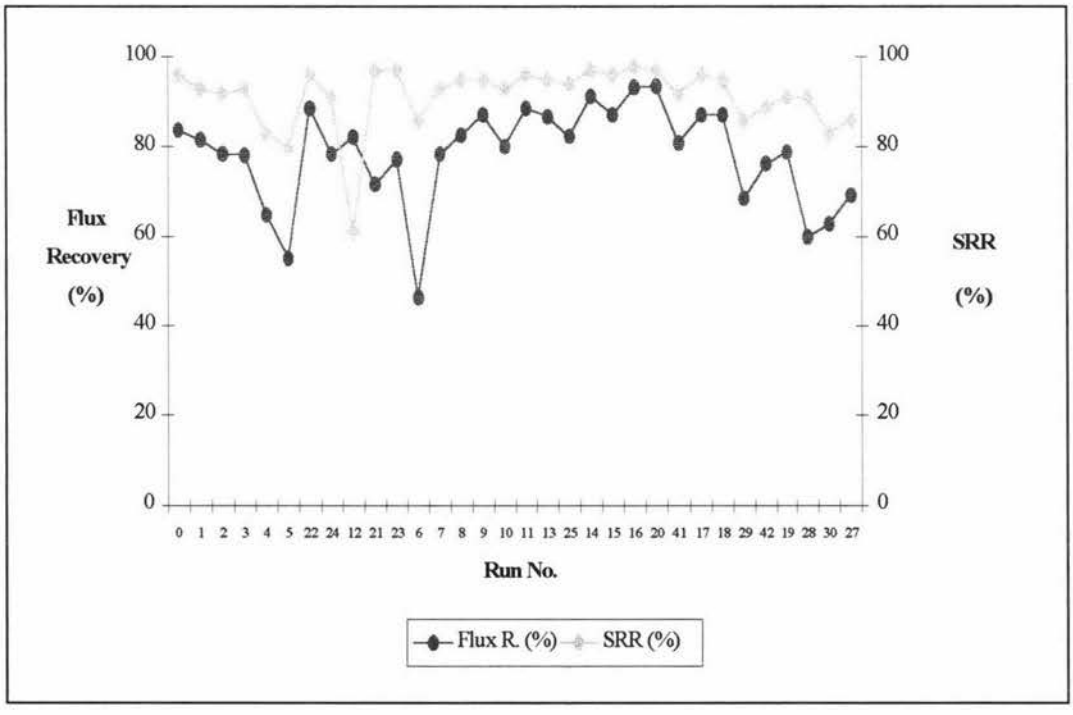

Figure 4.10 Cleaning effect of cleaning regimes A to F - flux recovery and solute resistance removal (SRR) after cleaning following fouling with skim milk and SMC (25°C, 2.1 bar ΔP_{TM})

A key to the above mentioned cleaning regimes can be found below:

regime A (18.5°C)
regime A (50°C)
regime B
regime C
regime D
regime E
regime F
regime G

Ten experiments were performed using skim milk concentrated to VCF 2. Cleaning regime A was used to clean the membrane after the first five runs while cleaning regime G was used to clean the membrane after the remaining 5 runs. The membrane was also fouled with SMC concentrated to VCF 2 and then cleaned using regime A (Appendix 10, Table A10.1, Run 26). Results of final water fluxes, flux recoveries and solute resistance removals (SRR) after cleaning are summarised in Figures 4.11 and 4.12.

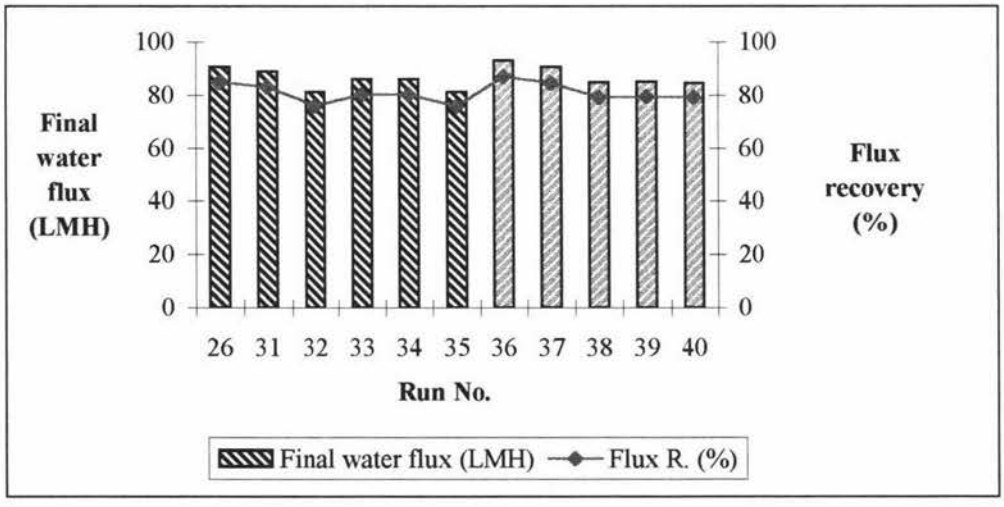

Figure 4.11 Cleaning effect of cleaning regimes A and G - final water flux and flux recovery after cleaning (25°C, 2.1 bar ΔP_{TM}, skim milk and SMC concentrated to VCF 2)

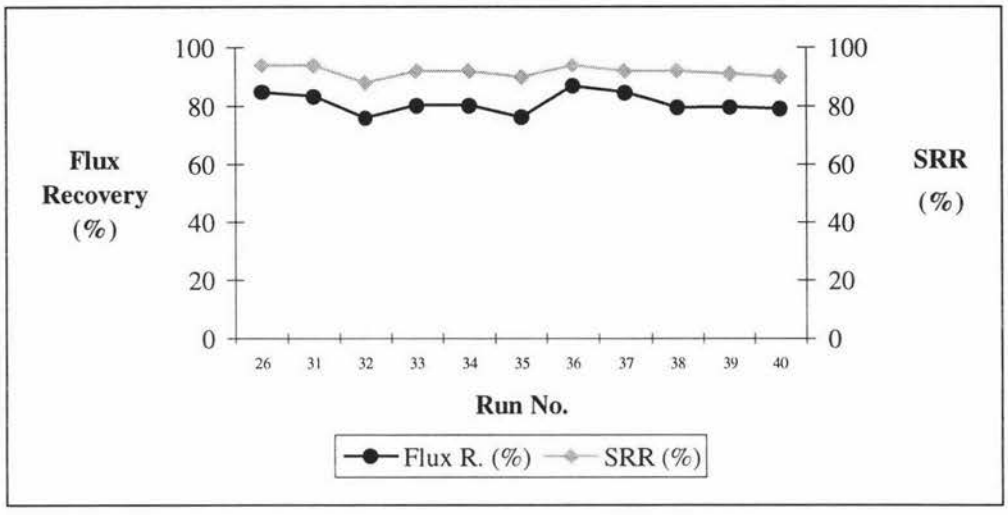

Figure 4.12 Cleaning effect of cleaning regimes A and G - flux recovery and solute resistance removal (SRR) after cleaning (25°C, 2.1 bar ΔP_{TM}, skim milk and SMC concentrated to VCF 2)

Flux recoveries of the seven cleaning regimes A to G can be arranged in the following order of decreasing cleaning efficiency:

C G B A D E F

decreasing cleaning efficiency

Differences between these regimes will be discussed later.

Data for cleaning efficiency can be expressed in terms of water flux recovery and relative solute resistance removal (SRR) as shown in Figures 4.9 to 4.12 above. According to Munoz-Aguado *et al.* (1996), it is insufficient to characterise cleaning efficiency by either flux recovery or solute resistance removal alone because large solute resistance removal values are often easily obtained when large amounts of foulant are deposited (for example, at the isoelectric point) but these high resistance removals do not necessarily equate with high flux recoveries.

Such examples can be found in these data. With reference to Table A7.2, low flux recoveries, 71.6% and 77.1% (Runs 21 and 23 respectively) did not correlate well with the high solute resistance removal values of 97% for both runs. Nevertheless, flux recovery curves and solute resistance removal curves (Figures 4.10 and 4.12) did overall follow the same trend. This was similarly observed by Munoz-Aguado *et al.* (1996). Solute resistance removal according to Daufin *et al.* (1992) provides a good but delayed picture of membrane cleanliness. It may have been helpful if a water flux was also performed after every cleaning stage in the regime tested.

Calculation of the residual solute resistances of the fouled membrane (R_{sw}) and residual solute resistances of the clean membrane (R_{sc}) after each experiment

(Appendix 7) showed that membrane performance was reasonably attained and maintained with repeated fouling and cleaning.

A combination of flux recovery and solute resistance removals is not enough to assess full cleaning performance. Microbiological swabbing and scanning electron microscopy (SEM) are other techniques that can be employed to study the nature of the protein deposits on the fouled and cleaned membranes. This is expensive and difficult to achieve on pilot-scale. While laboratory experiments can be performed easily and as many times, eventually work with real plant data is necessary. A real membrane was used for processing and hence performance (flux recovery and solute resistance removal) was accordingly measured on such a scale. Microbiological examinations have their limitations too, as much time is needed before getting the results. However, the microbiological status of pathogens will be tested in plants and if these meet specifications then it provides further evidence that all is well. Microbiological examinations are also used to test the efficacy of different cleaning solutions and regimes.

The FOSS NIRSystems LiquiFlow Analyser (NLA) was used to determine if feed samples used for each experimental run had comparable fat, protein, lactose and total solids content. Skim milk and SMC samples did show comparable contents of fat, protein, lactose and total solids.

4.2.2.2 Dosages of Orica cleaners

Figures 4.13 to 4.20 show the dosage volumes of Orica cleaners used in the seven cleaning regimes.

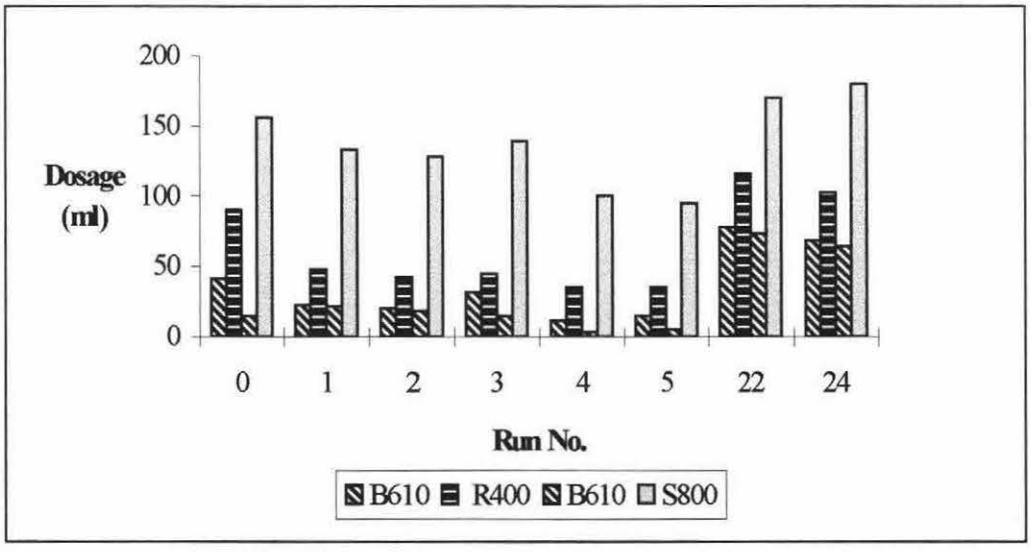

Figure 4.13 Dosage volumes of Reflux cleaners B610, R400 and S800 used for cleaning regime A after fouling with skim milk and SMC at 18.5°C (50°C, 2.5 bar ΔP_{TM}, 7 m^3h^{-1})

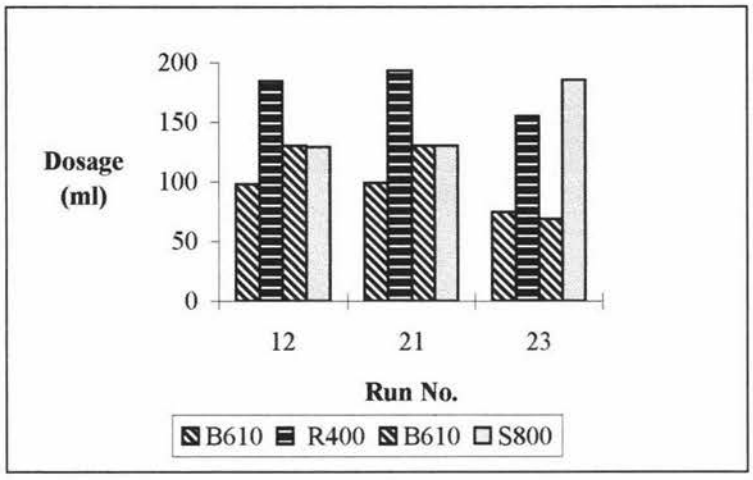

Figure 4.14 Dosage volumes of Reflux cleaners B610, R400 and S800 used for cleaning regime A after fouling with skim milk and SMC at 50°C (50°C, 2.5 bar ΔP_{TM}, 7 m^3h^{-1})

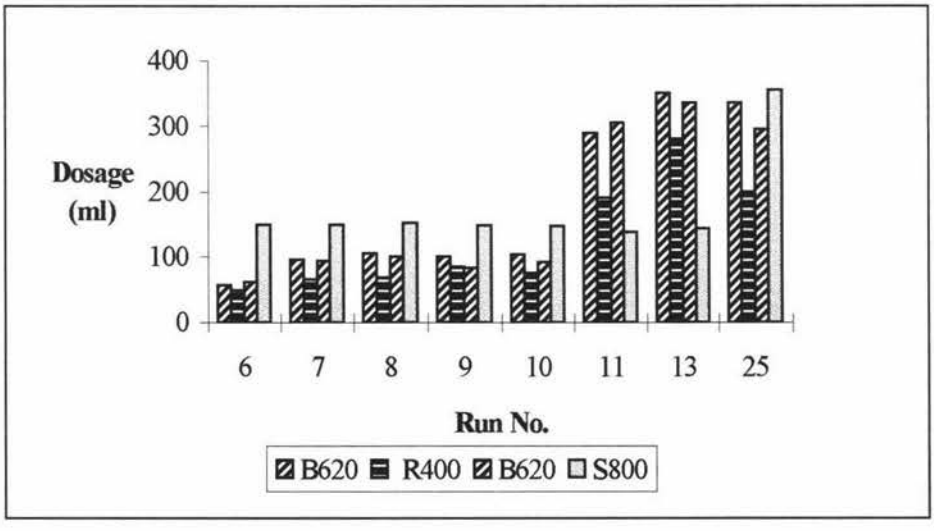

Figure 4.15 Dosage volumes of Reflux cleaners B620, R400 and S800 used for cleaning regime B after fouling with skim milk and SMC at 18.5°C (50°C, 2.5 bar ΔP_{TM}, 7 m^3h^{-1})

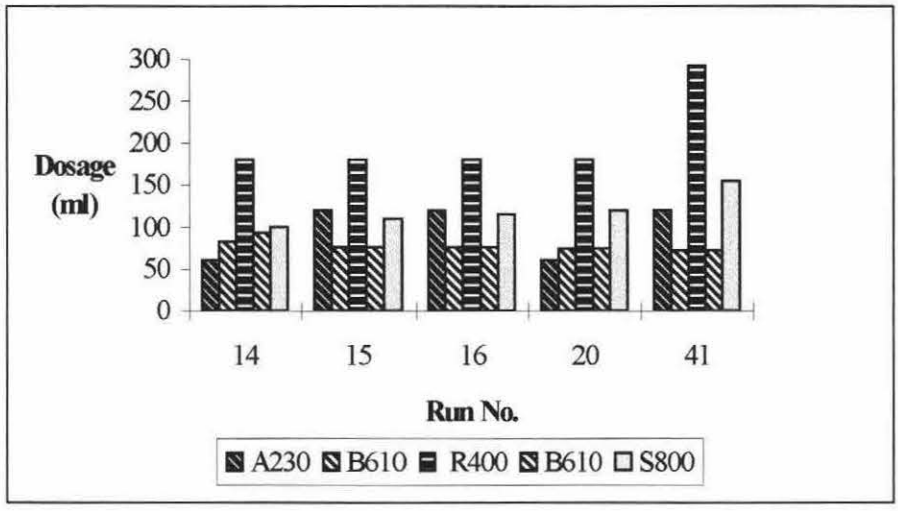

Figure 4.16 Dosage volumes of Reflux cleaners A230, B610, R400 and S800 used for cleaning regime C after fouling with skim milk and SMC at 18.5°C (50°C, 2.5 bar ΔP_{TM}, 7 m^3h^{-1})

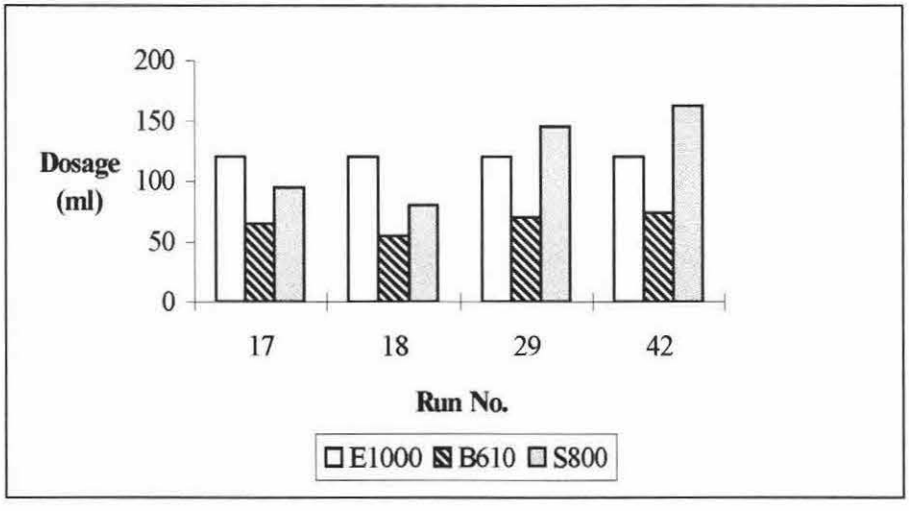

Figure 4.17 Dosage volumes of Reflux cleaners E1000, B610 and S800 used for cleaning regime D after fouling with skim milk and SMC at 18.5°C (50°C, 2.5 bar ΔP_{TM}, 7 m^3h^{-1})

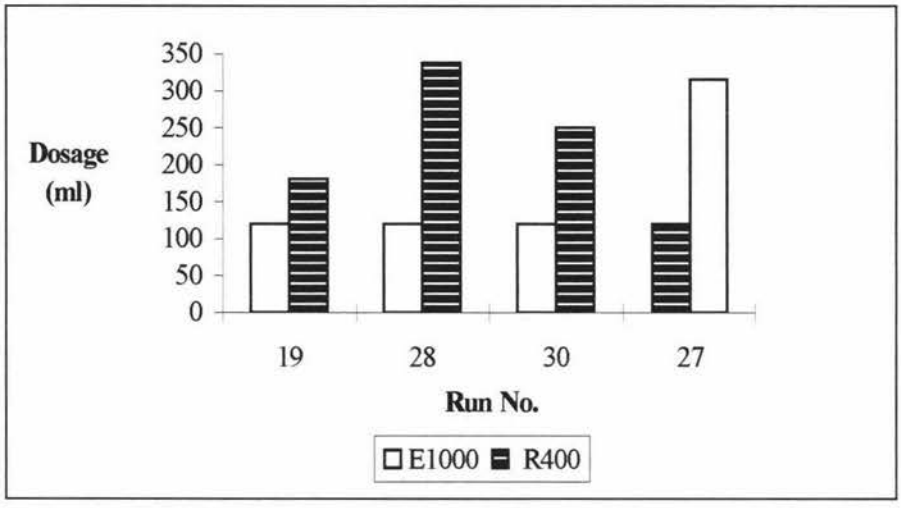

Figure 4.18 Dosage volumes of Reflux cleaners E1000 and R400 used for cleaning regimes E and F after fouling with skim milk and SMC at 18.5°C (50°C, 2.5 bar ΔP_{TM}, 7 m^3h^{-1})

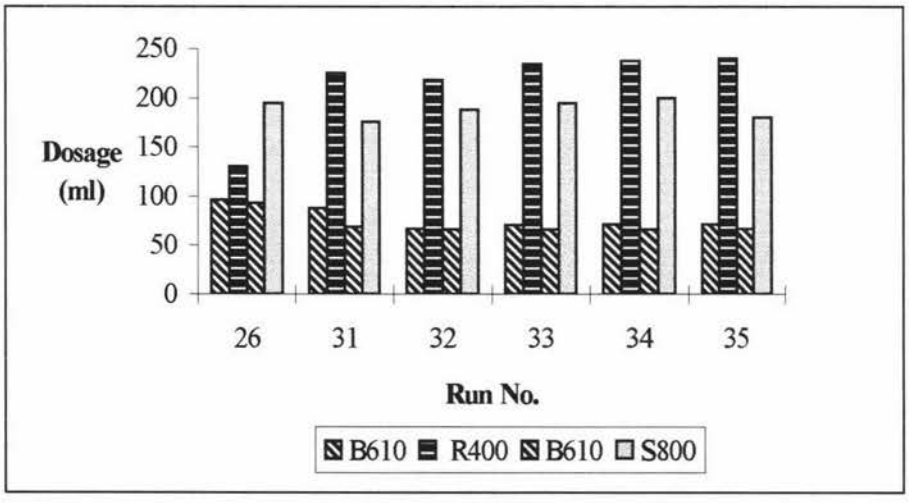

Figure 4.19 Dosage volumes of Reflux cleaners B610, R400 and S800 used for cleaning regime A after fouling with skim milk and SMC concentrated to VCF 2 at 18.5°C (50°C, 2.5 bar ΔP_{TM}, 7 m^3h^{-1})

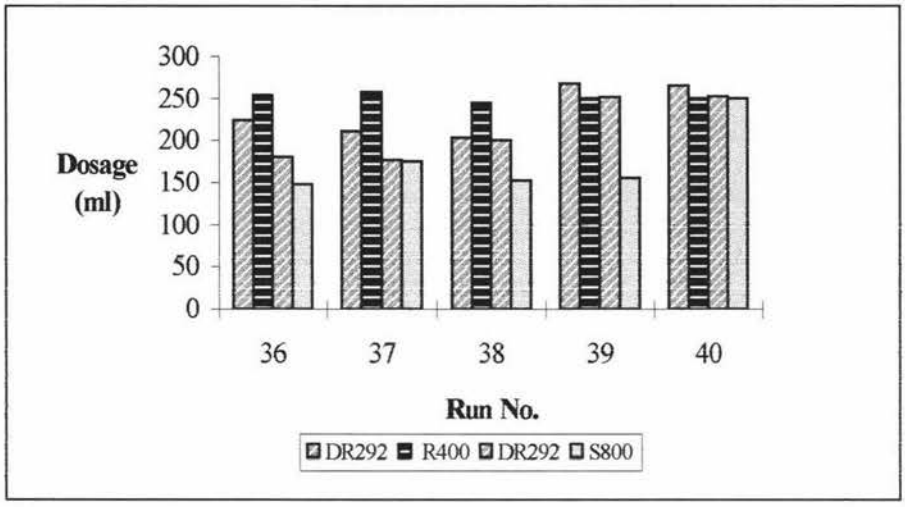

Figure 4.20 Dosage volumes of Reflux cleaners DR292, R400 and S800 used for cleaning regime G after fouling with skim milk concentrated to VCF 2 at 18.5°C (50°C, 2.5 bar ΔP_{TM}, 7 m^3h^{-1})

4.2.2.3 Comparison of alkali cleaners

Results show that the highest flux recoveries were obtained when using regime C. This was attributed to the presence of non-ionic surfactant Reflux A230 added with Reflux B610 in the alkali step giving rise to a product with a higher level of surfactants (Table 3.3 and 3.6).

To further investigate the validity of this statement, a new cleaner DR292 was formulated with more surfactant properties by incorporating both Reflux A230 and Reflux B610 into one product. The membrane was reproducibly fouled (five times) with skim milk concentrated to VCF 2 to model fouling characteristics on an industrial scale and was then cleaned using regime A after each run. At the end of this sequence, the membrane was again reproducibly fouled with skim milk concentrated to VCF 2 and this time the new formulation DR292 (regime G) was used to clean the membrane.

Figure 4.11 shows that the final water flux after cleaning with regime G was higher than the final water flux after regime A as expected (3.5% increase using regime G), but not as high as final water fluxes after regime C (9-11% increase using regime C compared to regime G) (Figure 4.9). The efficiency of subsequent acid cleaning was increased due to the wetting effect of the non-ionic surfactant (Reflux A230) which when used in conjunction with Reflux B610 (regime C) aided the convective cleaning solution flow through the membrane pores. Also, cleaner DR292 has an upper limit on the level of surfactant due to its high caustic content which causes the cleaning solution to cloud and become unstable.

t-Tests were performed on the 10 runs to determine if there was an improvement in using regime G over regime A. However, at the 1, 5 and 10% probability levels, it is certain that there was no improvement in using regime G over regime A.

Cleaning of the membrane after fouling with SMC concentrated to VCF 2 was also successful but further experiments were terminated because of the unavailability of SMC during this period.

Cleaning with Reflux B620 was found to yield higher flux recoveries than cleaning with Reflux B610 because as mentioned earlier (Section 3.2.2.4), the latter contains a lower concentration of additives and is therefore unlikely to wet as quickly and will clean more slowly.

Figures 4.13 to 4.20 show that as the membrane became progressively fouled, more cleaner was required to meet the required pH. Flux recoveries and solute resistance removal after cleaning (Runs 4, 5 and 6) were lower than expected because not enough cleaner was dosed to the required pH and concentrations used were below the recommended range.

4.2.2.4 Effectiveness of enzyme cleaners

All cleaning regimes using standard (non-enzyme) cleaners gave good flux recoveries except for regime E (enzyme-acid) and F (acid-enzyme). The same was observed in a study by Tran-Ha and Wiley (1998). This indicates that enzyme cleaning is milder to the membrane than surfactant cleaning. Experiments with the enzyme-sanitiser regime did produce good flux recoveries in the range of 68.4-87.3%. This is most likely because the sanitiser was capable of removing protein fragments reduced by the enzymatic reaction (Munoz-Aguado *et al.*, 1996),

Cleaning with enzyme and then acid gave an overall better flux recovery than a cleaning in the reverse order. The role of acid is to dissolve minerals while the enzyme removes fat and breaks down proteins. The acid causes the membrane pores to shrink or the foulant layer to contract making it difficult for the enzymatic detergent to further penetrate the foulant and remove it.

However, comparing runs 27 and 28 (Figure 4.18), flux recovery was higher for regime F than for regime E. The protease enzyme used reacts only with proteins and has no effect against fat. The non-ionic surfactants and alkaline buffers will however remove some fat, hence their inclusion in Reflux E1000 (Table 3.3).

On using regime F (Appendix 8, Table A8.14, Run 27), the acid may have denatured the protein to a point where the enzyme did not recognise the peptide bond it was designed to break. Therefore, less enzyme action took place, resulting in a lower final water flux (J_{wc}) of 74.2 LMH. After an acid-enzyme sequence (Regime F), the enzyme was still active in the next run (Appendix 8, Table A8.15, Run 28) after not being washed out and probably reacted with the milk proteins in skim milk, breaking them down into peptides. This further clogged the membrane pores causing a drastic decrease in flux to 64.2 LMH.

Overall, an acid-enzyme (regime F) sequence is not preferred in terms of cleaning efficiency, although in order to establish such a trend, further runs using this

protocol need to be conducted to a point where the membrane's permeability and selectivity can no longer be restored.

It is clearly evident that enzymatic cleaning did not restore membrane permeability as indicated by the downward trend in the two curves from Run 17 onwards (Figure 4.10), compared with surfactant based inorganic formulations.

4.2.2.5 Concentration of Orica cleaners versus pH

Figures 4.21 to 4.27 show the concentration levels of four Orica cleaners versus pH used in the cleaning regimes and the titration curves for each cleaner in the presence and absence of skim milk powder (SMP).

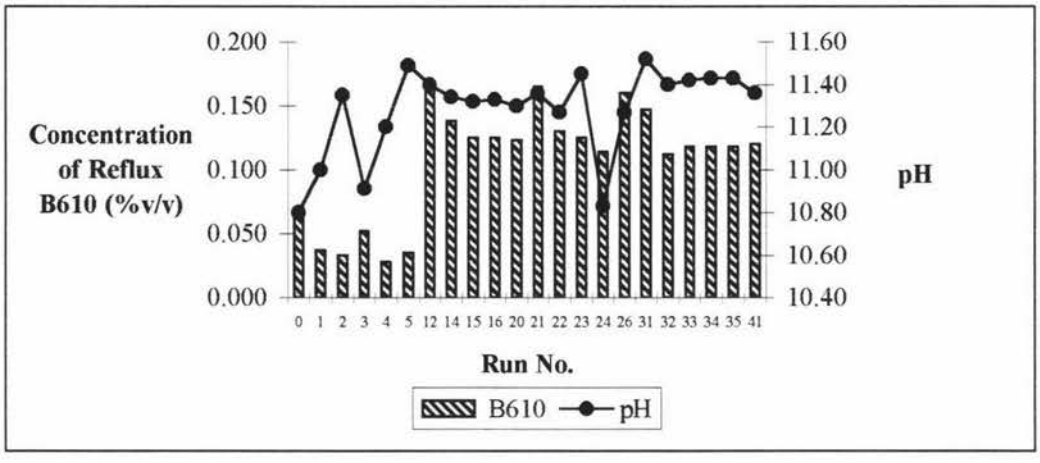

Figure 4.21 Concentration of Reflux B610 versus pH used for cleaning regimes A, C, and D following fouling with skim milk and SMC (50°C, 2.5 bar ΔP_{TM}, 7 m^3h^{-1})

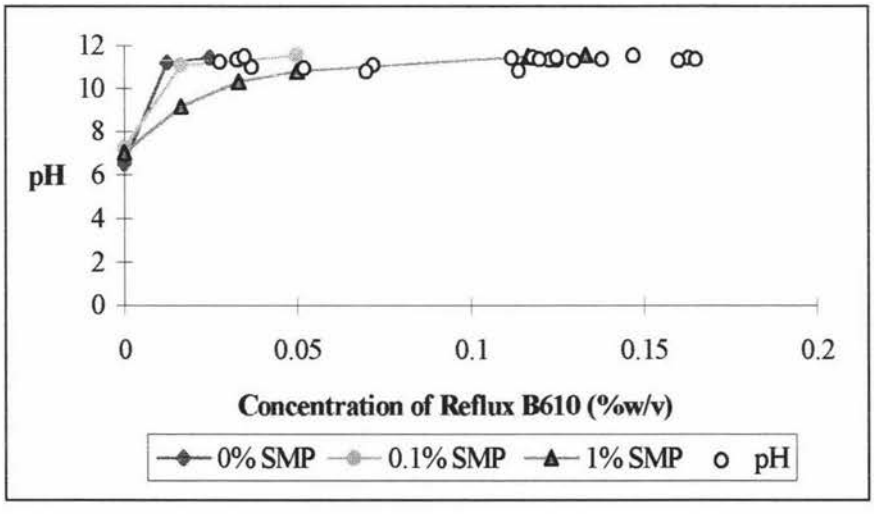

Figure 4.22 Comparison of pH versus concentration of Reflux B610 with titration curves

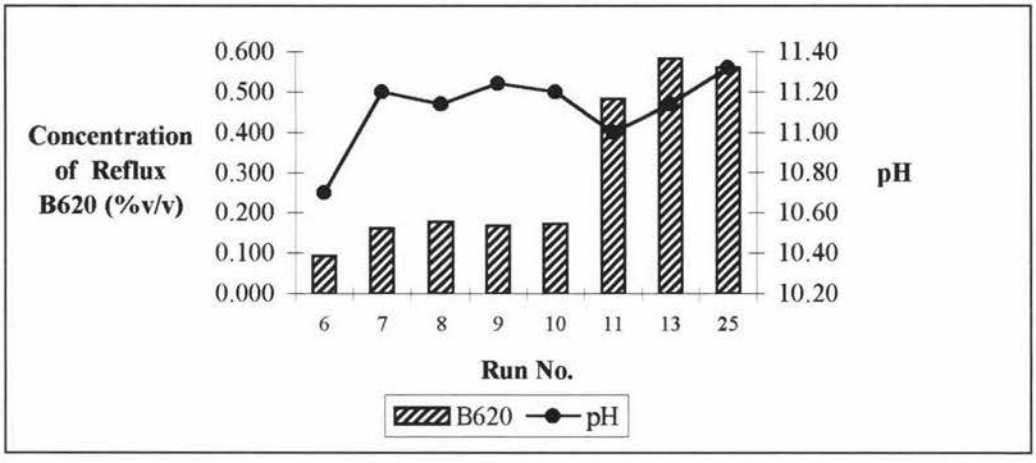

Figure 4.23 Concentration of Reflux B620 versus pH used for cleaning regime B following fouling with skim milk and SMC (50°C, 2.5 bar ΔP_{TM}, $7 m^3 h^{-1}$)

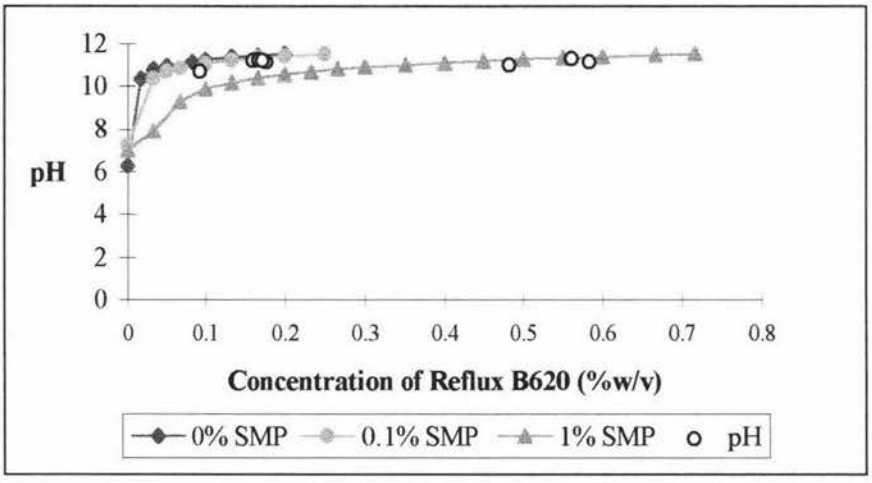

Figure 4.24 Comparison of pH versus concentration of Reflux B620 with titration curves

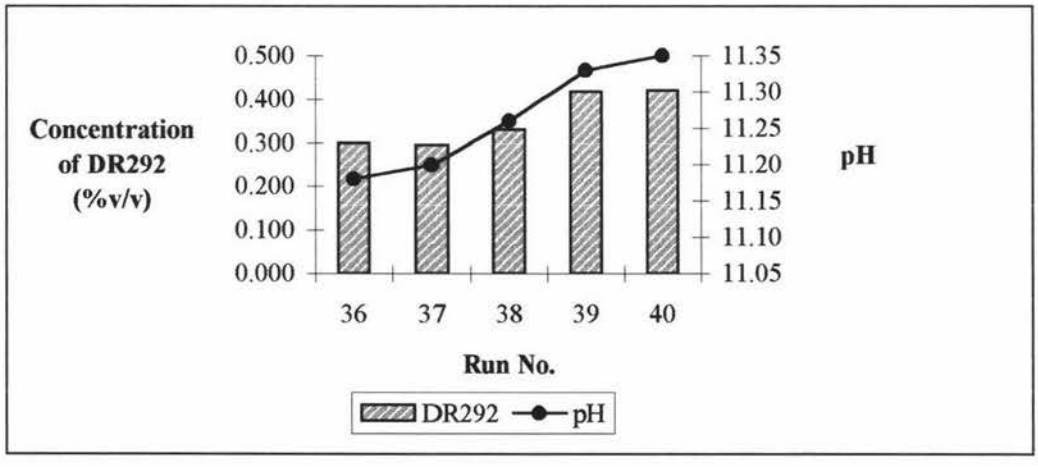

Figure 4.25 Concentration of cleaner DR292 versus pH used for cleaning regime G following fouling with skim milk (50°C, 2.5 bar ΔP_{TM}, 7 $m^3 h^{-1}$)

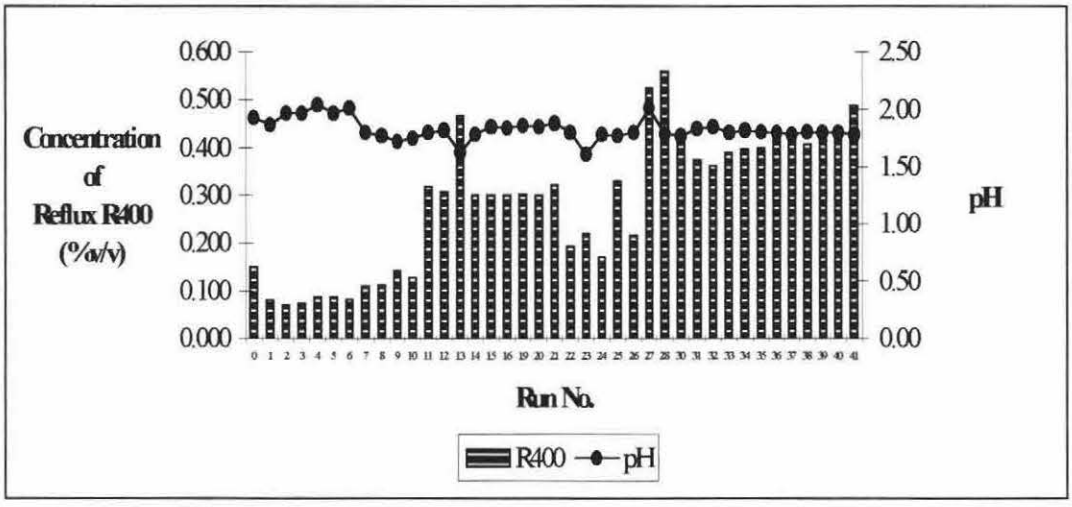

Figure 4.26 Concentration of Reflux R400 versus pH used for cleaning regimes A, B, C, E, F, and G following fouling with skim milk and SMC (50°C, 2.5 bar ΔP_{TM}, 7 m^3h^{-1})

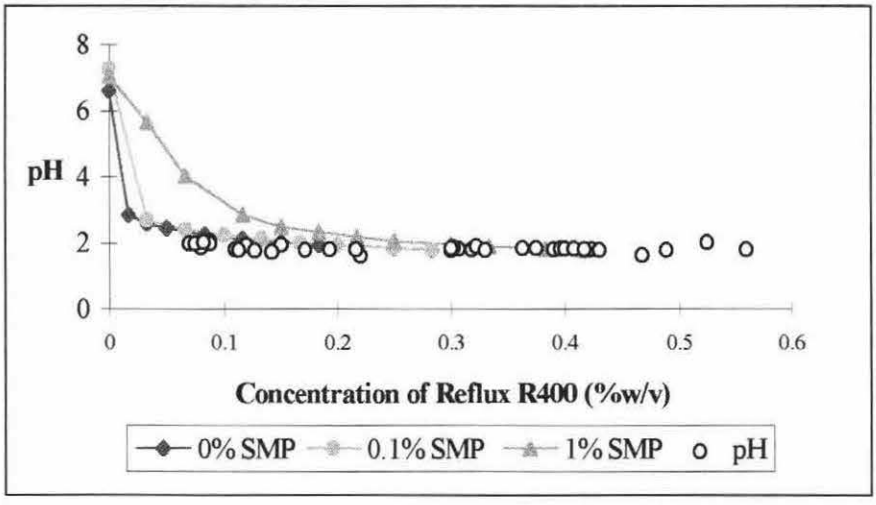

Figure 4.27 Comparison of pH versus concentration of Reflux R400 with titration curves

Figures 4.21 to 4.27 show concentration levels for four cleaners - Reflux B610, Reflux B620, DR292 and Reflux R400 versus pH. From all the experiments conducted on the pilot plant, it was found that flux recovery after cleaning improved when the acid cleaner Reflux R400 was dosed to a pH close to 1.8 and not any lower or higher. This is clearly evident in Runs 1, 2, 9,11,13,15,16, 22, and 23. The acid is essential for the removal of minerals. It was also necessary to dose the alkaline detergents, Reflux B610, Reflux B620 and DR292 to pH values above the recommended range (pH 10.5-11) in order to get a good clean (Runs 22-26, 31-40). The sanitiser in the sanitising step is responsible for the dissolution of organic matter and very often had to be dosed at chlorine concentrations of 200+ ppm in order to get a reasonably good clean. However, this is not recommended

because frequent use of such high concentrations could severely damage the membrane.

From Figures 4.13 to 4.27, it is clear that experiments performed on the pilot plant at the beginning did not require much cleaner to meet the required pH. However, as the membrane became progressively fouled, more cleaner volume was required to meet pH requirements. A reasonable explanation for this behaviour is that the membrane was relatively new at the start and so not much cleaner was required to restore membrane permeability. The following examples support this view:

- The amount of cleaner used for experiments using regime C (Figure 4.16) were relatively similar but run 41 required more cleaner than runs 14, 15, 16 and 20.

- A similar trend was observed for experiments using regime D (Figure 4.17).

- In Figures 4.19 and 4.20, an optimisation of the dosage volumes of each cleaner (regime G) was tried, but Run 40 required an equal quantity of all cleaners in regime G to clean the membrane and restore its permeability compared to earlier runs using the same regime.

It is impossible to get a 100% flux recovery as some material always remains bound to the membrane and subsequently reacts with the cleaners and reduces their effectiveness. Defining an optimum is not a simple task and needs to take these factors into account. In a study by Bartlett *et al.* (1995), increasing the cleaner concentration above the optimum value did not aid the cleaning process but instead resulted in lower maximum flux recovery values.

Titration curves were developed for three Reflux cleaners: B610, B620 and R400. Plots of pH versus concentration of these three cleaners were also plotted on their respective titration plots. Figures 4.22, 4.24 and 4.27 show that as the membrane got progressively fouled, the cleaning concentration had to be increased (due to the buffering capacity of these cleaners) to maintain pH in the effective range. Higher concentrations are required to influence pH (curves flatten). However, the presence of soil increases the buffering capacity of these cleaners at lower concentration ranges (hence the need to dose to the required optimum although this is not possible as shown above).

Cleaning will at least partially restore the permeability of the membrane. However, a gradual decrease in water flux as a function of the number of cleaning cycles, usually occurs. For instance, flux recoveries after using regime C (Runs 14, 15, 16 and 20) were in the range of 87.5-93.6%. However, subsequent fouling and cleaning reduced the flux recovery to 80.7% (Run 41). This is due to irreversible fouling and membrane deterioration and will eventually result in the membrane being removed from service.

There exist two conflicting factors that must be balanced in membrane replacement:

- an increase in the use of aggressive cleaners could increase flux recovery but decrease membrane life, and
- the use of less aggressive cleaners could decrease flux recovery but increase membrane life.

Overall, the role of surfactant points the need to improve additives to get mild cleaners (long "physical" life) with good cleaning properties (long "operational" life). To do this, further inclusion of surfactants in alkali solutions and knowledge of their interaction with soil is required. Also, if fouling can be minimised then advantages will accrue.

4.2.3 Industrial versus Pilot-scale

The Industrial plant, as outlined in Table 4.1, is a two-stage recirculation ultrafiltration plant based at Anchor Products, Lichfield used for the concentration of skim milk at 10°C. Each stage includes two cooling heat exchangers having approximately 2 x 2.5 m^2 cooling surface.

Table 4.1 Characteristics of the Industrial plant (McClunie Birch Limited, 1998)

Industrial plant Stage layout	
Number of modules parallel - stage 1	14; area = 852.6 m^2
Number of modules parallel - stage 2	12; area = 730.8 m^2
Number of cooling modules per stage	2
Number of membrane elements per module	3
Total number of cooling modules	4
Total number of membrane elements:	78
Total membrane area	1583.4 m^2
Membrane	
Element Specifications	
Membrane type	PES
Model	HP99
Spacer	31 mils
Operating and Design Parameters	
Rating	10,000 molecular weight cut-off
Typical operating pressure	136-952 kPa
Maximum temperature	60°C
Recommended pH	1.0-11.0 at 25°C 2.0-11.0 at 55°C
Module Dimensions	
Length	38″ (0.965 m)
Module outer diameter	3.8″ (0.0965 m)
Permeate tube inner diameter	0.830″ (0.021 m)

Figure 4.28 is a comparison of flux behaviour during ultrafiltration of skim milk on industrial and pilot-scales. Data used to plot Figure 4.28 was taken from Appendix 5 and 10.

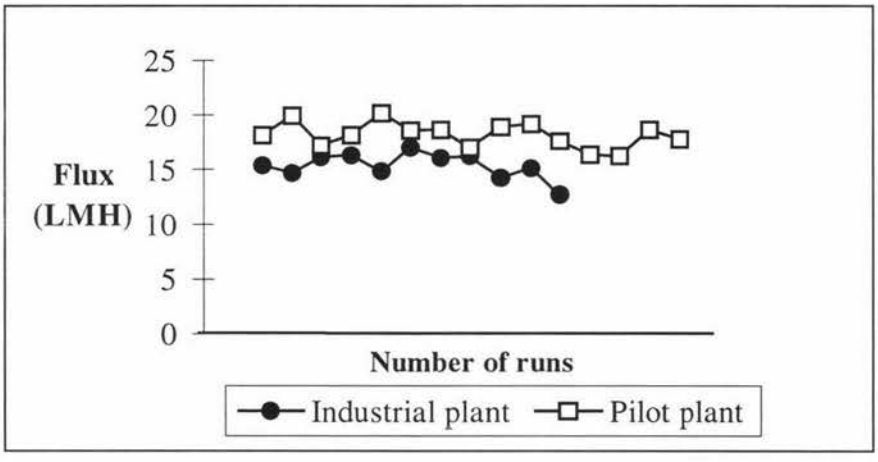

Figure 4.28 Comparison of flux behaviour during ultrafiltration on pilot scale (18.5°C, 2.5 bar ΔP_{TM}, VCF 2, 7.4 m^2 membrane area) and on industrial scale (~10°C, 3.2 bar ΔP_{TM}, VCF 2.7, 1583.4 m^2 membrane area)

Random flux data obtained during the processing of skim milk concentrated to VCF 2, was selected from Appendix 10 for the pilot-scale plant. Since each plant was operated at two different VCF's and temperatures, it is expected that flux would be lower for higher concentration factors as is the case with the industrial plant (Figure 4.28).

Flux data for the pilot plant was corrected to 10°C using Equation (6). The hydraulic membrane resistance (R_m) of each flux value obtained on the pilot plant was calculated using a transmembrane pressure of 2.5 bar and a viscosity of 1027.5 μPa.s at 18.5°C. Using the value of R_m calculated above and a viscosity of 1304 μPa.s at 10°C, the new flux value was determined. It was assumed that R_m did not change with operating conditions. The results are plotted in Figure 4.29.

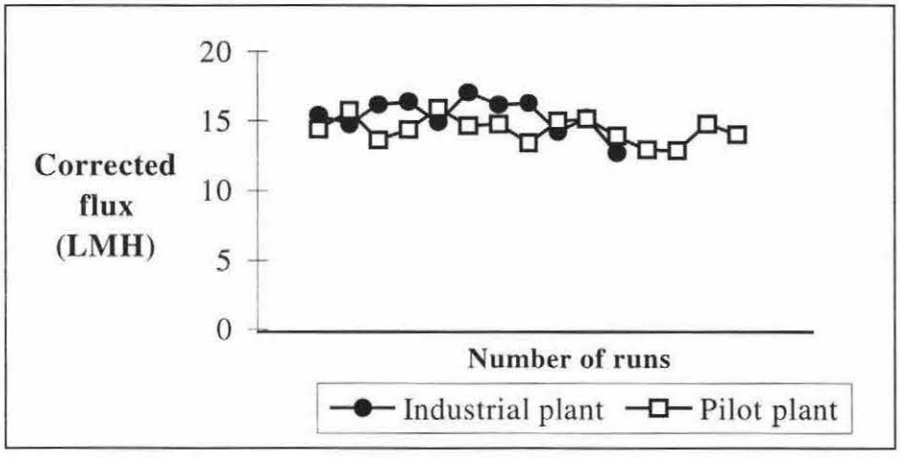

Figure 4.29 Comparison of flux behaviour on pilot and industrial scale after correcting for temperature differences

Assuming that differences between the two plants were independent of pressure, Figure 4.4 was used to convert flux values at VCF 2.0 to VCF 2.7. The results are plotted in Figure 4.30.

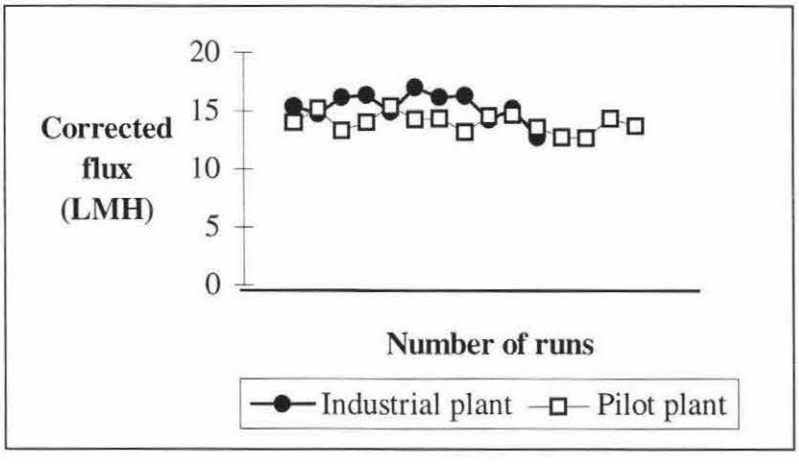

Figure 4.30 Comparison of flux behaviour on pilot and industrial scale after correcting for concentration differences

Hence, on the basis of temperature and concentration, it is evident that the PES membrane (7.4 m^2) was reproducibly fouled with skim milk and SMC to provide soil properties matching those found on fouled industrial membranes.

4.2.3.1 Circulation volumes of the two plants

Pilot-scale Plant

The average retentate flow rate (based on trial runs 31 to 40) can be taken as

= 253 Lh^{-1}
= 4.22 $Lmin^{-1}$
= 211 L based on 50 minutes of cleaning time
= 28.5 L per m^2 of membrane area
= circulation volume of the pilot plant

Industrial-scale Plant

The average retentate flow rate can be taken as

= 11,000 Lh^{-1}
= 183.3 $Lmin^{-1}$
= 19246.5 L based on 105 minutes of cleaning time
= 12.2 L per m^2 of membrane area
= circulation volume of the industrial plant

Hence, a greater amount of cleaner was associated with per m^2 of membrane area on the pilot plant as compared with the industrial plant. This needs to be taken into account in extrapolating data from pilot-scale to full scale. The amount of cleaning solution normally used in process plants today is between 4 and 5 L per m^2 membrane surface (Krack, 1995).

5.0 Conclusions And Recommendations

A polyethersulfone (PES) membrane was reproducibly fouled during the ultrafiltration of concentrated (VCF 2) and unconcentrated skim milk, and skim milk concentrate (SMC). Flux rates of concentrated (VCF 2) and unconcentrated skim milk were similar, with the former having lower flux values at the start of a run than the latter. In spite of this, very little flux decline was observed at these two concentrations. SMC gave the lowest flux values and so indicates the role of a higher concentration of proteins in the formation of a concentration polarisation layer and possibly additional fouling.

The effect of temperature and length of fouling cycles was also successfully studied. Overall, a run time of 3 hours for the processing of skim milk and 4 hours for the processing of SMC at 2.5 bar ΔP_{TM} and 18.5°C is recommended as it appeared that much of the fouling occurred within this time.

Higher operating temperatures (50°C) were found to increase the ultrafiltration flux because of the decreased solubility of certain feed components like proteins, minerals and fats, and the reduced viscosity. Fluxes at higher temperatures undergo a continuous decline for longer periods of time than at lower temperatures, and eventually decline to the flux values obtained at lower temperatures. An operating temperature of 18.5°C was chosen for all runs because solubility of calcium increases at lower temperatures and a larger amount of calcium will permeate the membrane without causing fouling problems. Also, less microbial activity occurs at low temperatures. It would also have been useful to check results at slightly lower temperatures (10-12°C) as is used in commercial plants.

A total of seven cleaning regimes consisting of a non-ionic surfactant, alkaline, acidic and enzymatic detergents, a sanitiser and a new formulated cleaner, were used to clean the membrane after each fouling cycle.

Results indicate that cleaning regimes with surfactant properties showed higher flux recoveries after cleaning than regimes using enzymatic detergents or inorganic cleaners with reduced surfactant properties. This is attributed to the wetting action of the surfactants capable of interacting with protein strands at specific points and solubilising any small loose fragments. A new cleaner DR292 was formulated with more surfactant action than Reflux B610 used as the standard conventional cleaner. While there appeared to be an increase in flux compared to results obtained with the conventional cleaner, t-Tests on these results showed that there was no improvement in using regime G over regime A. It is therefore recommended that a number of experiments using the conventional cleaner, and the new formulation need to be conducted on new membranes or on "new" aged membranes that is, membranes removed from a plant after 1-2 fouling and cleaning cycles, thereby using a "new" membrane for each experiment, to study the cleaning performance of the membrane. This could prove to be expensive on pilot-scale. It may also be useful to confirm the performance of new cleaners at lower temperatures.

Experiments using the non-ionic surfactant and the conventional cleaner produced the highest flux recoveries because the two cleaners together gave rise to a product with a higher level of surfactants.

Enzyme-acid and acid-enzyme regimes did not compare favourably with the other regimes. The role of acid in these regimes was to dissolve minerals while the enzyme removed fat and broke down proteins. It is postulated that the acid in the acid-enzyme regime caused the membrane pores to shrink or the foulant layer to contract thereby restricting the ability of the enzymatic detergent to further penetrate the foulant and remove it. Regimes using the enzymatic detergent followed by the sanitiser produced far better flux recoveries than other sequences using the enzymatic detergent, because the sanitiser was probably capable of removing protein fragments reduced by the enzymatic reaction.

Enzymatic cleaners are attractive in terms of presenting fewer disposal problems than caustic- or acid-based cleaners. Further work needs to be conducted to evaluate the performance of enzyme cleaners on a commercial scale to a point where the membrane's permeability and selectivity can no longer be restored. Enzyme cleaners are probably capable of removing foulants not easily removed by other cleaners. However, the lower flux recovery identified demonstrates that the current view of best practices with regard to these cleaners does not yield optimal cleaning.

A quantitative measure of the rate of decline of membrane cleaning performance was provided using a combination of flux recovery and solute resistance removals. While both generally follow the same trend, high resistance removals did not necessarily coincide with high flux recoveries.

Cleaning effectiveness decreased with subsequent cleaning as was observed with later runs requiring a higher concentration to achieve reasonable flux recovery and not being able to achieve high flux recoveries of previous runs using the same regime. This is attributed to irreversible fouling, the long-term gradual accumulation of recalcitrant material on the membrane, or membrane deterioration and will eventually result in the membrane being removed from service. If membrane life can be increased, significant savings can occur. Plots of concentration versus pH for three cleaners, Reflux B610, Reflux B620 and Reflux R400 showed that as the membrane got progressively fouled, the cleaning concentration had to be increased (due to their buffering capacity) to maintain pH in the effective range.

Finally, a comparison between the pilot plant and an industrial plant showed that flux on the pilot plant modelled that on an industrial scale with reference to temperature and concentration effects. Each plant operated at two different concentration factors and temperatures and flux was lower for higher concentration factors on the industrial plant. However, a greater amount of cleaner was associated with per m^2 of membrane area on the pilot plant as compared with the industrial plant which implies that the pilot plant may need longer cleaning to get the same effect as on the industrial plant, unless cleaning time on the pilot plant was greater than that needed to remove the soil, which was not tested.

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Appendix 1 Operating details for the pilot plant

A1.1 Start-up and Operating procedure

1. All valves (except V12 and V17) were turned off. Valves V12 and V17 were fully opened.

2. The desired flow routes were opened as follows:
   - For recirculation of permeate and retentate flows back to the balance tank, valves V3, V8, and V11 were opened.
   - If permeate was not to be recycled back to the balance tank, valve V7 was opened instead of valve V8. Similarly, if the retentate was not to be recycled back to the balance tank, valve V10 was opened instead of valve V11.

3. The balance tank was filled with product.

4. The feed pump (P1) was turned on and the system was allowed to fill and clear of air bubbles. Pump P2 was turned on and the recirculation loop was allowed to fill and clear of air bubbles.

5. Steady flow conditions were established by adjusting V12, V17, and the feed pump discharge pressure (on pressure gauge PI1). The feed pump discharge pressure was adjusted by turning the feed pump speed control knob. The membrane inlet pressure (on pressure gauge PI2) is the sum of the feed pump discharge pressure plus the recirculation pump pressure.

6. Operating temperature was controlled using valves V4, V15 and V16.

A1.2 Shut-down and CIP procedure

1. When the plant was ready to shut down, both the pumps were turned off.

2. If applicable all cooling was stopped by closing valve V16.

3. Valve V2 was opened and the balance tank contents sent to drain. Valve V14 was briefly opened to rinse the dregs of the feedstock from the balance tank interior to the drain.

4. For a good water flush through the membrane, valve V12 was fully opened, valve V17 was opened about one-third, V8 and V11 were closed while V7 and V10 were opened.

5. Valve V2 was closed and the tank was filled with demineralised water via valve V14.

6. Flush to drain was commenced by turning both pumps on. The membrane inlet pressure was set to 1.5 bar using the feed pump speed control knob. Flush to

drain continued until the retentate and permeate outflows were clean. Valves V8 and V11 were briefly opened in turn to ensure that the outflows were clean.

7. The spring cap/locknut assembly on the pressure relief valve was loosened for 20-30 seconds to flush out the valve spring chamber, the spring cap was then screwed down to its original position and locked in place with the locknut below.

8. Water recirculation conditions were set up by opening valves V8 and V11 and closing V7, V10 and V14. The water level was set to a little below the overflow level. The water recirculating around the plant was heated to the first chemical wash temperature of 50°C by adjusting the flow valves V15 and V16 via the spent water flow regulating valve V4, and then maintaining the CIP temperature.

9. The appropriate alkali cleaner was dosed to the correct pH and then recirculated at 50°C for 15 minutes.

10. Upon completion of the first chemical wash, both the pumps were turned off and the contents of the balance tank, were sent to drain via V2. Valve V14 was briefly opened to rinse the CIP dregs and froth from the interior of the balance tank to the drain.

11. Steps 4 to 7 were repeated until the permeate and retentate outflows were clean and fairly neutral (pH 7-8).

12. Water recirculation conditions were set up and the water was again heated to the second chemical wash temperature (50°C) by repeating step 8.

13. The appropriate acid cleaner was dosed to the correct pH and then recirculated at 50°C for 15 minutes.

14. Steps 10, and 4 to 7 were repeated until the permeate and retentate outflows were clean and fairly neutral (pH 6-7).

15. Water recirculation conditions were set up and the water was again heated to the third chemical wash temperature by repeating step 8.

16. The appropriate alkali cleaner was dosed to the correct pH. The sanitiser was then added until chlorine levels were in the right range, and then recirculated at 50°C for 20 minutes, keeping an eye on the chlorine levels.

17. Steps 10, and 4 to 7 were repeated until the permeate and retentate outflows were clean and fairly neutral (pH 7-8). Temperature of the system was brought down to 25°C, by adjusting the flow valves V15 and V16 via the spent water flow regulating valve V4. Both the pumps were turned off, valve V14 was closed and the balance tank emptied by opening valve V2. Valve V2 was then closed.

Appendix 2 Calibration of the pilot plant (permeate and retentate flowmeters)

Table A2.1. Calibration data for the pilot plant at 25°C using demineralised water

Feed (bar)	Loop (bar)	Ret. (bar)	ΔP_{TM} (bar)	RCF (m^3h^{-1})	R (%)	R_1 (mls^{-1})	R_2 (mls^{-1})	Av.R (Lh^{-1})	P (%)	P_1 (mls^{-1})	P_2 (mls^{-1})	Av.P (Lh^{-1})	Flux (LMH)
0.60	1.50	0.70	1.10	7	92	130.0	130.0	468.0	85	117.3	122.5	431.6	58.3
0.60	1.50	0.70	1.10	7	90	118.0	117.5	423.9	85.5	110.0	128.0	428.4	57.9
0.60	1.50	0.70	1.10	7	80	107.5	113.5	397.8	85	111.0	127.0	428.4	57.9
0.60	1.50	0.70	1.10	7	70	96.0	97.5	348.3	85	128.5	133.0	470.7	63.6
0.69	1.50	0.71	1.11	7	60	78.0	76.0	277.2	80	120.5	126.5	444.6	60.1
0.62	1.50	0.70	1.10	7	50	65.0	63.5	231.3	85	130.5	131.5	471.6	63.7
0.65	1.50	0.70	1.10	7	40	49.5	51.5	181.8	84	115.0	128.0	437.4	59.1
0.62	1.50	0.70	1.10	7	30	37.7	38.0	136.3	84	128.0	125.5	456.3	61.7
0.62	1.50	0.70	1.10	7	20	21.5	22.0	78.3	85	130.0	129.0	466.2	63.0
0.61	1.50	0.69	1.10	7	10	7.5	7.5	27.0	84	128.0	128.5	461.7	62.4
0.85	1.79	0.98	1.39	7	10	7.5	7.3	26.6	100	153.5	156.5	558.0	75.4
0.71	1.61	0.80	1.21	7	10	7.5	7.5	27.0	90	140.5	139.5	504.0	68.1
0.60	1.49	0.65	1.07	7	10	7.2	7.5	26.5	80	125.5	123.0	447.3	60.4
0.49	1.35	0.52	0.94	7	10	7.5	7.5	27.0	70	108.5	109.5	392.4	53.0
0.38	1.20	0.39	0.80	7	10	7.5	7.5	27.0	60	92.5	90.0	328.5	44.4
0.25	1.10	0.25	0.68	7	10	7.5	7.5	27.0	50	58.5	73.5	237.6	32.1
0.85	1.78	0.95	1.37	7	20	22.0	22.0	79.2	100	156.0	154.0	558.0	75.4
0.70	1.61	0.79	1.20	7	20	22.4	22.6	81.0	90	138.0	140.0	500.4	67.6
0.55	1.45	0.62	1.04	7	20	21.5	21.5	77.4	80	121.5	100.0	398.7	53.9
0.42	1.32	0.49	0.91	7	20	21.5	22.4	79.0	70	109.5	107.0	389.7	52.7
0.34	1.20	0.35	0.78	7	20	21.5	21.5	77.4	60	85.5	89.0	314.1	42.4
0.22	1.10	0.22	0.66	7	20	21.5	21.5	77.4	50	75.0	71.0	262.8	35.5
0.82	1.75	0.91	1.33	7	30	37.5	37.4	134.8	100	156.0	153.0	556.2	75.2
0.68	1.60	0.75	1.18	7	30	36.5	37.4	133.0	90	135.0	140.0	495.0	66.9
0.58	1.50	0.65	1.08	7	30	37.0	37.5	134.1	80	124.0	119.5	438.3	59.2
0.45	1.35	0.51	0.93	7	30	37.0	37.5	134.1	70	110.5	106.0	389.7	52.7
0.35	1.25	0.39	0.82	7	30	36.5	36.5	131.4	60	89.5	75.0	296.1	40.0
0.25	1.11	0.25	0.68	7	30	36.0	37.5	132.3	50	75.0	79.5	278.1	37.6
0.80	1.75	0.89	1.32	7	40	50.5	53.0	186.3	100	162.5	154.0	569.7	77.0
0.65	1.59	0.72	1.16	7	40	59.5	49.5	196.2	90	138.0	140.5	501.3	67.7
0.52	1.45	0.60	1.03	7	40	52.5	52.5	189.0	80	125.0	122.5	445.5	60.2
0.42	1.35	0.49	0.92	7	40	50.0	50.5	180.9	70	105.0	110.5	387.9	52.4
0.31	1.21	0.35	0.78	7	40	48.5	55.0	186.3	60	90.0	90.5	324.9	43.9
0.22	1.10	0.22	0.66	7	40	48.0	44.0	165.6	50	75.0	74.5	269.1	36.4
0.82	1.79	0.92	1.36	7	50	66.0	65.5	236.7	100	156.0	156.0	561.6	75.9
0.68	1.61	0.75	1.18	7	50	66.5	67.5	241.2	90	145.5	137.5	509.4	68.8
0.58	1.51	0.65	1.08	7	50	65.5	66.0	236.7	80	125.5	122.5	446.4	60.3
0.44	1.35	0.51	0.93	7	50	64.5	64.0	231.3	70	109.5	110.5	396.0	53.5
0.30	1.21	0.35	0.78	7	50	66.0	65.5	236.7	60	91.0	89.7	325.3	44.0

Feed (bar)	Loop (bar)	Ret. (bar)	ΔP_{TM} (bar)	RCF (m^3h^{-1})	R (%)	R_1 (mls^{-1})	R_2 (mls^{-1})	Av.R (Lh^{-1})	P (%)	P_1 (mls^{-1})	P_2 (mls^{-1})	Av.P (Lh^{-1})	Flux (LMH)
0.82	1.78	0.90	1.34	7	60	79.0	80.5	287.1	100	155.0	156.0	559.8	75.6
0.69	1.61	0.75	1.18	7	60	76.0	78.0	277.2	90	138.0	140.5	501.3	67.7
0.58	1.51	0.66	1.09	7	60	82.5	76.0	285.3	80	117.0	121.0	428.4	57.9
0.49	1.40	0.55	0.98	7	60	82.0	86.5	303.3	70	98.0	93.5	344.7	46.6
0.32	1.29	0.40	0.85	7	60	75.5	75.0	270.9	60	83.0	91.5	314.1	42.4
0.90	1.81	0.95	1.38	7	70	90.5	93.5	331.2	100	160.0	149.5	557.1	75.3
0.72	1.65	0.75	1.20	7	70	92.4	97.0	340.9	90	141.0	142.0	509.4	68.8
0.58	1.50	0.65	1.08	7	70	90.5	98.0	339.3	80	124.5	117.5	435.6	58.9
0.45	1.41	0.58	1.00	7	70	95.0	95.0	342.0	70	105.5	106.5	381.6	51.6
0.95	1.88	1.02	1.45	7	80	112.5	111.5	403.2	100	157.5	149.0	551.7	74.6
0.78	1.71	0.88	1.30	7	80	110.5	111.5	399.6	90	139.0	131.5	486.9	65.8
0.62	1.55	0.71	1.13	7	80	102.0	108.0	378.0	80	124.5	120.5	441.0	59.6
0.72	1.65	0.80	1.23	7	90	124.0	124.5	447.3	90	135.0	135.5	486.9	65.8
2.00	2.10	2.10	2.10	-	60	93.3	93.3	336.0	>100	220.0	220.0	792.0	107.0

Table A2.2. Calibration data for the pilot plant at 50°C using demineralised water

Feed (bar)	Loop (bar)	Ret. (bar)	ΔP_{TM} (bar)	RCF (m^3h^{-1})	R (%)	R_1 (mls^{-1})	R_2 (mls^{-1})	Av.R (Lh^{-1})	P (%)	P_1 (mls^{-1})	P_2 (mls^{-1})	Av.P (Lh^{-1})	Flux (LMH)
0.55	1.50	0.58	1.04	7	10	8.5	8.5	30.6	100	162.5	146.0	555.3	75.0
0.42	1.35	0.45	0.90	7	10	8.0	8.0	28.8	90	145.5	144.5	522.0	70.5
0.38	1.29	0.36	0.83	7	10	8.4	8.4	30.2	80	135.5	130.5	478.8	64.7
0.29	1.19	0.25	0.72	7	10	9.0	9.5	33.3	70	113.5	188.5	543.6	73.5
0.30	1.15	0.25	0.70	7	10	8.0	8.0	28.8	60	89.0	86.5	315.9	42.7
0.98	1.10	1.10	1.10	-	20	24.0	24.0	86.4	100	165.0	155.0	576.0	77.8
0.54	1.49	0.55	1.02	7	20	23.5	24.0	85.5	100	161.5	140.0	542.7	73.3
0.45	1.39	0.48	0.94	7	20	24.0	24.0	86.4	90	147.0	146.5	528.3	71.4
0.39	1.29	0.39	0.84	7	20	24.0	24.0	86.4	80	125.5	104.0	413.1	55.8
0.34	1.20	0.31	0.76	7	20	23.0	23.5	83.7	70	113.5	92.5	370.8	50.1
0.28	1.11	0.20	0.66	7	20	23.0	23.5	83.7	60	93.5	70.0	294.3	39.8
0.56	1.50	0.60	1.05	7	30	39.0	40.5	143.1	100	160.5	164.0	584.1	78.9
0.49	1.40	0.49	0.95	7	30	39.0	37.5	137.7	90	128.0	145.5	492.3	66.5
0.40	1.29	0.38	0.84	7	30	38.5	40.0	141.3	80	126.0	124.0	450.0	60.8
0.31	1.20	0.30	0.75	7	30	39.0	39.5	141.3	70	113.5	88.0	362.7	49.0
0.58	1.50	0.58	1.04	7	40	29.0	29.0	104.4	100	158.0	138.5	533.7	72.1
0.48	1.39	0.48	0.94	7	40	29.0	29.5	105.3	90	141.0	137.5	501.3	67.7
0.40	1.29	0.39	0.84	7	40	29.5	29.7	106.6	80	131.5	103.0	422.1	57.0
0.32	1.21	0.30	0.76	7	40	29.0	29.7	105.7	70	107.0	111.5	393.3	53.1
0.60	1.50	0.60	1.05	7	50	67.5	68.5	244.8	100	154.5	164.0	573.3	77.5
0.50	1.39	0.50	0.95	7	50	73.0	70.5	258.3	90	147.0	145.0	525.6	71.0
0.40	1.30	0.40	0.85	7	50	69.5	68.5	248.4	80	130.5	128.5	466.2	63.0

Feed (bar)	Loop (bar)	Ret. (bar)	ΔP_{TM} (bar)	RCF (m^3h^{-1})	R (%)	R_1 (mls^{-1})	R_2 (mls^{-1})	Av.R (Lh^{-1})	P (%)	P_1 (mls^{-1})	P_2 (mls^{-1})	Av.P (Lh^{-1})	Flux (LMH)
0.60	1.50	0.60	1.05	7	60	82.5	82.0	296.1	100	164.5	161.5	586.8	79.3
0.50	1.39	0.50	0.95	7	60	84.5	81.0	297.9	90	139.5	141.0	504.9	68.2
0.52	1.50	0.55	1.03	7	70	94.5	99.0	348.3	100	152.0	148.0	540.0	73.0
0.58	1.50	0.61	1.06	7	80	-	-	-	100	155.5	154.5	558.0	75.4

Table A2.3. Nomenclature

Symbol	Description	Units
Time	Time each reading was taken	min.
Feed	Feed pump pressure	bar
Loop	Membrane inlet pressure	bar
Ret.	Membrane outlet pressure	bar
Per.	Permeate pressure	bar
ΔP_{TM}	Transmembrane pressure	bar
RCF	Recirculation flow rate	m^3h^{-1}
R	Retentate flow rate on Retentate Rotameter	%
R_1	Retentate flow rate reading 1	mL/4s
R_2	Retentate flow rate reading 2	mL/4s
Av.R	Average retentate flow rate	Lh^{-1}
P	Permeate flow rate on Permeate Rotameter	%
P_1	Permeate flow rate reading 1	mL/5s
P_2	Permeate flow rate reading 2	mL/5s
Av.P	Average permeate flow rate	Lh^{-1}
Flux	Permeate flux	LMH
λ	Conductivity reading	µs
Temp.	Temperature of feed solution (read off pH meter)	°C
pHB	pH before cleaning	
pHA	pH after cleaning	
$Cl._{soln}$	Cleaning solution used	
$Cl._{conc}$	Concentration of cleaning solution	%v/v
$Cl._{vol.}$	Volume of cleaning solution used	mL
Flux R.	Flux recovery	%
T.S.	Total Solids	%
F/P ratio	Fat-Protein Ratio	
R_m	Hydraulic membrane resistance	m^{-1}
R_{sw}	Residual solute resistance of the fouled membrane	m^{-1}
R_{sc}	Residual solute resistance of the clean membrane	m^{-1}
SRR	Solute Resistance removal	%

Appendix 3 Calibration of the FOSS NIRSystems LiquiFlow Analyser (NLA)

Table A3.1 Calibration data for the FOSS NIRSystems Analyser using skim milk powder (SMP) samples.

	10% SMP	15% SMP	20% SMP
Fat (%)	0.093	0.100	0.103
Protein (%)	3.227	4.480	5.745
Lactose (%)	2.779	5.774	8.641
T.S. (%)	9.544	13.120	16.677
F/P ratio	0.029	0.022	0.018

Appendix 4 Titration data for Reflux chemicals

Table A4.1 Titration data for Reflux B610 at 25°C

mLs added	conc.	pH	mLs added	conc.	pH	mLs added	conc.	pH
0% SMP	%w/v	0% SMP	0.1% SMP	%w/v	0.1% SMP	1% SMP	%w/v	1% SMP
0.0	0.0000	6.53	0.0	0.0000	7.22	0.0	0.0000	7.04
0.1	0.0125	11.18	0.1	0.0167	11.08	0.1	0.0167	9.14
0.2	0.0250	11.45	0.2	0.0333	11.28	0.2	0.0333	10.3
			0.3	0.0500	11.55	0.3	0.0500	10.8
						0.7	0.1167	11.47
						0.8	0.1333	11.53

Table A4.2 Titration data for Reflux B620 at 25°C

mLs added	conc.	pH	mLs added	conc.	pH	mLs added	conc.	pH
0% SMP	%w/v	0% SMP	0.1% SMP	%w/v	0.1% SMP	1% SMP	%w/v	1% SMP
0.0	0.0000	6.3	0.0	0.0000	7.23	0.0	0.0000	7.02
0.1	0.0167	10.37	0.2	0.0333	10.36	0.2	0.0333	7.91
0.2	0.0333	10.81	0.3	0.0500	10.69	0.4	0.0667	9.28
0.3	0.0500	10.97	0.4	0.0667	10.84	0.6	0.1000	9.88
0.5	0.0833	11.14	0.6	0.1000	11.05	0.8	0.1333	10.17
0.6	0.1000	11.23	0.8	0.1333	11.20	1.0	0.1667	10.40
0.8	0.1333	11.37	1.0	0.1667	11.33	1.2	0.2000	10.56
1.0	0.1667	11.43	1.2	0.2000	11.39	1.4	0.2333	10.67
1.2	0.2000	11.52	1.5	0.2500	11.49	1.6	0.2667	10.79
						1.8	0.3000	10.89
						2.1	0.3500	11.00
						2.4	0.4000	11.10
						2.7	0.4500	11.18
						3.0	0.5000	11.27
						3.3	0.5500	11.33
						3.6	0.6000	11.38
						4.0	0.6667	11.46
						4.3	0.7167	11.52

Table A4.3 Titration data for Reflux R400 at 25°C

mLs added	**conc.**	**pH**	**mLs added**	**conc.**	**pH**	**mLs added**	**conc.**	**pH**
0% SMP	%w/v	0% SMP	0.1% SMP	%w/v	0.1% SMP	1% SMP	%w/v	1% SMP
0.0	0.0000	6.61	0.0	0.0000	7.28	0.0	0.0000	7.05
0.1	0.0167	2.85	0.2	0.0333	2.69	0.2	0.0333	5.66
0.2	0.0333	2.56	0.4	0.0667	2.40	0.4	0.0667	4.03
0.3	0.0500	2.43	0.6	0.1000	2.22	0.7	0.1167	2.85
0.5	0.0833	2.24	0.8	0.1333	2.10	0.9	0.1500	2.49
0.7	0.1167	2.10	1.0	0.1667	2.01	1.1	0.1833	2.32
0.9	0.1500	2.01	1.2	0.2000	1.93	1.3	0.2167	2.18
1.1	0.1833	1.93	1.5	0.2500	1.84	1.5	0.2500	2.06
1.3	0.2167	1.90	1.7	0.2833	1.79	1.8	0.3000	1.94
1.5	0.2500	1.83				2.0	0.3333	1.89
1.7	0.2833	1.78				2.3	0.3833	1.82
						2.5	0.4167	1.78

Appendix 5 Industrial plant flux data

Table A5.1 Flux data for the industrial plant

Flux (LMH)	Temperature correction factor	Pressure correction factor	Corrected flux (LMH)
10.7	1.441	1.000	15.4
11.4	1.441	0.897	14.7
12.2	1.441	0.920	16.2
11.7	1.441	0.970	16.4
11.9	1.441	0.870	14.9
11.8	1.441	1.000	17.0
11.8	1.441	0.950	16.2
11.3	1.441	1.000	16.3
11.4	1.441	0.870	14.2
13.0	1.441	0.810	15.2
10.9	1.441	0.810	12.7

$$\text{Flux} = \frac{\text{permeate flow } (lh^{-1})}{\text{membrane area } (m^2)}$$

Membrane area Stage 1 = 852.6 m^2
Stage 2 = 730.8 m^2

Corrected Flux = Flux * Ft * Pt

Ft = Temperature correction factor
= 1.441 at 10°C

Pt = Pressure correction factor
= 345 / P*101.2

P = baseline pressure (barg)

Appendix 6 t-Tests

1. t-Test to determine if fouling during Run 24 and Run 35 was reproducible

Time min.	Flux (LMH) Run 24	Flux (LMH) Run 35	d	$D-d_i$	$(D-d_i)^2$
0	20.3	19.1	-1.2	1.1	1.3
5	20.6	18.7	-1.9	1.8	3.4
10	20.4	18.5	-1.9	1.8	3.4
15	20.2	18.4	-1.8	1.7	3.0
20	19.8	18.7	-1.1	1.0	1.1
30	18.97	18.3	-0.67	0.6	0.4
40	19.3	20.0	0.7	-0.8	0.6
50	19.2	18.5	-0.7	0.6	0.4
60	17.5	18.2	0.7	-0.8	0.6
100	17.4	19.4	2	-2.1	4.2
120	16.9	18.5	1.6	-1.7	2.8
140	16.7	18.3	1.6	-1.7	2.8
160	16.8	18.7	1.9	-2.0	3.8
n	13	13			
mean (x)	18.77	18.72			
s	1.503	0.51			
D			0.06		
$(D-d_i)^2$					27.7

Null Hypothesis **Ho:** There is no difference between the two runs, that is, fouling is reproducible

Alternative Hypothesis **Ha:** Fouling is not comparable in the two runs

The standard deviation of the differences, $s_d = \sqrt{\frac{(D-d_i)^2}{n-1}}$

$s_d = 1.520$

Paired t-test $t = \frac{D\sqrt{n}}{s_d}$

$t = 0.14$

$t_{crit} = 3.055$ @ 1% $\Rightarrow$ $t<t_{crit}$ $\Rightarrow$ Accept Ho (two-tailed t-test)

$t_{crit} = 2.179$ @ 5% $\Rightarrow$ $t<t_{crit}$ $\Rightarrow$ Accept Ho (two-tailed t-test)

Therefore, the membrane was reproducibly fouled during the processing of skim milk (Run 24) and skim milk concentrated to VCF 2 (Run 35).

2. t-Test to determine if fouling increased with time during Run 22 and Run 2

Time min.	Flux (LMH) Run 22	Flux (LMH) Run 2	d	$D-d_i$	$(D-d_i)^2$
0	12.9	11.2	-1.7	1.0	1.0
5	12.9	12.1	-0.8	0.1	0.0
10	12.6	12.4	-0.2	-0.5	0.2
15	12.5	12.6	0.1	-0.8	0.6
20	12.6	12.2	-0.4	-0.3	0.1
30	12.4	11.7	-0.7	0.0	0.0
40	12.3	11.7	-0.6	-0.1	0.0
50	13.1	11.9	-1.2	0.5	0.3
60	12.4	11.8	-0.6	-0.1	0.0
80	12.04	11.7	-0.34	-0.3	0.1
100	12.5	11.2	-1.3	0.6	0.4
120	12.2	11.7	-0.5	-0.2	0.0
n	12	12			
mean (x)	12.54	11.85			
s	0.308	0.425			
D			0.69		
$(D-d_i)^2$					2.8

Null Hypothesis **Ho:** There is no difference between the two runs, that is, flux does not change

Alternative Hypothesis **Ha:** Flux increases with time, that is, more fouling

The standard deviation of the differences, $s_d = \sqrt{\frac{(D-d_i)^2}{n-1}}$

$s_d = 0.504$

Paired t-test $t = \frac{D\sqrt{n}}{s_d}$

$t = 4.74$

$t_{crit} = 2.718$ @ 1% $\Rightarrow$ $t > t_{crit}$ $\Rightarrow$ Reject Ho (one-tailed t-test)

$t_{crit} = 1.796$ @ 5% $\Rightarrow$ $t > t_{crit}$ $\Rightarrow$ Reject Ho (one-tailed t-test)

There is a significant difference between the two runs at the 1 and 5% probability levels. Therefore, flux increases with time.

3. t-Test to determine if fouling with water (Run 43) at 18.5°C and skim milk (Run 12) at 50°C was comparable

Time min.	Flux (LMH) Run 43	Flux (LMH) Run 12	d	$D-d_i$	$(D-d_i)^2$
0	105.2	36.5	-68.7	-7.9	62.2
5	107.6	28.5	-79.1	2.5	6.3
10	106.4	28.7	-77.7	1.1	1.2
15	105.2	29.9	-75.3	-1.3	1.7
20	100.3	26.8	-73.5	-3.1	9.5
30	100.9	25.1	-75.8	-0.8	0.6
40	99.7	24.1	-75.6	-1.0	1.0
50	100.9	25.5	-75.4	-1.2	1.4
60	105.2	26.5	-78.7	2.1	4.5
120	102.2	23.8	-78.4	1.8	3.3
140	98.5	24.1	-74.4	-2.2	4.8
160	100.9	22.1	-78.8	2.2	4.9
180	102.7	18.5	-84.2	7.6	58
n	13	13			
mean (x)	102.7	26.2			
s	2.87	4.32			
D			76.6		
$(D-d_i)^2$					159.3

Null Hypothesis **Ho:** There is no difference between the two runs as a result of temperature differences

Alternative Hypothesis **Ha:** Temperature influences the nature of fouling

The standard deviation of the differences, $s_d = \sqrt{\frac{(D-d_i)^2}{n-1}}$

$s_d = 3.64$

Paired t-test $t = \frac{D\sqrt{n}}{s_d}$

$t = 75.78$

$t_{crit} = 3.055$ @ 1% $\Rightarrow$ $t > t_{crit}$ $\Rightarrow$ Reject Ho (two-tailed t-test)

$t_{crit} = 2.179$ @ 5% $\Rightarrow$ $t > t_{crit}$ $\Rightarrow$ Reject Ho (two-tailed t-test)

There is a significant difference between the two runs at the 1 and 5% probability levels, indicating the influence of temperature in changing the nature of fouling.

4. t-Test to compare runs using regime A and G after fouling with concentrated skim milk (VCF 2)

	Regime G Runs 36-40 (Sample 1)	Regime A Runs 31-35 (Sample 2)
	92.9	89
	90.5	81.2
	84.9	85.9
	85.1	85.9
	84.6	81.2
n	5	5
mean (x)	87.6	84.6
s	3.84	3.39

Null Hypothesis **Ho:** There is no difference between regimes A & G

Alternative Hypothesis **Ha:** There is an improvement in using regime G over regime A

The pooled standard deviation,

$$s_p = \sqrt{\frac{(n_1 - 1)s_1^2 + (n_2 - 1)s_2^2}{n_1 + n_2 - 2}}$$

$$s_p = \sqrt{\frac{4x3.84^2 + 4x3.39^2}{5+5-2}}$$

$$s_p = 3.62$$

Two sample t-test

$$t = \frac{x_1 - x_2}{s_p\sqrt{1/n_1 + 1/n_2}}$$

$$t = 1.29$$

t_{crit} = 2.896 @ 1%	⇒	$t<t_{crit}$	⇒	Accept Ho (one-tailed t-test)
t_{crit} = 1.86 @ 5%	⇒	$t<t_{crit}$	⇒	Accept Ho (one-tailed t-test)
t_{crit} = 1.397 @ 10%	⇒	$t<t_{crit}$	⇒	Accept Ho (one-tailed t-test)

The observed value of 1.29 is less than the P = 0.01, 0.05 and 0.10 values. At the 1, 5 and 10% probability levels, it is safe to say that there is no improvement in using regime G over regime A.

Appendix 7 Summary of experiments using cleaning regimes A,B,C,D,E,F, and G

Table A7.1 Summary of experiments using cleaning regime A after fouling at 18.5°C

Run No.	Feed	Feed volume	Duration of fouling	Av. ΔP_{TM}	Av. Temp.	Av. λ	Av.R	Av. pH	Cl. vol.	J_{wc}	Flux R.	R_{sw}	R_{sc}	SRR	pH	Alkali		pH	Acid		pH	Sanitiser			
																B610	B610		R400	R400		B610	B610	S800	S800
		(L)	(hr)	bar	(°C)	(μs)	(Lh^{-1})		(L)	(LMH)	(%)	(x 10^{13} m^{-1})	(x 10^{12} m^{-1})	(%)		(mL)	(%v/v)		(mL)	(%v/v)		(mL)	(%v/v)	(mL)	(ppm)
0	skim milk	55	3	2.50	25.7	4250.0	282.1	6.54	60	89.6	83.8	3.54	1.47	96.0	10.80	41	0.070	1.93	90	0.150	11.20	14	0.023	156	248
24	skim milk	54	3	2.51	18.5	4244.7	260.9	6.77	60	83.9	78.4	2.60	2.33	91.0	11.27	68.5	0.114	1.78	102.5	0.171	11.40	64	0.107	180	204
1	SMC	55	2	2.52	18.1	3890.0	215.4	6.52	60	87.3	81.6	2.28	1.60	93.0	10.83	22	0.037	1.87	48	0.080	11.17	21	0.035	133	196
2	SMC	53	2	2.52	16.7	3910.0	214.4	6.20	60	83.9	78.4	2.62	2.08	92.0	11.00	20	0.033	1.97	42	0.070	11.20	18	0.03	128	200
3	SMC	55	4	2.52	18.8	3815.6	217.3	6.74	60	83.7	78.2	3.06	2.26	93.0	11.35	31	0.052	1.97	45	0.075	11.11	14	0.022	139	200
4	SMC	53	2	2.51	18.5	3566.7	226.2	6.61	40	69.3	64.8	2.58	4.43	83.0	10.91	11	0.028	2.04	35	0.088	11.16	3	0.008	100	200
5	SMC	55	2	2.54	18.6	3746.7	222.2	6.83	40	58.9	55.0	3.34	6.59	80.0	11.20	14	0.035	1.97	35	0.088	11.00	5	0.013	95	184
22	SMC	46	4	2.51	18.6	3801.2	213.4	6.82	60	94.9	88.7	2.48	1.08	96.0	11.49	78	0.130	1.80	116	0.193	11.51	73	0.122	170	176

Table A7.2 Summary of experiments using cleaning regime A after fouling at 50°C

Run No.	Feed	Feed volume	Duration of fouling	Av. ΔP_{TM}	Av. Temp.	Av. λ	Av.R	Av. pH	Cl. vol.	J_{wc}	Flux R.	R_{sw}	R_{sc}	SRR	pH	Alkali		pH	Acid		pH	Sanitiser			
																B610	B610		R400	R400		B610	B610	S800	S800
		(L)	(hr)	bar	(°C)	(μs)	(Lh^{-1})		(L)	(LMH)	(%)	(x 10^{13} m^{-1})	(x 10^{12} m^{-1})	(%)		(mL)	(%v/v)		(mL)	(%v/v)		(mL)	(%v/v)	(mL)	(ppm)
12	skim milk	55	3	2.51	49.5	4745.8	285.1	6.67	60	87.8	82.1	0.44	1.73	61.0	11.40	98	0.163	1.82	184	0.307	11.42	130	0.217	129	176
21	SMC	55	4	2.51	48.3	4591.2	251.3	6.60	60	76.6	71.6	9.52	3.20	97.0	11.36	99	0.165	1.88	193	0.322	11.47	130	0.217	130	72
23	SMC	55	4	2.52	49.8	4626.7	249.9	6.50	60	82.5	77.1	6.96	2.43	97.0	11.45	75	0.125	1.61	155	0.220	11.48	69	0.115	185	196

Table A7.3 Summary of experiments using cleaning regime B

Run No.	Feed	Feed volume	Duration of fouling	Av. ΔP_{TM}	Av. Temp.	Av. λ	Av.R	Av. pH	Cl. vol.	J_{wc}	Flux R.	R_{sw}	R_{sc}	SRR	pH	Alkali		pH	Acid		pH	Sanitiser			
																B620	B620		R400	R400		B620	B620	S800	S800
		(L)	(hr)	bar	(°C)	(μs)	(Lh^{-1})		(L)	(LMH)	(%)	(x 10^{13} m^{-1})	(x 10^{12} m^{-1})	(%)		(mL)	(%v/v)		(mL)	(%v/v)		(mL)	(%v/v)	(mL)	(ppm)
9	skim milk	53	3	2.50	19.4	-	268.6	6.88	60	93.4	87.3	2.35	1.18	95.0	11.24	100	0.167	1.72	85	0.142	11.14	83	0.138	149	-
11	skim milk	55	3	2.50	18.5	4083.6	271.4	6.82	60	94.9	88.6	2.59	1.12	96.0	11.00	289	0.482	1.80	191	0.318	11.00	305	0.508	137.5	226
13	skim milk	54	6	2.52	18.4	3983.7	268.7	6.83	60	92.9	86.8	2.44	1.29	95.0	11.14	350	0.583	1.63	280	0.467	11.34	335	0.558	143	240
25	skim milk	46	6	2.50	18.5	4154.4	265.9	6.85	60	88.1	82.3	3.02	1.80	94.0	11.32	335	0.560	1.77	200	0.330	11.50	295	0.492	355	248
6	SMC	54	4	2.50	18.4	2152.4	271.0	7.01	60	49.6	46.4	6.63	9.16	86.0	10.70	56	0.093	2.01	49	0.082	9.78	61	0.102	150	-
7	SMC	54	4	2.50	18.9	3600.0	226.7	6.81	60	83.9	78.4	4.40	3.11	93.0	11.20	96	0.160	1.80	66	0.110	11.20	94	0.157	150	-
8	SMC	54	4	2.50	22.8	3800.0	229.2	6.81	60	88.5	82.7	3.60	1.65	95.0	11.14	106	0.177	1.77	68	0.113	11.20	100	0.167	152	-
10	SMC	45	4	2.50	23.4	-	258.1	6.83	60	85.9	80.3	2.95	2.00	93.0	11.20	103	0.172	1.75	76	0.127	11.16	92	0.153	148	-

Table A7.4 Summary of experiments using cleaning regime C

Run No.	Feed	Feed volume	Duration of fouling	Av. ΔP_{TM}	Av. Temp.	Av. λ	Av.R	Av. pH	Cl. vol.	J_{wc}	Flux R.	R_{sw}	R_{sc}	SRR	pH	Alkali				pH	Acid		pH	Sanitiser		
																A230	A230	B610	B610		R400	R400		B610	B610	S800
		(L)	(hr)	bar	(°C)	(μs)	(Lh^{-1})		(L)	(LMH)	(%)	(x 10^{13} m^{-1})	(x 10^{12} m^{-1})	(%)		(mL)	(%v/v)	(mL)	(%v/v)		(mL)	(%v/v)		(mL)	(%v/v)	(mL)
14	skim milk	56	3	2.50	18.1	4304.3	267.1	6.80	60	97.8	91.4	2.63	0.79	97.0	11.34	60	0.100	83	0.138	1.78	180	0.300	11.42	93	0.155	100
15	skim milk	51	3	2.51	18.2	4241.4	265.2	6.85	60	93.4	87.3	3.18	1.22	96.0	11.32	120	0.200	75	0.125	1.85	180	0.300	11.30	75	0.125	110
16	skim milk	55	3	2.51	18.5	4394.3	267.9	6.82	60	100.0	93.4	2.59	0.58	98.0	11.33	120	0.200	75	0.125	1.84	180	0.300	11.28	74.8	0.125	115
20	SMC	52.5	4	2.51	19.9	3838.2	223.5	6.79	60	100.2	93.7	2.53	0.64	97.0	11.30	60	0.100	74	0.123	1.85	180	0.300	11.30	74	0.123	120
41	SMC	51	4	2.54	18.6	3922.5	214.3	6.86	60	86.4	80.7	2.37	1.92	92.0	11.36	120	0.200	72	0.120	1.78	292.5	0.488	11.37	72	0.120	155

Table A7.5 Summary of experiments using cleaning regime D

Run No.	Feed	Feed volume	Duration of fouling	Av. ΔP_{TM}	Av. Temp.	Av. λ	Av.R	Av. pH	Cl. vol.	J_{wc}	Flux R.	R_{sw}	R_{sc}	SRR	pH	Enzymatic		pH	Sanitiser			
																E1000	E1000		B610	B610	S800	S800
		(L)	(hr)	bar	(°C)	(μs)	(Lh^{-1})		(L)	(LMH)	(%)	(x 10^{13} m^{-1})	(x 10^{12} m^{-1})			(mL)	(%v/v)		(mL)	(%v/v)	(mL)	(ppm)
17	skim milk	55.5	3	2.51	19.3	4570.0	266.4	6.81	60	93.4	87.3	2.63	1.06	96.0	9.01	120	0.200	11.30	65	0.108	95	136
18	skim milk	54	3	2.50	19.0	4312.9	262.9	6.84	60	93.4	87.3	2.18	1.14	95.0	9.02	120	0.200	11.23	55	0.092	80	116
42	skim milk	45	3	2.50	18.3	4226.4	263.8	6.97	60	81.5	76.2	2.32	2.58	89.0	9.76	120	0.200	11.49	73.5	0.122	162.5	200
29	SMC	52.5	4	2.51	18.6	3875.9	203.6	6.67	60	73.2	68.4	2.60	3.74	86.0	9.13	120	0.200	11.49	70	0.120	145	196

Table A7.6 Summary of experiments using cleaning regime E

Run No.	Feed	Feed volume	Duration of fouling	Av. ΔP_{TM}	Av. Temp.	Av. λ	Av.R	Av. pH	Cl. vol.	J_{wc}	Flux R.	R_{sw}	R_{sc}	SRR	pH	Enzymatic		pH	Acid	
																E1000	E1000		R400	R400
		(L)	(hr)	bar	(°C)	(μs)	(Lh^{-1})		(L)	(LMH)	(%)	(x 10^{13} m^{-1})	(x 10^{12} m^{-1})	(%)		(mL)	(%v/v)		(mL)	(%v/v)
19	skim milk	55	3	2.50	18.8	4535.7	264.5	6.80	60	84.4	78.9	2.45	2.19	91.0	9.02	120	0.200	1.86	181	0.302
28	skim milk	55	3	2.51	18.4	4341.4	244.9	6.42	60	64.2	60.0	5.44	5.05	91.0	8.80	120	0.200	1.79	337.5	0.560
30	SMC	55	4	2.51	19.1	3913.5	203.2	6.86	60	67.1	62.7	2.79	4.77	83.0	9.17	120	0.200	1.77	250	0.417

Table A7.7 Summary of the experiment using cleaning regime F

Run No.	Feed	Feed volume	Duration of fouling	Av. ΔP_{TM}	Av. Temp.	Av. λ	Av.R	Av. pH	Cl. vol.	J_{wc}	Flux R.	R_{sw}	R_{sc}	SRR	pH	Acid		pH	Enzymatic	
																R400	R400		E1000	E1000
		(L)	(hr)	bar	(°C)	(μs)	(Lh^{-1})		(L)	(LMH)	(%)	(x 10^{13} m^{-1})	(x 10^{12} m^{-1})	(%)		(mL)	(%v/v)		(mL)	(%v/v)
27	skim milk	51.5	3	2.50	18.3	4435.0	262.1	6.47	60	74.2	69.3	2.50	3.62	86.0	2.01	315	0.525	8.76	120	0.200

Table A7.8 Summary of experiments using cleaning regimes A and G

Run No.	Feed	Feed volume	Duration of fouling	Av. ΔP_{TM}	Av. Temp.	Av. λ	Av.R	Av. pH	Cl. vol.	J_{wc}	Flux R.	R_{sw}	R_{sc}	SRR	pH	Alkali		pH	Acid		pH	Sanitiser			
																B610	B610		R400	R400		B610	B610	S800	S800
		(L)	(hr)	bar	(°C)	(μs)	(Lh^{-1})		(L)	(LMH)	(%)	(x 10^{13} m^{-1})	(x 10^{12} m^{-1})	(%)		(mL)	(%v/v)		(mL)	(%v/v)		(mL)	(%v/v)	(mL)	(ppm)
31	skim milk	32.5	3	2.50	18.6	4205.7	247.4	6.96	60	89.0	83.2	2.75	1.69	94.0	11.52	88	0.147	1.83	225	0.375	11.45	69	0.115	175	212
32	skim milk	25.5	3	2.51	18.5	4111.3	256.9	6.90	60	81.2	75.9	2.21	2.59	88.0	11.40	67	0.112	1.85	217.5	0.363	11.43	66	0.110	188.5	246
33	skim milk	31.25	3	2.51	18.5	4282.1	250.4	6.93	60	85.9	80.2	2.49	1.98	92.0	11.42	70.5	0.118	1.80	234	0.390	11.43	66	0.110	195	208
34	skim milk	28	3	2.50	18.7	4246.2	253.6	6.93	60	85.9	80.2	2.47	2.07	92.0	11.43	71	0.118	1.82	237.5	0.396	11.44	66	0.110	200	212
35	skim milk	27.5	3	2.50	18.7	4166.4	254.1	6.95	60	81.2	75.9	2.51	2.61	90.0	11.43	71	0.118	1.81	240	0.400	11.44	67	0.112	180	200
26	SMC	32.5	1.67	2.50	18.6	3614.0	222.1	6.65	60	90.7	84.8	2.72	1.64	94.0	11.27	96	0.160	1.80	130	0.216	11.45	93	0.155	195	216

Run No.	Feed	Feed volume	Duration of fouling	Av. ΔP_{TM}	Av. Temp.	Av. λ	Av.R	Av. pH	Cl. vol.	J_{wc}	Flux R.	R_{sw}	R_{sc}	SRR	pH	Alkali		pH	Acid		pH	Sanitiser			
																DR292	DR292		R400	R400		DR292	DR292	S800	S800
		(L)	(hr)	bar	(°C)	(μs)	(Lh^{-1})		(L)	(LMH)	(%)	(x 10^{13} m^{-1})	(x 10^{12} m^{-1})	(%)		(mL)	(%v/v)		(mL)	(%v/v)		(mL)	(%v/v)	(mL)	(ppm)
36	skim milk	27	3	2.51	18.6	4125.0	255.5	6.97	60	92.9	86.8	2.18	1.31	94.0	11.20	224	0.373	1.80	254	0.423	11.18	180	0.300	147.5	174
37	skim milk	32.5	3	2.51	18.3	4284.7	255.3	6.85	60	90.5	84.6	2.42	1.88	92.0	11.18	211	0.350	1.78	257.5	0.430	11.20	177	0.295	175	236
38	skim milk	26	3	2.50	18.4	4110.0	254.6	6.87	60	84.9	79.3	2.54	2.16	92.0	11.17	204	0.340	1.81	245	0.408	11.26	200	0.330	152.5	200
39	skim milk	30	3	2.50	18.4	4238.0	251.2	6.84	60	85.1	79.6	2.22	2.11	91.0	11.29	267	0.445	1.80	250	0.417	11.33	251	0.418	155	200
40	skim milk	32.5	3	2.51	18.6	4315.7	250.2	6.92	60	84.6	79.1	2.29	2.26	90.0	11.28	265	0.442	1.80	250	0.417	11.35	252.5	0.421	250	200

Table A7.9 Summary of the experiment using demineralised water

Run No.	Feed	Feed volume	Duration of fouling	Av. ΔP_{TM}	Av. Temp.	Av. λ	Av.R	Av. pH	Cl. vol.	J_{wc}	Flux R.
		(L)	(hr)	bar	(°C)	(μs)	(Lh^{-1})		(L)	(LMH)	(%)
43	water	55	3	2.50	18.4	2.18	305.5	6.29	-	92.4	-

Appendices 8, 9, 10, and 11