THE PURIFICATION OF CORN STEEP LIQUOR AS A FERMENTATION FEEDSTOCK BY ULTRAFILTRATION

by

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DEDICATION

I DEDICATE this thesis to my parents, Mr & Mrs. V.K.Govender for all their love and support in my academic endeavours, and to my spiritual master, Sri Sathya Sai Baba, for divine inspiration and strength.

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FOREWORD

This project was born out of significant inroads made by AECI Ltd. in the field of biochemical engineering and in particular to devise a process for the production of the amino acid Lysine. A period of eight years, 1990 to 1997, was spent in process development of the said technology and the subsequent commercialization. I have worked extensively on this project on a full time basis for the entire duration, with the project finally culminating in a fully commercialized production process. The process technology as developed by AECI Ltd. and encompassing the entire process including the raw material preparation, was lodged as a pending patent. The raw materials feedstock preparation process was lodged as two separate patents during this period, namely: *The pH treatment of corn steep liquor followed by the liquid-solid separation of precipitated material*; and *The use of membranes for the preparation of corn steep liquor for use as a protein feedstock for fermentations*, both under the auspices of AECI, with myself as the co-author.

The AECI Bioproducts plant in Umbogintwini, Kwazulu Natal, is the main production facility, constructed and commissioned in 1997. The raw material feedstock plant, the basis of this thesis, is a fully functional and commercialized facility at African Products in Germiston, Gauteng, constructed in 1995 and commissioned in 1996. This facility was developed based on an off-take agreement between AECI and African Products for the purchase of processed corn steep liquor. The construction of the facility was project managed by mtself.

At the time, technology and literature searches revealed that this process, as developed in this thesis, was indeed unique and the first of its kind worldwide. To date, minor modifications have been made to the production facility and this process technology remains tried and tested.

For this and many contributions to realizing this project, I remain eternally grateful to AECI Ltd.

SYNOPSIS

THE OBJECTIVE of this study was to devise a purification process, using ultrafiltration membranes as the core technology, for the preparation of corn steep liquor (CSL) as a fermentation feedstock. This process inherently required the development of a pretreatment system for the ultrafiltration membranes for the removal of suspended solids and high fouling material from corn steep liquor. The ultrafiltration membrane system was required for the separation and removal of colloidal solids from corn steep liquor, and to fractionate and separate out unwanted proteins, to render the feedstock suitable for sterilisation and subsequent fermentation.

THE CONCEPT of membrane technology was investigated in order to find a more practical alternative for what was deemed to be a difficult process problem. In particular, various pretreatment technologies were investigated to form a compact and robust process package.

THE CORN STEEP LIQUOR, a by-product of the corn wet milling process, was obtained from African Products, Germiston, in the form of a concentrated slurry directly from an evaporator system. A diagnostic of the feedstock was carried out and from this information, it was decided that three pretreatment options would be investigated. The first option was the pH treatment of the corn liquor, by the addition of ammonia which induced the precipitation of solids. This was followed by liquid-solid separation, and the clarified liquor was fed to the membrane system. The second option looked at the separation of suspended solids from the liquor by the use of broth conditioning additives and separation of the solids by a decanter centrifuge. The third option investigated was the use of a gyratory screening system for the removal of all solids greater than 100 μ in size.

IN THE pH TREATMENT of CSL, the process is effected by the addition of base to pH 7. The technology involves neutralisation of CSL in a mixing system, under predetermined conditions of temperature, agitation and rate of addition, followed by subsequent liquid-solid separation. Trials were conducted on a pilot plant to test the process. Initial trials, conducted on a small scale pilot filter press, proved to be successful for this application. A suspended solids removal of up to 98% was achieved. The average suspended solids in the filtrate was found to range between 0.1 to 0.25 %. Tests were also conducted on a hired “state of art” filtration plant under various conditions. A diaphragm membrane press was found to provide the best performance. Protein recoveries of above 95 % at fluxes of 35 L/m^2h at temperatures above 50 °C, and an incremental application of feed pressure was most suited for the process. The removal of the colloidal solids by the above-mentioned process was found to improve the quality of sterilisation. A reduction of more than 90 % in coagulated solids was achieved.

IT WAS OBSERVED that the separation of suspended solids from CSL is enhanced by the use of coagulation and flocculation. Although not commonly used for this purpose, it was felt that a decanter centrifuge was well suited for the subsequent separation of the flocs from the clarified liquor. This work describes the results of the trials with such a device and the impact of broth conditioning on the efficiency of the separation.

Trials have been conducted using an Alfa-Laval Model NX210 decanter, which was not specifically built for the work and therefore imposed several limitations on its performance. Despite these shortcomings, preliminary trials proved to be successful in achieving the separation objective. Tests were conducted using five different batches of CSL. With a maximum suspended solids loading of 4.3 % and a feed rate of 700 L/h, a solids recovery of 90 % was achieved. The clarified liquor contained residual solids between 0.5 and 0.8 %. The sludge had a solids concentration that ranged between 43 % and 65 %.

COAGULATION AND FLOCCULATION dosages were kept within the limits of the laboratory evaluations. Flocculant dosages were controlled between 100 and 200 ppm, with the coagulant operating at higher dosages of between 400 and 2000 ppm. The only controllable parameter on the machine itself was the scroll differential speed. The best performance in terms of the cake dryness and centrate clarity was obtained at the lowest scroll differential speed of 4 rpm.

THE USE OF GYRATORY SCREENS entailed passing the raw liquor through a set of two screens. The technology involves the use of a gyratory mechanism, which aids in the cleaning of the screens during continuous operation. Trials have been conducted on a pilot plant to test the system. Since the unit used was designed specifically for quick on-site screening exercises, it did not possess the added flexibility and robustness of a properly designed full scale unit. This imposed some limitations on its performance. However, despite these shortcomings, the trials conducted on the pilot plant proved to be successful in meeting the outlined objectives.

A NUMBER OF TRIALS were performed on various batches of CSL. There was considerable batch to batch variation in the suspended solids content of the CSL and this was found to ultimately affect the throughput of the screening process. The feed suspended solids varied between 10 and 18 %. The highest throughput achieved was 400 L/h at a feed suspended solids loading of 14.5 %. It was found that temperature made a significant impact on the separation. The loss of heat in the feed stream caused excessive coagulation to occur thus increasing the suspended solids loading and lowering the throughput. The total solids in the sludge stream varied between 45 and 77 %. Protein loss in the sludge stream was around 1 %. Careful attention had to be given to the handling of the sludge stream. This stream displayed rheological characteristics typical of a non-Newtonian thixotropic fluid. The 100 μm screen operated best

when prior separation was done using a 180 to 200 μm screen. This reduced the solids loading on the tighter screen and increased the throughput by 10 to 15 %. The self cleaning mechanism also performed more efficiently under these conditions.

THE SELECTED OPTION was then based on the influence the operation had on the ultrafiltration membranes, sterilisation of the product prior to fermentation and ultimately the fermentation performance. Subsequent testing of the pretreatment options were performed on an ultrafiltration membrane test cell. The product from the gyratory screens were found to produce the best overall results, where the highest fluxes and least amount of fouling occurred on the membranes tested.

ONCE THE PRETREATMENT OPTION was decided, the development of the membane ultrafiltration system was then pursued. Trials were conducted on a laboratory scale, in a membrane test cell, to determine the preliminary screening of the membrane type, fouling effects and fluxes. It was found that polyvinylidene and polyacrylonitrile membranes produced the best overall fluxes of 11.25 and 10.96 L/m^2h respectively. These membranes produced permeate protein concentrations of 121 and 115 g/L respectively. Sterilisation tests conducted on the permeate streams produced also showed that these two membranes had the lowest suspended solids concentrations.

FERMENTABILITY tests conducted, showed that the ultrafiltered CSL, from these two membranes, produced increased cell counts and protein utilisation along with an increased product yield. Approximately 42 g/L of biomass was generated with lysine yields of 46 g/L. Further testwork revealed the non-Newtonian nature of CSL and its inherent viscosity effects.

BENCH-SCALE testwork was conducted for various membrane configurations. With tubular membranes and hollow fibre membranes, average fluxes of 6.23 and 4.5 L/m^2h were achieved respectively. Spiral wound membranes were found to be more consistent in their performance, with average fluxes of around 6.25 L/m^2h. For the spiral wound membranes, it was found that the Desal-2 mesh spacer with a 80 mil thickness was most appropriate for the duty.

PILOT PLANT testwork was conducted to scale-up the membrane system and to eliminate possible risks associated with the technology. The pilot plant studies showed up a number of principle design variables which needed careful attention. The flaws in the piloting system were subsequently rectified and this helped to improve the overall performance of the system.

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NOMENCLATURE

AS	atomic spectrophotometer
CCSL	concentrated corn steep liquor
CSL	corn steep liquor
HPLC	high pressure liquid chromatography
LCSL	light corn steep liquor
MS	mass spectroscopy
WC	wet chemistry
XR	X-ray

α	Collision parameter (Smoluchhowski equation)
μ	viscosity (Pa.s)
β	collision parameter (Smoluchowski equation for mono-sized particles)
Φ_v	particle volume fraction
ε	energy dissipation per unit mass of fluid
σ	constant indicating mean binding strength with respect to the net cross-sectional area of the aggregate
η	turbulence microscale
$\Delta\rho$	difference in density between particle and fluid ($kg.m^{-3}$)
Ω_b	rotational speed of centrifuge bowl ($rev.s^{-1}$)

A	area (m^2)
A_B	net cross-sectional area of aggregate (m^2)
C_p	permeate concentration (g/L)
C_r	reject concentration (g/L)
D	diffusion coefficient (Smoluchowski equation)
d	particle diameter (m)
D	impeller diameter in stirred tanks (m)
d_p	pore diameter (m)
F_b	binding force of an aggregate (N)
F_V	turbulent breaking force of fluid for the aggregate (N)
G	average shear rate (s^{-1})
g	gravitational constant (ms^{-2})
h	cake height (m)
J	baffle width in stirred tanks (m)
J	permeate flux ($L/m^2.h$) or LMH
K_A	agglomeration constant (Smoluchowski equation)
k_B	Boltzmann's Constant (J/K)
L	distance between centrifuge feed inlet and overflow (m)
L	blade length in stirred tanks (m)
M_W	molecular mass (g/gmol)
N	particle number concentration (Smoluchowski equation)

n	impeller speed in stirred tanks ($rev.s^{-1}$)
N_p	impeller power number in stirred tanks
N_{pi}	power number
P_0	power consumed (W)
ΔP	Pressure drop over the filter (Pa)
q_f	filtrate flow rate ($m^3.s^{-1}$)
r	local point value of cake resistance ($m.kg^{-1}$)
R	membrane rejection
r_0	specific resistance of cake at unit pressure drop ($m.kg^{-1}.Pa^{-1}$)
R_b	centrifuge bowl radius (m)
R_M	Filter medium resistance (m)
S	impeller diameter in stirred tanks (m)
s	compressibility coefficient of filter cake
T	absolute temperature (K)
t	time (s)
T	tank diameter in stirred tanks (m)
U	bulk flow velocity ($m.s^{-1}$)
V	vessel volume stirred tanks (m^3)
v^c	cake volume per unit filtrate volume
v_f	final volume of filtrate (m^3)
V_s	settling velocity ($m.s^{-1}$)

w	Concentration of solids in the slurry (volume fraction)
W	blade width in stirred tanks (m)
X_F	mass flowrate of feed ($kg.s^{-1}$)
X_L	mass flowrate of centrate ($kg.s^{-1}$)
X_S	mass flowrate of cake ($kg.s^{-1}$)
X_Y	mass flowrate of polymer ($kg.s^{-1}$)

CHAPTER 1

INTRODUCTION

1.1 Background

Corn steep liquor (CSL) is a by-product of the corn wet milling process in the production of starch. The wet milling process entails the steeping of maize in water under controlled conditions of temperature, pH and time, which is very similar to a fermentation process, except that the primary biological activity is by enzymes. During the steeping process the maize is enzymatically broken down into constituent fractions. These enzymes occur naturally in the maize and are activated by this controlled environment. The solubilised fraction is then separated from the rest of the maize constituents by being allowed to pass through a coarse screen.

This filtrate, which is rich in kernel extractives, microbes (principally *lactobacilli*), numerous products of fermentation processes, dissolved sulphur dioxide (SO_2), phytin, proteins, vitamins, mineral nutrients and carbohydrates, is called Light Corn Steep Liquor (LCSL) and contains between 10 % to 15 % dissolved solids and approximately 0.5 % to 1 % suspended solids by mass. These suspended solids are mostly un-solubilised fines, which have slipped through the screening process. The LCSL is then concentrated in an evaporator to about 40 % to 50 % solids and the resulting stream is called Concentrated Corn Steep Liquor (CCSL). In this thesis, CCSL will be commonly referred to as Corn Steep Liquor (CSL)

The outermost cell layer of the endosperm of grain (maize) is called the aleurone layer. The aleurone consists of thick-walled cells, which contain no starch but are rich in protein, oil, sugars and nicotinic acid[1]. The aleurone cells contain small granules which consist mostly of phytic acid and a small amount of associated protein. The phytic acid exists as calcium, magnesium and potassium salts, called phytin. The phytic acid is comprised of inositol phosphates, where the predominant specie appears to be inositol hexaphosphate. A large amount of phytin is solubilised during the steeping process and ultimately the CSL may contain as much as 4.2 % m/v of phytin, adding significantly to its nutritional value.

CSL is commonly used as a high protein-value feedstock in the animal nutrition industry, particularly as a high protein supplement in food recipes for cattle, pigs, sheep and, to a much smaller extent, in the poultry industry. The rich composition of the CSL adds a significant proportion of nutritional value to animal feedstocks.

Recently, CSL been identified as a suitable protein and nutrient source for the fermentation industry. Most bacteria, yeast and certain fungal organisms require protein and essential amino acids for their metabolism and sustenance. These organisms are grown and nurtured in a controlled environment called a fermentation, and the organisms produce important products such as enzymes, amino acids and various pharmaceutical products, amongst others. CSL is particularly suitable as a raw material for aerobic type fermentations, where the organisms require oxygen for their living functions, since CSL is a cost-effective source of protein, containing an abundance of essential amino acids, vitamins, minerals and carbohydrates.

There are several other alternatives of protein sources, of equivalent protein value to CSL, that are available on a low volume industrial scale. Some examples are :- soy meal which is extracted from the soy bean; yeast extract; cell debris hydrolysates from bacteria and fungi; protein extracts from leguminous plants; and extracts from algae. However, all of these protein sources have been targeted for specialised and established markets and are therefore exhorbitantly priced. On a cost basis they are not economically feasible for use as a fermentation feedstock. CSL is significantly cheaper since it is a by-product of the corn wet milling process. It is also available in much higher volumes for use on an industrial scale.

However, despite its high nutritional value and relatively low cost, CSL is presently not widely used as a feedstock in the fermentation industry internationally. This is primarily due to the fact that maize is only grown on a major scale in certain areas of the world. Further, most maize producers sell off their product to dry milling operations, where the maize is processed for various maize derived products such as corn flour and maize meal. CSL is a by-product of the wet milling process, where the major product is starch and starch derived products such as high fructose corn syrup, maltose, glucose and dextrose.

South Africa currently produces large quantities of maize and maize derived products. A significant proportion of raw maize is exported to Europe and the Far East, while the rest is sold to local dry milling and wet milling operations. Maize gluten, a concentrated protein feedstock, is a product of the wet milling process and is produced primarily for the local animal feed market. Hence, relative to starch derived products from maize, it is inexpensive and produced in surplus to local requirements. Accordingly, the use of CSL as a fermentation feedstock is very feasible in the local market.

However, “raw” CSL is not suitable for direct use in fermentations due to several reasons arising from the complex composition of CSL. These include :

(i) Contamination by suspended and colloidal material :- A relatively large fraction of the solids in CSL is suspended and this is one of the contributing factors which make the material unsuitable for direct use in fermentation. A small portion of the suspended solids are microscopic and fibrous in nature. This fraction of suspended colloidal solids varies from batch to batch and is a result of seasonal variations in the maize, coupled with process variations in the maize steeping process.

Incomplete steeping of the maize leaves a higher proportion of unsolubilised material, which tends to remain as a colloidal suspension. The over-steeping of the maize tends to release a higher fraction of polysaccharides into the liquid phase. This is primarily due to the presence of lactic acid forming bacteria, which breaks down the inner starch fractions, releasing polysaccharides and forms lactic acid. At the end of the steeping process the pH of the CSL is 4.0 to 4.3. At this pH, complexes like phytin appear to be partially soluble and partially colloidal in nature. The rheological behaviour of corn steep liquor is therefore unpredictable and leads to complications which aggravates the processing problems.

(ii) Difficulties with sterilization :- In fermentation processes, it is customary to either pasteurise or sterilize the feedstock prior to fermentation[2]. Sterilisation is a standard methodology adopted in the fermentation, food and pharmaceutical industries. It refers to the removal or destruction of micro-organisms, including all bacterial spores. Pasteurisation on the other hand, is the thermal destruction of vegetative micro-organisms, excluding thermoresistant bacterial spores. The main difference between sterilisation and pasteurisation is that temperatures required for sterilisation are significantly higher than for pasteurisation (> 120 ^{o}C compared with 70 to 90 ^{o}C). As most bacterial spores will survive pasteurisation, the process is used with streams in which spore forming bacteria do not grow, or in products where the shelf life is too short to allow the spores to germinate and grow to unacceptable levels.

For bacterial fermentations, sterilisation has been adopted as the standard methodology[3]. Sterilisation of feedstocks prior to fermentation is aimed at eliminating the risk of contamination and is used to extend the life of an aseptic environment. Most fermentations usually consist of one desired type of organism. The organism is introduced into the aseptic environment under sterile conditions. Due to the fact that only one organism type is allowed to flourish in the fermentation system, the system is therefore known to be monoseptic.

There are several techniques of media sterilisation. These could be specific to a particular process and is based on the stringent requirements of the process or the product itself. In most fermentation processes a convenient method of sterilisation is heat treatment. There are two categories of thermal sterilisation systems commonly used in industry, viz. *direct* and *indirect*[4]. The choice depends on many factors related to the product characteristics, like viscosity, density and susceptibility to fouling.

Direct heating of the media involves the condensation of steam brought in direct contact with the product. There are two types of direct heating : steam injection and steam infusion. In steam injection, the steam is injected directly into the media, whereas in an infusion process the media is sprayed into a steam atmosphere. In an indirect heating system, the heating medium (steam or hot water) is separated from the media by a physical barrier; heat is transferred across the barrier to heat the media. Indirect heating systems are probably the most widely used for sterilising liquid media, and are generally much less complex than direct systems.

Another form of sterilisation commonly used in the pharmaceutical industry is *sterile liquid filtration*. Here, an absolute rated depth filter, ranging between 0.1 to 0.22 micrometers, is used to filter the media prior to addition into the fermenter. These filters are sterilised and cleaned chemically with various sanitation chemicals or thermally by direct electrical heating or steam injection. These filters are generally constructed of specialised woven polymers, sintered stainless steel or ceramics. These systems, which are available in various configurations, are extremely expensive, and generally only used for low volume throughput.

In the case of CSL, the choice of the sterilisation system is difficult, since the rheology, physical and chemical characteristics of "raw" CSL are never constant. Earlier testwork had indicated that CSL in its raw form is extremely difficult to sterilise with any of the established sterilisation techniques[5]. The high level of fibrous suspended solids and colloidal solids make *sterile liquid filtration* impractical. The filters are rendered inoperable because they block and foul irreversibly after processing only a small volume. Thermally sterilising CSL results in copious coagulation of suspended solids and colloidal solids of high molecular mass. The presence of the suspended solids in vessels, pipes, heat exchanges, etc. retards the sterilisation, necessitating higher temperatures, and/or longer heating times. The presence of thermally sensitive nutrients, such as the vitamins, amino acids, complexed minerals, some proteins and sugars, makes thermal sterilisation even more difficult, since the preservation of these nutrients is essential to the fermentation process.

An analytical breakdown of the coagulated CSL showed significantly large fractions of phytin and its associated salts, lactic acid, vegetable fats and various carbohydrate forms. Those components, which appear to cause the coagulation due to heat treatment, have been identified as phytin complexed salts, high molecular weight protein and lactic acid. Also, prior to fermentation, the media, which includes the protein feedstock, is adjusted to a neutral pH. The addition of the base for neutralisation induces copious precipitation of solids, which also adds to the problems of fouling and subsequent sterilisation.

(iii) Presence of non-fermentable components :- A further problem is the existence of large amounts of solubilised proteinaceous material, the associated salts, starch, fats, etc. in raw CSL. A large fraction of the dissolved protein, particularly of high molecular weight, remains unused in fermentations. These proteins are considered to be undesirable for fermentations since they precipitate out when neutralised with ammonia gas during the course of fermentations. These suspended solids are known to limit oxygen transfer during the fermentation process as well as cause severe separation problems in downstream processing unit operations.

Therefore, if CSL is to be exploited as a fermentation feedstock it is necessary to devise a method to prepare a substantially clean and easily sterilisable protein feedstock for fermentation. It was also desirable to obtain a stream consisting of only useable protein, amino acids, carbohydrates, vitamins, and the other low molecular weight organic and salt nutrients.

In recent developments in the area of membrane technology, and *ultrafiltration* in particular, great strides have been made in solving many difficult separation problems. Accordingly, in this work, membrane technology was chosen as the core unit operation for the purification of CSL. However, the performance of membrane systems can be substantially reduced by fouling of the membranes. Hence, for the successful operation of membrane processes, it is necessary to incorporate a pretreatment operation for the removal of abrasive suspended solids and other high fouling species.

A literature search, and subsequent enquiries to producers of CSL as well as membrane vendors worldwide, has indicated that membranes have not been used before for this particular application. This study will focus on determining a suitable pretreatment process and membrane system to treat CSL as a feedstock for fermentation.

1.2 Objectives

The overall objective of this study is to develop and evaluate a membrane system to treat raw CSL and produce a stream suitable for use as a feedstock to fermentation processes.

The specific objectives are:

(i) to devise a pretreatment system for the for the removal of suspended solids and high fouling material from CSL, and render it suitable as a feed to ultrafiltration,

(ii) to devise an ultrafiltration membrane system for the separation and removal of colloidal solids and unwanted proteins from CSL, to render the feedstock suitable for sterilisation and subsequent fermentation, and

(iii) to select, develop and configure the said technology by means of laboratory, bench-scale and pilot-scale engineering to obtain realistic performance data for design and economic evaluations.

1.3 Approach

It was decided from the outset that it made practical and economic sense to perform all testwork on the more concentrated stream of CSL. The product is required in the concentrated form, hence the volumetric throughput for processing is significantly reduced. There is also a greater consistency in the solids concentration of the CSL coming out of the evaporation system and the associated significant reduction in the cost of transporting the concentrated stream.

The approach taken in this study was as follows :

(i) Selection of candidate pretreatment processes :- a detailed literature search was undertaken to identify pretreatment processes that could be suitable for this application.

(ii) Optimisation of pretreatment processes :- the selected pretreatment processes were evaluated experimentally, and the operating conditions and equipment variables were experimentally optimized to yield the optimum product quality for the particular process. Each of the pretreatment options investigated were tested as far as possible on both the bench scale and pilot scale. This phase of research covered the design and construction of laboratory equipment, bench-scale systems, followed by piloting systems.

(iii) Selection of candidate membranes :- a detailed survey of membrane literature and membrane manufacturer's specifications was performed. From this, a list of candidate membranes for the application were identified

(iv) Determination of the optimal pretreatment-membrane combination :- a matrix of pretreatment processes and candidate membranes was drawn up. The optimized product from each pretreatment process was filtered through each candidate membrane, using bench-scale membrane rigs. The final permeates were assessed in terms of permeate flux, protein recovery, suitability for sterilization and fermentability. From this the optimal pretreatment-membrane combination was determined.

(v) Scale-up of membrane system :- the results of the bench-scale testing then enabled the design and construction of a pilot plant. The design basis captured specific scale-up parameters, robustness and ease of operation. Statistical design was used to optimise the operation of the pilot plant. The pilot plant was then operated under the optimised conditions for a prescribed period for process validation. The CSL product generated was used to validate the various areas of uncertainty, such as the following:- its ability to be sterilised without copious precipitation of valuable protein, the recovery of useable protein, the CSL product shelf-life, and its fermentability on a larger scale.

1.4 Thesis Organisation

A review of current technology on the candidate pretreatment processes is given in Chapter 2. The review of current membrane technology, applicable to bioseparations, is given in Chapter 3. In Chapter 4 the effects of the operating variables and equipment variables on the performance of each selected pretreatment option are investigated and optimised. The determination of an optimal pretreatment-membrane combination is investigated in Chapter 5. The scale-up of the membrane system is covered in Chapter 6. The Conclusions and Recommendations of this study are presented in Chapter 7.

CHAPTER 2

REVIEW OF PRETREATMENT OPTIONS

2.1 Introduction

A literature scan was performed to identify possible pretreatment processes for the preparation of a suitable feed to an ultrafiltration membrane process. From this scan, three candidate processes were identified for further investigation and evaluation, viz.

(i) Precipitation by pH Treatment:- this involves changing the pH of the mother liquor to force the precipitation of unwanted components, followed by a solid-liquid separation step to remove the precipitated components. Based on evidence that the addition of base to CSL affects the precipitation of solids, pH precipitation was selected as a candidate process to precipitate and remove unwanted colloidal solids prior to ultrafiltration. The pH of CSL is very close to the iso-electric point of the protein, and the pK's of lactic acid and phytic acid. Hence, small changes in the pH or temperature may also affect changes in the solubility of these complexes. Water soluble constituents, including phytin, may precipitate with the protein as a result of occlusion.

Current technology on the process of base addition, the design and testing of an efficient mixing system and the subsequent liquid-solid separation process for the removal of the precipitated solids, is reviewed in Section 2.2.

(ii) Centrifugation. This is probably the most common form of liquid-solids separation used in industry, for difficult slurry separations. Based on initial laboratory trials, it was decided that a scroll decanter centrifuge would be most suited for this function. Current technology on decanter centrifuges in the pretreatment operation is reviewed in Section 2.3.

(iii) Gyratory Screens. The use of screens for the removal of suspended solids has been successfully used in many challenging duties. Gyratory screens have provided an added innovation to the separation process. The use of gyratory screens as a pretreatment step is reviewed in Section 2.4.

2.2 Precipitation by pH Treatment

2.2.1 Introduction

Precipitation as a bioseparation step is an established method that has been in existence for many years. It is a method in which the solubility of macro-molecules, such as proteins, polysaccharides and phytate, is reduced by the addition of solvents, salts, acid or base, metal ions or high molecular weight polymers. The principle of reduced solubility of neutral molecules with increasing ion strength was already published in the 1880's. In 1946, Cohn[6] described the concept of methanol fractionation of plasma-proteins, which is a well known method today. Presently in industry, many bulk enzymes are recovered by precipitation.

Although precipitation displays similarities to coagulation or flocculation, it must not be confused with these two concepts. In the case of coagulation, it is the destabilisation of colloidal particles, induced by electrolytes, which reduces the thickness of the electrical double-layer. In flocculation, the colloidal particles or cells grow to flocs that can be more easily separated from the liquid. In this process the formation of molecular bridges by macromolecules and electrolytes plays an important role. Coagulation is used primarily in clarification and in the waste-water treatment processes. Flocculation is used quite extensively in the pre-treatment of whole cells or cell debris from fermentations or other liquid streams prior to filtration or centrifugation.

The approach of a precipitation process is usually empirical, because the theory of solubilisation cannot be applied directly to complex mixtures such as corn steep liquor (CSL) or fermentation liquor. Often, not all compounds in the feed liquor are accurately known and are frequently subject to change during the lifetime of the liquor. Precipitation can be considered as a purification, a fractionation, or as a concentration method. Here it is considered as a purification method.

2.2.2 Colloidal foulants in CSL

Phytate, the hexakis-o-phosphate of myo-inositol, is widely distributed in the cells and tissue of higher plants. Seeds, such as maize, accumulate up to 90 % of stored organic phosphate as phytate. The sysnthesis of phytate starts with the formation of myo-inositol-1-phosphate from glucose-6-phosphate, followed by complete phosphorylation by a kinase enzyme. In mature maize kernels, phytase accounts for 0.9 % of the dry weight and about 88 % is found in the germ. According to Bolley, Watchung and McCormack[7] , phytate has great utility in the field of nutrition and is also used to a limited extent as fermentation nutrient.

During the fermentation process, bacteria or yeast apparently provide the enzyme in sufficient quantities to hydrolyse the soluble phytin to an available form of phosphate.

Phytic acid acts as a nutrient chelate and interferes with the availability of certain mineral, especially calcium, magnesium, zinc and iron. In excess, phytic acid could therefore have an inhibitory effect on fermentations. This is especially severe if insufficient phytase enzyme is made available for the breakdown of phytin. The phytate with its extensive chelating properties therefore behaves as a multiple complexing agent possessing varying properties.

Small changes of pH and temperature also effects changes in the solubility of the phytate complexes, since the pH of the CSL, usually 4 to 4.5, is very close to the isoelectric point of the protein, and the pK's of lactic acid and phytic acid. Water soluble constituents, including phytin, may precipitate with the protein as a result of occlusion. Furthermore, the suspended colloidal material in CSL, whether organic or inorganic, microscopic or sub-microscopic, possesses certain properties associated with interfacial phenomena. Such phenomena include the effects of surface charges carried by particles and the degree of hydration (or solvation) of the particles surface layers. It is due to the overriding influence of surface phenomena that fine particulate matter (microscopic) and colloidal matter (sub-microscopic), which possess a colossal surface area to mass ratio, have the ability to exist as stable dispersions.

For a given mass of liquor, the higher the concentration of suspended material in the microscopic to submicroscopic range, the more predominant the influence of phenomena associated with interfaces. The influence of gravity effects on mass becomes reduced. It is therefore apparent that if the hydrodnamic effects alone are considered, large time scales are required for the colloidal material to settle through a significant distance. The feasibility of removing such colloidal particles from dispersions like CSL, by methods other than those relying on gravity effects, needs to be investigated.

The processes which convert fine particulate, colloidal or dissolved material into a form whereby separation from the dispersion or solvent is practicable are important. According to Bratby[3] such processes could alter the surface properties of particulate material, thereby increasing the adsorptivity of the particles to a given filter medium and generating a tendency for aggregation of small particles into larger units. It could also precipitate dissolved material thereby creating particulate material for which separation by sedimentation and/or filtration is feasible. Such a conversion of the stable state of a given dispersion or solution to an unstable state is termed *destabilisation*. The term '*stability*' describes the ability of individual particles to remain as separate entities or, in other words, to maintain a dispersed state. The stability of the colloidal material arises from the predominance of forces associated with the solid-liquid interface.

Earlier work by Priesing[8] on biological material suggests two general classes of colloids which are given the names *lyophobic* and *lyophilic*, more generally termed *hydrophobic* and *hydrophilic.*

These terms refer to the degree of affinity of the colloids for the liquid phase. Hydrophilic or lyophilic colloids generally include gelatin, starch, gums, proteins and all biocolloids. A solution such as CSL is difficult to classify as being either lyophobic or lyophilic. Both types of colloidal dispersions may co-exist and furthermore, there may be a continuous transition from one state to the other. A further difficulty in classification is that in some instances both hydrophobic and hydrophilic areas may exist on the colloids together.

2.2.3 Principle options of the precipitation process

There are various methods for the precipitation of phytin, protein and other colloidal particles:

(a) addition of neutral salts, such as ammonium phosphate, to reduce the solubility of high molecular weight protein, an operation known as "salting-out",

(b) addition of organic solvents such as ethanol, methanol, acetone and propanol, to reduce the dielectric constant. In this way, the electrostatic interaction between the molecules is enhanced until precipitation occurs, and

(c) adjustment of the pH, which has a strong influence on the ionisation of the weakly acidic and basic groups of side chains of proteins and phytic acid. The solubility depends on the net charge of these groups. Those molecules with a zero net charge at some pH (iso-electric point) will tend to precipitate.

In addition, there are some other methods which belong, more strictly speaking, to the group of flocculation and coagulation techniques:

(d) the addition of uncharged polymers (non-ionics) to reduce the amount of available water for salvation,

(e) the addition of charged poly-electrolytes, to induce flocculation under the appropriate pH conditions, and

(f) the addition of polyvalent metal ions, in particular Fe^{3+} or Al^{3+}.

The method to be chosen depends primarily on the application. For animal consumption, the addition of polymers and metal ions are not always allowed. Residual alcohol in the product could be poisonous. In

the use of the treated product in fermentations it is not desirable to have such polymers and metal ions present, due to the toxic effects on the bacteria. In the case of CSL, only the removal of colloidal foulants and suspended solids are required. It is therefore necessary to ensure that the valuable low molecular weight proteins, amino acids, vitamins, fatty acids and carbohydrates, are not removed from the CSL stream. Based on earlier evidence by Govender[9], that the addition of base for the neutralisation of CSL induces precipitation of colloidal solids, it was decided that pH treatment be used as a method for pretreatment. Furthermore, ammonium hydroxide or ammonia gas is preferred as the base for such a pretreatment process, since ammonia and ammonium salts are considered to be non-toxic and are readily utilised in fermentations as a nitrogen source. Most aerobic fermentations use ammonia and ammonium salts in there nutrient recipes.

2.2.4 Iso-electric Precipitation

The solubility of most colloidal solids such as phytin and proteins is substantially influenced by the pH-value. The iso-electric point (IEP) is defined as the pH at which the molecule has a net zero charge and minimum solubility. The precipitation at this pH is called iso-electric precipitation. The advantage of iso-electric precipitation is that all protein-like compounds with a higher or lower IEP will stay in solution. In this way a purification can be achieved.

2.2.5 Kinetics for solids aggregation

It was noted that although much has been published in the kinetics of precipitation, very little data of practical relevance has been published. Important work on the kinetics of protein and protein-like solids aggregation has been carried out at the University College London, which has one of the best non-industrial downstream pilot plant facilities[10,11,12]. Some of this work and extensions of it will be summarised in this section. The following aspects can be considered in the mechanism of the colloidal solids aggregation:

(i) For very small particles, inner particle collision will be governed by their random movements, characterised by a diffusion coefficient, and referred to as perikinetic growth.

(ii) For larger particles, collisions will be governed by the flow and shear pattern, referred to as orthokinetic aggregation.

(iii) If particles collide, they may aggregate, but the collision may also result in breakage.

(iv) The factors that enhance breakage on collision of a particle with another particle or a wall will become more predominant for larger particle sizes. Hence, there will exist a maximum aggregate diameter.

(v) If there is a wide particle size distribution, small particles are "eaten away" by larger particles. Hence, ageing of a dispersion of aggregates improves the quality of the precipitate.

(vi) Theoretical considerations tend to be restricted to mono-size dispersions. To deal with the wide particle size distribution encountered in an actual aggregation process, macroscopic models are required, for example population balance models.

2.2.5.1 Perikinetic Growth

The rate of decrease of the particle number concentration for small mono-sized particles, is given by the following Smoluchowski equation:

$$-\frac{dN}{dt} = \alpha K_A N^2 \tag{2.1}$$

with

$$K_A = 8\pi D d \tag{2.2}$$

where N = particle number concentration

α = collision parameter

K_A = agglomeration rate constant

D = diffusion coefficient

and the diffusion coefficient **D** is given by the Stokes-Einstein equation:

$$D = \frac{k_B T}{3\pi\mu d} \tag{2.3}$$

where k_B = Boltzmann's Constant

T = absolute temperature

μ = viscosity

d = particle diameter

For perikinetic aggregation of 0.8 to 3 μm particles of urea denatured oval-albumin, the Smoluchowski theory was found to describe the iso-electric point precipitation quite well. In general however, various parameters influence the efficiency factor α to be much smaller than 1. For example the equations above do not account for the presence of an electrical barrier or hydration layer around the protein particles. Hence the particulars of the attractive and repulsive forces between the particles will influence the collision efficiency. Also, particle non-sphericity is not taken into account. The particle size distribution can be taken into account in the Smoluchowski theory as follows:

$$\frac{d\,N_k}{dt} = \frac{1}{2}\alpha\left\{\sum_{i=1}^{i=k-1} 2\pi\left(d_d + d_j\right)\left(D_i + D_j\right)N_i N_j\right\}$$

$$-\alpha\, N_k\left\{\sum_{i=1}^{\infty} 2\pi\left(d_i + d_k\right)\left(D_i + D_k\right)N_i\right\} + \frac{1}{2}\alpha\left(8\pi\, d_k\, D_k\right)N_k^2 \qquad (2.4)$$

where, I, j, and k define particle sizes such that:

$$d_k^3 = d_i^3 + d_j^3 \qquad (2.5)$$

The first term on the right hand side of Eq. (4) describes the formation of particles of diameter d_k , by collisions of smaller particles. The second term represents the rate of loss of particles of diameter d_k by collisions. The third term accounts for collisions between like particles in the second term, which have been counted twice. **D** is the effective particle diffusivity. Eq. (4) is too cumbersome to be used in practice, but it can be used , for example, in perikinetic aggregation where dN/dt is only a weak function of the particle size. Assuming that:

$$M_w \sim d^3 \qquad (2.6)$$

where M_w is the molecular mass, Smoluchowski's growth kinetics may be related to change in molecular mass M_w of the aggregate with time:

$$M_w(t) = M_w(0)\left(1 + K_A\, m_0\, t\right) \qquad (2.7)$$

where, M_0 is the molar concentration of the aggregate species. Thus, the measurement of the average molecular mass versus time will provide values for the rate constant K_A.

2.2.5.2 Orthokinetic Growth

In a sheared suspension of particles greater than approximately 1 μm in diameter, fluid motion will cause particles to collide and hence aggregate. Also, for this case there is a Smoluchowski equation for mono-sized particles in a uniform shear field:

$$-\frac{dN}{dt} = \beta \frac{4}{\pi} \phi_v \bar{G} N \tag{2.8}$$

where β = collision parameter

G = average shear rate

ϕ_v = particle volume fraction

in which the particle volume fraction is defined as follows:

$$\phi_v = \frac{1}{6} \pi d^3 N \tag{2.9}$$

Eq. (8) can be rewritten in terms of the ratio of final to initial number concentrations after exposure to shear for a time *t*:

$$\frac{N_t}{N_0} = \exp\left(-\frac{4}{\pi} \beta \phi_v \bar{G} t \right) \tag{2.10}$$

This Smoluchowski's rate equation assumes that the fluid flow is laminar. However, this is not the case for most practical circumstances as in stirred vessels. Despite this, Camp and Stein[6] have attempted to estimate the mean shear rate in stirred vessels and applied this to the rate equation. So the average shear rate *G* in Smoluchowski's orthokinetic growth equation can be estimated on the basis of the power dissipation per unit volume:

$$\bar{G} = \sqrt{\frac{\varepsilon}{\nu}} \tag{2.11}$$

where, υ is the kinematic viscosity and ε is the energy dissipation per unit mass of fluid. For a stirred tank ε:

$$\varepsilon = \frac{N_p \quad n^3 \quad S^5}{V} \tag{2.12}$$

where, *Np* is the impeller power number, depending on the type of impeller, *n* the impeller speed, *S* the impeller diameter and *V* the vessel volume [7].

The collision effectiveness factor β takes into account the influence of a large number of variables:

- the same effects as mentioned for the effectiveness factor α for perikinetic growth.
- particles tend to follow the streamlines; this effect will reduce the chance of collision.
- the shear rate is not the same everywhere, in particular not in turbulent flow.

2.2.5.3 Maximum aggregate diameter during precipitation

Solids aggregate formation is generally carried out under turbulent agitation conditions and the maximum aggregate size appears to decrease with the increase of the agitation intensity. The maximum aggregate diameter under a given agitation condition is controlled by two counteracting forces: the binding force of the aggregate, F_b, and the turbulent breaking force of the fluid for the aggregate, F_v. The first is proportional to the nett cross sectional area A_B :

$$F_b = \sigma A_B \tag{2.13}$$

where, σ is a constant that shows the mean binding strength with respect to the net cross sectional area of the aggregate. A_B should be taken at the plane of rupture. Hence, it is known in detail, but it will be proportional to d^2. Tambo and Hozumi[7] have derived the following expressions for the break-up force:

$$F_U = \sigma_f \quad _l\left(\varepsilon\nu\right)^{2/3} d^{2/3} \qquad when \;\; d >> \eta \tag{2.14}$$

$$F_U = \sigma_f \quad _l\left(\varepsilon\nu\right) d^4 \qquad when \;\; d << \eta \tag{2.15}$$

ε is given by Equation (12) and η is the so called turbulence micro-scale, which gives a measure of the size of the eddies in a fluid in turbulent flow:

$$\eta = \left(\frac{\nu^3}{\varepsilon} \right)^{0.25} \tag{2.16}$$

The critical condition of break-up of an aggregate is considered to be the break-up force equal to the binding force. When the binding force and break-up force are equated, a maximum aggregate diameter is obtained. The relationship eventually found is a rather complex function depending on various effects such as pH, agitation intensity, aggregate density, fluid characteristics, dosage of the precipitation agent and the colloidal solids concentration. For the design of stirred vessels for the colloidal solids precipitation, the main result can be expressed as follows:

$$d_{\max} \propto \overline{G}^{-2y} \tag{2.17}$$

where G is given in Eq. (11). This implies, inter alia, for the dependence on the stirrer speed n:

$$d_{\max} \propto n^{-3y} \tag{2.18}$$

For aggregates larger than the turbulent microscale η and hence exposed to break-up by inertial forces due to particle-particle and particle-surface collisions, y approaches a value of 1. For break-up by viscous forces, where aggregates are smaller than η, y approaches a value of 0. Maximum surface shear effects occur when the particle is about the same size as the turbulent microscale; for this case **y** is assumed to be 0.5. Experimental values range from 0.1 to 0.8 for precipitation processes in standard stirred vessels.

2.2.6 Mixing

The processes of nucleation, particle growth and ageing are distinct and controlled by different mechanisms. The time for nucleation is of the order of less than a second whereas the particle growth and ageing is of the order of minutes or many minutes. Nucleation takes place in the Golmogorov micro-scale which is a function of the power input per unit volume. During the nucleation stage, mixing is very important to ensure a uniform distribution of the precipitating agent. The effect of mixing during particle growth is less pronounced.

2.2.6.1 Mixing technology for pH treated CSL

Mixing is very broad and diffuse and occurs quite commonly in many unit operations. As discussed earlier, the desired process objective for mixing is to obtain a mixture of the precipitating agent and the stream being treated. As such, mixing is an integral part of this process infrastructure. It is also important

to note that the optimal mixing conditions for process streams are unique and not transferrable from one to the other. In many instances it is poorly understood and often leads to inefficient process performances.

CSL has already been identified as being a highly complex stream possessing unique rheological characteristics. The addition of ammonium hydroxide for the pH treatment of this stream complicates the rheological behaviour even further. A two phase system such as this is affected by many variables, hence a thorough understanding of the rheological behaviour, whether Newtonian or non Newtonian, a shear thinning or thickening fluid, Bingham plastic or visco-elastic fluid, needs to be understood. The time effects of the chemical reaction and the product particle size distribution are in essence some of the most important key parameters.

Numerous types of geometries are used for mixing applications. Tank mixing geometries include laminar, turbulent and multiphase configurations and is also dependant on whether the operation is batch or continuous. In batch operation all distinct processes will take place at the same time. During the precipitant feed phase the concentration gradually increases leading to relatively large particles. The stirring during this phase is very important, since the large particles initially formed will be fractured. However, a batch operation is easy to perform and flexible in operation and hence, will be used in the testwork.

In continuous operation, one is able to separate the distinct phases. The precipitant can be added in the ratio required at once. This stage can be performed in a dynamic pre-mixer or static mixer. The nucleates formed are allowed to grow in the stirred vessel or tubular reactor continuously. Finally the precipitates may be exposed to gentle shear or ageing in a separate stirred vessel or tubular reactor. In the case of stirred vessels, the maximum level of shear in the impeller zone is of particular importance. Due to the more controlled conditions with respect to the mixing and shear, the particle size distribution will become smaller. Such continuously operated systems are by far less flexible than batch systems.

In any precipitation process, the particle size distribution is an important parameter with respect to the ease of solid-liquid separation. The rate of addition of precipitant largely determines the particle size. A fast addition will result in the formation of a number of small sized particles. As explained earlier, mixing has a pronounced effect on the particle size obtained, since shear forces are introduced leading to fragmentation of aggregated particles. Shear effects may also be induced by pumps, especially centrifugal and gear pumps.

The requirements of this process, therefore, are to establish the controlling parameters and process variables that significantly affect the accomplishment of the process objectives. Hence, a detailed study is required to obtain the correct perspective and adequate information. Mixing tests have to be performed to gather the data as well as to determine the importance of certain process variables. Classical methods of determining such data, is to change the impeller rotational speed and record the changes in the process result, or changing the feed rate, feed location, any sparging and power distribution in the system.

2.2.7 Selection of a solid-liquid separation process for precipitated CSL

Liquid-solid separation embraces a wide range of techniques such as filtration, centrifugation, gravity sedimentation and flotation. There is also a wide range of solid-liquid separation equipment that is commercially available, including:

- Gravity separators
- Flotation devices
- Centrifuges (sedimenting, tubular bowl, disk-stack, decanter scroll)
- Hydrocyclones
- Batch filters (pressure leaf, filter presses)
- Continuous filters (drum, disc, horizontal belt)
- Filtering centrifuges (peeler, pusher, oscillating and tumbling)

The selection of the best equipment for a particular operation is dependent on many factors such as the operating conditions, the required product quality, and scale-up characteristics, amongst others.

In order to determine the most appropriate solid-liquid separation equipment for precipitated CSL, a *decision flowsheet procedure* was developed. The procedure essentially chooses the most suitable equipment for a solid-liquid separation application based on :

(i) the duty (scale) of the final operation

(ii) the settling characteristics of the feed

(iii) the filtration characteristics of the feed

From this decision flowsheet procedure, **filtration** was identified as the most appropriate separating technique, and the following were identified as the most appropriate equipment for separation of precipitated CSL :

Batch filters : pressure leaf, filter presses

Continuous filters : drum filters

The theory related to filtration is reviewed in the next section.

2.2.8 General theory of filtration relevant to filtration tests

2.2.8.1 Types of filters

The separation of solids by filtration may be divided into three broad areas of interest:

(i) Surface filtration of a dilute suspension where the liquid is usually the desired product.

(ii) Depth filtration in which small contaminants are retained in the filter medium itself.

(iii) Cake filtration where the solids act as the filter medium.

In surface filtration a small quantity of deposits form a highly resistant layer and, once covered, the filtering element must be cleaned or rejected. In contrast, depth filtration provides a relatively large solids capacity. In cake filtration the solids deposited gradually increase in thickness with the overall effect of reducing flow rates and/or increasing pressure drops over the system. The principal objective here is to choose a filter medium which produces a clear separation without major penetration of particles into the pores of the medium. However, some penetration is inevitable and cake filtration is usually a combination of surface and depth processes.

The technique chosen depends largely on the solids concentration in the feed. Below 0.1 % by volume, depth filtration is preferred. Above 3 % by volume, cake filtration is likely to perform the best. Surface filtration is usually applied in between. When studying pressure filters or "dead-end" filters, it is recommended to consider only cake filtration when examining practical results. Bosley[13] showed how some of the equations, evolved by Carman and Kozeny from the earlier equations of Hagen and Poisseule, could be used in this respect.

2.2.8.2 Filtration equations

The flow rate (dv/do) of filtrate at any time may be related to the volume of filtrate passed up to that time (V), the pressure drop over the system, P_T, and the area of the filter A, by:

$$\frac{dv}{d0} = \frac{A^2 P_T}{\mu(rwV + A R_m)} \tag{2.19}$$

where *r* is the local point value of the cake resistance, *w* the concentration of solids in the slurry, R_M the filter medium resistance and μ the liquid viscosity.

If the differential pressure varies throughout the test, the specific resistance changes for those systems exhibiting compressibility. In these cases the local value may be expressed as :

$$r = r_0(\Delta P)^S \tag{2.20}$$

where r_0 is the specific resistance at unit pressure drop and *s* the compressibility coefficient of the filter cake. The exponent generally varies from 0 for incompressible material to 1 for highly compressible sludges.

In turn the cake height is a function of time and can be related to the filtrate volume V_f via :

$$h.A = v^c.v_f^* \tag{2.21}$$

where v^c is the cake volume per unit of filtrate volume. As the pores in the filter medium and the cake are small, and the flow rate is low, laminar flow conditions are invariably obtained. In this case Darcy's law may be applied. This law relates the filtrate flow rate Q_f of viscosity μ through a porous bed with resistance R_f and area *A* to the driving force ΔP

$$q_f = \frac{\Delta P.A}{\mu.R_t} \tag{2.22}$$

Substitution of equation 21 into 22 and some arrangements gives:

$$q_f = \frac{\Delta P.A}{\mu}\left\{\frac{1}{r.v^c.\frac{v_f}{A} + R_m}\right\} \tag{2.23}$$

Based on Darcy's law, the equation derived relates the flow rate of filtrate as a function of the feed or broth's properties (μ , c), the specific cake resistance r, the filter area A, the medium resistance R_m and the volume of the filtrate v_f . Because : $v_f = {dQ_f}/{dt}$ in equation 23 which can be integrated. It should be noted here that there are two modes of filter operation:

- at constant pressure difference
- at constant flow rate

Since constant pressure filtration is probably the most common type of filtration in biotechnology, equation 23 will be solved first for this mode of operation. In batch mode filtration at constant pressure, all variables are assumed to be independant of the applied filtration pressure. Therefore :

$$\int_0^t dt = \frac{\mu.r.v^c}{A^2\,\Delta P}\int_0^V V.dV + \frac{\mu.R_m}{\Delta P.A}\int_0^v dV \tag{2.24}$$

Integration yields :

$$t = \frac{\mu.r.v^c}{2.A^2.\Delta P}v_f^2 + \frac{\mu.R_m}{\Delta P.A}v_f \tag{2.25}$$

Using equation 25, the time required to filter a volume *v* and visa versa may be calculated, provided the specific cake resistance is known.

In constant rate filtration the flow is kept constant by varying the operating pressure. Substitution of $Q = v_f.t$ and the integration of equation 23 gives :

$$\Delta P = r.\mu.v^c\left(\frac{q}{A}\right)^2 + \mu.R_m\frac{q}{A} \tag{2.26}$$

or simplified further :

$$\Delta P = a_1 . t + b_1 \qquad (2.27)$$

in which $a_1 = r\mu v^c$ *and* $b_1 = \mu r$

Constant rate filtration as such has limited application in biotechnology. However, in many cases the filtration is operated by a centrifugal pump, where the early stage of the filtration is conducted at nearly constant rate. As the cake becomes thicker, it offers more resistance to flow, the pressure development by the pump becomes a limiting factor and the filtration proceeds at a nearly constant pressure due to the typical centrifugal pump characteristics.

2.2.8.3 Fitration Mechanisms

There are three mechanisms that determine the retention capability of filters :

- mechanical screening effect
- adsorptive retention of sludge particles
- surface filtration

In the case of mechanical screening effect, the particles are retained in the filter media or filter labyrinth by virtue of their size. They gradually block the pores causing the filtration rate to be reduced while the pressure remains constant. In addition to mechanical screening, adsorptive forces take effect in filter media, causing the separation of finer particles and solutes. For instance, sludge particles and colloids in neutral to slightly acidic solutions often have a negative surface charge. Filter media with a positive potential will have a strong adsorptive effect on the particles. These adsorptive mechanisms of charge are frequently termed *zeta-potential*. This is defined as the electrical charge built up around solid particles in an electrolytic liquid. Figure 2.1 shows the development of this potential diagrammatically, as postulated by Raistrick[14]. The phenomenon of the zeta-potential depends on the pH of the solution, shown in Figure 2.2.

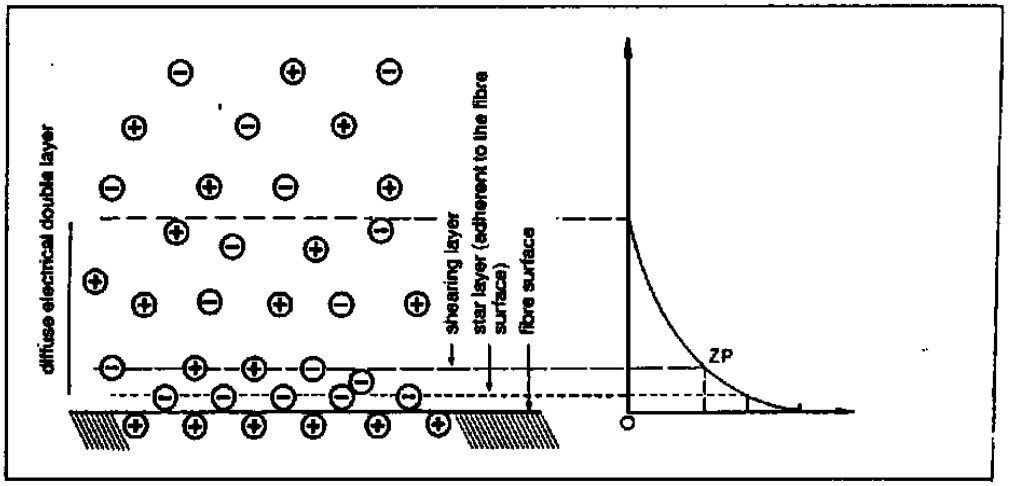


Figure 2.1 : Build-up of the zeta-potential at a positive zeta-potential fibre surrounded by electrolytic liquid

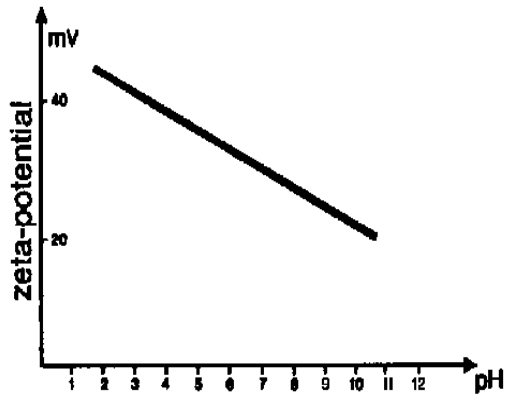


Figure 2.2 : Dependence of zeta-potential on pH

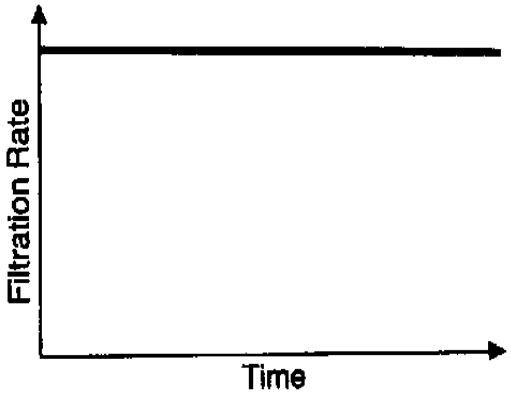


Figure 2.3 : Filtrate rate vs. time

As particles and molecules that are retained purely by adsorption hardly impede the free passage of liquid, the filtration rate remains nearly constant over the entire filtration time if the process is entirely an adsorptive one, as seen in Figure 2.3**.** The difference in size of the particles to be separated varies over a wide range, therefore filtration purely by the screening method or purely through adsorptive mechanisms, is the exception. Both processes will take place with one or the other dominating and this will be dependent on the charge characteristics of the feed solution, together with the filtration media. Surface filtration displays different characteristics.

In addition to the effects described above, particles larger than the inlet pores are retained at the filter media surface. In connection with surface filtration, one can distinguish between two types of particles, namely compressible (i.e. deformable) and incompressible. The higher the content of compressible particles, such as gel-type particles, the sooner the blockage on the surface of the filter media. The filtration rate is reduced proportionately. These particles block the surface pores and after a short period of time they form a nearly impermeable thin layer. Liquids with a relatively high proportion of these deformable slimy particles are usually of very poor filterability.

In this case of CSL this layer can consist of a host of substances. In order to prevent an early superficial blocking of the filter media, the filter media and the individual filtration steps should be selected for reasons of economy. This should be implemented in such a way that depth filtration takes place and not surface filtration. Figure 2.4 shows a comparison by Brenner[15] of surface filtration and depth filtration. Figure 2.5 shows the performance curve of true depth filtration. Data acquired from true depth filtration makes filter sizing and scale-up to continuous or batch operation simple with minimum risk on operability.

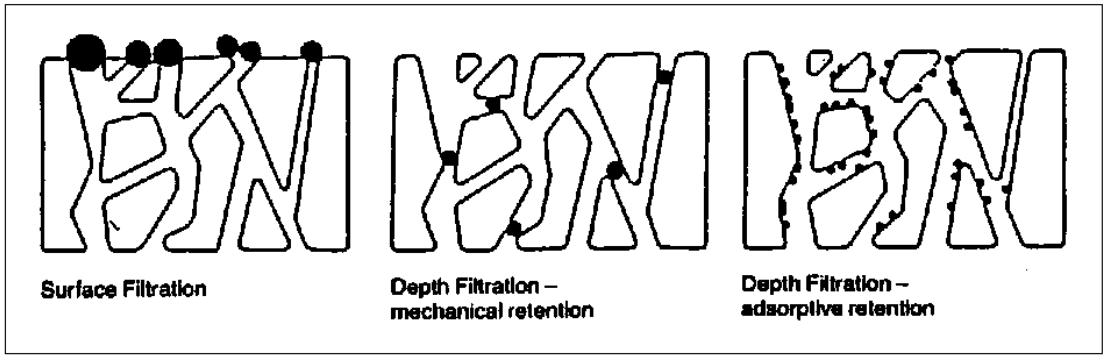


Figure 2.4 : Comparison : surface filtration vs depth filtration

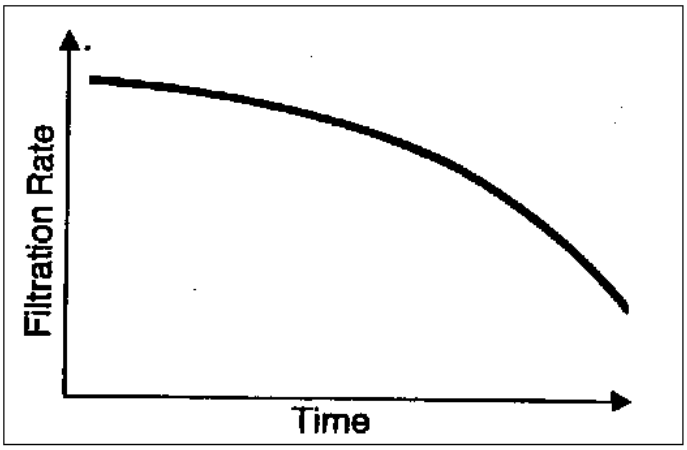


Figure 2.5 : Development of the filtration rate curve as a function of time in true depth filtration

2.2.8.4 Effect of pre-filtration viscosity on filtration efficiency

The viscosity of the liquid to be filtered has a significant influence on the filterability. With most liquids the viscosity is a function of the temperature. If an increase in filtration temperature is allowed by the process, then an increase in filtration rate, equal to the viscosity decrease, will result in accordance with equation 19. The manipulation of viscosity as a variable will have a direct impact on the performance of filtration equipment and also the sizing of such equipment.

2.2.8.5 Filter Media

The filter medium is the heart of any filtration step and should therefore be selected carefully. There exists, however, no proper method or even clear criteria to select media. The selection depends largely on experience in small and large-scale operation. Only rough guidelines can be given here. The performance of any filter medium may be characterised by the next three criteria :

- clarity of the filtrate
- resistance to flow
- durability

The clarity of the filtrate depends on the aperture of the filter medium and the particle size as well as the ability of the particles to form bridges to cover the pores. As a rule of thumb the aperture is 3-7 times larger than the particle size. Initially there will be a breakthrough of the particles, which will stop as the bridges are formed.

So in cake filtration the function of the filter medium is limited to the first few particles layers of the cake. If no clear filtrate can be obtained, a pre-coat can be necessary sometimes. The resistance to flow depends to a great extent on the porosity or free area of the medium, which, in turn depends on the material used and the type of manufacturing. Table 2.1 gives an overview of the filter media available for filtration in biotechnology.

Table 2.1 : Overview of filter media for bio-filtration.

Filter Medium	Examples	% Free Area
Woven fabrics	Cloths, Natural and synthetic fibres	20-40
Rigid porous media	Ceramics, sintered metal, Glass	50-70
Metal sheets	Perforated, woven wire	5-20
Non woven sheets	Felts, paper, mats	60-80
Loose solids	Sand, diatomaceous earth, perlite, carbon	60-95

The resistance to flow can be determined experimentally at bench scale by passing water or air through the medium. The ability to pass air or water is a measure for the medium permeability. The durability depends on a large number of factors:

- broth/slurry characteristics
- abrasiveness of the particles
- medium material and manufacturing
- cleanability
- filtration temperature and pH
- type of filter and the size

Selection of filter media is usually done in close co-operation with the supplier.

2.2.8.6 Filter aids

If the specific cake resistance is too high i.e. >> 10^{14} m^{-1} or the cake is too compressible, an addition of filter aid could be a solution to the problem. Filter aids can improve the filtration rate considerably, in some cases, by orders of magnitude. Two modes of operation are common:

- body feed filtration
- pre-coat filtration

In body feed filtration, the broth is mixed with filter aid up to 10% m/m but is usually applied in the range of 3 to 5% m/m. Here the filter aid serves as a body builder to obtain high cake porosities in order to maintain high rates.

When the particles are too small to be retained by the filter medium, a layer of filter aid called pre-coat can be formed on the medium.

This is commonly referred to as "deep bed filtration". Pre-coat filtration is also frequently applied as a polishing filtration. Among the various filter aids commercially available, diatomaceous earth is by far the most commonly used. Filter cakes formed by diatomite are highly porous (~ 85%) and non-compressible.

2.2.8.7 Cake dewatering and drying

Proper filter cake removal, handling and deposition, makes dewatering, and sometimes drying, necessary. Dewatering can be done in various ways :

- Displacement by a gas
- Squeezing the cake
- Centrifugal dewatering

A necessary condition for displacement by a gas is that the applied pressure exceeds the capillary pressure. Dewatering with a (gas) is far from perfect. It seldom succeeds in removing more than 50% of the cake liquid. Cakes are frequently dewatered by sqeezing the cake between two membranes in a specially designed filter press. Squeezing can be accomplished either by compressed air or liquid. Centrifugal dewatering is one of the features of filtering centrifuges and not commonly used in biotechnology, due to the rheological nature of bio-materials. Cake drying can be done with hot air or gas, the efficiency is low and therefore seldom applied in biotechnology.

2.3 Liquor Conditioning Followed by a Decanter Centrifuge

2.3.1 Introduction

Centrifuges harness the very strong G-forces generated by high speed rotation. So, they are often the equipment of choice for solid-liquid systems in which the solid phase does not readily drop out of suspension or where the separation must be made rapidly. Centrifuges are widespread in the chemical, food processing and pharmaceutical industries as well as in mining operations and waste water treatment plants, and they are important in other processing situations as well. They are used not only for straightforward recovery of solids or liquids from slurries, but also to clarify liquids or to classify solids.

Centrifuges can be divided into two categories, filtering and sedimentation. The former, using basically a rotating basket fitted with a filtering medium, is like filtration except that the centrifugal action rather than pressure difference is the major driving force that expels the fluid. The sedimentation version relies instead on a difference in density between the solid phase and the mother liquor. As the incoming slurry is made to spin, the denser solid moves out towards the wall of the centrifuge bowl while clear liquor overflows weirs or is picked up by a skimmer. In each version the solids are recovered intermittently or continuously.

Most naturally occurring colloidal particles have negative charges. As a result they repel one another and resist the tendency to agglomerate (flocculate) upon colliding. In their natural state, these colloids are not removed efficiently by granular media filters because of their small size and because the media are also negatively charged and tend to repel colloidal particles. Centrifuges also have difficulty in separating such solids due to the small density difference between the solids and the liquor.

These difficulties are overcome by using coagulants-positively charged polymeric compounds that are capable of neutralising the negative charges on colloids. Coagulants include organic polyelectrolytes, alum (aluminium sulphate), and iron salts. These are generally added to the feed liquor upstream of the centrifuge. Once the negative charges have been neutralised, collisions between colloidal particles are likely to result in flocculation of the particles and centrifugation improves significantly. This subsequent agglomeration of particles increases the density difference between the liquor and the agglomerated particles, and sedimentation under centrifugal force becomes easy.

2.3.2 Theory of operation of sedimentation devices

The centrifuge length and the throughput to be handled impose a minimum required settling rate for the solid material if it is not to leave with the overflow. Meanwhile, the properties of the feed and the radius and rotational speed of the centrifuge determine the settling rate that is available.

2.3.2.1 The settling rate required

Consider the operation of a sedimenting centrifuge in its simplest terms. Feed slurry brought up to the rotational speed of the unit forms an annulus, sometimes called a pool or pond, adjacent to the bowl wall. Assume that re-entrainment is minimal and that the solids are removed once they settle on the bowl wall. Also assume that the particles entering the centrifuge are distributed uniformly across the depth ***h*** of the pool through which they have to settle. Then an average particle must travel a radial distance equal to ***h/2*** while settling.

The upper limit on the time available for settling is given by the residence time ***t*** that a particle would otherwise reside in the centrifuge before being carried to the overflow. Assuming plug flow, this is simply

$$t = \frac{L}{U} = L\left(\frac{A}{Q}\right) \tag{2.28}$$

where L is the distance between the feed inlet and the overflow (i.e., the length of the sedimentation portion of the centrifuge) and U is the bulk flow velocity, estimated from the volumetric throughput Q and the cross-sectional area A of the annulus.

Given the height required to settle and given the residence time, the "required" settling rate in order to assure that the average particle is removed through sedimentation is :

$$V_{S\ (req.)} = \frac{\left(\frac{h}{2}\right)}{t} = \frac{1}{2}\left(h/L\right)\left(Q/A\right) \tag{2.29}$$

after making substitution from equation (28).

We can visualise the trajectory of an average particle as it enters at *h/2* on one end of the sedimentation section and settles to the bowl surface of the centrifuge while being carried a distance L by the bulk flow.

It follows that if the settling velocity is less than the value prescribed by equation (29), an average particle would not reach the settling surface in time and would be carried out in the overflow. Conversely, any higher settling velocity will enable the average particle to settle out before reaching the overflow exit.

Equation (29) also brings out the equivalence between sedimentation centrifugation and odinary sedimentation (under the normal force of gravity). Because *L(A)* is the volume of the pool and *h* is its depth, *L (A/h)* is roughly the "cross-sectional area" through which the outward-moving settlable material passes en route to the wall.

Therefore, equation (29) suggests that the required settling rate for the average particle is the throughput divided by the settling surface area, a very familiar result in sedimentation.

2.3.2.2 The settling rate available

The most useful mathematical relationship in sedimentation is the simple one given by Stokes, who derived the terminal velocity of a discrete particle settling in an infinite fluid medium of viscosity μ. At that velocity, the net weight of the particle (after discounting the effects of buoyancy) balances the viscous drag on it.

This settling velocity V_S can be obtained from the equation,

$$V_S = \left(\Delta\rho / 18\mu\right) g\, d^2 \left(G/g\right) \tag{2.30}$$

where, *d* is the particle diameter in meters, μ is in kilograms per-meter second, Δρ is the difference in density between the particle and the fluid, *g* is the gravitational constant and the ratio *G/g* is defined by the equation,

$$G/g = \Omega_b{}^2 R_b / g \tag{2.31}$$

where, Ω_b is the rotational speed of the bowl in radians per second and R_b is the bowl radius in meters. This ratio measures the centrifugal acceleration developed in units of gravity.

For gravity settling, G/g equals 1. For centrifuges, however, the ratio can have a value in the order of thousands, depending on the radius and rotational speed of the bowl.

2.3.2.3 Putting the rates together

The required rate from equation (29) can be equated with the available rate from equation (30) and the equation rearranged as follows:

$$Q = 2V_{S\ (1g)}\left(\Omega_{b^2}\quad R_{av}/g\right)\left(L\quad A/h\right) \tag{2.32}$$

where, $V_{s(1g)}$ is the settling velocity under gravity settling and R_{av} is the average radius of the bowl and the pool. This equation shows that the throughput Q increases with the Stokes settling velocity, the intensity of centrifugation G/g, and the surface area for settling.

For centrifuges with a cylindrical bowl,

$$A = \pi\left(R_{b^2} - R_{p^2}\right) \tag{2.33a}$$

$$h = R_b - R_p \tag{2.33b}$$

Where, R_b and R_p are the radii of the bowl and the pool, respectively. Substituting these equations into equation (32) gives

$$Q = 2V_{S\ (1g)} \times \left(\Omega^2\quad R_{av}/g\right) \times 2\pi\, R_{av} L \tag{2.34}$$

or

$$Q = \textit{Stokes settling} \times G \times \textit{surface area}$$

This relationship, based strictly on the limiting-trajectory concept and Stokes's law, has also been derived for centrifuges of different geometries. It has also been modified[10] to take into account the effect of radius on *G*. In all cases, throughput remains proportional to the three parameters discussed above: particle settling characteristics, *G*, and surface area.

Any observed discrepancies from equation (34), for instance during field trials, are due to complex factors not taken into account here. These fall into main categories. One is the effect of Coriolis forces[11], particle size distribution, hindered settling and particle shape on the settling process. The other is the fluid dynamic effect of rotation upon the flow through the centrifuge, a consideration especially relevant for continuous centrifuges.

2.3.3 Decanter Centrifuge Specifications

The scroll-type continuous-conveyor-discharge decanter is characterised by a horizontal conical or conical cylindrical bowl. The bowl has a length-to-diameter ratio ranging from 1,5 to 3,5. The Alfa-Laval Model NX 210 used in these trials has a length-to-diameter ratio of approximately 1,5. It contains a screw conveyor that rotates in the same direction, but at a slightly higher or lower speed than the bowl. On this particular model the speed difference can be adjusted between 4 and 100 rpm. The bowl speed has been fixed at 3286 rpm, which results in a lower centrifugal force than that of a high speed disk stack centrifuge.

Feed enters through an axial tube at the centre of the rotor, passes through openings in the screw conveyor and is fed to the rotor wall. Solids deposited on the wall are moved by the helical screw conveyor up a sloping beach out of the liquid and discharged at a radius smaller than that of the liquid discharge. The liquid level is maintained by ports or weirs that can be adjusted to the desired pool depth.

It has been shown elsewhere[16] that a settling force of 2000 to 3000 g's is usually produced, but up to 4000 g is possible on some machines. For this particular model the centrifugal force is approximately 3000 g. Feed flowrates range from 0,4 to 60 m^3/hr depending on the machine and application. When operating as a clarifier, the scroll-type centrifuge recovers medium and coarse particles from a wide range of feed concentrations, 2 to 50% by volume according to Mackay and Salusburg[17]. Particles smaller than 2 μm are normally not collected. Since bacteria range between 1 and 2 μm in size, and some protein particles and cell debris are even smaller than 1 μm, separation in a decanter is most unlikely. Chemical pretreatment of the CSL is therefore necessary.

Polyelectrolytes are used for the agglomeration and subsequent flocculation of the particles. This increases the particle size and density which in turn improves settling and dewatering characteristics. To aid centrifugation, a fast acting flocculant is required, as the residence time within a decanter is of the order of seconds. To increase the contact time, the point of addition of the flocculant may be varied. Anionic flocculants are usually dosed upstream of the centrifuge, while cationics, which react faster, may be added within the centrifuge.

In decanters, considerable variations occur in the design of the shell contour, flight angle and pitch, beach angle and length, conveyor speed and feed position. An alternative to the open liquid overflow-outlet is a paring tube for skimming of the liquid.

It has been shown by Records[18] that the residual moisture content of the sludge solids can be as low as the equilibrium saturation point. This can be obtained at very low feed rates because of shear effects in the solids moving up the sloping beach above the liquid level.

2.3.4 Coagulation and Flocculation

Predicting particle settling behaviour in biological broths such as CSL is complicated because of variations in the rheology. The addition of chemical reagents destabilises the liquor's colloidal system, increases the particle size and improves the settling rates. Settling behaviour primarily depends on the degree of flocculation and solids concentration. Svarovsky[19] shows that there are four basic regimes of settling behaviour: particulate settling, flocculation clarification, zone settling and compression. This is illustrated in Figure 2.6

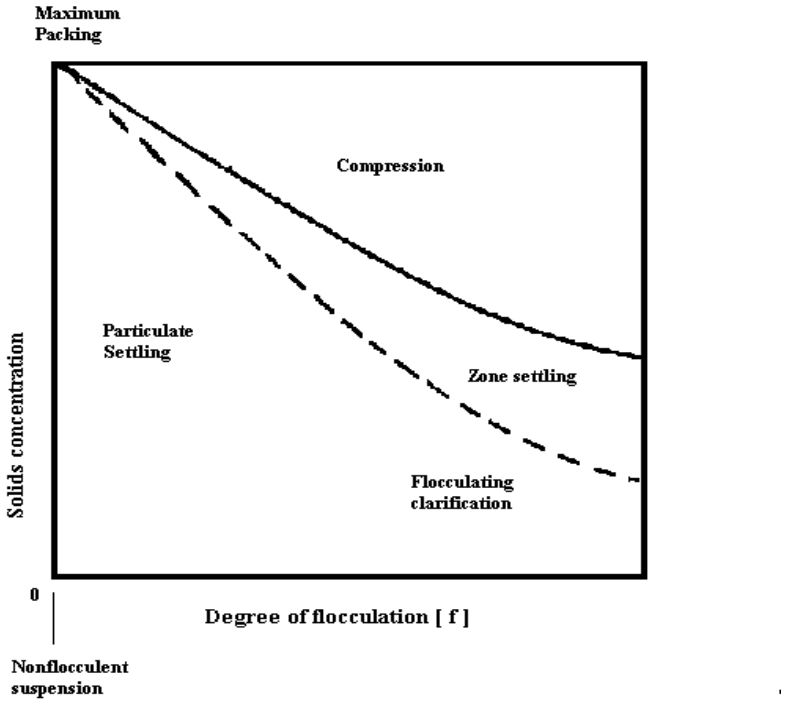


Figure 2.6 : The four basic regimes of settling behaviour

In particulate settling, particles settle independantly, with the settling velocity being a function of concentration and particle size**.** This type of regime is exhibited by non-flocculant suspension (such as coarse particulate mineral slurries), in which particles remain separate at all concentrations up to final packing, and their weight is borne solely by hydraulic forces.

In flocculation clarification, particles agglomerate into separate flocs that settle at their own rate. In both particulate settling and flocculation clarification, the supernatant liquid gradually clarifies. With a flocculating suspension, the flocs crowd closer together as concentration increases, until they come into very loose contact, forming a plastic structure. At this point, the suspension enters the zone settling regime, which is characterised by essentially all particles, regardless of size, moving at the same velocity. A visible interface occurs that moves downward from the surface of the suspension. As seen in Figure 2.6, there is no single concentration at which zone settling begins. It depends on the degree of flocculation of the system.

As concentration increases further, the structure becomes firmer, eventually entering the compression zone where it attains compressive strength.

Thus, in addition to being supported by hydraulic forces, it is now supported mechanically from underneath. The structure (now sludge) becomes a porous medium that continues to consolidate solids, but settles at a much slower rate.

Based on laboratory evaluations and screening of chemical reagents, Sedipur CF 803, a high molecular weight (10^6), high charge density cationic flocculant has been chosen from the BASF range. For the process of coagulation, an in-depth study has indicated polyaluminium chloride (PAC) to be the best choice.

2.4 The use of Gyratory Screens for the Separation of Suspended Solids

2.4.1 Introduction

A large proportion of the suspended solids in CSL were found to be fibrous in nature. These type of solids pose an especially severe problem to membrane systems. Fibrous type solids tend to penetrate and entangle in membrane mesh spacers and are extremely difficult to remove. Moreover, the formation of gel layers tend to attract fibrous solids which become emeshed in the gel. As a result of this, flow channel blockages are common occurrences, and the membrane is subjected to a large pressure drop on the concentrate side.

This obviously puts the membrane under severe stress, and the recommended tolerable pressure drop is quite easily exceeded under these conditions. The deleterious effects of exceeding the maximum tolerable pressure drop is quite well documented in the literature[20] on membranes.

It is understood that the level of screening required for an operating membrane system is dependant on the application. For this particular application, a screening cutoff of 100μ has been stipulated. It is also common practice for membrane plants to be equipped with "safety" filters or mesh screens as a protective device. In the processing of CSL, this feature is inadequate to meet the demands of the very high solids loading in the feed stream. It is primarily due to the above mentioned shortcoming that an alternative method of screening has been devised.

As shown earlier, a number of separating techniques have been investigated to help solve this problem. This selection procedure[21] was simplified by using the modified decision tree developed for such separations. Centrifugation is certainly a very effective option for the total removal of suspended solids, but this is also very capital intensive and does have high operating costs. Another viable option, investigated on a pilot scale, was the use of sieve bends. These are used quite extensively in industry and certainly meet the economic requirements of low capital and operating costs. For this particular application, problems were experienced with the cleaning of the screens, which fouled quite readily. To implement the same separating principle and to overcome the problem of screen fouling, gyratory screens were investigated.

2.4.2 Gyratory Screens

This type of screening technique has been in existence for many years, being used extensively in the mining, pharmaceutical and chemicals industries. It has only recently been incorporated into the area of

biotehnology. Its operating principle enables it to be used for both wet and dry separations. Figure 2.7 shows the simple screening operation. Basically, this separator is a screening device that vibrates about its centre of mass. Vibration is accomplished by accentric weights on the upper and lower ends of the motion generator shaft. Rotation of the top weight creates vibration in the horizontal plane, which causes material to move across the screen cloth to the periphery. The lower weight acts to tilt the machine, causing vibration in the vertical and tangential planes. The angle of lead given to the lower weight with relation to the upper weight provides variable control of the spiral screening pattern.

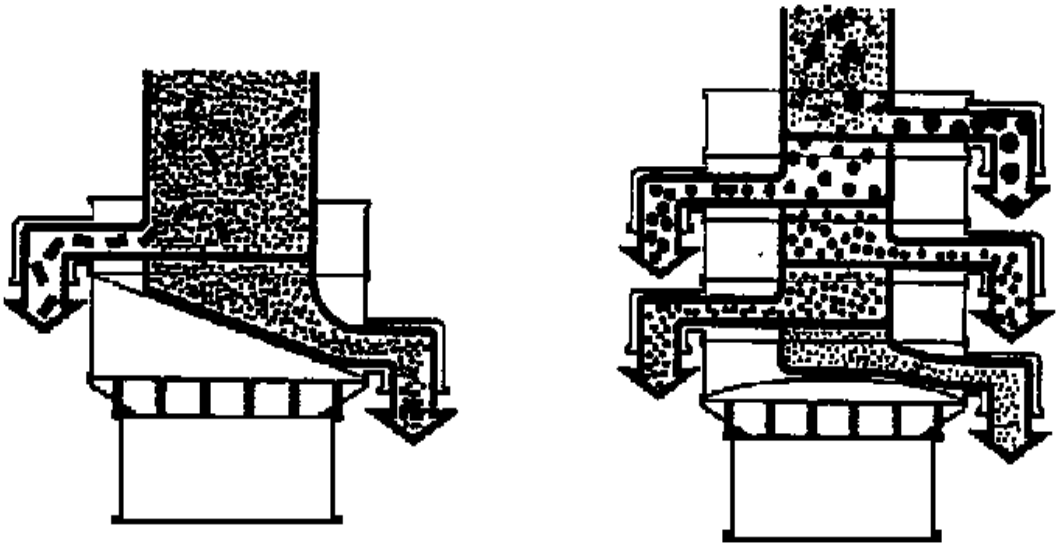


Figure 2.7 : The gyratory separator classifying solid particles

The manipulation of the speed and spiral pattern of the material can be set for maximum throughput and screening efficiency of any screenable product, wet or dry. Figure 2.8 shows the operating principles of the separator. These diagrams show the screen patterns obtainable when you change the angle by which the the lower motion-generator weight leads the upper one. Adding or removing the weight plate amplifies or increases horizontal or vertical amplitudes, thus effecting throughput rate and efficiency ratio.

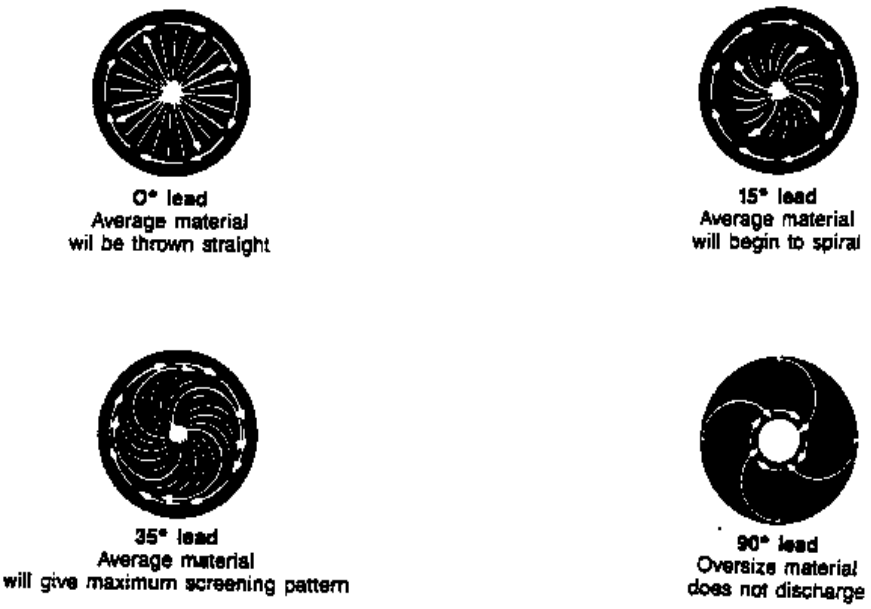


Figure 2.8 : The weight adjustment effects on screening patterns

Another useful feature of the separator is the simple self cleaning mechanism which improves the efficiency of the separation. The action of the separator causes sharp edge sliding cylinders to scrape the underside of the screen, cutting off dangling fibres as well as freeing near sized material lodged in the openings. By reducing blinding, the self cleaning mechanism improves the liquid-solid separation. Also, a system of rotating brushes is used to remove oversized material which have a tendency to staple over or entrap themselves in the screen. No external drive mechanism is required to rotate the brushes. The 3-dimensional vibro-energy motion of the separator forces the brushes to move in a preset direction.

CHAPTER 3

REVIEW OF MEMBRANE ULTRAFILTRATION PROCESSES

3.1 Introduction

A precise and complete definition of a membrane which covers all its aspects is rather difficult, even when the discussion is limited to synthetic structures as in this outline. In the more general sense, a synthetic membrane is a barrier which separates two phases and restricts transport of various chemical species in a rather specific manner. A membrane can vary, being homogeous or heterogenous, symmetric or asymmetric in structure; it may be solid or liquid; it may neutral or charged, or may be bipolar. Its thickness may vary between 100 nm to more than a centimetre. The term "membrane", therefore, includes a great variety of materials and structures, and a membrane can often be better described in terms of what it does rather than what it is.

In recent years, membranes and membrane separation techniques have grown from a simple laboratory tool to an industrial process with considerable technical and commercial impact[22]. Today, membranes are used on a large scale to produce potable water from the sea by reverse osmosis, to clean industrial effluents and recover valuable constituents, to fractionate macromolecular solutions in the food and drug industry[23], and numerous other significant applications. Although membrane processes may be very different in their mode of operation, in the structures used as separating barriers, and in the driving forces used for the transporting of the different chemical components, they have several features in common which make them attractive as a separation tool. In many cases, membranes processes are faster, more efficient and more economical than conventional separation techniques.

The membrane process most commonly used in biotechnology separations is ultrafiltration. Ultrafiltration membranes have a molecular weight cutoff ranging from about 100 000 Dalton to about 20 000 Dalton. This makes them ideal for the removal of proteins and other large organic macromolecules from suspensions.

Ultrafiltration can be operated both in continuous and batch modes and therefore presents several advantages over other separation methods. With membranes, the separation is usually performed at ambient temperatures, thus allowing the temperature-sensitive solutions to be treated without the constituents being damaged or chemically altered. It is specially suitable when dealing with thermally degradable substances because no heat is added. On the other hand, they have the ability to operate at higher temperatures, such as in some biotechnology applications where viscosity limiting conditions may

prevail. For such applications membranes are usually "tailor-made" so that their properties can be adjusted to the specific separation task. This is why ultrafiltration is substituting some concentration and separation processes in a variety of industries, mainly in biotechnical applications with proteins and other sensible biomolecules[24,25].

There are some disadvantages as well with ultrafiltration. Given that a membrane retains an interesting biomolecule or group of bio-components, it should also give high fluxes in order to increase the operating efficiency of ultrafiltration. However, it is known that permeability decreases until being more or less constant for high pressures[26]. The existence of such a maximum for the flux has been attributed to concentration-polarisation, i.e., the accumulation of the rejected solute in a boundary layer in contact with the membrane surface. In these conditions, the resulting mechanism of flux reduction has been variously thought[6] to consist of :- a reduction in the driving force due to the increases in the osmotic pressure at the membrane surface; the gelation of the retained solute with the appearance of an extra hydraulic resistance; or a fouling process.

Usually, only the nominal molecular weight cutoff is given by manufacturers of ultrafilters to specify their product's characteristics. Nevertheless, in practice, this cutoff is not clearly defined attending to the membrane heteroporosity and solute polydispersity. On other hand, the solute-membrane interface characteristics influence the molecular weight cutoff, making it dependant on the applied pressure and the velocity of circulation used in the retentate (concentrate) loop. Consequently, the retention and separation characteristics for each type of membrane will be very different and will also differ from application to application.

The aim here is to study tangential ultrafiltration of CSL proteins through several types of membranes, where the "best" membrane type and configuration is selected for the subsequent process design and long term testing by a piloting programme. It is also important to note the preceding research performed on the CSL pre-treatment process. All the research and development on the ultrafiltration process uses the assumed base case of a clarified CSL stream as the feed to the membrane system.

3.2 Theoretical Background

3.2.1 Fundamentals of Membrane Processes

Membranes used in mass separations differ significantly in their structure, function, and application. The type of membrane used depends directly on the characteristics of the application, therefore membrane separation processes can be rather different in their process design. In ultrafiltration, the membrane structures are heterogenous to meet the demands of both simple and intricate operations. A multitude of very different structures is summarised under the term "membrane".

All these structures have a common phenomenon, in that they affect permeation of different chemical components in a specific way. Membranes achieve the separation of molecular mixtures by restricting the permeation of certain components while others may pass unhindered.

In ultrafiltration the driving force for mass transport is the hydrostatic pressure difference, but depending on the type of membrane, the separation mechanism may be different. For instance, separation can be achieved by a "sieving effect", where the components of a mixture are sorted out according to their size. Separation can also be based on different solubilities and diffusion coefficients of the single components in the membrane matrix.

Technically relevant[27] membranes are summarised in Table 3.1. Structures of various membranes are shown in the scanning electron micrographs in Figure 3.1.

Table 3.1. Properties and Applications of Technically Relevant Synthetic Membranes.

Membranes	Basic Materials	Manufacturing Procedures	Structures	Applications
Ceramic membranes	Clay, silicate, aluminiumoxide graphite, metal powder	Pressing, sintering of fine powders	Pores from 0.1 to 10 microns	Filtering of suspensions, gas separations
Stretched membranes	Polytetrafluoro-ethylene, polyethylene, polypropylene	Stretching of partially crystalline foil perpendicular to the orientation crystallyts	Pores of 0.1 to 1 microns	Filtration of aggressive media, air, sterile filtration, medical uses
Etched polymer films	Polycarbonate	Radiation of a foil and subsequent acid etching	Pores of 0.5 to 10 microns	Sterile filtration, medical, analytical
Symmetrical microporous membranes	Cellulose derivatives, polyamide, polypropylene	Phase inversion reaction	Pores of 50 to 5000 nm	Sterile filtration, dialysis, distillation
Integral asymmetric membranes	Cellulose derivatives, polyamide, polysulfone	Phase inversion reaction	Pores of 1 to 10 nm	Ultrafiltration, hyperfiltration, gas sep., pervaporation
Composite asymmetric membranes	Cellulose derivatives, polyamide, polysulfone, polydimethyl-siloxane	Application of a film to a microporous membrane	Homogenous polymer or pores from 1 to 5 nm	Ultrafiltration, hyperfiltration, gas sep., pervaporation
Ion exchange membranes	Polyethylene, polysulfone, polyvinyl-chloride	Foils from ion-exchange resins, sulfonation of polymers	Matrix with positive or negative charges	Electrodialysis, electrolysis

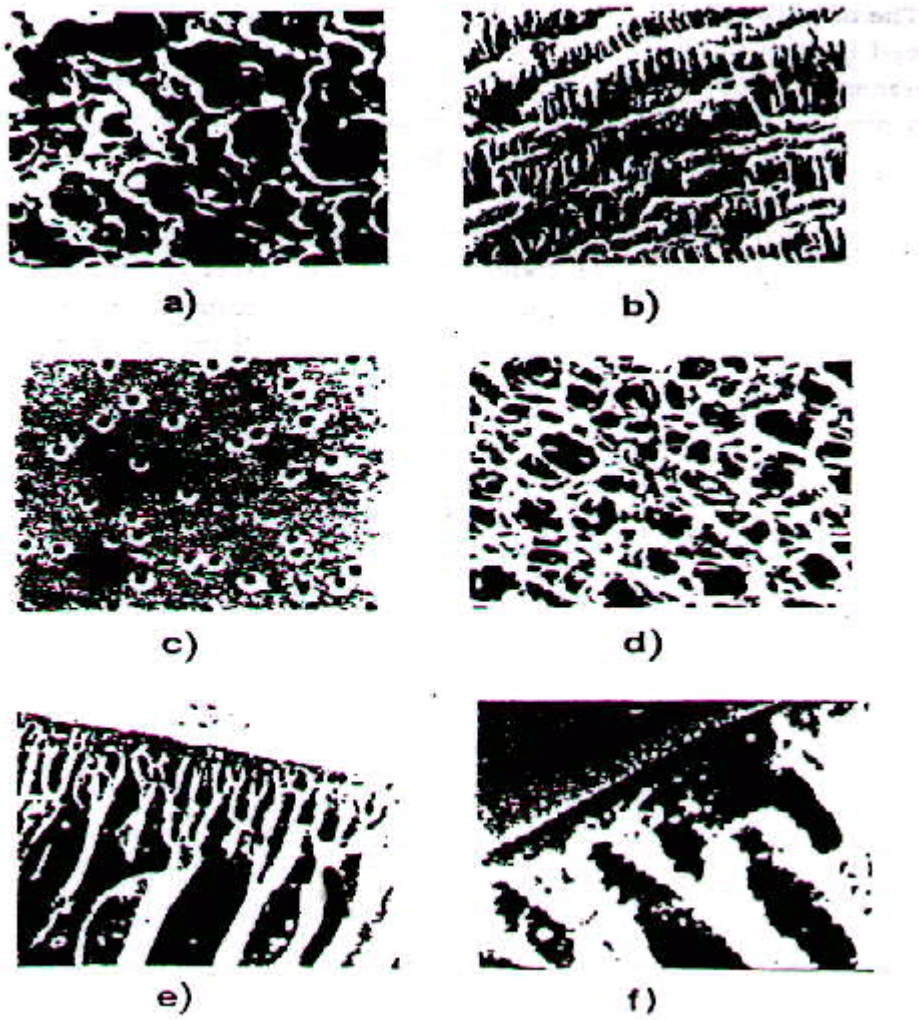


Figure 3.1 : Scanning electron micrographs of membrane structures:

a) PTFE-sintered membrane; b) stretched PTFE membrane;

c) capillary pore membrane; d) symmetric MF membrane;

e) asymmetric UF-membrane; f) composite membrane

The most simple form of synthetic membranes are porous plates or foils. They are produced by pressing and sintering a polymeric, ceramic, or a metal powder. These membranes have relatively large pores, a wide pore size distribution and a low porosity. The symmeric or asymmetric phase inversion membranes are more complex in their production as well as their structure. They are produced by precipitation of a polymer solution. These membranes are used today in micro- and ultrafiltration and as well as in gas separation. Composite membranes are more and more employed in the above mentioned processes. The

selective layer and the support structure of these membranes consist of different materials. The membranes with functional groups are gaining increasing importance in various applications.

3.2.2 Membrane Modules

For a membrane to be useful in industrial separation processes it has to be installed in an appropriate device generally referred to as a membrane module. Typical membrane modules used in biotechnological processes are :

- plate and frame module
- tubular module
- capillary module
- hollow fibre module
- spiral wound module

In the plate and frame module the membranes are installed as flat sheets and are mainly used for micro- and ultrafiltration. The advantage of this system is that it can be easily disassembled for membrane replacement and cleaning. In tubular modules, the membranes are installed in porous support tubes with an inner diameter of 1-2 cm. They are used mainly in micro- and ultrafiltration. Tubular systems normally operate at higher cross flow velocities, which in turn helps to overcome the concentration polarisation and fouling. In capillary membrane modules, they are manufactured as capillaries and installed in an outer shell tube. The feed solution is introduced into the inner lumen of the capillary. This type of membrane is extensively used in ultrafiltration applications.

In hollow fibre modules the installation of the membranes is similar to that of a capillary module. However, the feed solution penetrates the fibre from the outside and the product leaves from the inner lumen. Hollow fibres are very sensitive to membrane fouling and are mainly used for reverse osmosis with relatively "clean solutions".

In the spiral-wound membrane module, which is used extensively for reverse osmosis, ultrafiltration and microfiltration, the membranes are placed as a sandwich on a porous support and then wound in a spiral type configuration. A relatively high surface area can be installed per unit volume and investment costs are low.

3.2.3 Fluxes through Membranes

The important characteristics of membrane separations are the **rejection** of solutes and the magnitude of the transmembrane transport of the solvent and solute species (**flux**).

The rejection is defined as :

$$R = 1 - \frac{C_p}{C_r} \tag{3.1}$$

where C_r and C_p are the concentrations of the partially rejected species in the retentate and permeate respectively. Rejection and transmembrane flux are strongly dependant on the extent of partitioning of solvent and solute over the solution and membrane phase, as well as the extent of specific interaction during transport through the membrane. The partitioning effect provides the basic selectivity of the membrane, which is not dependant on the operating conditions (equilibrium selectivity) whereas the different interactions of the various solvent and solute species with the membrane lead to a selectivity (kinetic) which is dependant on the operating conditions. The quantification of the equilibrium partitioning as well as for the driving force for the transport through the membrane will be outlined in following sections.

The consequence of the partial or total rejection of solutes by the membrane, is an accumulation of that species in the boundary layer adjacent to the membrane surface. This phenomenon is referred to as "concentration polarisation" and the resulting boundary layer is called the "polarization layer". The extent of concentration polarization is determined by convective transport towards the membrane and diffusion from the membrane back into the bulk solution. The occurrence of concentration leads to an extra resistance to mass transfer. In contrast, with the transport through the membrane, this extra mass transfer resistance is strongly dependant on the hydrodynamic conditions at the feed side of the membrane.

3.2.4 Steric hindrance

The pore size of UF membranes has the same order of magnitude as the solvent and solute molecules transporting through it. Using a hard sphere model for a molecule, it cannot utilise the complete pore volume, but is 'excluded' from a volume fraction near the pore wall. This fraction corresponds with the diameters of the molecule and the pore. Krishna and Wesselingh (1990) as well as Van Oers (1994) used this 'sphere in tube' model which yields the following relation between liquid and pore composition purely on the basis of steric hindrance:

$$\frac{x^M}{x^L} = \left(1 - d/d_{pore}\right)^2 \qquad (3.2)$$

in which d is the solute/solvent diameter and d_p is the pore diameter. This relation is plotted in the figure below, indicating a strongly increasing rejection when the diameter of the solute or solvent molecule approaches that of the pore.

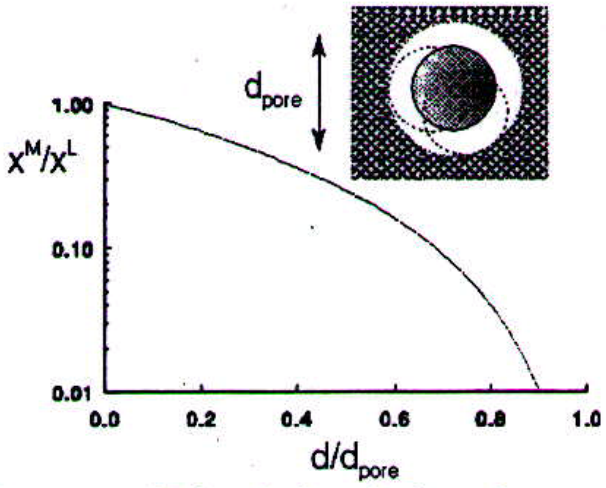


Figure 3.2 : Steric exclusion of solute when approaching pores with similar size.

Therefore the rejection of solute is never a discontinuous function, being zero when the solute is below the pore size and being unity when the solute exceeds the pore size. Therefore, in general, the rejection is a gradually increasing function of molecular size (molecular mass). However, deviation of molecular shape from the idealized 'hard' spherical form, which is more a rule than exception, leaves the above relation for rejection on the basis of steric hindrance as a first estimate only.

3.2.5 Osmotic and Donnan Phenomena

Membrane surface effects and fixed charges in the membranes lead to pressure and potential differences over the membrane and liquid phase respectively. As the pressure difference or the potential difference are equal for any species in the system, this constraints the partitioning for solutes and solvents according to the relation for thermodynamic equilibrium indicated earlier:

$$\frac{x_i^M}{x_i^L} = K_i = \frac{\gamma_i^L}{\gamma_i^M} \exp\left(\frac{\nu_i \quad \Delta \quad P}{RT} + \frac{Z_i \quad F \quad \Delta \quad \Phi}{RT} \right) \tag{3.3}$$

Taking the electrostatic Donnan exclusion as an example, and neglecting the (osmotic) pressure contribution, the above equation simplifies into:

$$\Delta\Phi = \frac{\Delta \quad \mu_i}{Z_i \quad F} + \frac{RT}{Z_i \quad F} \ln\left(\frac{a_i^n}{a_i^I} \right) = \ldots \tag{3.4}$$

The first term on the right hand side corrects for the possible difference in standard state.

3.2.6 Transport equations

A rigorous and unifying approach to describe multicomponent transport processes is the use of the generalised Maxwell-Stefan equation (GMS), which relates the net driving force on a species, in terms of gradients of molar Gibbs energy to the intermolecular frictions with other solutes or solvents as well as with the membrane matrix. The GMS equation in differential form reads:

$$\nu_i x_i \frac{d}{dz} + z_i x_i F \frac{d\Phi}{dz} + x_i \frac{d\mu}{dz} = RT \sum_j \frac{x_i \quad j_j - x_j \quad J_i}{c_t \quad D_{ij}} \tag{3.5}$$

The membrane is considered as a separate component (M=c+1 for slutes/solvents), to be seen as a giant molecule with an infinite mass and uniform distribution in space.

Linearization

Assuming linear gradients over the mass transfer zone with thickness δ, yields a linearized approximation of the GMS relation. The linearized relation, however, contains the essentials of the coupled transport in multicomponents systems and is given by:

$$x_i^* \frac{\Delta P}{P_i^*} + x_i^* \frac{\Delta \Phi}{\Phi_i^*} + x_i^* \frac{\Delta \quad (\gamma\chi)_i}{(\gamma\chi)_i^*} = \frac{1}{c_t} \sum_j \frac{x_i^* \quad J_j - x_j^* \quad J_i}{k_{ij}} \tag{3.6}$$

with

$$P_i^* = \frac{RT}{\nu_i}$$

$$\Phi_i^* = \frac{RT}{(Z_i \quad F)}$$

$$k_{ij} = \frac{D_{ij}}{\delta}$$

The variables indicated with a '*' are linearly averaged over the membrane phase, e.g.

$$x_i^* = 0.5(x_i(0) + x_i(\delta)) \tag{3.7}$$

The difference values over the membrane are treated in a similar way :

$$\Delta x_i^* = (x_i(\delta) - x_i(0))$$

3.3 Membrane Selection

The design of the membrane package or module and the fluid management within that module will profoundly affect membrane performance. Further, the optimum design for one application may be totally unsatisfactory for another application. For example, thin channels promote higher mass transport and flux, but this must be balanced against their greater propensity to foul. In addition, high performance modules must be evaluated in terms of cost, ease of cleaning and replacement. As indicated earlier, there are currently four generic configurations for UF membranes in industrial use: tubes, hollow fibres, plate and frame units, and spiral wound modules. These configurations are available in a variety of polymeric materials. In addition, tubular membranes are also available in sintered stainless steel and ceramics.

In this study, the ultrafiltration of CSL is tested on several membrane types. These filters were selected utilising vendor recommendations with respect to their special characteristics caused by their molecular structures. For example, the SO_2 group in the polymeric sulfone is quite stable due to the electronic attraction of resonating electrons between adjacent aromatic groups. The oxygen molecules projecting from this group, each have two pairs of unshared electrons to donate to strong hydrogen bonding of solute or solvent molecules. This makes polysulfone membranes very durable with a pH range of 1-14, quite good chlorine resistance, and a wide temperature range with hydrophobic properties if untreated.

Similarly, other polymeric membranes such as polyvinylidene difluoride (PVDF), polyacrylonitrile (PAN), polyethersulfone (PES), etc., each have unique chemical properties.

Fouling could be avoided or limited if the solute-surface interactions are minimised by decreasing the membrane-protein affinity. This could be done by controlling the pH level, for example, as shown by Bowen and Gan[28]. Nevertheless, usually low fouling levels are found with tangential filtration devices, especially for high enough tangential velocities of circulation over the retentate face. On other hand, the concoction of proteins present in CSL have iso-electric points spanning a vast pH range and could lead to the formation of protein aggregates.

3.3.1 Molecular weight cut-off

Ultrafiltration membrane pore sizes range from 0.001-0.1μ. It is difficult to measure the pores directly by any of the techniques used for microfiltration membranes. The anisotropic structure and wide distribution of pore sizes makes this almost impossible. Instead we are accustomed to think of the molecular weight of the macromolecules which are retained by or pass through the membrane. Unfortunately, existing UF membranes do not have "sharp cut-offs", because of the wide distribution of pores in the skin of the membrane. Most UF membranes have "diffuse cut-off" characteristics. It is imperative to know what is meant by the molecular weight cut-off of a "diffuse cut-off" membrane, which has to be clearly defined.

The convention established by Amicon, a major membrane vendor, and adopted by most UF membrane manufacturers is based on the retention of globular proteins (spherical macromolecules).

The retention R (in percent) may be defined as follows:

$$R = 100\left(1 - \frac{C_{UF}}{C_R}\right)$$

where C_{UF} = concentrate of the solute in the ultrafiltrate

C_R = concentration of the solute in the retentate.

The convention states that the molecular weight cut-off of the membrane is equal to the molecular weight of globular proteins which are 90% retained by the membrane.

Figure 3.3 shows how this is determined. The retention curves[29] of a series of globular proteins are measured on the same membrane. The molecular weight at which the retention curve crosses a retentivity

of 90% is the “molecular weight cut-off” of the membrane. This means that larger molecules are said to be retained by the membranes and the smaller molecules are said to pass.

Normally UF membranes are designated by prefix letters, which refer to the membrane type, followed by one or more digits, which refer to the molecular weight cut-off in thousands of daltons. For example in Figure 3.3, UM, PM and XM refer to three different polymers, where PM 10 indicates that the membrane has a 10 000 molecular weight cut-off (MWCO). The approximate molecular diameter (angstroms) at the top of Figure 3.4 is taken from radius of gyration data reported in the literature. This may be used to estimate the effective pore size.

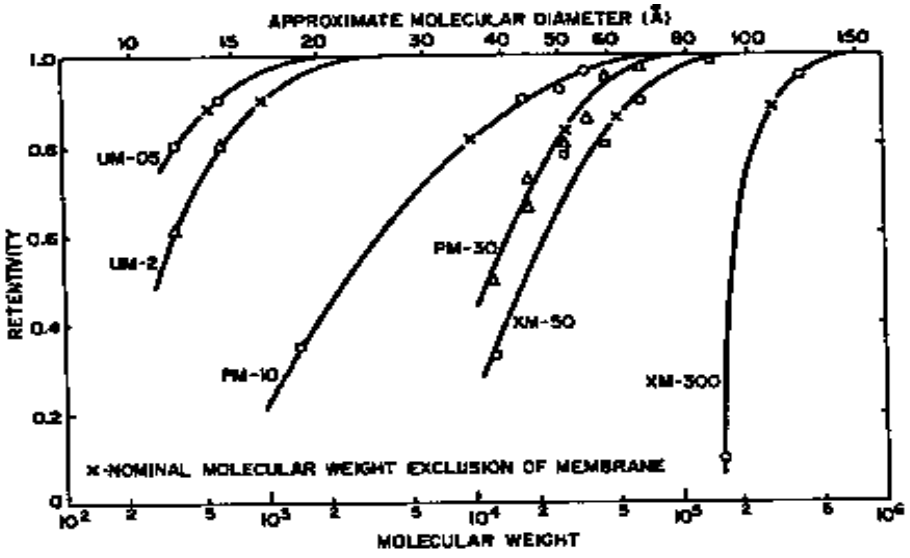


Figure 3.3 : Retentivity of a series of globular proteins on various UF membranes.

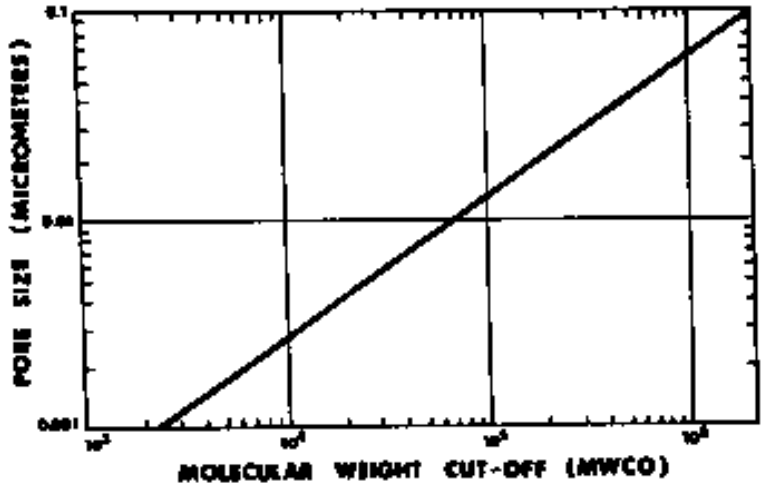


Figure 3.4 : Pore size variation with molecular weight cut-off (MWCO).

3.3.2 Molecular Weight Distribution of Proteins in CSL

In order to achieve maximum benefit from the separation and purification of proteins from CSL, it is important to characterise its actual protein molecular weight distribution. For a highly complex mixture of components in CSL this task proved to be rather difficult. Earlier research conducted by Rech[30] at AECI Research Department, using the SDS PAGE method, as described by Laemmli SDS Polyacrylamide Gel Electrophoresis Instruction Booklet, was used with certain modifications to improve the resolution of protein bands.

A combination of dialysis, centrifugation and pH adjustment together with the standard method, provided reasonable separation of CSL into bands of 14 000D and 21 000D.

The utilisable portion of CSL protein is represented mainly by single free amino acids. However, bacteria in fermentative mode are also capable of breaking down peptides of higher molecular weight. Proteins up to approximately 25000-30000 MW are generally broken down to smaller peptide units and single amino acids. Thus, the ultimate value of the CSL rests largely in the quantity of final free amino acids that can be made available to the fermentation organisms.

The attempt to elucidate the larger protein fractions between 6000 and 30000 daltons using polyacrylamide gel electrophoresis (PAGE), was successful. Appendix II shows the flowchart of the modified procedure used by Rech.

Selected electrophoretograms are shown in Figure 3.5 and Figure 3.6.

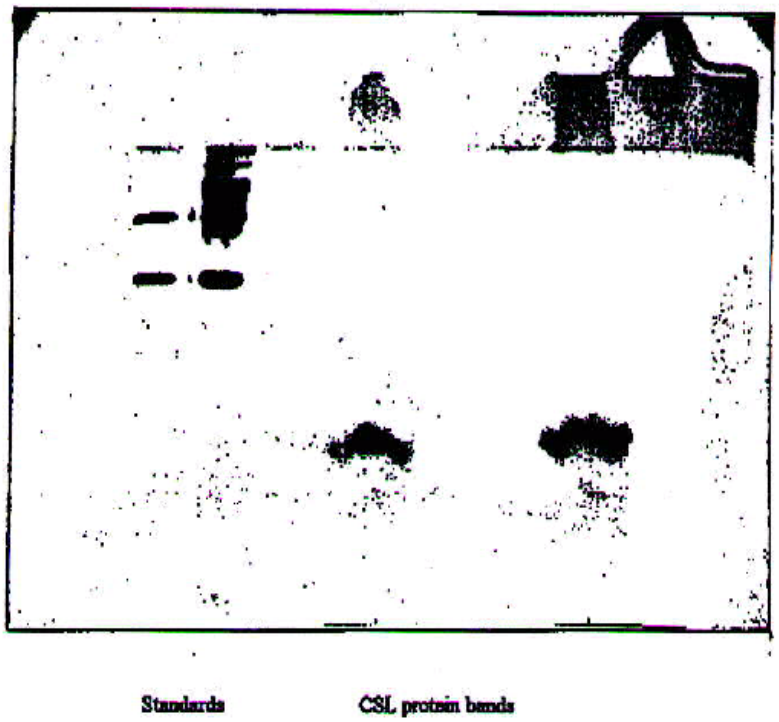


Figure 3.5 : Electrophoretogram of CSL using denser gel to improve resolution.

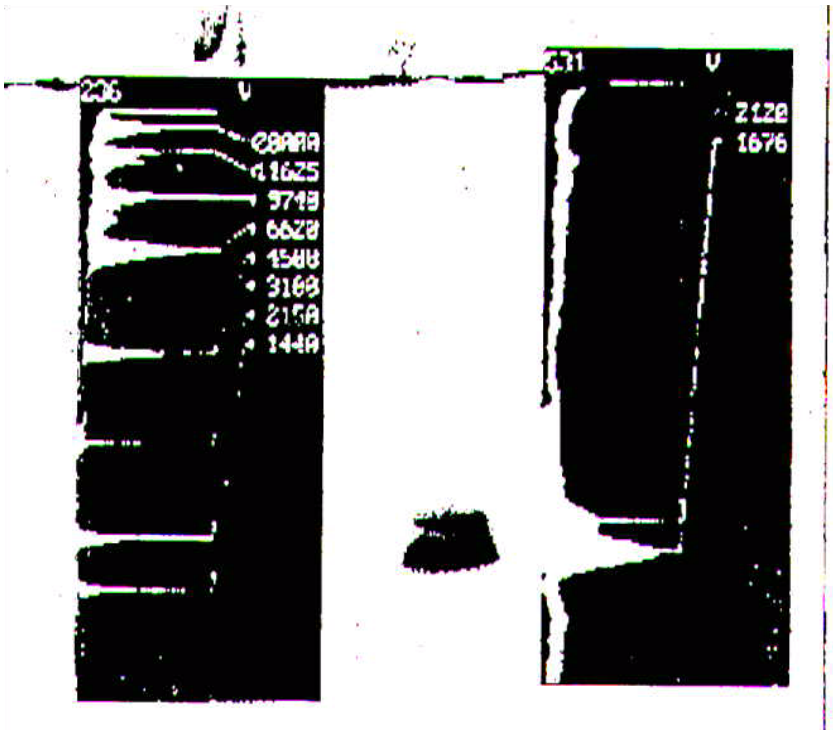


Figure 3.6 : Electrophoretogram showing standard and CSL protein bands. Note CSL proteins are visible as bands of 16 670 daltons and 21200 daltons.

3.3.3 Selection of Membrane Molecular Weight Cut-off (MWCO)

Two different molecules of the same molecular weight can have different configurations such that their molecular diameter is different. For example, a linear protein molecule may snake through the pores while a spherical polymer of the same molecular weight, but of greater diameter, is retained. It is also known[31] that the pH and ionic strength of solutions of proteins can have a marked influence on their retentivities. The more the protein polymer is charged in solution, and the lower the ionic strength of the medium, the larger the effective size of the protein polymer for a given molecular weight.

The polymer from which a UF membrane is made does not generally affect the retention characteristics of the membrane. However, the nature of the polymer can affect adsorption of species onto the membrane surface. Strong adsorption of the solute can diminish its concentration in both the retentate and in the permeate (filtrate), and this can affect the apparent retention of the membrane.

Further, the retention of a single solute is determined solely by the properties of the membrane (pore size distribution, charge, and adsorption characteristics) and by the operating conditions such as pressure, pH and ionic strength of the solution.

The retention of individual solutes from a mixture is more complicated. Fractionation may or may not be possible. Proteins retained by the membrane form a “gel layer” which acts as a retentive barrier for other proteins, even those of lower molecular weight. Without the presence of the “dynamic secondary membrane”, these proteins would pass the primary membrane.

Generally bacteria in fermentations are capable of utilising proteins up to 30000D. It was shown earlier through the SDS Page Gel that CSL contains sizeable fractions of proteins in the 16000-22000D range. Very little protein is found above this range. It therefore seemed reasonable to select membranes with a 30000D cut-off for all the experimentation. This would ensure maximum recovery of the useable protein present in CSL as well as compensate for the globular protein in the higher range. The orientation of the larger molecules (22000D) would also be compensated for, to a certain extent.

3.4 Membrane Fouling, Flux Decay and Restoration

With some process streams the flux can be stable for months or even years without cleaning or membrane replacement. However, for most applications there is a gradual flux decay with time. This is not due to internal pore fouling (as in symmetrical microfiltration membranes), rather it is the result of the

accumulation of materials on the surface of the membrane. In effect, they "blind" small sections of the membrane, thereby reducing the effective area and the flux through the membrane.

Often preventative measures may be taken to avoid fouling the membrane. Pre-filters or screens are generally used to remove large particles which block thin channels or accumulate in stagnant areas of the membrane module. High cross-flow velocities tend to sweep deposits away. However, configuration and module design can also limit the cross-flow velocity.

Also, low pressures avoid compaction of gels on the membrane. Some polymers have a higher susceptibility to fouling and chemical modification of the membrane surface can have a profound effect on the propensity to foul. CSL has a very complex composition and also consists of many "fouling precursors" in the form of organic, inorganic or intricate complexes of both and therefore presents a unique challenge.

If fouling does occur, the membrane deposits can sometimes be removed by aggressive cleaning agents such as detergents, acids, bases, enzymes or even organic solvents. The advantage of a chemically resistant membrane is that severe cleaning agents may be used. However, even with periodic cleaning, the flux cannot always be restored to the initial value. This results in overall long term decay.

3.4.1 Effect of Cross Flow Velocity

High cross flow velocities tend to prevent fouling and also aid in the cleaning process as illustrated[32] in Figures 3.7 and 3.8. The log-log plot in Figure 3.7 shows the flux decay low, medium and high recirculation rates (Q_L, Q_M and Q_H). Plotting the data in this way often permits a reasonably good extrapolation of the flux for much longer times-up to 2 or 3 years. The flux decay data usually plots on a straight line and because of the cyclical nature of the log-log plot, 10 days often permits extrapolation to 100 or even 1000 days.

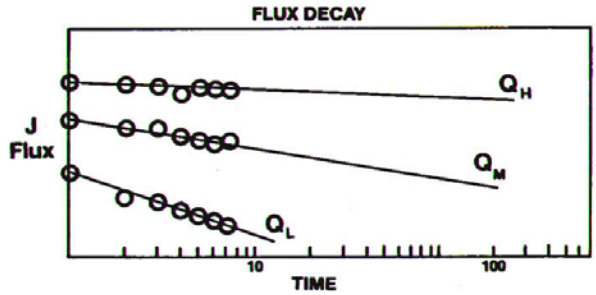


Figure 3.7 : Effect of cross flow velocity on long term flux decay.

High cross velocities also facilitate cleaning. Figure 3.8 shows that the flux is restored more rapidly and to a higher level with higher velocities.

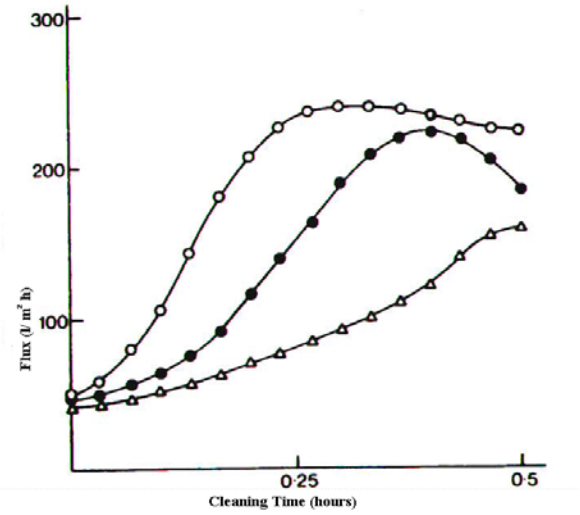


Figure 3.8 : Effect of recirculation rate on detergent cleaning.

3.4.2 Effect of Pressure

If no fouling occurs, the maximum flux will be obtained in the gel-polarised regime above the threshold pressure (P_T). However, for solutes which form semi-gels on the membrane, pressure (P_H) higher than the threshold pressure may compact the gel layer resulting in greater fouling. Flux decay data like that of Figure 3.9.[33] may show greater flux stability at pressures (P_L) lower than the threshold pressure. Even though the initial flux at P_L is lower (since it is not gel polarised), the long term flux at this pressure may be higher.

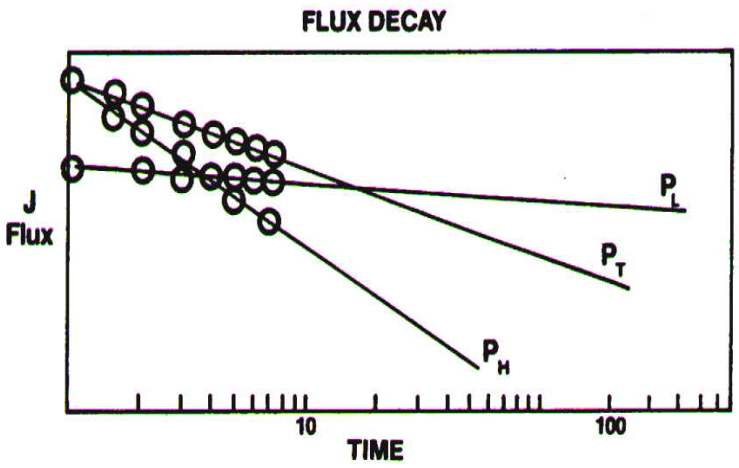


Figure 3.9 : Effect of pressure on long term flux decay.

The flux drops if the feed pressure is increased above a few bars. For most products, the maximum useful pressure is 3 to 5 bar with very few exceptions. This means that in reality a UF plant has a capacity which depends more on the product than on the membrane itself. The best way of operating, generally, is to observe the flux and choose the most advantageous operating pressure.

3.4.3 Membrane Cleaning and Flux Restoration

Periodical cleaning is a necessity for membrane systems. It is necessary to ensure optimal operation, but it should only be performed when absolutely necessary, due to the adverse effect on membrane life. Also, the cost of cleaning chemicals and the volume of water used for cleaning could be substantial.

Generally, the best strategy to avoid cleaning as far as possible and to achieve easy cleaning when necessary, is to have good pre-treatment of the feed stream. It is also necessary to choose optimum operating parameters with emphasis on the prevention of scaling (gel layers), fouling by plugging and the precipitation of organic and inorganic material.

Most membrane manufacturers recommend regular cleaning to avoid the buildup of foulants on membrane surfaces, which reduce the permeate flow and quality. A precipitant deposited on the membrane surface may reduce flow, cause permanent chemical damage to the membrane and reduce membrane element life. Therefore regular removal of such foulants, which is more effective than sporadic cleaning, extends the membrane life and enhances the overall system performance.

Cleaning of membrane systems is essentially very simple provided certain rules are observed and followed. There are many different cleaning regimens, and the exact procedure for a given membrane system depends on the product treated, the membrane type and the system design. When selecting a cleaner or sanitiser, several things must be considered, including the foulant to be removed, its chemical and physical nature, adverse reactions with the cleaning chemicals, quantity of cleaning chemicals required and the environmental impact of the chemicals.

It is important that cleaning solutions fall within the specified pH ranges, for the specific membrane type. Table 3.2, shows pH regimes generally recommended by membrane manufacturers for some of the more common membrane polymers.

Table 3.2 : Recommended pH ranges for cleaning solutions for some common membranes.

MEMBRANE TYPE	CLEANING pH RANGE
Cellulose Acetate (CA)	2-8
Polysulfone (PS)	1-12
Fluorinated Polymer (PVDF)	1-11
Polyamide (PA)	1-12
Polyacrylonitrile (PAN)	1-12.5

In addition, the cleaner must not contain certain chemical substances that are incompatible with the membrane element, such as certain surface-active agents and, in some instances, oxidising agents such as chlorine. The presence of these chemicals sometimes cannot be avoided, due to contaminated cleaning solutions. Therefore the source of such cleaning solutions is very important. Contact time of the cleaning solutions should always be considered and should be minimised wherever practical.

This is especially critical when the cleaning solutions pH reaches the upper or lower limits of the recommended ranges.

Feed water composition, seasonal water quality variability, residual free chlorine concentration, system recovery rates, flow rates, operating pressure and feed water temperatures all affect the rate of fouling. As a result, these variables should be studied for each application before determining how to clean the membrane system. Small changes in these variables may require changes in the cleaning regimes.

Some of the common foulants encountered in UF systems include: mineral (inorganic) scale, biological matter, organic and organic-mineral complexes, iron and organic-iron complexes, colloids (gel-layers), silica based contaminants and insoluble particulates. Some of these are known to alter the polymer integrity of the membrane. The most common problem is that the build-up of scale deposits cause increased differential pressure across the membrane element or membrane housing. This in turn leads to compaction of the deposits on the membrane surface, which sometimes causes irreversible damage.

3.4.4 Corn Steep Liquor Protein Deposition on UF Membranes

The understanding of protein fouling is fundamental in designing and controlling membrane processes for many biotechnology applications. Direct observation[34] of protein deposits after fouling has revealed varying types of fouling on UF membranes. During filtration, significant surface deposits may occur, some in large aggregates, many times the size of the protein molecules and pores. However, internal deposition, in the form of monolayers or multilayers, is still difficult to determine by direct observation and must still be deduced by analysis of total amount of protein on the membrane surface by using spectroscopic methods, by radiolabelling, or other techniques[35, 36]. It is thus necessary to examine protein deposition provided by the differing membrane morphologies to further identify the contributing factors to fouling revealed by electron microscopy.

While protein adsorption levels have already been reported for many filtration conditions and different membranes, the variation between membrane polymers and, hence different morphologies, makes the values from different membranes difficult to interpret on the same basis. CSL has already been recognised as being potentially a high fouling solution. Therefore to aid in the selection of membranes passive adsorption studies were found to be necessary.

In this work several membranes of various polymer types were studied with controlled exposure (constant filtration-time experiments) to CSL under static (no transmembrane pressure) and dynamic conditions. Although each membrane has the same reported nominal molecular weight cut-off, distinct differences in morphology exist between the membranes. The protein deposition and permeate flowrates are examined for patterns of fouling and the controlled determinants of fouling. Previous investigations[37,38] using scanning electron microscopes (SEM) and field emmission electron micrscopy (FESEM) of membrane surfaces have suggested that two types of fouling occur: (a) surface adsorption by low flux membranes, and (b) pore blocking due to shear denaturation or supersaturation by high flux membranes.

3.4.5 Viscosity effects of CSL

Corn steep liquor is a highly concentrated solution consisting of a wide range of components. The presence of components such as starch (among other polysaccharides), gums, polypeptides and phytin presents unique problems in understanding the flow behaviour in ultrafiltration. These components, and other unidentified organic and inorganic compounds, are considered to be viscosity precursors which contribute to the non-newtonian character of CSL.

Non-newtonian fluids are frequently encountered in various industrial processes, e.g. concentration by reverse osmosis of fruit juices[39,40] and egg white[41], ultrafiltration for producing clarified fruit juice directly from puree[42] and the purification of polysaccharides produced in a fermentation broth[43]. As reported in these processes, the variations in permeate flux with respect to operating conditions revealed unusual effects: the shear rate exponent in laminar flow for non-newtonian fluids give unusual values, and the fall in permeate flux is not proportional to the logarithm of the bulk concentration, which is obtained for newtonian fluids and predicted by the concentration polarisation model with a constant mass transfer coefficient.

In spite of the importance of non-newtonian cross-flow filtration, very little has been published. A qualitative study on the effect of pseudoplasticity, upon mass transfer in ultrafiltration, was performed by Aimar[44], using scleroglucan and concentrated skimmilk solutions. He considered that a pseudoplastic fluid should create better mass transfer than a Newtonian fluid which has the same viscosity at rest because the pseudoplastic fluid has a higher shear rate and lower viscosity at the wall.

Pritchard[45] proposed an expression for the laminar mass transfer coefficient, which incorporates the effect of pseudoplastic rheological behaviour. The model is a tool for understanding the cubic shape of the plot of flux versus log (feed concentration) rather than for a flux prediction.

Moreover, little has been published on the direct effect of boundary layer rheology on mass transfer in cross-flow filtration. The layer of concentrate adjacent to the membrane upstream surface may have substantially different rheological and mechanical properties from that of overlying (more dilute) solution, which is reported for the ultrafiltration of whey protein solution[46], wheat starch effluent[47] and mineral slurry[48].

Because of its high viscosity and stress properties, the layer of concentrate does not migrate with the flowing upstream fluid, or else it moves with a substantially reduced velocity relative to that of the overlying fluid. Leonard and Vassilief[49] postulated that particles do not return to the bulk but rather flow along the surface. The role of the rheology of the layer of concentrate was emphasised.

CSL, like many of these non-newtonian liquids, exhibits complex rheological behaviour which may be represented by sophisticated models. However, in order to keep this analysis of CSL free of such complexities, only simple viscosity measurements are made to check the influence of cross flow velocity and temperature on the separation process.

3.5 Effect of Configuration on Fluid Flow Path and Flux

Successful application of membrane technology requires not only high-performance membranes, but also modules which provide good fluid management at the membrane surface. Fluid management determines performance because it induces mass transport, controls concentration polarisation, and controls fouling. The popular module concepts for industrial scale UF operations are mostly spiral wound, tubular and hollow fibre. The tubular configuration relies strongly on high cross flow velocity by pumping, with turbulent fluid velocities between 5-10 m/s. Hollow fibre modules on the otherhand, operate with a very low Reynolds number, and relies on the choice of the correct lumen diameter of the fibres.

For spiral wound modules, net type spacers are a key feature in the fluid management. The spacers have the dual function of keeping adjacent membranes apart to form a feed channel and of promoting turbulence, i.e., facilitating the mixing between the bulk of fluid and the fluid adjacent to the membrane surface thus reducing the thickness of the boundary layer and increasing local shear and enhancing flux. The effect of spacer configuration and its link to orientation and geometric characteristics to UF performance, has been described by Da Costa et al., 1991, 1993, 1994. Other authors Glatzel and Tomaz, 1966; Hicks, 1967; Farkova, 1991; studied the effect of net-type spacers on pressure drop and heat and mass transfer phenomena, and also observed that changing the orientation of the spacer in the channel caused a marked effect on the results.

In this work only the effects on flux and fouling is determined by means of a simple experimental setup, to identify the optimal spacer configuration for CSL separation.

3.6 Scale-up of Membrane Systems

Since the productivity of a crossflow system is proportional to the membrane area, it might be thought that to achieve higher productivities, one simply has to increase the membrane area in proportion to the productivity. Thus, it might seem possible to move directly from laboratory-scale experiments to large-scale plants.

The reality is that the operational conditions are not the same everywhere on the membrane, and laboratory experiments do not provide the full picture of the issues likely to be encountered on a larger plant. Another key point is that different feedstocks have different needs, and thus there is no general solution to designs. CSL has already been highlighted as being a difficult stream to process through a membrane system.

In order to map out a development path and to ensure that all pertinent testing is pursued, it is important to understand the information and products of the different tests. Table 3.3 highlights the different sorts of information resulting from tests at different scales.

Table 3.3 : Different tests yield different information.

Feature	**Aspect**	**Laboratory**		**Field**	
		Membrane	**Element**	**Pilot**	**Full-scale**
Challenge	Timescale	~ 1 day	~ 1 week	~3 months	~ 3 years
	Type	Synthetic	Reconstitute	Real	Real
	Variation	Constant	Constant	Variable	Variable
Conditions	Pressure	- Reducing range with scale -			
	Temperature	Controlled	Controlled	Real,daily	Real,season
	Recovery	~ 0-10%	25-50%	With recycle	With recycle
Performance	Productivity	Maximum	Maximum	Closer to	Better than
	Rejection	Maximum	Maximum	Closer to	Better than
	Lifetime	Short-term	Short-term	Medium-term	Long-term
	Fouling	Membrane-	Element-	Allows	Disturbance
Design	Flowsheet	Recirculating	Total recirc.	Single-pass internal	
	Pretreatment	- Increasing options with scale of process -			
	Cleaning	Compatibility	-Effectiveness of cleaners-		Procedure
	Pump	- Limited -		- Useful and real -	
	Instruments	- Limited -		- Useful and real -	
	Robustness	- No information -		- Plant problems -	

Crossflow technologies do have the capability of operating on the bench-scale with very small sample sizes. Such experiments help to eliminate membrane materials rather than to select ones; the membrane with the best laboratory performance may not be the most cost-effective solution when scaled-up. A major weakness of laboratory trials is that they do not a full picture of the serious fouling issues. This is because invariably for laboratory trials the feed will continually reconstituted.

Since foulants are usually well rejected and accumulate on the membrane, the real fouling challenge is not assessed. It is particularly for this reason that pilot trials are of such great value. One of the most important aspects of any testwork is to define the required pretreatment and cleaning methods. Appropriate sizing of the pretreatment process is an essential element in all system designs, and can usually only be assessed by carrying out pilot studies. In some plants the pretreatment can make up 50% of the total capital cost.

3.6.1 Scale-up of Flat Sheet Membranes to Elements

Probably the single most important scale-up issue is to select how the membrane should be packaged. Fortunately, while there are countless varieties of membranes, there are only a few ways in which membranes are packaged. Table 3.4 summarises how the different configurations perform against various criteria, as suggested by various membrane vendors. To some extent, the rating of each feature does depend on the membrane type. Also, different processes have different needs, so the weighting given to each feature will be different. Thus, even for a given application there may be more than one choice.

An important difference between tests on membranes and elements is the recovery under which they are carried out. The recovery is the fraction of material removed from the feed as it passes through the element, and provides a useful measure of the operational conditions. An alternative is to look at the ratio of concentration between the concentrate stream and the feed stream is known as the concentration factor. These two measures are related through a mass balance. Hence, it is essential that in any testwork the unit is run under the system recovery likely to be encountered. In practice one of the key objectives of any pilot work is to set the operational limits.

Table 3.4. How different element configurations give different combinations of features.

Feature		Element design			
Aspect	Property	Plate&frame	Spiral wound	Tubular	Hollow fibre
Geometry	Packing density	**	***	*	****
	Membrane availability	***	***	***	***
	Dead volume	**	**	*	***
	Reynolds no.	Low-medium	Low	High	Very low
Operational	Fouling	**	**	***	*
	Cleanability	***	**	****	*
	Life	***	***	**	**
	Pretreatment	***	**	****	*
Economics	Cost/area	**	****	*	***
	Energy cons.	**	***	*	***
	Replacement	*	***	**	****
Application	Viscous feeds	***	**	****	*
	Suspended solids	***	**	****	*
Key : From * (poor) to **** (very good)					

3.6.2 Scale-up from Elements to Systems

One of the first decisions to be made on scaling-up is whether the process should be ‘batch’ or ‘continuous’. At the small scale the decision between these is dependant on a number of factors that are not related to the average flowrate, but to the variability of the feed and demand of both quantity and quality, level of automation required etc.

The modular nature of crossflow systems suggests that the productivity can be doubled by doubling the membrane area. This can be done by either adding membrane elements in parallel or in series. If elements are added in parallel, the average crossflow falls and hence fouling becomes greater. If elements are added in series, the crossflow falls through the series, so the final element also sees low crossflow and hence higher potential fouling problems.

To alleviate this problem, it is conventional in UF systems to operate at low recoveries and recirculate a large proportion of the reject to the feed, using a pump to make up for the pressure loss. In essence the recirculating pump provides the crossflow while the feed pump provides the system pressure. The design of a system is therefore a compromise between the best possible design for performance and minimising costs.

CHAPTER 4

OPTIMISATION OF PRETREATMENT PROCESSES

4.1 Introduction

Three candidate technologies have been selected to pretreat raw CSL prior to ultrafiltration, as discussed in Chapter 2. One of the eventual aims of this study is to identify which of these pretreatment processes would provide the "best quality" feed to ultrafiltration. However, the performance of each pretreatment process would be very dependant on operating conditions and equipment variables. Hence, it is important to firstly optimize each process for operation on raw CSL, prior to evaluating their performance.

The aim of this chapter is to determine the effects of operating conditions and equipment variables on performance for each pretreatment process, and hence optimize each process for the pretreatment of raw CSL.

pH treatment followed by solid-liquid separation is discussed in Section 4.2, Broth Condition followed by centrifugation is discussed in Section 4.3, and Gyratory screens are discussed in Section 4.4. For each pretreatment process the developmental/experimental program is outlined, followed by the results obtained.

4.2 pH treatment followed by solid-liquid separation

4.2.1 Experimental program

4.2.1.1 Introduction

The experimental program for this pretreatment option consisted of 3 stages :

(i) Quantifying the effects of shear rate and temperature on viscosity

(ii) Developing the protocol for the pH treatment

(iii) Design and optimization of the filtration stage. This was done in three stages :- *filtration screening trials* to determine basic choices between pressure and vacuum filtration, addition of precoat or body feed etc; pilot scale trials on a *plate and frame filter press* ; and pilot scale trials on a *diaphragm membrane filter press* to optimize operating and equipment variables and quantify performance.

4.2.1.2 Determination of the effects of shear rate and temperature on viscosity

Samples of pH treated CSL were prepared and tested on a Brookfield Viscometer. The viscosity was determined as a function of spindle speeds and temperatures.

4.2.1.3 Protocol for pH Treatment

Raw material and Treatment Equipment

CSL was obtained from African Products, Germiston Mill, a major corn wet milling company, and stored at 50 ^{0}C in a stirred tank. The precipitation of the colloidal solids was effected by the slow addition of a suitable alkali or base. For the test purposes ammonium hydroxide was chosen as a non-toxic base, suitable and compatible for fermentations, although any alkali metal hydroxides such as sodium hydroxide, and alkaline earth metal oxides or hydroxides, such as those of calcium could be used.

The base was added in the form of an aqueous solution. A variable speed peristaltic pump was employed for this purpose. The variable speed tank stirrer was adjusted to just keep the precipitated solids in suspension. Ammonium hydroxide was added to the liquor with careful monitoring of the pH. When the slurry in the tank reached pH 7, the dosage was terminated. The temperature in the tank was maintained until the next stage of the process. Figure 4.1 shows an outline of the equipment used for the pH treatment.

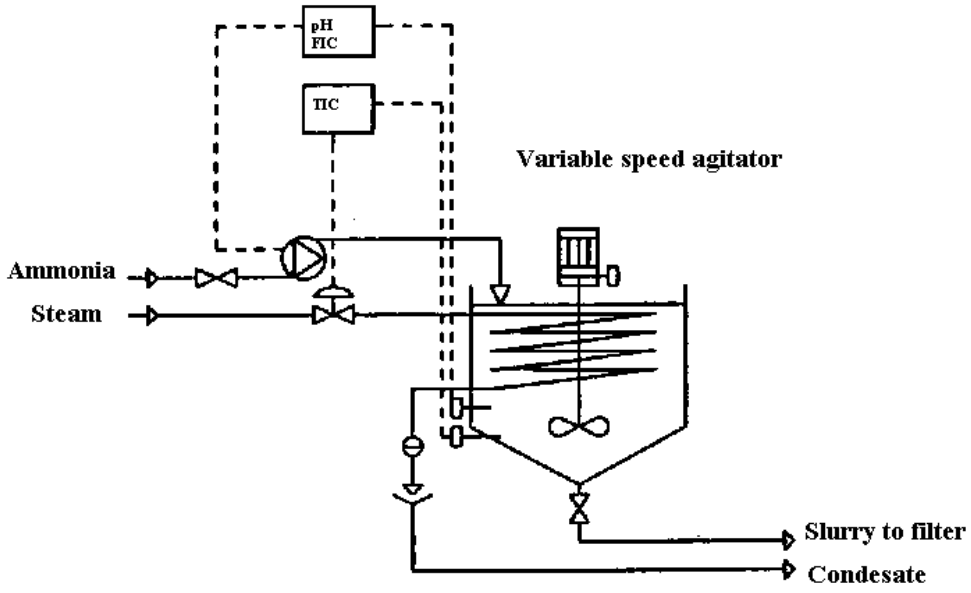


Figure 4.1 : Schematic of pH treatment process of CSL

Optimisation of the mixing stage

The objectives of the mixing equipment shown in Figure 4.1 are twofold :

(i) to change the pH of the raw CSL to the desired final value, and thus precipitate the undesirable components

(ii) to achieve a product slurry that can be easily treated by the downstream process, i.e. that can be easily filtered.

There are three operating variables in the treatment equipment shown in Figure 4.1, viz. the agitator speed, the rate of addition of the base and the operating temperature. These are likely to affect the properties of the final slurry, including the size distribution of the slurry, and thus could affect the performance of the filtration step. Hence, these operating variables need to be optimized to produce a final slurry that can be easily filtered.

A statistical design program called "Design Ease" was used for this purpose. The statistical design of the experiment allowed the process of planning the experiment so that appropriate data was collected for analyses, and also provided the capability to see interactions among experimental variables.

The variables to be investigated in the experiment were selected, viz. agitator spped, rate of addition of base and temperature. The ranges, over which these factors are varied, and the number of levels, at which the experiments are made, was then determined based on limitations of the experimental equipment It was necessary to select a response variable, which could provide real information about the problem. The probable accuracy of the measurements was checked before any further steps.

The difference in true response was checked against the magnitude of risk, which then led to a choice of experimental design. It was necessary to take into account the balance between cost and statistical accuracy. Also, the design was kept as simple as possible.

The basic experiment was repeated to allow for an estimate of experimental error and a more precise estimate of the effect of each variable. Allocation of the experimental material and the order in which the individual runs of the experiment were performed, were randomly determined.

This made the statistical assumptions of independantly distributed observations (or errors) valid and reduced bias. In the experimental plan a factorial design was selected where all combinations of variable conditions were investigated. A uniform environment was maintained as far as possible for each

experiment. The performance of the mixing system was determined by analysing samples for particle size distribution.

The experimental setup consisted of the following: a 5 litre glass vessel fitted with a 4-baffle system, an overhead variable speed agitator fitted with a 4-blade turbine type impeller, a heating plate, pH meter, temperature indication, a variable speed peristaltic pump with silicone tubing, with suction connected to a holding vessel and delivery to the mixing vessel. A tachometer was connected to the shaft of the impeller. The feed material used consisted of fresh CSL, and 25% (v/v) ammonium hydroxide.

The same batch of CSL was used in all the experiments for the sake of consistency. CSL was added to the mixing system and the conditions of temperature, agitation and the rate of ammonium hydroxide addition, were set according to the routine of the experimental design. The peristaltic pump was used to dose the base into the mixing system. Samples were removed at the end of the procedure (i.e. when the pH reached 7) and analysed for particle size distribution. Hence, the combination of operating conditions that gave the best product particle size distribution could be selected.

Quantification of power requirements

Once the optimal mixing strategy has been determined, it is important to quantify the power requirements for the pH treatment stage. This is required for scale-up, and any subsequent economic evaluation, of the process.

Tank configuration

The following tank and mixer geometry relations were used:

a) 4 blade turbine type agitator
b) Impeller diameter, $D = T/3$
c) Liquid height, $H = T/3$
d) Blade width, $W = T/5$
e) Blade length, $L = T/4$
f) Liquid height, $H_2 = T$
g) 4 symmetrical baffles
h) Baffle width, $J = T/10$

Where, T = Tank diameter.

Determination of Power consumption

In addition to the above geometric quantities, the following input data was utilised:

	Symbol	**Units**
Rotation speed	N	rpm
Liquor density	P	kg/m^3
Tank dimensions:		
Diameter	T	m
Cross section area	A	m^2
Liquid height	H_L	m
Liquid volume	V_L	m^3
Impeller dimensions:		
Diameter	D	m
Length of blades	L	m
Width of blades	W	m
Number of blades	B	
Spacing	S	m
Baffle dimensions:		
Width	J	m
Number	R	m

A computer program then generated the following output data:

Tip speed		cm/s
Power number	Npi	
Power consumed	Po	W
Power consumption per volume		W/m^3

The following equations were used to calculate the above output data:

a) Tip speed $= \left\{\frac{N}{60}\right\}\left[(D)\ \ (P)\ \ (100)\right] cm/s$

b) Npi $= \left[336{,}5\left(\frac{W}{D}\right)\left(\frac{L}{D}^{1{,}5}\right)\left(\frac{J}{D}\right)^{0{,}3}\left(\frac{B}{6}\right)^{0{,}56}\left(\frac{R}{4}\right)^{0{,}4}\right]$

c) Po $= (Npi)(P)\left[\left(\frac{N}{60}\right)^{3}\ \ (D)^{5}\right] W$

d) Power consumption per volume $= \frac{P_0}{V_L}$

4.2.1.4 Filtration screening trials

Pressure filtration

Equipment

The equipment selection technique used to identify the pressure filter, had to cover all the factors that could have a significant influence on filter operation. A simple system as outlined in Figure 4.2 was used for the laboratory test work. The system was made up of a vertical cylindrical vessel with a capacity of approximately 1.5 litres. A horizontal filter medium and a wire mesh screen, was located at the base. The upper cylindrical section was detachable to provide easy access for cleaning. In order to perform tests at different temperatures, the cylindrical portion and the bottom filter coupling were jacketed. The system was also equipped with a pressure gauge.

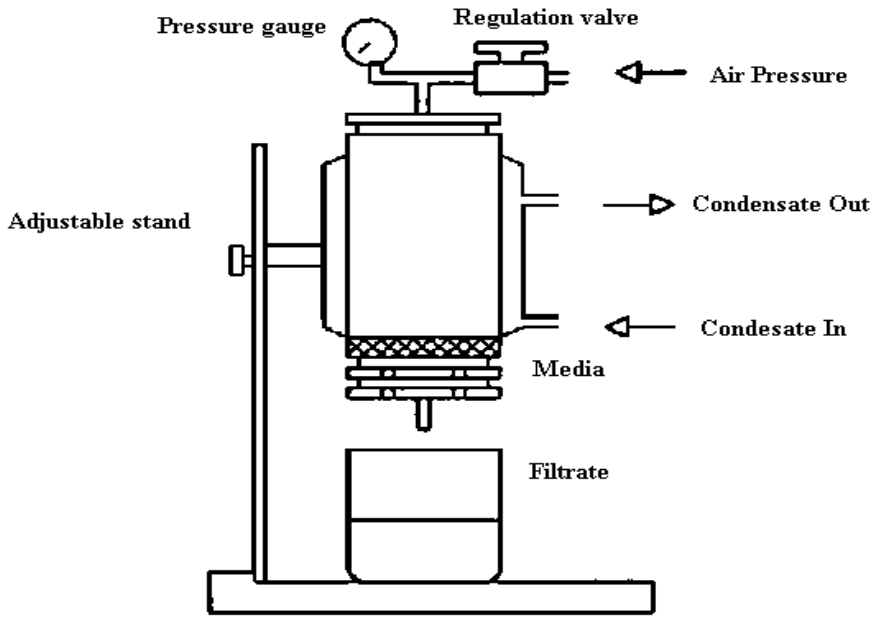


Figure 4.2 : Schematic of laboratory pressure filter

Procedure

The CSL slurry was gently stirred until a homogeneous suspension was obtained. The upper part of the filter was dismantled and the sample was transferred into the vessel. The filtrate valve was maintained in a closed position. All the upper parts were re-assembled, the air supply connected and adjusted to the operating pressure. The filtrate was then "cracked" open gradually and at the same time the pressure was adjusted to compensate for the pressure drop. The filtrate volumes were noted at intervals.

After a filtration time of 10 minutes the non-filtered volume was drained away via the drain valve, and the cake was blown dry by pressurising with air. The filter cake was then inspected for cake thickness and dryness. The filtrate was also examined for suspended solids. The tests were repeated for various types of filter media (varying materials of fabrication and pore sizes). Once a suitable filter medium has been chosen, an improvement in filtrate quality was sought.

Precoat pressure filtration

Precoat filtration was tested by adding diatomaceous earth on to the filter medium. Various bed thicknesses ranging from 1-5 mm were used.

Body feed

Diatomaceous earth of a predetermined mass was added to the slurry and the tests were conducted in the same manner as outlined above.

Precoat with body feed

The filtration tests were repeated with the combination of precoat and body feed.

Vacuum filtration

Equipment

A typical leaf test system was used for the vacuum filtration. The system contained a circular disk with a plane area of 25 cm^2 . The face of the disk had numerous holes for filtrate drainage. The filtrate medium was clamped on to the disk by an 'o-ring' type clamp which had a slight overlay for cake build-up. The underside of the disk had a common drainage or suction port which was connected to a vacuum receiver by way of a flexible rubber hose.

Procedure

The test leaf was fitted with a selected filter medium. The hose at the back of the leaf was hand-crimped to prevent the suction from reaching the leaf. The vacuum pump was switched on and the bypass valve on the pump was adjusted to give the desired vacuum. The test leaf was immersed face down into a beaker filled with pH treated CSL slurry, so that the filter medium was immersed one-half the depth of the slurry. The crimp on the hose was released and a timer was started simultaneously. The leaf was gently swirled to prevent clogging or blinding by fine particles. At the end of three minutes (the time set aside for cake formation) the leaf was removed from the slurry. The leaf was maintained in an upright position (cake surface on top) so that all the liquor in the drainage passages were drawn into the receiver. At the end of the run the filtrate volume was recorded along with the cake thickness, cake mass and cake discharge characteristics.

Precoat vacuum filtration

A slurry of diatomaceous earth was prepared in a beaker. The leaf was immersed into the slurry in the beaker and a cake was allowed to form in exactly the same manner as above.

Body feed vacuum filtration

Diatomaceous earth of a predetermined mass was added to the slurry and the tests were conducted in exactly the same manner as outlined earlier. Body feed trials were performed with and without a precoat layer.

4.2.1.5 Pilot scale filter press tests

Trials were performed on a bench scale filter press to investigate the following :

(i) Filter performance in terms of filtration time, separation efficiency, filtrate clarity, filter cake solids content and filter cake bulk density.

(ii) The effect on filter performance of filter feed rate, rate of increase of pressure, and of maximum operating pressure.

(iii) The effect of variations in cake thickness on filter performance.

(iv) A comparison of alternative pretreatment chemicals (flocculants and coagulants) at varying dosage levels and their effect on filter performance.

(v) The need for and the effect on efficiency of filter aids as precoat or as a body additive.

(vi) Alternative filter media.

(vii) The effect of elevated operating temperatures on filter performance.

Equipment

The tests were carried out on a Carlson Princess-Ariston Mark II filter press. The system comprised of 8 plates and frames (40 cm × 40 cm) providing an effective filtration area of 0.96 m^2. Figure 4.3 shows a process flow diagram of the system used on the pilot plant.

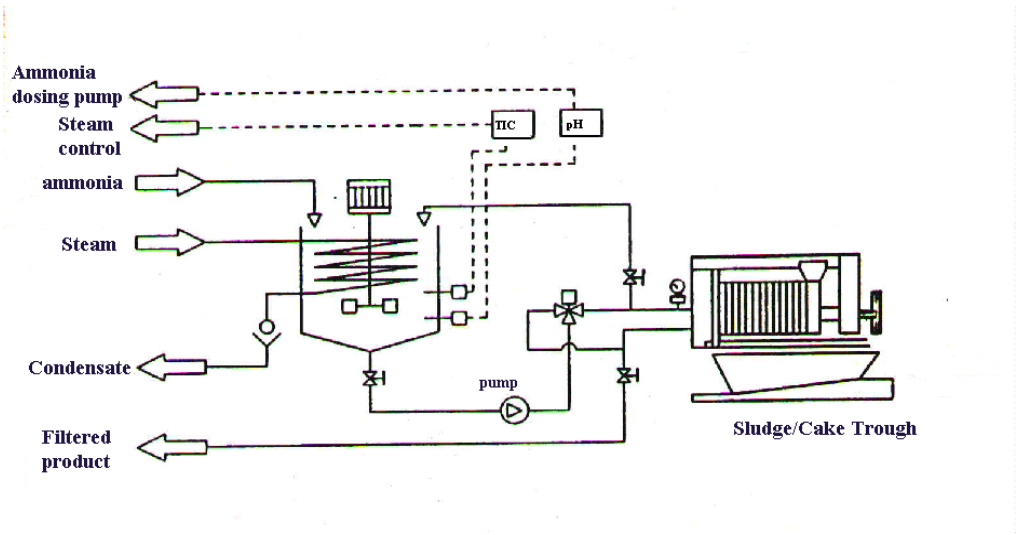


Figure 4.3 : Process flow of pilot plant filter press system

The operation consisted of a feed tank equipped with heating coils (steam) and agitation, a centrifugal pump (maximum feed delivery pressure of 8 bar) with a recycle loop valve for feed pressure regulation, a rotameter, feed inlet pressure gauge, a diaphragm valve for feed flow regulation, the filter press, a recycle loop and a product recovery tank.

Test programme

The requirement was to produce a clear filtrate free of suspended solids and to recover solids in the form of a filter cake at maximum solids concentration. Within these limitations it was desirable to operate at optimum flow rate, filter cake thickness and optimum pressure to obtain the shortest optimum filtration cycle time.

The tests were performed on various batches of feed where each batch was similarly treated prior to the test work. The programme consisted of three groups of tests where the filtrate volume flow was measured at equal increments of time during each test, as follows:

1. Over a range of constant flow rates with the same cake chamber thickness being maintained throughout, the time taken to reach a predetermined maximum pressure (6 bar) was recorded and the pressing time as determined by the point at which filtrate flow was 5% of maximum flow, was obtained during the test.

   Comparison of the results obtained for maximum cumulative volume filtrate flow in minimum total time indicated the optimum feed rate.

2. Over different cake chamber thicknesses, the optimum feed rate and the same pre-determined maximum pressure being maintained, and the total pressing times were recorded. The optimum cake thickness was that which produced the desired solids content in the filter cake, as measured by cumulative filtrate removed, and the maximum output per unit of operating time.

3. Over a range of maximum pressures, the optimum feed rate and optimum cake chamber thickness being maintained, the cumulative filtrate volumes were removed and the total pressing times recorded. The optimum maximum pressure was indicated by the maximum output of filter cake on a dry mass basis per unit of total operating time.

At the conclusion of each test in a series, the filter cake was weighed, the solids content of the cake was determined and the total volume of feed sample used was recorded. Also, observations were made of filter cake release from the filter medium and the degree of blinding of the filter medium. A further series of tests were run at the optimum operating parameters with a range of filter media.

Assessment of the filter performance was used to indicate whether a particular medium was likely to offer any particular advantages in improved cake discharge or lesser media blinding. The wear and tear characteristics of the filter medium and its utilisation between successive washings for cleaning purposes were also observed. The handling characteristics of the discharged filter cake were noted.

4.2.1.6 Pilot scale trials on Diaphragm Membrane Filter Press

Based on the performance of the pilot scale filter press, improvements in the separation were sought. A fully automated unit from Delkor Technik, a local filtration equipment vendor, was used for the test program. The filter unit had the following specifications:

Plate types and sizes:	Recessed chamber 500 × 500 mm^2; cake thickness 15 mm to 40 mm.
	Recessed chamber 500 × 500 mm^2 with rubber membrane diaphragm; cake thickness 40 mm.
Filter media/cloth types:	Polypropylene, mono-filament and multi-filament composite weaves.
Press closing pressure :	44 Mpa
Compressed air pressure :	0 - 1200 kPa
Feed pump pressure :	0 - 1500 kPa
Feed tank :	800*l*, with agitation and heating

The unit was also equipped with a filtrate recycle facility. Figure 4.4 shows an outline of the pilot process.

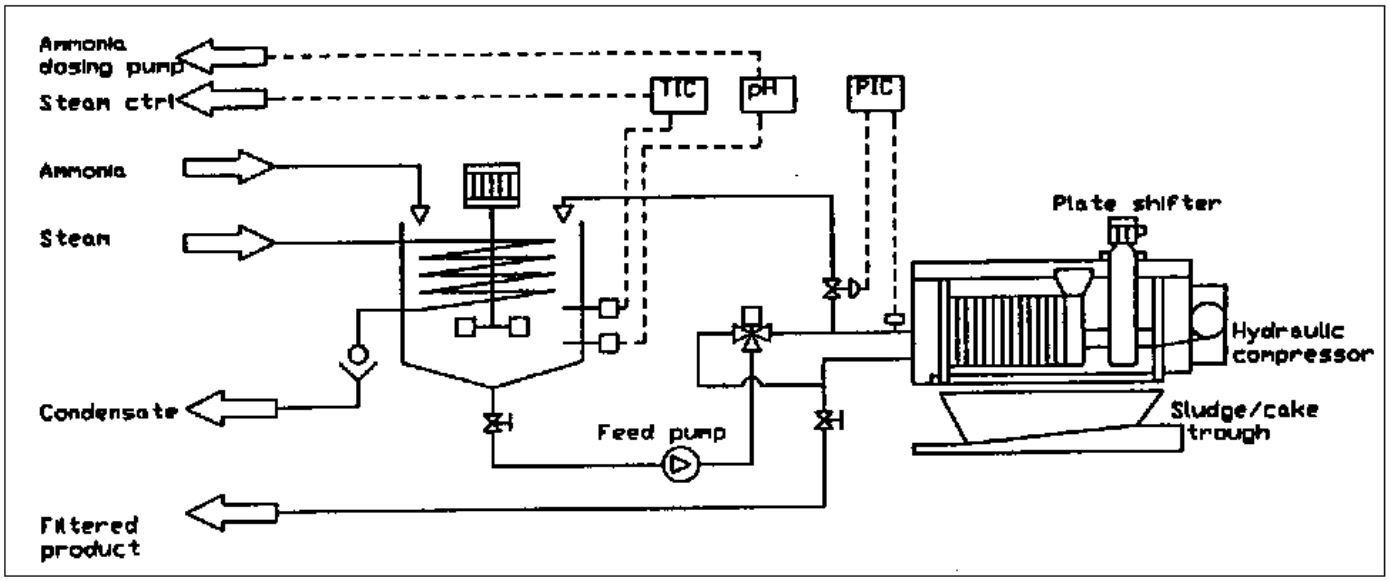


Figure 4.4 : Schematic of Delkor filter press system

Recessed Chamber Plates

The optimum parameters of the earlier filter press tests were used as a basis for the operation of the Delkor rig equipped with recessed chamber plates. Figure 4.5 shows the various press types tested and the manner in which they operate. Tests were conducted with 15 mm and 20 mm recessed chamber plates. The feed pressure was increased progressively from 300 kPa to 1500 kPa in all tests. The trials were conducted with low and high permeability filter cloths, air permeability greater than 1 cfm (at 1/2 inch water gauge), and with air blowing for cake drying. The effect of temperature on filtration was also tested. The feed was heated and the filtration was performed at the higher setpoint temperatures.

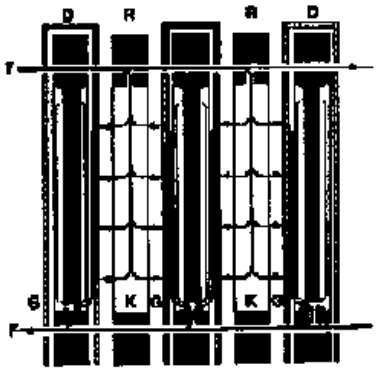


Plate and frame press - filtration phase

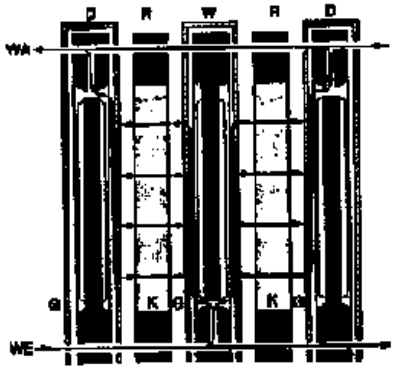
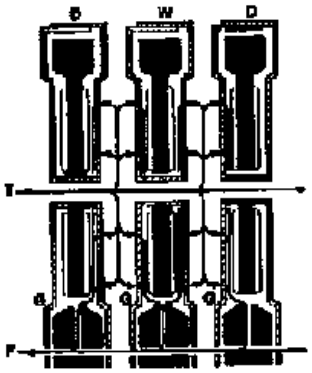
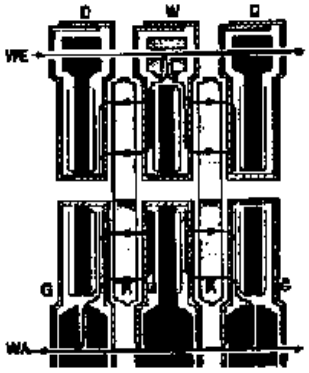


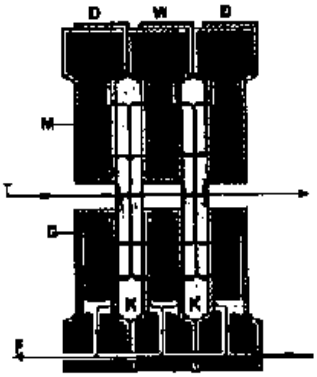
Plate and frame press - wash phase



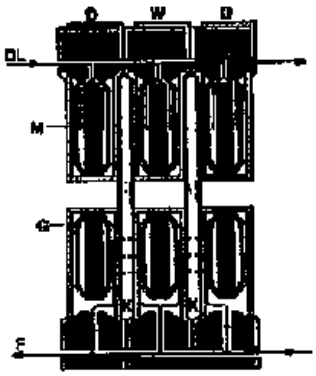
Chamber press - filtration phase



Chamber press - wash phase



Membrane press - filtration phase



Membrane press - compression phase

D = pressure plate
R = frame
W = wash plate
K = cake

G = filter weave (media)
T = slurry feed
F = filtrate
WE = wash fluid - inlet

WA = wash fluid - outlet
DL = compressed air
M = membrane

Figure 4.5 : Flow patterns of the various press systems

Recessed Chamber Plates with Membrane Diaphragms

In order to incorporate the wide range in dewatering rates observed, due to variations in dissolved solids and suspended solids contents of the feed, further filtration tests were carried out with recessed chamber plates which contain a rubber diaphragm to squeeze the cake. The tests were carried out two stages, where initial dewatering was achieved at a moderate feed pressure of 700 kPa, followed by a secondary dewatering with diaphragm squeeze at pressures in excess of 1000 kPa. These tests were conducted at the optimum temperature as assessed from the previous experiments.

Sample Points and Analyses

Samples were taken at various stages of the trials to allow mass balances to be compiled, and to enable the flow of important species to be followed through the process. The pH was monitored throughout the process and volumes were recorded where possible. In addition the filtrate samples were sterilised in an autoclave at 120 °C for 60 minutes. After sterilisation the samples were analysed for coagulated solids. The sampling points and analyses performed are tabulated in Table 4.1.

Table 4.1 : Sampling points and analyses conducted

Sample point	**Protein**	**Solids**	**Phytic acid**	**Lactic acid**	**Ash**
Untreated CSL	Yes	Yes	No	No	No
pH treated CSL	Yes	Yes	Yes	Yes	No
Filtrate	Yes	Yes	Yes	Yes	No
Cake	Yes	Yes	Yes	Yes	Yes
Sterilised coagulated solids	Yes	Yes	Yes	Yes	Yes

4.2.2 Results and Discussion

4.2.2.1 Effects of shear rate and temperature on viscosity

The effects of spindle rate on viscosity are shown in Appendix III, Figures 1-7, and the effects of spindle speed as a function of time shown in Appendix III, Figure 8**.** The effects of temperature on viscosity are given in Appendix III, Figures 9-11. These are reflected at various spindle speeds.

The trends observed are summarized below :

(i) An increase in the spindle speed of the viscometer at constant temperature, showed a significant decrease in the viscosity. A further observation was the time dependence on constant spindle speed. An increase in the time spent at a specific spindle speed also produced a decrease in the viscosity, clearly denoted in the results. This is typical thixotropic behaviour which classifies pH treated CSL as a non-Newtonian fluid.

(ii) An increase in the temperature at constant spindle speed showed a predictable decrease in the viscosity. Due to limitations on the test equipment, temperatures above 80°C could not be tested. However, the behaviour of temperature versus viscosity beyond this point is fairly predictable and can be addressed by the process and its limitations.

4.2.2.2 Design and optimization of mixing system

Optimisation of mixing variables

Selected results of the optimisation experiments performed to optmise the combination of agitator speed, operating temperature and base addition rate, are given in Table 4.2. Figure 4.6 shows the best particle size distribution achieved reflected as a percentage over a range.

Table 4.2 : Results of the mixing system trials

TEMP (°C)	Agitation Rate (rpm)	Base Addition Rate (ml/min)	Particle size distribution (PSD) (present in > 50% of solids) (um)
60	50	10	Gel-mass
60	80	10	Gel-mass
60	100	10	59.6
60	120	10	43.4
60	150	10	39.1
60	200	10	32.7
60	300	10	28.5
60	400	10	26.8
60	500	10	22.3

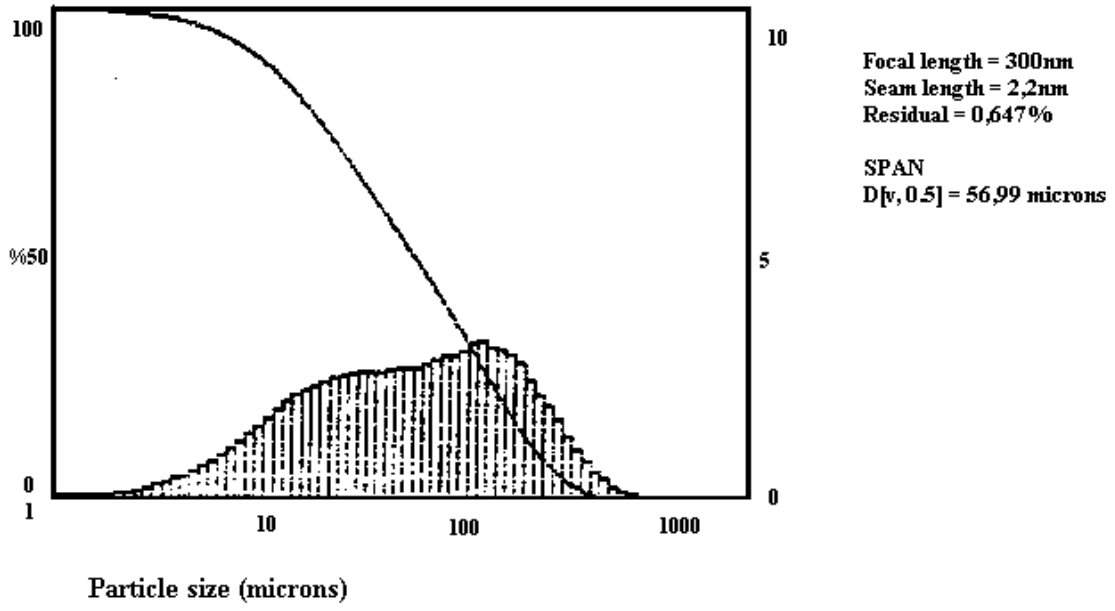


Figure 4.6 : Optimised particle size distribution

The manipulation of the three variables of temperature, rate of base addition and the rate of agitation has shown marked influence on the particle size distribution. From Table 4.2 it would seem that a low agitation rate (100 rpm) followed by a low base addition rate of 10 ml/min, at a high temperature of 60°C was favoured for the production of larger particles. Although the system seemed to be less sensitive to the base addition rate than to the agitation rate, from the experimentation it seemed that the agitation rate, from the experimentation it seemed that the agitation required should be just enough to keep the solids in suspension or to prevent settling. High agitation rates notably caused smaller sized particles to form. This was probably due to high shear imparted by the impellers causing the particles to break up. Extremely low agitation, below 80 rpm, caused the aggregates to clump together and settle into gel-like mass.

One of the major characteristics in study is the state of aggregation of the sample material. The particles that make up the solid phase are not separate and distinct but were found to be clumped or tightly stuck together. At the extreme low rate of agitation larger clumps (flocs) form and these occupy a large volume in dispersion. The viscosity of the dispersion tends to be a lot higher than if the floc volume was smaller. This is due to greater force required to dissipate the solid component of the dispersion.

As shear rate is increased, the aggregates are broken down, decreasing the friction and there viscosity. At the agitation rate of 100 rpm the bonds of the aggregate seemed to be sufficiently strong to prevent further break up with time.

These results, obtained from the experimental design on the standard tank configuration, has indicated that great care should be taken in the design of such a system. The earlier work performed on shear and viscosity was validated to a large extent on the test system. As indicated earlier, liquid-solid separations performed on various separation equipment are dependent on many factors. One of the most influential factors is the quality of the feed suspended solids material that needs to undergo the separation process. For instance, the mechanisms operating in a filtration process are dependent on variable such as pressure, residence time, particle size distribution, etc. Hence, adequate care is required in upstream processing to optimise the effects of some of these variables.

Power Consumption

The calculated power consumption data is given in Appendix IV, and is summarized in Figure 4.7.

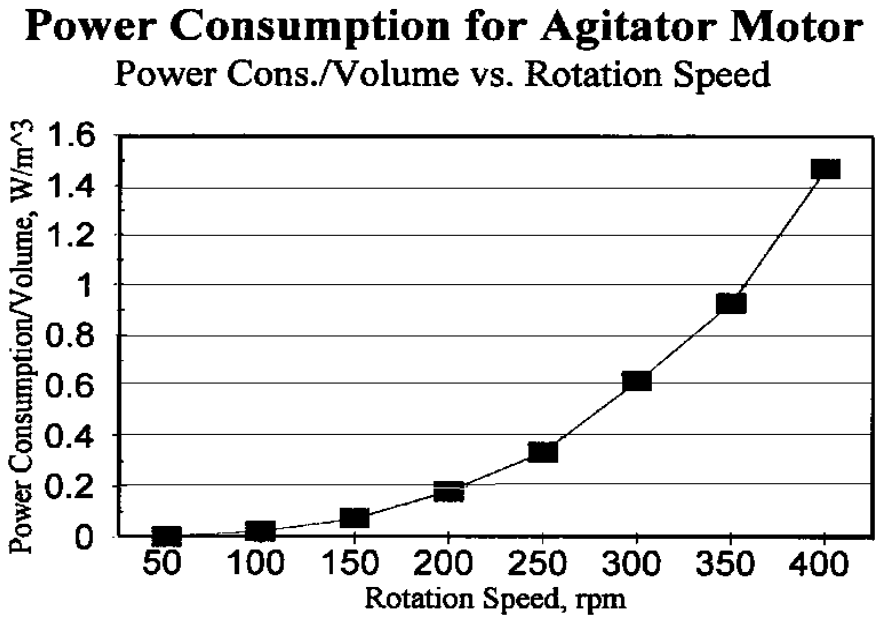


Figure 4.7 : Power consumption per unit volume vs rotation speed

Data for the power consumption showed predictable results. There was an increase in the power consumption per unit volume with an increase in impeller speed.

4.2.2.3 Filtration Screening Trials

The mass balances presented in this section do not include protein, phytic acid and lactic acid. As these trials were used primarily for assessing filtration parameters, only total solids analysis (dissolved solids and suspended solids) were performed. The runs were labelled according to the following convention. The first digit denotes the batch of CSL and the suffix denotes the filtration trial. For example, the fourth filtration trial using the third batch of CSL is labelled 3b.

The results are presented in the order in which they were processed, namely, run 1a, 2a, 3a, etc. All yields and recoveries are quoted on a mass basis. Ideally the feed solids should equal cake solids plus filtrate solids. However, due to the removal of samples, mass losses during processing (such as leaks on filter

press, volume holdup of pipes and pump) and errors in the solids analyses, mass balances were difficult to close. This was also the case for protein (measured by the Lowry method), phytic acid and lactic acid.

Pressure Filter Trials

The results of the pressure leaf filtration tests are presented in **Table 4.3**.

Table 4.3 : Results of laboratory pressure filtration tests

Test Number	**Units**	**1a**	**1b**	**2a**	**2b**	**3a**
Temperature	°C	60	60	60	60	60
Feed Characteristics						
Dissolved solids	% m/m	34	34.3	33.8	32	30
Suspended solids	% m/m	10	10.5	9.2	10.5	11.5
Protein (Lowry)	g/l	127	119	108	115	114
Filtrate Characteristics						
Dissolved solids	% m/m	33.8	34	32	31.5	30.5
Suspended solids	% m/m	0.2	0.15	0.16	0.18	0.11
Protein (Lowry)	g/l	128	125	114	118	98
Dewatering time	Min.	10	10	10	10	10
Dewatering rate	$l/m^2/hr$	31	28	26	20.5	12
Cake solids	% m/m	48	49.5	50.5	50.2	55
Cake thickness	Mm	5	5	5	5	5
Protein recovery	%	92	93	93.5	95	96
Filter medium						
Pore size		100	80	60	50	30

Material		PW1	CW2	CW2	CW2	CW2
Pressure	kPa	350	350	350	350	350
Precoat addition						
Dewatering rate	$l/m^2/hr$	23	22.5	19	14	9
Body feed						
Dewatering rate	$l/m^2/hr$	24	22.8	18.5	11	10
Precoat and body feed dewatering rate	$l/m^2/hr$	20	18	16	8	6

Key: PW1 = Polyester weave monofit

CW2 = Composite weave multifilament

Vacuum Filtration Trials

a) The filter was found to blind within a minute of initiating vacuum. No filtrate reached the receiver.

b) The addition of a precoat did not improve the situation.

c) Body feed addition did not improve the technique.

d) Addition of both body feed and precoat showed no improvement in the filtration.

Discussion

Laboratory scale filtration screening trials, when properly designed, provides very useful data for scale-up. In the pressure filtration trials, the fluxes averaged out at 18 $L/m^2/hr$ under un-optimised conditions. It was also noted that the input of body feed and precoat had little or no impact on the filtration. In some instances such as runs 1b, 2a and 2b, there were marked decreases in the fluxes.

The vacuum leaf test proved to be unsuccessful. Surface filtration effects caused immediate blinding. On examination of the surface film, very fine particles which accumulated into an almost gelatinous-like layer, were found. It was apparent that vacuum pressure filtration was not suitable for this application.

4.2.2.4 Pilot Trials on Carlson Filter Press

A summary of the results are presented in Table 4.4.

Table 4.4 : Results of pilot trials on Carlson Filter Press with multifilament composite weave as filter medium

Test Number	**Units**	**1a**	**2a**	**3a**	**3b**	**4a**
Temperature	°C	40	50	55	60	70
Feed : TDS	%m/m	37.7	32.66	31.04	33.50	29.46
TSS	%m/m	15.84	11.76	10.13	10.15	9.32
Filtrate : TDS	%m/m	34.24	31.47	31.03	33.35	29.15
TSS	%m/m	0.32	0.19	0.21	0.25	0.19
Cake Solids	%m/m	51.27	50.22	51.23	52.33	52.25
Cake Thickness	Mm	10	10	10	10	10
Chamber volume	*L*	0.95	0.75	0.73	0.80	0.71
Time⇒350 kPa	Hr	0.25	0.25	0.25	0.25	0.25
Pressing time	Hr	1.00	1.00	1.00	1.00	1.00
Volume used	*L*	25	22	21	23	20
Weight used	Kg	30.25	25.96	24.68	27.37	23.40
Bulk density of	kg/*l*	0.253	0.238	0.227	0.24	0.210

Initial trials on the small pilot filter, the Carlson filter press, were very useful for gaining experience on the operability of a filter press. The trials showed that filtration at higher temperatures, 50°C and above, were more effective. An increase in filtration rates of up to 25 % was noted.

Also, much drier cakes were obtained at the higher temperatures and this effectively improved cake dislodging from the filter medium. Table 4.4 shows that despite variations in the feed solids composition from batch to batch, fairly consistent filtration quality was generated. The pressing time required for all the batches was the same at 1 hour. The maximum pressure was 350kPa. Higher pressures could not be tested on this system due to limitations on the equipment. The fluxes generated average around 20 $1/m^2/hr$ with notable decreases with an increase in the feed solids content.

The results shown in Table 4.4 indicate reasonable agreement between the laboratory test filter and the filter press. The cake moisture content and bulk density was found to be fairly consistent. The only notable difference was the "sloppiness" of the cake seen on a few runs. Runs 1a and 3a showed incomplete cake formation in the centre of the filter cake. Run 2a showed improved cake formation, which was possibly due to the higher temperature of 50°C. This immediately suggested that scale-up was to be determined with extreme care. On the other hand, the recorded comparison was very encouraging and suggested that scale-up was possible.

Mass balance information for the Carlson filter press was not compiled fully as the trials were used primarily to gain experience and to establish the workable filtration parameters.

4.2.2.5 Delkor Pilot Trials

Results – Recessed Chamber plates

Tests were conducted on 15 mm and 20 mm recessed chamber plates. The feed pressure was increased progressively from 300 kPa to 1500 kPa, in all the tests. The results of these tests together with the mass balances, are given in Appendix V. The filtration curves obtained are shown in Figure 4.8.

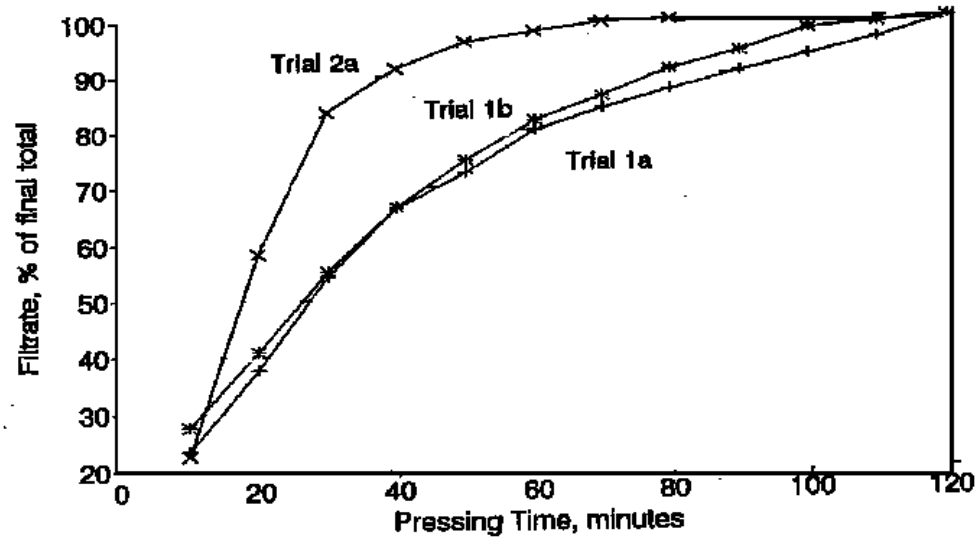


Figure 4.8: Filtration curves for Delkor pilot trials using recessed chamber plates

The following observations were made.

(i) Cake thickness :- It was observed that 20 mm plates produced incompletely formed cakes, where approximately 20% of the cake at the centre was floppy. Tests carried out with 15 mm plates produced competent and completely formed cakes with good discharge characteristics.

(ii) Dewatering rate :- On average, dewatering rates in excess of 20 $1/m^2/hr$ were obtained. The dewatering time ranged from 80 minutes to 120 minutes.

(iii) Cake moisture content :- The cake moisture was found to be less than 50%. Tests carried out to dry the cake with air blowing were unsuccessful. This was found to be due to the impermeable nature of the cake.

(iv) Filtrate clarity :- Tests conducted with highly permeable cloths, air permeability greater than 1 cfm (at ½ inch water guage) produced cloudy filtrates. The suspended solids were found to be between 0,5 and 1%. However, with low permeability cloths, significant improvement in filtrate clarity was observed. On average, the overall filtrate clarity was measured at 0,19% (TSS). The filtrate clarity was further improved by recyclying the initial portion of the filtrate, 5 - 10% of the overall filtrate volume, back into the feed tank.

Results - Recessed Chamber plates with diaphragms

Tests were conducted with 15 mm and 40 mm recessed plates. The feed pressure was gradually increased to 700 kPa with the diaphragm squeeze being applied directly at 1000 kPa. The results of these tests are given in Appendix V. The filtration curves are presented in Figure 4.9.

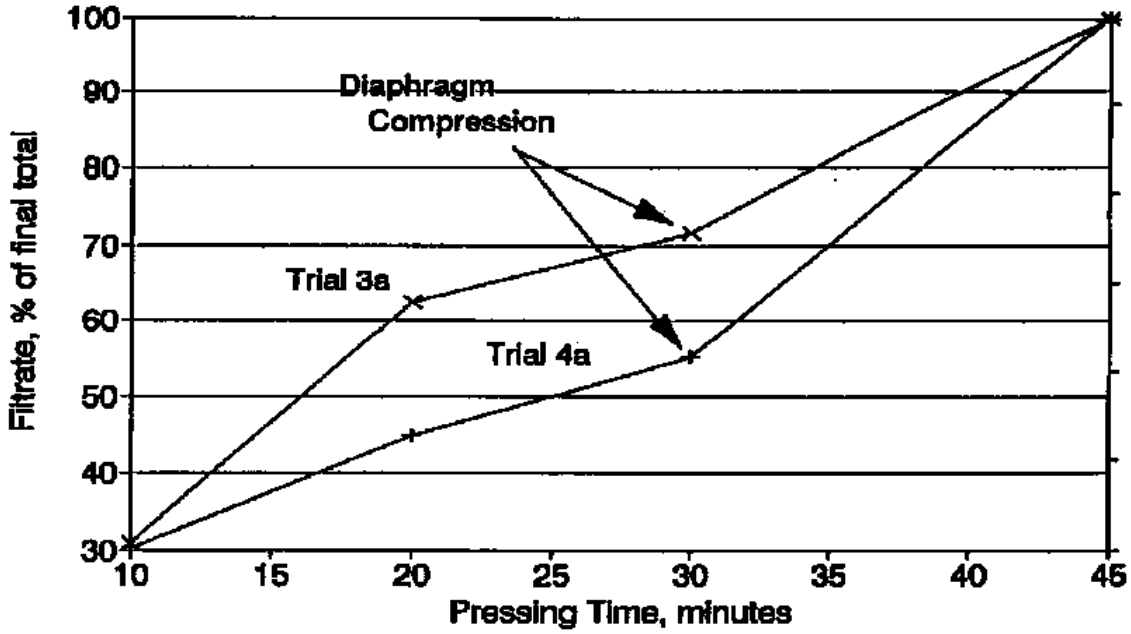


Figure 4.9 : Filtration curves for Delkor pilot trials using diaphragm squeeze

The following improvements were noted.

(i) Dewatering rate :- On average the overall dewatering rate, including the diaphragm squeeze stage, was approximately 36 1/m2/hr. The total dewatering time was approximately 45 minutes.

(ii) Cake moisture :- The cake moisture content improved by approximately 2% as compared to the trials without cake squeeze.

Sterilisation of clarified liquor

The results of the heat treatment for sterilisation tests performed on the clarified liquor from each of the Delkor runs are summarised below in **Table 4.5**.

Table 4.5 : Results of sterilisation trials on clarified CSL (quantities shown on a % m/m basis)

Trial Number	**Crude CSL**	**1a**	**1b**	**2a**	**3a**	**4a**	**5a**
Before sterilisation							
Total solids	46.32	36.40	29.34	34.71	28.07	45.92	9.95
dissolved solids	41.56	36.13	29.15	34.24	27.70	45.75	9.90
suspended solids	4.76	0.25	0.18	0.17	0.37	0.17	0.05
Phytic acid	5.83	1.95	0.83	0.57	0.85	0.99	0.96
Lactic acid	7.12	8.94	6.93	6.19	6.77	8.80	1.65
Protein	12.52	15.45	10.14	14.06	12.81	15.86	3.16
After sterilisation							
Total solids	46.32	36.40	29.21	34.23	28.04	46.10	9.93
dissolved solids	37.36	35.55	28.11	33.95	26.90	45.68	9.75
suspended solids	8.96	0.85	0.47	0.33	1.23	0.41	0.18
Phytic acid	3.75	0.39	0.18	0.12	0.50	0.18	0.07
Lactic acid	3.36	0.28	0.16	0.18	0.77	0.20	0.09
Protein	10.56	15.03	10.23	13.89	13.26	15.14	3.20

The sterilisation by heat tests showed clearly that its success was dependent on the quality of filtrate produced. Increased amounts of suspended solids showed increased coagulation during the sterilisation process. This is seen in Figure 4.10. Although the amount of coagulated suspended solids was as high 1,23% (m/m), this was within tolerable limits and marked a significant improvement in sterilisation quality.

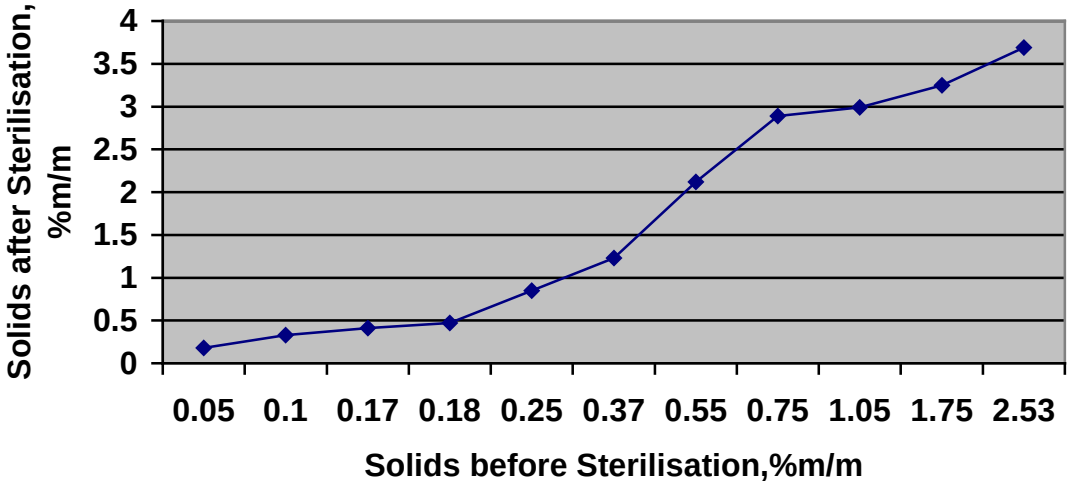


Figure 4.10 : Plot of suspended solids before sterilisation vs. suspended solids after sterilisation.

The surface charge effects of the colloidal solids become enhanced at the higher temperatures and is especially vigorous for the larger suspended particles. These particles act as "seeding" points for the coagulation process to take place. Analyses of the coagulated solids show major compositions of phytic and lactic acids, the latter appearing in higher proportions.

Overall Performance and Characterization

The Delkor pilot system provided an up-to-date filter system with facilities to incorporate the most recent technological advances in filter presses. To establish accurate design parameters it was important to test the process on such a system that possessed both flexibility and full scale equipment characteristics. The performance of the system is discussed under the following headings.

Selection of the optimum filter medium

As a general rule, increasing filtration capability reduces the filtration rate of a filter cloth/sheet. This means that the selection of the most suitable filter medium requires optimisation efforts aimed at the highest possible filtration rate on the one hand and a satisfactory filtration efficiency on the other.

In following the objectives of the separation, filter media with very high filtration efficiency (with a tight pore matrix) may certainly be the safest solution. However, with CSL it was proven to be unsuitable as early exhaustion or blocking occurred because of the presence of very small particularly matter. The tight medium also showed a tendency to prefer lower flows and higher pressures.

Alternatively, the looser filter media showed frequent sludge breakthrough or light contamination of the filtrate. It was found in the past on other applications, was not suitable for this application. An imported fabric, Propex 46, was the most satisfactory performer. Although this was a relatively coarse filter sheet (approximately 75 micron pores), the bridging effect was excellent and prevented particles from being squeezed through.

Filter rinsing and cleanability

The selected filter medium possessed good cleanability characteristics. A rinsing time of 10 to 15 minutes at a rate of 1,5 to 2 times the specific filtration rate was required to obtain a fully cleaned system. Acid condition of the filter sheets was required once very 5 runs in order to solubilise and remove residual debris from the media matrix. A 1% phosphoric acid solution was found to be suitable for this purpose. A change in the pH value caused the precipitated material to be solubilised and this led to the material being easily washed out of the media.

Special consideration was given to the fact that the low pH rinse and the clean water rinse was first done at low pressure (between 250 - 350 kPa) and then carried out with the filter stack loosened. This allows the free flow of liquid in the outer zone of the sealing edge.

Cake Compressibility

The volume versus time information at each constant pressure level shows a clear indication that the solids are compressible. In Run 1a a gradual decrease in the filtered volume is seen at 10 bar. In the final 10 minutes the pressure was increased to 15 bar and an increased volume of filtrate was obtained. The different slopes obtained on the plot of cumulative filtrate volume versus filtration time, as the pressure is altered, indicated the presence of a compressible cake. This phenomenon is seen in the subsequent runs and is especially apparent with the use of diaphragms. Approximately 55-75% of the filtrate is removed under a moderate pressure of 7 bar, as obtained in Runs 3a and 4a, and the remaining filtrate is removed by membrane squeeze at a higher pressure of 10 bar.

It is clearly seen that the effectiveness of the diaphragms is dependent on the degree of cake compressibility. The compressibility factors for these runs were found to vary between 0.28 and 0.36.

Differential Pressure

As already mentioned, increasing the differential pressure will only be successful if the compressibility factor is zero, or close to zero. In this case, however, the increase in the differential pressure is necessary for improving the filtration but must be applied with caution. In Run 2a, the maximum pressure was applied after only 30 minutes of pressing time. The resultant effect was a decrease in the dewatering time from 120 minutes to 80 minutes and a significant decrease in the average flux. Although a part of the decreased flux could be attributed to increased solids loading, it is fairly apparent that the differential pressure should be increased gradually in equal increments, within the dewatering period.

Run 1b showed a significant improvement in both the solids rate and the flux rate when compared to 1a. The only difference between the two runs is in the application of the pressure, where Run 1b was subjected to a gradual increase in pressure.

Solids Content

The volume of filtrate produced in a filtration cycle is influenced by the amount of solids to be removed. Increased feed solids content decreased the total filtrate volume and also showed significant decrease in the flux. Run 2a had a feed solids content of 53.3% solids and had a flux of 14.38 $l/m^2/hr$. This flux was lower than Run 1a which was in turn lower than 1b.

Recessed Chamber Plates

The performance of the recessed chamber plates was dependent on many criteria. The first being the cake depth with its associated dryness factor. Cake thickness above 15 mm had progressively higher moisture content. The solids rate was found to be poor despite the increase in chamber depth. The dewatering rates also decreased with the increase in chamber depth.

It was also noted that pressure surges had a direct impact on the filterability of the material. Sudden variations in the pressure partly destroy the bridging effect or the more ordered build-up of the particle deposits.

The solid particles are washed off, and in the most unfavourable case, pass through into the filtrate. Although this behaviour of breakthrough is only of a short duration, the overall quality of the filtrate was considerably reduced.

The best cake formation was achieved at a temperature of 60 °C and chamber depth of 15 mm. The total dewatering time required was 120 minutes. All attempts to reduce the dewatering period failed as this produced incomplete and "sloppy" cakes.

Recessed Chamber Plates with Diaphragms

The pilot data obtained on the recessed chamber plates were fairly inconclusive in that large improvements were required in all of solids rate, fluxes and the dewatering time. The recessed chamber plates with diaphragms showed marked improvements in all of these areas. The chamber depth was increased to an optimum 40 mm which increased the solids rate by approximately three times that of 15 mm plates. Although a larger chamber depth was used, in contradiction to what was discussed earlier, the principle of operation was different.

The initial dewatering stage was performed with an incremental increase in pressure and this was followed by a compression stage, using the diaphragms, at high pressure. This process reduced the cycle time to 45 minutes and also increased the fluxes by approximately 30%. The moisture content of the cake was found to be consistently less than 50%. The bulk density of the cake was considerably less than those achieved with recessed plates without diaphragms.

4.3 Decanter Centrifuge

4.3.1 Experimental Equipment and Protocol

For the evaluation of the decanter performance, it was necessary to identify the fixed parameters and those that could be adjusted during operation. The fixed parameters on the NX 210 were bowl diameter, bowl length, bowl geometry (conical), scroll pitch, bowl internal design and bowl speed. The variable parameters were the feed rate, operating temperature, sedimentation aids, pond depth and the scroll differential speed.

The following were required to be set up for the trials:

- a well stirred feed tank equipped with heating coil
- a variable speed positive displacement pump for precise feed control
- a calibrated floating head rotameter
- an in-line mixer (set up for turbulent mixing)
- a peristaltic pump (calibrated for flocculant dosage)
- piping connections
- an adequate supply of representative feed CSL
- a sufficient quantity of uniformly mixed flocculant.

The scroll differential speed was adjusted to the lowest possible setting and the pond depth was adjusted to that most commonly used for this type of application according to the decanter centrifuge supplier. The coagulant for the trials, Gilufloc 40 (polyaluminium chloride, PAC), was obtained from Giulini Chemicals, Germany. The flocculant, Sedipur CF 803, strongly cationic, high-charge density, and high molecular weight polyacrylamide was obtained from BASF, Germany. Runs were conducted at a range of feed rates and a fixed temperature of 50 °C. For each feed rate the centrate clarity and cake dryness were determined.

On assessment of the samples, the optimum feed rate was chosen for investigations at different speeds, from which samples were taken for analysis. Assuming some improvement in the results, the optimum

speed was fixed and four more runs were conducted in an attempt to increase machine capacity without dropping product quality below the required level.

The flocculant dosage was altered in proportion to the feed rate of CSL such that the concentration was kept constant. On selecting the optimum feed rate and speed, the flocculant concentration was varied. Samples were taken and analysed for cake dryness, suspended solids in the centrate. Feed rates were then adjusted to determine the correct floc dosage. Tests were also conducted to check if reduced polymer concentration can reduce the required dosage. Once the required dosage for a given CSL feed rate was determined, this dosage was used to re-evaluate the earlier experiments to determine whether a further reduction in the floc dosage was possible.

Mass balances were determined as described below. Figure 4.11 defines the terms, as used in the following discussion, namely mass flow of feed (F), centrate (L), cake (S) and polymer (Y) and mass fractions X_F, X_L, X_S, and X_Y for the feed, centrate, cake and polymer respectively.

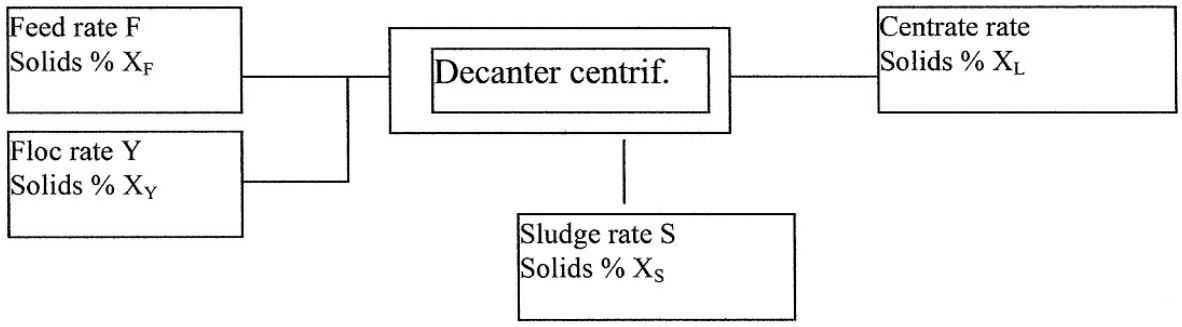


Figure 4.11: Mass Balance Diagram for the Decanter Centrifuge

The following equations can now be derived by an overall and component mass balance:

$$F + Y = L + S$$

$$FX_F + YX_Y = LX_L + SX_S$$

By eliminating S (as this is difficult to measure accurately)

$$F = L(X_L - X_S) / (X_F - X_S) + Y(X_S - X_Y) / (X_F - X_S)$$

In the situation where the densities of the F, L and S are close to unity, then the mass flows can be converted to volumetric flows ($F = Q_f$). If no precipitation or dissolution occurs, then the dissolved solids may be ignored. In this case, the solids fraction represents the suspended solids only, and the value of Xy will be zero.

The recovery (R) was defined as the percentage of the feed solids that have reported to the cake discharge, quoted as per cent of suspended solids.

$$R = 100\left(1 - \frac{LX_L}{FX_F}\right)$$

While floc dosage, FD, is given by :

$$FD = \frac{YX_Y}{FX_F} \times 1000(kg / tonne)$$

4.3.2 Results and Discussion

The results of the decanter trials are shown in Table 4.6.

Table 4.6 : Results for decanter centrifuge trials

Run number	**47**	**53**	**55**	**56**	**57**
Machine Conditions					
Bowl speed, rpm	3286	3286	3286	3286	3286
Beach angle, deg.	8	8	8	8	8
Scroll pitch, cm	3	3	3	3	3
Scroll differential, rpm	4	4	4	4	4
Feed Conditions					
Solids % m/m, dry	2.5	2.1	3.6	4.3	2.12
Temperature, °C	60	60	60	60	60
Feed rate, l/hr	600	600	700	700	700
pH	9.0	8.45	8.47	8.55	8.43
Coag. Conditions					
Type	PAC	PAC	PAC	PAC	PAC
Concentration, % m/m	40	40	40	40	40

Dosage, % m/m	0.4	0.05	0.18	0.1	0.1
Floc Conditions					
Type	CF 803	CF 803	CF 803	CF 803	CF 803
Concentration % m/m	0.1	0.25	0.35	0.5	0.2
Rate, l/hr	0.08	0.08	0.08	0.08	0.08
Dosage, %m/m	0.01	0.2	0.028	0.04	0.016
FD, kg/tonne solids	0.05	0.1	0.088	0.106	0.087
Product Conditions					
Centrate rate, l/hr	570	520	630	640	650
Centrate solids, %m/m	0.2	0.73	0.55	0.85	0.5
Cake solids, %m/m	58.0	65.87	43.0	44.4	49.3
Solids recovery, %m/m	92.4	70.0	86.25	89.4	78.1

The performance of the decanter is governed by four crucial factors:

a) centrifugal force required to sediment the solids

b) sedimentation area necessary to capture the solids

c) differential speed required between the bowl and scroll to convey the solids

d) hydrodynamic design to minimise turbulence.

Control of only one of the above four was possible, that being the differential speed between the bowl and the scroll. Table 4.7 shows the effect of the scroll differential on cake dryness.

Table 4.7 : Effect of scroll differential on cake dryness (Run 53)

Trial no.	**1**	**2**	**3**	**4**	**5**	**6**
Feed rate (l/hr)	600	600	600	600	600	600
Scroll diff. (rpm)	4.0	6.5	8.8	11.2	13.6	15.9
Dry solids, % m/m	65.87	58.0	40.50	31.80	22.15	12.63
Centrate dry solids, % m/m (suspended)	0.73	0.68	0.59	0.58	0.79	1.20

Reduced scroll speed differential showed improved dryness but, at the lower limit, there were restrictions in capacity. Also, the centrate clarity deteriorated as the equilibrium solids loading in the bowl increased.

At the upper end of the scroll differential, centrate clarity was seen to deteriorate again due to resuspension of the solids from the turbulence in the centrate pool as well as insufficient residence time for the solids "beach-out". The differential speed was investigated with a constant feed rate.

In this way the optimum differential speed was chosen. This differential speed was then fixed and an attempt was made to increase machine throughput. However, product quality deteriorated when the feed rate was increased. The solids carryover in the centrate also increased from 0.73% to 1.2%. An interesting feature of the trials was that the CSL obtained for the testwork contained far less suspended solids than normal. Typically CSL contains 10% to 15% suspended solids. This situation was as a result of total dependency on the supplier for CSL and was therefore subject to the existing process conditions. The sudden change in solids consistency could be attributed to evaporation conditions during the concentration process in the production of CSL or certain changes during the steeping process.

From these trials it was fairly apparent that feed solids concentration would severely affect the optimal operation of the centrifuge, due to the sensitivity of the settings of these variables. Sudden changes in feed solids concentration would result in significant carryover of un-sedimented suspended solids.

One of the improvements in the hydrodynamics design was the inclusion of a baffle in the centrifugal bowl. The baffle helps to prevent carryover of fines and gelatinous solids by creating a sludge barrier. It also assists in the scrolling and and the compaction of solids.

It was apparent that the incorporation of the baffle-design enabled the decanter to operate at a very deep pond setting. Although theory suggests that an increased pond depth produces a wetter solid, the trials showed the reverse. It was found that deeper ponds reduced turbulence as the Reynolds number decreased and so allowed improved settling. Expressed differently, with deeper ponds there is reduced suspension of solids in the vicinity of the liquid weir ports.

In some runs the performance was unsatisfactory. In run 56, the carryover of solids in the centrate was found to be 0.85%, which was approximately 20% of solids contained in the feed. Reduction of the bowl speed together with the increased pond depth may improve this figure. The bowl speed on the centrifuge was fixed, however, and so this could not be tested. The flocculated particles tend to be delicate and operating at the correct bowl speed and pond depth are essential for better performance in their sedimentation.

It was difficult to assess the degree of floc breakup and other shear effects in the centrifuge. Laboratory assessment of floc strength and the shear effect due to turbulent mixing seemed to be sufficient for the prelimnary decanter trials.

Subsequent analyses of the centrate samples for particle size distribution showed that approximately 0.2% m/m of the suspended solids were greater than 100 μm. This represented a significant proportion of suspended solids. In addition, microscopic evaluation revealed that these solids were fibrous in nature. It is possible that these solids are unaffected by the coagulation and flocculation conditions due to their ability not to agglomerate.

It is also feasible that the fibrous nature of the solids enables them to escape the “sweeping” effects of flocculation and the accelerated settling. It is certain that the densities of these solids are very close to unity with the CSL solution, and so separation by centrifugation would be relatively difficult, unless higher centrifugal force is utilised.

The carryover of this type of solids would pose severe problems for ultrafiltration, since the safety filters, slotted upstream of ultrafiltration, are rated to 100μm. Blinding of these “dead-end” filters would be far too frequent under normal operating conditions. Furthermore, fibrous solids are known to cause severe fouling problems on membrane surfaces as well as the entrapment in small diameter tubes and mesh spacers.

4.4 Gyratory Screens

4.4.1 Equipment and Experimental protocol

4.4.1.1 Equipment and Objectives

The trials on the pilot plant were conducted on a Sweco Vibro-energy separator, model LS30S66, equipped with 0.164m^2 of screen area. A schematic diagram of the unit is shown in Figure 4.12**.**

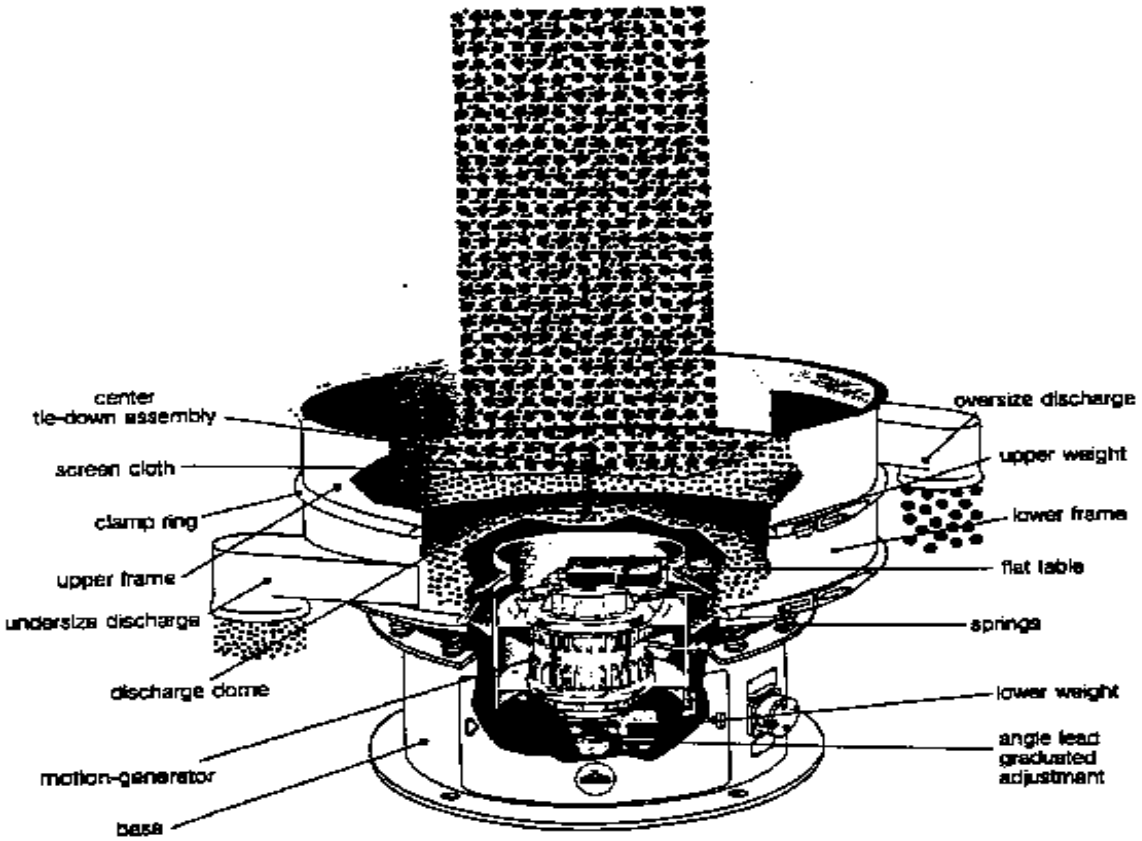


Figure 4.12 : The gyratory screen separator

CSL was obtained from African Products, Germiston, and stored in a heated 500*l* stirred tank. A centrifugal pump was used to transfer the feed material to the separator. The discharge side of the pump was equipped with a flowmeter, a floating head rotameter, and a manual diaphragm valve for flow control. Both the filtrate and sludge streams were collected in respective holding vessels. The experiments were conducted to determine the following criteria:

(i) To ascertain the relationship between feed rate, spiral screening pattern, vibration frequency, solids rejection and discharge characteristics.

(ii) To determine the number of screens required for the duty.

(iii) To ascertain the cleanability of the screens or the efficacy of the self-cleaning mechanism.

4.4.1.2 Experimental Procedure

The test procedures entailed the following:

1. The separator was adjusted to a standard zero lead setting, so that a base case was established for the separation.

2. A low feed rate was initiated for a uniform cake thickness. The feed rate was increased in stages with samples of all the streams being taken before each increase in flowrate.

3. The feed rate was increased until the separator "slopped". At the "slop-limit" the filter area was too small for the flowrate.

4. The lead setting was increased to see whether the "slop-limit" could be raised.

5. The lead setting was adjusted or fine tuned to give the best screening pattern.

6. The tests were conducted with and without self-cleaning mechanism.

7. The optimised conditions were repeated on several batches and the results compared.

8. The tests were conducted with feed material passing through two screens in series, i.e. first through a loose screen of 180-200μ and then through the 100μ screen. The same procedures were adhered to in order to achieve the optimum operating conditions.

The screened material was then processed through a 100μ safety filter. The safety filter was examined at the end of the run for retained solids.

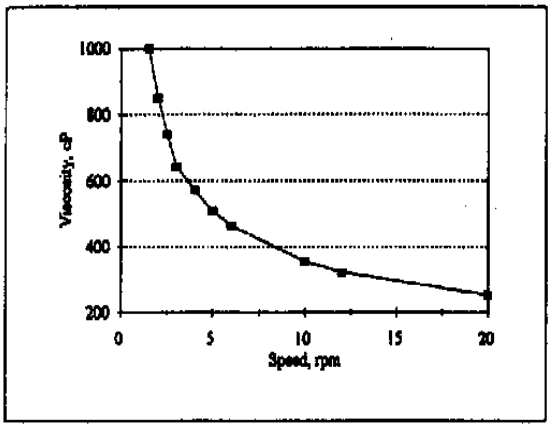
4.4.1.3 Sample Points and Analyses

Samples were taken at various stages of the trials to allow mass balances to be compiled, and to enable the flow of important species to be followed through the process. The volumes were recorded where possible. The samples were analysed for protein, suspended solids and dissolved solids. Viscosity tests were conducted using a Brookfield viscometer.

4.4.2 Results and Discussion

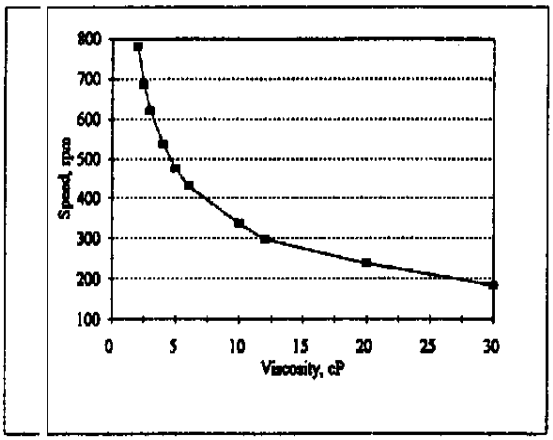
4.4.2.1 Effects of shear rate and temperature on viscosity

The effects of spindle rate on viscosity at various temperatures are shown in Figure 4.13 (a), (b) and (c).. The viscosity data presented here illustrates clearly the rheological nature of the separated streams. An increase in the shear at constant temperature, showed a significant decrease in the viscosity. The results indicate typical non-Newtonian behaviour, and in particular that of a thixotropic fluid. The sludge stream showed that the viscosity could reach very high levels.



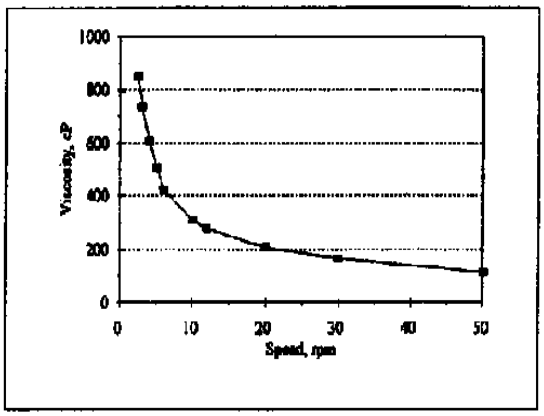
Speed rpm	Torque %	Viscosity cP	Temperature C
1.5	25.0	999.8	31.0
2.0	28.3	848.8	31.0
2.5	30.8	739.0	31.0
3.0	32.2	643.9	31.0
4.0	38.2	572.9	31.0
5.0	42.4	508.7	31.1
6.0	46.4	463.9	31.0
10.0	59.3	355.7	31.1
12.0	64.4	321.9	31.1
20.0	84.0	251.9	31.1

Figure 4.13 (a) : Viscosity vs speed at 31°C



Speed rpm	Torque %	Viscosity cP	Temperature C
2.0	26.1	782.8	40.5
2.5	28.6	686.3	40.5
3.0	31.1	621.9	40.5
4.0	35.9	538.4	40.5
5.0	39.7	476.3	40.5
6.0	43.1	430.9	40.5
10.0	56.1	336.5	40.5
12.0	59.5	297.4	40.5
20.0	79.4	238.1	40.5
30.0	91.8	183.6	40.5

Figure 4.13 (b) : Viscosity vs speed at 40,5°C



Speed rpm	Torque %	Viscosity cP	Temperature C
2.5	35.4	849.4	50.5
3.0	36.8	735.8	50.4
4.0	40.4	605.9	50.4
5.0	42.2	506.3	50.5
6.0	42.1	420.9	50.4
10.0	51.5	308.9	50.4
12.0	55.6	277.9	50.5
20.0	69.5	208.5	50.5
30.0	81.8	163.6	50.5
50.0	94.7	113.6	50.5

Figure 4.13 : Viscosity vs speed at 50,5°C

An important observation made during the trials is that the sludge stream gels into a solid mass when allowed to cool down. This could pose specific problems for pumping and re-slurrying. It is therefore important that the sludge be kept agitated at all times and also that there should be a minimum loss in temperature to prevent this phenomenon from occurring.

4.4.2.2 Pilot Plant Testwork on Gyratory Screens

The mass balances presented in this section only detail the flows of protein, suspended solids and dissolved solids, since these trials were used primarily to test separation parameters. The results are

presented in Table 4.8 in the order in which they were processed. All yields and recoveries are quoted on a mass basis. There were significant losses from the various process streams due to the removal of samples, spillages during processing and the volume holdup of the pump and piping. Mass balances were difficult to close as a result of this.

Table 4.8 : Results of gyratory screen tests

	Feed		**Filtrate**		**Sludge**		**Closure**
Run 1	**%m/m**	**kg**	**%m/m**	**kg**	**%m/m**	**kg**	**%**
Total solids	44.72	25.74	42.66	23.04	45.60	0.19	109.74
Water	55.28	31.81	57.34	30.97	54.40	0.23	101.95
Total	**100**	**57.55**	**100**	**54.01**	**100**	**0.42**	**105.43**
Suspended solids	10.22	5.88	10.10	5.45	17.40	0.07	106.12
Protein(Lowry)	11.98	6.89	10.96	5.92	16.26	0.07	113.06
Run 2							
Total solids	43.63	25.13	43.97	24.08	44.07	0.15	103.58
Water	56.37	32.47	56.03	30.69	55.93	0.19	104.88
Total	**100**	**57.60**	**100**	**54.77**	**100**	**0.42**	**104.31**
Suspended solids	10.42	6.00	12.02	6.58	24.70	0.09	88.83
Protein(Lowry)	10.87	6.26	13.37	7.32	15.81	0.06	82.11

Run 3							
Total solids	43.85	56.22	43.89	55.80	45.20	0.74	99.43
Water	56.15	71.99	56.11	71.33	54.80	0.89	99.68
Total	**100**	**128.21**	**100**	**127.13**	**100**	**1.63**	**99.57**
Suspended solids	11.22	14.39	11.61	14.76	19.20	0.31	95.27
Protein(Lowry)	15.20	19.49	14.27	18.14	15.44	0.25	105.64
Run 4							
Total solids	44.24	56.54	44.81	55.56	44.74	0.33	101.15
Water	55.76	71.26	55.19	68.43	55.26	0.40	103.41
Total	**100**	**127.80**	**100**	**123.99**	**100**	**0.73**	**102.41**
Suspended solids	12.38	15.82	12.00	14.88	15.08	0.11	105.25
Protein(Lowry)	9.69	12.39	12.55	15.56	24.29	0.18	72.96
Run 5							
Total solids	57.10	40.16	50.80	29.43	58.86	0.75	124.85
Water	42.90	30.17	49.20	28.50	41.14	0.52	103.80
Total	**100**	**70.33**	**100**	**57.93**	**100**	**1.27**	**115.82**
Suspended solids	14.51	10.21	5.59	3.24	26.52	0.34	164.94
Protein(Lowry)	8.60	6.05	9.36	5.42	1.72	0.02	110.08

There was significant variation in the suspended solids composition of the various batches processed. It was also difficult to obtain a particle size distribution that was representative of all batches. The feed suspended solids content was found to range between 10 % and 18 %. Of this, only a small fraction, 1 to 2% m/m, was greater than 100μm in size. It is also important to note that the CSL was allowed to cool down during transportation and this induced the coagulation of solids.

The reported suspended solids are therefore higher than usual. There is also no evidence to suggest that these solids redissolve on heating. this phenomenon also occurs during the sampling of the various separated streams, where the samples cool down before actual analysis.

Despite these shortcomings the general trends in the removal of suspended solids is apparent. The total solids content of the sludge varied between 44 and 59%. The suspended solids content of the filtrate was still fairly high with, with the exception of run 5, where the sample was treated differently. The suspended solids were centrifuged out fairly quickly without allowing significant cooling of the sample to occur. The suspended solids content of the filtrate was 5.6%. This is the typical figure that could be expected on a continuous process where the operating conditions are bound to be more stable.

Protein Loss

The loss of protein to the sludge stream was found to range between 0 and 1.5%. This clearly indicates that although protein coagulation is a common phenomenon, a very small fraction of the coagulated protein particles in the feed stream was greater than 100μm in size and retained by the screen. Even though small amounts of protein are lost, most of this is present in the moisture of the sludge stream.

Gyratory Screen Cleaning

One of the major disadvantages of conventional screening systems is the inability to prevent fouling. Particles that are near-sized and over-sized easily block the screen pores and reduce the screening area. The principles used in the operation of this machine means that it has tremendous advantages over the conventional screening methods. The gyratory screens can be fined tuned to efficiently remove such foulants without disrupting the screening operation. Unfortunately on this pilot scale unit there was little room for the manipulation or fine tuning of variables. An important variable such as the vibration frequency was fixed on this machine.

Nevertheless, for a liquid as viscous as this, a lead angle of 45-60° was required. Anything less than this range caused the failure of particles to migrate to the periphery of the screens. The sludge was found to accumulate on the screen, thus reducing the screen area significantly. Lead angles greater than this range caused definite spiralling of sludge towards the centre of the screens. Here again, the accumulation of the solids in the centre of the screens caused severe blinding. It is envisaged that the manipulation of vibration frequency together with the correct lead setting will further improve the screening efficiency.

The inclusion of the sliding cylinders, situated on the underside of the screen, made a significant difference to the operation. Fibrous type material, which often wedges into the mesh, is easily dislodged by the sliding cylinders and conveyed away from the screen surface. Also, the continuous sliding action helped in the spiral conveyance of the sludge to the discharge port.

Feed Port

It was established that the position of entry of the feed into the system was very important. Feed entrance on the periphery of the screen caused the bulk of the feed to be discharged into the sludge port. Best distribution was obtained when the feed pipe was located at the centre of the screen. This allowed sufficient retention of the feed stream so that the laminar flow conditions were adhered to. In this way a more concentrated sludge stream was produced. This is seen in the result of run 5, where a sludge concentration of 59% was obtained.

CHAPTER 5

MEMBRANE SCANNING TRIALS

5.1 Introduction

The objectives of this section are :

(i) To identify candidate membranes that could be applicable for the purification of pretreated CSL as a fermentation feed

(ii) To determine the combination of pretreatment process and membrane type that could give the best quality of fermentation feed

(iii) To quantify the performance of the selected pretreatment-membrane system

5.2 Experimental Protocol

A phased program of experimentation was followed due to the complexity of the outlined objectives. As shown earlier, the research and development of the pre-treatment of CSL to produce a "suitably clarified" feedstock to a membrane separation process, is fundamental for the success of the ultrafiltration process.

5.2.1 CSL Feed Material

Corn steep liquor was obtained from African Products, Germiston Mill. This was received as an evaporated concentrate, with a solids concentration of 50% (m/m) and pH 4.2. The concentrate was diluted using RO water to a concentration of 43% (m/m). The sample was divided into sufficient amounts for the various pre-treatment processes. The samples were then processed using the method for pH treatment and subsequent filtration, centrifugation by scroll decanter and screening by the gyratory double screen system. The products of the pre-treatment processes were stored at 50 °C prior to use.

5.2.2 Membranes

The ultrafiltration membranes, in the form of flat sheets and laboratory hollow fibre modules, were obtained from various membrane vending companies, as outlined in Table 5.1. All the membranes were prepared by soaking in demineralised water, except for the polysulfone and polyacrylonitrile membranes, which were wetted by a 50% ethanol solution for 5 minutes before use. A pure water flux was measured

for each membrane at 100 kPa before any of the filtration experiments were conducted. Clean water was obtained from a PALL-D-MIN system.

Table 5.1 : Membranes for laboratory screening

Membrane	MWCO	Type	Vendor
Cellulose acetate (CA)	25K-30K	flat sheet	Koch/Abcor
Polysulfone (PS)	30K-40K	flat sheet	Osmonics Inc.
Polyvinylidene difluoride	30K	flat sheet	Osmonics Inc.
Polyacylonitrile (PAN)	20K-35K	hollow fibre	Asahi Corp. Japan
Polyamide (PA)	30K-35K	flat sheet	Desalination Sys.
Regenerated cellulose acetate (RCA)	30K-33K	flat sheet	Hoechst
Polyethersulfone (PES)	30K	flat sheet	Kiryat Weizman

5.2.3 Laboratory Rig and Procedures

5.2.3.1 Experimental Apparatus

The primary focus of initial laboratory experimentation was to determine the filtrate flux for a variety of membrane types. Product (useable protein) permeation and fouling was examined as well. Attention was also given to the effect of the pre-treated feedstock on membrane performance. The laboratory system used is illustrated schematically in Figure 5.1.

The system comprised of a magnetically-stirred feed reservoir. An immersion heater with an electric coil was used to heat the feed in the resrvoir. A variable speed Watson-Marlow peristaltic pump was used to feed a Mini-Tan flat cell filtration system, constructed from stainless steel, and obtained from the Millipore Corporation. The system offered flexibility and could be adapted to utilise a variety of membranes, both hydrophobic and hydrophilic. For the use of hollow fibre membranes, the Mini-Tan test cell was uncoupled at the feed, retentate and permeate ports and removed. Adapter couplings were then

used for the installation of the hollow fibre module, which took up the exact same position in the system as the test cell.

The membranes selected for the initial testwork were recommended by the vendors, outlined in Table 5.1**,** where each membrane polymer provided unique separation and cleaning characteristics. The MWCO's ranged from 20 000 daltons to 40 000 daltons.

Although the molecular range of required proteins was already known, it was important to test the actual passage and/or rejection of the proteins bands. Two pressure transducers were placed before and after the membrane cell, in the feed and retentate loops. They were equipped to measure a range of 0-500 kPa above atmospheric pressure, with an accuracy of ± 0.25% of full scale. Given that the pressure loss along the hydraulic channel of the permeate loop is small and maybe assumed as almost linear, the trans-membrane pressure can be taken as the average of the values taken up and down the membrane cell. In all cases, the applied trans-membrane pressure was below 500 kPa.

Using $0.024m^2$ of membrane area, a cross flowrate of 5 litres/min and an initial trans-membrane pressure of 100 kPa, a working temperature of 50 °C, 10 litres of feed solution was concentrated for 1 hour in each experiment. In order to measure the retentate flow, two electromagnetic flowmeters were used, both with errors lower than ± 0.2% at full scale. The pressure and velocity in the retentate loop are independantly controlled by means of the pump regulation and a needle valve on the retentate loop. The permeate flow was measured by collection in a graduated cylinder and stop watch. Flux was measured periodically as were the permeate and retentate volumes, trans-membrane pressure and temperature. Samples of permeate and retentate were collected over time. Protein concentrations in the feed, retentate and permeate streams were measured by the Lowry method for protein assay.

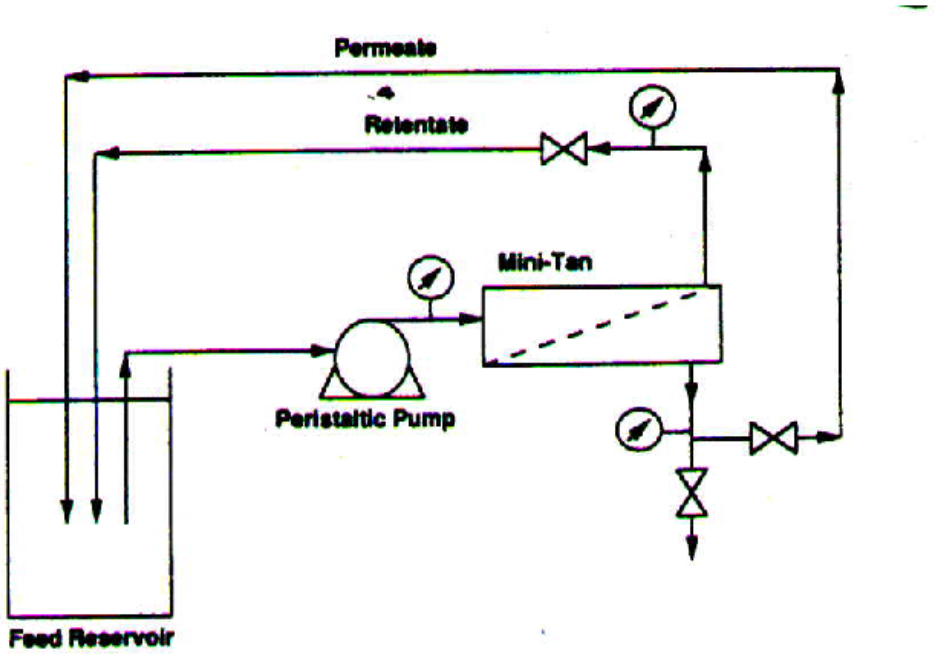


Figure 5.1 : Schematic of laboratory scale crossflow filtration system.

5.2.3.2 Effects of Heat Sterilisation on Permeate

After the ultrafiltration of the various samples of CSL, 500 ml of permeate solution was removed from each batch processed. An untreated sample of CSL was used as the experimental standard. The permeate samples were then transferred into heat resistant conical flasks and weighed. The volume transferred was approximately 200 ml. The flasks were then sealed by inserting cotton wool bungs into the necks of the flasks. The untreated sample of CSL was also transferred into a flask and weighed.

The flasks were placed in a laboratory steam autoclave and sterilised for a period of one hour at 121 °C. After sterilisation at the prescribed period, the samples were allowed to cool down to room temperature and then weighed to check for vapourisation losses during the sterilisation process. Each sample was then centrifuged in a Joune laboratory solid bowl centrifuge for 10 minutes at 14 000 RPM. The separated solids were then oven dried at 60 °C for 24 hours. The dried samples were then weighed.

5.2.3.3 Corn Steep Liquor Fermentability

The ultimate performance of all the testwork would definitely have to be reflected directly by fermentation. Since, the quality of the protein feedstock would impact on fermentability. Fermentations were performed in CHEMAP laboratory fermentors, of 8 litre capacity, under monoseptic conditions

(only one type of bacterial strain survives and flourishes) and prescribed media components of salts, water, thiamine, biotin, sugar and CSL permeate as the protein source. All the components were added to the fermentor and steam sterilised in-situ for 1 hour at 121 °C. One fermentor served as the standard where the only component different was untreated CSL.

After sterilisation, the fermentors were automatically adjusted to the operating temperature of 31 °C. An incubation flask containing 500 ml of seed bacteria, a genetically mutated strain of *Corynebacterium flavum*, was transferred into each of the fermentors under aseptic conditions. The fermentations were conducted for a period of 48 hours under controlled aerobic and temperature conditions. Foaming in the fermentations were monitored automatically and were controlled by the addition of corn-oil as the antifoaming agent.

Samples of fermentation broth were taken at 4 hour intervals to check bacterial growth and residual protein concentration. Bacterial cell growth was determined by taking 20 ml of the fermented broth, weighing the sample, and then centrifuging out the solids.

The supernatant was used for protein determination by the Lowry method. The separated solids were dried in an oven at 60 °C for 24 hours. The dried solids were then weighed and the mass of bacterial cells expressed in mass %.

5.2.3.4 Viscosity Effects of CSL

The experimental setup was adapted for conducting highly viscous and non-newtonian fluid experiments: the feed was recirculated through the Mini-Tan flat sheet membrane cell using a positive displacement pump. A helicoidal impeller was used for mixing the fluid in the feed tank. The retentate and permeate streams leaving the module were returned to the feed tank so as to maintain a constant feed concentration. The flow rate through the module was monitored through a rotameter calibrated for the CSL feed solution.

The permeate rates were measured volumetrically. Two pressure gauges were used to measure inlet and outlet pressures, the transmembrane pressure, P*m*, is the mean of the inlet and outlet pressures. Average transmembrane pressure was maintained by adjusting the back pressure on the retentate leaving the module. The measurements were performed at 20, 30 and 50 °C, with average excursions of ± 2 °C.

The filtration module contained a flat sheet polymeric membrane, polyvinyldifluoride (PVDF), with a contact area of 0.013 m^2 and flow mesh spacer of 2mm. The nominal molecular weight cut-off was

30 000 daltons and the membrane water permeability was 130 ± 10 L/m^2/h at 2 bar. Before the start of each run , the water permeability was measured to check the stability of the membrane.

The viscosity measurements were made with a Brookfield viscometer . The CSL feed was very stable under the shear rate conditions and the bulk rheological properties did not change due to mechanical degradation during all the experimental runs. A clear permeate was obtained during the separation process.

5.2.4 Sample analyses

The CSL is complex, contain organic and inorganic compounds, which often interact in ways not predictable by simple solution chemistry. The composition of the CSL is not completely known and it is likely to differ from batch to batch due to variations in the steeping process and also to seasonal attributes. Variations in the analytical results were observed and a review of analytical procedures has been undertaken, especially for the analysis of proteins, dissolve solids, ammonia and phytic acid. Trends can, however, be observed from the mass balances and it is these trends that are more important.

The largest analytical errors were in the ammonia, dissolve solids component, phytic acid and protein analyses with the latter two being less conspicuous. Ammonia and the dissolved solids content of the filtrate can be seen to be inconsistent with the mass balance (see Appendix V). The large errors seen in the dissolved solids content could be attibuted to the loss of volatile organics during the sample drying process.

At the neutral pH of the CSL, a fraction of the ammonia remains as “free” or unbound ammonia, which is often lost at the high process temperatures. Preliminary experiments have indicated the phytic acid response factor is dependant on the “phytin” phosphorus content. Conventional methods for phytic acid analysis rely upon precipitated phosphorus by supernatant difference.

Here, non-phytin phosphorus could easily be mistaken as phytin phosphorus. Subsequent liquid chromatography analyses were performed with minor problems in the mobile phase. Protein analysis by the Lowry method is dependant on many factors, such as dilution factors, protein hydrolysis, etc. The mass balances show closures of above 90% which is reasonable for a stream as complex as CSL.

The analyses of lactic acid, chlorides, sulphates and phosphates appear to be consistent as can be seen from the mass balances in Appendix V. The laboratory equipment that was used to perform the analyses are listed in Table 5.2.

Table 5.2 : List of Laboratory equipment that performed analyses

Type of Analysis	Analytical Laboratory
Protein	-
Sulphates	HPLC, XR, WC
Phosphates	HPLC, XR, WC
Chlorides	HPLC
Ammonia	WC
Phtyic Acid	LC, XR, WC
Lactic Acid	LC

HPLC = High pressure liquid chromatography

XR = X-ray

WC = Wet chemistry

AS = Atomic

MS = Mass spectroscopy

The consistency of lactic acid, sulphates, chlorides and phosphate analyses throughout the mass balance serves to validate the samples and the mass balance.

5.3 Results and Discussion

After the thorough investigation into the pretreatment of CSL prior to membrane ultrafiltration, the intense phased program of experimentation for the membrane ultrafiltration was completed in tandem. From the outset of the experimental program, problems were experienced with the consistency of the CSL obtained from African Products. It was for this particular reason it was decided that the pretreated concentrate would be diluted with RO water to a consistent concentration of 43% m/m. The concentration and dilution factor was based on subsequent viscosity evaluations and osmotic pressure implications on the hydrodynamic conditions in the membrane systems.

5.3.1 Screening of Membranes in Laboratory Cross-flow System

5.3.1.1 Membrane Characteristics

Before determining the transport properties of the various membranes in relation to their application, the effect of their compactness and transmembrane pressure on water filtration was tested. It is known that the flow of water through the membrane is mainly associated with a number of phenomena of significance for the technological process of ultrafiltration. In addition, standardization of the membranes is crucial in determining performance and fouling.

Before these measurements were made, the membranes were subjected to the process of conditioning. Investigations were carried out with a cross flow velocity of water equal to 3 m/s, feed pressure of 100 kPa and temperature of 25 °C. The characteristics obtained are shown in Table 5.3**.**

For membranes of different permeability's, a dependence of water transport on transmembrane pressure was obtained. A decrease in water flux was associated with an increase in membrane compactness.

Table 5.3 : Standardisation of membranes prior to laboratory screening

Membrane	**Transmembrane Pressure (kPa)**	**Water flux, *J* (*l/m^2/hr*)**
Cellulose acetate	45	75
Polysulfone	47	80
PVDF	52	96
Polyacrylonitrile	51	92
Polyamide	44	70
Regenerated cellulose acetate	48	85
Polyethersulfone	42	60

Very similar characteristics, of flux and transmembrane pressure, were displayed by the PVDF and PAN membranes.

5.3.1.2 Membrane Screening

Permeate Fluxes

It was imperative to test each membrane with all three of the pretreated material samples in order to achieve a valid assessment. A new membrane was used for each run, except in the case of the hollow fibre membrane, where thorough cleaning of the membrane was required before starting a new run. In total, 21 batches were processed. Since each experiment was conducted for a total period of 1 hour, the total cumulative volume of the permeate was measured. Although the flux was measured periodically, it is expressed here as an average over this period. A summary of the results are given in Table 5.4**.** After the run, the membrane system was thoroughly flushed with water at low pressure, followed by a water standardization to check the water flux.

Table 5.4 : Summary of membrane screening results

Membrane	**Pretreatment 1**			**Pretreatment 2**			**Pretreatment 3**		
	Volume (ml)	Flux, *J* $L/m^2.hr$	Water flux, *J*	Volume (ml)	Flux, *J* $L/m^2.hr$	Water flux, *J*	Volume (ml)	Flux, *J* $L/m^2.hr$	Water flux, *J*
Cellulose acetate	220	9,20	21	190	7,92	22	230	8,98	19
Polysulfone	205	9,54	42	165	8,47	39	215	9,46	45
PVDF	250	10,42	75	225	9,37	73	270	11,25	76
Polyacrylo-nitrile	240	9,99	70	180	7,50	51	263	10,96	70
Polyamide	190	7,92	33	157	6,54	27	192	7,99	29
RCA	225	9,37	27	194	8,08	25	228	9,10	28
Polyether-sulfone	187	7,79	17	132	5,49	10	189	7,87	21

Key : Pretreatment 1 ⇒ pH Treatment of CSL by base addition followed by filtration

Pretreatment 2 ⇒ Removal of suspended solids from CSL by decanter centrifuge

Pretreatment 3 ⇒ Removal of suspended solids from CSL by gyratory screens

The results obtained from these runs provided good comparisons in terms of revealing the true membrane characteristics. The best overall flux performance was achieved with PVDF membranes, although the hollow fibre, polyacrylonitrile membranes, were very close in terms of performance except for the run using pretreated material from the decanter centrifuge, which produced much lower fluxes.

Contrary to expectations, the pH treated CSL, in spite of the incorporation of a filtration process, produced marginally lower fluxes than that of the gyratory screens. This could be explained in terms of the pH of the feed solution. pH treated CSL has a pH of 7,0-7,2 which drastically changes the "charge state" of the protein molecules and their relative surface activity with respect to their pK values. These changes in the charge have the propensity to make the molecules "bigger" and also drastically change the conformational state of the proteins. Typically the solution concentration and the surface concentration of the protein will be different; there is also a likely time-dependent redistribution of protein. Therefore, actual permeation and rejection of the membranes are affected. Also, residual phytin complexes, i.e. not removed by the treatment process and now remain as colloidal solids, will retard the separation process by the formation of gel layers and by interaction with protein molecules as chelating complexes.

The overall results using material from the decanter centrifuge was very poor. Severe fouling of the membranes were seen, especially those of cellulose acetate and polyethersulfone. Although the average fluxes do not seem to be far off in comparison to the other pretreatment runs, higher fluxes were seen at the beginning of the runs and this decreased rapidly during the course of runs. This indicated rapid fouling of the membranes.

Subsequent examination of the membranes showed a "shiny layer" deposited on the surface of the membranes. The layer was polymeric in nature and this suggested that it was residual flocculent carried over during the centrifugation process. This means that even very small quantities of charged polymeric material is of detriment to the membrane process, since accumulation is inevitable. Polymers used as flocculents generally have high molecular weights and readily adsorb onto charged substrates.

Adsorption onto the membrane surface occurs quite readily due to concentration polarization and the boundary layer effects of adsorption. The water flush at the end of the run seemed to have no impact on the removal of the polymer.

Of major significance is the performance of the hollow fibre membrane during the processing of the pretreated material from the decanter centrifuge. A severe pressure drop was experienced during the course of the run. On examination, vast amount of solids had accumulated at the entrance of the fibre lumen, thus restricting the feed flow and creating a higher pressure drop. The solids, which were fibrous in nature, seemed to agglomerate into a mesh-like mass. In retrospect, these solids were not removed by the flocculation and centrifugation process and were therefore present in the centrate and, subsequently as feed material to the membrane system. Hence, the feed material from the decanter centrifuge presented two major problems for the membrane ultrafiltration process. These could be looked upon as major shortcomings, which render the process unsuitable as a pretreatment option.

Contrary to expectations, membrane trials using material from the gyratory screening process were by far the most consistent and produced the highest overall fluxes.

Here again, PVDF and PAN membranes produced the highest fluxes, significantly higher than the other five membranes. These membranes also seemed to be least affected by fouling during the course of the runs. The PAN hollow fibre membrane showed no signs of having any fibrous solids trapped at the feed port either.

A very important observation is that greater values of adsorbed mass were found on the hydrophobic as opposed to hydrophilic surfaces. This is due to the presence of hydrophobic “pockets” in the protein molecule. This interaction gives the molecule an extended structure, covering a relatively large area of the surface. This means that there is relatively a greater number of adsorbed molecules per unit area on a hydrophobic surface. On a hydrophilic surface, the interaction is in general quite different: forces acting between the surface and the molecule may be smaller in magnitude, and since the resulting conformational change will be smaller, a larger repulsive force will be present between the molecules.

Therefore, the packing of adsorbed molecules will not be as close as that on a hydrophobic surface. In general, a smaller number of adsorbed molecules are found on hydrophilic surfaces.

PVDF and PAN membranes are relatively more hydrophilic in nature when compared to the other membranes and therefore show low binding affinity for the proteins in the CSL. This is clearly seen in the results by way of higher fluxes and the higher water flowrates during standardization.

Protein production

Having assessed the impact of the pretreated CSL samples on fluxes and fouling, focus was directed at the protein flow across the membrane. Table 5.5 shows the concentrations of protein, measured by Lowry, in each of the permeates collected.

Table 5.5 : Protein concentrations of permeates produced

Membrane	**Pretreatment 1**	**Pretreatment 2**	**Pretreatment 3**
	Permeate protein concentration (Lowry) (g/l)		
Cellulose acetate	89	78	95
Polysulfone	101	98	112
PVDF	112	110	121
Polyacrylonitrile	104	102	115
Polyamide	102	83	109
RCA	109	87	115
Polyethersulfone	92	81	101

The PVDF and PAN membranes show consistently high permeation of protein from all three pretreatment samples. Feed from the gyratory screens produced the highest protein concentrations. Low protein permeation, as those seen in cellulose acetate and polyethersulfone membranes, could be attributed to the fouling rate of the membranes, as well as the porosity coupled with the differing membrane morphologies, which have a direct influence on the flow of the various protein bands. Also, as discussed earlier, the relative hydrophobicity of the membrane.

5.3.1.3 Effects of Heat Sterilization on Permeate

As is customary in fermentations, sterilization of nutrient components is essential to prevent contamination. The sterilization of protein feedstocks is generally considered to be a difficult practice, mainly due to the lack of control on protein behavior. One component protein solutions are relatively simple to predict with respect to high temperature exposure. CSL on the other hand, is a highly complex stream. Results of the sterilization tests are given in Table 5.6**.**

Table 5.6 : Results of sterilization tests for the various membranes and pretreatment processes

Membrane	Pretreatment 1	Pretreatment 2	Pretreatment 2
	Precipitated solids, % m/m		
Cellulose acetate	0,53	0,65	0,52
Polysulfone	0,56	0,67	0,51
PVDF	0,35	0,54	0,32
Polyacrylonitrile	0,33	0,55	0,32
Polyamide	0,51	0,62	0,47
Regenerated cellulose acetate	0,49	0,59	0,49
Polyethersulfone	0,36	0,56	0,34

Of the three pretreatment processes, ultrafiltered material from the gyratory screens produced the best results, where the lowest precipitation of solids occurred. It is highly likely that the pretreatment processes have very distinct effects on protein-membrane-surface interactions, thus affecting the protein molecular band separations and conformational stability. Therefore, the make-up and composition of the permeates are very different from their respective mother liquors, giving the permeates certain characteristics.

It was also quite apparent that the more hydrophilic membranes, PVDF and PAN, produced the least amount of precipitated solids. This was seen in permeate samples from all three pretreatment processes.

In general, protein precipitation is dependent on the temperature, solution pH, ionic strength, conformational stability of the protein in solution, solids surface charge and hydrophobic-hydrophilic balance. High temperatures tend to affect the conformational stability of proteins which in turn affect the pH and ionic strength of the solution. The protein then precipitates by a number of interactions such as electrostatic, hydrophobic, or van der Waals forces.

During high temperature exposure, foaming due to surface-active components are not uncommon, tending to produce nucleation points for precipitation and colloidal protein agglomeration.

If electrostatics constitute the major interactions, adsorbed mass is generally greater at pH values below the isoelectric point than above it. The relationship between adsorbed mass and changes in pH and ionic strength becomes intimately tied up to the protein conformational stability. Another observation of importance is that the protein precipitation process tends to be an irreversible process.

It is also important to note that protein concentration in a fermentation medium plays an important role in the precipitation process. Other nutrients such as the salts, vitamins, thiamine, biotin, sugars and components of yeast extract have a significant influence on the protein stability. For instance, protein interaction with sugar under high temperature forms Mailard products. These products are sometimes insoluble in the medium and also act as "seeding" points for other colloidal protein, thus facilitating coagulation. The effect of protein concentration on coagulation due to sterilization in a fermentation medium is shown in Figure 5.2**.** Three samples, permeate from ultrafiltration, "raw" CSL and the concentrate of the UF, with each containing fermentation nutrients, were used to show the impact of protein concentration and protein type on coagulation.

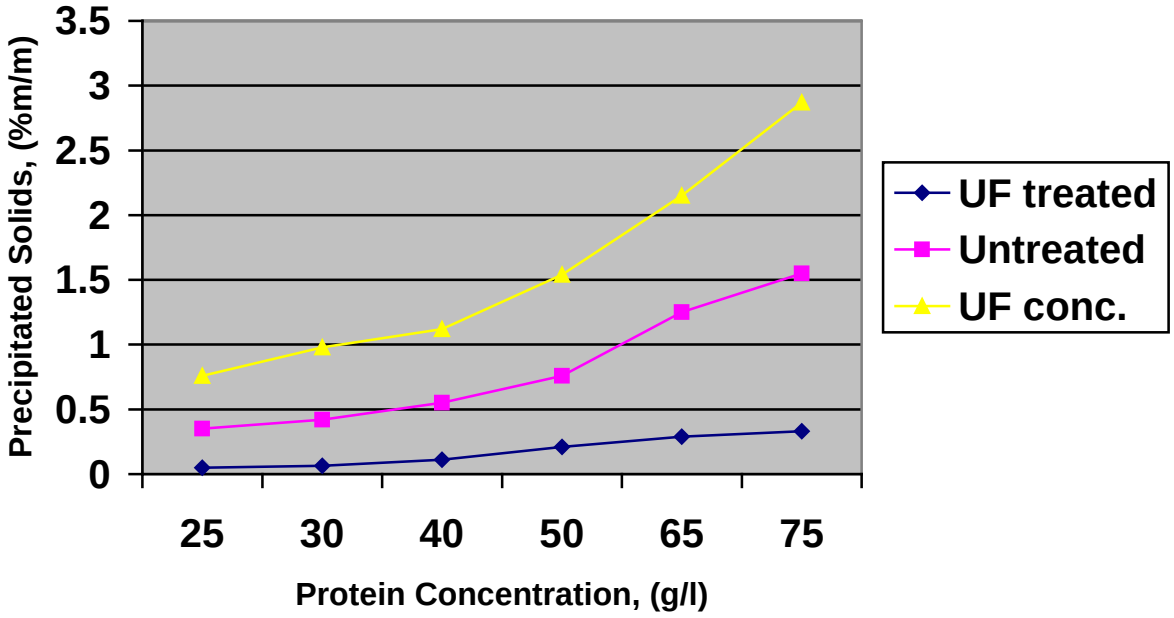


Figure 5.2 : Effect of protein concentration on coagulation due to sterilization.

The ultrafiltered sample produces the least amount of coagulated solids when compared to the raw CSL and the UF concentrate. The UF concentrate was used specifically to show the effects of coagulation, due

to high temperature, on high molecular weight protein. Here the level of coagulation is almost three fold. Untreated CSL, on the otherhand, contains protein components of both the UF filtered material and the UF concentrate. It can also be seen that coagulation is accelerated at a threshold concentration of 50 g/l. The ultrafiltered material shows a gradual increase in coagulation as the concentration of protein increases. These results clearly indicate that high molecular weight proteins are more susceptible to conformational changes as a result of high temperatures.

5.3.1.4 CSL Permeate Fermentability

From the earlier results of flux, protein throughput and solids precipitation during sterilization, it was clear that gyratory screens were the best pretreatment process for this application. Thus, it was decided that only ultrafiltration samples processed through gyratory screens would be used in all subsequent fermentation trials. This helped to substantially reduce the number of fermentations to be conducted.

Prior to the fermentations, free-amino acid profiles of selected amino acids were processed by HPLC. The results obtained are shown in Table 5.7**.** These selected amino acids were deemed to be important in the metabolism of the selected micro-organism.

Table 5.7 : Free amino acid profiles of UF treated CSL

Membrane	**Amino acids, g/l**							
	Thre	**Met**	**Leu**	**Asp**	**Glu**	**Ser**	**Gly**	**Lys**
Cellulose acetate	1,54	2,04	4,53	1,87	6,93	2,20	1,44	3,09
Polysulfone	1,79	2,45	8,12	2,23	8,08	2,58	1,39	3,52
PVDF	3,53	5,71	14,22	2,99	9,79	4,65	2,82	5,64
Polyacrylonitrile	3,45	5,45	10,89	3,45	9,93	4,34	2,87	5,34
Polyamide	2,09	3,79	6,03	3,02	6,41	2,61	1,91	3,49
RCA	1,89	2,23	5,78	2,15	7,63	2,21	1,63	3,22
Polyethersulfone	1,33	1,78	4,33	1,27	5,05	1,83	1,23	3,18

The free-amino acid profile of the permeate from PVDF membrane showed the highest concentrations. These were followed very closely by the polyacrylonitrile membrane. Of these amino acids, threonine and methionine are considered to be the most important for the fermentation, where low concentrations would require supplementation. However, the concentrations of these amino acids were sufficient for the fermentation trials. These results can be considered to be in good agreement when compared with the overall protein throughput of the various membranes.

The summarised results of the fermentation trials are presented in Table 5.8**.** Each trial is given as a number followed by a suffix, a group of letters, which represents the membrane type in the order presented in Table 5.7**.**

Table 5.8 : Results of fermentation trials using CSL permeate

Trial no.	Biomass prod.	Lysine prod.	Residual sugars	Residual protein
	g/l			
1-CA	27,19	13,10	60,45	49,75
2-PS	30,12	21,35	48,50	41,23
3-PVDF	42,22	46,43	10,65	9,08
4-PAN	42,13	45,98	11,22	10,97
5-PA	33,56	37,76	21,34	15,88
6-RCA	29,66	16,12	56,77	47,54
7-PES	21,24	11,98	78,65	55,43
8 (Std)	18,88	6,55	79,34	65,45

The genetically mutated strain of *Corynebacterium flavum* was designed to produce the amino acid lysine as a secondary metabolite, which is passed into the extra-cellular fermentation medium. The biomass produced in these fermentations showed significant differences in concentration for the various membrane permeate samples, with the highest concentration of cells being produced by Trials 3 and 4 (PVDF and PAN membranes respectively). This concentration is close to the maximum tolerable cell

concentration for the hydrodynamics of the laboratory fermentor. Approximately 46 g/l of lysine was produced in both these fermentations. Also, low residual sugar and protein concentrations were recorded for these two fermentations. When considering the amino acid profiles of the permeates of the PVDF and PAN membranes, these results came as no surprise.

However, of major importance is the in-situ sterilization of the protein prior to fermentation. On examination, no visible suspended solids were seen in any of the fermentors, except for the fermentor labelled Standard, where untreated CSL was utilized for the fermentation. Copious precipitation occurred. The first batch of samples taken showed small amounts of sedimented solids in **Trials 1, 5, 6** and **7.** In essence, the sedimented solids were proteins which were consequently unused in the course of the fermentation. The production of lysine seemed to be directly related to the concentration of bacterial cells, where a high concentration of cells produced a corresponding high concentration of lysine. This could also be related to the amount and type of available protein and free amino acids.

These trials further proved that ultrafiltered CSL enhanced the overall quality of the fermentation by increasing the bacterial cell count, increasing the protein utilisation, reducing the amount of coagulated solids after sterilisation and also increasing the product yield.

5.3.2 Viscosity Effects of CSL

Viscosity is measured as a function of shear rate. The rheological measurements were performed at 30 °C, 40 °C and 50 °C. The reported results, as shown in Table 5.9, are mean values of 3 measurements. CSL solutions are highly viscous, pseudoplastic and obey the power-law model, as discussed earlier in the pH treatment of raw CSL.

The results show that at each temperature, the feed viscosity decreases as the shear rate increases. The resultant increase in axial flow velocities shows a steady increase in the permeate flux. In all cases, the results were recorded with the feed pressure maintained at 250 kPa. However, gradual changes in the freed pressure to check the effects on the flux showed that the flux was independant of pressure around 265 kPa. The transmembrane pressure showed definite changes under the steady state conditions for at least 5 minutes until it settled down.

On examining the flux increase on increase of the axial velocity, there was a negligible increase in the flux after an axial velocity of 1 m/s. This indicated that permeate flux was independant of axial velocity at this stage onwards. This was also calculated as being the change from laminar to turbulent flow, but

still within the critical zone i.e. Re = 2200 which is the critical Reynolds number. However, this does not account for the presence of the mesh spacer in the membrane cell, which acts as a turbulence promoter.

At the lower velocities the flow was most likely to be laminar in nature. The lower velocity coupled with lower temperature showed phenomenal increases in viscosity, in the extreme range, a four-fold increase in viscosity is seen. Under these conditions, the rheological behavior of the layer adjacent to the membrane surface is likely to be gel-like in nature, and would contribute significantly to low fluxes. The experimental observation is that the higher axial velocity would certainly reduce the bulk concentration at the surface, thereby influencing the permeate flow.

Table 5.9 : CSL rheological properties and its effects on permeate flow

Temperature **°C**	**Axial velocity** **m/s**	**Viscosity** **cP**	**Shear rate** **1/sec**	**Flux, *J*** ***l/m²/hr***	**Pressure, ΔP** **kPa**
30	0,2	26,75	14,72	6,75	75
	0,5	23,97	24,55	6,98	80
	1,0	21,62	36,76	7,12	83
	2,0	18,35	61,53	7,35	100
40	0,2	16,23	14,75	7,15	78
	0,5	14,56	24,45	7,49	85
	1,0	13,44	36,73	7,75	110
	2,0	12,97	61,23	7,97	135
50	0,2	12,20	14,69	7,53	85
	0,5	10,86	24,52	7,86	97
	1,0	8,63	36,71	8,42	120
	2,0	6,03	61,22	8,63	140

All these experiments were conducted on a total recycle mode, where both the permeate and concentrate streams are returned to the feed tank. It was important to note the increase in viscosity of the feed when permeate was removed. In one experiment, the ultrafiltration was conducted at 50 °C and allowed to continue until there was minimal permeate flow. Figure 5.3 shows the results from the experiment.

As the retentate becomes more concentrated, a phenomenal increases in suspended solids are seen. This is followed by drastic increases in the viscosity.

This poses a point of major concern in the design of the membrane system, since the hydrodynamics of such systems have definite limitations in terms of viscosity. The processing of fluids with viscosities between 15-20 cP is certainly impractical. Therefore, this places limitations in terms of the processing of CSL. According to the results, suspended solids concentration cannot be allowed to increase beyond 6-7 % m/m.

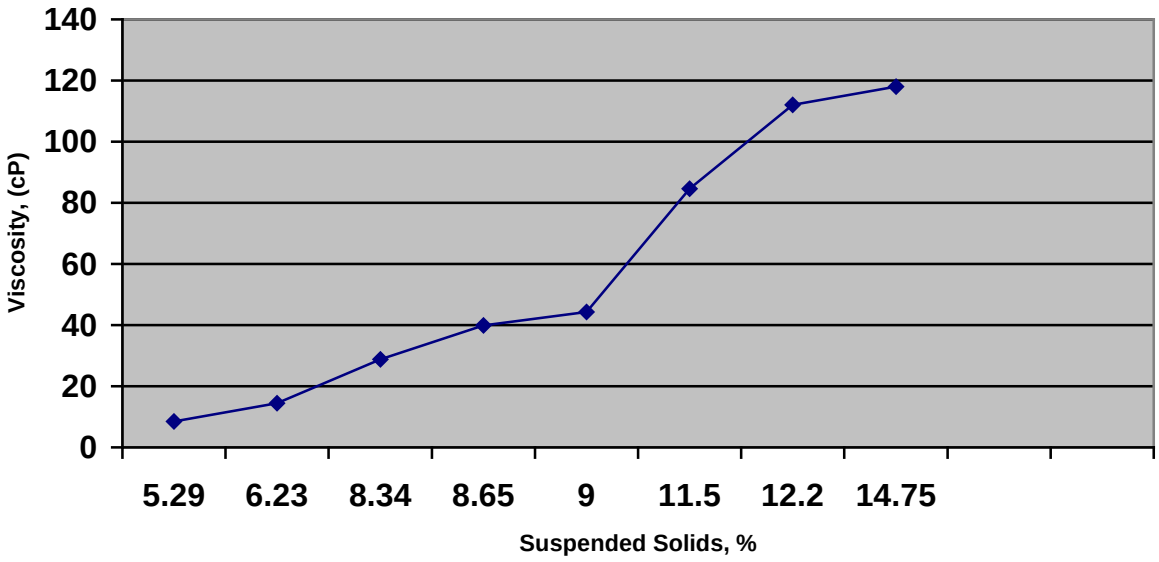


Figure 5.3 : Effect of CSL suspended solids on viscosity

CHAPTER 6

MEMBRANE SCALE-UP

6.1 Introduction

In the previous section, the optimal membrane type for the application was identified, and the performance of the selected membrane type was quantified. Experimentation was based on laboratory rigs using flat-sheet membranes.

In this section, the flat-sheet membranes are scaled up to a pilot plant membrane systems.

6.2 Experimental Protocol

6.2.1 Investigations into module configurations

With the feasibility of the membrane filtration established for this feedstock, subsequent development efforts were directed towards the design of a scaled-up membrane package or module. Under recommendations from membrane vendors, it was decided that three generic configurations, commonly used in industry, would be tested. These are tubular membranes, hollow fibres and spiral wound modules. These tests would provide a qualitative comparison of the capabilities of these configurations and the advantages and disadvantages of the fluid management within these systems.

To test these configurations, a flexible and robust system was designed to meet the hydraulic requirements of the three configurations. A variable speed, rotary lobe positive displacement pump system and a centrifugal transfer pump, were employed to provide the required cross flow velocity and pressure. Hydraulic balance was achieved through manipulating the variable speed drive unit on the circulation pump and by employing a needle valve on the retentate loop. Figure 6.1 illustrates the configuration of the system which included a 60 litre jacketed feed tank, equipped with agitation. Stainless steel pipe sections were made up into spool pieces to connect the three types of membrane modules to the mini-plant system. In this way each configuration could be tested on the same rig. A heat exchanger was connected in-line with the retentate loop.

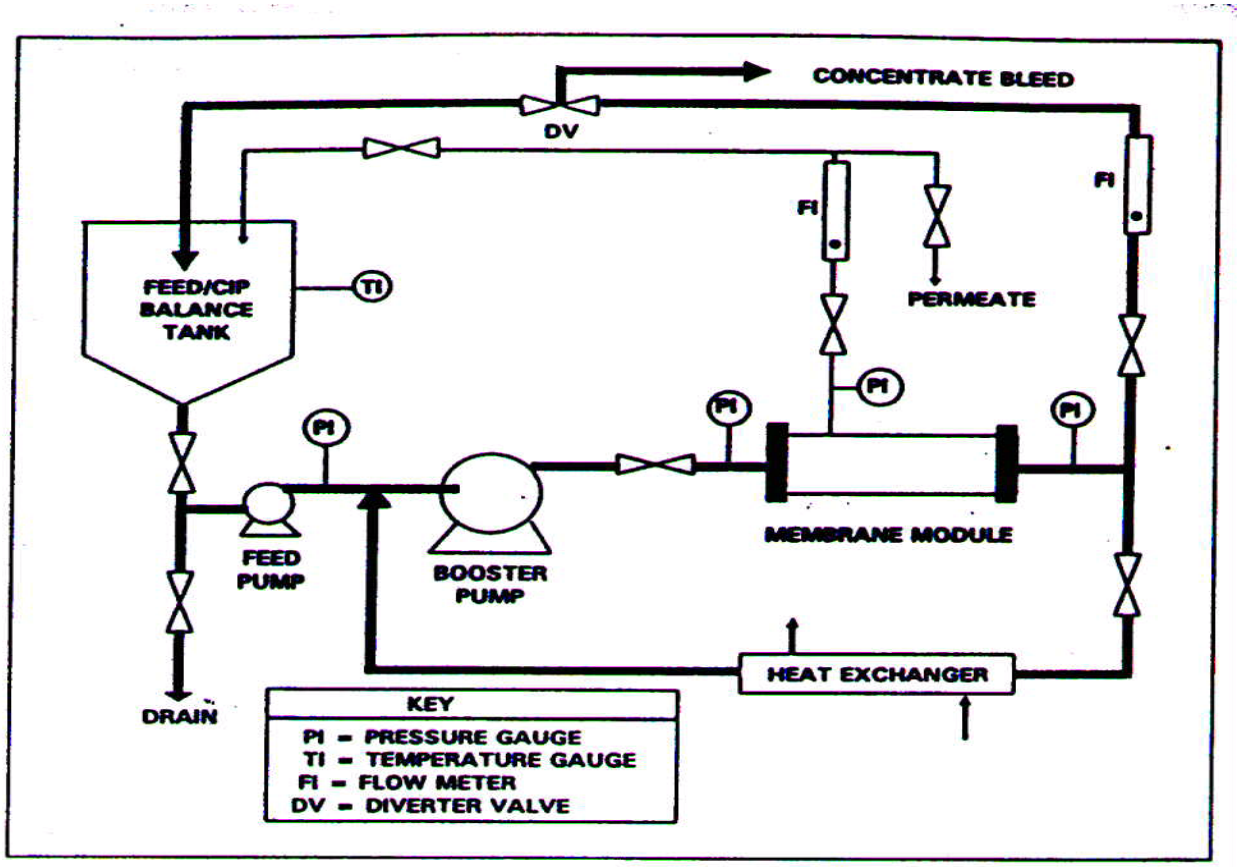


Figure 6.1 : Schematic of bench-scale crossflow filtration system.

6.2.1.1 Tubular Membrane Module

A tubular membrane module was obtained from Envig S.A. This was a 1 metre long polysulfone membrane with a MWCO of 30 000 and pore diameter of 6mm. The membrane was fitted into a porous stainless steel support tube. This was inturn fitted into a reinforced polycarbonate collection tube. The tubular module was connected by means of the specially designed adapter spool pieces to the bench-scale system.

The system was equipped with a variable speed positive diplacement pump to achieve the high cross flow velocity and an additional sponge ball dispenser/collector. The sponge ball system was also connected by means of specially designed adapter spool pieces. The sponge balls had a diameter of approximately 6.2mm and were used periodically to pass through the system. The sponge ball system helped to clean the membranes by removing gel layers and other precipitates from the surface. The feed reservoir and peripheral instrumentation was the same as for the bench-scale system used earlier.

The tests were conducted with 50 litres of “screened” CSL at 50 °C. The feed flowrate was maintained at 4-5 m/s at a feed pressure of 2.5 bar. A maximum pressure drop of 1.5 bar was allowed. The experiments

were conducted in total recycle, where the concentrate was returned to the suction side of the circulation pump. The experiment was conducted for a period of 3 hours. Samples of the permeate and concentrate were taken at 30 minute intervals. At the end of the run the system was flushed with water until no product was visible. At this stage a standard water flux was taken to check the degree of fouling. The standard cleaning method recommended by the membrane vendor was then applied to attempt to restore the clean water flux.

The regeneration of the tubular membrane employed the following protocol:

(i) flush of system with de-ionised water to remove residual broth,

(ii) 30 min recycle of 2 g/l Tergazyme (Alconox Inc., New York, NY) detergent solution at ambient temperature to remove proteinaceous foulants,

(iii) 30 min recycle of 0.1 mol/l sodium hydroxide solution at 50 °C to remove lipids and polysaccharides,

(iv) flush of system to remove Tergazyme and sodium hydroxide solution.

The effectiveness of the regeneration procedure was tested by measuring water fluxes through the membrane system, over a range of transmembrane pressures and by comparing these values with those for a new membrane.

6.2.1.2 Hollow Fibre Module

A hollow fibre module ACP 0030 was obtained from the Asahi Glass Co., Japan, for the testwork. The module was easily fitted to the bench-scale system by using the specially designed adapter spool pieces.

The membrane unit was cast in a polycarbonate pressure vessel, sealed at both ends by means of a 'U' cup seal with dairy type clamps. The membrane fibre bundle was made of polyacrylonitrile (PAN) with a membrane area of 1.3 m^2 and MWCO of 30 000. The recommended feed flowrate was 8 litres/min with a feed pressure of 2.5 bar. The pressure drop measured on the retentate side did not exceed 0.5 bar. The experiments were conducted in a total recycle mode with "screened" CSL at 50 °C. The separation was carried out for a period of 3 hours, with samples of the permeate and retentate removed at 30 minute intervals.

At the end of the run the module was flushed with water until all traces of product were removed. A test water flux was then recorded. The standard cleaning procedure as outlined above was then applied.

6.2.1.3 Spiral Wound Membrane Module

The spiral wound element type is said to be the workhorse in the membrane world. Although made almost exclusively for water desalination, its compact design and low price made it very attractive for testwork on CSL. For this particular application, the elements had to be redesigned to meet the stringent requirements of the process. Spiral wound elements are produced by a number of companies but only a few can really develop and supply special elements for stringent applications.

Two companies, Osmonics Inc. and Desalination Systems, both from the USA, supplied specially designed modules for the duty. Each of these companies manufactured the membrane elements with specific polymer types (patented and proprietory). Table 6.1 outlines the types of spiral wound membrane elements and their specific design variables.

Table 6.1 : Types and Variables of Spiral Wound Elements

	MANUFACTURER	
	Osmonics Inc.	**Desalination Systems**
Type	PVDF	PAN
Dimension	2.0 inches D, 40 inches L	2.1 inches D, 40 inches L
Outer wrap	loose fit-type	loose fit-type
Product spacer	80 mil (2 mm)	80 mil (2 mm)
Spacer type	diamond mesh	square type mesh
Membrane support	Polyester	polypropylene
Brine seal	no seal	lip seal
Anti-telescopic device	star type	hole plate type
Glue	high temperature bonding	high temperature bonding
Membrane area	2.2 m^2	2.4 m^2
MWCO	30 000	30 000

Each of these membranes were housed in their own stainless steel pressure vessels. The stainless steel housing was coupled onto the bench-scale rig by means of specially designed stainless steel spool pieces. Screened CSL at 50 °C was used for the experimentation.

A recommended crossflow of 13 litres/min was used. The transmembrane pressure of 100 kPa was set at the start and was allowed to reach a maximum of 140 kPa.

Flow Channel Mesh Spacer

The effect of the mesh spacer configuration has been deemed to be very important in the overall design of the spiral wound module. Prior to ordering of the bench-scale spiral modules, it was necessary to test the various spacer options available. Each geometric configuration had its own merits and de-merits and selection was strictly dependant on the application. The general characteristics of mesh spacers were made up of : angle, mesh size, thickness, filament size and voidage.

Ultrafiltration experiments were performed in a flat channel test cell with dimensions of 150 mm wide and 280 mm long. A schematic representation of the cell and system layout is shown in Figure 6.2 It had a stainless steel base plate housing the membrane support, with an outlet port for the permeate. The body of the cell was machined from stainless steel with an inlay, tapered inlet and outlet regions, to define the channel width. The base plate and body sections sandwiched the membrane support. Silicon rubber tubes were attached to the outlet permeate port, the feed port and the retentate port.

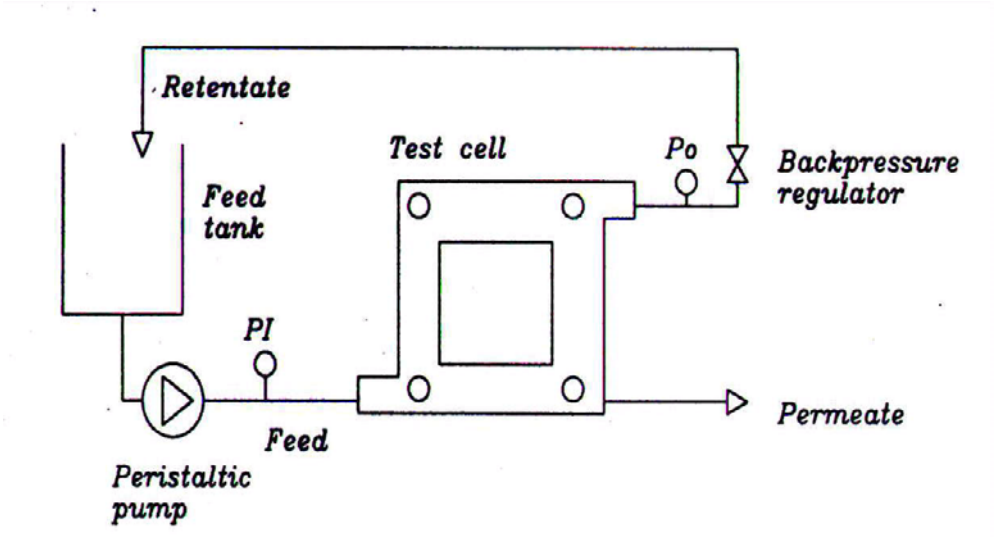


Figure 6.2 : Schematic of flat sheet cell system used for the testing of mesh spacers.

Within the base plate was a porous stainless steel plate supporting the membrane against the pressure differential. Its area was equal to the membrane active area. Between the edge of the base plate and the support plate was an o-ring to seal the cell and avoid leakage. Within the stainless steel body, the spacer can be fitted in the grooved channel. To avoid bypassing (channelling) at the edges, the spacers were cut acurately to fit in the channel.

The membrane used was a PVDF membrane with a molecular weight cutoff of 30 000, supplied by Osmonics Inc., and several commercially available netlike feed spacers were used. The photograph of the spacers used are depicted in Figure 6.3 , and Table 6.2 summarises the configuration of the spacers. The spacers are made of polypropylene and polyethylene, and some samples were supplied by Desalination Sytems, Osmonics Inc., Nalle Plastics Inc. and Conwed Plastics.

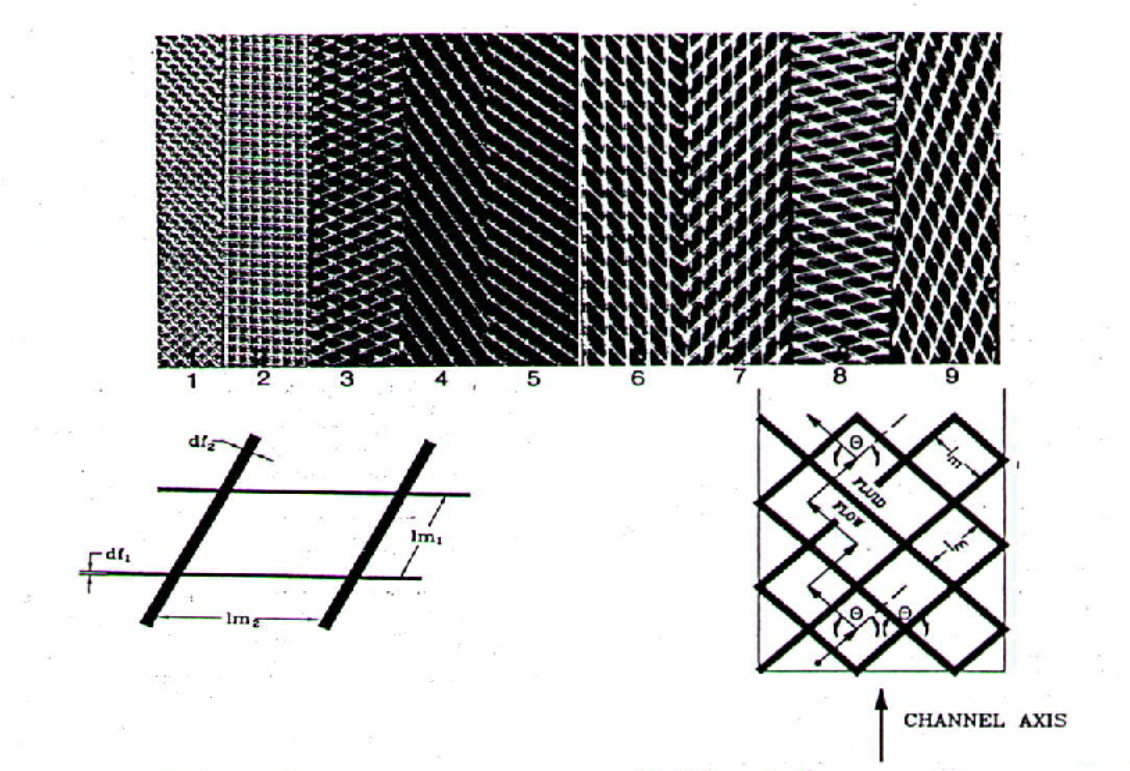


Figure 6.3 : (a, top) Feed spacers (from left to right: CONWED-1, CONWED-2, NALTEX-124, NALTEX-51-1, NALTEX-51-2, DESAL-1, DESAL-2, OSMO-1, OSMO-2).
(b, bottom left) Definition of dimensions.
(c, bottom right) Definition of hydrodynamic angle θ.

After the spacer was inserted in the channel and after the membrane was placed on the porous plate, the stainless steel plates were held together by tightening screws with a torque wrench at 30 Nm. In the case of spacers thinner than the channel, polycarbonate plates were placed between the channel roof and the spacer to fill the channel. The gap between the polycarbonate plates and the channel side were filled with a silicon rubber gasket to eliminate channeling of fluid.

Before each run the membrane was cleaned to remove glycerol from the pores by simply soaking it in water/ethanol mixture for about 20 minutes. Experimental solutions were prepared by diluting CSL to a 43% m/m dissolved solids concentration and heated to a temperature of 50 °C. In a typical run about 10 litres of CSL was circulated at the required flowrate and pressure for 5-10 minutes to allow for stabilisation. The series of experiments included the measurement of permeate flux and the pressure drop across the spacer-filled channel.

This was performed in duplicate for a particular spacer at various flowrates and desired transmembrane pressure. Flow rates ranged from 0.4 to 4.0 L/min and the feed pressure was 300 kPa. A measuring cylinder and stopwatch was used to measure permeate flowrate. A new membrane was used for each spacer tested. Protein concentrations were measured by the Lowry protein assay.

Table 6.2 : Summary of spacer configurations.

Configuration	Angle (deg)	Symmetry	Figure 3a
CONWED-1	90	rhomboid mesh, 45° to channel axis	1
CONWED-2	0	filaments perpendicular to each other	2
NALTEX-124	124	filaments are 62° to channel axis	3
NALTEX-51-1	51	parallelogram mesh, thick filaments 30° to channel	4
NALTEX-51-2	0	thick filaments are 51° to channel axis; thin	5
DESAL-1	0	parallelogram mesh	6
DESAL-2	0	parallelogram mesh; thick filaments 40° to channel	7
OSMO-1	135	parallelogram mesh; thick filaments 60° to channel	8
OSMO-2	45	parallelogram mesh; thick filaments 20° to channel	9

Membrane Cleaning

The progressive development work on the spiral wound modules soon showed shortcomings in the standard cleaning procedures and difficulties in restoring clean water fluxes as a result of severe fouling. There was therefore a dire requirement to develop a cleaning regimen specifically for this process. It was decided that the development of the cleaning regimen would follow two phases. The first phase was to test the fouling and cleaning on the laboratory flat sheet cell system, followed by testing on the bench-scale spiral module.

The flat sheet cell system was set up with a PVDF membrane and a Desal-2 mesh spacer. The system was standardised with RO water at 25 °C. Screened CSL was ultrafiltered on a total recycle mode, with feed flowrate at 3 litres/min and feed pressure of 300 kPa, until the permeate flow was reduced to a minimum flowrate. It was important to operate the system in this manner to determine the limiting fouling components as well determine a "worst case" fouling situation.

On completion of the run, the system was flushed with RO water at a reduced feed pressure of 100 kPa and increased flowrate of 4 litres/min. The product was flushed to drain until the concentrate and permeate appeared reasonably clean. The CIP procedure was very much on a "trial and error" setup, based on visual (microscopic) inspection of the membrane surface and the analysis of the composition of CSL.

The solubilities of components were looked at, especially higher molecular weight proteins, starch, lipid compounds, phytin complexes, fibrous compounds and precipitated salts. The modified procedure encompassed the following:

- ***First alkaline rinse***. Recycled RO water in the system, where the permeate and concentrate were returned to the feed/CIP tank. The water was heated to 50 °C. An alkaline detergent, Ultrasil 93 from Henkel Products, was added to the water to a concentration of approximately 0.5% m/v at a pH of 10. The detergent was recycled for 60 minutes. The pH was checked at regular intervals.
- The system was then flushed out with RO water until pH of permeate and concentrate was the same as pure RO water.
- ***Acid rinse***. An acid detergent, Ulrasil 75 from Henkel Products, was added to the tank containing water at 50 °C to a pH of 2.5 and approximate concentration of 0.5% m/v. The acid detergent was recycled for 60 minutes. The pH was checked at regular intervals.
- The system was flushed out with RO water until pH was equivalent to that of pure RO water.
- ***Second enzymatic/alkaline rinse.*** Ultrasil 56 from Henkel Products was circulated at a temperature of 50 °C, pH of 10 and approximate concentration of 1% m/v. Recirculation for 30 minutes.
- Flush out with RO water.
- ***Disinfection***. Ultrasil Active from Henkel Products or Divosan Forte from Diversey, was circulated at a concentration of 0.1% m/v, at room temperature, for a period of 30 minutes. The feed pressure was increased to 300 kPa, to increase the permeate flowrate for disinfection of the permeate side of the system.

- Flush out with RO water.
- Measured water flux at specified temperature and pressure and compared with clean water flux.

The procedure was subsequently evaluated on the bench-scale system on the spiral wound module. The procedure was modified as follows:

- The acid rinse step was reduced to 20 minutes.
- An additional step was added before disinfection and after the second alkaline rinse. An enzyme, BAN 480L, a fungal amylase, was circulated at a concentration of 0.01% m/v for 20 minutes and then flushed out with RO water.
- For severe fouling, a neutral enzyme detergent, Ultrasil 53 from Henkel Products, was used at a solution concentration of 1% m/v. The detergent was first circulated for 1 hour and left to "soak" for 3 hours. The system was then flushed out with RO water and the water flux checked against the standard clean water flux.

6.2.2 Pilot Plant System

Having established the feasibility of using membrane technology and the testing of the various configurations thereof, subsequent development focused on a pilot-scale crossflow filtration system. Based on the research and development of laboratory and bench-scale experimentation, a dedicated spiral wound, skid mounted system was designed, constructed and commissioned for the operation, with the assistance of the chosen vendor Desalination Systems.

6.2.2.1 Equipment

Figure 6.4 illustrates the configuration of the system. Desalination Systems also supplied the 4 inch PVDF membrane elements equipped with 80 mil (2mm) Desal-2 mesh spacers and hollow plate ATD's.

The system was designed to operate in either batch or continuous, consisting of 3 membrane pressure vessels, constructed of stainless steel, connected in series. The pressure vessels were designed to accomodate 4 inch membrane elements with the flexibility of using 1 to 2 or 3 membranes in series. This configuration was designed as such to determine maximum/minimum pressure drop conditions as a result of the concentration ratio.

A 800 litre jacketed vessel was used for the feed, connected to a centrifugal transfer pump and two in-line cartridge safety filters. These safety filters, rated at 100 microns, were connected in parallel and equipped with isolation valves so that there was flexibility to use either one or both during operation. A multistage centrifugal pump was used for the circulation of the feed.

Flowrates for the feed, concentrate, retentate loop (recirculation) and permeate were measured by Krohne magnetic induction flowmetres, with accuracies of ± 0.1% of calibrated scale. Pressure transducers, ± 0.2% accuracy, were used to measure the feed pressure and the concentrate pressure exiting each vessel. In this way the pressure drop across each vessel was obtained. Manual needle valves were employed for the retentate recirculation and concentrate loops. The permeate was collected via a permeate manifold into a 500 litre stainless steel collection tank, graduated for volume.

In addition, the system was equipped with two supplementary feed systems, for the injection of CIP chemicals directly into the feed transfer line.

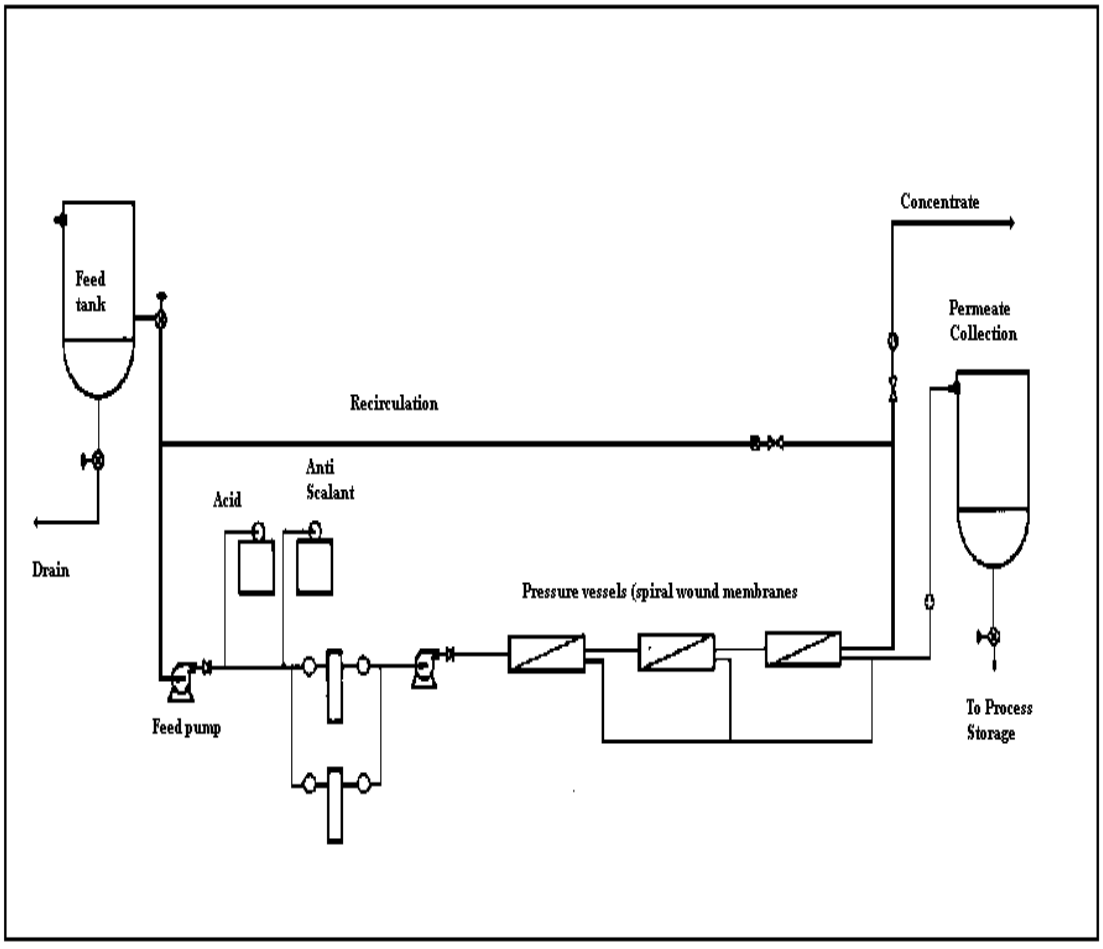


Figure 6.4 : Schematic diagram of skid-mounted pilot-scale system

6.2.2.2 Experimental Procedure

As is customary for membrane separations in biotechnology, the plant was operated in a "semi-continuous mode", i.e., 20 hours of processing and 4 hours for clean-in-place (CIP). The skid mounted system and pretreatment system was positioned at the main CSL supply tank at African Products. Fresh feed at 50 °C was supplied to the pre-treatment plant as and when required, processed and fed into the UF feed tank. On start-up of the UF plant, the concentrate and permeate streams were allowed to first flow back into the main supply tank for a period of 5 minutes. This was to allow the water in the system to be displaced and thereby prevent excessive dilution of the feed and product streams. The plant was then operated on a "semi-continuous" mode.

Readings of the flows, pressures and temperature were performed on an hourly basis, while samples of the feed, concentrate and permeate streams were taken every 4 hours.

Initial testing focussed on finding the maximum number of elements that could be utilised in series, while studying the effects of pressure, pressure drop, temperature, concentration ratio and fouling.

6.2.2.3 Optimising Flux, Pressure and Temperature

Flux as Function of Pressure

A well operating membrane filtration system must have a reasonable and stable fux and the energy consumption should be as low as possible. In order to achieve these goals, the process must be optimised with respect to product flux, pressure and temperature.

Flux as a function of pressure was checked by manipulating the flow of the concentrate and retentate streams. The maximum design pressure of the system was 1000 kPa. The recommended maximum operating feed pressure was 800 kPa. The flux was observed for at least one hour at each pressure set point. The most advantageous pressure set point was then chosen. The pressure drop on start up was set at 100 kPa and was allowed to progress to a maximum of 140 kPa per membrane element.

Flux as Function of Temperature

If it is at all possible to change the temperature of the feed, it is mostly recommended to increase the temperature as much as possible. A trial was conducted to check the influence of temperature on permeate flow. The feed tank heating system was used to gradually heat up the feed to the required temperature and the corresponding flux was recorded.

6.2.2.4 Optimisation of Plant Operation

First the operating temperature was chosen based on the sustained membrane flux and the overall long term effects on membrane life. The optimum feed pressure was then found in combination with feed flowrate and pressure drop across each membrane element. The maximum allowed pressure drop was 140 kPa and the minimum allowed exit pressure from the last element was 100 kPa. The effect of concentration on the hydraulic parameters was then tested by running the system on batch mode, where varying degrees of the concentrate is returned to the retentate circulation loop. The change in the concentration ratio and the subsequent effects on feed flowrate, pressure and permeate flow were measured. In this way the maximum number of elements in series were determined.

6.3 Results and Discussion

6.3.1 Selection of membrane material

The results of the initial flat sheet membrane screening experiments were used as the basis for selecting the material type. Initial best fluxes ranged from 11,25 $l/m^2/hr$ for the 30K MWCO polyvinylidene fluoride membrane, 10,96 $l/m^2/hr$ for the 25-35K polyacrylonitrile membrane to 9,46 $l/m^2/hr$ for the polysulfone membrane. These were taken as average flux rates. The fluxes declined to approximately one-half of their initial values after only 1,5-fold concentration.

Although the best results were obtained by the more hydrophilic membranes such as PVDF and PAN, other hydrophilic membranes such as cellulose actetate and regenerated cellulose actetate produced very poor fluxes. This is because these membranes are sometimes more hydrophobic than expected. Also, membrane pore structure plays a significant role in determining actual permeation rates. The permeation rates of these membranes were found to be very dependent on the protein conformation and the protein-membrane-surface interaction.

All future testwork focussed on polyvinylidene and polyacrylonitrile membranes, since these were most suited for the application. The exception, however, was for the tubular membrane testwork, where both these membranes were unavailable in this format for the testwork. The closest obtainable membrane, in terms of performance, was the polysulfone membrane obtained from Envig S.A.

6.3.2 Investigations into module configurations

6.3.2.1 Tubular Membrane Module

The bench-scale system used in the studies proved to be very flexible and performed well within the design expectations. A standard water flux of 95 l/m^2/hr was recorded for the membrane module. Coupling of the tubular membrane module using the adapter spool pieces was simple, and the module could be assembled and stripped down without any complications. However, some difficulty was experienced when trying to commission the sponge ball dispenser/collector. This was due to the "sticky" nature of CSL which tended to trap the sponge balls in the dispensing pipeline. The problem was partially overcome by increasing the cross-flow velocity from 4 m/s to 5 m/s. The results shown are an average of three runs performed, where very little difference was seen in performance in each of the runs.

The results are shown in Figure 6.5**,** where the flux is shown as a function of time. A relatively high initial flux was recorded at 15 l/m^2/hr. However, by the time a 1,2-fold concentration was reached, the initial flux value had halved and continued to decline steadily to the end of the run. The average flux rate was calculated as 6,23 L/m^2/hr.

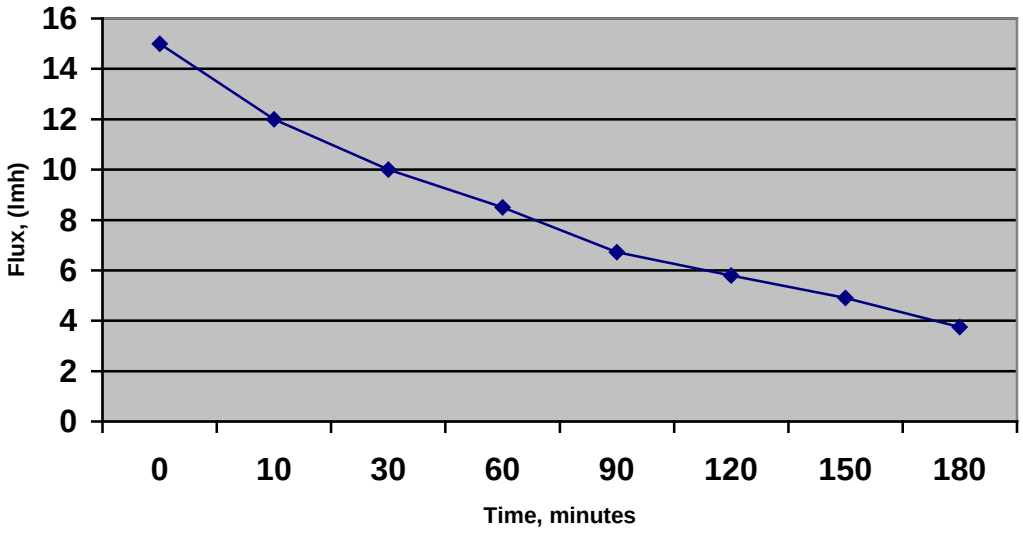


Figure 6.5 : Filtration performance of 30K tubular membrane

The flux drop after 3 hours of processing time was quite severe, since only 50% of the volume was recovered. At the high cross-flow velocity, the initial pressure drop was 140 kPa which steadily progressed to 180 kPa. Controlling to the 150 kPa limit was difficult, since cross-flow velocity had to be sacrificed. The permeate was a clear liquid, visually of good quality. Subsequent protein analysis, by the

Lowry method, showed a pooled permeate concentration of 90 g/l. This protein concentration was relatively low when compared to protein flows in the flat sheet membrane tests.

The overall performance of the system for the CSL separation was somewhat disappointing. Low overall fluxes were not assisted by the sponge ball mechanism, which seemed to take great strain in contending with the rheology of the CSL. After each run the sponge balls were examined. On each occasion the sponge ball was covered by a "gel-like" layer, which was cleaned off with great difficulty. In this application, this particular operation did not seem feasible and certainly complicated the process.

The water standardisation after the run was recorded as 12 $l/m^2/hr$. This showed that severe fouling had taken place. On regeneration, using the recommended CIP protocol, a water flux of 50 $l/m^2/hr$ was obtained. This was still a long way off the original clean flux. The system was subsequently cleaned in 3 more CIP cycles, with a final clean flux of 68 $l/m^2/hr$. This was only 72% of the original water flux.

Earlier experimentation had showed that the cross flow velocity was only effective up to a certain point and was then independant of both cross flow velocity and applied pressure. The high transmembrane pressure certainly contributed to fouling of the membrane and, in this case, fouling was irreversible.

Also, the diminished fluxes measured here versus the higher values obtained during the prelimnary studies using flat sheet membranes, illustrate an important principle of crossflow filtration scale-up. Defining membrane loading, i.e. the feed volume to membrane area ratio is critical. In the laboratory experiments, the feed volume was 10 litres to a membrane area of 0,024 m^2. In this experiment, 50 litres of feed was used for a membrane area of 0.1 m^2. By ratio, this is approximately 20% more feed than that used in the bench-scale tubular module experiment.

The higher feed ratio creates a higher exposure to foulants and gel polarisation. By mere recirculation at the higher velocity, the exposure to the feed material is many times higher, hence the greater propensity to foul.

6.3.2.2 Hollow Fibre Module

Further development efforts were conducted employing a hollow fibre membrane module. The feasibility of scaling up this system was examined by separating 50 litres of CSL using a 30K polyacrylonitrile membrane. A crossflow rate of 8 litres/min and an initial transmembrane pressure of 40 kPa were chosen, as recommended by the manufacturer. The results of this test, which was performed at 50 °C, is shown in Figure 6.6, in which flux is plotted against time.

An average flux of 4,5 l/m^2/hr was obtained, which is slightly less than the earlier results using the laboratory module. This is also in good agreement when compared to the results obtained with the tubular membranes. A 1,3-fold concentration of CSL was obtained, after which transmembrane pressure and inlet pressure began to rise rapidly. This is not surprising considering that the CSL contained approximately 1,5% suspended solids and the concentration resulted in the solids approaching 2%, which is approaching the upper limit of suspended solids concentration that could be handled by a hollow fibre membrane.

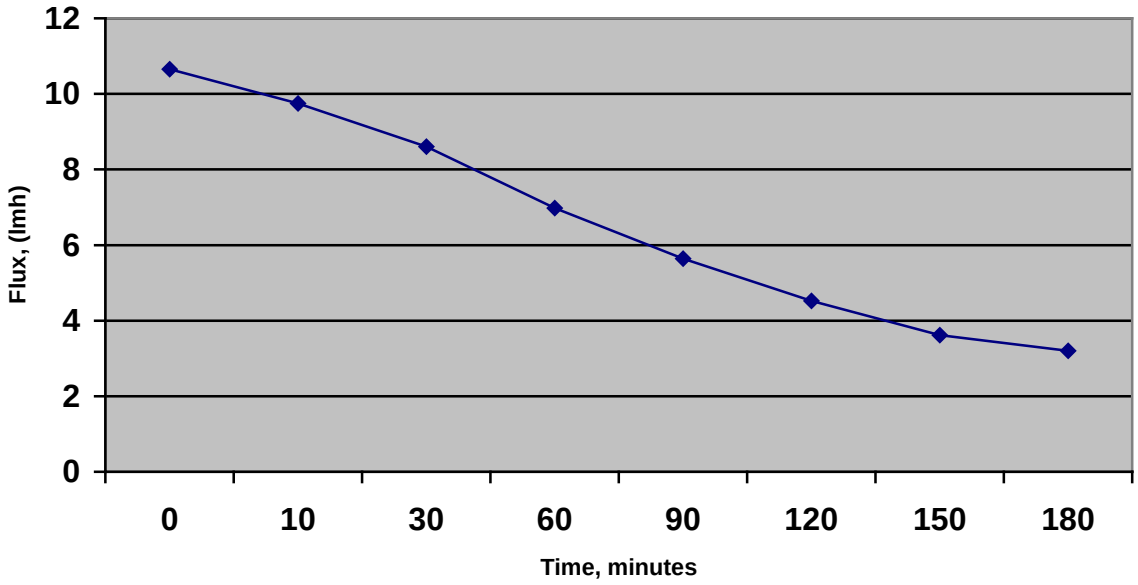


Figure 6.6 : Plot of flux versus time for polyacrylonitrile hollow fibre membrane.

In order to better understand the reason for this limit, one has to consider the lumen of the fibres at the feed port. Conveyance of the solids through the lumen is extremely difficult, even though the CSL solids are deformable. These solids tend to have a higher close-packed volume fraction, and so the mobility is restricted especially at the entrance of the fibre tubes. The restricted flow of these solids leads to an accumulation of solids at the feed port. Hence, there is a restriction in the flow, which causes the increase in feed pressure and the increased pressure drop.

Towards the end of the run, the fibre bundle seemed to bulge, as if stretching under the strain of the high feed pressure and transmembrane pressure. These membranes are generally constructed for very “clean solutions”, while any form of suspended solids will lead to an immediate deterioration of separation performance. While these limitations were not witnessed during the laboratory trials on the smaller module, it is important to note the scale-up flowrates and throughputs, which are notably different.

Analysis of the permeate stream for protein, showed a concentration of 110 g/l by Lowry assay. This was a relatively good concentration of protein in the permeate, especially when comparing this to the earlier tubular membrane trial.

Regeneration capacity of the hollow fibre element was examined by comparing the water flux of the virgin membrane to that of the regenerated membrane. The results indicate that greater than 85% of the original water flux was regained after the membrane was cleaned with the standard protocol. A repeat of the cleaning procedure restored the clean water flux to 100%.

6.3.2.3 Spiral Wound Membrane Module

Flow Channel Mesh Spacer

Effect of Spacer Configuration on Flux

The effects of flow channel mesh spacers can be categorised according to their hydrodynamic angle and detailed symmetry. These variables, however, are purely dependent on the rheological phenomena of the fluid being separated by the membrane system. The hydrodynamic angle has a direct bearing on the developing velocity and concentration profiles for laminar flow, thus causing the mass transfer to be maximised. These categories enable the fluid to flow either in a zigzag format, i.e. continuous changes in flow direction or by straight flow past transverse filaments.

The influence of the mesh spacers on flux was tested. Figure 6.7 shows the plot of flux on three selected flowrates for the various mesh spacers tested.

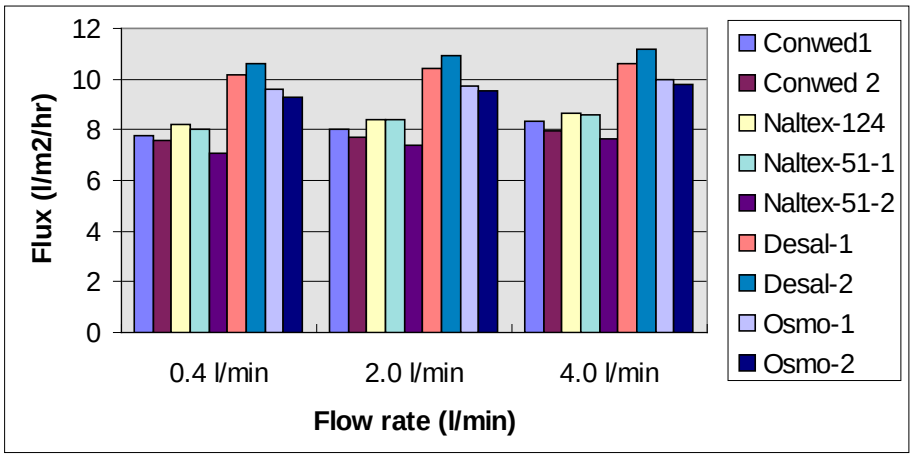


Figure 6.7 : Effect of feed spacers on flux at various flowrates.

Under the standardardised experimental conditions, the best fluxes were obtained with the Desal-2 mesh spacer, although the Desal-1 spacer was not far off. These mesh spacers are characterised by a parallelogram mesh, where the Desal-2 has in addition, thick filaments mounted 40° to the channel axis. In this arrangement, the thick filaments act as baffles in a tubular flow channel.

Being mounted at an angle to the channel axis enables the fluid to be "gently" deflected, thus inducing localised turbulence, even at low cross flow velocity. It is clearly seen that this spacer is consistent in providing higher fluxes at all the cross flow rates tested.

However, results from the literature show higher rates in other applications of non-Newtonian fluids for mesh spacers with the zigzag arrangement. This discrepancy can be explained in terms of the local mass transfer. The higher local velocities generate wakes big enough to affect mass transfer on the opposite wall, beneath the filaments. In this way the efficiency of the attached filaments in breaking up the boundary layer is increased due to the increased local velocity. For the zigzag arrangement, the local velocity is lower due to the frequent change in the direction of flow.and the overhanging filaments which retard velocity, and are therefore less effective in breaking up the boundary layer.

Filament Size and Angle of Transverse Filaments to Flow Direction

The results given in Figure 6.7 also shows the effect of filament size and angle of transverse filaments to channel axis. The UF spacers are asymmetric consisting of parallelogram meshes and thicker filaments overlaying thinner ones. In configuration Osmo-1 the thicker filaments are 60° to channel axis and the mesh is oriented with the longer diagonal perpendicular to flow. Fluid moves in a zigzag changing direction by 135°. In configuration Desal-2, the thicker filaments are parallel to the channel axis, and thinner filaments are transverse at 40°. Most of the fluid flows parallel to the *x*-axis; a small proportion of fluid might be diverted especially at low velocities.

At high flowrates, the difference in the flux becomes smaller because a limit is reached to the rate of increase in mass transfer and the greater part of the kinetic losses does not contribute to the enhancement. However, the difference in kinetic losses is enormous with pressure drops showing distinct differences.

Configuration Desal-2, with the thinner filaments transverse to flow at 40° on the membrane, gives significantly higher fluxes than when the thicker filaments parallel to flow are on the membrane forming a series of parallel channels, as seen in Desal-1. In this latter case because the transverse filaments in contact with the channel roof are thin, the wakes formed are not big enough to affect the opposite wall (membrane).

It should be noted that although the above trends were reproducible, the absolute values have a likely experimental error of about ±5%.

In spiral wound membrane elements channels are limited by membranes on both sides. Therefore, results obtained for symmetric spacers are the same for both surfaces, whereas for asymmetric ones flux will be given by an average. It should also be noted that although the experiments reported in this work were performed with a membrane at the bottom of the channel, similar performance would be expected for a membrane located above the channel. For example in a recent study of membrane orientation (Youm et al., 1994) using the same type of simulator, no effect of orientation on ultrafiltration of proteins has been observed, provided that the channel is spacer-filled and the flow rate exceeds about 0.3 l/min.

The outcome of this analysis indicates that thicker filaments have a higher impact on mass transfer at the wall they are attached to and are more likely to promote mass transfer on the opposite wall than thinner filaments. These results are specific for the non-Newtonian rheology and fluid character demonstrated by CSL.

Spacer Optimisation

It is shown that flux enhancement with spacers is achieved at the expense of high pressure losses. Increasing the flow rate causes energy costs to rise due to increase in pressure losses. Membrane costs decrease due to the enhancement in flux. Typical of optimisation problems, the optimum is determined by the sum of both costs. Figure 6.8 shows a comparison of Desal-2 mesh spacers of varying thickness, and their effects on feed flow rate and pressure drop.

The effects of feed spacer thickness is also to a large extent determined by the density or solids concentration of the feed. CSL, being typically processed at 43% solids concentration, with the solids concentration increasing on the retentate side as the filtration progresses, has a tremendous impact on the pressure drop. It is also worth noting that typical spiral wound elements for ultrafiltration have an upper limit for cross flow velocity of about 0.6 m/s. This upper limit is largely dictated by the maximum allowable pressure losses across the element to avoid telescoping.

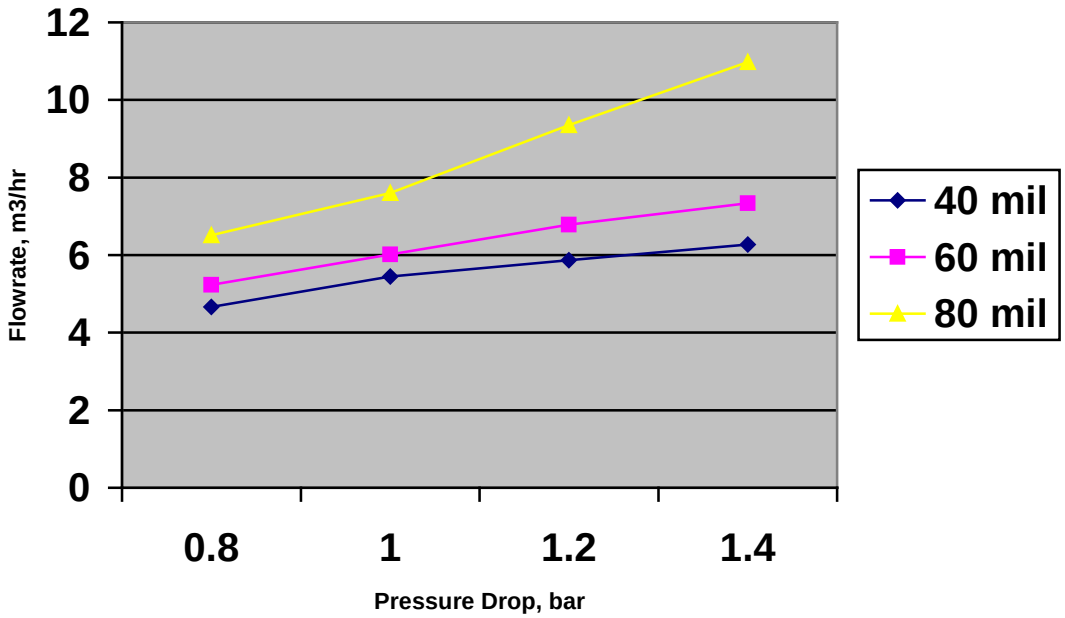


Figure 6.8 : Effect of spacer on feed flow and pressure drop.

Given these severe restrictions, the 80 mil spacer was most appropriate for the application. The cross flow velocity could easily progress towards reasonable limits, without exceeding the 0.6 m/s, and the pressure drop remaining between 1and 1.4 bar.

Membrane Cleaning

One of the main problems in large-scale membrane systems is to ensure the stationary conditions of the membrane process. Even in cases when all operating parameters are kept on a constant level, permeate flux declines systematically with time. This is the consequence of reversible and irreversible changes in the membrane and its closest vicinity.

Concentration polarisation is the primary reason for the flux decline during the initial period of operation (Fane et al., 1983, 1985, 1987; Abulnor, 1988; Aimar, 1988, 1989; Finnigan, 1989; Fell, 1990). Accumulation of the solute retained on the membrane surface leads to increasing permeate flow resistance at the membrane wall region. The most important reason for flux decline is membrane fouling, which is considered as a group of physical, chemical, and biological effects leading to irreversible loss of membrane permeability.

The first set of experiments on the flat sheet cell system helped to elucidate the intensity and type of fouling. Having selected the type of membrane to be used in the scaled-up process, it was important to identify the key fouling components.

The standard water flux at 25°C of the virgin membrane was 98 l/m^2/hr. The initial product flux was 12 l/m^2/hr. The system was operated for a total period of 20 hours, by which stage, the flux had reduced to 2.1 l/m^2/hr. This was a significant reduction in the flux rate over a normal production period of 20 hours. The water standardisation showed a water flux rate of 18 l/m^2/hr.

Approximately 82% of the membrane flux was lost due to fouling in one form or another. A visual inspection of the fouled membrane was carried out prior to implementing the cleaning procedure. Thick deposits of brown and creamy layers were seen, compacted into a polymeric-like structure. A small portion of this was carefully scraped off and analysed. Determinations by liquid chromatography, AA spectroscopy and NMR, showed an intricate web of complexes. The adsorbed material consisted of salts, predominantly of calcium, magnesium, phosphates, iron and sulphates; polypeptides, polysaccharides (starch identified), lipids and organic acids.

Because suspended solids were totally rejected by the membrane, due to their size, it is likely that reversible fouling was built as a cake of biological particles accumulated at the membrane surface. Some molecules, such as the proteins, peptides, salts, lipids, etc. could induce concentration polarisation and participate to the reversible fouling. These could invariably form layers which would become compacted over time. The assumption is that the cake layer could be considered as a net which was clogged by broth components depending on the hydraulic parameters of the crossflow filtration.

Previous attempts to clean the membranes using standard techniques had failed, hence a more constructive approach was taken to develop procedures. The cleaners had to be classified under the following areas:

- alkaline cleaning
- fat removal
- protein removal
- enzyme cleaning
- acid cleaning
- sanitizers

Alkaline cleaning

Most cleaning can be done with a good alkaline product, since most types of soil are best removed with alkalinity. Fats are saponified by alkaline cleaners, and most proteins are more easily removed at high pH values. At protein values greater than 11.0 the protein is hydrolysed, making it soluble. As neutral values are approached, the solubility decreases, and at pH 4-5 many proteins can even be precipitated, they become quite insoluble and difficult to remove.

Great care has to be taken to ensure that the membrane pH tolerance levels be adhered to. Prolonged exposure to extreme pH's is detrimental to membrane material structure and will severely shorten the life-span. For PVDF membranes, a pH of 10.5-10.8 is considered to be the top end for the cleaning cycle. Also, considering the operating temperature, a combination of high temperatures and higher pH's administer greater severity on the membranes. Therefore, a more balanced approach was required. A pH of 10.3 was considered to be safe at an operating temperature of 50°C.

The selection of suitable cleaning agents was limited to three suppliers, namely; Alconox, Henkel Products and Diversey. The best product for the duty was Ultrasil 93, an amine-based product from Henkel, Germany. A 0.5% m/v concentration produced a pH of 10.3. The dosing and pH correlation was fairly consistent, provided that RO water is used for the CIP.

Fat

Under normal conditions of cleaning (time, temperature and alkalinity usually encountered), not much hydrolysis or saponification occurs. The emulsification properties of wetting agents is a significant factor in fat removal at lower temperatures and alkalinity necessary for maintaining membrane life. The higher the alkalinity, the higher the temperature, the more fat will be hydrolysed, but membrane life is shortened. So great care must be taken to strike a good balance.

It was also noted that, in some of the cleaners used, the presence of calcium ions forms insoluble deposits, which can clog up filters and the flow channels in membranes. This phenomenon often occurs when the cleaner does not have enough chelating power.

Alkalinity based on caustic alone is not sufficient. pH control was found to be very difficult since no buffer system was present. The caustic does not have any detergency or wetting agents, hence the lack of soil carrying capacity. Builders are a strong requirement. The correct type and molecular size must be used to prevent fouling or swelling or cracking of membranes. The best builders were found to be sodium

carbonate or phosphates which also served as excellent buffer systems. Ultrasil 93, adjusted with an addition of 100 ppm of phosphates served as an excellent fat removal detergent.

Protein Removal

Protein solubility data suggests that the higher the pH the better the cleaning. It is also known that membranes have severe limitations in terms of prolonged exposure to very high pH's. pH values above 11 are rarely used. Even at these high values exposure must be limited to safe-guard the membrane.

Built detergents, such as Ultrasil 93, have an enormous advantage over straight caustic due to the inclusion of various sequestrants, chelating and complexing agents. A reduction in pH with the retention of cleaning efficiency is therefore possible.

Enzyme Cleaners

Not all proteins are solubilised by high pH cleaning. These proteins require enzymes which slowly digest the protein molecules and makes them into water soluble fragments. However, the optimum activity of enzymes normally require neutral pH's and moderate temperatures. Balanced products such as Tergazyme from Alconox and Ultrasil 56 from Henkel Products were found to be fairly efficient in solubilising adsorbed protein. Although Ultrasil 56 showed much better sustainable performance.

The presence of starch on the membrane initially posed severe problems. The normal detergents were ineffective in removing the thin starch layer. The only alternative was the use of a fungal amylase, obtained from Enzymes S.A., called BAN 480L. A concentration of 50 ppm was sufficient to solubilise all the starch on the membrane.

Acid Cleaners

Acid cleaning was found to be necessary since high amounts of mineral deposits such as Calcium, Magnesium and Iron were found on the membrane surface. Phytin, which normally has limited solubility at pH's above 4.5, was also detected on the membrane. Phytin was found to be readily soluble at pH 2. A blend of acids was produced, containing nitric and phosphoric acids. Here again, care had to be taken to limit the exposure time to 20 minutes. Prolonged exposure of the membrane to very low pH's causes brittleness and cracking.

Sanitizers

It is customary to sanitize membrane systems after cleaning. This prevents microbial growth and also serves to keep the membrane free of colour adsorbing compounds. The experience in CSL processing showed distinct changes in the membrane colour, even after CIP. In general, chlorine is by far the most common sanitizer used. However, there are a number of shortcomings to contend with when chlorine is used. The higher concentration limits is around 200 ppm, with exposure time not more than 20-30 minutes. Membrane vendors generally stipulate very strict measures with regards to chlorine exposure. The polymeric material is very susceptible to chlorine attack, which causes severe destabilisation of the compound structure.

In order to alleviate these dangers, a suitable alternative was found. Hydrogen peroxide was used at a concentration of 1000 ppm. This was found to be fairly efficient and not as destructive as chlorine.

The modified procedure for the CIP on the test cell was as follows:

- ***First alkaline rinse.*** RO water was recycled in the system, where the permeate and concentrate were returned to the feed/CIP tank. The water was heated to 50°C. The alkaline detergent, Ultrasil 93 from Henkel Products, was added to the water to a concentration of approximately 0.5% m/v and pH of 10.3. The detergent mixture was recycled for 60 minutes. The pH was checked at regular intervals.

- ***Water flush.*** The system was then flushed out with water until the pH of the permeate and concentrate was the same as the incoming flush water.

- ***Acid rinse.*** Acid detergent, Ultrasil 75 from Henkel Products, was added to the CIP tank containing water at 50°C, to a pH of 2.5. The approximate concentration was 0.5% m/v. The acid detergent was recycled for 60 minutes and the pH checked at regular intervals.

- ***Water flush.*** The system was then flushed out with water until the pH of the permeate and concentrate was the same as the incoming flush water.

- ***Second alkaline/enzymatic rinse.*** Ultrasil 56 from Henkel Products was circulated at a temperature of 50°C, approximate concentration of 1% and pH of 10. The recirculation was conducted for 30 minutes.

- ***Water flush.*** The system was then flushed out with water until the pH of the permeate and concentrate was the same as the incoming water.

- ***Disinfection.*** Ultrasil Active from Henkel Products or Divorsan Forte from Diversey, was circulated at a concentration of 1000 ppm, at room temperature, for a period of 30 minutes. The feed pressure was increased to 300 kPa to increase the permeate flowrate to increase the permeate flowrate for proper disinfection of the permeate side.

- ***Water flush.*** The system was then flushed with water.

- ***Standardization.*** The water flux was measured at 25°C and 1 bar pressure and compared with the original clean water flux.

The procedure was subsequently evaluated on the bench-scale system on the spiral wound module. The procedure was modified as follows:

- The ***acid rinse step*** was reduced to 20 minutes.

- An ***additional step*** was added before disinfection and after the second alkaline rinse. An enzyme, BAN 480L, a fungal amylase, was circulated at a concentration of 0.001% m/v for 20 minutes and then flushed out with RO water.

- For ***severe fouling***, a neutral enzyme detergent, Ultrasil 53 from Henkel Products, was used at a solution concentration of 1% m/v. The detergent was first circulated for 1 hour and left to "soak" for 3 hours. The system was then flushed out with RO water and the water flux checked against the standard clean water flux.

6.3.3 Pilot Plant System

This was truly the culmination of all the research and development performed on CSL to render it suitable as a fermentation feedstock. In order to obtain the "process confidence" for a novel process, it was necessary to somehow configure the pilot system to generate real data. It was therefore necessary to set up the entire pilot system as close to the raw material source as possible, given that the feedstock was a biological stream and was highly susceptible to changes. There was also an added advantage for the spent material (concentrate and permeate) to be re-blended and returned back to the wet milling process. This minimised unnecessary losses of valuable CSL.

6.3.3.1 General Performance

A series of five batches of CSL were processed with good reproducibility. Each run included a volume recovery of permeate of approximately 50%, except for *Run 2*, where a 60% volume recovery was obtained. As noted earlier, the pilot plant system employed a centrifugal pump for recirculation of CSL through the membranes, which provided an inlet pressure of 3.5 bar; transmembrane pressure was controlled by adjustment of the outlet and filtrate pressures.

The results from the five runs in the series are shown in Figure 6.9 where the flux is plotted against time. A steady drop in the flux occurs as permeate is recovered. The drop in the flux is seen to be more pronounced in the first 10 hours of the run. During this period the flux steadily drops to less than half of the initial value. The remaining 10 hours then shows a more gradual drop in the flux. The run data is given in Appendix VI. It can also be seen from the data that approximately 75% of the volume recovered occurs in the first 10 hours of the run.

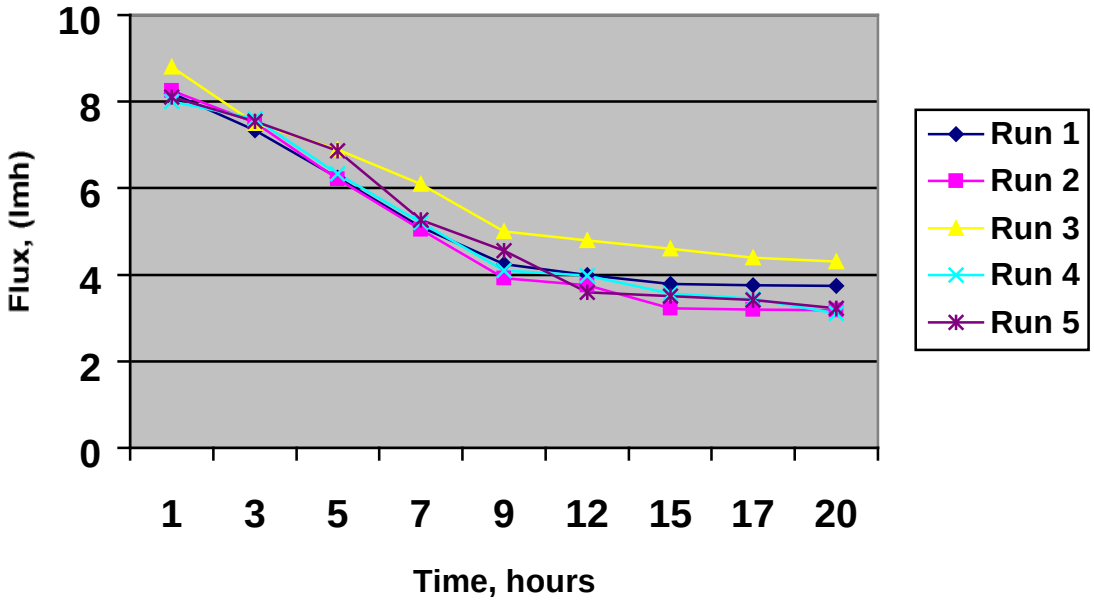


Figure 6.9 : Plot of flux versus time for the five batches.

The trend in the cross flow rate follows the trend in flux, as is seen in Appendix VI**.** The reduction of volume in the feed tank as well as the increased viscosity of the concentrated CSL, made the feed more difficult to pump. This increase in viscosity, also shown earlier in laboratory trials, is caused primarily by

viscosity precursors such as polypeptides, polysaccharides and lipids. These precursors are rejected by the membrane and therefore remain in the retentate, increasing in concentration as permeate is removed.

Due to the non-Newtonian nature of the fluid, the increased concentration of the viscosity precursors and the subsequent reduction in the cross flow rate, has a tremendous impact on the overall rheology.

Further, the difficulty does not result just from the higher pressure drop required to pump the more viscous broth the membrane lumen, but also results form reduced from reduced net positive suction head available to the pump, which ultimately leads to pump cavitation. The transfer pump was found to be severely affected by this and ultimately affected the circulation pump. The problem was rectified in subsequent batches by applying 50-100 kPa of air pressure to the head space of the feed tank. This resulted in sufficient pressure at the transfer pump inlet to eliminate cavitation, resulting in a more constant cross flowrate.

In spite of the uniform operating conditions, which resulted from the improvement in the system design, there was still a notable decrease in the during the initial concentration phase.

The fact that flux decays significantly in the first 10-12 hours and then does not decay further, but varies between 3 and 4 $l/m^2/hr$ as the CSL is concentrated, suggests that this fouling is in some way self-limiting. One might hypothesise that the accumulation of a stable, dense layer of CSL solids may result from attractive interactions which only come into play when the inter-particle and particle-surface distances are reduced as at the membrane surface.

Extending this hypothesis, once at play these interactions are too strong to be disrupted by the enhanced shear, which results from the presence of the net-spacer. The gel-layer remains and the flux remains depressed for the remainder of the run. The thickness of this layer would be proportional to the maximum CSL concentration. Another hypothesis, is based on specific chemical interactions that occur between proteins, inorganic components, lipids, polysaccharides, phytin etc. These interactions are highly likely, as seen in earlier experimental observations on fouling. In terms of bulk concentrations, protein and phytin or myo-inositol, are by far of the highest concentrations. Phytin, in particular, behaves as a multi-chelating complex. Minor changes of pH, concentration or zeta-potential will affect the pK's of phytin and proteins. Thus, in these charged states, interactions are highly likely. Phytin-protein complexes become insoluble under these conditions and are relatively hydrophobic in nature. They then gel onto the surface of the membrane.

6.3.3.2 Membrane Loading Effects

One pilot-scale experiment was performed to evaluate the membrane performance at a higher loading capacity. This was done to eliminate any uncertainties on the hydraulic design at higher retentate concentrations and to expose potentially problematic fouling. It also provided an opportunity to avoid unrealistically high flux projections. Even when a fouling problem exists, maintaining a constant loading at least allows reliable scale-up, regardless of the underlying fouling mechanism.

The run was conducted for 40 hours under identical conditions of flow and pressure. The results of this experiment are shown in Figure 6.10**.** The results show a similar flux trend to the other runs in the first 20 hours**.** Thereafter, the flux remains relatively constant for the remainder of the run period, at approximately 3,2 L/m^2/hr.

The accumulation of the gel-layer on the membrane surface ultimately becomes the controlling resistance. As the solids concentration of the feed changes, the rate at which the cake accumulates is slowed down, thus slowing the rate of flux decline. This phenomenon can be seen after the first 20 hours of operation, after which the flux decline is minimal. However, this analysis ignores several other possible factors, which may affect the performance of the membranes.

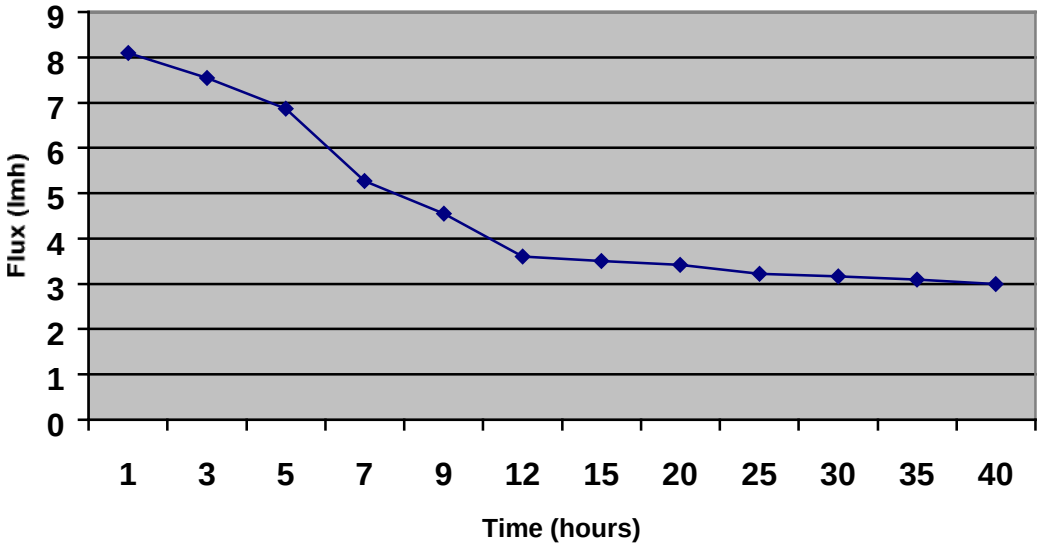


Figure 6.10 : Plot of flux against time.

Another important characteristic of this run is shown in Figure 6.11. A significant drop in the flux is seen as the solids concentration of the retentate increases. This could be attributed to the preferential movement of water, along with low molecular weight material, across the membrane. The solids concentration of the permeate in the initial stages does appear to be more dilute. It then stabilises after the first seven hours of the run and remains relatively constant for the remainder of the run, until the feed concentration exceeds 48%. Flux decline at this point is fairly rapid. Given that the CSL is non-Newtonian in nature, rheology probably has the most influence on the rapid flux decline. The high solids concentration is difficult to move at high cross flow velocities, thus significantly influencing the boundary layer.

Therefore, diafiltration could be a feasible solution to maintain a solids concentration between 43 and 48%. However, given the fact that this would produce a more dilute permeate stream, there will be significant implications in the fermentation recipe make-up as well as the transportation costs associated with the larger water fraction. Concentration of the permeate stream would be considered to be an expensive option, although other drawbacks such as protein damage and losses could be singled out as well. Careful consideration of the feed and bleed design configuration of the membrane system could potentially solve the problem. With an incoming feed concentration of 43%, there is a considerable amount of recirculation. The purge from the system could be set so as to prevent the system average concentration from exceeding 48% solids.

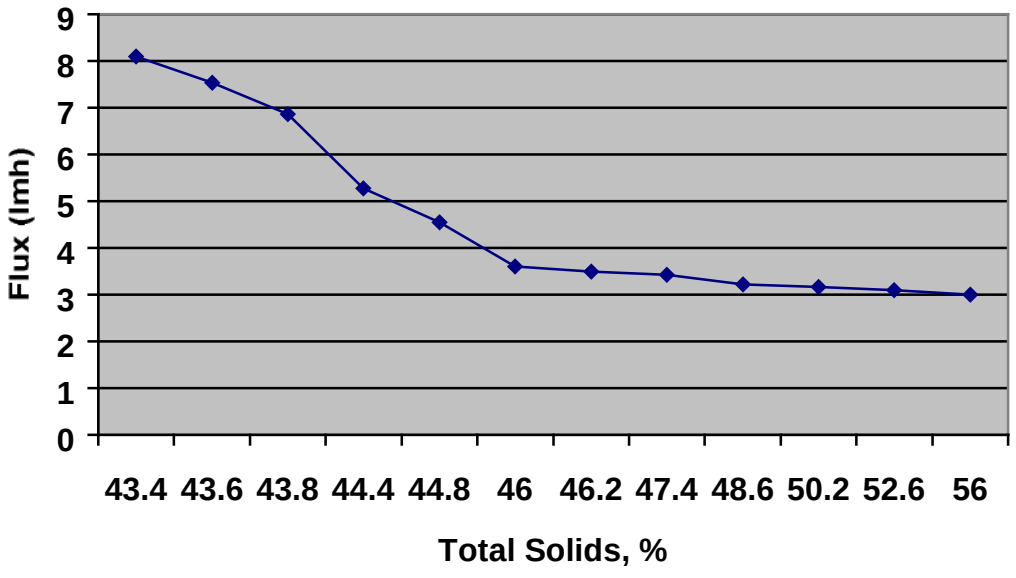


Figure 6.11 : Plot of solids concentration in retentate vs. flux

6.3.3.3 Reproducibility

The reproducibility of the five pilot plant batches is illustrated in Figure 6.12, where the retentate volume recovery is plotted versus time, for the concentration of each of the batches. The same volume of feed was employed for each of the runs. The average flux was calculated as 6,25 l/m^2/hr. The data for Run 5 is only plotted for the first 20 hours. The effect of the observed batch to batch variation in flux was that the percentage of total solids in the feed varied slightly, hence the difference in the end concentration of the retentate.

Approximately 99% of the original water flux of the system was recovered after post-run cleanings. Furthermore, filtration performance did not steadily decrease with each subsequent run, indicating that the developed cleaning protocol was sufficient to regenerate the membrane.

These tests provided a clear indication that the system was robust enough to cope with inherent batch variations, without affecting the quality of the end product. It might be said that the overall system flux was low when compared to other processes. Given the complexity of the task and inherent nature of the CSL, cognisance of the value-added benefit to CSL as a fermentation feedstock is of primary importance. Low fluxes are definitely attributed to the nature of CSL, hence a much larger membrane area would be required for the full scale duty.

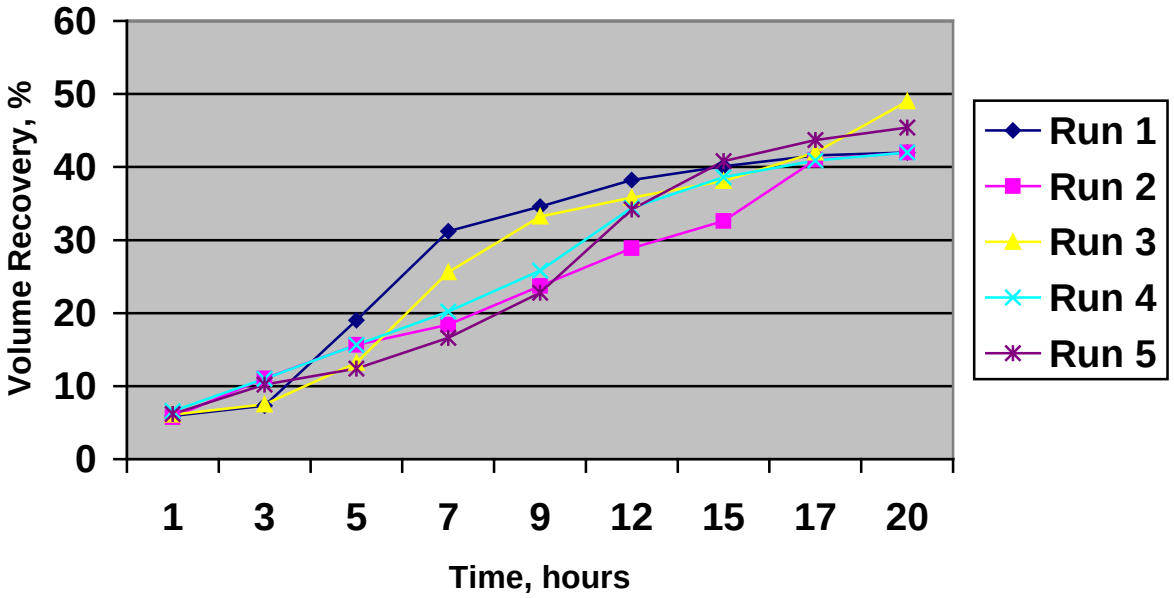


Figure 6.12 : Plot of batch volume recovery versus time.

CHAPTER 7

CONCLUSIONS AND RECOMMENDATIONS

7.1 Conclusion

7.1.1 Corn Steep Liquor Characterisation as a Feedstock

CSL was found to inherently possess many nutritional components which added great value to fermentation media. These nutritional components were found to be inaccessible due to the many problems associated with the sterilisation of CSL. The beneficial use of CSL is therefore clearly dependant on the pretreatment techniques employed. It was also evident that treatment of CSL in its concentrated form was more appropriate since it created spin-offs on reduced capital for the pretreatment processes, significantly reducing transport costs and eliminating a concentration process that would be required after pretreatment.

However, in its concentrated form there are certain processing disadvantages. These are associated with the non-Newtonian fluid behaviour of CSL, which has ramifications on the hydrodynamic design of processing equipment, and the high level of suspended solids which complicates the separation processes. The suspended solids had a direct impact on the viscosity, where increasing levels of suspended solids showed increasing viscosity.

The CSL from African Products was available as a 50% m/m solids concentrate. For all intensive purposes a solids concentration of 43% was found to be most suitable for the membrane separation process and the subsequent use in fermentations.

The characterisation of the protein showed various molecular weight bands, where the range between 16000 and 22000 daltons seemed to be most pronounced. Fermentability testing revealed that the protein in this range was easily broken down and utilised by the bacteria. Bacterial dry cell masses of 30-46 g/l were achieved

7.1.2 Pre-treatment

7.1.2.1 pH Treatment

The success of the separation process of pH treated CSL was dependant on the quality of the upstream processing, i.e. the pH treatment operation. A properly designed tank with the correct geometry, baffle system and mixing system, with inherent system design for a highly viscous solution, is a primary requirement. A low agitation rate coupled with a low base addition rate was required for good particle size distribution. The pH treatment was best effected at temperatures higher than 50°C, where a significant drop in viscosity was noted. The treated liquor showed typical thixotropic behaviour, which classifies the slurry as a non-Newtonian fluid.

Various techniques have been used to ascertain the best equipment for the liquid-solid separation duty. A pressure filter, in particular, a diaphragm membrane filter press, produced the best filtration results. Reasonable agreement was obtained in the results of the laboratory screening trials and large-scale pilot testing. The performance of the pressure filter was dependant on a gradual increase of pressure during the dewatering stage and for the operation to be performed at temperatures higher than 50°C. In addition a specialised filter medium, Propex 46 or equivalent, was required for the separation to be a success.

In following the operation under the optimised conditions, protein recoveries of above 95% at fluxes of 35 $l/m^2/hr$ were achieved.

This process had a significant impact on the sterilisation of the CSL. The removal of the colloidal solids was found to improve the quality of sterilisation. A reduction of more than 90% in coagulated solids was achieved.

7.1.2.2 Broth Conditioning followed by Decanter Centrifuge

It was observed that the separation of suspended solids from CSL is enhanced by the use of coagulation and flocculation. The scroll decanter centrifuge was well suited for the subsequent separation of the flocs from the clarified liquor.

Due to fact that the centrifuge was not specifically built for the duty, it therefore imposed several limitations on its performance. Despite these shortcomings, preliminary trials proved to be somewhat successful in meeting the separation objectives.

The tests were conducted on various batches of CSL and in this way feed variations were tested. With a maximum suspended solids loading of 18% and a feed rate of 700 l/hr, a solids recovery of 90% was

achieved. The clarified liquor contained residual solids between 0,5 and 0,8%. The CSL sludge had a solids concentration that ranged between 43 and 65%. Although these results looked impressive, there was an area of concern. The residual solids of the clarified liquor contained fibres or fibrous type solids, which were not removed by the decanter centrifuge. This was due to the very small density difference between the solids and the liquor. More importantly, fibres are known to be problematic to membrane systems. Also, the sludge produced by the decanter centrifuge, required dilution almost immediately, to enable the slurry to be conducive to pumping.

Coagulation and flocculation doses were kept within the limits of the laboratory evaluations. Flocculant dosages were controlled between 100 and 200 ppm, with the coagulant operating at higher dosages between 400 and 2000 ppm. The only controllable parameter on the machine itself was the scroll differential speed. The best performance in terms of the cake dryness and centrate clarity was obtained at the lowest scroll differential speed of 4 rpm.

7.1.2.3 Separation by Gyratory Screens

The pretreatment process was devised to pass raw CSL through a set of two screens. The technology entails the use of a gyratory mechanism which aids in the cleaning of the screens during continuous operation. The trials conducted on the pilot plant utilised a specifically designed unit for quick-on-site screening, which did not possess the added flexibility and robustness of a properly designed full scale unit. This imposed some limitations on its performance. However, despite these shortcomings, the trials conducted on the pilot plant proved to be successful in meeting the above objectives.

A number of trials were performed on various batches of CSL. There was considerable batch to batch variation in the suspended solids content of the CSL and this was found to ultimately affect the throughput of the screening process. The feed suspended solids concentration varied between 10 and 18%. The highest throughput achieved was 400 l/hr, at a feed solids loading of 14,5%. It was found that temperature made a significant impact on the separation. The loss of heat in the feed stream caused excessive coagulation to occur thus increasing the suspended solids content and lowering the throughput. The total solids in the sludge stream varied between 45 and 77%. Protein loss in the sludge stream was around 1%. Careful attention had to be given to the handling of the sludge stream. This stream displayed rheological characteristics typical of a non-Newtonian thixotropic fluid.

The 100 μ screen operated best when prior separation was done using a 180-200 μ screen. This reduced the solids loading on the 100 μ screen and increased the throughput by at least 10-15%. The self-cleaning mechanism also performed more efficiently under these conditions. The success of the operation was

dependant on the sub-optimised lead angle setting of 45-60°, the feed entrance at the centre of the screen and the inclusion of the sliding cylinders as a self-cleaning mechanism.

In summary, it was found that the gyratory screens were well suited to this application, demonstrating tremendous flexibility in handling the batch to batch variations. The results presented here demonstrates a reasonable degree of confidence over the operation.

7.1.3 Membrane Ultrafiltration

7.1.3.1 Membrane Selection

The results obtained in the laboratory screening trials showed that the components of CSL have a direct effect on the ultrafiltration performance. These component attributes were intrinsically linked to the complex nature of CSL. Therefore, some standard practices were adopted to achieve a decent basis of comparison. These included the temperature of operation, the feed solids consistency, the crossflow rate, the feed pressure and the pressure drop. Having taken into account all the latest technological advances made on the membrane front, two membrane types were selected on the basis of performance. Laboratory screening on a specialised test cell showed polyvinylidene (PVDF) and polyacrylonitrile (PAN) to be the best performers. Further testwork showed that PVDF membranes were more suited for the operation. Although, both the PVDF and PAN membranes displayed low protein binding attributes.

A molecular weight cut-off of 30 000 was determined as being best suited for providing a CSL permeate which was readily utilised in the bacterial aerobic fermentation. Evaluation of membranes with differing morphologies and material compositions, but similar molecular weight cut-off's, showed significant differences in permeability and surface roughness. These qualities affected the fouling characteristics during filtration. Also, the degree of hydrophobicity and hydrophilicity of these membranes had a direct effect on adsorption type fouling characteristics.

7.1.3.2 Pretreatment prior to Ultrafiltration

There was conclusive evidence that pretreatment of the feed CSL was necessary, thus forming an important step in the development of the ultrafiltration process. The various studies performed, exploited most of the known possibilities and techniques. However, in this particular application for CSL, the process is novel. pH treatment of CSL provided a very clean feedstock to the membrane process. The product of the process had virtually no suspended solids. There was also a significant reduction in the amount of suspended solids after sterilisation.

However, there are two major drawbacks in the process. The first, is that significant amounts of nutrients, especially the phosphate complexes, are stripped out of the CSL and lost to the precipitated material. Therefore, subsequent testwork on fermentations showed poor results. The second drawback, is that the process was fairly complicated with the unit operations being capital intensive and generating significant amounts of waste material. No appropriate use was found for the sludge generated during the solid-liquid separation. The mixing technology for the process requires very careful monitoring and process control.

The decanter centrifuge also provided a relatively clean stream, but failed to remove a crucial portion of the suspended solids. Fibrous solids were found to be "too light" to be removed by centrifugation, and therefore posed a threat to the membrane system. Part of the membrane process guarantee, as proposed by membrane vendors, required a stream that was free of fibrous solids.

Of major concern, is the addition of broth conditioners. The work performed in this area did not cover the possible deleterious effects of these chemicals to the fermentation. This remains an area of doubt since dosages are never constant. Further, the option of a decanter centrifuge was found to be very capital intensive.

The most effective and cheapest option for the pretreatment was the use of the gyratory screens. This system removed all suspended solids down to 100 μ . The double screening system employed ensured that all fibrous type solids were also removed. The system was also low in capital cost and had minimal operating costs. The second biggest advantage was that the product of the gyratory screens produced the highest membrane fluxes and lowest fouling potential, when compared to the other pretreatment methods.

Therefore, coupling the gyratory screen process as a pretreatment step for the ultrafiltration system, seemed to be the logical option. All subsequent pilot studies conducted, used CSL feedstock treated through the gyratory screen system.

7.1.3.3 CSL Solids and Concentration Limitations

The study showed that a 40-50% volume recovery is the practical limit for the CSL ultrafiltration process. Recoveries above this range are possible, but have severe repercussions on fouling and the system hydrodynamics, which cannot support a feed with solids concentrations exceeding 47% m/m. Therefore, the initial feed concentration was found to operate best at 43% total solids.

The flow characteristics of CSL, quickly changes as liquid is removed from the system and the solids concentration approaches 47%. As this value is approached, the retentate behaves as a high viscosity pseudoplastic liquid. The ratio of this maximum solids concentration, to that of the feed, sets the practical

limit of concentration which can be achieved in the system. The use of a high pressure positive displacement (rotary lobe, moving cavity or diaphragm pump), instead of a centrifugal pump, can extend this limit. However, the high viscosity of the concentrated retentate results in very high pressure drops across the membrane flow channels. The inlet pressure rating may then be exceeded, leading to structural damage to the membrane.

It is important to note that a high concentration of solids in the retentate is not a problem in and of itself and does not necessarily correlate with poor filtration performance. It is only because at high concentrations most filtration systems cannot maintain adequate flow, and thus adequate shear rate at the membrane surface, that they have a problem. The reduction of wall shear rate, upon concentration of CSL solution in an ultrafiltration system, accounts for much of the observed drop in flux in an otherwise well balanced filtration process; this should be expected.

Truly poor performance usually results from the presence of gel-forming soluble and in-soluble compounds; identified as protein, phytin, inorganic complexes, lipids and starch, compounds which adsorb onto the membrane surface or into its pores, or which promote the adhesion of solids to the membrane surface.

7.1.3.4 Comparison and Selection of Membrane Modules

In depth study of four commercially available modules were performed. For a CSL medium, spiral wound modules gave significantly higher fluxes when compared to the tubular, hollow fibre and flat sheet systems. However, a fair amount of optimisation was required in terms of selecting an efficient spiral modular design. Screening trials on a number of mesh spacers samples, showed that the DESAL-2 parallelogram type mesh spacer was best suited for the application. A significant improvement in flux and reduced fouling was seen with this particular mesh spacer.

7.1.3.5 Membrane Cleaning

Conventional cleaning methods proved to be unsatisfactory for this particular application. This was due to certain fouling components not being removed from the membrane surface by conventional detergents. These components were subsequently identified by laboratory analyses and a method of removal was devised. A new cleaning protocol was developed, where, enzyme solutions were utilised to remove the foulants. This technique was highly successful and was demonstrated repeatedly on a number of trials.

7.1.4 Membrane Process Scale-up

The results of this work confirmed earlier experiences with laboratory and bench scale trials. Hence, the scale-up is generally straight forward. Assuming the same modular system is employed, the key variables, which must be employed and maintained, are the transmembrane pressure, cross flow velocity and the membrane loading. The latter parameter, which is the ratio of feed volume to membrane area, is often overlooked during early laboratory studies, which are carried out using relatively small volumes of liquor, resulting in overly optimistic predictions of membrane performance. However, when higher loadings are employed at the pilot or production scale, where costs often restricts system size, lower average fluxes are often obtained. In this case, by adjusting the membrane loading from bench scale to pilot scale, good agreement in flux was obtained.

Pump selection is another variable, which is often ignored upon scale-up. The selection of the correct type of pumping system was found to have a tremendous impact on ultrafiltration performance. Many laboratory systems employ positive displacement pumps, especially peristaltic pumps, since they are mechanically simple and most laboratory workers are familiar with them. While for the more exotic and costly products, this design can be maintained upon scale-up. For cheaper applications it is usually desirable to employ centrifugal pumps at the production scale. The operating curves for these devices are significantly different and must be considered in the design. As noted in this work, this relates particularly to the net positive suction head requirements of a centrifugal pump.

As the liquid becomes more viscous upon concentration, the head requirement increases and loss of proper head can result in cavitation. The problem was solved, in this instance, by the application of a positive pressure to the feed vessel head space, to compensate for the increased head requirement.

Other aspects of scale-up similarly require the observance of good chemical engineering practice. Elevations and pressure drop through ancillary piping can have a major impact on the flow and transmembrane pressure available to a large scale filtration system, whereas these factors are essentially non-existent at the laboratory scale where all components are on the same bench top. These are usually connected using short lengths of tubing.

In a production environment, equipment location can be dictated by space constraints, existing equipment availability and other factors, which result in a less than optimal design. Proper hydraulic design can often compensate for these shortcomings. For example, the pressure head required to return a retentate stream to the top of a large feed vessel can add significantly to the pressure on the feed/retentate side of

the filtration module. In such cases control of the transmembrane pressure requires control of the filtrate discharge pressure, which is often uncontrolled in laboratory experiments.

7.1.4.1 Membrane Elements in Series or Parallel

The modular nature of the cross flow system suggests that the productivity can be doubled by doubling the membrane area. This can be done by either adding membrane elements in parallel or in series. If elements are added in parallel the average cross flow falls, thus having a direct effect on increased fouling. If elements are added in series, the cross flow falls through the series, so the final element also sees low cross flow, hence having higher potential to foul.

From the piloting experiments, the results show that the system should not be operated with a series of elements, at greater than 47% recovery of the feed. To achieve the higher recoveries, a cascade of elements are required, i.e. for a system with 60-70% recovery, there should be two sets of elements in series operating in parallel, both feeding into a third.

As mentioned earlier, the limitations are clearly seen in viscosity, solids build-up and the drop in cross flow velocity. As a result, the lowest feed pressure to an element is in the region of 2,8-3,0 bar. The maximum feed pressure to an element is in the region of 5,8-6,0 bar. The elements are definitely designed to handle up to 10 bar feed pressure, but for a continuous operation this eventually leads to membrane telescoping and membrane compaction , as experienced on the pilot studies.

Given that the maximum allowable pressure drop is 1,4 bar, it is therefore only possible to have two membranes elements operating in series or housed in one pressure vessel. Interstage pumping is a good solution in cascade systems, since the retentate from one set of elements in series, can be re-pumped to the next set, thus increasing the feed pressure and cross flow velocity. In general, this option adds significant cost to the system and could render the application uneconomic. One way of solving this dilemma, is to return some of the reject back to the feed. In this way, high recoveries can be maintained, without letting the recovery of any stage go above 50%. The penalties for this approach are both in performance and economics, in that additional pumping energy is being used to pump material over the membrane several times.

However, the interstage pumping is necessary to make up for the pressure loss and cross flow velocity. In essence, the recirculating pump provides the cross flow, while the feed pump provides the system pressure. With this format, pressure vessels with the limited number of elements in series, can then be

arranged in parallel with the appropriately sized interstage pump. This has the advantage of lower energy cost and easier operation.

The increasing concentration within the system has an impact on the performance, where the increasing concentration of solute means that the permeate from the last element is of a higher concentration than the first and has a lower flux.

It can be seen that while cross flow membrane technology seems to be straightforward, the doubling of the throughput requires the doubling of the area, the reality is that as the scale changes, the issues of concern change. On a small laboratory scale test cell, the costs are associated with a person's time, achieving targets etc. On a larger scale, the important factors are the aspects which relate to the capital and operating costs

Cleaning a membrane in the laboratory is relatively quick and easy. On a plant scale, the issues are time, cost, waste disposal, etc. Another important process variable is temperature. In the laboratory, the ambient temperature might be 20°C, while in the plant the operational temperature might fall to 10°C or rise as high as 70°C. Since the productivity changes by more than 2% per degree, this has a significant impact on the plant design.

There is no unique scale-up procedure for cross flow filtration systems, since in most cases alternate designs and alternate membranes can meet the same challenge. However, within a specific application, there is an optimal solution. To reach this solution requires in-depth study and development. Without previous experience or test data, scaling-up can only be done with excessive over design or an excessive risk of under performance. The testwork conducted at the various stages provides a simple method of reducing risks. The starting point of the process is the assessment of the feed, from which an outline flowsheet is devised, followed by an assessment as to what further information is required from laboratory or field testing. Field testing is of particular importance in assessing the fouling potential. Such data provides invaluable information for the pretreatment requirements and subsequent cleaning techniques.

A key decision point in the scale-up, is what element configuration to use. The exact choice, it was seen, depends on the application and its inherent characteristics. In depth testwork for CSL was clearly required to eliminate all risk.

7.2 Recommendations

The product from the pH treatment process was by far the cleanest stream for the membrane system, but unfortunately produced poor fermentation results. This was probably due to the low phosphate levels in the treated CSL as a result of phytin removal. Phosphate is considered to be an essential nutrient, which is used extensively in enzyme reactions and energy transfer in the bacterial metabolism. It is recommended that research be conducted to investigate the use pH treated CSL in fermentations, with the supplementary addition of measured amounts of phosphate. Also, the precipitate produced in this process is rich in phytin. Potential uses as an organic feedstock should be investigated.

In selecting the gyratory screen system, certain modifications in the design, such as a flexible range for the frequency of vibration and the inclusion of a self-cleaning mechanism, are necessary for enhanced performance and should be considered before any final design. The handling of the sludge, produced by the gyratory system, requires careful consideration. There is a definite requirement, based on rheological characteristics, for properly designed agitation and pumping systems.

It is also recommended that work be performed on the membrane system to achieve longer run times. One possible way, is to investigate the use of hydrophilising polymers of suitable molecular weight to coat the membranes. This has the potential of reducing and even preventing certain types of fouling, thus extending the run time. Other techniques, such as low frequency vibration and permeate flushing should also be investigated.

Further, fractionation of the permeate by membranes into various molecular weight streams should now be a strong possibility. Other uses for the separated peptides and amino acids could be found in the fermentation and pharmaceutical industries.

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