INVESTIGATION INTO THE DECOLOURISATION OF JOHNSON SWEETWATER USING ULTRAFILTRATION

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Preface

I hereby declare that this entire dissertation is my own work, unless stated otherwise in the text, and that it has not been submitted, in whole or in part, for a degree to any other University or Institution.

Grant Michael Hubbard

December 1993
Abstract

The purpose of the investigation was to assess the ability of ultrafiltration to retain colour in Johnson sweetwater and to determine whether the improved quality of the Johnson sweetwater ultrafiltration permeate will have a positive influence on the refinery decolourisation processes. Ceramic membrane modules were used due to the high temperature of the Johnson sweetwater stream.

Johnson sweetwater is a recycle stream and affects the decolourisation processes downstream of the melter. For colour retention to be effective, the ultrafiltered Johnson sweetwater must have lower concentrations of the high molecular weight colourant molecules which have a high probability of being included in refined sugar crystals (the potentially included molecules). ICUMSA colour does not indicate the relative amounts of the various colourant types and therefore does not indicate how a particular solution will decolourise. Hence, ultrafiltration runs were performed using refined sugar solutions and colour transfer experiments were performed to determine whether the membrane retains the potentially included colourants.

Point ICUMSA colour retention values ranged from 28 to 50 % using the CeraMem LMDA-20-P1 module, the CeraMem LMA-0005-P module, the Membralox 1P19-40 (0,02 μm pore size) module, the modified Membralox 1P19-40 (0,02 μm pore size) module with dual layer ZrO2/PAA dynamic membrane, and the M5 Micro-Carbosip 60 (10 000 dalton cut-off) module. The highest ICUMSA colour retention was achieved using the Micro-Carbosip module. Ultrafiltration of the refined sugar solutions using the CeraMem LMDA-20-P1 membrane module retained 34 and 52 % of ICUMSA colour in solutions of H1 refined sugar and affinated H1 refined sugar respectively. Ultrafiltered Johnson sweetwater achieved lower colour transfer, from solution to crystal, ranging from 19 to 27 %. Hence, ultrafiltration retains the high molecular weight potentially included colourant molecules in Johnson sweetwater and the colour removal is effective.

It is proposed that future investigations into the ultrafiltration of Johnson sweetwater regard sugar colour as a mixture of: low molecular weight colourants which are easily removed by ion exchange and crystallisation, and high molecular weight molecules which are potentially included in the final refined sugar crystals, as opposed to the single grouped solute referred to as ICUMSA colour. Analytical techniques need to be developed which can distinguish between the two types of colour. The quality of ultrafiltered Johnson sweetwater will be able to be effectively quantified on the basis of retained potentially included colour and the effect of recycled Johnson sweetwater ultrafiltration permeate on ion exchange and crystallisation will be able to be predicted. An economic evaluation of the membrane process, based on improved decolourisation in the ion exchange and crystallisation processes, may then be performed.
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<td>A3-3</td>
</tr>
<tr>
<td>Figure A3.2</td>
<td>Cross-section of the Membralox membrane module.</td>
<td>A3-7</td>
</tr>
<tr>
<td>Figure A3.3</td>
<td>Cross-section of the M5 Micro-Carbosep ultrafiltration membrane module.</td>
<td>A3-10</td>
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<tr>
<td>Figure A5.1</td>
<td>Johnson sweetwater average ICUMSA colour and brix calculated using weekly average quality control data from April 1991 to October 1993</td>
<td>A5-2</td>
</tr>
</tbody>
</table>
# Glossary

<table>
<thead>
<tr>
<th>WORD</th>
<th>DESCRIPTION</th>
</tr>
</thead>
<tbody>
<tr>
<td>Affination</td>
<td>The washing of sugar crystals to remove surface film colourants.</td>
</tr>
<tr>
<td>Bagasse</td>
<td>The shredded cane-fibre residue following juice extraction.</td>
</tr>
<tr>
<td>Boiling</td>
<td>The process of sugar crystallisation in the vacuum pans.</td>
</tr>
<tr>
<td>Brix up</td>
<td>To increase concentration of a sugar solution by sugar addition or evaporation.</td>
</tr>
<tr>
<td>Brix</td>
<td>Brix is the sum of the dissolved solid matter in a sugar solution expressed as a percentage by mass or as an actual mass.</td>
</tr>
<tr>
<td>Brixing</td>
<td>Changing the concentration of total dissolved solids in a sugar solution by evaporation, addition of water or addition of sugar.</td>
</tr>
<tr>
<td>Brown liquor</td>
<td>The clarified liquor produced by refinery carbonatation.</td>
</tr>
<tr>
<td>Calandria</td>
<td>The heating element of an evaporator or a crystalliser.</td>
</tr>
<tr>
<td>Clear juice</td>
<td>The liquor following sugar-mill clarification.</td>
</tr>
<tr>
<td>Colour precursors</td>
<td>Those molecules, which are not actually coloured, but can react during the refining process to produce colour.</td>
</tr>
<tr>
<td>Composite permeate quality</td>
<td>The ratio of mass of solute in the total permeate volume to the volume of permeate.</td>
</tr>
<tr>
<td>Concentration polarisation</td>
<td>This phenomena occurring when retained solute molecules accumulate on or near the membrane surface as a result of their exclusion from the permeate.</td>
</tr>
</tbody>
</table>
Critical water recovery

The water recovery value at which relative permeate quality becomes equal to zero.

Cross-flow

The mode of operation of a membrane filter where the feed flows parallel to the membrane surface producing two outgoing streams, the permeate and retentate.

Crystallisation pan

A vessel in which sugar crystallisation takes place (usually under vacuum).

daltons

molecular weight units.

Easily removed molecules

Molecules which are preferentially removed by the decolorisation processes of ion exchange and crystallisation.

First boiling sugar

The first crop of sugar produced from a particular liquor by the crystallisation pans. It represents the purest sugar in the refinery.

Flux

The volume of permeate passing through a membrane per unit time and per unit membrane surface area.

Grade

Grade is a measure of the quality of a sugar solution and is defined as the ratio of brix to ICUMSA colour.

Grain

The term describing the introduction of crystal nuclei to initiate crystal growth in a saturated liquor.

H1 refined sugar

The refined white sugar product consisting of a mixture of 1st to 4th boiling sugars.

H11 Superfine sugar

A speciality sugar produced by Hulett Refineries having a size distribution between 150 and 355 mm.

Point retention

If sufficiently small samples are taken so that there is no change in the concentration of the feed before and after the samples are taken, then the retentions are termed point retentions.
<table>
<thead>
<tr>
<th>Term</th>
<th>Definition</th>
</tr>
</thead>
<tbody>
<tr>
<td>Johnson sweetwater</td>
<td>The sweetwater produced by the Johnson filter presses.</td>
</tr>
<tr>
<td>Linear velocity</td>
<td>The rate at which the process fluid flows parallel to the membrane surface.</td>
</tr>
<tr>
<td>Magma</td>
<td>A mixture of saturated sugar liquor and sugar crystals.</td>
</tr>
<tr>
<td>Massecuite</td>
<td>A molasses/sugar-crystal mixture.</td>
</tr>
<tr>
<td>Melter</td>
<td>The unit operation where sugar crystals are dissolved in hot water.</td>
</tr>
<tr>
<td>Membrane</td>
<td>A membrane is a thin permeable barrier, interposed between two phases, which offers varying degrees of selectivity to the passage of different constituents, as a function of their specific transport properties, under the influence of a driving force.</td>
</tr>
<tr>
<td>Milk-of-lime</td>
<td>A calcium hydroxide slurry.</td>
</tr>
<tr>
<td>Mill</td>
<td>The unit operation used to extract juice from sugar cane by applied pressure.</td>
</tr>
<tr>
<td>Molasses</td>
<td>The highly coloured <em>mother liquor</em> following final boiling of a sugar solution.</td>
</tr>
<tr>
<td>Mother liquor</td>
<td>The liquor from which a batch of crystals is boiled.</td>
</tr>
<tr>
<td>Mud</td>
<td>Thickened tri-calcium phosphate or calcium hydroxide precipitate recovered from the mill and refinery clarification processes.</td>
</tr>
<tr>
<td>off-spec</td>
<td>Refers to a parameter that is above or below required specifications.</td>
</tr>
<tr>
<td>Permeate</td>
<td>The filtered feed forced through a membrane under the influence of pressure.</td>
</tr>
<tr>
<td>Pol</td>
<td>Pol is the apparent sucrose in a substance, given as a percentage by mass or as an actual mass.</td>
</tr>
<tr>
<td>Potentially included molecules</td>
<td>Molecules which are preferentially included in the final refined sugar crystal.</td>
</tr>
<tr>
<td>Term</td>
<td>Definition</td>
</tr>
<tr>
<td>----------------------</td>
<td>-------------------------------------------------------------------------------------------------------------------------------------------</td>
</tr>
<tr>
<td>Reducing sugars</td>
<td>These are the chemically reducing sugars found in sugar solutions, the main ones being glucose and fructose.</td>
</tr>
<tr>
<td>Refractometer</td>
<td>An optical instrument used to determine brix concentration. The instrument measures the amount that a ray of light, passing from air, is refracted (bent) at the surface of a particular solution. This is then related to total dissolved solids in the solution.</td>
</tr>
<tr>
<td>Relative permeate</td>
<td>The difference between point permeate ICUMSA colour and original feed ICUMSA colour.</td>
</tr>
<tr>
<td>Retentate</td>
<td>The concentrate solution which does not pass through the membrane.</td>
</tr>
<tr>
<td>Retention</td>
<td>Retention is defined as the degree of separation of a particular species and is calculated from the analysis of feed and permeate solutions.</td>
</tr>
<tr>
<td>Secondary liquor</td>
<td>The decolourised liquor following ion exchange in the sugar refinery.</td>
</tr>
<tr>
<td>Seeding</td>
<td>This is the term describing the addition of crystal nuclei to a saturated syrup to induce crystal growth.</td>
</tr>
<tr>
<td>Solute loss</td>
<td>The ratio of mass of solute in the permeate to the mass of solute in the original feed.</td>
</tr>
<tr>
<td>Strike</td>
<td>The process of recovering a massecuite from a crystallisation pan.</td>
</tr>
<tr>
<td>Sugar colour</td>
<td>The complex collection of molecules which increases the light absorbance of a sugar solution at a particular wavelength.</td>
</tr>
<tr>
<td>Sweetwater</td>
<td>A dilute sucrose containing stream not actually part of the actual sugar refining process.</td>
</tr>
<tr>
<td>Syrup</td>
<td>Concentrated clear juice following evaporation in the mill.</td>
</tr>
<tr>
<td>Trans-membrane</td>
<td>The average pressure across the membrane from feed (retentate) side to permeate side.</td>
</tr>
</tbody>
</table>
Water recovery  The ratio of volume of permeate to volume of original feed.
# List of Abbreviations

<table>
<thead>
<tr>
<th>Abbreviation</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>ADF</td>
<td>Alkaline degradation products of fructose</td>
</tr>
<tr>
<td>CEA</td>
<td>Commissariat a l'Energie Atomique</td>
</tr>
<tr>
<td>CGE</td>
<td>Compagnie Generale d'Electrite</td>
</tr>
<tr>
<td>CGEC</td>
<td>Compagnie Generale d'Electroceramique</td>
</tr>
<tr>
<td>CSR</td>
<td>Colonial Sugar Refiners</td>
</tr>
<tr>
<td>DGU</td>
<td>3,4-dideoxyglucosulose-cnc</td>
</tr>
<tr>
<td>HMF</td>
<td>5-hydroxymethyl-2-furfural</td>
</tr>
<tr>
<td>HMW</td>
<td>High molecular weight</td>
</tr>
<tr>
<td>HPLC</td>
<td>High performance liquid chromatography</td>
</tr>
<tr>
<td>ICUMSA</td>
<td>International Commission for Uniform Methods of Sugar Analysis</td>
</tr>
<tr>
<td>IV</td>
<td>Indicator value</td>
</tr>
<tr>
<td>MW</td>
<td>Molecular weight</td>
</tr>
<tr>
<td>Ret</td>
<td>Retention</td>
</tr>
<tr>
<td>SASTA</td>
<td>South African Sugar Technologists Association</td>
</tr>
<tr>
<td>SCT</td>
<td>Societe des Ceramiques Techniques</td>
</tr>
<tr>
<td>Abbreviation</td>
<td>Full Form</td>
</tr>
<tr>
<td>--------------</td>
<td>-----------</td>
</tr>
<tr>
<td>SFEC</td>
<td>Société de Fabrication d'Éléments Catalytiques</td>
</tr>
<tr>
<td>SMRI</td>
<td>Sugar Milling Research Institute</td>
</tr>
<tr>
<td>SPRI</td>
<td>Sugar Processing Research Institute</td>
</tr>
<tr>
<td>UCLA</td>
<td>University of California, Los Angeles</td>
</tr>
<tr>
<td>USA</td>
<td>United States of America</td>
</tr>
<tr>
<td>USSR</td>
<td>The former Union of Soviet Socialist Republics</td>
</tr>
<tr>
<td>VHMW</td>
<td>Very high molecular weight</td>
</tr>
<tr>
<td>VHP</td>
<td>Very high pol</td>
</tr>
<tr>
<td>WR</td>
<td>Water recovery</td>
</tr>
</tbody>
</table>
Chapter 1

Introduction

Refined white sugar, an essential ingredient in our everyday lives, is produced by Hulett Refineries Limited. However, the sucrose making up the sugar crystals, has a history that goes back much further than the sugar refinery.

The sugar industry is well established and has its own characteristic terminology. The particular terms are defined in the glossary.

Sucrose originates in sugarcane, a giant grass of the genus *Saccharum*. The sugar mills receive cane stalks, which have had their roots, leaves and tops removed, from the growers. The growers are paid according to the sucrose content of the cane they produced. The stalks are then prepared for sucrose extraction by being cut and shredded at the front end of the sugar mill (Figure 1.1).

Extraction involves the separation of the sugar juice from the cane-fibre by milling and/or diffusion. Because of the high water retention of sugarcane, the juice in the cane-fibre is diluted by addition of water or *thin juice* (a dilute sugar solution). The milling extraction process involves crushing the cane-fibre between a set of rollers to *squeeze* out the diluted juice. The diffuser extraction process consists of an enclosed carrier through which a bed of prepared cane is slowly dragged. Large volumes of water are sprayed onto the bed surface to effectively flush out the sucrose bearing juice from the cane-fibre.

Following the extraction process, the juice requires purification and clarification. The first step involves the screening of the juice to remove any fibrous material prior to the clarification reactors. The purpose of clarification is to produce a clear juice that is neutral, light in colour and free of suspended matter. The process involves the addition of milk-of-lime (calcium hydroxide slurry) which reacts with the naturally occurring phosphates in the juice to produce a tri-calcium phosphate precipitate. Impurities and suspended particles occlude within the precipitate and become trapped as the precipitate compacts and settles. The settled precipitate, referred to as *mud*, is pumped out of the clarifier vessels and filtered. The filtrate is recycled while the retained filter cake is used as a soil conditioner.
Figure 1.1: Simplified flow diagram of the sugar production process from sugarcane to refined sugar.
The clarified product, *clear juice*, is *briised up* (concentrated), from 11 to 65% total dissolved solids in the multiple effect evaporators. The evaporators boil off water under vacuum. The syrup (concentrated juice) is sent to the vacuum pans for *boiling* (crystallisation).

The function of the pans is to grow crystals in as many steps as may be required to maximise the amount of sugar recovered. The resulting mother liquor is termed *molasses*. The pans are seeded to induce crystal growth in the saturated syrup. The *massecuite* (crystal/molasses mixture) is struck from the crystallisers and centrifuged to separate the crystals which are then dried in the dryers. The dried product constitutes *VHP* (very high pol) sugar and has an average apparent sucrose content (pol) usually of about 99.3% by mass [Pillay (1990)].

VHP sugar is sent directly to the sugar refinery or is stockpiled at the South African Sugar Association (SASA) sugar terminals on Maydon Wharf, Durban harbour.

The goal of a cane-sugar refinery is to remove all non-sugars from raw, VHP sugar crystals as far as is commercially possible. Although the VHP sugar is about 99.3% sucrose when it reaches the refinery from the various sugar mills, it is still highly coloured and unsuitable for the local and export markets. It therefore undergoes a series of clarification and decolourisation processes to remove the remaining impurities.

Because the majority of the non-sugar impurities are coloured, it is common practise to use colour as a measure of the level of impurity of a sugar solution. The term *sugar colour* refers to that complex collection of molecules which increases the light absorbance of a sugar solution at a particular wavelength. The ICUMSA (International Commission for Uniform Methods of Sugar Analysis) procedure is the standard method of sugar colour analysis in the sugar industry.

The first sugar refining process is the *raw sugar melter* where the VHP sugar is dissolved using refinery *sweetwater* and make-up water (Figure 1.1). Sweetwater is the general term used to define dilute, sucrose-containing recycle streams not part of the actual colour removal process.

The raw liquor from the melter is pumped to the saturation vessels for clarification by the process of carbonatation. During carbonatation, boiler flue-gas is bubbled through a mixture of raw sugar liquor from the melter and milk-of-lime (calcium hydroxide slurry) which was added to the stream prior to the reactor. The calcium hydroxide reacts with the carbon dioxide in the flue-gas to form a calcium carbonate precipitate. Impurities occlude within the precipitate, thereby clarifying the raw liquor.

The calcium carbonate *mud* is removed from the clarified raw liquor, referred to as brown liquor, in the auto-filters and is sent to the mud tank. The brown liquor is sent for decolourisation in the ion exchange plant. Here, the anionic colourants are adsorbed by the ion exchange resin and displace
chloride ions from the active sites in the resin matrix. The decolourised ion exchange product (secondary liquor) is sent to the evaporators for brixing up (concentration), by evaporation of water, prior to crystallisation in the vacuum pans. Up to four crops (crystallisation stages) of sugar are boiled in the pans. The crystals are separated from the molasses by centrifuging.

The final molasses may be boiled to produce sugar crystals that will be remelted, recycled to raw house syrup, or sold as a by-product. The four separate crops of sugar are dried before being mixed together to produce the final commercial refined sugar product. This is then conditioned (further dried) to prevent any possible caking of the packaged product.

1.1 The Recycle of Impurities to The Melter

The raw sugar melter is the one process in the sugar refinery where impurities, or non-sugars, are returned to the sugar solution. This is due to the highly coloured nature of the recycled refinery sweetwater used for dissolving the VHP sugar. The vast majority of recycled sweetwater is produced by the Johnson filter presses and is termed Johnson sweetwater. The origin of Johnson sweetwater is described in Section 1.2.

It is important to note that the various recycled sweetwaters are comprised of rejected, off-spec materials which have a high concentration of non-sugars and a low concentration of sucrose.

Some of the non-sugars contained in the Johnson sweetwater stream are similar to those in the incoming raw sugar. However other non-sugars, often colour bodies, have been physically changed and made more intractable by their initial pass through the refinery. These non-sugars are returned to the start of the refining process effectively doubling, at least, their demand on the refining processes.

In a study by the Sugar Processing Research Institute (New Orleans, USA) it was found that, in general, 24 to 59% of the colour load in melt liquor comes from the recycle of various sweetwaters and remelt sugars [James et al. (1986)]. Furthermore, it has been reported that the colour of melt liquor has been frequently observed to be higher than that of washed raw sugar and that, on average, 20 to 30% of melt liquor colour was contributed either by colourants in the melter sweetwater or by colour generated by heat in the melter [Clarke et al. (1987)]. Experiments by Godshall et al. [1988] confirm that an increase in both high molecular weight colourant and polysaccharide colourant occurs in the melt liquor due to recycled sweetwaters.

In the course of this investigation it was estimated that the average increase in ICUMSA colour load to the melter at Hulett Refineries, due to Johnson sweetwater, can be up to 31% based on weekly average quality control data from April 1991 to October 1993.
It is clear that recycled Johnson sweetwater contributes a significant amount to the colour load in the melter and that this problem is not specific to Hulet Refineries. This increase in colour load in the melter due to Johnson sweetwater increases the colour load to the decolourisation processes following the melter - reducing their efficiency and ultimately the efficiency of the entire sugar refinery. The removal of colour bodies from the Johnson sweetwater recycle stream will theoretically reduce colour and result in more efficient decolourisation in the ion exchange process and the crystallisation pans. Also, it is possible that savings will be experienced with regard to raw materials such as ion exchange resin and regenerant.

The objective of reducing the colour load from recycled Johnson sweetwater would be the production of refined sugar with a lower average colour content than is presently being achieved at Hulett Refineries.

Johnson sweetwater poses a problem in that, although it is not a product stream *per se*, it still has some intrinsic value due to its sucrose content and cannot simply be discarded. From an economic point of view, the melting of raw sugar in high quality sweetwater is correct and is general practice in sugar refining. However, little attention has been paid to the merits of improving the quality of this sweetwater prior to the melter [James et al. (1986)]. To date it has been considered to be uneconomic to devote a colour removal plant, based on existing sugar decolourisation processes, specifically to the decolourisation of Johnson sweetwater. However the strive for higher efficiency in sugar refining and the strive to produce higher quality refined sugar for the local and export markets has prompted the investigation into methods for the decolourisation of Johnson sweetwater.

The science of membrane separation technology offers an alternative colour removal process to those currently being employed by the sugar refinery.

### 1.2 The Origin of Johnson Sweetwater

As mentioned above, sweetwater is the term given to dilute, sucrose-containing streams not part of the actual sugar refining process. It is normally generated by the washing of various stages in the refinery to recover sucrose and contains a high concentration of non-sugars. The vast majority of sweetwater arises from the filtrate and wash product of the Johnson filter presses which, when mixed together in the Johnson Sweetwater Tank, make up the Johnson sweetwater stream.

The filter cake retained by the Johnson presses is the unwanted by-product of the carbonatation clarification process. The calcium carbonate slurry, removed by the auto-filters following carbonatation, is sent to the mud tank prior to being filtered in the Johnson presses where the solid calcium carbonate is recovered as a filter cake. The filtrate from the Johnson presses constitutes the majority of Johnson sweetwater.
Once fully loaded, the Johnson presses are flushed with hot water to recover the sucrose contained within the filter cake interstices and adhering to the crystal surfaces of the filter cake. The sucrose enriched product of this hot wash makes up the remainder of the Johnson Sweetwater.

Johnson sweetwater from the presses is pumped to the Johnson Sweetwater Tank prior to being sent either directly to the High Grade Sweetwater Tank or to the Pan-house Melter for dissolving reject sugars from the crystallisation pans. The dissolved reject sugar stream from the Pan-house Melter is pumped back to the High Grade Sweetwater Tank. Sweetwater from this tank, refinery sweetwater, is recycled to the Raw Sugar Melter for dissolving the VHP sugar - completing the Johnson sweetwater recycle system. The Johnson sweetwater flow system is depicted graphically in Figure 1.2.

![Flow diagram of the Johnson sweetwater generation and recycle system.](image)

Johnson sweetwater, like all sugar solutions, is a highly degradable stream. Degradation takes the form of sucrose inversion and/or colour formation. Colour formation is often linked to inversion and degradation of the resulting reducing sugars.
The inversion of sucrose is dependent on (i) time, (ii) temperature and (iii) degree of acidity. The longer a particular sugar solution is held, the higher the temperature and the lower the pH, the greater the rate of sucrose inversion. Inversion involves the acid catalysed splitting of the sucrose molecule to glucose and fructose (reducing sugars). The fructose molecule forms colour precursors under conditions of high temperature and pH.

The degradation of Johnson sweetwater, and sugar solutions in general, due to colour formation is described extensively in Section 2.2.3. The cause of colour formation is the reactions which take place between sucrose, the reducing sugars and the non-sugars present in the Johnson sweetwater solution. The rate of colour formation increases with increasing temperature and pH of the solution. Alkaline degradation products of fructose (ADF) are formed by the reaction of fructose with colour precursors in the sugar refinery. Melanoidins are formed when the Maillard reaction products of the reducing sugars with amines, amino acids and proteins, rearrange to form a mixture of dark polymers. Melanins result from the high temperature oxidation of phenolic compounds, while caramel are formed by the thermal degradation of polyhydroxyl-carbonyl compounds in the absence of amino nitrogen compounds.

1.3 The Nature of Ultrafiltration

Ultrafiltration is a relatively new separation technique using a selective membrane to fractionate a mixture of solutes.

The definition of a membrane is not a simple one and has been the subject of much debate among membrane researchers. Most agree that the definition of a membrane should be based on the membranes function rather than its physical properties and, as the functions of the membrane broaden, so too must the definition of the membrane.

The following definition was compiled from several definitions listed by Lonsdale [1989]:

A membrane is a thin permeable barrier, interposed between two phases, which offers varying degrees of selectivity to the passage of different constituents, as a function of their specific transport properties, under the influence of a driving force.

The science of membrane separation has gained popularity since the development of the first asymmetric membranes by Loeb and Sourirajan in the late 1950’s at the University of California, Los Angeles (UCLA) [Lonsdale (1987)]. The original asymmetric membranes were made from cellulose acetate and were designed for desalination applications. They consisted of a very thin, dense retention layer on the outer surface with the remainder of the membrane consisting of a finely porous substrate acting as a support for the thin retention layer.
Pressure driven industrial membrane processes can be divided into three categories based on their size separation characteristics. Other membrane processes such as dialysis and electrodialysis utilise driving forces such as concentration differences and electric potential differences. The pressure driven membrane separation categories are described as follows:

- **Ultrafiltration**

  Ultrafiltration technology is a membrane filtration process with the ability to continuously separate two or more components from a fluid stream. The membrane acts as a selective barrier, retaining certain solutes while allowing the passage of others, resulting in the enrichment of either the retentate or the permeate in one or more components of the process fluid. Due to their property of selective retention, ultrafiltration processes are more versatile than reverse osmosis processes, described below, and can be used to purify, concentrate and fractionate molecules or fine colloidal suspensions.

  Ultrafiltration membranes retain molecules or particles in the range 0.002 to 0.02 μm. From a molecular weight point of view, ultrafiltration retains particles larger than 500 daltons [Gekas (1988)]. Hence, all suspended particles are retained by ultrafiltration, including bacteria and viruses.

  Nanofiltration is a relatively new category of membrane processes designed to fill the gap between reverse osmosis and ultrafiltration. Nanofiltration membranes are generally charged and retain solutes of about 0.001 μm. They are designed to retain particles, colloids, macromolecules and dissolved polyvalent salts.

- **Reverse Osmosis**

  Reverse osmosis is a dewatering process ideally retaining all solute molecules other than water itself. A reverse osmosis membrane is designed to retain particles, colloids, macromolecules and dissolved monovalent salts sized from 0.0001 to 0.002 μm [Gekas (1988)].

- **Microfiltration**

  Microfiltration processes are designed to retain suspended particles in the micron range from about 0.02 μm to about 10 μm [Gekas (1988)]. Microfiltration can be used to continuously separate solid particles from dissolved substances.

  Filtration of particles larger than 10 μm requires conventional depth or media filters where the
particles are retained within the structure of fibres making up the filter cloth or medium. The size ranges of the various classes of pressure driven membrane separation technology are depicted in Figure 1.3.

![Diagram of Particle Size Retention Ranges](image)

**Figure 1.3**: Particle size retention ranges for conventional filtration, microfiltration, ultrafiltration and reverse osmosis based on the size retention ranges in Gekas [1988].

Particular membranes of the above classes can be further classified according to the following criteria:

- **The membrane material, which may be**
  - organic (polymeric)
  - inorganic e.g. porous ceramic or carbon
  - liquid

- **The criteria for retention by the membrane, based on**
  - the size of the membrane pores
  - the shape of the membrane pores
  - the chemical composition of the membrane
  - the physical state of the membrane

Most ultrafiltration applications operate under cross-flow filtration conditions as opposed to dead-end conditions. Cross-flow utilises the shearing effect, caused by the flow of the feed solution parallel to the retention surface, to prevent the formation of a filter cake and limit the blocking of the membrane pores by the solute molecules. This is in contrast to dead-end filtration where flow is perpendicular to the
retention surface resulting in the rapid formation of a flux limiting filter cake. The difference between cross-flow filtration and dead-end filtration is depicted graphically in Figure 1.4.

![Cross-flow Filtration and Dead-end Filtration Diagrams](image)

**Figure 1.4**: Graphical representation of the difference between cross-flow filtration and dead-end filtration [Patel (1990)].

1.4 The Ultrafiltration of Johnson Sweetwater

In order to achieve the goal of decolourising Johnson sweetwater using ultrafiltration, a membrane is required which will pass the sucrose in the feed stream while retaining the colourants.

It has been reported by Patel [1992] that a colour retention of 60% is possible using a Carbosep 10 000 dalton molecular weight cut-off membrane for the ultrafiltration of refinery sweetwater from Hulett Refineries. Strohwald [1990] observed a colour retention of 43% using a 20 000 dalton molecular weight cut-off, polymeric, ultrafiltration membrane for the ultrafiltration of refinery sweetwater. The ultrafiltration of raw sugar was investigated by Mak [1991] who observed a maximum colour retention of 80% using a 10 000 dalton molecular weight cut-off, hollow-fibre, membrane module.

Concentrations of high molecular weight colour in white sugar crystals are dependent on the starting raw sugar composition and extra input load from remelt sugars and dilution sweetwaters. It has been
found that colour of size greater than 20 000 daltons comprises on average 30 to 50 % of colour in raw sugar [Godshall et al. (1988)].

It is evident, from the above experimental work, that sugar colour retention is achievable using ultrafiltration membranes. It is not clear what degree of retention is required to be achieved to benefit the sugar refinery. Simply improving the colour of the Johnson sweetwater is meaningless if the membrane only retains those colourants which are effectively and easily removed by the ion exchange and crystallisation decolourisation processes. However, if the membrane retains those molecules which are not removed by ion exchange, which foul the ion exchange resin or which are occluded during final crystallisation, the ultrafiltration of Johnson sweetwater will be beneficial irrespective of the degree of colour retention based on ICUMSA colour.

1.5 Objectives of the Investigation

The objective of the investigation was to research the various requirements for the ultrafiltration of Johnson sweetwater and to set up a series of experiments designed to assess the effectiveness of ultrafiltration for the decolourisation of Johnson sweetwater.

To achieve the above, the project was divided into the following investigations to:

- survey the available membrane technology and to select a suitable membrane based on the available literature.

- assess the effectiveness of the membrane for the decolourisation of Johnson sweetwater. The variables assessed were ICUMSA colour retention, brix retention and permeate flux decline during membrane fouling.

- assess the effectiveness of the membrane for the decolourisation of H1 refined sugar, affinated H1 refined sugar, affination wash liquor and raw VHP sugar.

Affinated refined sugar is sugar that has been washed, using a saturated sugar solution, to remove the colour associated with the crystal surface film. Affination wash liquor is the liquor resulting from the affination of refined sugar.

- assess the quality of the Johnson sweetwater ultrafiltration permeate by investigating the colour transfer from the Johnson sweetwater and ultrafiltration permeate solutions to their respective sugar crystals by pilot-pan boiling.
Chapter 2

Literature Review

This chapter contains the findings of a review into the literature relating to various aspects of sugar chemistry, sugar refining and ultrafiltration technology.

The first part of the review investigates the chemistry of sugar and its associated colour. This includes studies of the various types of sugar colour, the influence of the various types of colour in the sugar refinery and the colour removal processes in the sugar refinery. It is divided into the following sections:

2.1 The Structure of Refined Sugar
2.2 Colour in the Sugar Refinery
2.3 The Distribution of Non-sucrose in Sugar Following Crystallisation
2.4 The Ion Exchange Process.

The second part of the review investigates aspects of ultrafiltration technology, especially pertaining to inorganic membranes. Inorganic membranes were investigated due to their ability to tolerate high process temperatures and a wide range of pH values. The temperature of the Johnson sweetwater is typically between 70 and 80 °C. The review is divided into the following sections:

2.5 The Historical Development of Membrane Technology
2.6 The Development of Inorganic Membranes.
2.7 Relevant Ultrafiltration Theory

2.1 The Structure of Refined Sugar

Common refined table sugar produced by the sugar refinery is D-sucrose, the pure disaccharide α-D-glucopyranosyl-β-D-fructofuranoside. The most common source of sucrose in South Africa is sugar cane which is defined as a tall grass of the genus *Saccharum*. More commonly, sugar cane is produced from hybrids which are the progeny of a number of *Saccharum* species [SASTA (1985)].
Sucrose is a disaccharide falling under the broader definition of carbohydrates. It has the chemical formula C₁₂H₂₂O₁₁. On hydrolysis, by dilute aqueous acid or by the action of the enzyme invertase, sucrose yields equal amounts D-(−)-glucose and D-(−)-fructose but, in contrast to most monosaccharides and disaccharides, sucrose is not a reducing sugar. This means that the reducing groups in both the monosaccharide components must be involved in the glycosidic linkage between the two sugars. Thus the C-1 and C-2 carbon atoms of the glucose and fructose moieties must be covalently linked by a glycoside bond [Morrison and Boyd (1987)].

The structure of sucrose is presented in Figure 2.1 while those of the reducing sugars, glucose and fructose, are presented in Figure 2.2 and Figure 2.3 respectively.

![Figure 2.1: The molecular structure of sucrose (Moeller et al. (1984)).](image)

![Figure 2.2: The molecular structure of glucose (Moeller et al. (1984)).](image)
Figure 2.3: The molecular structure of fructose [Moeller et al. (1984)]
2.2 Colour in the Sugar Refinery

The term sugar colour is defined as that complex collection of molecules which contribute to the increased light absorbance of sugar solutions at a particular wavelength.

In sugar refining, colour is conveniently used as a measure of the level of non-sugars, or purity, of a sugar solution due to the fact that most non-sugars are coloured. The ICUMSA method of colour measurement is generally used in the sugar industry.

\[
\text{ICUMSA Colour} = \frac{\text{Absorbance (at 420 nm) x 10000}}{\text{Cell Length (mm) x Concentration of Total Solids (g/l cm}^2\text{)}}
\]  

(2.1)

The ultimate goal of a cane-sugar refinery is to remove all non-sugars from raw VHP (very high pol) sugar crystals. VHP sugar is the raw sugar supplied by the sugar mills. Removal of colour constituents rather than colour masking, by bleaching or pH adjustment, is practised in the sugar refinery. Hence, a knowledge of the constituents that are removed would be beneficial to the sugar refiner and assist in the understanding of the various decolourisation processes taking place. Knowledge of the different types of sugar colour and their interactions in the refinery decolourisation processes could explain the varying results achieved when processing sugars of similar colour and quality factors.

The process of ultrafiltration selectively retains certain types of molecules, with large molecules more likely to be retained than small molecules. It would be beneficial to predict the range of molecules making up the retained colourant species and the range of molecules making up the non-retained colourant species which permeate through the membrane. The composition and relative quality of the retentate and permeate streams could then be predicted.

Sugar colour is made up of a complex mixture of molecules some permanently coloured and some only becoming coloured on exposure to specific refinery conditions e.g. benzoic acid derivatives. In recent years there has been much research into the composition and chemical nature of sugar colourants.

This section summarises the findings of a literature survey into the origin, effects and removal of the various sugar colourant types.

2.2.1 The Characterisation of Sugar Colour

Since sugar colour does not consist of discrete, easily characterised components, it is convenient to divide it into the following categories based on origin and basic chemical type:
**Sugarcane Plant Derived Colour**
- Phenolic acid colour
- Flavonoid colour

**Factory Produced Colour**
- Melanoidin Colour
- Melanin Colour
- Caramel colour
- Colour associated with the alkaline degradation products of sucrose

**Colour Associated with Polysaccharide Compounds**

Note: The term sugar colourant, when applied to individual molecules, is not limited to molecules which are actually coloured but also applies to colour precursors which will react under refinery conditions to produce colour.

Molecular weight and pH sensitivity are two additional methods which may be used to distinguished between the different classes of sugar colourant.

### 2.2.1.1 Classification of Colour by Molecular Weight

Generally speaking, polymeric colourants have the highest molecular weight (MW) (MW greater than 25 000 daltons), followed by intermediate substances such as degradation products (MW from 10 000 to 25 000 daltons) and flavonoids (MW less than 10 000 daltons). A further class of sugar colourant is high molecular weight (HMW) colourant (MW greater than 100 000 daltons). HMW colourant is generally associated with polysaccharide material.

### 2.2.1.2 Classification of Colour by Degree of pH Sensitivity

At a pH value of 4.0 most sugar cane colourants are not ionised and are relatively lightly coloured. However, at a pH value of 9.0 ionisation of the colourants is almost complete, the colourants are anionic and are highly coloured.

Plant derived pigments have the greatest sensitivity to changes in pH due to the molecular rearrangements that occur under alkaline conditions, to give a series of conjugated double bonds. Conjugated double bonds are the structural requirement for visible colour. These rearrangements also occur in non-coloured phenolics as they react with ferric or ferrous iron to form coloured complexes.
It is the phenolic acid and flavonoid compounds that are mainly responsible for the change in sugar colour with pH making it impossible to measure sugar colour reproducibly without constant pH. The relative quantity of phenolics and flavonoids is determined by comparing the indicator value (IV) of different sugars and sugar solutions. The IV is defined as the ratio of sugar colour at a pH value of 9.0 to the colour at pH 4.0:

\[
IV = \frac{Colour \text{ at pH } 9.0}{Colour \text{ at pH } 4.0}
\]

If the IV is greater for a particular batch of sugar crystals, then the relative percentage of phenolics and flavonoids is greater in that particular batch. Since the phenolics and flavonoids are easier to remove than the other types of sugar colourant, it is a good indication that the sugar will decolourise satisfactorily. Sugars with low indicator values have high levels of amine and caramel colour.

Reported indicator values of the various classes of colourants vary. Table 2.1 lists these differences in reported IV and gives a combined result.

<table>
<thead>
<tr>
<th>Colourant type</th>
<th>IV [Bardwell et al. (1985)]</th>
<th>IV [Clarke et al. (1984)]</th>
<th>IV (Combined)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Melanoidins</td>
<td>1.2 to 1.6</td>
<td>1.0 to 1.2</td>
<td>1.0 to 1.6</td>
</tr>
<tr>
<td>ADF</td>
<td>2.0 to 2.5</td>
<td>1.5 to 3.2</td>
<td>1.5 to 3.2</td>
</tr>
<tr>
<td>Caramels</td>
<td>2.0</td>
<td>1.0 to 1.5</td>
<td>1.0 to 2.0</td>
</tr>
<tr>
<td>Phenolics &amp; flavonoids</td>
<td>5 to 14</td>
<td>5 to 14</td>
<td></td>
</tr>
</tbody>
</table>

ADF = alkaline degradation products of fructose

4.2.2 Sugar Colour Types - Sugarcane Plant Derived Pigment

Plant derived pigments are mainly phenolic or polymeric in nature and exist as glycosides attached to sugar residues in the cane plant. The phenolics of relevance to cane-sugar processing are phenolic acids and flavonoids. Other plant colourants such as anthocyanins, chlorophylls and carotenes exist in cane juice but are easily removed during processing.

Plant colourants tend to be charged, especially at high pH values and, if unreacted, are of low to mid molecular weight (less than 5 000 daltons). In general, phenolic and flavonoid colourants are more
easily removed by clarification and decolourisation processes than factory produced colourants. This is due to their low molecular weight and charged nature at refinery process pH values.

2.2.2.1 Phenolic Acid Colour

Common sugarcane plant derived phenolic acids are derivatives of benzoic and cinnamic acids. They do not occur as free acids, but as esters and glycosides with the free acid being formed by acid or alkaline hydrolysis. Non-removed phenolics in the refining process may react further with amino compounds or aldehydes in the refinery process to form higher molecular weight material with a lower charge distribution or density.

Phenolics are best removed by processes which utilise the charged nature of the compound e.g. ion exchange. Carbonatation has been found to remove up to 34 % of phenols [Godshall and Roberts (1982)].

Some phenolics are not actually coloured but react (usually with amines), complex with iron, or oxidise to form coloured compounds when exposed to the refinery process. Colour precursors such as reducing sugars, amino acids and other hydroxyacids and aldehydes, that are classed as simple phenolic compounds, are also sugarcane plant derived and combine with the non-coloured phenolics under refinery conditions to produce colour.

Colour Forming Reactions Of Phenolic Acids [Godshall and Roberts (1982)] :

(i) The formation of oxidised brown pigments :
These are produced by both enzymatic and non-enzymatic action involving free radical formation and random polymerisation leading to high molecular weight brown pigments.

(ii) Phenol-aldehyde condensation :
This mechanism involves a condensation between resorcinol and the acid decomposition products of sucrose to produce a red coloured compound.

(iii) Phenol-amine reactions :
Intensely red-brown and bright red products are formed from the reaction of quinones with amines. These are also condensation reactions which ultimately lead to polymeric brown or black pigments known as melamins.
(iv) **Reactions with metal ions:**
Ferric and ferric salts are most reactive towards phenols and organics containing o-dihydroxy groups. They react to form highly coloured compounds.

(v) **Enhancement of other reactions:**
Reactions between phenols and reactive aldehydes (e.g. furfural) during caramelisation (thermal degradation of sucrose) enhance and speed browning due to concurrent phenol-aldehyde reactions. Quinones, which are oxidised phenols, enhance the Maillard sugar/amino-acid browning reactions.

Some phenol compounds were isolated by Godshall and Roberts [1982] and are listed in Table 2.2.

<table>
<thead>
<tr>
<th>Table 2.2 : Phenolic compounds isolated by Godshall and Roberts [1982].</th>
</tr>
</thead>
<tbody>
<tr>
<td>Benzoic acid</td>
</tr>
<tr>
<td>Phenylacetic acid</td>
</tr>
<tr>
<td>Catechol</td>
</tr>
<tr>
<td>2-Methyl-benzoic acid</td>
</tr>
<tr>
<td>Acetyl salicylic acid</td>
</tr>
<tr>
<td>4-Methyl catechol</td>
</tr>
<tr>
<td>Acetyl formoin</td>
</tr>
<tr>
<td>2-Hydroxy-benzoic acid</td>
</tr>
</tbody>
</table>

Various phenolic cane colourants have been isolated using electrophoresis [Farber and Carpenter (1971), (1972)]. These are listed as derivatives of benzoic acid (Table 2.3), derivatives of cinnamic acid (Table 2.4) and derivatives of coumarin (Table 2.5).

![Figure 2.4: The basic structure of benzoic acid and associated derivatives [Farber and Carpenter (1971), (1972)]. See Table 2.3 for structures of R1, R2 and R3.](image-url)
Table 2.3: Benzoic acid derivatives and corresponding aldehydes relating to Figure 2.4 [Farber and Carpenter (1971), (1972)].

<table>
<thead>
<tr>
<th>Compound</th>
<th>$R_1$</th>
<th>$R_2$</th>
<th>$R_3$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Vanillic acid</td>
<td>OCH$_3$</td>
<td>H</td>
<td>OH</td>
</tr>
<tr>
<td>Vanillin</td>
<td>OCH$_3$</td>
<td>H</td>
<td>H</td>
</tr>
<tr>
<td>3,4-Dihydroxybenzoic acid</td>
<td>OH</td>
<td>H</td>
<td>OH</td>
</tr>
<tr>
<td>3,4-Dihydroxybenzaldehyde</td>
<td>OH</td>
<td>H</td>
<td>H</td>
</tr>
<tr>
<td>p-Hydroxybenzoic acid</td>
<td>H</td>
<td>H</td>
<td>OH</td>
</tr>
<tr>
<td>p-Hydroxybenzaldehyde</td>
<td>H</td>
<td>H</td>
<td>H</td>
</tr>
<tr>
<td>Syringic acid</td>
<td>OCH$_3$</td>
<td>OCH$_3$</td>
<td>OCH$_3$</td>
</tr>
</tbody>
</table>

Figure 2.5: The basic structure of cinnamic acid and associated derivatives [Farber and Carpenter (1971), (1972)]. See Table 2.4 for structures of $R_1$, $R_2$ and $R_3$.

Table 2.4: Cinnamic acid derivatives and corresponding alcohols and esters relating to Figure 2.5 [Farber and Carpenter (1971), (1972)].

<table>
<thead>
<tr>
<th>Compound</th>
<th>$R_1$</th>
<th>$R_2$</th>
<th>$R_3$</th>
</tr>
</thead>
<tbody>
<tr>
<td>p-Hydroxycinnamic acid</td>
<td>OH</td>
<td>H</td>
<td>H</td>
</tr>
<tr>
<td>Caffeic acid</td>
<td>OH</td>
<td>OH</td>
<td>H</td>
</tr>
<tr>
<td>4-Hydroxy-3-methoxycinnamic acid</td>
<td>OH</td>
<td>CH$_3$OCH$_2$OCH$_3$</td>
<td>H</td>
</tr>
<tr>
<td>4-Hydroxy3,5-dimethoxycinnamic acid</td>
<td>OH</td>
<td>OCH$_3$</td>
<td>OCH$_3$</td>
</tr>
<tr>
<td>Chlorogenic acid</td>
<td>OH</td>
<td>OH</td>
<td>H - Quinic acid ester</td>
</tr>
<tr>
<td>Coniferin</td>
<td>O - Glucose</td>
<td>OCH$_3$</td>
<td>H - Alcohol</td>
</tr>
</tbody>
</table>
Flavonoids are alkaline stable grass flavones and, in sugar cane, are derivatives of tricin, luteolin and apigenin. They form one of the largest class of naturally occurring phenolic compounds and are widely distributed in nature, mostly as their glycosides.

Because of their conjugated polyphenolic structure, many flavonoids possess colour with a high pH sensitivity. As a class, tricin based flavonoids are more pH sensitive than luteolin based flavonoids. Flavonoids can be classified as flavones, catechins, anthocyanins and others. These compounds contribute to colour either by being coloured themselves or by their involvement in colour forming reactions. Anthocyanins are the principle red, violet and blue pigments in plants, mostly found in flower petals and in fruits.

Australian sugar colour research had, up until 1985, concentrated on plant derived pigment of which flavonoids were believed to be the dominant contributors to colour in refinery process streams and products [Bardwell et al. (1985)]. Earlier estimates of their contribution to total colour suggested that flavonoids could be responsible for two thirds or more of the colour in the sugar refinery process streams [Smith, in : Clarke et al. (1987)]. This estimate was made on the basis of indicator value data. Bardwell et al. [1985], conclude that flavonoids alone cannot be responsible for the large increase in colour between pH 4 and pH 9 and that those estimates made by Smith, above, are inaccurate.
Consequently there must be other colourants, particularly factory formed colourants, which are sensitive to pH.

Using high performance liquid chromatography (HPLC), Bardwell et al. [1985] measured the concentration of flavonoid compounds relative to apigenin (a flavone of glycone). Many of the flavonoids in cane-sugar are known to be glycoside derivatives of apigenin and tricin. Fourteen flavonoids were identified of which thirteen were found to be glycosides or methyl ethers of apigenin, luteolin and tricin, and the other was tricin itself. Five of the fourteen were identified as major and represent at least 50 percent of all flavonoids in raw sugar that is rich in flavonoids, and considerably more in sugars with fewer total flavonoids present. The five major flavonoids identified were: iso-schafloside; schaftoside; swertisin; iso-orientin 7,3'-o-dimethylether; tricin 7-o-rhamnoseyl-o-galacturonile.

Paton [1987] found that the five flavonoids listed above may contribute up to 10% of the colour, measured at pH 7, of the particular raw sugar solution. It was estimated that the maximum contribution from all flavonoids could only be about double this. Thus the non-flavonoids may contribute as much as 75% of the colour of raw sugar at pH 7.

Hence, non-flavonoids contribute the major part of sugar colour at near neutral pH values. However flavonoids are still important, especially with regard to ion exchange processes, as they are only fully ionised at a pH value of 9. Refinery process pH values are usually about 8.0.

The structures of the 14 flavonoids identified by Bardwell et al. [1985] are presented in papers by Paton et al. [1987] and by Mabry et al. [1984]. Flavonoids have a skeleton built up from 15 carbon atoms and are composed of two phenolic nuclei connected by a three carbon unit. The general structure of flavonoids is presented in Figure 2.7 and the associated table (Table 2.6).

![Figure 2.7: The general structure of flavonoids (Paton (1987)]. See Table 2.6 for structures of R1, R2, R3, R4 and R5.
<table>
<thead>
<tr>
<th>Compound</th>
<th>R₁</th>
<th>R₂</th>
<th>R₃</th>
<th>R₄</th>
<th>R₅</th>
</tr>
</thead>
<tbody>
<tr>
<td>Apigenin</td>
<td>H</td>
<td>H</td>
<td>H</td>
<td>H</td>
<td>H</td>
</tr>
<tr>
<td>Luteolin</td>
<td>H</td>
<td>H</td>
<td>H</td>
<td>OH</td>
<td>H</td>
</tr>
<tr>
<td>Tricin</td>
<td>H</td>
<td>H</td>
<td>H</td>
<td>CH₃₀</td>
<td>CH₃₀</td>
</tr>
<tr>
<td>Apigenin 6-C-glucosyl-7-o-methyl ether (Swerpisin)</td>
<td>GLU</td>
<td>CH₃</td>
<td>H</td>
<td>H</td>
<td>H</td>
</tr>
<tr>
<td>Apigenin 6-C-glucosyl-8-C-arabinoside (Schaftloside)</td>
<td>GLU</td>
<td>H</td>
<td>ARA</td>
<td>H</td>
<td>H</td>
</tr>
<tr>
<td>Apigenin 6-C-arabinosyl 8-C-glucoside</td>
<td>ARA</td>
<td>H</td>
<td>GLU</td>
<td>H</td>
<td>H</td>
</tr>
<tr>
<td>Apigenin 6,8-Di-C-glucoside (Vicemin)</td>
<td>GLU</td>
<td>H</td>
<td>GLU</td>
<td>H</td>
<td>H</td>
</tr>
<tr>
<td>Luteolin 6-C-glucoside (Isoorientin)</td>
<td>GLU</td>
<td>H</td>
<td>H</td>
<td>OH</td>
<td>H</td>
</tr>
<tr>
<td>Luteolin 6-C-glucosyl 7-o-methyl ether</td>
<td>GLU</td>
<td>CH₃</td>
<td>H</td>
<td>OH</td>
<td>H</td>
</tr>
<tr>
<td>Isoorientin-7,3'-O-dimethyl ether</td>
<td>GLU</td>
<td>CH₃</td>
<td>H</td>
<td>CH₃₀</td>
<td>H</td>
</tr>
<tr>
<td>6-Methoxyluteolin</td>
<td>CH₃₀</td>
<td>H</td>
<td>H</td>
<td>OH</td>
<td>H</td>
</tr>
<tr>
<td>Luteolin 8-C-glucoside (Orientin)</td>
<td>H</td>
<td>H</td>
<td>GLU</td>
<td>OH</td>
<td>H</td>
</tr>
<tr>
<td>Orientin-7,3'-O-dimethyl ether</td>
<td>H</td>
<td>CH₃</td>
<td>GLU</td>
<td>CH₃₀</td>
<td>H</td>
</tr>
<tr>
<td>Luteolin 6-C-glucosyl 8-C-arabinoside</td>
<td>GLU</td>
<td>H</td>
<td>ARA</td>
<td>OH</td>
<td>H</td>
</tr>
<tr>
<td>Tricin 7-o-rhamnosyl-o-galacturonide</td>
<td>H</td>
<td>Rha-Galur</td>
<td>H</td>
<td>CH₃₀</td>
<td>CH₃₀</td>
</tr>
<tr>
<td>Tricin 7-glucoside</td>
<td>H</td>
<td>GLU</td>
<td>H</td>
<td>CH₃₀</td>
<td>CH₃₀</td>
</tr>
<tr>
<td>Tricin 7-glucoside sulphate</td>
<td>H</td>
<td>GLU-SO₄</td>
<td>H</td>
<td>CH₃₀</td>
<td>CH₃₀</td>
</tr>
</tbody>
</table>

ARA = arabinoside, Rha-Galur = rhamnosylgalacturonide, GLU = glucoside

2.2.3 Sugar Colourant Types - Colour Produced in the Refinery

Even though the primary purpose of the sugar refinery is to remove colour bodies, some colour is produced during the sugar refining process due to the influence of specific operating conditions on various types of molecules.

Sucrose, like all organic compounds, is unstable and reacts under refinery conditions to form coloured compounds. Thus, even while the majority of colour is being removed by the refinery process, some colour molecules are being formed. The longer a liquor is held, and the higher the process temperature, the greater the fraction of refinery colourants produced and also the greater the sucrose loss and invert decomposition which will occur. Refinery formed colour may be generated under either acidic or basic conditions and by a number of different reactions.

* Acid Reactions :
Under acidic conditions, the predominant colour forming reactions in sugar solutions are through a degradation of the sucrose molecule by a process that includes fructose, 3,4-dideoxyglucosulose-3-ene (DGU) and 5-hydroxymethyl-2-furfural (HMF).

The first step is the inversion of sucrose to glucose and fructose, followed by further reaction of the reducing sugars which are inherently more reactive (or less stable) than sucrose. When fructose is heated at low pH values, two of the substances formed are cis-isomers and trans-isomers of DGU. These are immediate precursors of HMF which is a well known colour producing molecule.

There are many other intermediate products in the formation of DGU most of which are created by the Maillard reaction involving amines and fructose. Carpenter et al. [1974] conclude that there are 13 intermediates, or alternative routes, in the formation of DGU. None of the intermediate compounds are coloured, but all fall into the category of colour precursors.

**Basic Reactions**

Under alkaline conditions, the first step in the degradation of sugar solutions is the dehydration of the fructose moiety of sucrose. This is in contrast to the splitting of sucrose to glucose and fructose in the acid media case. The mechanism of fructose degradation in alkaline solution is highly complex and beyond the scope of this investigation.

The various classes of refinery produced colourants are presented below.

### 2.2.3.1 Melanoidin Colour

Melanoidins are formed when the Maillard reaction products of the reducing sugars with amines, amino acids and proteins, rearrange to form a complex mixture of dark polymers. Melanoidins only form if the mixture is subjected to heat. Low heat over long periods, as under storage conditions, can cause this type of colour formation.

The initial, colourless, stages of the reaction comprise the sugar-amine condensation and Amordi rearrangement. The intermediate stage consists of dehydration, fragmentation and degradation reactions producing colourless or yellow products. The final stage involves aldol condensation followed by aldehyde-amine polymerisation and formation of highly coloured heterocyclic nitrogen compounds [Shore et al. (1984)].
Melanoidins are usually negatively charged at refinery process pH values, but with diminishing charge as molecular weight increases. The charge can be reversed by acidification. Melanoidins are generally of high molecular weight.

In a survey done on Russian white sugar colourants, 22 amino acids were found of which 18 were identified. The principle colourants of Russian white sugar colourants were concluded to be melanoidins of molecular weight approximately 21,000 Daltons [Bugaenko et al. (1987)].

2.2.3.2 Melanin Colour

A sub-class of high molecular weight, uncharged compounds are called melanins. These are black enzymatic oxidation products of phenolics such as tyrosine (a monophenol) and dihydroxyphenylalanine (a polyphenol).

The colour formation depends on the enzyme, polyphenol-oxidase, and oxygen. Polyphenol-oxidase catalyses hydroxylation of monohydroxyphenols to ortho-dihydroxyphenols followed by oxidation of the latter products to ortho-quinones. The initial oxidation steps are followed by the formation of an aromatic ring system of the indole type which then reacts further by polymerisation, oxidation and partial loss of carbon dioxide to form the melanin complexes [Shore et al. (1984)].

Melanins can be removed during processing but are otherwise preferentially included in the sugar crystal during crystallisation. Granular activated carbon is the only process reported to be effective in removing uncharged high molecular weight melanins [Clarke et al. (1985)].

2.2.3.3 Alkaline Degradation Products of Fructose (ADF)

These are formed in the refinery under alkaline conditions. They are relatively uncharged and of medium to high molecular weight (5,000 to 25,000 daltons). As mentioned in Section 2.2.3, the mechanism of alkaline degradation of fructose is complex and beyond the scope of this investigation, however, a proposed mechanism is presented in a paper by De Bruijn et al. [1986].

The following compounds were extracted from the fourth strike syrup of a refinery. They are all decomposition products of reducing sugars and may be colour precursors under refinery conditions [Roberts and Godshall (1980)].
Table 2.7: Alkaline degradation products of fructose
[Roberts and Godshall (1980)].

<table>
<thead>
<tr>
<th>Maltol</th>
<th>Catechol</th>
</tr>
</thead>
<tbody>
<tr>
<td>Acetic acid</td>
<td>4 Methyl Catechol</td>
</tr>
<tr>
<td>Propionic acid</td>
<td>Isobutyric acid</td>
</tr>
<tr>
<td>Butyrolactone</td>
<td>N,N-Dimethylformamide</td>
</tr>
<tr>
<td>Dimethoxy-methane</td>
<td>Furfuryl alcohol</td>
</tr>
<tr>
<td>Butyric acid</td>
<td>Valeric alcohol</td>
</tr>
<tr>
<td>Acetol</td>
<td>5-Hydroxymethyl furfural</td>
</tr>
</tbody>
</table>

2.2.3.4 Caramel Colour

Caramel colourants (caramels) are the thermal degradation products of polyhydroxy-carbonyl compounds, e.g. sucrose, which form in the absence of the amino nitrogen compounds.

Caramels are polymers and their formation can be catalysed by both acids and bases. Organic acids formed by the degradation of reducing sugars can also catalyse caramelisation. They are only slightly charged (negative) and the molecular weight increases with time and temperature development.

2.2.4 Sugar Colourant Types - High Molecular Weight Colour Associated With Polysaccharide

There are three major types of high molecular weight colourant associated with polysaccharide which are identifiable by gel permeation chromatography. The first type is called the very high molecular weight (VHMW) colourant and has a molecular weight greater than 1 000 000 daltons. This elutes as a doublet on a gel permeation chromatograph, is associated with both polysaccharide and a hazy turbidity and has a light yellow colour. The turbidity will pass through an 8 μm filter but not through a 0.45 μm filter. This peak is rarely missing from raw sugars. The second peak represents the bulk of the visible brown colour and shows a great deal of variability. The molecular weight of this second type of colourant lies in the range 100 000 to 500 000 daltons. The third peak is less well defined. Its molecular weight is in the range 20 000 to 50 000 daltons and the colour is light brown. The above three colourants are said to comprise, on average, 30 to 50% of the colour in raw sugar [James et al. (1986)].
Polysaccharides are generally classified as high molecular weight and, in raw sugar, can range up to several million daltons. The lower molecular weight range is not well defined, but may be in the range 5,000 to 10,000 daltons, with the fraction below 3,000 more properly classified as oligosaccharides.

The two major types of polysaccharide which come from sugar cane are starch and arabinogalactan. Total polysaccharides occur in much higher concentration levels than total starches or gums [Clarke et al. (1986a)].

Other soluble polysaccharides include sarkaran, from stale cane, and Roberts glucan. Roberts glucan is a lower molecular weight component of the indigenous sugar cane polysaccharide (MW less than 50,000 daltons) and is found in all cane. It appears similar in structure to amylopectin and is very soluble. It is only present in small amounts (0.01%) in cane. Glucan has no deleterious effects on processing [Clarke et al. (1986a)]. The influence of these two polysaccharides is minor and will not be considered further.

Polysaccharides decrease filtration rates and can block resin systems. If polysaccharides continue through to crystallisation, turbidity problems arise. White sugars with high levels of polysaccharide will retain moisture and store poorly [Clarke et al. (1984)].

Polysaccharide colourants of molecular weight greater than 1,000,000 daltons are not removed by refinery processes and are found in the white sugar crystal. This fraction of colourant contributes only a small proportion of colour to raw sugar but, because it is preferentially occluded during crystallisation, contributes a much greater proportion to refined or white sugar. It is probable that most of the high molecular weight polysaccharide material is not high molecular weight colourant per se, but comprises compounds formed by the interaction between polyphenolics and polysaccharides either through adsorption or covalent bonding during the refinery process. It is for these reasons that much research has been done in this field recently [Clarke and Godshall (1990)].

The indigenous sugarcane polysaccharide (ISP) is an arabinogalactan with glucuronic acid units and may be regarded as a soluble hemicellulose. Arabinogalactan is the non-sugar of greatest concentration in cane juice after organic and amino acids. In the plant ISP may serve to link phenolic and flavonoid residues to the insoluble cell wall glycans.

The glucuronic acid units account for the negative charge of ISP at high pH values. ISP has a molecular weight ranging from 100,000 to 300,000 daltons but can reach up to 1,000,000 daltons [Clarke et al. (1986a)].

At temperatures between 85 and 95 °C the ISP is soluble [Roberts et al. (1978)]. At room temperatures, substituted ISP is in colloidal suspension.
There are two possible structures of the colourant polysaccharide complex:

**In the first case**, phenolic compounds such as substituted hydroxybenzoic acids, which are covalently linked to the carbohydrate backbone of cell wall polysaccharides in the growing plant, react during processing to form coloured substituents while remaining part of the polysaccharide structure. These coloured complexes are shown to be of very high molecular weight (VHMW) (molecular weight greater than 1 000 000 daltons) and are preferentially retained throughout processing, entering the final sugar crystal [Godshall and Clarke (1988)].

Indigenous sugarcane polysaccharides can be cross linked by small substituted phenolics. An example is ferulic acid which is a pale yellow compound and has been shown, upon inclusion in refined sugar crystals, to produce rapid yellowing and darkening of the crystals. The ferulic acid ester linkage is less easily hydrolysed than natural glycosidic linkages, non-glycosidic covalent linkages and hydrogen bonds and remains attached to the backbone of the polysaccharide even when the polysaccharide is degraded into smaller units. The natural linkages are less likely to withstand the high process temperatures and pH values experienced in the factory and are therefore more easily broken down. Ferulic acid is always observed in raw unrefined sugars [Clarke et al. (1988)].

Ferulic acid is not the only phenolic compound that has been found in these cell wall complexes. Others compounds include - coumaric acid, vanillin, p-hydroxybenzaldehyde and syringaldehyde. Several of these, especially ferulic acid, can dimerise to a dehydroxy-ferulic acid. The dimer has more intense colour at a higher wavelength in the visible range than the monomer. It is possible that ferulic acid (or another phenolic acid) carried into the sugar crystal by the polysaccharide complex, dimerises as time passes and causes colour increase in the crystal [Clarke and Godshall (1990)].

**In the second case**, the colourant-polysaccharide complex arises from the cross linking of acidic polysaccharides (e.g. ISP) with lignin. Less is known about this type of complex although there is evidence of bonding, again through an ester linkage, but in this case through the acid group on the polysaccharide [Clarke et al. (1988)].

Charged sites on the ISP would be expected to be effectively adsorbed onto anion exchange resins, but in practise this is not the case. This is due to the resin sites, capable of holding such large molecules, becoming rapidly saturated with respect to polysaccharides.

Carbonatation is relatively effective in removing polysaccharides from unrefined liquor owing to the large polysaccharide molecules showing a tendency to be occluded in the calcium carbonate crystal during liming. Also, temperatures are generally lower in the carbonatation process thereby decreasing
the amount of dissolved polysaccharide. Press filtration after carbonatation is known to take out macromolecules.

Good crystallisation and less recycle of impurities will lower polysaccharide levels in the refinery [Roberts and Godshall (1978)].

The total polysaccharide level in a raw sugar is important for the following reasons [Godshall and Clarke (1988)]:

- High molecular weight colourant changes structurally throughout the refining process to a higher average molecular weight compounds.
- Very high molecular weight colour is associated with polysaccharides.
- Very high molecular weight colour is preferentially retained throughout the refining process and is not removed by the decolourisation operations.
- Very high molecular weight colour is increased by recycling of sweetwater and remelt sugars.
- Very high molecular weight colour preferentially gets included in the sugar crystal.

2.2.4.1 The Structure of the Indigenous Sugar Cane Polysaccharide

Indigenous sugarcane polysaccharide arabinogalactans were found to be chromatographically homogeneous with molecular weights of about 110 000 daltons (referenced to B-512 dextran) [Blake and Clarke (1984)]. The molecular weights of the more highly branched arabinogalactans show little correlation with the more linear dextrans.

Overall, the ISP can be categorised as a 3,6-type polysaccharide possessing a framework of 1,3-β-D-galactopyranose residues to which galactosyl and arabinosyl side chains are attached at position 6. They may also carry other less abundant monosaccharides such as L-rhamnopyranose, D-xylopyranose, D-rhamnopyranose, D-glucopyranose and D-gluconuric acid, usually as terminal substituents [Blake and Clarke (1984)].

2.2.5 Sugar Colourant Types - Dextrans

Although not classed as colourants, dextrans constitute undesirable non-sugars in the process streams. Dextrans are formed in damaged or diseased cane and in cane which has been left to lie through the off season, resulting in microbial infections.

Dextran are usually of high molecular weight (greater than 20 000 daltons) and, although they can be broken down in the refining process, may be expected to have an average molecular weight higher than
those in raw sugar. Dextran concentration has been found to increase in lower grade sugars [Clarke et al. (1986b)].

Carbonatation has been found to be the only significant dextran removing process especially with regard to the low molecular weight dextrans.

Sweetwaters are known to be potential sources of dextran production, especially if maintained below operating temperatures [Clarke et al. (1986b)].

2.2.6 The Influence of Colour in the Refinery

The removal of colourants generally follows one or a combination of four mechanisms. These can be summarised as follows:

• Adsorption, where the colour bodies are trapped into a crystal or porous adsorbent.

• Adsorption through hydrophobic bonding, e.g. aromatic colour removal by carbon.

• Ion exchange, where acidic colourant is retained by resin in an anionic form.

• Precipitation followed by occlusion and/or adsorption via van de Waals forces.

These mechanisms occur during carbonatation, ion exchange and crystallisation.

2.2.6.1 Affination and Melter

The melter is the one operation in the refinery where non-sugars are put back into the process sugar solution. Most refineries recycle a certain amount of remelt sugar back to the melter, and all use high grade sweetwaters as melter water.

These streams not only contain sugar, but also non-sugars, some similar to those in the incoming raw sugar, and others which have been physically changed and made more intractable by their initial pass through the refinery. These non-sugar outputs from other parts of the refinery are put back at the start of the refining process effectively doubling, at least, the work done on them by the refinery processes. From an economic point of view, the practise of melting sugar in high quality sweetwater is correct, and is general practise internationally. However, little attention has been paid to the merits of improving the quality of this sweetwater prior to the affination melter [James et al. (1986)].
2.2.6.2 Carbonatation

Carbonatation involves the addition of lime to the raw liquor from the melter. This is followed by the bubbling of carbon dioxide through the lime/liquor mixture. The lime reacts with the carbon dioxide to produce a calcium carbonate precipitate. Non-sugar impurities are trapped within the precipitate thereby clarifying the liquor.

The many variables over the carbonatation stage include melt liquor composition, retention time and temperature. It is generally known that coloured phenolics can be generated during clarification, an important reason for keeping residence time and temperatures low. As a result, there may be simultaneous removal and generation of phenolic colour in the carbonatation stage [Clarke et al. (1984)].

Carbonatation has a high affinity for removing polymeric colourants and amino nitrogen colourants. However, it removes few low molecular weight pigments. Alkaline degradation products of fructose are constantly formed during carbonatation [Kennedy and Smith (1976)].

Carbonatation has been found to remove up to 34% of phenols [Godshall and Clarke (1982)]. Also, carbonatation is the only refining unit operation found to achieve significant dextran removal [Fowler (1981)]. Over-carbonatation tends to desorb any pH sensitive colourants which were previously adsorbed by the calcium carbonate precipitate.

2.2.6.3 Ion Exchange

The process of ion exchange is dealt with extensively in Section 2.4 of this chapter.

The removal of factory produced polymeric by ion exchange is poor but is enhanced at low feed pH values to the detriment of the removal of other colourants. Good removal of low molecular weight charged compounds is achieved. Organic fouling of the resin by phenolic acid compounds can occur, particularly in combination with iron. Ash (inorganic salts) competes for ion exchange resin sites [Kennedy and Smith (1976)].

Ion exchange exhibits excellent removal of phenolics owing to their low molecular weight and highly charged nature. Paton and Smith [1982], observed a 70% removal of total flavonoid concentration from clarified liquor by ion exchange.
The charged sites on polysaccharides are generally negative and would be expected to react with the anion exchange resin. However, the sites capable of holding such large molecules rapidly become filled, causing the resin to become saturated with respect to polysaccharides soon after start-up.

The factor which has most influence on resin performance is the size of the colourant molecules relative to the pore size distribution of the resin. This decreases with increased resin cross linking. The larger the molecule, the more its diffusion into the pores is restricted, and the lower the probability of its being adsorbed.

2.2.6.4 Evaporation

A general colour increase and an increase in phenolics has been observed during evaporation. This could be important as some of the heat generated phenolics might not be coloured in the heavy liquor, but may react further to produce colour in the pans [Clarke et al. (1985)].

2.2.6.5 Crystallisation

The occlusion of colour in sugar crystals during crystallisation is dealt with extensively in Section 2.3.

Excellent removal of most colour constituents is observed during crystallisation. However, as in the case above, poorer removal of amino-nitrogens, polysaccharides and very high molecular weight colourants is observed.

It is well known that during boiling, factory colourants, notably caramels, are formed and the total colour of the massecuite increases. The pattern of colour transfer from mother liquor to crystal is different from that in raw crystallisation. With refined granulated sugar, more than 50% of the original colour remains in the crystal after dissolving 10% of the crystal whereas, with raw sugar, less than 25% of the original colour remains after the same degree of crystal dissolusion. Hence, the fraction of occluded colour to total crystal colour (occluded and film colourants) is greater for refined sugar than for raw VHP sugar [Clarke et al. (1985)].

Excellent removal of most constituents from the mother liquor, in all four white boilings of a particular sugar refinery, has been observed. However, amino-nitrogen compounds, polysaccharides and very high molecular weight colourants were relatively less well removed by crystallisation [Godshall et al. (1988)].

Phenolic colourants are less likely to be included in the crystals than colourants containing amino-nitrogen. An increase in IV from the massecuite to the crystal indicates that pH sensitive colourants (flavonoids) are also preferentially included. The levels of flavonoids and phenolic acids in
the refined crystal depends on their levels in the original fine liquor. Levels of polymeric and other pH-insensitive colour increases relative to phenolic levels during serial boiling [Clarke et al. (1985)].

2.2.6.6 The Effect of Some Inorganic Ions on Colour Formation

The effects of various ionic constituents on sugar solution colour formation at constant pH are presented below [Carpenter and Roberts (1974)]:

- Calcium ions inhibit colour formation at high pH values and enhance colour formation at low pH values.
- Sodium ions enhance colour formation at high pH values and inhibit colour formation at low pH values.
- Potassium ions enhance colour formation at a pH value of 8 with less colour formation at other pH values.
- Chloride ions have no effect on colour formation.
2.3 The Distribution of Non-sucrose in Sugar Following Crystallisation

Although crystallisation is an effective purification process, non-sugars can still be found in sugar crystals.

Sugar crystals developing in pure sucrose solutions show inclusions of solution and air according to rate of crystallisation and the condition of the solution from which crystallisation is taking place. If sugar is crystallised from an impure solution, non-sugars can be found in the final crystal as a function of the nature of the non-sugars, the operating conditions during crystallisation and the degree of impurity of the mother liquor. The impurities may be ionic or non-ionic, molecular dispersed substances dissolved in the mother liquor such as saccharides, salts and colourants, or they may be colloid-dispersed or coarse-dispersed substances such as residues of sugar cane, oil and starch [Delavier (1968)].

2.3.1 Mechanisms of Impurity Transfer to the Sugar Crystal

Inclusions in the sugar crystal may be divided into solid inclusions and fluid inclusions [Powers (1969)].

Delavier [1968] found that if, during crystallisation of sugar, a change occurs in the purity of the mother liquor, it may be expected that crystal layers of different purity degrees may form. There are three mechanisms of uptake of non-sucrose by crystals, namely, adsorption, inclusion and co-crystallisation.

2.3.1.1 Solid Inclusions

The mechanism of solid inclusion in sugar crystals is described in Powers [1969].

(i) Inclusion of Small Crystals

During crystallisation, other crystals of foreign matter, e.g. mineral salts, do occasionally occur when sufficiently concentrated to nucleate and grow during sugar boiling. These crystals can be overgrown by larger sucrose crystals, trapping the non-sucrose crystals within the sugar crystals themselves. The extent of the inclusion of small crystals is expected to be low.

(ii) Insoluble Particles

Low purity cane syrups exhibit large amounts of insoluble particles which have the potential to be included during crystallisation. These include calcium and magnesium silicates, oxalates,
aconitates, caramels, pectins (gums), lipids (fatty acids, cane wax, alcohols) and many others. Even living micro-organisms have been found in the crystal body itself, or in larger fluid inclusions.

(iii) **Nucleation by foreign particles**:

Workers have found samples of sugar which, when viewed with a microscope, reveal a solid particle within each crystal, indicating that the particle had probably acted as a catalyst for nucleation. Although foreign particles can aid nucleation, nucleation within the sugar industry is essentially homogeneous, caused by fragments of the growing crystals forming new nuclei.

### 2.3.1.2 Fluid Inclusions

The mechanism of fluid inclusions in sugar crystals is described in Powers [1969].

(i) **Inclusion patterns**:

There are three groups of fluid inclusions. The first occurs in random unsymmetric positions - sometimes a parallel sequence of *fjord-like* forms, sometimes irregular and formless. The second is of hourglass shape, symmetrical to the crystal axis, but frequently unbalanced, the *waist* not being at the centre point of the crystal. Occasionally the pattern is of a *Maltese cross* shape like two hourglasses at right angles to one another. The third type of inclusion is of small *veil-like* shapes. These are created when strains develop which form cracks into which solution is drawn. This changes to forms with a lower free energy level by local dissolution and crystallisation. The crack breaks up into a network of canals which slowly break down into a series of isolated pools, still marking the initial plane of the crack. These later become spherical in form and tend to produce a slightly milky haze in refined sugar. Strength and reactivity are also affected.

(ii) **Causes of liquid inclusions**:

The presence of micro-cavities on the various faces of the crystal surface, makes the inclusion of large or small droplets of the mother solution possible, increasing the colour of the crystal. The formation of these cavities is directly related to the face structure and growth rate of the crystal.

A widely held view is that the mechanism of liquid inclusion is via etch pit formation due to periods of subsaturation during the growth of the crystal. This occurs during vacuum pan boiling when the pan is diluted or heated to subsaturation to remove unwanted fine grains. When supersaturation is reached and growth recommences, the depression of the etch pits is overgrown.
sealing in some of the mother liquor.

It is generally accepted that the more rapid the crystal growth and the larger the crystal, the more pronounced the inclusion.

(iii) **Gaseous inclusions**:

The mechanism of gaseous inclusion is relatively simple. The gas, usually air, becomes concentrated to produce supersaturation, then is nucleated on the surface of a growing crystal. During subsequent growth, the presence of a bubble masks that small area of the crystal surface to which it is attached, so causing an inclusion. The whole bubble may be included together with the immediately surrounding solution or, if the bubble is being fed sufficiently rapidly, it will act as a blockage on the crystal face whilst continuing to feed the inclusion as the crystal grows.

### 2.3.2 The Effect of the Interface and Exhaustion Sleeve on Crystallisation

The effect of *crystal interface* and *exhaustion sleeve* (boundary layer) on crystallisation is described by Powers [1969].

It has been shown that the distribution of impurities between the crystalline solid and the interfacial liquid from which it grows cannot be described in terms of the usual phase diagrams. There are kinetic processes taking place at the interface resulting in changes in concentration and other properties of the interfacial medium [Lionnet (1987)]. Powers [1969] stresses that the molecular properties at the crystal/massecruiite interface must be considered. The process of non-sucrose inclusion in crystals cannot only be treated as simple entrapment of mother liquor into the crystal.

It has been shown that sugar crystals include colourants on particular faces of the crystal in the presence of high supersaturation and temperature and that colouring matter includes as the crystal growth kinetic conditions vary [Montovani et al. (1985)].

During crystallisation, individual molecules of widely differing substances come under the influence of many short range forces. Several intermediate stages are passed before a particular molecule takes up a position of least free energy. The crystal is composed of a vast number of individual molecules capable of individual migrations under favourable conditions, progressing towards ultimate perfection which, in practise, is never achieved. Faults abound and are necessary to aid the growth of the crystal.
The crystal can be viewed as a three-dimensional sieve which is full of faults. Smaller molecules, atoms and electrons migrate through the crystal under favourable conditions, as do the faults, to occupy more stable positions of lower free energy.

The composition of the liquid in contact with the surface of the growing crystal is not the same as the composition of the bulk mother liquor. The liquid film, or boundary layer, at the crystal surface is referred to as the exhaustion sleeve and has a lower concentration of the sucrose solute and a higher concentration of impurities. The mechanism of deposition of molecules on the crystal surface in this sleeve is preceded by the formation of molecular aggregates of sucrose and water in solution, which are also important in nucleation. Also present are many impurity molecules, all in constant fluidised motion. Individual molecules will be subjected to constantly changing surrounding attractions and migrate under their influence to achieve a state of least free energy. It is this constantly changing sleeve that causes the crystal to develop such high concentrations of faults, and to include foreign molecules.

Due to the sleeve of exhaustion, the composition of the included material will not necessarily be the same as that of the mother liquor because of the above-mentioned interfacial kinetic processes. The concentration of impurities in the sleeve will have been increased due to the loss of sucrose during crystallisation. The proportions of the impurities will also have been affected by their different rates of diffusion to and from the bulk liquor. Hence one cannot calculate the amount of a particular impurity expected to be included in the crystal based on the composition of the bulk liquor. A further complication in attempting to predict the composition of the final crystal is due to certain molecules being temporarily held at the growing face and then being released. This is a natural consequence of the complex possible affinities between a particular impurity and the crystal lattice. High molecular weight molecules are retained in the grain much more than the low molecular weight molecules [Yamane in : Powers (1969)].

Montovani et al., [1985] propose the following reason for the inclusion of high molecular weight molecules in the bulk of the refined sugar crystal. The coloured solution droplets trapped in the first step of the crystallisation process remain during the whole period of the boiling at the temperature conditions of the boiling itself. The mother solution around the crystal at the final stages of the boiling is made up of fresh sugar juices which have not had sufficient time to polymerise.

The inclusion of various types of crystals often causes a change or modification in the crystal habit of certain surfaces. Faster growing surfaces tend to grow away from the bulk solid, leading to a change in the crystal form.
2.3.3 The Surface Film

The surface of all commercial sugar crystals is covered by a layer of refinery molasses, which is not static, but in a constant state of molecular migration. In high quality sugars, this layer is only a few molecules thick, but is of significance being the highly active layer interchanging sucrose molecules with the crystal face and water molecules with the atmosphere. The direction of migration of the latter is a function of the relative humidity of this layer and of the surrounding atmosphere [Montovani et al. (1985)].

In raw sugar, three layers have been observed. The outer layer (5% of crystal mass) contributes only slightly to the total colour, the second layer (25% of crystal mass) contributes the majority of the colour, while the third "inner" layer (70% of crystal mass) contributes about 20% to the total colour. It is presumed that the colour in the various layers is not distributed uniformly. The inner layer corresponds to crystal growth following nucleation, the highly coloured middle layer corresponds to the conditions in the latter stages of the massecuite formation, while the outer layer corresponds to the slow crystallisation following the removal of the massecuite from the pan [Montovani et al. (1985)].

With regard to refined sugars, Montovani et al. [1985] observed two layers, with the outer layer (25% of crystal mass) contributing about 20% to the total colour of the crystal. This is due to the different process conditions occurring in the refinery as opposed to the mills. Droplet inclusion in the crystal occurs under conditions of high viscosity at the crystal solution interface. As the viscosity increases, so does the surface tension, increasing both the number and size of the liquid inclusions. During refined sugar crystallisation, the variation of the mother liquor viscosity between the start and end of the boiling is very low, whereas in the case of raw sugar boiling the viscosity increases ten fold [Montovani et al. (1985)].

2.3.4 The Effect of Process Conditions

(i) Viscosity

It has already been mentioned above that viscosity enhances droplet capture [Montovani et al. (1985)]. Mackintosh and White [1969] observed that decreasing temperature resulted in increasing quantities of inclusions at a given growth rate. This phenomenon was assumed to be due to the increasing viscosity of the solution (and decreasing diffusivity coefficient) with decreasing temperature. As the viscosity increases, it becomes more difficult for fresh solution to reach the bottom of pits and grooves in the growing crystal.
(ii) Crystal Growth Rate

Montovani et al., [1986] have observed experimentally that the inclusion of colouring matter occurs preferentially in the more rapidly growing faces. They also showed that the inclusion of colour requires kinetic conditions which cause one or more of the faces to grow rapidly enough to promote inclusion. Hence, general inclusion of colour will only occur above a certain temperature and degree of supersaturation which promotes rapid crystal growth. Some colourants may, however, be included at conditions below the critical conditions due to a structural affinity with the crystal face.

The presence of certain non-sugars (e.g. dextrins) cause crystal habit modification by the slowing down of the growth rate of certain faces of the crystal. This varies the degree of inclusion of particular types of colourant molecules resulting in different colour inclusions under the same conditions of temperature and supersaturation. Hence, different crystal faces will have inclusions dependent on their particular growth rate.

(iii) Crystal Size

It has been shown that the relative amount of impurities trapped by the crystal increases with crystal size [Moritsugu and Payne (1965)], [Guo and White (1984)].
2.4 The Use of Ion Exchange for the Decolourisation of Sugar Solutions

This survey into the use of ion exchange for the decolourisation of sugar solutions is a summary of an extensive literature survey reported in Getaz, MA [1988].

This review is limited to acrylic, strong-base anion exchange resins currently employed by Hulett Refineries Limited.

2.4.1 Introduction

*Ion exchange is the reversible exchange of ions between a solid and a liquid in which there is no substantial change in the structure of the solid.*

In the area of sugar cane refining, ion exchange has been employed mainly for the decolourisation of liquors prior to crystallisation operations, and for the decolourisation and de-ashing of liquors in the production of liquid sugar.

Ion exchange is a unique technology. The chemical and physical structure of each ion exchange resin process possesses a particular selectivity which is advantageous to that specific application.

The fundamental features of ion exchange are listed below:

- Ion exchange reactions are stochiometric. For every mole of exchanging ion taken up by the resin, a mole of ion is released from the resin to the solution.

- Ion exchange reactions are generally reversible.

- All the ion active groups in an ion exchange resin are accessible as exchange sites for small ions.

- In general, any compound which is soluble and will ionise is capable of undergoing an ion exchange reaction.

- The economics of an ion exchange process are linked to the type and quantity of the ions to be exchanged.

An ion exchange resin is a high molecular weight polymer containing ionic groupings as integral parts of the polymer structure. Synthetic ion exchange resins consist of crosslinked polyelectrolytes that can
be visualised as an elastic three dimensional hydrocarbon network to attached a large number of ion active groups are attached.

The resin contains cations and anions in a condition of electroneutrality. The state of ions differs from that of an electrolyte in that only one of the two ionic species is mobile. The immobile ions constitute an integral part of the polymer to which the mobile ions are attached.

2.4.2 The use of Ion Exchange Resins in the Sugar Industry

The use of ion exchange resins, in the chloride form, as colour polishers following the traditional decolourisation processes using granular activated carbon and bone char, dates back to the early 1950's. In that era efforts were made to optimise the resins to achieve lower crosslinking and higher moisture content in an attempt to speed up the diffusion rates of the larger colour bodies to the polymeric adsorption sites in the resin polymer backbone. However, this was limited by the physical instability of high moisture, gelular resins. The backbone of these resins was a styrene/divinylbenzene copolymer with very small passageways dictated by the distance between the crosslinks.

In the early 1960's a revolution in structure occurred in that the copolymers could be made to consist of macroreticular pores. This allowed further incorporation of moisture with no loss in physical stability. The practical capacity of these resins for colour removal was greatly enhanced leading to their widespread commercial use as polishing agents after bone-char or granular carbon. In the late 1960's acrylic based ion exchange resins were developed. This allowed the possibility of an all ion exchange decolourisation system in sugar refineries without the use of bone-char or activated carbon. Acrylic resins offer high decolourisation efficiency coupled with the ability to be regenerated with a 10% brine solution.

Decolourisation by ion exchange in South Africa has been limited, commercially, to gross decolourisation of refinery liquors. At present there are two such ion exchange plants in South Africa.

The first experimental work was begun in 1974 and was conducted by the Sugar Milling Research Institute (SMRI) on a pilot-plant set-up at Hulett Refineries. It was shown that the decolourisation of brown liquor by ion exchange was economically viable. Hulett Refineries currently employ an acrylic, strong-base, anion exchange resin plant for the decolourisation of brown liquor prior to crystallisation. This was the first commercial ion exchange resin plant to be installed in a sugar refining capacity in South Africa and was commissioned in 1978.
2.4.3 Physical Structure of Ion Exchange Resins

2.4.3.1 Resin Manufacture

Several aspects are important in the manufacture of ion exchange resins:

- **Durability**

  Resins must be able to resist physical breakdown, chemical degradation and solubility. The economic viability of an ion exchange resin depends on its durability as much as on its capacity.

- **Particle Size**

  Decreasing the size of the resin particles materially decreases the time required for a resin to reach equilibrium with a contacting solution. As the time is decreased, the efficiency of a given volume of resin increases, or the volume of resin required for a specific operation is decreased.

2.4.3.2 Macroreticular Resin Structures

Macroreticular resins possess a pore structure that is superimposed on the crosslinked copolymer structure. This is similar to that of the classical adsorbents e.g. carbon.

Macroreticular pores and true porosity refer to the structure in which the pores are larger than the atomic distances and are not part of the gel structure. Their size and shape are not greatly influenced by environmental changes. The macroreticular ion exchange resins have both a macroreticular as well as a microreticular structure. The latter refers to the distances between the chains and crosslinks of the swollen gel structure, while the former refers to the pores that are not part of the actual chemical structure. The macroreticular portion of the structure may actually consist of micro, macro and transitional pores depending on the pore size distribution.

The macroreticular structure permits the preparation of physically and chemically stable ion exchange resins and also the introduction of functional groups that ordinarily could not have been introduced effectively into a microreticular crosslinked copolymer structure.
2.4.3.3 Polymer Crosslinkage

The amount of crosslinkage affects the capacity of the resin in two ways:

(i) As crosslinkage increases, the wet volume capacity increases. This is due to the fact that highly crosslinked resins do not swell as much as the more porous resins. Capacity based on volume of resin will be greater.

(ii) As crosslinkage increases, the dry weight capacity decreases. This results from the greater difficulty of substituting active groups on the aromatic rings in the copolymer because of steric effects. This is minor in comparison with wet volume capacity increase.

Several other physical and chemical properties of the resin are affected by the amount of crosslinkage:

- As crosslinkage decreases and the resin swells, diffusion of ions within the resin becomes faster resulting in faster equilibrium rates. As crosslinkage decreases, the diffusion paths become smaller. This offers the possibility of separation based on ionic size.

- As the crosslinkage is decreased, the selectivity of the resin is decreased due to the resulting larger pores having reduced selectivity based on ionic size.

- Resins of low degrees of crosslinkage are soft and easily deformed.

- Highly crosslinked resins are brittle.

2.4.4 The Polymeric Backbone of the Acrylic Ion Exchange Resin

The nature of the ion exchange matrix plays a very important role with regard to selectivity, particularly when considering the anion exchange resins. This factor becomes more important as the size of the anionic species to be adsorbed increases. The kinetics and equilibria of anion exchange become more favourable as the skeletal structure of the matrix is changed from the hydrophobic aromatic structure associated with styrene to the hydrophilic structure associated with acrylic esters.
2.4.4.1 Acrylic Structures

The nature of the skeletal polymer structure represents the basic difference between acrylic and styrenic structures. Styrenic structures are aromatic whereas acrylic structures are aliphatic with a minor amount of aromatic crosslinkage incorporated into the polymer.

Discussion of acrylic structures will be limited to the strongly basic anion exchange resins presently employed at Hulett Refineries Limited.

The unique behaviour of acrylic-based strongly basic anion exchange resins arises from the fact that, although they are as basic as their styrenic counterparts, they exhibit a higher degree of hydrophilicity. This makes the resins more suitable for the removal of colourants from sugar liquors with a degree of reversibility that is orders of magnitude greater than that exhibited by styrene-based anion exchange resins. Hence, the acrylic resins generally foul to a much lower degree than the styrenic resins when used in applications where high levels of organic compounds are present.

The nature of the ion exchange matrix plays a very important role with regard to selectivity. This factor becomes more important as the size of the anionic species to be adsorbed increases. The kinetics and equilibria of anion exchange become more favourable as the skeletal structure of the matrix is changed from the hydrophobic aromatic structure associated with styrene to the hydrophilic structure associated with acrylic esters.

2.4.5 Factors Affecting Resin Selectivity

♦ The type of functional groups

The effect of the functional group on resin selectivity is directly dependent on acid or base strength. While the distinction between the strong and weak exchange resins is rather sharp, there are shadows of strength in both categories.

♦ The valence and nature of exchanging ions

In general, at total concentrations of less than 0.1 N, divalent ions are more tightly held by the resin than monovalent ions and trivalent ions more tightly than divalent ions.
The nature of non-exchanging ions

These have little effect on the selectivity unless they tend to form complexes with the exchanging ions.

The ionic form of the resin

Selectivity for a particular ion varies, usually decreasing, as the resin is converted to that ionic form. In most cases the effect is slight.

The total ionic solution strength

Monovalent exchanges are affected only slightly by changes in total ionic strength of the solution. However it becomes very important for exchanges between ions of different valences as in mono-divalent exchanges.

2.4.6 The Functional Groups of Strong-base Anion Exchange Resins

Strong base anion exchange resins all incorporate quaternary ammonium groups. They are highly ionised and can be used over the entire pH range.

The regeneration of strong base anion exchange resins is generally performed with moderate concentrations of sodium hydroxide solutions. The regeneration reactions are not as easily reversed and regenerant levels of 150 to 200 percent of the stoichiometric requirements are frequently employed. The resins show marked affinity relationships depending on ion size and valence. The order of affinity for common anions is: \( \text{PO}_4^{3-} > \text{SiO}_4^{2-} > \text{SO}_4^{2-} > \text{NO}_3^- > \text{Cl}^- > \text{CO}_3^{2-} > \text{OH}^- \).

Resins with strongly basic anion functional groups have proved to be most suitable for the decolourisation of sugar liquors. The functional groups are quaternary ammonium groups which are regenerated with an alkaline common salt solution.

There are two types of strong-base resins available commercially. The first type has a quaternary ammonium functional group, while the second type has a slightly modified quaternary ammonium functional group in which one of the methyl groups is replaced with an ethanol group. The two types differ in their affinities for chloride and hydroxide anions and in their chemical stabilities. The first type has less exchange capacity, but is more stable than the second type.

Colour bodies are adsorbed onto the resin by ionic and a combination of electrostatic and hydrophobic forces. Not all these bodies are removed during brine regeneration and this accumulation of organic
matter in the resin matrix impairs the effectiveness of the resin. The form in which the regenerated resin is employed plays a major role in the extent and ease of decolourisation. Usually the anion exchangers are employed in the OH\(^{-}\) or Cl\(^{-}\) form. It is accepted that resins in the Cl\(^{-}\) form give the best decolourising results. Alkalis are the best regenerants for dislodging the adsorbed colour bodies from the resin. A combination of NaCl with NaOH or NH\(_4\)Cl has been proven to be more effective than any single regenerant [Joshi in : Getaz (1988)].

2.4.7 Decolourisation Mechanisms of Ion Exchange Resins

Because of the complex nature of sugar colourants and because of the fact that resin selectivity is dependent on its physical structure, its ionic functional groups and its polymeric backbone, the mechanism of decolourisation will also be complex.

2.4.7.1 Selectivity

The selectivity of an ion exchange resin increases markedly as the aromaticity of the organic ion increases or the aqueous solubility of the ion decreases. This cannot be explained by electrostatic interactions alone since the charge densities of the organic ions are considerably less than the chloride ions which they displaced. A combination of electrostatic and hydrophobic bonding produce this high selectivity. The selectivity of organic ions increases with an increase in organic loading for acrylic resins.

2.4.7.2 Kinetics

There are three reversible reactions which can proceed simultaneously in a resin-liquor system. The first reaction is the exchange of chloride ions for colourants, the second is the competing exchange of non-coloured anions from liquor ash and the third is the decolourising reaction with the resin converted to the ash-anionic form.

In continuous fixed bed ion exchange processes, the thermodynamic equilibria are not necessarily of overriding importance. More important are the rate of transport of exchanging ions from the bulk liquor to the resin surface and through the resin matrix to the active sites - and vice versa.

Thus, under dynamic conditions, fast-diffusing ions are preferentially exchanged even if the equilibrium favours slower-diffusing ions. There is a continuous change of these preferences and, as the process continues, the slower ions replace the faster ones bringing the whole system to a state of thermodynamic equilibrium between the resin and feed liquor. A simplified model based on the above is as follows:
Resin decolourisation of refinery liquors is basically an ion exchange process.

With the exception of the earliest stages, decolourisation proceeds as a two stage process. In the first stage, the main exchange reaction is the substitution of chloride ions from the resin by anions introduced through the liquor ash. The second stage is the decolourisation itself, in which colourants substitute for ash anions in the converted resin.

Strong base resin and favourable feed pH are essential for good decolourisation.

2.4.7.3 Summary of Decolourisation Mechanisms

Evidence has been found, at Hulett Refineries Ltd, that both a drop in moisture holding capacity (a measure of pore blockage) and in ion exchange capacity result in a drop in decolourising performance. It has been concluded from this that both ion exchange and adsorption play significant roles in the resin decolourisation process [Loker, C (1983)].

Part of the colourants are removed in exchange for chloride ions, but a significant portion of the colour is removed without being exchanged by another anionic species. Such sorptive processes involve primarily the matrix of the anion exchange resin rather than the ionic functionality. In other words, colourants are bound to the resin by a combination of electrostatic and hydrophobic bonding.
2.5 The Historical Development of Membrane Technology

The development of the science of membrane technology is summarised in this section. Most of the information was obtained from the works by Cheryan [1986] and Belfort [1981].

1748 The process of osmosis was discovered by Abbe Nollet, using an animal bladder, who observed that water diffuses from a dilute solution to a more concentrated one when separated by a semi-permeable membrane.

1845 Matteucci and Cima observed that the osmosis membranes were anisotropic, that is, their behaviour was dependent on which side of the membrane faced the feed solution.

1865 Fick developed the first synthetic membrane made of nitrocellulose. He formulated the first laws of diffusion through colloidon membranes for solutions. Two years later, Traub also prepared artificial membranes.

1877 Pfeffer reported the first successful manufacture of an inorganic membrane by precipitating copper ferrocyanide in the pores of porcelain.

1907 Bechhold developed methods for controlling the pore size of the original colloidon membranes by controlling the rate of evaporation of the solvents and by water washing of the film. He was the first to suggest the use of air pressure for improving flux rates and for measuring the relative pore size of the membranes by determining the difference in surface tension. He is generally credited with first using the term ultrafiltration.

1877 to 1920 This period saw the rapid development of the theory of solution thermodynamics. Of note are the van't Hoff's theory of dilute solutions and Gibbs theory of the relationship between osmotic pressure and other thermodynamic properties.

1927 Membrane filters were commercially available from the Sartorius Company in Germany. Up until 1945 membranes were used primarily for the removal of micro-organisms and particles from fluid streams.

1957 The United States Public Health Service officially adopted the membrane filtration process for drinking water analysis.
1950's  Samuel Yuster of The University of California, Los Angeles, predicted that, based on the Gibbs adsorption isotherm, it should be possible to produce fresh water from brine. Sourirajan reported some success with this concept using commercially available homogeneous membranes. However, fluxes were too low to make the process viable.

1958 to 1960  Sourirajan and Loeb attempted to increase the size of the pores by heating the membrane under water. The opposite occurred in that the membrane pores contracted on heating. However, flux and retention increased markedly.

The heating, or annealing, process created a phenomenon known as anisotropy or asymmetry in the ultrastructure of the membrane, that is, the behaviour of the membrane was different depending on which side of the membrane faced the feed solution. The anisotropy of the Loeb-Sourirajan membrane is characterised by a thin microporous skin on one surface of the membrane while the remainder of the membrane exhibits a macroporous, sponge like, structure. The major resistance to the transport of molecules through the membrane is due to the thickness of the membrane. The effective thickness of the asymmetric membrane is only that of the thin retention layer on the membrane surface resulting in the higher observed fluxes. The retention of salt remained high due to the effective decrease in the pore size of the retention surface.

Late 1960’s  Asymmetric, non-cellulosic ultrafiltration membranes were developed.

Late 1960’s to present  Since the development of the non-cellulosic, asymmetric membrane, membrane separations technology, in its modern form, has found application in a vast array of applications ranging from chemical separation to medical applications.
2.6 The Development of Inorganic Membranes

Inorganic membranes were investigated due to their ability to tolerate the high temperature process conditions of the Johnson sweetwater stream.

The following description of the development of inorganic membranes is a summary of an extensive literature survey by Gillot [Gillot in: Bhave (1991)] :

The development of inorganic membranes for common industrial solute separation started in the 1940's and can be divided into two distinct periods :

(i) The development and mass production of membranes for the separation of uranium isotopes by the process of gas diffusion.

(ii) The development of inorganic membranes for the ultrafiltration and microfiltration of process fluids.

2.6.1 The Nuclear Period

The active uranium isotope $^{235}$U, used in the production of nuclear weapons and in power generating plants, was originally separated during the Manhattan Project (World War II) using mass spectroscopy. This process became too expensive, prompting the development and implementation of gaseous diffusion technology as a separation technique.

The process of uranium recovery by gaseous diffusion requires the conversion of uranium to UF$_6$ which is then allowed to diffuse across a porous membrane with a nominal pore diameter in the range 0.006 to 0.04 µm. The lighter $^{235}$UF$_6$ molecules flow faster than the $^{238}$UF$_6$ molecules and are thus separated. Because of the low enrichment factor, the required gaseous diffusion plants were large, requiring the mass production of porous inorganic membrane supports.

Essentially three French companies were involved in the development of tubular macroporous supports for the Commissariat a l'Energie Atomique (CEA) :

(i) Desmarquest, now a subsidiary of Pechiney.

(ii) Le Carbone Lorraine, a producer of carbon and graphite products, now also a subsidiary of Pechiney.
(iii) Compagnie Generale d'Electroceramique (CGEC), then a subsidiary of Compagnie Generale d'Electrite (CGE), which later became Ceraver, the membrane department now belonging to Societe des Ceramiques Techniques (SCT), a subsidiary of Alcoa.

In France, the first period of industrial production of inorganic membranes was aimed at making the membranes for the Pierrelatte military enrichment plant in the late 1960's and early 1970's. Most of the tubular supports were made by CGEC, while the rejecting layers were made by SFEC (Societe de Fabrication d'Elements Catalytiques - a subsidiary of the CEA). The original ceramic membranes are still in operation in this plant.

After the oil crisis of 1973, several European countries (Belgium, France, Italy and Spain) decided to build the Eurodif gas diffusion plant to supply nuclear fuel to the large number of new nuclear power plants. The ceramic supports for this plant were made by private companies with the separating layer being manufactured by SFEC. Ceraver and Euroceral proposed ceramic oxide based supports with each company winning 50% of the market to produce 2,000,000 m² of ceramic supports within six years. The plans to build another such plant, the Coredif project, fell through as the oil crisis came to an end leading to a marked decrease in the demand for gaseous diffusion membranes.

In the USA, similar developments of inorganic membranes took place with several large gaseous diffusion plants being constructed. These were located at Oak Ridge (1953), Paducah (1953) and Portsmouth (1954). Union Carbide played a major role in the field of membrane development.

Inorganic membranes were also developed in the USSR. However, little is known of these developments.

Gaseous diffusion has now been replaced by alternative, more economical uranium enrichment technologies. This brought to an end the demand for new ceramic membrane supports. However, during the nuclear period, it was demonstrated that inorganic membranes can be produced on a large scale to meet stringent specifications. The inorganic membrane was proven to have a long life span under extremely harsh conditions.

2.6.2 The Development of Inorganic Ultrafiltration and Microfiltration Membranes for use on Process Fluids

The development of industrial inorganic ultrafiltration and microfiltration membranes for process fluid applications resulted from three factors:

(i) Experience accumulated by the companies involved in the nuclear gas diffusion plants.
(ii) The existence of ultrafiltration using polymeric membranes as an established industrial process.

(iii) The limitations of polymeric membranes in terms of temperature, pressure and durability.

The first attempts to use the high mechanical strength of inorganic membranes for process fluid applications dates back to the 1960's in the USA, where the Oak Ridge National Laboratory created dual-layer dynamic membranes consisting of hydrous zirconium oxide and polyacrylic acid deposited onto a porous carbon or ceramic support. The dual-layer dynamic membrane acts as the retention layer. This later developed into dynamic zirconium oxide membranes applied to porous stainless steel supports marketed by CARRE, a subsidiary of du Pont.

The Ucaresep* membrane was also developed from dynamic membrane technology. It consisted of a non-sintered ceramic oxide membrane deposited onto a porous carbon support. These membranes were patented by Union Carbide in 1973. SFEC added a further step to the development of the inorganic membrane when they sintered ZrO₂ particles onto a Union Carbide 6 mm internal diameter tubular carbon support. In 1980 SFEC began marketing these ultrafiltration membranes under the trademark of Carbosep®.

Since membranes had no important future applications in the nuclear field, SFEC was sold in 1987 by the CEA to Rhone-Poulenc who merged them with their existing organic membrane division to form the subsidiary Tech Sep. The sintered ZrO₂ based membranes on 6 mm diameter supports continues to be the main product line of Tech Sep.

Ceraver, in contrast to SFEC, developed a range of α-alumina microfiltration membranes on an α-alumina support. Since 1984 these membranes have been sold under the trademark MembraLox®.

The MembraLox® membrane offers two innovative features, the first being its multi-channel design and the second being its ability to be back-flushed. The multi-channel design comprises a multi-channel support made of sintered oxide with each channel carrying a sintered metallic-oxide retention layer. The design offers sturdiness, lower production costs when compared with the tube-bundle geometry and lower energy requirements in the cross-flow loop. The back-flushing feature involves the pressurisation of the permeate side of the membrane module thereby forcing permeate back through the membrane. This removes a substantial amount of the fouling layer on the retention surface and restores high fluxes. Ceraver initiated the development of cross-flow microfiltration with back-flushing as a new industrial processes. The MembraLox® ultrafiltration membranes with sintered ZrO₂ rejecting layers were commercialised in 1988.

In 1986, CGE sold the ceramic part of Ceraver to Alcoa. Under the name SCT it is now a subsidiary of the recently formed Alcoa Separations Technology, Inc.
A few other companies involved in the nuclear program have also developed ultrafiltration membranes:

- Norton-USA developed α-alumina membranes and supports. These membranes, produced by Norton, are sold by Millipore under the trademark Ceraflo®.

- Le Carbonc-Lorraine developed tubular ultrafiltration and microfiltration membranes made of carbon fibre with a carbon separating layer which have been marketed since 1988.

- Ceram-Filtre was formed by former employees of Euroceral who now produce a range of multi-channel microfiltration membrane modules.

- Asymmetric alumina membranes developed by the anodic oxidation of alumina sheet were also first developed for uranium enrichment in the 1950’s. Such membranes are now marketed under the trademark Anopore® by Anotec, a British subsidiary of Alcan.

2.6.3 Conclusions

It is clear that ceramic membrane technology first developed as an uranium enrichment process and that this is still the major application of ceramic membrane technology to date. However, ceramic membranes are increasingly being applied in a wide range of separation applications in the chemical process industry, often at the expense of existing polymeric ultrafiltration membranes.
2.7 Relevant Ultrafiltration Theory

This section summarises various aspects of ultrafiltration theory relative to the investigation into the decolourisation of Johnson sweetwater using ultrafiltration. The basic principles of ultrafiltration are dealt with in virtually all the available texts on membrane separation technology.

The theory covered in this section deals firstly with the phenomena influencing the permeate flux and retention characteristics of an ultrafiltration membrane and secondly with the equations used to predict brix, absorbance and ICUMSA colour for high water recovery ultrafiltration experiments. Also included is multi-solute high water recovery ultrafiltration theory.

2.7.1 Phenomena Influencing the Permeate Flux and the Retention Characteristics of a Membrane

The various phenomena influencing the membrane are described in Bhave [1991]. Factors such as concentration polarisation, adsorption and internal fouling influence the flux and separation characteristics of the membrane.

2.7.1.1 Concentration Polarisation

Ultrafiltration involves the pressure induced separation of two or more chemical constituents of a solution which have different permeabilities through the membrane. Solvent passes through the membrane while retained solute accumulates in the vicinity of the membrane. In order for steady state mass transfer to be satisfied, the net rate of convective transport towards and parallel to the membrane surface must equal the net rate of transport by convection and diffusion away from the membrane surface.

The net result is a layer of solution adjacent to the membrane surface of substantially greater solute concentration than that of the bulk solution within the channel. This concentrated layer results in the phenomenon of concentration polarisation comprising a laminar boundary layer between the bulk solution and the membrane surface.

In the case of solutions composed of high molecular weight solutes, where osmotic pressure contributions are practically negligible, solute concentration at the surface continues to increase until limits are reached at which point a gelatinous precipitate matrix is formed upon the membrane. The gel layer offers an additional hydraulic resistance to solvent flow. This occurrence is termed gel polarisation.
It must be noted that concentration polarisation is purely a surface phenomenon. Fluxes of asymmetric membranes can be restored to their original values by simple cleaning or washing techniques.

Figure 2.8 shows schematically the phenomenon of concentration polarisation. At a given temperature, pressure difference and feed rate, the permeate crossing the surface carries a certain amount of solute. This can be represented by the permeate flux (J) and solute concentration (C). As a result of solute transport across the membrane, the concentration of solute near the membrane surface can be higher than near the bulk. However, due to the higher solute concentration near the wall, there will be a back-diffusion of solute from the wall into the bulk liquid phase. This can be expressed as $D(\frac{dC}{dy})$

Thus, at steady state:

$$J\dot{C} = -D\frac{dC}{dy}$$

integrating from bulk concentration ($C_b$) to membrane wall concentration ($C_w$):

$$\frac{C_w}{C_b} = \exp\sqrt{\frac{\delta}{D}}$$

where the boundary layer thickness is represented by the symbol $\delta$.

The mass transfer coefficient, $k$, is given by:

$$k = \frac{D}{\delta}$$

The permeate flux, $J$, is obtained from:

$$J = k \ln\left(\frac{C_w}{C_b}\right)$$

The value of permeate flux is influenced by a number of hydraulic parameters such as cross-flow velocity, wall roughness and solution viscosity. When the wall concentration ($C_w$) reaches the concentration ($C_g$) at which gel formation occurs, the permeate rate is given by:

$$J = k \ln\left(\frac{C_g}{C_b}\right)$$

The permeate flux under these conditions is strongly influenced by the back-diffusion of solute from the gel layer to the bulk feed. The permeate flux can be increased by increasing the value of $k$, or by decreasing the gel layer thickness or, less frequently, by increasing the diffusion coefficient through an increase in temperature. In practice, this is often accomplished by an increase in the value of cross-flow
velocity. Under gel polarisation conditions, trans-membrane pressure can no longer influence the permeate flux due to the insensitivity of $C_g$ to pressure variations, which is essentially controlled by mass transfer parameters.

![Diagram of concentration polarisation](image)

Figure 2.8: A schematic representation of the phenomenon of concentration polarisation [Bhave (1991)].

### 2.7.1.2 Adsorption

Almost all macromolecules show an interaction with the particular surface in contact. This phenomenon, commonly referred to as fouling, is due to adsorption. To simplify the analysis of adsorption, a mono-molecular layer is assumed to be formed covering the membrane layer in contact with the feed solution (with or without permeation across the membrane surface area). A significant flux reduction can occur even with a mono-molecular adsorption layer. The tendency to form adsorbed layers on the membrane surface may be a function of the nature of the membrane surface. For example, it is commonly observed that hydrophilic surfaces adsorb less strongly than hydrophobic surfaces.

Fouling due to adsorption is more likely in ultrafiltration than in microfiltration. This is due to the smaller pore size distribution of the ultrafiltration membrane surface. At high solute concentrations, a number of layers progressively build up on the membrane surface. These secondary layers are responsible for flux reduction.
2.7.2 The Equations Used to Predict Brix, Absorbance and ICUMSA Colour for High Water Recovery Ultrafiltration Experiments

The definitions of the various terms used in the equations are presented in Section 2.7.2.1 while the nomenclature used in the equations is presented in Section 2.7.2.4. The equations used to predict high water recovery data are derived and presented in Section 2.7.2.2. Multi-solute ultrafiltration theory is presented in Section 2.7.2.4.

2.7.2.1 Definitions

(i) **Retention** :
   A measure of the perfection of a membrane for retaining a particular solute.

(ii) **Water Recovery** :
   The ratio of volume of permeate to volume of original feed.

(iii) **Point Retention** :
   If sufficiently small samples are taken so that there is no change in the concentration of the feed before and after the samples are taken, then the retentions are termed point retentions.

(iv) **Composite Permeate Quality** :
   The ratio of mass of solute in the total permeate volume to the volume of permeate.

(v) **Solute Loss** :
   The ratio of mass of solute in the permeate to the mass of solute in the original feed.

(vi) **Grade** :
   Grade is a measure of the quality of the sugar solution and may be defined as the ratio of brix to ICUMSA colour.

(vii) **Relative permeate quality** :
   The difference between permeate colour and original feed colour.
2.7.2.2 Equations

2.7.2.2.1 Retention

Retention (\( \sigma \)) is defined as the degree of separation of a particular species and is calculated from the analysis of feed and permeate solutions. Mathematically, retention is defined as follows:

**General Equation**:

\[
\sigma = 1 - \frac{C_p}{C_f}
\]  

(2.2)

where \( C_p \) is the concentration of the solute species in the permeate and \( C_f \) is the concentration of the solute species in the feed.

For the purpose of assessing the decolourisation performance of a membrane operating on sweet water, two specific retention values are defined, namely ICUMSA colour retention and brix retention. Any further reference to the term colour in this section refers to ICUMSA colour.

**Colour Retention**:

\[
\sigma = 1 - \frac{I_p}{I_f}
\]  

(2.3)

where \( I_p \) is the permeate colour and \( I_f \) is the feed colour.

**Brix Retention**:

\[
\sigma = 1 - \frac{B_p}{B_f}
\]  

(2.4)

where \( B_p \) is the permeate brix and \( B_f \) is the feed brix.

A membrane which entirely retains a particular solute is said to have a retention value of 1 (or 100 %) relative to that solute. Equation (2.2) can be rewritten as:

\[
\sigma = \frac{C_f - C_p}{C_f}
\]  

(2.5)
From Equation (2.5) it is evident that, if the concentration of a specific species in the permeate is zero, then the retention is 1 (or 100%) and the membrane is ideal.

### 2.7.2.2.2 Water Recovery

Water recovery (R) is defined as the ratio of volume of permeate to that of initial feed at any one time during the run of the experiment. Mathematically it is defined as:

\[ R = \frac{V_p}{V_f^0} \]  

(2.6)

As water recovery increases, so does the concentration of the retained solute species in the feed.

When sufficiently small permeate samples are taken, the permeate flow is essentially zero and so is the water recovery. In this case there is no observed change in the feed composition. Although no permeate has been produced the definition of retention can be used to calculate the point permeate concentration.

\[ C_p = C_f (1 - \sigma) \]  

(2.7)

For a batch process, the increase in volume of the permeate is equal to the decrease in volume of the feed.

\[ V_p = V_f^0 - V_f \]  

(2.8)

Substituting this into equation (2.1) gives:

\[ R = \frac{V_f^0 - V_f}{V_f^0} \]

\[ R = 1 - \frac{V_f}{V_f^0} \]  

(2.9)

### 2.7.2.2.3 Feed Quality

The concentration of the solute in a batch process, in both the feed and the permeate, increases as the batch concentration proceeds. The composition of the composite permeate will be somewhere between that of the initial (zero water recovery) permeate and the most recently produced permeate.
At any time the mass of solute in the feed tank is given by:

\[ V_f C_f \]

After a period of time \((t + dt)\):

Feed Volume \(= V_f + dV_f\)

Feed Concentration \(= C_f + dC_f\)

At time \((t + dt)\), the mass of solute in the feed tank will be:

\[(V_f + dV_f)(C_f + dC_f)\]

The volume of permeate produced will be \(-dV_f\) with a solute concentration of \(C_p\).

Total mass must be conserved, therefore:

\[
\text{Original feed mass} = \text{Current feed mass} + \text{Permeate mass}
\]

\[ V_f C_f = (V_f + dV_f)(C_f + dC_f) + dV_p C_p \]

but,

\[ dV_p = (-dV_f) \]

therefore,

\[ V_f C_f = (V_f + dV_f)(C_f + dC_f) - dV_f C_p \]

from equation (2.7),

\[ C_p = C_f(1 - \sigma) \]

substituting this into the above equation and multiplying out, we get:

\[ V_f C_p = (V_f + dV_f)(C_f + dC_f) - dV_f C_f(1 - \sigma) \]

\[ V_f C_f = V_f C_f + V_fdC_f + C_fdV_f + dC_fdV_f - C_fdV_f - \sigma C_f dV_f \]

neglecting \(dC_f dV_f\), then
\[ V_f dC_f = -\alpha C_f dV_f \]
or,
\[ \frac{dV_f}{V_f} = -\frac{1}{\sigma} \frac{dC_f}{C_f} \]

Integrating this expression from the original feed conditions where \( C_f = C_f^o \) and \( V_f = V_f^o \) :

\[ \int_{V_f}^{V_f^o} \frac{dV_f}{V_f} = -\frac{1}{\sigma} \int_{C_f}^{C_f^o} \frac{dC_f}{C_f} \]

\[ \ln \frac{V_f^o}{V_f} = -\frac{1}{\sigma} \ln \frac{C_f}{C_f^o} \]

\[ \left( \frac{C_f}{C_f^o} \right) = \left( \frac{V_f}{V_f^o} \right)^{\sigma} \]

(2.10)

From the above it is evident that if we have perfect retention (\( \sigma = 1 \)), then the mass of solute in the initial feed is equal to the mass of solute at any time \( (V_f^o C_f^o = V_f C_f) \)

From equation (2.9) :

\[ R = 1 - \frac{V_f}{V_f^o} \]

Substituting into equation (2.10) gives

\[ C_f = C_f^o (1 - R)^{-\sigma} \]

(2.11)

Equation (2.11) represents the feed quality as a function of water recovery.

Expressions for feed absorbance and the feed brix are derived in a similar fashion.

**Feed Colour** :

\[ I_f = I_f^o (1 - R)^{-\sigma} \]

(2.12)

**Feed Brix** :

\[ B_f = B_f^o (1 - R)^{-\sigma} \]

(2.13)
It must be noted that these equations were derived without taking permeate flux, osmotic pressure and precipitation into account. These effects will pose additional physical limits to the process.

### 2.7.2.2.4 Composite Permeate Quality

Composite permeate composition is defined as:

\[
\overline{C_p} = \frac{\text{Mass of Solute in the Total Permeate Volume}}{\text{Volume of Permeate}}
\]  
(2.14)

The mass of solute in the permeate is the same as the loss of solute from the feed. Similarly, the volume of permeate is the same as the loss of feed volume.

\[
\overline{C_p} = \frac{V_f^0 C_f^0 - V_f C_f}{V_f^0 - V_f}
\]  
(2.15)

but from equation (2.9),

\[
R = 1 - \frac{V_f}{V_f^0}
\]

and from equation (2.11),

\[
C_f = C_f^0 (1 - R)^\alpha
\]

substituting these into (2.15) and rearranging gives:

\[
\overline{C_p} = \frac{C_f^0 (1 - (1 - R)^{1-\alpha})}{R}
\]  
(2.16)

Similarly for colour and brix:

**Composite Permeate Colour**:

\[
\overline{T_p} = \frac{T_f^0 (1 - (1 - R)^{1-\alpha})}{R}
\]  
(2.17)

**Composite Permeate Brix**:

\[
\overline{B_p} = \frac{B_f^0 (1 - (1 - R)^{1-\alpha})}{R}
\]  
(2.18)
2.7.2.5 Solute Loss

Solute loss ($\delta$) represents the amount of solute lost to the permeate.

\[
\delta = \frac{\text{Mass Solute in the Permeate}}{\text{Mass Solute in the Feed}} = \frac{v_f c_f^0 - v_f c_f}{v_f c_f^0}
\]

\[
= 1 - \left( \frac{v_f}{v_f^0} \right) \left( \frac{v_f}{v_f^0} \right)^{\sigma} 
\]

\[
= 1 - \left( \frac{v_f}{v_f^0} \right)^{1-\sigma}
\]

Substituting from equation 2.9 and introducing water recovery:

\[
\delta = 1 - (1 - R)^{1-\sigma}
\]

Similarly for sugar and colour,

Fraction Colour Passing the Membrane:

\[
\delta_f = 1 - (1 - R)^{1-\sigma_f}
\]

Fraction Brix Recovered:

\[
\delta_B = 1 - (1 - R)^{1-\sigma_B}
\]

2.7.2.6 Grade

Grade is a measure of the quality of the sugar solution and is refined as the ratio of brix to colour.

Permeate Grade:

\[
G_p = \frac{B_p}{I_p}
\]
Feed Grade:

\[ G_f = \frac{B_f}{I_f} \]  \hspace{1cm} (2.25)

2.7.2.2.7 Relative Permeate Quality

Relative permeate quality is the difference between the permeate and original feed colour.

\[ \text{Relative permeate quality} = \frac{I_f^0 - I_p}{I_f^0} \]  \hspace{1cm} (2.26)

From Equation (2.7) and introducing colour,

\[ I_p = I_f (1 - \sigma) \]

and from Equation (2.12),

\[ I_f = I_f^0 (1 - R)^\sigma \]

Equation (2.26) becomes:

\[ \text{Relative permeate quality} = \frac{I_f^0 - I_f^0 (1 - R)^\sigma (1 - \sigma)}{I_f^0} \]  \hspace{1cm} (2.27)

\[ \text{Relative permeate quality} = 1 - (1 - R)^\sigma (1 - \sigma) \]  \hspace{1cm} (2.28)

Relative permeate quality is independent of the feed colour. For a particular value of water recovery, it is dependent on retention only.

2.7.2.3 Multi-solute Ultrafiltration Theory

In the course of this investigation it became evident that the evaluation of membrane performance based on ICUMSA colour was not sufficient due to the complex nature of sugar colour and the effect of the different types of colourant molecules on the refining process. An ultrafiltered sugar solution will have different chemical and decolourisation properties due to certain types of molecules being retained by the
membrane. The colourant types which are important to this investigation may be divided into two groups, namely, molecules which are preferentially included in final refined sugar crystallisation and molecules which are easily removed by the ion exchange and crystallisation decolourisation processes. The molecules which are included in the refined sugar crystals are generally the same as those which are not effectively removed by the ion exchange process and tend to foul the ion exchange resin. The various colourant types are described in Section 2.2, the inclusion of colour in refined sugar crystals is described in Section 2.3 while the ion exchange decolourisation process is described in Section 2.4.

The theory in this section proposes that the colourant molecules contained in a sugar solution be divided into the groups mentioned above and that the performance of the membrane be assessed on the basis of its potential for the removal of one or both of the colourant types.

The two colourant groups of interest are referred to as follows:

- potentially included colour ($I_1$)
- easily removed colour ($I_2$)

The easily removed colourant molecules are the sugarcane plant derived colourant species, namely, phenolic acids and flavonoids. These are charged and have a low molecular weight distribution (below 5 000 daltons). The potentially included molecules are generally the high molecular weight, uncharged, colourants. These include colour associated with polysaccharide molecules and the colour molecules produced in the refinery, namely, melanins, melanoidins, alkaline degradation products of fructose and caramels.

Assuming that the two colour groups have constant retention values, equations relating the colour contribution of the two components, in the feed and permeate solutions, to water recovery can be derived as for the single component case above (Section 2.7.2).

From Equation (2.3) for a particular colourant group ($i$) of a multi-component system, the retention is given by:

$$\sigma_i = 1 - \frac{I_{ip}}{I_{if}}$$  \hspace{1cm} (2.29)

where $I$ represents ICUMSA colour.

For the potentially included colourant species:
For the potentially included colourant species:

\[
\sigma_1 = 1 - \frac{I_{1p}}{I_{1f}}
\]

(2.31)

For the easily removed colourant species:

\[
\sigma_2 = 1 - \frac{I_{2p}}{I_{2f}}
\]

(2.31)

Assuming that the two components of colour are additive:

\[
I_{Total} = I_1 + I_2
\]

(2.32)

At the start of the batch ultrafiltration \((t = 0)\), assume:

\[
I_{2f}^0 = F(I_{1f}^0)
\]

(2.33)

Therefore,

\[
I_{Total}^0 = I_1^0 (1 + F)
\]

(2.34)

2.7.2.3.1 Component Feed Colour Contribution

The equation relating feed colour to water recovery for an individual colour component may be derived in the same way as Equation (2.12).

Potentially Retained Colour in the Feed:

\[
I_{1f} = I_{1f}^0 (1 - R)^{-\sigma_1}
\]

(2.35)

Easily Removed Colour in the Feed:

\[
I_{2f} = I_{2f}^0 (1 - R)^{-\sigma_2}
\]

(2.36)
2.7.2.3.2 Composite Permeate Quality

The composite permeate colour is defined as follows:

\[ I_p = \frac{\text{Total Colour in the Permeate Volume}}{\text{Volume of Permeate}} \]  
(2.37)

where \( I_p \) represents the total composite permeate colour.

From Equation (2.17):

\[ I_p = \frac{I_{\text{Total},f}^0 (1 - (1 - R)^{(1 - \sigma_1)})}{R} \]  
(2.38)

but colour is assumed additive (Equation 2.32) Equation 2.38 becomes:

\[ I_p = I_{1,f}^0 (1 - (1 - R)^{(1 - \sigma_1)}) + I_{2,f}^0 (1 - (1 - R)^{(1 - \sigma_2)}) \]

from Equation (2.26),

\[ I_{2,f}^0 = F(I_{1,f}^0) \]

substituting above gives:

\[ I_p = \frac{I_{1,f}^0 (1 - (1 - R)^{(1 - \sigma_1)}) + F(I_{1,f}^0) (1 - (1 - R)^{(1 - \sigma_2)})}{R} \]

\[ I_p = \frac{I_{1,f}^0 [(1 - (1 - R)^{(1 - \sigma_1)}) + F (1 - (1 - R)^{(1 - \sigma_2)})]}{R} \]  
(2.39)

It may be assumed that the retention of the easily removed colourant species will be very low due to the fact that they constitute the low molecular weight sugarcane plant derived colourants (less than 5000 daltons). Assuming a zero retention for the easily removed colourant group, Equation (2.39) simplifies to:

\[ I_p = \frac{I_{1,f}^0 (1 - (1 - R)^{(1 - \sigma_1)}) + FR}{R} \]  
(2.40)
2.7.2.3.3 Fraction of Original Colourant Group in the Feed

From Equation (2.22), the fraction of original feed colour in the permeate is given by:

\[ \delta = 1 - (1 - R)^{(1-\sigma)} \]

For the two colourant groups the equations may be modified to give:

**Fraction Potentially Retained Colour Passing the Membrane**:\[ \delta_1 = 1 - (1 - R)^{(1-\sigma_1)} \] (2.41)

**Fraction Easily Removed Colour Passing the Membrane**:\[ \delta_2 = 1 - (1 - R)^{(1-\sigma_2)} \] (2.42)

2.7.2.3.4 Relative Permeate Quality

From Equation (2.28) the relative permeate quality based on the potentially included and easily removed colourant groups are defined as follows:

Relative permeate quality based on potentially included colour \( = 1 - (1 - \sigma_1)(1 - R)^{-\sigma_1} \) (2.43)

Relative permeate quality based on easily removed colour \( = 1 - (1 - \sigma_2)(1 - R)^{-\sigma_2} \) (2.44)
2.7.2.4 Equation Nomenclature

The symbols used in the above equations are defined as follows:

- $I'_f$ - Original feed colour
- $I_f$ - Feed colour
- $I_p$ - Permeate colour
- $\bar{I}_f$ - Composite permeate colour
- $B'_f$ - Original feed brix
- $B_f$ - Feed brix
- $B_p$ - Permeate brix
- $\bar{B}_f$ - Composite permeate brix
- $C'_f$ - Original feed concentration
- $C_f$ - Feed concentration
- $C_p$ - Permeate concentration
- $G_p$ - Permeate grade
- $G_f$ - Feed grade
- $R$ - Water recovery
- $\sigma$ - Retention
- $\sigma_I$ - Retention based on colour
- $\sigma_B$ - Rejection based on brix
- $\delta$ - Solute loss through membrane
- $\delta_I$ - Fraction colour passing the membrane
- $\delta_B$ - Fraction brix recovered
Chapter 3

Experimental Equipment

This Chapter describes the equipment used in the experimental work performed during this investigation. The equipment includes the inorganic membrane modules, the ultrafiltration pilot rigs, the Sugar Milling Research Institute's (SMRI) pilot evaporator and the SMRI pilot vacuum crystallisation pan. Also described are sundry analytical instruments used for colour and brix determination.

3.1 The Inorganic Membrane Modules

3.1.1 The CeraMem® Series LMDA and LMA Membrane Modules

The CeraMem series LMDA and LMA membrane modules are laboratory-scale ultrafiltration units designed for pilot evaluations or small process flows. They are identical in configuration and have a honeycomb monolith structure. The honeycomb monolith comprises a tubular, porous ceramic support containing sixty, square section, 2 mm wide feed channels. A Cross-sectional view of the honeycomb monolith design is presented in Figure 3.1.

Specifications for the two modules are presented in Table 3.1 and Table 3.2 respectively, while further descriptions are included in Appendix A3.1.
Figure 3.1: Cross-section of the CeraMem series LMDA and series LMA membrane modules.

Table 3.1: Specifications of the CeraMem LMDA-20-P1 ceramic ultrafiltration membrane module.

<table>
<thead>
<tr>
<th>Specification</th>
<th>Specification Details</th>
</tr>
</thead>
<tbody>
<tr>
<td>Manufacturer</td>
<td>CeraMem Separations</td>
</tr>
<tr>
<td>Membrane material</td>
<td>Zirconium oxide</td>
</tr>
<tr>
<td>Support material</td>
<td>Zirconium oxide (CeraMem Separations standard 0.01 μm module)</td>
</tr>
<tr>
<td>Membrane nominal pore diameter</td>
<td>Not specified</td>
</tr>
<tr>
<td>Membrane molecular weight cut-off</td>
<td>10 000 to 15 000 daltons</td>
</tr>
<tr>
<td>Geometry of support element</td>
<td>Tubular monolith with sixty square-section feed channels</td>
</tr>
<tr>
<td>Channel width</td>
<td>2 mm</td>
</tr>
<tr>
<td>Channel length</td>
<td>33 mm</td>
</tr>
<tr>
<td>Total membrane surface area</td>
<td>0.1584 m²</td>
</tr>
<tr>
<td>Maximum operating temperature</td>
<td>130 °C</td>
</tr>
<tr>
<td>Maximum operating pressure</td>
<td>700 kPa</td>
</tr>
<tr>
<td>pH operating range</td>
<td>pH 5 to 12</td>
</tr>
</tbody>
</table>
Table 3.2 Specifications of the CeraMem LMA-0005-P ceramic ultrafiltration membrane module.

<table>
<thead>
<tr>
<th>Feature</th>
<th>Specification</th>
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</thead>
<tbody>
<tr>
<td>Manufacturer</td>
<td>CeraMem Separations</td>
</tr>
<tr>
<td>Membrane material</td>
<td>γ-alumina</td>
</tr>
<tr>
<td>Support material</td>
<td>Silica</td>
</tr>
<tr>
<td>Membrane nominal pore diameter</td>
<td>0.005 μm</td>
</tr>
<tr>
<td>Membrane molecular weight cut-off</td>
<td>Not specified</td>
</tr>
<tr>
<td>Geometry of support element</td>
<td>Tubular monolith with sixty square-section feed channels</td>
</tr>
<tr>
<td>Channel width</td>
<td>2 mm</td>
</tr>
<tr>
<td>Channel length</td>
<td>33 mm</td>
</tr>
<tr>
<td>Total membrane surface area</td>
<td>0.1584 m²</td>
</tr>
<tr>
<td>Maximum operating temperature</td>
<td>Limited by inorganic cement (greater than 130 °C)</td>
</tr>
<tr>
<td>Maximum operating pressure</td>
<td>700 kPa</td>
</tr>
<tr>
<td>pH operating range</td>
<td>pH 5 to pH 12</td>
</tr>
</tbody>
</table>

3.1.2 The Membralox 1P19-40 (0.02 μm) Membrane Module

The Membralox 1P19-40 (0.02 μm) membrane module is an industrial scale ultrafiltration unit, consisting of a single element, having a multi-channel, hexagonal monolithic structure.

Specifications for the module are presented in Table 3.3, while a further description is included in Appendix A3.2. A cross-sectional view of the multi-channel design is presented in Figure 3.2.
Figure 3.2: Cross-section of the Membralox 1P19-40 membrane module.

Table 3.3: Specifications of the Membralox 1P19-40 (0.02 μm) ceramic ultrafiltration membrane.

<table>
<thead>
<tr>
<th>Specification</th>
<th>Details</th>
</tr>
</thead>
<tbody>
<tr>
<td>Manufacturer</td>
<td>Alcoa/SCT</td>
</tr>
<tr>
<td>Membrane material</td>
<td>zirconium oxide</td>
</tr>
<tr>
<td>Support material</td>
<td>α-alumina</td>
</tr>
<tr>
<td>Membrane nominal pore diameter</td>
<td>0.02 μm</td>
</tr>
<tr>
<td>Membrane molecular weight cut-off</td>
<td>Not specified</td>
</tr>
<tr>
<td>Geometry of support element</td>
<td>Hexagonal monolith with 19 circular-section channels</td>
</tr>
<tr>
<td>Channel inside diameter</td>
<td>4 mm</td>
</tr>
<tr>
<td>Channel length</td>
<td>869 mm</td>
</tr>
<tr>
<td>Total membrane surface area</td>
<td>0.2075 m²</td>
</tr>
<tr>
<td>Maximum operating temperature</td>
<td>1000 °C</td>
</tr>
<tr>
<td>Maximum operating pressure</td>
<td>Bursting pressure specified as 10 MPa</td>
</tr>
<tr>
<td>pH operating range</td>
<td>pH 1 to 14</td>
</tr>
</tbody>
</table>

3.1.3 The Carbosep Membrane Module

The M5 Micro-Carbosep 60 membrane module is a pilot-scale ultrafiltration unit suited for laboratory evaluations or small process flows. It consists of a single tubular element of porous carbon.
Specifications for the module are presented in Table 3.4, while a further description is included in Appendix A3.3. A cross-sectional view of the tubular design is presented in Figure 3.3.

**Figure 3.3**: Cross-section of the M5 Micro-Carbosep 60 membrane module.

**Table 3.4**: Specifications of the M5 Micro-Carbosep 60 inorganic ultrafiltration membrane module.

<table>
<thead>
<tr>
<th>Specification</th>
<th>Value</th>
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</thead>
<tbody>
<tr>
<td>Manufacturer</td>
<td>Tech Sep, a division of Rhone-Poulenc/SFEC</td>
</tr>
<tr>
<td>Membrane material</td>
<td>Zirconium-oxide/titanium-oxide</td>
</tr>
<tr>
<td>Support material</td>
<td>Carbon</td>
</tr>
<tr>
<td>Membrane nominal pore diameter</td>
<td>Not specified</td>
</tr>
<tr>
<td>Membrane molecular weight cut-off</td>
<td>10 000 dalton</td>
</tr>
<tr>
<td>Geometry of support element</td>
<td>Tubular</td>
</tr>
<tr>
<td>Channel inside diameter</td>
<td>6 mm</td>
</tr>
<tr>
<td>Channel length</td>
<td>600 mm</td>
</tr>
<tr>
<td>Total membrane surface area</td>
<td>0.01131 m²</td>
</tr>
<tr>
<td>Maximum operating temperature</td>
<td>300 °C</td>
</tr>
<tr>
<td>Maximum operating pressure</td>
<td>1 500 kPa</td>
</tr>
<tr>
<td>pH operating range</td>
<td>pH 1 to 14</td>
</tr>
</tbody>
</table>
3.2 Pilot Ultrafiltration Rigs

3.2.1 The Membrane Cleaning Rig

![Diagram of the membrane cleaning rig]

**Figure 3.4:** Flow diagram of the membrane cleaning rig.

The *membrane cleaning rig* was used for chemical cleaning of the inorganic membrane modules as well as for membrane pure water permeability (PWP) determinations. Cleaning procedures are described in Appendix A2.3, while the procedure for the determination of membrane PWP is described in Appendix A2.2.

The particular membrane module, in its stainless steel housing, is attached to a separate stand by means of U-bolts. Flexible, stainless steel hoses are used to connect the membrane module feed and discharge ends to the rig. A similar hose is used to connect the permeate return line, on the housing, to the feed tank.
The rig has a 40 ℓ feed tank which is connected to a M-range, S32M Mono pump (Mono Pumps Africa (Pty) Limited). A 2 kW immersion heating element is inserted in the feed tank. A temperature sensor in the tank is connected to a Eurotherm controller which is used to switch the immersion heater on and off to maintain a set temperature in the feed tank.

Feed solution may be pumped directly to the membrane module, may be returned to the feed tank via a bypass line, or may be pumped to drain. Retentate flows through a metric 24 G rotameter (GEC - Elliot Process Instruments Ltd) before returning to the feed tank. The retentate may also be diverted to drain. Feed solution can be drained directly from the feed tank without pumping.

Pressure is controlled by adjusting the control valves in the retentate return and bypass return lines. Pressure gauges are located at the inlet and outlet ends of the housing module. They are both glycerine filled and have a maximum pressures tolerance of 2 500 kPa.

All flow lines, except the pump supply and discharge lines and the flexible stainless steel hoses, are tubes of half inch diameter. The pump supply and discharge lines are half inch diameter pipes.

The entire rig, including pipework, tubes, connections, valves, gauges and the feed tank are of 316 stainless steel.
3.2.2 The Refined Sugar Ultrafiltration Rig

The refined sugar ultrafiltration rig was used for Experiment Series B, Experiment Series C and Experiment D (all described in Chapter 4). Solutions used were of H1 refined sugar, affinated H1 refined sugar, affination wash liquor, raw VHP sugar and Johnson sweetwater.

The rig is a modified version of the membrane cleaning rig described in Section 3.2.1. The entire configuration is identical except for the feed tank heating arrangement. The sugar solutions could not be heated using the 2 kW heating element used in the membrane cleaning rig due to the high film temperatures of the element. This could cause burning and consequent colour formation in the sugar solution. To avoid burning, the sugar solution was heated using a heating coil through which hot water was passed. The heating system is described below.

The 2 kW immersion element, used in the membrane cleaning rig, is placed in a separate tank containing water. Temperature in the water tank is measured by a probe and controlled by means of a
Eurotherm controller connected to the heater element. The controller is used to switch the element on and off to maintain a set water temperature.

The water tank is connected to the stainless steel coil (half inch diameter tube) inside the refined sugar ultrafiltration rig feed tank, by means of rubber hoses, completing the hot water circuit. A temperature probe in the rig feed tank is connected to another Eurotherm temperature controller dedicated to switching on and off a small centrifugal pump in the hot water circuit. The pump is a Serfilco Model A magnetic centrifugal pump. This is used to maintain a set temperature in the feed tank.

3.2.3 The Refinery Ultrafiltration Rig

![Flow diagram of the refinery ultrafiltration rig]

Figure 3.6: Flow diagram of the refinery ultrafiltration rig

The refinery ultrafiltration rig was used for the ultrafiltration of Johnson sweetwater in Experiment Series A and to collect Johnson sweetwater feed and permeate samples for Experiment Series E. The experiments are described in Chapter 4.

The rig is designed to run using Johnson sweetwater directly from the Johnson sweetwater tank at Hulett Refineries. A three inch pipeline, connected to the Johnson sweetwater pump discharge line, supplies
the *ultrafiltration-rig booster pump*. The booster pump is an ETB 40-20 centrifugal pump manufactured by KSB Pumps (S.A.).

The *ultrafiltration-rig booster pump* discharges to a half inch line connected to the ultrafiltration rig frame. The ultrafiltration rig is self contained and is constructed on a frame of angle iron. The entire unit may be disconnected from the booster pump and transported. The membrane module housing is connected to the rig by U-bolts. The feed and discharge ends are connected to the rig pipework by means of flexible rubber hoses.

Prior to connecting to the housing feed hose, three separate lines are connected to the feed line from the booster pump. The first line is the *continuous feed sample port*. This sample port has a control valve (needle valve) allowing feed sample flow rate to be regulated. The second line is the *feed purge line*. This allows feed to be purged to the sump. The *membrane isolation valve* in the feed line is closed when feed is being discharged to the sump, allowing the membrane module to be bypassed. A rubber hose runs from the *purge valve* to the sump. The third line is the *feed sample port*. This is conveniently located to allow rapid sampling of the feed stream.

The discharge line has a control valve allowing the system back pressure to be regulated and hence, the trans-membrane pressure to be controlled. A rubber hose is connected to the *back-pressure valve* allowing the retentate to be discharged to the sump. A rubber hose is also connected to the permeate valve on the particular membrane module housing to allow permeate to be discharged to the sump.

Glycerine filled pressure gauges are located at the feed and discharge ends of the membrane module housing. A temperature gauge is connected in the feed line.

Permeate flux was measured using a measuring cylinder and a stopwatch, while feed flow rate was measured using a 30 ℓ container and a stopwatch.
3.3 The SMRI Pilot Evaporator

![Flow diagram of the SMRI pilot evaporator](image)

Figure 3.7: Flow diagram of the SMRI pilot evaporator

The SMRI pilot scale evaporator, described by Lionnet and Reid [1993], is a two-effect evaporator designed to evaporate water at a rate of 12 L/h.

The first effect evaporator vessel is made up of two sections. The first section, the calandria, consists of a stainless steel tube, 100 mm in diameter and 600 mm long, around which three plate elements, each of 1.25 kW, are wrapped. A fourth element of 1.4 kW is arranged in a central tube fitted on the bottom flange. The second section consists of a glass cylinder, also 100 mm in diameter and 600 mm long, which is attached above the calandria and constitutes the boiling column.

The juice inlet to the first effect is located at the bottom of the stainless steel calandria. Juice flow rate into the calandria is controlled manually by means of a needle valve in the juice inlet line (the first effect feed valve). A level sensor is situated in the boiling column. The level controller associated with the sensor opens and closes a solenoid valve in the parallel feed line to maintain a minimum level in the
boiling column. The level sensor is not relied upon to maintain actual boiling level in the evaporator. It is more reliable to control boiling level manually by observing the boiling in the glass column and controlling the feed flow rate by adjusting the first effect feed valve.

A small sight glass is situated at the top of the stainless steel calandria. The vapour outlet is located at the top of the glass boiling column and is fitted with a simple droplet eliminator. The vessel is fitted with a safety valve set at 30 kPa gauge.

The second effect evaporator consists of three stainless steel tubes, each of 16 mm diameter and 1 200 mm long, welded into tube plates. The tube plates are fitted into a 50 mm diameter, stainless steel calandria using O-rings to facilitate quick replacement. The second effect operates on the climbing-film principle. The top of the vessel is provided with a sight glass and a mirror so that the boiling operation can be observed from ground level.

Juice from the first effect calandria enters the second effect tubes from the bottom. The rate of flow of juice is controlled manually by adjusting the second effect feed valve. Hot vapour from the first effect enters the top of the second effect on the shell side. The vapour supplies the heat to boil the juice on the inside of the tubes. The intensity of boiling in the tubes is controlled by increasing or decreasing the amount of splashing on the sight glass by manipulating the second effect feed valve. The vapour and juice from the top of the second effect vessel are separated in the separator (a small cyclone), the vapour being condensed in the condenser (a water cooled heat exchanger).

The condensates, from the second effect shell and the condenser, and the final syrup, from the separator, are collected in stainless steel vacuum vessels which have sufficient capacity to allow about 4 hours of continuous operation.

The evaporation procedure is described in Appendix A2.8.3.
3.4 The SMRI Pilot Crystallisation Pan

![Diagram of the SMRI pilot crystallisation pan]

Figure 3.8: Flow diagram of the SMRI pilot crystallisation pan.

The pilot-scale vacuum pan was originally designed and built at SMRI in 1964 [Bruijn (1964)]. Extensive modifications have been made to the pan instrumentation in recent times [Lionnet and Reid (1993)].

The pan consists of a brass vessel 229 mm in diameter and 107 mm high which forms the *calandria*. Around the sides of the brass vessel are wound four electric heating elements which are covered by asbestos insulation. The body of the pan consists of a Quickfit quartz pipe segment of 229 mm diameter by 457 mm high. This quartz segment is fixed to the calandria by a stainless steel ring held by four stainless steel rods. Rubber washers provide an airtight seal. In the bottom of the pan are three needle valves for feed, water and seed slurry.
Through the lid of the pan passes a stainless steel shaft carrying three impellers in a perforated draft tube. The draft tube is perforated to compensate for varying liquid level. A reduction gearbox, made of lathe change wheels, is fitted on the top of the shaft to reduce the shaft speed to 140 rpm.

The pan instrumentation is described below [Lionnet (1987)].

(i) Conductivity measurements are taken using a conventional two electrode system which is situated in the pan saucer.

(ii) Massicuie temperature is measured by a semiconductor sensor extending about 50 mm into the calandria vessel.

(iii) Stirrer torque is measured electronically at the DC motor.

(iv) Pan absolute pressure is measured electronically.

(v) Boiling point elevation, the difference between the massicuie temperature measured in (ii) above and the boiling temperature of water at the same absolute pressure, is measured electronically.

The measurements are converted to 0 to 10 V signals, which are then fed into a data logging computer through an A/D card. The five quantities mentioned above are displayed numerically and graphically on the computer monitor. The measurements are stored on disc and can be printed if desired [Lionnet (1987)].

The procedure for the boiling operation is described in Appendix A2.8.4.

### 3.5 Sundry Analytical Equipment

#### 3.5.1 Spectrophotometer

The spectrophotometer was used to measure the absorbance of sugar solutions for colour analysis. The procedure for ICUMSA colour analysis is presented in Appendix A2.1.

<table>
<thead>
<tr>
<th>Manufacturer</th>
<th>Phillips</th>
</tr>
</thead>
<tbody>
<tr>
<td>Make</td>
<td>PU8670 VIS/NIR Spectrophotometer</td>
</tr>
<tr>
<td>Serial number</td>
<td>GE 388491</td>
</tr>
</tbody>
</table>
3.5.2 Digital Refractometer

The refractometer was used to measure the brix of sugar solutions for colour analysis. The procedure for ICUMSA colour analysis is presented in Appendix A2.1.

Manufacturer : Bellingham and Stanley Limited
Make : RFM 80 Digital Refractometer
Serial number : N83210
Chapter 4

Experimental

Chapter 4 describes and discusses the experimental work performed in the investigation into the decolourisation of Johnson sweetwater using ultrafiltration. The preliminary investigations are described in Section 4.1 while the individual experiments are each contained in a separate section.

The results of the ultrafiltration of Johnson sweetwater (Experimental Series A) led to additional experimental work being performed in an attempt to clarify the colour retention results achieved. The motivation and reasons for the additional experimental work, Experiment Series B to Experiment Series E, are discussed in Section 4.4.4.

The experimental result sections contained in this chapter are as follows:

4.1 Preliminary Investigations

4.2 Original Pure Water Permeability

4.3 The Formation of a Dynamic, Dual-layer, Zirconium(iv)oxide/Polyacrylic-acid Membrane on the Membralox IP19-40 (0.02 μm) Membrane Module

4.4 Experiment Series A
The Ultrafiltration of Johnson Sweetwater

4.5 Experiment Series B
The Ultrafiltration of H1 Refined Sugar, Affinated H1 Refined Sugar, Affination Wash Liquor and Raw VHP Sugar - using the CeraMem LMDA-20-P1 Membrane Module

4.6 Experiment Series C
The Ultrafiltration of H1 Refined Sugar and Affinated H1 Refined Sugar Under Conditions of High Water Recovery - using the CeraMem LMDA-20-P1 Membrane Module
4.7 Experiment series D
The Ultrafiltration of Johnson Sweetwater Under Conditions of High Water Recovery- using the CeraMem LMDA-20-P1 Membrane Module

4.8 Experiment Series E
Johnson Sweetwater Feed and Permeate Colour Transfer Analyses

Each section discusses the aim of the particular experiment, the experimental procedure and equipment used, and the results obtained. Results are summarised to compliment only the specific aims of that experiment. Detailed experimental results and raw data are presented in Appendix A1, while stepwise experimental procedures are contained in Appendix A2. Descriptions of experimental equipment are contained in Chapter 3.
4.1 Preliminary Investigations

4.1.1 The Ultrafiltration of Johnson Sweetwater Using Flat-sheet Organic Membranes

4.1.1.1 Aim of the Experiment

The process of ultrafiltration, as an effective method for the removal of colour from Johnson sweetwater solutions, was investigated using several organic membranes of known molecular weight cut-off.

4.1.1.2 Experimental Method and Equipment

The membranes were of the flat-sheet variety and were installed in a flat-sheet rig for ultrafiltration investigations.

The flat-sheet rig consists of an 8ℓ feed tank, a Hydrocell D10 pump and three membrane cells in series. The cells were each fitted with discs of flat-sheet membrane, 47 mm in diameter. The rig was run at a pressure of 500 kPa and at a temperature of 80 ℃, with the permeate and retentate being returned to the feed tank. A 2 kW immersion heater, connected to a Eurotherm controller and temperature probe, was used to maintain the temperature of the feed tank at 75 ℃. The run-time of each experiment was 1 h.

The specifications of the organic, flat-sheet membranes are presented in Table 4.1.

<table>
<thead>
<tr>
<th>Table 4.1</th>
<th>Organic, flat-sheet membrane specifications.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Membrane</td>
<td>Molecular weight retention range (daltons)</td>
</tr>
<tr>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
</tr>
<tr>
<td>Koch HFK131</td>
<td>1 000 to 10 000</td>
</tr>
<tr>
<td>Koch HFM100</td>
<td>10 000 to 30 000</td>
</tr>
<tr>
<td>SEPA AG02</td>
<td>3 000</td>
</tr>
</tbody>
</table>
4.1.1.3 Experimental Results and Discussion

The ICUMSA colour retention and brix retention results using the flat-sheet organic membranes are presented in Table 4.2.

<table>
<thead>
<tr>
<th>Membrane</th>
<th>ICUMSA colour retention (%)</th>
<th>Brix retention (%)</th>
<th>Permeate flux (L/m²h)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Koch HFK131</td>
<td>54</td>
<td>9</td>
<td>121</td>
</tr>
<tr>
<td>Koch HFM100</td>
<td>66</td>
<td>9</td>
<td>91</td>
</tr>
<tr>
<td>SEPA AG02</td>
<td>55</td>
<td>8</td>
<td>123</td>
</tr>
</tbody>
</table>

The ICUMSA colour retention values achieved using the three organic membranes range between 54 and 66%. These are relatively high, but may be exaggerated due to the high feed ICUMSA colour value of 5 500.

The highest ICUMSA colour retention value was achieved using the Koch HFM100 membrane. This membrane also exhibited the lowest permeate flux value of 91 L/m²h. This is contrary to expectations when one considers that the specified retention range of the Koch HFM100 membrane is an order of magnitude greater than the retention ranges of the Koch HFK131 and SEPA AG02 membranes (Table 4.1).

It may be assumed that the HFM100 membrane was more conducive to the formation of a dynamic secondary layer on the membrane surface due to its larger pore size distribution. The formation of the dynamic secondary layer, or concentration polarised layer, is a function of the membrane surface structure, the operating conditions and the nature of the Johnson sweetwater and results from the concentration of retained solute species at the solution/membrane interface due to the passage of water and non-retained solute species through the membrane. This phenomenon causes an increase in the retention of the high molecular weight solute species and a decrease in the permeate flux due to increased resistance to transport at the membrane surface. Concentration polarisation is described in Section 2.7.1.1.

Experimentation using the flat-sheet, organic membranes was discontinued for the following reasons:

Firstly, colour formation due to excessive heating of the feed Johnson sweetwater was observed. This was caused by the long residence time of the feed Johnson sweetwater in the tank due to the low feed
circulation rate, the low feed volume in the system and the high film temperature of the heating element. Secondly, the extent of compaction and plastic deformation of the membrane surface, due to operation at high temperature and pressure, could not be effectively quantified. Thirdly, the respective manufacturers discounted the possibility of their available membrane housing modules being able to tolerate the high process temperatures associated with the Johnson sweetwater system (70 to 80 °C). Also, the membrane manufacturers predict greatly reduced operating lives of the organic membranes when operating at temperatures close to their maximum limits.

Work on the organic membranes was discontinued. However, the preliminary work did indicate the ability of ultrafiltration to retain ICUMSA colour from Johnson sweetwater. The ultrafiltration investigation was subsequently focused on the potential use of inorganic membranes.

### 4.1.2 The Selection of Inorganic Membranes for the Ultrafiltration of Johnson Sweetwater

Following the decision to discontinue investigating the organic ultrafiltration membranes, a suitable inorganic membrane had to be found which would be able to achieve similar results to those of the organic membranes.

The advantages of inorganic ultrafiltration media over their organic counterparts are:

- long lifetime and reliability
- high resistance to temperature and pressure
- high stability in organic media
- rigidity, with no creep or deformation of the membrane surface
- stability over a wide pH range
- corrosion and abrasion resistance
- insensitivity to bacterial action
- ability to be repeatedly sterilised by steam and chemicals
- ability to be back-washed
- possibility of regeneration after fouling
• greater void area per unit area of filtration surface
• strong bonding of filtrate to substrate by sintering
• ability to process highly viscous fluids

The criterion for the selection of inorganic membranes for the ultrafiltration of Johnson sweetwater was based primarily on pore size or specified molecular weight retention of the membrane.

Patel [1992] reported a colour retention of 60% using a Carbosep 10 000 dalton molecular weight cut-off membrane for the ultrafiltration of refinery sweetwater. Refinery sweetwater is the sweetwater from the high grade sweetwater and is used as melter water. It is made up of Johnson sweetwater, dissolved reject sugars from the pan-house melter and fine water makeup (Figure 1.2). Refinery sweetwater has a higher brix value and will have a higher concentration of high molecular weight potentially included colour molecules than Johnson sweetwater due to the recycle of reject sugar. Strohwald [1990], observed a colour retention of 43% for refinery sweetwater, using a 20 000 dalton molecular weight cut-off, organic ultrafiltration membrane.

Based on the reported colour retentions for the ultrafiltration of refinery sweetwater, and on the preliminary work performed during the course of this investigation, a survey was performed to isolate the lowest molecular weight cut-off (tightest) inorganic membrane modules available. The membranes are required to tolerate a process temperature of about 80 °C and process pH values ranging between 6 and 9.

A list of available ceramic membrane manufacturers and their addresses is presented in Table A4.2 (Appendix A4). The manufacturers were contacted and information regarding their available inorganic membrane products requested. Bhave [1991] also performed such a survey, the results of which are summarised in Table A4.1 (Appendix A4).

To date, the majority of inorganic membrane manufacturers only produce microfiltration membranes of pore size greater than 0.02 µm. The membranes that were not considered were disregarded because of their large pore sizes, except for the Asahi Glass range of membranes which are sensitive to pH values of 9 and above, and the Membralox ultrafiltration membranes which are also pH sensitive.

The CeraMem and Carbosep range of ultrafiltration membranes were the tightest available liquid processing. The CeraMem membranes have a honeycomb monolith structure which provides high

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1 Potentially included colour molecules are those colourants which tend to be included in the refined sugar crystals.
membrane surface area in a compact design. In contrast to the CeraMem module, the Carbossep membrane module is tubular and has a surface area an order of magnitude lower. On the basis of this, it was decided to purchase two CeraMem series LM pilot-scale membrane modules, the CeraMem LMA-0005-P module, having a specified nominal pore size of 0.005 μm, and the CeraMem LMDA-20-P1 module, having a specified molecular weight cut-off between 10 000 and 15 000 daltons.

An M5 Micro-Carbossep 60 membrane module with a specified nominal molecular weight cut-off of 10 000 daltons was borrowed from the Sugar Milling Research Institute. A Membralox 1P19-40 membrane module, with a nominal pore size of 0.02 μm, was borrowed from MEMBRASEP, a division of the Atomic Energy Corporation of South Africa Limited.

The specifications for the CeraMem series LM, the Micro-Carbossep 60 and the Membralox membrane modules are presented in Section 3.1.
4.2 Original Pure Water Permeability

4.2.1 Aim of the Experiment

The aim of the experiment was to determine the characteristic permeate flux rates of the original membranes, using pure water (reverse osmosis permeate water) as the process fluid.

4.2.2 Experimental Method and Equipment

Pure water permeabilities were determined for the CeraMem LMDA-20-P1 module, the CeraMem LMA-0005-P module, the M5 Micro-Carbosep 60 (10 000 dalton pore size) module and the Membralox 1P19-40 (0.02 μm cut-off) module.

<table>
<thead>
<tr>
<th>Experimental rig used</th>
<th>Membrane cleaning rig (described in Chapter 3.2.1)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Feed solution</td>
<td>Reverse osmosis permeate water</td>
</tr>
<tr>
<td>Feed temperature</td>
<td>40 °C</td>
</tr>
<tr>
<td>Volumetric flow rate</td>
<td>21 g/min (CeraMem and Membralox modules)</td>
</tr>
<tr>
<td></td>
<td>4 g/min (Carbosep module)</td>
</tr>
<tr>
<td>Linear flow rate</td>
<td>1.5 m/s (CeraMem and Membralox modules)</td>
</tr>
<tr>
<td></td>
<td>2.5 m/s (Carbosep module)</td>
</tr>
</tbody>
</table>

The stepwise experimental procedure for pure water permeability determination is presented in Appendix A2.2.
### 4.2.3 Experimental Results and Discussion

<table>
<thead>
<tr>
<th>Membrane</th>
<th>Original pure water permeability (l/m²h)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>300 kPa</td>
</tr>
<tr>
<td>CeraMem LMDA-20-P1</td>
<td>300</td>
</tr>
<tr>
<td>CeraMem LMA-0005-P</td>
<td>400</td>
</tr>
<tr>
<td>M5 Micro-Carbosep 60 (10 000 dalton cut-off)</td>
<td>170</td>
</tr>
<tr>
<td>Membralox 1P19-40 (20 nm pore size)</td>
<td>700</td>
</tr>
</tbody>
</table>

The purpose of determining the pure water permeability (PWP) of a particular membrane is to be able to assess the degree of fouling of that membrane, following its exposure to a particular sugar solution, relative to the original PWP when it was first purchased. The difference between the value of the PWP of a particular membrane and its original PWP is a measure of the degree of fouling of that membrane. The original pure water permeability values of the new membranes were determined prior to exposing them to any sugar solution or process fluid.

Pure water permeability (PWP) is directly proportional to the applied trans-membrane pressure and is a characteristic of a particular membrane, being dependent on the pore structure and associated resistance of that membrane. No secondary flow resistance such as concentration polarisation or membrane fouling occurs due to the absence of solute molecules. Hence, PWP is only a function of the membrane surface structure, applied trans-membrane pressure which is the driving force, and system temperature which affects fluid viscosity.

The original membrane pure water permeability values, presented in Table 4.3, were used as reference values when assessing the degree of membrane fouling following experimental runs on sugar solutions.
4.3 The Formation of a Dynamic, Dual-layer, Zirconium(iv)oxide/Polyacrylic-acid Membrane on the Membralox 1P19-40 (0,02 μm) Membrane Module

4.3.1 Aim of the Experiment

The aim of the experiment was to modify the retention characteristics of the Membralox 1P19-40 (20 μm) membrane module by forming a dynamic, dual-layer, zirconium(iv)oxide/polyacrylic-acid (ZrO₂/PAA) membrane on the ceramic membrane surface.

4.3.2 Experimental Method and Equipment

The procedure for the formation of the dynamic, dual layer, ZrO₂/PAA membrane is presented in Appendix A2.9. The procedure was adapted from Neytzel-de Wilde [1986] for the formation of the same dynamic membrane on porous stainless steel supports.

The experimental rig used was the membrane cleaning rig which is described in Section 3.2.1.

4.3.3 Experimental Results and Discussion

An in-depth study of the science of dynamic membrane formation on ceramic membrane supports was not intended. The experiment was merely an attempt to investigate whether or not membrane surface modification could improve the retention characteristics of the 0,02 μm Membralox membrane.

The maximum retention of sodium nitrate, based on conductivity difference between feed and ultrafiltration permeate solutions, was only 15 %. This is lower than the 30 % retention achieved using porous, stainless steel supports [Neytzel-de Wilde (1986)]. However the decrease in pure water permeability of the membrane from 1 200 to 60 μm²/h confirms the formation of the dynamic membrane on the surface pores of the membrane.

The modified Membralox membrane was run using Johnson sweetwater as the feed solution (Experiment A4). The results are presented in Section 4.4.3 and in Appendix A1 2.2.4.
4.4 Experiment Series A: The Ultrafiltration of Johnson Sweetwater

4.4.1 Aim of Experiment Series A

The aim of Experiment Series A was to assess the ability of the various inorganic membranes to retain colour in Johnson sweetwater.

4.4.2 Experimental Method and Equipment

The stepwise experimental procedure for the ultrafiltration of Johnson sweetwater using the inorganic membranes is described in Appendix A2.4. The experiments were performed using the refinery ultrafiltration rig which is described in Section 3.2.3.

Experiments A1 to A5 correspond to the ultrafiltration of Johnson sweetwater using the CeraMem LM0A-20-PI module, the CeraMem LMA-0005-P module, the Membralox 1P19-40 (0.02 μm pore size) module, the modified Membralox 1P19-40 (0.02 μm pore size) module with dual layer ZrO₂/PAA dynamic membrane, and the MS Micro-Carbosep 60 (10 000 dalton cut-off) module, respectively. The membrane modules are described in Section 3.1.

Johnson sweetwater from the Johnson sweetwater tank was pumped through the membrane module using the ultrafiltration-rig booster pump. Retentate and permeate were allowed to flow continuously into the sump. Feed pressure was maintained at 400 kPa, while feed temperature, brix, absorbance, pH and ICUMSA colour varied with the condition of the Johnson sweetwater.

The membranes were exposed to the Johnson sweetwater for varying periods of time, depending on the degree of fouling and associated flux decline of the particular membrane. Feed and permeate samples were taken periodically from the feed and permeate sample ports respectively. Permeate flow rate was measured at the permeate sample port using a measuring cylinder and stopwatch and converted to a permeate flux value by dividing by the particular membrane surface area. Feed flow rate was determined using a 25 ℓ container and a stopwatch.

The samples were analysed for brix, pH, absorbance and ICUMSA colour in the laboratory at Hulett Refineries. The values of brix retention, absorbance retention and ICUMSA colour retention were calculated by determining the percentage difference between the respective feed and permeate values and are presented in Section 4.4.3.
4.4.3 Experimental Results and Discussion

Complete feed data, permeate flux data and retention data are presented in the tables and figures in Appendix A1.2. The data for each particular experiment is presented in similar tables and figures to allow membrane performance to be compared. Each experiment has two associated tables of results, the titles of which are listed below.

Note : ( ) denotes a particular membrane module.

(i) Point feed variables and permeate flux values for the ultrafiltration of Johnson sweetwater using the ( ) membrane module.

(ii) Point brix retention, absorbance retention and ICUMSA colour retention values for the ultrafiltration of Johnson sweetwater using the ( ) membrane module.

Each experiment has five associated figures containing experimental results, the titles of which are listed below.

Note : ( ) denotes a particular membrane module.

(i) Point feed and permeate variables for the ultrafiltration of Johnson sweetwater using the ( ) membrane module.

(ii) Point feed and permeate brix values, absorbance values and ICUMSA colour values for the ultrafiltration of Johnson sweetwater using the ( ) membrane module.

(iii) Point brix retention, absorbance retention and ICUMSA colour retention values for the ultrafiltration of Johnson sweetwater using the ( ) membrane module.

(iv) Mathematically predicted feed and permeate absorbance values, ICUMSA colour values and brix values for the ultrafiltration of Johnson sweetwater using the ( ) membrane module.

(v) Mathematically predicted % colour passing the membrane and % sugar recovered, composite permeate grade, and relative permeate quality as functions of water recovery for the ultrafiltration of Johnson sweetwater using the ( ) membrane module.

Brix retention, absorbance retention and ICUMSA colour retention values for Experiment A1 to A5 are presented in Table 4.4. The average feed and permeate brix values, absorbance values and ICUMSA colour values for the five experiments are presented in Table 4.5.
### Table 4.4: Experiment Series A
Point brix retention, absorbance retention and ICUMSA colour retention for the ultrafiltration of Johnson sweetwater.

<table>
<thead>
<tr>
<th>Experiment Number and associated membrane</th>
<th>Brix Retention (%)</th>
<th>ICUMSA Colour Retention (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Max</td>
<td>Min</td>
</tr>
<tr>
<td>Experiment A1 (CeraMem LMDA-20-P1)</td>
<td>10</td>
<td>0</td>
</tr>
<tr>
<td>Experiment A2 (CeraMem LMA-0005-P)</td>
<td>23</td>
<td>7</td>
</tr>
<tr>
<td>Experiment A3 (Membralox 1P19-40 (20 μm))</td>
<td>4</td>
<td>1</td>
</tr>
<tr>
<td>Experiment A4 (Modified Membralox 1P19-40 (20 μm))</td>
<td>19</td>
<td>0</td>
</tr>
<tr>
<td>Experiment A5 (M5 Micro-Carbosep 60)</td>
<td>9</td>
<td>4</td>
</tr>
</tbody>
</table>

Max = maximum, Min = minimum

### Table 4.5: Experiment Series A
Average point feed and permeate brix values, absorbance values and ICUMSA colour values.

<table>
<thead>
<tr>
<th>Experiment number and associated membrane</th>
<th>Brix</th>
<th>Absorbance</th>
<th>ICUMSA Colour</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Feed</td>
<td>Permeate</td>
<td>Feed</td>
</tr>
<tr>
<td>Experiment A1 (CeraMem LMDA-20-P1)</td>
<td>10,4</td>
<td>10,0</td>
<td>0,334</td>
</tr>
<tr>
<td>Experiment A2 (CeraMem LMA-0005-P)</td>
<td>8,1</td>
<td>7,2</td>
<td>0,272</td>
</tr>
<tr>
<td>Experiment A3 (Membralox 1P19-40 (20 μm))</td>
<td>9,8</td>
<td>9,5</td>
<td>0,374</td>
</tr>
<tr>
<td>Experiment A4 (Modified Membralox 1P19-40 (20 μm))</td>
<td>6,2</td>
<td>5,6</td>
<td>0,192</td>
</tr>
<tr>
<td>Experiment A5 (M5 Micro-Carbosep 60)</td>
<td>6,6</td>
<td>6,3</td>
<td>0,168</td>
</tr>
</tbody>
</table>

Point values of feed and permeate brix, absorbance and ICUMSA colour, as well as the corresponding point retention values are presented graphically in Figure 4.1 to 4.5 for Experiment A1 to A5 respectively. The point permeate flux values are presented in Figure 4.6.
Figure 4.1: Experiment A1
Point brix retention, absorbance retention and ICUMSA colour retention values for the ultrafiltration of Johnson sweetwater using the CeraMem LMDA-20-P1 membrane module.
Figure 4.2: Experiment A2
Point brix retention, absorbance retention and ICUMSA colour retention values for the ultrafiltration of Johnson sweetwater using the CeraMem LMA-0005-P membrane module.
Figure 4.3: Experiment A3
Point brix retention, absorbance retention and ICUMSA colour retention values for the ultrafiltration of Johnson sweetwater using the Membralox 1P19-40 (20 nm) membrane module.
Figure 4.4: Experiment A4

Point brix retention, absorbance retention and ICUMSA colour retention values for the ultrafiltration of Johnson sweetwater using the modified Membralox 1P19-40 (20 nm) membrane module with dual-layer dynamic membrane.
Figure 4.5: Experiment A5
Point brix retention, absorbance retention and ICUMSA colour retention values for the ultrafiltration of Johnson sweetwater using the M5 Micro-Carbosep (10 000 dalton cut-off) membrane module.
The results of Experiment Series A represent typical values of brix retention and ICUMSA colour retention for the ultrafiltration of Johnson sweetwater using the inorganic membranes. The experiments are not reproducible, due to the varying nature of the feed Johnson sweetwater, and each point value of brix or colour retention is unique for a particular membrane at the particular feed and operating conditions. However, the experiments do give an indication as to what range of colour retentions the membranes are capable of achieving.

The performance of each membrane is compared relative to the performance of the CeraMem LMDA-20-P1 membrane module, used in subsequent experimental work.
4.4.3.1 ICUMSA Colour Retentions

The term *colour*, used in this section, always refers to ICUMSA colour. ICUMSA colour is defined in Section 2.2. The procedure for the determination of ICUMSA colour is described in Appendix A2.1.

The CeraMem LMDA-20-P1 and the M5 Micro-Carbosep 60 membrane modules were expected to achieve the highest values of colour retention due to their low, specified molecular weight cut-off characteristics. The CeraMem LMDA-20-P1 module has a specified cut-off of between 10 000 and 15 000 daltons, while the Carbosep membrane has a specified cut-off of 10 000 daltons. These molecular weight cut-off values were determined by the membrane manufacturers using polymers of known molecular weight. The specified cut-off’s cannot always be relied upon due to the retention of a particular species being dependent, not only on the membrane pore structure, but also on the dynamic secondary membrane formed by the concentration of solute molecules at the membrane/solution interface. This phenomenon is known as concentration polarisation and is described in Section 2.7.1.1. The extent of formation and the retention characteristics of the dynamic secondary membrane layer are dependent on the membrane surface structure, the nature of the dissolved species and the experimental operating conditions.

The M5 Micro-Carbosep module did achieve the highest maximum (56 %) and average (50 %) colour retentions (Table 4.4). These values are strongly dependent on the nature of the Johnson sweetwater and the interaction of the non-sugars in the sweetwater with the membrane surface. The point feed and permeate ICUMSA colour values, absorbance values, brix values, and the corresponding retention values, are presented in Figure 4.5. The average feed and permeate ICUMSA colour values, absorbance values and brix values are presented in Table 4.5.

Patel [1992] observed a colour retention of 60 % using the identical Micro-Carbosep membrane module on refinery sweetwater. Refinery sweetwater, from the high grade sweetwater tank, has a lower ICUMSA colour value than Johnson sweetwater due to the higher sucrose concentration from reject sugar addition. Refinery sweetwater is made up of Johnson sweetwater, dissolved reject sugars from the pan house and finely water make-up.

The CeraMem LMDA-20-P1 module was expected to exhibit an ICUMSA colour retention of similar magnitude to the Carbosep membrane. However, this was not the case with the maximum and average colour retentions for the CeraMem module being only 37 and 31 % respectively. The reasons for this can only be attributed to the nature of the membrane surface and the characteristics of the dynamic membrane (concentration polarised layer) formed on the original membrane surface. The phenomenon of concentration polarisation is described in Section 2.7.1.1. The Carbosep membrane fouled much quicker than the CeraMem module which is evident in the greater permeate flux decline for the
Carbosep module (Figure 4.6, Experiment A5 and A1 respectively). After 22 h, the flux for the Carbosep module had decreased to 15 dm²/h whereas the flux for the CeraMem module had decreased to 70 dm²/h from similar starting fluxes. Even though the respective Johnson sweetwater solutions were of differing composition, the difference in the extent of flux decline is high enough to conclude that the Carbosep membrane module shows a tendency to be more rapidly fouled than the CeraMem module. In fact, the average brix and absorbance of the feed Johnson sweetwater during Experiment A5, using the Carbosep module, were lower than during Experiment A1 using the CeraMem LMDA-20-P1 module (Table 4.5). Hence the feed solution for Experiment A5 was of higher quality and should have been less conducive to fouling, supporting the above conclusion that the Carbosep module is more prone to fouling.

The difference in the rates of flux decline for the M5 Micro-Carbosep 60 membrane module and the CeraMem LMDA-20-P1 membrane module, indicates the varying rate and magnitude of solute absorption onto the surface and into the pores of the membrane surface, and also the differences in the extent of concentration polarisation at the membrane surface. The Carbosep membrane module achieves a greater colour retention, but becomes more rapidly fouled than the CeraMem LMDA-20-P1 module.

The LMDA-20-P1 module comprises a sintered zirconium oxide membrane formed on the CeraMem standard 0.01 µm membrane module. It has a specified molecular weight retention range from 10 000 to 15 000 daltons which corresponds to a nominal pore size ranging from about 0.004 to 0.005 µm. This is tighter than the CeraMem LMA-0005-P module which has a specified nominal pore size of 0.005 µm. The CeraMem LMDA-20-P1 module was expected to produce higher colour retentions than the CeraMem LMA-0005-P module.

The CeraMem LMA-0005-P module achieved an average colour retention of 28%, which is not significantly lower than the retention of 31% achieved by the LMDA-20-P1 module. The maximum colour retention for the LMA-0005-P module was 41% as opposed to 36% for the LMDA-20-P1 module (Table 4.5, Experiment A2 and A1 respectively). However, this occurred under extremely low values of 3 °brix and 0.083 absorbance units and may be disregarded. The LMA-0005-P module exhibited lower fluxes than the LMDA-20-P1 module (Figure 4.6, Experiment A2 and A1 respectively). However, these are not significant and may be attributed to differences in the feed quality of the Johnson sweetwater.

No further work could be performed using the CeraMem LMA-0005-P module as it was broken during removal from the housing module.

The colour retention values obtained using the Membralox 1P19-40 (0.02 µm) membrane module were greater than expected when comparing its pore size of 0.02 µm with the 0.004 to 0.005 µm pore size of
the CeraMem LMDA-20-P1 module. Average colour retention for the Membralox membrane was 27% as opposed to 31% for the CeraMem module (Table 4.4, Experiment A3 and A1 respectively). Again, this can be attributed to the influence of a dynamic secondary membrane and solute adsorption on the original membrane surface following its exposure to the Johnson sweetwater.

The rate of flux decrease for the Membralox membrane was significantly higher than for the CeraMem LMDA-20-P1 membrane module with flux values of 23 and 72 l/m²h being observed after 22 h for the Membralox and CeraMem LMDA-20-P1 membrane modules respectively (Figure 4.6, Experiment A3 and A1 respectively). This supports the theory of the formation of a dynamic (concentration polarised) retention layer and adsorption of the retained solute species. The larger pore size distribution of the Membralox membrane results in larger and greater numbers of solute molecules becoming adsorbed and trapped within the surface pore structure, thereby causing an obstruction to flow. This phenomenon is known as flux paradox, where lower fluxes are observed using membrane of larger pore size.

The modified Membralox 1P19-40 (0.02 μm) membrane module consists of the original Membralox support module, described in Section 3.1.2, with a dual-layer, dynamic zirconium(iv)oxide/polyacrylic-acid (ZrO₂/PAA) membrane formed on the membrane surface. The procedure for the formation of the dynamic membrane is described in Appendix A2.9, while the results of the formation are described in Section 4.2.

The ICUMSA colour retention of the original membrane was greatly improved by the formation of the dynamic ZrO₂/PAA membrane. The average colour retention value was 44% for the modified membrane, compared with 27% for the original membrane (Table 4.4, Experiment A4 and A3 respectively). However, the flux values observed were extremely low, 30 l/m²h after just 1 h of operation (Figure 4.6). This makes the process impractical.

### 4.4.3.2 Brix Retentions

Brix is defined as the percentage, by mass, of total dissolved solids in a sugar solution. In Johnson sweetwater it is made up of sucrose and dissolved non-sucrose impurities (colourants). Sweetwater is a highly coloured stream having a low brix value. It can therefore be assumed that the non-sucrose solute molecules contribute significantly to the solution brix. Sucrose retention will therefore be lower than the total brix retention.

Average brix retentions for the inorganic membranes ranged from 2.6%, for the Membralox 1P19-40 (0.02 μm) module, to 14% for the CeraMem LMA-0005-P membrane module (Table 4.4). Point feed and permeate brix values and the corresponding retention values are presented in Figure 4.1 to 4.5 for Experiment A1 to A5 respectively.
The average retention value of 14% obtained for the CeraMem LMA-0005-P membrane module is relatively high. This value was inflated by the two high brix retention values corresponding to the extremely low feed brix at sample times of 21 and 26 h. The lower the feed brix, the higher the relative retention value. However, the actual mass brix retained will be very low.

Brix retention values vary considerably as the nature of the Johnson sweetwater varies. However, brix retention was generally well below 10%.

4.4.3.3 Membrane Fouling

The extent of fouling of a particular membrane was assessed by determining the pure water permeability (PWP) of the membrane following its exposure to the Johnson sweetwater solution and comparing this with the original pure water permeability. The original PWP values are presented in Section 4.1. The procedure for the determination of PWP is presented in Appendix A2.2.

The results of the membrane PWP determinations following Experiment A1 to A5 are presented in Table 4.6.

<table>
<thead>
<tr>
<th>Experiment</th>
<th>PWP following experiment (L/m²·h)</th>
<th>Original PWP (L/m²·h)</th>
<th>Run-time of experiment (h)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Experiment A1 (CeraMem LMDA-20-P1)</td>
<td>8</td>
<td>500</td>
<td>149</td>
</tr>
<tr>
<td>Experiment A2 (CeraMem LMA-0005-P)</td>
<td>13</td>
<td>600</td>
<td>60</td>
</tr>
<tr>
<td>Experiment A3 (Membralox 1P19-40 (20 μm))</td>
<td>13</td>
<td>1200</td>
<td>46</td>
</tr>
<tr>
<td>Experiment A4 (Modified Membralox 1P19-40 (20 μm))</td>
<td>6</td>
<td>30</td>
<td>92</td>
</tr>
<tr>
<td>Experiment A5 (M5 Micro-Carbasep 60)</td>
<td>5</td>
<td>60</td>
<td>22</td>
</tr>
</tbody>
</table>

The pure water permeability values for the inorganic membranes were all extremely low following the experimental runs. The membranes were severely fouled by solute molecules which were adsorbed onto the membrane pore surfaces and trapped within the pores themselves. The rate of fouling is dependent on the membrane surface structure, the experimental conditions and the nature of the Johnson sweetwater, that is, on the types and concentrations of non-sucrose molecules present in the sweetwater.
Original pure water fluxes were successfully restored using chemical cleaning procedures. The procedures were based on those suggested by the respective membrane manufacturers and are presented in Appendix A2.3.

Membrane cleaning was most difficult for the Membralox membrane module following Experiment A3. This was due to the larger pore size distribution of the module allowing the adsorption of larger, more resistant molecules into the surface pores. A wider range of molecules will be able to enter the larger membrane pores. Membrane fouling is highly dependent on the nature of the solute molecules, and will vary as the condition of the Johnson sweetwater varies.

Time constraints prevented an investigation into alternative membrane cleaning procedures. Also, the back-flushing technique, described in Appendix A3.2.4.1 was not investigated. Back-flushing involves the temporary regeneration of flux by applying pressure on the permeate side of the membrane and reversing the flow of permeate through the membrane. This destroys the concentration polarised layer on the membrane surface.

4.4.3.4 Mathematically Predicted High Water Recovery Data

Mathematically predicted feed and permeate absorbance values, ICUMSA colour values and brix values, as functions of water recovery, are presented graphically in figures in Appendix A1.2. Also predicted are values of percent sugar recovered and percent colour passing the membrane, composite permeate grade, and relative permeate quality as functions of water recovery. These are also presented in figures in Appendix A1.2.2.

The relevant equations used to predict the values are presented in Section 2.7.2.2 (p 2-48). The values were calculated using average values of feed and permeate brix, absorbance and ICUMSA colour, and average values of brix retention, absorbance retention and ICUMSA colour retention, for Experiment A1 to A5.

The water recovery plots for Experiment A1, using the CeraMem LMDA-20-P1 membrane module, are included below as an example.

Feed values of brix, absorbance and ICUMSA colour increase as water recovery tends to a value of 1.0. The feed variables at zero water recovery are the average experimentally determined point feed variables over the duration of the experiment. Composite permeate variables tend towards the average experimental feed values as water recovery tends to a value of 1.0. The composite permeate variables at zero water recovery are the average point experimental values of the particular permeate variables over the duration of the experiment.
A zero retention value will result in constant feed and composite permeate variables, of the same value as the average experimental point feed variable values. The greater the retention value of a particular variable, the lower the average composite permeate value at zero water recovery. For a high retention value, a particular composite permeate variable will remain at a value much lower than the corresponding feed variable value and will display a low rate of increase over a wide range of water recovery values. The particular composite permeate variable will display a high rate of increase only at a very high water recovery value.

The plots of percent sugar recovered and percent colour passing, composite permeate grade, and relative permeate quality as functions of water recovery give an indication of the high water performance of the particular membrane for the retention of ICUMSA colour from Johnson sweetwater.

Percent sugar recovery was based on brix values which represent the total dissolved solids in the Johnson sweetwater. Due to the high relative concentration of non-sucrose molecules in the Johnson sweetwater, sucrose (sugar) retention will always be lower than brix retention. Because of the low brix retention, the curve of percent sugar recovered versus water recovery is essentially a straight line following the diagonal of the plot. This is evident in Figure 4.8, for Experiment A1, and is the case for all the experiments. A brix retention of zero will result in percent sugar recovered values equal to the water recovery values, e.g. a water recovery of 50 % corresponds to a percent sugar recovered value of 50 %.

The percent colour passing the membrane is a function of the ICUMSA colour retention. The curve takes the form concave-up. The greater the colour retention, the greater the deviation of the percent colour passing curve from the diagonal and from the percent sugar recovered curve. The greater the deviation, the better the membrane performance for the decolourisation of Johnson sweetwater and the recovery of sugar (brix). The two curves for Experiment A1 are presented in Figure 4.8. When comparing the performance of two or more membranes, a particular water recovery value is selected and the percent colour passing and percent sugar recovered values compared. The greater the difference between the two values at a particular water recovery, the better the performance of that particular membrane for the decolourisation of Johnson sweetwater.

At a water recovery value of 50 % for the CeraMem LMDA-20-P1 membrane, the percent sugar recovered is about 48 % while the percent colour passing is about 38 % (Figure 4.8). For the M5 Micro-Carbos ep (10 000 dalton cut-off) membrane, used in Experiment A5, the percent sugar recovered, also at a water recovery of 50 %, is about 47 % while the percent colour passing the membrane is about 29 % (Figure A1.25). Hence, the Carbos ep membrane has better colour retention and sugar recovery characteristics than the CeraMem LMDA-20-P1 membrane at values of high water recovery.
Composite permeate grade is defined as the ratio of feed colour to composite permeate colour at a particular water recovery value. The highest composite permeate grade is achieved at a water recovery of zero and tends to the original feed grade value of 1.0 as water recovery tends to 1.0. The greater the colour retention value of a particular membrane, the higher the composite permeate grade at a particular water recovery.

The relative permeate quality plots for the various membranes are important in that they show to what value of water recovery the process will be viable (based on ICUMSA colour). Relative permeate quality is the percentage difference between original feed colour and the permeate colour at a particular water recovery.

At a water recovery of zero, the relative permeate quality value is the same as the retention value. As water recovery increases, the permeate colour increases and relative permeate quality decreases, tending to zero. When relative permeate quality is equal to zero (at the critical water recovery value), the permeate has the same colour as the original feed. For Experiment A1, relative permeate quality becomes equal to zero at a water recovery of about 70% (Figure 4.8). The higher the ICUMSA colour retention of a particular membrane, the greater the water recovery value at which the relative permeate quality becomes equal to zero. When permeate colour becomes greater than the original feed colour, relative permeate quality becomes negative. The negative values are not shown in the figures.

The predicted high water recovery values are theoretical and are based on average data from Experiment A1 to A5. The experiments were run continuously, with retentate and permeate being discarded to the sump. This is in contrast to a batch experiment with retentate being returned to the feed tank and permeate being collected in a separate tank. Consequently, there was no re-circulation and accumulation of retained species which can effect the retention characteristics of the membrane at high water recovery values.

A batch high water recovery run was performed in Experiment D, using the CeraMem LMDA-20-P1 membrane. The results of this are discussed in Section 4.7 and are presented in Appendix A1.5. Also discussed in Section 4.7 is the possibility of applying multi-solute separation theory to the ultrafiltration of Johnson sweetwater.
Figure 4.7: Experiment A1
Mathematically predicted feed and composite permeate absorbance values, ICUMSA colour values and brix values as functions of water recovery, for the ultrafiltration of Johnson sweetwater using the CeraMem LMDA-20-P1 membrane module.
Figure 4.8: Experiment A1
Mathematically predicted % colour passing the membrane and % sugar recovered, composite permeate grade, and relative permeate quality, as functions of water recovery, for the ultrafiltration of Johnson sweetwater using the CeraMem LMDA-20-P1 membrane module.
4.4.4 Motivation for Subsequent Experimental Work

The results of the ultrafiltration of Johnson sweetwater gave an indication as to which membranes achieved good decolourisation of Johnson sweetwater based on the brix and ICUMSA colour retention values.

The best decolourisation performance was achieved by the M5 Micro-Carbosep 60 (10 000 dalton cut-off) membrane module which achieved an average ICUMSA colour retention value of 50% with a corresponding average brix retention value of 5%.

From an economic point of view, the colour and brix retention characteristics of a particular membrane would have to be considered together with the particular membrane's permeate flux and fouling characteristics. Hence, high effective colour retention, high sugar recovery, high permeate fluxes and low cost cleaning requirements are the prerequisites for the economic ultrafiltration of Johnson sweetwater.

The factor preventing further evaluation of the membranes investigated in Experiment Series A was the question of what constitutes effective colour retention.

Johnson sweetwater is a recycle stream, as opposed to a product stream, and influences the decolourisation processes following the melter by increasing the concentration of those specific colourant types contained in the Johnson sweetwater. For colour retention to be effective, the recycled ultrafiltration permeate would have to have lower quantities of those colourants which adversely effect the existing decolourisation processes of ion exchange and crystallisation.

ICUMSA colour does not indicate the relative concentrations of the various types of sugar colour. It is simply a colour measurement based on the absorbance per unit sucrose concentration of a particular sugar solution. Consequently, the effectiveness of the removal of colour from the feed Johnson sweetwater cannot be judged solely on the basis of ICUMSA colour retention.

Sugar colour is made up of a complex mixture of colour molecules of varying molecular weight, molecular structure and chemical properties. Some colourant species are easily removed by the refinery decolourisation processes, namely, ion exchange and crystallisation, while others pass through the refinery process entering the final refined sugar crystal.

From the literature review into the types and influences of the various classes of colour (Section 2.2), and into the decolourisation processes of ion exchange and crystallisation (Section 2.3 and 2.4), it is the high molecular weight colourants which tend not to be removed by ion exchange and are preferentially included in the refined sugar crystals. Ion exchange resin becomes rapidly saturated with respect to the
high molecular weight colourants, which also tend to foul the resin. Hence, a colour retention of 30% (based on ICUMSA colour) from Johnson sweetwater may appear relatively low, but may result in refined sugar of lower colour than is presently achieved if it is the potentially included colourants which are retained by the membrane. Lower rates of ion exchange resin fouling may also be observed due to the retention of the high molecular weight molecules from Johnson sweetwater.

If ultrafiltration retains those colourant molecules which are easily removed by the existing decolourisation processes of ion exchange and crystallisation, the ultrafiltration of Johnson sweetwater will be ineffective. Ultrafiltration, being a filtration process, preferentially retains the higher molecular weight solutes in a solution. The lower molecular weight molecules pass, unhindered, through the ultrafiltration membrane. Consequently, it is the retention of the higher molecular weight range of colour molecules which is of interest to this investigation.

Colour retention based on ICUMSA colour does give an indication as to the relative performance of different membranes for the decolourisation of Johnson sweetwater. A membrane which displays higher average ICUMSA colour retention characteristics will perform better than a membrane with lower retention characteristics due to the fact that a wider range of molecules in the high molecular weight range are being retained in the former case. However, as far as predicting the influence of the decolourised Johnson sweetwater permeate on the rest of the sugar refinery, retention values based on ICUMSA colour are meaningless. This discounts the possibility of any economic evaluation of the ultrafiltration process based on ICUMSA colour retention.

The complex nature of sugar colour does not allow the analysis of the sugar solutions for specific types and relative quantities of colourant molecules. Consequently, the quality of the Johnson sweetwater feed and permeate could not be compared on the basis of retained colourant species. Alternative methods had to be employed in an attempt to determine the influence of ultrafiltration for the decolourisation of Johnson sweetwater.

A series of experiments were devised to investigate whether the process of ultrafiltration could remove colour from refined sugar. The results of this are presented in Section 4.5 and 4.6 (Experiment B and Experiment C) and in Appendix A1.3 and A1.4. A positive retention of colour from solutions of refined sugar would mean that ultrafiltration has the ability to retain those colourant types which are preferentially included during final crystallisation.

Generally, it is the larger molecules that tend to be retained by the membrane filter. It is also these larger molecules which tend to be included in the final refined sugar crystal. Hence, by observing the effect ultrafiltration has on the removal of colour from various refined sugar solutions, an insight will be gained as to what type of, and to what extent, sugar colourant is being retained.
Following the ultrafiltration of the refined sugar solutions, experiments were performed to examine the colour transfer characteristics of the Johnson sweetwater ultrafiltration permeate relative to the colour transfer characteristics of the feed Johnson sweetwater. Colour transfer involves the crystallisation of the feed and permeate solutions and comparison of the respective crystal colours.

The CeraMem LMDA-20-P1 membrane was selected for subsequent experimental work due to the following reasons:

- The permeate flow rate of the M5 Micro-Carboserp (10 000 dalton cut-off) membrane was very low due to the small membrane surface area and due to the rapid fouling observed (Experiment A5).

- The permeate flux of the Membralox 1P19-40 (0.02 μm cut-off) membrane module decreased rapidly (Experiment A3).

- The permeate flux of the modified Membralox 1P19-40 (0.02 μm cut-off) membrane module was very low - about 30 L/m²h after 1 h (Experiment A4).

- The CeraMem LMA-0005-P membrane module was accidentally broken.

The focus of the investigation shifted from the selection of the optimum membrane for Johnson sweetwater decolourisation, to establishing whether or not ultrafiltration of Johnson sweetwater results in effective colour retention, that is, the retention of potentially included colourant molecules.

1 Potentially included molecules are those colour molecules which have a high probability of being included in the final refined sugar crystal.
4.5 Experiment Series B:
The Ultrafiltration of H1 Refined Sugar, Affinated H1 Refined Sugar, Affination Wash Liquor and Raw VHP Sugar - using the CeraMem LMDA-20-P1 Membrane Module

4.5.1 The Aim of Experiment Series B

The aim of Experiment Series B was to assess the ability of the CeraMem LMDA-20-P1 ultrafiltration membrane to retain ICUMSA colour and brix in solutions of H1 refined sugar, affinated H1 refined sugar, affination wash liquor and VHP sugar.

4.5.2 Experimental Methods and Equipment

The stepwise experimental procedure for Experiment Series B is presented in Appendix A2.5.

The refined sugar ultrafiltration rig was used in order to prevent colour formation, due to caramelisation and burning of the sugar solution, by the application of excessive heat. The rig is described in Section 3.2.2. It is essentially the same as the membrane cleaning rig, but uses a stainless steel coil, through which hot water is passed, instead of a heating coil to heat the feed solution.

The rig was thoroughly cleaned prior to experimentation to prevent any external colour influences. This was important when dealing with the very low-colour refined sugar solutions.

Retention characteristics were investigated at three refined sugar concentrations except for the affination wash liquor where only two concentrations were possible due to insufficient feed liquor.

The sugar solutions were made up from the following sugar types:

- **H1 Refined Sugar (Lot 405)**

  *H1 refined sugar* is a mixture of 1st to 4th boiling sugars produced by the crystallisation pans at Hulett Refineries. It constitutes the final refined white sugar product marketed by the sugar refinery. The particular batch of H1 sugar used for these experiments was from Lot 405.

- **Affinated H1 Refined Sugar (Lot 405)**

  Affination involves the washing of the sugar crystals to remove the surface film. A significant
amount of colour is found in the surface film which is caused by the crystals remaining in contact with the mother liquor during crystallisation and also from contact with the atmosphere following crystallisation. The stepwise affination procedure is as follows:

(i) A mass of 1 000 g H1 refined sugar was added to 800 g saturated sugar solution (made from H1 refined sugar). The sugar and saturated liquor magma was mixed for 15 min.

(ii) Following mixing, the magma was centrifuged in a Martin Christ laboratory centrifuge at 4 000 rpm for a period of 5 min to recover the crystals. The speed was then increased to 5 000 rpm whereafter a volume of 50 mL distilled water was sprayed evenly over the crystal cake surface in the spinning centrifuge basket.

(iii) The sugar was centrifuged for a further 3 min after which the affinated sugar was scraped off the sides of the basket and allowed to air dry. This constitutes affinated H1 refined sugar.

(iv) The rejected liquor from the magma was collected at the centrifuge drain and bottled. This constitutes the affination wash liquor.

♦ Affination Wash Liquor (Lot 405)

The origin of the affination wash liquor is described in the affination procedure above. The affination wash liquor is a sugar solution with a high concentration of surface film colourants.

♦ Raw VHP Sugar

Raw VHP (very high pol) sugar is the raw sugar feed to the refinery from the various sugar mills.

A volume of 10 L reverse osmosis permeate water was added to the feed tank of the refined sugar ultrafiltration rig. This was heated to 40 °C prior to adding the required mass of sugar to achieve a feed concentration of about 10 °brix. This solution was circulated for 30 min to allow the membrane to attain a state of equilibrium with the feed solution. Point feed and permeate samples were then taken for subsequent analysis. Additional sugar was then added to increase the feed concentration to the next desired value. Experimental runs were performed at concentrations of about 10, 25 and 50 °brix. In the case of the affination wash liquor, specific volumes of the concentrated liquor were added to achieve the desired concentrations of about 10 and 25 °brix.

The experimental operating conditions were as follows:

 Feed temperature = 40 °C
 Trans-membrane pressure = 400 kPa
Feed volumetric flow rate $= 21 \, \ell/\text{min}$
Feed linear flow rate $= 1.5 \, \text{m/s}$

The experiment was run under zero water recovery conditions with permeate and retentate being returned to the feed tank.
4.5.3 Experimental Results and Discussion

![Graphs showing Colour Retention, Absorbance Retention, and Brix Retention](image)

- **Low Brix** = about 10 °brix
- **Medium brix** = about 25 °brix
- **High brix** = about 50 °brix

**Figure 4.9:** Experiment Series B

Point ICUMSA colour retention, absorbance retention and brix retention values for the ultrafiltration of H1 refined sugar, affinitated H1 refined sugar, affination wash liquor and VHP sugar, under conditions of zero water recovery.
4.5.3.1 ICUMSA Colour Retentions

The ICUMSA colour retention values achieved using the CeraMem LMDA-20-P1 membrane module for the various sugar solutions are presented in Figure 4.9.

Of the three refined sugar solutions, the colour retention achieved for the affinity wash liquor was greatest with values of 60 and 58 % for the 10 and 25 °brix solutions respectively. The affinated H1 refined sugar solution displayed the next highest retention values with 48, 62 and 47 % for the 10, 25 and 50 °brix solutions respectively. The H1 refined sugar solution displayed colour retention values of 29, 48 and 26 % for the three concentrations respectively.

The affinity wash liquor had a colour value of about 110 ICUMSA units compared to about 52 units for the H1 refined sugar. This confirms the high percentage of sugar colour contained in the surface film of the refined sugar crystals. The average colour retention value for the affinity wash liquor was 59 % as opposed to 34 % for the H1 refined sugar. The high colour retention in the case of the affinity wash liquor can be attributed to a greater concentration of non-sugar solute molecules effecting the retention characteristics of the concentration polarised layer. The phenomenon of concentration polarisation is described in Section 2.7.1.1.

The ICUMSA colour of the affinated H1 refined sugar solution was about 37 units. This is 29 % lower than the colour of the H1 refined sugar. The affinated sugar crystal has a lower concentration of coloured matter per mass sucrose than the original refined sugar crystal. This is due to the high proportion of colour in the surface film. The average colour retention value achieved for the affinated H1 refined sugar was 52 % as opposed to 34 % for the unaffinated H1 refined sugar. The affinated sugar solution therefore has a higher relative percentage of high molecular weight colourant present than the unaffinated sugar. That is, the included colour molecules have a high average molecular weight.

The retention values, corresponding to the medium brix case (about 25 °brix), for the H1 refined sugar solution and the affinated H1 refined sugar solution were both significantly higher than for the other two concentrations. The only possible reason for this is the dynamic, concentration polarised layer having improved colour retention characteristics at the particular operating conditions and solution brix.

ICUMSA colour retention for raw VHP sugar was also investigated. Retention over the three concentrations did not vary significantly. The average retention value obtained was 49 %. This is higher than the 34 % retention achieved in the H1 refined sugar solution and similar to the 52 % retention achieved for the affinated H1 refined sugar solution. The concentration of both low and high molecular weight impurities will both be high for the raw VHP sugar. The high ICUMSA colour
retention achieved for the high molecular weight colourants will be reduced by the low ICUMSA colour retention achieved for the low molecular weight colourants. ICUMSA colour does not differentiate between the various colourant types. The high total concentration of non-sugars will effect the retention characteristics of the dynamic membrane layer. Colour transfer experiments would have to be performed to assess the effectiveness of the ultrafiltration of VHP sugar to produce a raw liquor of higher quality, which will decolourise more easily in the existing refinery processes.

The aim of Experiment Series B was to ascertain whether or not, colour included in the refined sugar crystals could be retained by ultrafiltration. The results showed a positive ICUMSA colour retention ranging from 29 to 62 % for the various refined sugar solutions at the various concentrations. Further conclusions from the available results would be unsubstantiated due to the varying nature of sugar. Many similar experiments would have to be performed to be able to draw statistically significant conclusions regarding retention trends for the ultrafiltration of refined sugar solutions.

It was decided to perform high water recovery ultrafiltration runs using solutions of H1 refined sugar and affinated H1 refined sugar to assess the ability of the CeraMem LMDA-20-P1 membrane module to retain ICUMSA colour, which was included in the refined sugar crystals, at high water recovery values. This was to observe the effects of increasing the concentration of the potentially included colour molecules on the membrane retention characteristics. The results of this are presented in Experiment Series C (Section 4.6 and in Appendix A1.4).

4.5.3.2 Brix Retentions

In all cases, for the refined sugar solutions and for the VHP sugar solution, the brix retention values were extremely low. For the refined sugar solutions, the brix retentions ranged between 0 and 2.2 %, for all feed concentrations. The brix retention values for the ultrafiltration of VHP sugar ranged between 2 and 3 %.
4.5.3.3 Permeate Fluxes

![Bar chart showing permeate flux for different conditions.

Flux (l/m².h)

160
140
120
100
80
60
40
20
0
H1 Refined
H1 Affinased
Affination Wash
VHP Sugar

Low Brix = about 10 °brix
Med Brix = about 25 °brix
High Brix = about 50 °brix.

Figure 4.10: Experiment Series B
Point permeate flux as a function of brix for the ultrafiltration of H1 refined sugar, affinated H1 refined sugar, affination wash liquor and raw VHP sugar under conditions of zero water recovery.

Flux values for the three refined sugar solutions are similar for a particular concentration. The flux values are presented in Figure 4.10. The run time of each experiment was only 30 min, minimising the effect of any membrane fouling.
4.6 Experiment Series C:  
The Ultrafiltration of H1 Refined Sugar and Affinates H1  
Refined Sugar Under Conditions of High Water Recovery - 
using the CeraMem LMDA-20-P1 Membrane Module

4.6.1 The Aim of Experiment Series C

The aim of Experiment Series C was to assess the ability of the CeraMem LMDA-20-P1 membrane 
module to retain ICUMSA colour and brix in solutions of H1 refined sugar and affinates H1 refined 
sugar, under conditions of high water recovery. This was to observe the effect of the increased 
concentration of the retained high molecular weight solute molecules on the retention characteristics of 
the membrane.

4.6.2 Experimental Method and Equipment

The stepwise experimental procedure for the high water recovery experiments is presented in 
Appendix A2.6. The refined sugar ultrafiltration rig was used in order to prevent colour formation, due 
to caramelisation and burning of the sugar solution, by the application of excessive heat. The rig, 
described in Section 3.2.2, uses a stainless steel coil, through which hot water is passed, to heat the feed 
solution.

The rig was thoroughly cleaned prior to experimentation to prevent any external colour influences. This 
is important when dealing with the very low coloured refined sugar solutions.

The two sugar solutions used were made up of H1 refined sugar and affinated H1 refined sugar, and are 
described in Section 4.5.2.

A mass of 4.500 g of the particular feed sugar was dissolved in 38 L of reverse osmosis permeate water 
in the feed tank of the ultrafiltration rig. This solution was heated to 40 °C and circulated at the 
following operating conditions:

\[
\begin{align*}
\text{Feed temperature} & = 40 \, ^\circ\text{C} \\
\text{Trans-membrane pressure} & = 400 \, \text{kPa} \\
\text{Feed volumetric flow rate} & = 21 \, L/\text{min} \\
\text{Feed linear flow rate} & = 1.5 \, \text{m/s}
\end{align*}
\]
The rig was run for 30 min at zero water recovery to allow the membrane to attain a state of equilibrium with the feed solution, whereafter the permeate was directed to a separate permeate collection tank and the retentate returned to the feed tank. The solution in the permeate collection tank constituted the composite permeate sample.

Point feed and permeate samples, as well as permeate flux measurements, were taken at water recovery values of 0,0; 23,7; 50,0; 64,5; 75,0 and 86,8 %. The maximum attainable water recovery, due to dead volume in the system, was 86,8 % which corresponded to 33 € of permeate collected. Composite permeate samples were taken from the permeate collection tank at water recovery values of 50 and 86,8 %.

4.6.3 Experimental Results and Discussion

The results of Experiment Series C are presented in Table 4.7 and Table 4.8, and in Appendix A1.4. Table 4.7 contains point ICUMSA colour values and associated point retention values at the particular water recovery values. Table 4.8 contains composite feed and composite permeate values of brix and ICUMSA colour as well as the mathematically predicted composite feed and composite permeate values. The equations used for the prediction of composite values are presented in Section 2.7.2.

<table>
<thead>
<tr>
<th>Table 4.7 : Experiment Series C</th>
</tr>
</thead>
<tbody>
<tr>
<td>Point ICUMSA colour values and associated retention values as functions of water recovery for the high water recovery ultrafiltration of H1 refined sugar and affinated H1 refined sugar.</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>WR (%)</th>
<th>Experiment C1 (H1 refined sugar)</th>
<th>Experiment C2 (affinated H1 refined sugar)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Time (min)</td>
<td>Flux (L/m²h)</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>0,0</td>
<td>0</td>
<td>125</td>
</tr>
<tr>
<td>23,7</td>
<td>33</td>
<td>117</td>
</tr>
<tr>
<td>50,0</td>
<td>72</td>
<td>113</td>
</tr>
<tr>
<td>64,5</td>
<td>95</td>
<td>107</td>
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<td>75,0</td>
<td>112</td>
<td>103</td>
</tr>
<tr>
<td>86,8</td>
<td>132</td>
<td>81</td>
</tr>
</tbody>
</table>

Note : Ret = retention, WR = water recovery, Perm = permeate
Table 4.8: Experiment Series C
Composite feed and composite permeate brix and ICUMSA colour values as functions of water recovery for the high water recovery ultrafiltration of H1 refined sugar and affinated H1 refined sugar.
(Mathematically predicted composite feed and composite permeate values, based on zero water recovery retentions, are presented in brackets)

<table>
<thead>
<tr>
<th>WR (%)</th>
<th>Experiment C1 (H1 refined sugar)</th>
<th></th>
<th>Experiment C2 (affinated H1 refined sugar)</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Composite %brix</td>
<td>Composite ICUMSA Colour</td>
<td>Feed</td>
<td>Permeate</td>
</tr>
<tr>
<td>0,0</td>
<td>10,4 (10,4)</td>
<td>10,1 (10,1)</td>
<td>61 (61)</td>
<td>27 (27)</td>
</tr>
<tr>
<td>23,7</td>
<td>10,5 (10,5)</td>
<td>10,1 (10,1)</td>
<td>60 (71)</td>
<td>29 (29)</td>
</tr>
<tr>
<td>50,0</td>
<td>10,7 (10,6)</td>
<td>10,3 (10,2)</td>
<td>83 (90)</td>
<td>33 (32)</td>
</tr>
<tr>
<td>64,5</td>
<td>10,7 (10,7)</td>
<td>10,2 (10,2)</td>
<td>108 (108)</td>
<td>35 (35)</td>
</tr>
<tr>
<td>75,0</td>
<td>10,9 (10,8)</td>
<td>10,3 (10,3)</td>
<td>129 (132)</td>
<td>37 (37)</td>
</tr>
<tr>
<td>86,8</td>
<td>11,2 (11,0)</td>
<td>10,4 (10,3)</td>
<td>158 (191)</td>
<td>44 (42)</td>
</tr>
</tbody>
</table>

At zero water recovery, the ICUMSA colour retention for the H1 refined sugar solution was 55.7% as opposed to 48.7% for the affinated H1 sugar solution. The colour retention value for the 10 %brix H1 refined sugar solution in Experiment Series B was significantly lower, 29.3% even though feed solution colour was similar to Experiment C1. The reason for this is unclear. The colour retention values for the 10 %brix affinated H1 refined sugar solutions for Experiment Series B and Experiment Series C2 were identical.

The feed and permeate ICUMSA colour values, as well as the corresponding ICUMSA colour retention values mentioned above were used for the mathematical prediction of composite permeate values.

The experimental point feed, point permeate and composite permeate variables show excellent correlation with the predicted values (Table 4.8). At the maximum water recovery of 86.8%, the experimental composite permeate colour was only 5% greater than the predicted value for H1 refined sugar, while the experimental composite permeate colour for the affinated H1 refined sugar was 20% greater. At a water recovery of 50% these values were only 3 and 4% respectively.

ICUMSA colour retention for the H1 refined sugar increases by 16% from 55.7 to 71.9% over the range of water recovery values, while for the affinated H1 refined sugar run, the ICUMSA colour retention increases by 5% from 48.7 to 53.8% (Table 4.7). The reason for the higher increase in the
case of the unaffinated H1 refined sugar is the higher concentration of non-sucrose solute molecules which effect the retention characteristics of the dynamic secondary membrane formed by the process of concentration polarisation on the membrane surface. The high concentration of non-sucrose solute molecules and greater influence of the dynamic secondary layer is confirmed by the more rapid flux decrease in the case of the unaffinated H1 refined sugar (Table 4.7).

Although ICUMSA colour retention increases, the permeate and composite permeate colour values increase at a faster rate with increase in water recovery. Hence, the quality, based on ICUMSA colour, of the permeate decreases as water recovery increases and feed quality decreases.

Plots of point feed, point permeate and composite values of ICUMSA colour and brix are presented in Figure A1.29 and A1.30 in Appendix A1.4.2.

Composite permeate brix values show excellent correlation with the predicted values (Table 4.8). Brix retentions, like the ICUMSA colour retentions, also increase over the range of water recovery values. However this increase is very low, less than 1%.

The results obtained in Experiment C1 and C2 will vary with the varying nature of the feed H1 sugar. As in Experiment Series B, many similar experiments would have to be performed to be able to draw statistically significant conclusions regarding retention trends for the ultrafiltration of refined sugar solutions. The experiment did, however, confirm the ability of ultrafiltration to retain ICUMSA colour from refined sugar solutions at high water recovery values. The membrane therefore has the ability to retain those colourant molecules which are included in the refined sugar crystals.
4.7 Experiment D: The Ultrafiltration of Johnson Sweetwater Under Conditions of High Water Recovery - using the CeraMem LMDA-20-P1 Membrane Module

4.7.1 The Aim of Experiment D

The aim of Experiment D was to assess the ability of the CeraMem LMDA-20-P1 membrane module to retain ICUMSA colour and brix in Johnson sweetwater under conditions of high water recovery.

4.7.2 Experimental Method and Equipment

The stepwise procedure for the high water recovery ultrafiltration of Johnson sweetwater is described in Appendix A2.7. The refined sugar ultrafiltration rig was used in order to prevent colour formation, due to caramelisation and burning of the Johnson sweetwater solution, by the application of excessive heat. The rig is described in Section 3.2.2. It uses a stainless steel coil, through which hot water is passed, to heat the feed solution.

A volume of 38 l of Johnson sweetwater from the sugar refinery was added to the feed tank of the ultrafiltration rig. This solution was heated to 75 °C and circulated at the following operating conditions:

- Feed temperature = 75 °C
- Trans-membrane pressure = 400 kPa
- Feed volumetric flow rate = 21 l/min
- Feed linear flow rate = 1.5 m/s

The rig was run for 30 min at zero water recovery to allow the membrane to attain a state of equilibrium with the feed solution, whereafter the permeate was directed to a separate permeate collection tank and the retentate returned to the feed tank. The solution in the permeate collection tank constituted the composite Johnson sweetwater permeate sample.

Point feed and permeate samples, as well as permeate flux rates, were taken at water recovery values of 0.0; 23.7; 50.0; 64.5; 75.0 and 82.9 %. The maximum attainable water recovery, due to dead volume and frothing of the Johnson sweetwater, was 82.9 % - corresponding to 31.5 l of permeate. Composite permeate samples were taken at water recovery values of 50 and 82.9 %.
4.7.3 Experimental Results and Discussion

The experimental results are presented in Table 4.9 and 4.10 and in Appendix A1.5. Table 4.9 contains point feed and permeate brix, absorbance and ICUMSA colour values as functions of water recovery. Corresponding point retention values are also presented. Table 4.10 contains composite feed and composite permeate values of brix and ICUMSA colour as well as the mathematically predicted composite feed and composite permeate values. The equations used for the mathematical prediction of composite values are presented in Section 2.7.2.

| Table 4.9: Experiment D
| Point feed and permeate brix and ICUMSA colour values, and corresponding retention values as functions of water recovery for the high water recovery ultrafiltration of Johnson sweetwater. |
| WR (%) | Time (min) | Flux (L/m²h) | °Brix | ICUMSA Colour |
|        |           |              | Feed | Perm | Ret (%) | Feed | Perm | Ret (%) | Rel. Perm Quality (%) |
| 0.0    | 0         | 128          | 11.3 | 11.1 | 1.7      | 2892 | 1867 | 35.4    | 35.4                 |
| 23.7   | 40        | 104          | 11.4 | 11.2 | 1.8      | 3092 | 1997 | 35.4    | 30.9                 |
| 50.0   | 90        | 93           | 11.7 | 11.4 | 2.6      | 3549 | 2252 | 36.5    | 22.0                 |
| 64.5   | 112       | 86           | 11.8 | 11.7 | 1.7      | 3582 | 2314 | 35.3    | 19.9                 |
| 75.0   | 136       | 81           | 12.5 | 12.3 | 1.6      | 4562 | 2522 | 44.7    | 12.8                 |
| 82.9   | 160       | 60           | 13.8 | 13.5 | 2.2      | 4269 | 2700 | 36.7    | 6.6                  |

Ret = retention, WR = water recovery, Perm = permeate
Rel. Perm Quality = Relative permeate quality (the difference between permeate colour and original feed colour)
Table 4.10: Experiment D
Composite feed and composite permeate values of brix and ICUMSA colour, as functions of water recovery, for the high water recovery ultrafiltration of Johnson Sweetwater.
(Mathematically predicted composite feed and composite permeate values, based on zero water recovery retentions, are presented in brackets)

<table>
<thead>
<tr>
<th>WR (%)</th>
<th>Composite °Brix</th>
<th>Composite ICUMSA Colour</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Feed</td>
<td>Permeate</td>
</tr>
<tr>
<td>0,0</td>
<td>11,3</td>
<td>11,1</td>
</tr>
<tr>
<td></td>
<td>(11,3)</td>
<td>(11,1)</td>
</tr>
<tr>
<td>23,7</td>
<td>11,4</td>
<td>11,1</td>
</tr>
<tr>
<td></td>
<td>(11,4)</td>
<td>(11,1)</td>
</tr>
<tr>
<td>50,0</td>
<td>11,7</td>
<td>11,2</td>
</tr>
<tr>
<td></td>
<td>(11,4)</td>
<td>(11,2)</td>
</tr>
<tr>
<td>64,5</td>
<td>11,8</td>
<td>11,2</td>
</tr>
<tr>
<td></td>
<td>(11,5)</td>
<td>(11,2)</td>
</tr>
<tr>
<td>75,0</td>
<td>12,5</td>
<td>11,2</td>
</tr>
<tr>
<td></td>
<td>(11,6)</td>
<td>(11,2)</td>
</tr>
<tr>
<td>82,9</td>
<td>13,8</td>
<td>11,5</td>
</tr>
<tr>
<td></td>
<td>(11,7)</td>
<td>(11,2)</td>
</tr>
</tbody>
</table>

Figure 4.11: Experimentally determined and mathematically predicted values of relative permeate quality as a function of water recovery for the high water recovery ultrafiltration of Johnson sweetwater.

The experiment was performed to assess the colour retention characteristics of the CeraMem LMDDA-20-P1 membrane under conditions of high water recovery. Predicted high water recovery values were presented for Experiment Series A, however, these are theoretical and may not hold true in reality. In practice, the re-circulation and subsequent concentration of the retained high molecular weight
species may effect the retention characteristics of the membrane by influencing the dynamic secondary layer on the membrane surface. The influence of the retained solute species generally increases as their concentration increases with water recovery.

The maximum water recovery achieved was 82.9%. This was due to dead volume in the refined sugar ultrafiltration rig, and due to frothing of the Johnson sweetwater.

Over the range of water recovery values, feed colour increased from 2.892 to 4.269 ICUMSA units. Corresponding colour retention values did not increase significantly and remained relatively constant at about 36%. The constant colour retention value resulted in a poorer quality permeate, at higher water recovery values, than was expected. The greater concentration of retained, high molecular weight solute molecules in the feed, at high water recovery values, was expected to increase colour retention by increasing the extent of development of the concentration polarised layer on the membrane surface. Increased retention at higher water recoveries will result in composite permeate solutions of higher quality than the experimental and mathematically predicted results, presented in Table 4.10, which assume a constant colour retention for all water recovery values.

Feed brix increased from 11.3 to 13.8, while permeate brix increased from 11.1 to 13.5 over the range of water recovery values. The brix retention values were relatively constant, ranging from 1.7 and 2.2%.

The mathematically predicted composite feed and composite permeate results were calculated using the point feed and permeate brix and colour values and the associated retention values at zero water recovery. The results are presented in Table 4.10. The experimental composite permeate brix values of brix and colour showed good correlation with the mathematically predicted values. The experimental composite permeate ICUMSA colour at 50% water recovery was 2.260 compared with a predicted value of 2.088 units, a difference of 8%, while at 82.9% water recovery, the difference between the experimental value of 2.431 and the predicted value of 2.377 was only 2%. The excellent correlation is due to the relatively constant point colour retentions which could have been be due to a relatively homogeneous feed solution. Feed colour values are slightly lower than the predicted colour values over the entire range of water recovery values.

Composite permeate brix values also show good correlation with the predicted values. Experimental feed brix values were somewhat higher than the predicted values. At a water recovery of 82.9%, the experimental feed brix was 13.8 compared with a predicted value of 11.7 - a difference of about 15%. The fact that brix can only be measured to one decimal place does effect the accuracy of comparison between actual and predicted values.

The most significant results from this experiment are the relative permeate quality values. Relative permeate quality is the difference between the actual permeate colour at a particular water recovery and
the original feed colour at zero water recovery, expressed as a percentage. These are presented in Table 4.9 and in Figure 4.11. At a water recovery of zero, the relative permeate quality value is the same as the ICUMSA colour retention value, however, as the permeate colour increases with increasing water recovery, the relative permeate quality will decrease.

At zero water recovery the relative permeate quality was 35.4%, while at a water recovery value of 50% the quality had decreased to 22%, that is, the permeate had 22% less ICUMSA colour than the original feed. At a water recovery value of 82.9%, the relative permeate quality had decreased to 6.6%. The experimental and predicted values of relative permeate quality are presented in Figure 4.11. The experimental relative permeate quality values were higher than the mathematically predicted values over the entire range of water recovery values.

When relative permeate quality becomes equal to zero, at a particular water recovery (the critical water recovery value), the permeate ICUMSA colour is the same as that of the original feed and the ultrafiltration of Johnson sweetwater no longer achieves positive colour removal (based on ICUMSA colour). At water recovery values above the critical value, relative permeate quality becomes negative and the recycled permeate will be of higher ICUMSA colour than the original Johnson sweetwater.

Although the ICUMSA colour of the permeate is greater than that of the original feed at water recovery values higher than the critical water recovery, this may not mean that colour retention is no longer effective, and that the recycle of ultrafiltered Johnson sweetwater will no longer have a positive influence on the refinery decolourisation processes downstream of the melter. The higher colour of the permeate and the negative values of relative permeate quality may be due to the passage of low molecular weight, *easily removed* colourant molecules through the membrane. The retention of the high molecular weight, *potentially included* colourants may still be very high. These are the colourant molecules which tend not to be removed by ion exchange and are preferentially included in the refined sugar crystals. Hence colour retention may still be effective even at zero to negative relative permeate quality values based on ICUMSA colour.

It is proposed that future investigation into the decolourisation of Johnson sweetwater regard sugar colour as a multi-solute mixture as opposed to the homogeneous solute termed ICUMSA colour. Some basic multi-solute ultrafiltration theory is included in Section 2.7.3.

---

1 *easily removed* colourant molecules are those which are effectively removed by ion exchange and crystallisation.

2 *potentially included* colourant molecules are those which pass through ion exchange and have a high probability of being included in the refined sugar crystal.
As mentioned previously, Johnson sweetwater is a recycle stream and influences the decolourisation processes downstream of the melter. The colourant types of interest to the investigation are those that:

- are not removed by the ion exchange decolourisation process
- foul the ion exchange resin
- are preferentially included in the refined sugar crystals

From the literature review into the types of sugar colour and the decolourisation processes of ion exchange and crystallisation (Chapter 2), it is the high molecular weight colourants which tend to be included during crystallisation and are not removed by the ion exchange process. It would be convenient, therefore, to divide sugar colour into two groups of molecules - potentially included colour molecules and easily removed colour molecules. The easily removed molecules are generally the low molecular weight, charged colourants originating in the sugar cane plant, namely, phenolic acids and flavonoids (Section 2.2.2). The potentially included molecules are the high molecular weight refinery produced colourants (Section 2.2.3) and the colour associated with polysaccharide molecules (Section 2.2.4).

Ultrafiltration is expected to retain most of the high molecular weight refinery produced and polysaccharide molecules, while passing the low molecular weight phenolic acids and flavonoids. The high water recovery characteristics of the membranes will have to be based on potentially included colour and easily removed colour as opposed to ICUMSA colour. The relevant equations based on the above two colourant groups are derived and presented in Section 2.7.2.3.

Possibly the most important variable in assessing the performance of a particular membrane is the relative permeate quality based on potentially included colourant and is used here as an example. Relative permeate quality investigation will result in two curves, namely, relative permeate quality based on potentially included colour and relative permeate quality based on easily removed colour. New analytical techniques will have to employed to determined the fraction of colour molecules greater than a particular weight (mass) in the feed and permeate solutions. This will constitute the fraction of potentially included molecules in the feed or ultrafiltration permeate solution. The fraction of colour of molecular weight lower than the particular value constitutes the fraction of easily removed colourants in the feed or permeate solution. Retentions based on potentially included or easily removed colourants can be determined experimentally, from the analysis of the solutions, and mathematically using the equations below. Curves may also be plotted.

An example of what the curves will possibly look like is presented in Figure 4.12.
Figure 4.12 presents proposed curves for \textit{relative permeate quality} based on \textit{potentially included} and \textit{easily removed colour}. The retention value based on \textit{potentially included} colour is expected to be much higher than that of the \textit{easily removed} colour due to the large molecular weight difference, and hence the retention difference between the two colourant groups. This results in the \textit{relative permeate quality} curve, based on \textit{potentially included} colour, having much higher values than the corresponding \textit{relative permeate quality} curve based on \textit{easily removed} colour for all water recovery values.

The \textit{critical water recovery} value, where \textit{relative permeate quality} becomes equal to zero, will be much higher for the \textit{potentially included} colour case due to the higher retention value. This means that the membrane will achieve \textit{effective decolourisation} up to a much higher water recovery value than was indicated by the \textit{relative permeate quality} curves based on ICUMSA colour.

Other quantities such as \textit{composite permeate colour}, \textit{percent colour passing the membrane} and \textit{composite permeate grade} can all be viewed from a multi-solute point of view. The equations for these are presented in Section 2.7.3.

The limiting factor in performing the multi-solute investigation is the lack of available analytical equipment and expertise. Researchers at SPRI and CSR have reported the effective use of HPLC for the fractionation of sugar colour and the determination of the relative quantities of high and low molecular weight species.
An example of what is required would be the fractionation of the Johnson sweetwater feed and ultrafiltration permeate solutions. The fraction of molecules having a molecular weight greater than a particular value, 10 000 daltons say, could be determined for each solution. The performance of the membrane could then be determined based on high molecular weight (potentially included) colour and low molecular weight (easily removed) colour. The influence of the ultrafiltered Johnson sweetwater on the refinery decolourisation processes could then be predicted.
4.8 Experiment Series E: Johnson Sweetwater Feed and Permeate Colour Transfer Analyses

The colour transfer experiments were performed in an attempt to determine whether the ultrafiltration of Johnson sweetwater has the potential to positively influence the refinery decolourisation processes, that is, to assess whether the retention of colour achieved by the ultrafiltration of Johnson sweetwater was effective.

As discussed previously, the recycle of ultrafiltered Johnson sweetwater will affect the decolourisation processes downstream of the melter, namely, ion exchange and crystallisation. It is unlikely that any improvement in the quality of the recycled Johnson sweetwater will affect the carbonation clarification process due to the fact that the solution constituting Johnson sweetwater has already passed through the carbonation stage. The decolourisation processes have greater capacities for the removal of certain types of colourant types. Ion exchange has a high capacity for the removal of the anionic low molecular weight sugar-cane plant produced colourants. The high molecular weight colourants tend to pass through the ion exchange process, while those that do get adsorbed saturate and foul the resin - lowering the efficiency of the process. The high molecular weight sugar-cane plant and factory produced colourants, which pass through the ion exchange process, tend to be included in the final refined sugar crystals during boiling. The process of colour removal by ion exchange and that of colour inclusion in refined sugar crystals are discussed in Section 2.3 and 2.4 respectively.

Sugar colour is a highly complex mixture of molecules ranging, in molecular weight from several hundred to several million daltons with varying chemical and physical properties. The various types of sugar colour are described in Section 2.2. ICUMSA colour does not indicate the types or proportions of the different colourant species contained in a particular sugar solution. Hence, it cannot be used to predict how a particular solution will decolourise in the species selective processes of ion exchange and crystallisation. In fact, no effective analytical technique has been established which can easily and accurately be used to determine the proportions of the individual sugar colour types.

Because the potential influence of recycled Johnson sweetwater ultrafiltration permeate could not be predicted on the basis of ICUMSA colour, and due to the lack of analytical techniques for determination of the relative proportion of sugar colourant types, an alternative method was devised to measure the quality of the Johnson sweetwater ultrafiltration permeate relative to the original feed.

It was decided to investigate the quality, based on ICUMSA colour, of the crystals which could be grown from the respective feed and permeate Johnson sweetwater solutions. The difference between the feed and permeate crystal colour, that is, the difference between the colour transfer characteristics of the feed
and permeate, would give an indication as to the relative quality of the Johnson sweetwater permeate. A lower colour transfer value for ultrafiltration permeate would mean that those colourant molecules which tend to be included during crystallisation were retained by the ultrafiltration membrane. The colour molecules which tend to be included are also those molecules which tend not to be removed by ion exchange, indicating that the Johnson sweetwater ultrafiltration permeate will be more effectively decolourised than the original feed Johnson sweetwater.

It has already been shown that ultrafiltration of refined sugar solutions, using the CeraMem LMDA-20-P1 membrane module, has the ability to retain those colourants which are included in the final refined sugar crystals (Experiment Series B and Experiment Series C, Section 4.5 and 4.6 respectively). It remains to be shown whether these molecules are present in Johnson sweetwater and whether the ultrafiltration of Johnson sweetwater prior to crystallisation improves the colour transfer characteristics of the Johnson sweetwater.

4.8.1 The Aim of Experiment Series E

The aim of Experiment Series E was to assess the difference in colour transfer, from solution to sugar crystals, for the Johnson sweetwater feed and corresponding ultrafiltration permeate. The colour transfer results were aimed at indicating whether the ultrafiltration of Johnson sweetwater retains those colour molecules which are preferentially included in sugar crystals.

4.8.2 Experimental Method and Equipment

The stepwise experimental procedure for the colour transfer experiments is presented in Appendix A2.8.2.

The refinery ultrafiltration rig, described in Section 3.2.3, was used to collect feed and permeate samples for colour transfer analysis. The feed and permeate samples were collected at the same rate to ensure that each composite sample was representative. This was necessary due to the varying nature of Johnson sweetwater composition. To achieve a feed sample rate equivalent to the permeate flow rate, the latter was measured and the control valve on the continuous feed sample port adjusted accordingly. The 38 litre samples were collected in 50 litre containers and transferred to the Sugar Milling Research Institute (SMRI) for evaporation, crystallisation and colour analysis.

Due to the dilute nature of Johnson sweetwater, the samples required brining up, or concentration, by the addition of first boiling sugar from Hulett Refineries. First boiling sugar constitutes the first strike from a particular liquor and is the purest sugar produced by the refinery. For a full pilot-pan boiling, a
total of about 20 kg brix was required while for a half boiling, about 13 kg brix was required. Following brixing, the samples were evaporated to achieve the required pan feed liquor brix of about 60.

The reasons for concentrating the samples by brixing and evaporation are discussed further in Section 4.8.3.1. The pilot evaporator is described in Section 3.3 while the evaporator operating procedure is described in Appendix A2.8.3.

Following evaporation, the concentrated feed or permeate liquor was boiled in the Sugar Milling Research Institute pilot vacuum pan. The pilot-pan is described in Section 3.4, while the operating procedure for the pan is described in Appendix A2.8.4. The resulting massecuite, following boiling of the feed or permeate Johnson sweetwater solution, was struck from the pan and centrifuged to separate the crystals from the mother liquor. The crystals were washed, by mixing with a saturated H1 refined sugar solution, to remove the mother liquor costing from the crystal surfaces. This mixture was then centrifuged to recover the washed crystals, which were allowed to air dry.

A portion of the sugar crystals was affinated according to the ICUMSA procedure given in Appendix A2.8.2 (xvii). The purpose of the affination procedure was to remove the surface film of colourants surrounding the sugar crystals and any traces of the mother liquor remaining on the crystal surfaces.

The affinated and unaffinated, feed and permeate, sugar crystals were analysed for colour by the ICUMSA method presented in Appendix A2.1. The colour of the unaffinated crystals represents general sugar colour, while that of the affinated crystals represents crystal colour, that is, colour that was included in the growing crystals. The colour transfer difference was calculated from the difference between the colour of the affinated Johnson sweetwater feed crystals and the colour of the affinated ultrafiltration permeate crystals.

Due to the length of time required by the evaporation and crystallisation processes, the solution had to be stored in a cold room below 4 °C to prevent biological degradation. The exact time sequence was followed for all the colour transfer experiments. The samples were collected and brixed up by the addition of first boiling sugar. They were then stored overnight in the cold room at the Sugar Milling Research Institute. The following morning they were heated and concentrated by evaporation. The concentrated solution was stored in the cold room overnight prior to evaporation the following morning.

The experimental method is presented pictorially in Figure 4.13.
4.8.3 Experimental Results and Discussion

The results of the three colour transfer investigations in Experiment Series E are presented in Table 4.12 (Section 4.8.3.2) and in Appendix A1.6.

The colour transfer experiments posed several problems which were due to the low sugar concentration (brix) of the Johnson sweetwater and low permeate flow rate of the CeraMem LMDA-20-P1 membrane module. This lead to the samples requiring brixing, by the addition of sugar, and evaporation prior to crystallisation boiling. The problems are discussed in Section 4.8.3.1 prior to further discussion of the experimental results.

4.8.3.1 Problems Associated With the Colour Transfer Experiments

The SMRI pilot-pan requires a minimum of 20 kg brix for a full boiling and a minimum of 13 kg brix for a half boiling. Johnson sweetwater has an average brix of about 10 (Appendix 5). To satisfy the minimum, half boiling, requirements of the pilot-pan, a mass of 130 kg Johnson sweetwater and
corresponding ultrafiltration permeate would have to be collected to supply the 13 kg brix required. A full boiling would require 200 kg of Johnson sweetwater.

Using the CeraMem LMDA-20-P1 membrane module, the time required to collect 130 kg (about 130 \( \ell \)) of Johnson sweetwater ultrafiltration permeate, assuming a permeate flux rate of 100 \( \ell/\text{m}^2\text{h} \), would be about 10 h. The average permeate flux rate will probably be lower than 100 \( \ell/\text{m}^2\text{h} \) over a 10 h period resulting in a sample time in excess of 10 h being required. This is not feasible due to the fact that the Johnson sweetwater will degrade over the sample time. The long permeate collection time was the reason for not being able to use the Micro-Carbosep 60 (10 000 dalton cut-off) membrane which has a surface area an order of magnitude lower than that of the CeraMem LMDA-20-P1 module.

The pan requires a minimum of 13 kg brix at a concentration of about 60 \(^\circ\)brix. To concentrate the minimum mass of 130 kg Johnson sweetwater from 10 \(^\circ\)brix to 60 \(^\circ\)brix would require the evaporation of 100 kg water. Assuming the SMRI pilot evaporator operates at its maximum specified evaporation rate of 12 \( \ell \) per hour, the required evaporation time would be greater than eight hours. Sugar solutions form colour over long periods of exposure to heat, hence the need to avoid long evaporation times.

The long permeate collection times and long evaporation times were not feasible and would result in degradation of the feed and permeate samples, affecting the colour transfer results. Consequently, an alternative permeate collection and concentration procedure was devised.

Volumes of 36 \( \ell \) feed and ultrafiltration permeate were collected. Equal masses, from the same batch of first boiling sugar were added to the respective solutions to increase the total mass brix of each solution to the desired value greater than the minimum of 13 kg brix. First boiling sugar is the first crop of crystals produced from a particular liquor in the refinery. It constitutes the purest, lowest colour, of all the refined sugars produced by Hulett Refineries.

The addition of first boiling sugar will decrease, or mask, the colour transfer differences due to the fact that sucrose is being added. This decreases the ratio of potentially included colourant molecules to sucrose molecules. In the experiments, the minimum mass sugar added was 12 kg (Experiment E2 and E3). The original mass brix in the feed and permeate solutions was 4.7 and 4.3 kg for E2 and E3 respectively. Hence, the mass brix added was about 2.5 times the original mass brix. In Experiment E3, 18 kg sugar was added to feed and permeate solutions containing 3.6 and 3.4 kg brix respectively. This was about 5 times the original mass brix.

By adding sugar to the feed and permeate samples, colour was also added. This colour was made up of those molecules which were included in the first boiling sugar crystals. The colour of the brixing sugar was only about 30 ICUMSA units, while that of the affinited brixing sugar was 21 units. However, the addition of colour to the feed and permeate solutions effectively decreases the relative difference
between feed and permeate potentially included colour. The process is complicated by the fact that a molecule which was previously included in a sugar crystal may not be included in a subsequent boiling due to operating conditions or localised effects during inclusion.

Following brixing, the sugar solution then had to be evaporated to increase its concentration to 60 °brix. The evaporation time required was reduced due to the increased concentration of the evaporator feed solution following brixing. This decreased the effect of heating the solution and possible colour formation during evaporation.

Experiment E0 was performed to assess the extent of colour formation due to pilot evaporation and pilot-pan boiling of a sugar solution. The experiment involved the evaporation of a solution of first boiling sugar followed by re-crystallisation in the SMRI pilot-pan. The evaporator feed solution was made to the same concentration as the brixed solutions in Experiment E1 and E2. No increase in final sugar colour compared to the original first boiling feed sugar was observed. The affinated final pilot-pan sugar colour was 15 ICUMSA units as opposed to 21 for the original first boiling sugar.

4.8.3.2 Colour Transfer Results

<table>
<thead>
<tr>
<th>Sugar Type</th>
<th>Experiment E1</th>
<th>Experiment E2</th>
<th>Experiment E3</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Feed crystal colour</td>
<td>Perm crystal colour</td>
<td>Colour transfer difference (%)</td>
</tr>
<tr>
<td>Unaffinated pan sugar</td>
<td>25</td>
<td>18</td>
<td>28</td>
</tr>
<tr>
<td>Affinated pan sugar</td>
<td>17</td>
<td>13</td>
<td>24</td>
</tr>
</tbody>
</table>

Colour = ICUMSA colour, Perm = permeate

Higher colour transfer, from solution to sugar crystal, was observed for the feed Johnson sweetwater as opposed to the ultrafiltration permeate in all three experiments. The colour transfer results are summarised in Table 4.11.

For Experiment E1, the difference between the Johnson sweetwater feed and ultrafiltration permeate affinated crystal colour, was 24%. That is, the affinated feed crystals had 24% more included colour than the affinated permeate crystals. For Experiment E2 and E3, the affinated crystal colour transfer differences were 27 and 19% respectively.
The colour transfer values are dependent on the relative concentrations of the various types of colour molecules present in the feed and permeate solutions. In all three cases, the colour transfer was lower for the ultrafiltration permeate by 19 to 27%. Due to the fact that a certain amount of potentially included colour was added during brixing of the feed and permeate solutions, the retention of potentially included molecules by the membrane will be higher than that indicated by the colour transfer differences. The addition of included colour deflates the colour transfer differences. The actual amount by which the added colour deflates the transfer values cannot be quantified due to the fact that potentially included molecules are not always included during crystallisation. Not all the colour that was added to the solutions due to the addition of brixing sugar will again include during crystallisation. The molecules may have constituted part of a fluid inclusion comprising a wide range of molecules. Some of the colourants in the inclusion may not actually be potentially included molecules, but may have been included due to localised viscosity or supersaturation effects. Certain molecules do, however, show a regular tendency to be included in the refined sugar crystals, however the relative quantities of these cannot be determined. The mechanism of colour inclusion during sugar crystallisation is described in Section 2.3.

The ultrafiltration of Johnson sweetwater during Experiment E1 achieved the highest colour retention of 34.2% (Table A1.25). This resulted in a colour transfer difference of 24%. The retentions achieved in Experiment E2 and E3 were 21% and 24% respectively (Table A1.26 and A1.27) resulting in colour transfer differences of 27% and 19% respectively. The colour transfer difference for Experiment E1 was expected to be higher than that for the other two experiments due to the colour retention for E1 being higher. This was not the case, the reason being the greater quantity of brixing sugar added to the original solutions in Experiment E1 - lowering the ratio of potentially included colourants to sucrose. This lowers the colour transfer difference between the feed and permeate crystals. The colour transfer difference for Experiment E2 was expected to be lower than that for Experiment E3 due to the colour retention being lower. This was not the case with colour transfers differences of 27 and 19% being achieved for E2 and E3 respectively. The actual colour of the feed and permeate solutions for Experiment E2 were higher which could have been the reason for the lower colour transfer difference. However, ICUMSA colour does not indicate the concentrations of the various types of molecules in the solutions. Hence, the composition of the solutions with regard to potentially included molecules was unknown.

The mechanisms of inclusion of colour in refined sugar crystals is highly complex and dependent on the types and concentrations of molecules present. Short range forces then determine whether the potentially included molecules do get included. However, the colour transfer experiments did show improved colour transfer for the ultrafiltered Johnson sweetwater in all cases. Although the results do not allow the accurate prediction of the types and quantities of molecules which were retained, it can be concluded that ultrafiltration produces a permeate of higher quality (lower concentration of potentially
included molecules) than the feed and that the recycle of ultrafiltered Johnson sweetwater has the potential to positively influence the refinery decolourisation processes. The colour transfer results confirm that the retention of colour from Johnson sweetwater is effective.

### 4.8.3.3 Colourant Types Likely to be Retained During The Ultrafiltration of Johnson Sweetwater

Although it is not possible, from the above results, to quantify the types of sugar colour included in the feed and permeate crystals, comparison of the results with the literature review presented in Section 2.1 to 2.4 allows the prediction of those molecules which are likely to be retained by the ultrafiltration membrane. This allows the prediction of the possible influence the recycle of ultrafiltered Johnson sweetwater will have on the refinery decolourisation processes.

The inclusion of colour in sugar crystals takes place by the mechanism of solid and/or liquid inclusion. In the case of refined sugar, the extent of solid inclusion is assumed to be negligible. Fluid inclusions are described in detail in Section 2.3.1.2.

The presence of micro-cavities on the various faces of the crystal surface, makes the inclusion of large or small droplets of the mother solution possible, increasing the colour of the crystal. The faster growing faces have been observed to have the highest colour inclusion. As temperature and/or degree of supersaturation increase, other crystal faces can become involved in non-sucrose liquid inclusion [Montovani et al. (1985)].

It has been shown that the distribution of impurities between the crystalline solid and the interfacial liquid from which it grows, cannot be described in terms of the usual phase diagrams. There are kinetic processes taking place at the interface resulting in changes in concentration and other properties of the interfacial medium [Lionnet (1987)]. Powers [1969] stresses that the molecular properties at the crystal/massequite interface must be considered. The process of non-sucrose inclusion in crystals cannot only be treated as simple entrapment of mother liquor into the crystal.

The composition of the liquid in contact with the surface of the growing crystal is not the same as the composition of the bulk mother liquor. The liquid film, or boundary layer, at the crystal surface is referred to as the exhaustion sleeve and has a lower concentration of sucrose and a higher concentration of impurities. The mechanism of deposition of molecules on the crystal surface in this sleeve is preceded by the formation of molecular aggregates of sucrose and water in solution. Also present are many impurity molecules, all in constant fluidised motion. Individual molecules will be subjected to constantly changing surrounding attractions and migrate under their influence to achieve a state of least
free energy. It is this constantly changing sleeve that causes the crystal to develop such high concentrations of faults and to build in foreign molecules.

Due to the sleeve of exhaustion, the composition of the included material will not necessarily be the same as that of the mother liquor. The concentration of impurities in the sleeve will have been increased due to the loss of sucrose during crystallisation. The proportions of the impurities will also have been affected by their different rates of diffusion to and from the bulk liquor. Hence one cannot calculate the amount of a particular impurity expected to be included in the crystal based on the composition of the bulk liquor. A further complication in attempting to predict the composition of the final crystal is due to certain molecules being temporarily held at the growing face and then being released. This is a natural consequence of the complex possible affinities between a particular impurity and the crystal lattice. High molecular weight molecules are retained in the grain much more than the low molecular weight molecules [Yamane in: Powers (1969)].

During crystallisation, the individual molecules are influenced by many short range forces. Several intermediate stages are passes before a particular molecule takes up a position of least free energy. The crystal is composed of a vast number of individual molecules capable of individual migrations through the crystal under favourable conditions, progressing towards ultimate perfection which, in practise, is never achieved. Faults abound and are necessary to aid the growth of the crystal. Larger molecules have lower transport rates and do not migrate out of liquid inclusions formed in the early stages of crystallisation.

Droplet inclusion in the crystal occurs under conditions of high viscosity at the crystal solution interface. As the viscosity increases, so too does the surface tension, increasing both the number and size of the liquid inclusions. High molecular weight molecules can cause isolated local sites of high viscosity on the crystal surface. These are preferentially included in crystal flaws. Also, the slower rate of transport of the high molecular weight (HMW) species limits the migration of the HMW non-sucrose molecules from the crystal back to the solution.

Montovani et al. [1986] observed experimentally that colouring matter includes preferentially in the more rapidly growing faces. They also showed that the occlusion of colour requires the presence of kinetic conditions which cause one or more of the faces to grow rapidly enough to promote inclusion. Hence, general inclusion of colour will only occur above a certain temperature and supersaturation level which promote rapid crystal growth. Some colourants may, however, be included at conditions below the critical ones owing to a structural affinity with the crystal face. The high molecular weight molecules are often highly branched and have many side chains which may show an affinity for the sugar crystal surface. The probability of affinity with the crystal surface for the high molecular weight colourant molecules is higher than that for the low molecular weight molecules.
It is evident that it is the high molecular weight molecules which have a higher probability of being included during crystallisation due to: - their low transport rates, the fact that they can cause localised sites (pools) of high viscosity and the fact that they have a higher probability of sharing a structural affinity with the growing crystal. High molecular weight colourants are associated with polysaccharide molecules from sugar cane and are generated in the sugar mill and the sugar refinery by the high temperature process conditions (Section 2.2.2). Refinery produced colour comprises melanoidins, melanins, alkaline degradation products of fructose (ADF's) and caramels.

The ultrafiltration of Johnson sweetwater using the CeraMem LMDA-20-P1 membrane module is likely to retain the majority of colourant molecules having a molecular weight greater than 15,000 daltons. This comprises most of the low and uncharged factory formed colourants, and the colour associated with polysaccharide molecules from the sugar cane. The retained molecules are assumed to be the high molecular weight colourants while the non-retained colourants are assumed to be the low molecular weight sugar cane derived colourants. Sugar cane derived colourants are relatively easily removed by the refinery decolourisation processes.

Hence, the retention of the high molecular weight range of colour molecules prior to boiling will result in less inclusion of colour in refined sugar crystals. This was evident in the colour transfer experiments.
Chapter 5

Conclusions

Johnson sweetwater is a recycle stream and affects the decolourisation processes downstream of the melter, namely, ion exchange and crystallisation. For the retention of colour by ultrafiltration to be effective, the ultrafiltered Johnson sweetwater will have to positively influence the decolourisation processes by improving their colour removal efficiency. During the course of this investigation, the maximum ICUMSA colour load to the melter was calculated to be 31% based on weekly average quality control data.

The high molecular weight refinery and factory produced colourants, as well as the high molecular weight colourants associated with polysaccharide molecules from the sugarcane were concluded to be the molecules most likely to pass through the ion exchange process, foul the ion exchange resin (if adsorbed) and be included in the final refined sugar crystals. These are termed potentially included molecules. Low molecular weight sugarcane derived colourants are effectively removed by the decolourisation processes and are less likely to be included in the refined sugar crystal.

Ultrafiltration, being a filtration process, preferentially retains the high molecular weight, potentially included components in a solution, in contrast to ion exchange and crystallisation which preferentially remove the low molecular weight sugarcane derived colourants, that is, the easily removed colourants. ICUMSA colour does not indicate the relative amounts of the various fractions of sugar colour. Hence, the quality and potential influence of ultrafiltered Johnson sweetwater on the refinery decolourisation processes cannot be adequately quantified on the basis of ICUMSA colour.

In the course of this investigation, several ceramic membrane modules were used to assess the ability of ultrafiltration, as a process, to decolourise Johnson sweetwater. Point ICUMSA colour and brix retentions were investigated using the various membranes. This led to subsequent experimental work being required due to the inability of the process to be effectively assessed based on ICUMSA colour. The ultrafiltration of refined sugar solutions was performed to determine whether ultrafiltration has the ability to retain those molecules which are included in refined sugar crystals (Experiment Series B and Series C). Following this, colour transfer experiments were performed to determine whether the colour transfer, from solution to sugar crystal, is lower for the ultrafiltered Johnson sweetwater
compared to the original feed Johnson sweetwater (Experiment Series E). The results of this would confirm whether ultrafiltration retains those molecules which are preferentially included in the crystals during crystallisation.

The ultrafiltration of Johnson sweetwater achieved point ICUMSA colour retentions ranging from 28 to 50% (Experiment Series A) using the various membrane modules. Hence, the recycle of ultrafiltered Johnson sweetwater has the potential to decrease ICUMSA colour load to the melter and subsequent decolourisation processes by a maximum ranging from 8.7 to 15.5% using the above membranes.

Brix retentions were generally below 10% in Johnson sweetwater solutions. For refined sugar solutions, brix retention was observed to be about 2%. Hence, the retention of sucrose in Johnson sweetwater solutions can be assumed to be much less than the brix retentions.

Ultrafiltration of refined sugar solutions achieved average point ICUMSA colour retentions of 34% in \textit{H1 refined sugar} and 52% in \textit{affinated H1 refined sugar}. The retention in the affinated sugar solution was higher due to the greater relative percentage of high molecular weight potentially included colour in the crystal as opposed to the unaffinated crystal which comprises the surface film contained colourants as well. These refined sugar solutions were also ultrafiltered under conditions of high water recovery where similar colour retentions were observed.

The ultrafiltration of Johnson sweetwater decreased the colour transfer, from solution to crystal, for the ultrafiltration permeate solution by between 19 and 27%, relative to the feed Johnson sweetwater solutions. The actual colour transfer differences are probably greater than these experimentally determined values due to the fact that sugar, and associated colour, was added to brix up the feed and permeate solutions prior to evaporation and crystallisation. Ultrafiltration therefore retains those colourants which have a high potential to be included in sugar crystals during crystallisation.

The ultrafiltration of refined sugar solutions and the colour transfer experiments showed that the membrane preferentially retains potentially included molecules. Hence, ultrafiltration of Johnson sweetwater is effective and will positively influence the decolourisation processes downstream of the melter. More colour transfer experiments would have to be performed to be able to propose correlations between ICUMSA colour retention and improved colour transfer, due to the varying nature of Johnson sweetwater.

High water recovery ultrafiltration experiments were performed on Johnson sweetwater (Experiment D). Contrary to indications, the ICUMSA colour retention did not increase with water recovery. The varying nature of Johnson sweetwater means that the results of a particular experiment are unique for
the particular operating conditions and feed composition. However, the results do give an indication as to membrane performance.

Relative permeate quality, the difference between the point permeate ICUMSA colour and the original feed ICUMSA colour, decreased to 6.6% at a water recovery of 82.9% for Johnson sweetwater. When the relative permeate quality becomes equal to zero (at the critical water recovery value), the point permeate ICUMSA colour is the same as that of the original feed and ultrafiltration is no longer effective as a colour removal process. However, in the case of Johnson sweetwater, it is concluded that relative permeate quality based on ICUMSA colour is not an accurate measure of the effectiveness of the process. Ultrafiltration may still be effective at water recoveries higher than the critical water recovery value due to the fact that the membrane may still be retaining high molecular weight potentially included colourants. The high ICUMSA colour of the permeate is likely to be largely due to the passage of low molecular weight easily removed colourants. Hence, ultrafiltration will be effective at water recoveries greater than the critical water recovery value based on ICUMSA colour.

It is proposed that future investigations into the ultrafiltration of Johnson sweetwater regard colour as a mixture of easily removed and potentially included molecules as opposed to the single grouped solute referred to as ICUMSA colour. Analytical techniques should be developed which can distinguish between the two types of colour. Many experiments will have to be performed to determine the average fractions of potentially included molecules due to the varying nature of Johnson sweetwater. A knowledge of the amount of potentially included colour retained by a membrane will enable the influence of the recycled Johnson sweetwater ultrafiltration permeate to be determined and an economic evaluation could be undertaken based on the improved efficiency of the ion exchange and crystallisation processes.

The design of a full-scale ultrafiltration process for the decolourisation of Johnson sweetwater would require extensive on site work to investigate long term trends in flux and flux regeneration. Johnson sweetwater is a high volume stream with a low brix and high ICUMSA colour concentration. Hence, the process would require high permeate fluxes to make it economically viable. Alternative chemical cleaning methods and the back-flushing technique would have to be investigated to determine optimum operating cycles. This would require a full scale membrane module.

Also, more information regarding the condition of the Johnson sweetwater is required. It is recommended that a flow meter be installed in the Johnson sweetwater pump discharge line and that regular sampling, for Johnson sweetwater quality analysis, include corresponding flow rate information. A more accurate assessment of the colour load of the Johnson sweetwater stream could then be made.

Although the CeraMem LMDA-20-P1 membrane module was used for most of the work, the M5 Micro-Carbosep 60 module achieved higher point ICUMSA colour retentions in Johnson sweetwater. It
is possible that this module would have achieved better colour transfer results than the CeraMem module. However, the Micro-Carbosep module could not be used because of the low permeate flow rate associated with the low membrane surface area of the laboratory scale module.

Ceramic membrane manufacturers are continually developing new products which could produce better results than those in this investigation. It is recommended that the literature be continually monitored for developments in ceramic ultrafiltration technology.
References


CLARKE, MA; ROBERTS, EJ; TO; TBT (1986b) Recent studies on dextrins and polysaccharides in refinery processes. *Proceedings of the Sugar Processing Research Conference held in Savannah, Georgia, USA.* 74-81.


CLARKE, MA; TSANG, WSC; GODSHALL, MA (1988) Structure of colorants. *Proceedings of the Sugar Processing Research Conference held in New Orleans, Louisiana, USA.*


processes. Proceedings of the Sugar Processing Research Conference held in Savannah, Georgia, USA. 74-81.


APPENDICES
Appendix 1

Raw Data and Experimental Results
A1.1 Original Pure Water Permeabilities

A1.1.1 Aim of the Experiment

The purpose of determining the pure water permeability (PWP) of a particular membrane was to be able to assess the degree of fouling of that membrane, following its exposure to a particular sugar solution, relative to the original PWP when it was first purchased. The difference between the value of the PWP of a particular membrane and its original PWP is a measure of the degree of fouling of that membrane. The original pure water permeability values of the new membranes were determined prior to exposing them to any sugar solution or process fluid.

The procedure for determination of the pure water permeability of a particular membrane is described in Appendix A2.2.

A1.1.2 Experimental Conditions

<table>
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<tr>
<th>Experimental rig used</th>
<th>Membrane cleaning rig (Chapter 3.2.1)</th>
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<tbody>
<tr>
<td>Feed water</td>
<td>Reverse osmosis permeate water</td>
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<tr>
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<tr>
<td>Volumetric flow rate</td>
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</tr>
<tr>
<td></td>
<td>4 ³/min (Carbosep module)</td>
</tr>
<tr>
<td>Linear flow rate</td>
<td>1,5 m/s (CeraMem and Membralox modules)</td>
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<tr>
<td></td>
<td>2,5 m/s (Carbosep module)</td>
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</table>

A1.1.3 Experimental Results

<table>
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<tr>
<th>Table A1.1: Original pure water permeabilities of the CeraMem LMDA-20-P1 membrane module.</th>
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</thead>
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<td>Pressure</td>
</tr>
<tr>
<td>----------</td>
</tr>
<tr>
<td>500 kPa</td>
</tr>
<tr>
<td>400 kPa</td>
</tr>
<tr>
<td>300 kPa</td>
</tr>
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Table A1.2: Original pure water permeability of the CeraMem LMA-0005-P membrane module.

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</thead>
<tbody>
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<td>600 $\mu$m$^2$/h</td>
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<td>400 kPa</td>
<td>500 $\mu$m$^2$/h</td>
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<td>300 kPa</td>
<td>400 $\mu$m$^2$/h</td>
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Table A1.3: Original pure water permeability of the Membralox 1P19-40 (20 nm nominal pore size) membrane module.

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<th>Pure Water Permeability</th>
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<td>500 kPa</td>
<td>1 200 $\mu$m$^2$/h</td>
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<tr>
<td>400 kPa</td>
<td>950 $\mu$m$^2$/h</td>
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<tr>
<td>300 kPa</td>
<td>700 $\mu$m$^2$/h</td>
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Table A1.4: Original pure water permeability of the M5 Micro-Carbosep 60 (10 000 dalton cut-off) membrane module.

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<tr>
<td>400 kPa</td>
<td>200 $\mu$m$^2$/h</td>
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<tr>
<td>300 kPa</td>
<td>170 $\mu$m$^2$/h</td>
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A1.2 Experiment Series A:  
The Ultrafiltration of Johnson Sweetwater

A1.2.1 The Aim of Experiment Series A

The aim of Experiment Series A was to assess the ability of the various inorganic membranes, listed below, to retain colour in Johnson sweetwater.

The membranes used were the CeraMem LMDA-20-P1 module, the CeraMem LMA-0005-P module, the Membralox 1P19-40 (20 nm nominal pore size) module and the M5 Micro-Carbosep 60 (10 000 dalton cut-off) module.

The series of experiments were performed using the refinery ultrafiltration rig which is described in Chapter 3.2.3. The experimental procedure is described in Appendix A2.4.
A1.2.2 Experimental Results

A1.2.2.1 Experiment A1:
The Ultrafiltration of Johnson Sweetwater using the CeraMem LMDA-20-P1 Ceramic Membrane Module

Table A1.5: Experiment A1
Point feed variables and permeate flux values for the ultrafiltration of Johnson sweetwater using the CeraMem LMDA-20-P1 membrane module.
Date: 27/07/1993 to 29/07/1993

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<tr>
<th>Sample Time (h)</th>
<th>Feed Temperature (°C)</th>
<th>Pressure (kPa)</th>
<th>Linear Flow Rate (m/s)</th>
<th>pH</th>
<th>Permeate Flux (L/m²h)</th>
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<td>1.9</td>
<td>7.5</td>
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Table A1.6 : Experiment A1
Point brix retention, absorbance retention and ICUMSA colour retention values for the ultrafiltration of Johnson sweetwater using the CeraMem LMDA-20-P1 membrane module.
Date : 27/07/1993 to 29/07/1993

<table>
<thead>
<tr>
<th>Sample Time (h)</th>
<th>°Brix</th>
<th>Absorbance</th>
<th>ICUMSA Colour</th>
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<td></td>
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<td>Perm</td>
<td>Ret (%)</td>
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Note : Ret = retention, Perm = permeate
Figure A1.1: Experiment A1
Point feed and permeate variables for the ultrafiltration of Johnson sweetwater using the CeraMem LMDA-20-P1 membrane module.
Figure A1.2: Experiment A1
Point feed and permeate brix values, absorbance values and ICUMSA colour values for the ultrafiltration of Johnson sweetwater using the CeraMem LMDA-20-P1 membrane module.
Figure A1.3: Experiment A1
Point brix retention, absorbance retention and ICUMSA colour retention values for the ultrafiltration of Johnson sweetwater using the CeraMem LMDA-20-PI membrane module.
Figure A1.4: Experiment A1
Mathematically predicted feed and composite permeate absorbance values, ICUMSA colour values and brix values as functions of water recovery, for the ultrafiltration of Johnson sweetwater using the CeraMem LMDA-20-P1 membrane module.
Figure A1.5: Experiment A1
Mathematically predicted % colour passing the membrane and % sugar recovered, composite permeate grade, and relative permeate quality as functions of water recovery, for the ultrafiltration of Johnson sweetwater using the CeraMem LMDA-20-P1 membrane module.
A1.2.2.2 Experiment A2:
The Ultrafiltration of Johnson Sweetwater using the CeraMem LMA-0005-P Ceramic Membrane Module

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<td>1.8</td>
<td>no sample</td>
<td>235</td>
</tr>
<tr>
<td>1</td>
<td>75</td>
<td>400</td>
<td>1.8</td>
<td>7.1</td>
<td>184</td>
</tr>
<tr>
<td>2</td>
<td>75</td>
<td>400</td>
<td>1.8</td>
<td>no sample</td>
<td>136</td>
</tr>
<tr>
<td>3</td>
<td>80</td>
<td>400</td>
<td>1.9</td>
<td>10.6</td>
<td>110</td>
</tr>
<tr>
<td>21</td>
<td>80</td>
<td>400</td>
<td>1.6</td>
<td>7.9</td>
<td>60</td>
</tr>
<tr>
<td>26</td>
<td>80</td>
<td>400</td>
<td>1.4</td>
<td>7.8</td>
<td>60</td>
</tr>
<tr>
<td>45</td>
<td>80</td>
<td>400</td>
<td>1.8</td>
<td>6.3</td>
<td>18</td>
</tr>
<tr>
<td>60</td>
<td>75</td>
<td>400</td>
<td>1.5</td>
<td>6.7</td>
<td>13</td>
</tr>
</tbody>
</table>

Table A1.8: Experiment A2
Point brix retention, absorbance retention and ICUMSA colour retention values for the ultrafiltration of Johnson sweetwater using the CeraMem LMA-0005-P membrane module.
Date: 21/06/1993 to 23/06/1993

<table>
<thead>
<tr>
<th>Sample Time (h)</th>
<th>°Brix</th>
<th>Absorbance</th>
<th>ICUMSA Colour</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Feed</td>
<td>Perm</td>
<td>Ret (%)</td>
</tr>
<tr>
<td>1</td>
<td>8.9</td>
<td>8.3</td>
<td>6.7</td>
</tr>
<tr>
<td>3</td>
<td>10.9</td>
<td>9.5</td>
<td>12.8</td>
</tr>
<tr>
<td>21</td>
<td>3.0</td>
<td>2.4</td>
<td>20.0</td>
</tr>
<tr>
<td>26</td>
<td>3.0</td>
<td>2.3</td>
<td>23.0</td>
</tr>
<tr>
<td>45</td>
<td>10.3</td>
<td>9.1</td>
<td>11.7</td>
</tr>
<tr>
<td>60</td>
<td>12.6</td>
<td>11.4</td>
<td>9.5</td>
</tr>
</tbody>
</table>

Note: Ret = retention, Perm = permeate
Figure A1.6: Experiment A2
Point feed and permeate variables for the ultrafiltration of Johnson sweetwater using the CeraMem LMA-0005-P membrane module.
Figure A1.7: Experiment A2

Point feed and permeate brix values, absorbance values and ICUMSA colour values for the ultrafiltration of Johnson sweetwater using the CeraMem LMA-0005-P membrane module.
Figure A1.8: Experiment A2
Point brix retention, absorbance retention and ICUMSA colour retention values for the ultrafiltration of Johnson sweetwater using the CeraMem LMA-0005-P membrane module.
Figure A1.9: Experiment A2
Mathematically predicted feed and composite permeate absorbance values, 1CUMSA colour values and brix values as functions of water recovery, for the ultrafiltration of Johnson sweetwater using the CeraMem LMA-0005-P membrane module.
Figure A1.10 : Experiment A2
Mathematically predicted % colour passing the membrane and % sugar recovered, composite permeate grade, and relative permeate quality as functions of water recovery, for the ultrafiltration of Johnson sweetwater using the CeraMem LMA-0005-P membrane module.
A1.2.2.3 Experiment A3:
The Ultrafiltration of Johnson Sweetwater Using the Membralox 1P19-40 (20 nm) Membrane Module

Table A1.9: Experiment A3
Point feed variables and permeate flux values for the ultrafiltration of Johnson sweetwater using the Membralox 1P19-40 (20 nm) membrane module.
Date: 01/11/1993 to 03/11/93

<table>
<thead>
<tr>
<th>Sample Time (h)</th>
<th>Feed Temperature (°C)</th>
<th>Pressure (kPa)</th>
<th>Linear Flow Rate (m/s)</th>
<th>pH</th>
<th>Permeate Flux (l/m²h)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>75</td>
<td>400</td>
<td>1.8</td>
<td>7.25</td>
<td>192</td>
</tr>
<tr>
<td>8</td>
<td>78</td>
<td>400</td>
<td>1.8</td>
<td>7.50</td>
<td>90</td>
</tr>
<tr>
<td>22</td>
<td>75</td>
<td>400</td>
<td>1.8</td>
<td>7.34</td>
<td>23</td>
</tr>
<tr>
<td>46</td>
<td>75</td>
<td>400</td>
<td>1.8</td>
<td>7.67</td>
<td>15</td>
</tr>
</tbody>
</table>

Table A1.10: Experiment A3
Point brix retention, absorbance retention and ICUMSA colour retention values for the ultrafiltration of Johnson sweetwater using the Membralox 1P19-40 (20 nm) membrane module.
Date: 01/11/1993 to 03/11/93

<table>
<thead>
<tr>
<th>Sample Time (h)</th>
<th>°Brix Feed</th>
<th>°Brix Perm</th>
<th>Ret (%)</th>
<th>Absorbance Feed</th>
<th>Absorbance Perm</th>
<th>Ret (%)</th>
<th>ICUMSA Colour Feed</th>
<th>ICUMSA Colour Perm</th>
<th>Ret (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>12.3</td>
<td>11.8</td>
<td>4.1</td>
<td>0.393</td>
<td>0.308</td>
<td>21.6</td>
<td>3 050</td>
<td>2 496</td>
<td>18.2</td>
</tr>
<tr>
<td>8</td>
<td>7.9</td>
<td>7.8</td>
<td>1.3</td>
<td>0.290</td>
<td>0.222</td>
<td>23.4</td>
<td>3 566</td>
<td>2 730</td>
<td>23.4</td>
</tr>
<tr>
<td>22</td>
<td>10.3</td>
<td>9.9</td>
<td>3.8</td>
<td>0.457</td>
<td>0.265</td>
<td>42.0</td>
<td>4 269</td>
<td>2 579</td>
<td>39.5</td>
</tr>
<tr>
<td>46</td>
<td>8.5</td>
<td>8.4</td>
<td>1.2</td>
<td>0.354</td>
<td>0.260</td>
<td>26.6</td>
<td>4 036</td>
<td>3 001</td>
<td>25.6</td>
</tr>
</tbody>
</table>

Note: Ret = retention, Perm = permeate
Figure A1.11: Experiment A3

Point feed and permeate variables for the ultrafiltration of Johnson sweetwater using the Membralox 1P19-40 (20 nm) membrane module.
Figure A1.12: Experiment A3
Point feed and permeate brix values, absorbance values and ICUMSA colour values for the ultrafiltration of Johnson sweetwater using the Membraflex 1P19-40 (20 nm) membrane module.
Figure A1.13: Experiment A3

Point brix retention, absorbance retention and ICUMSA colour retention values for the ultrafiltration of Johnson sweetwater using the Membralox 1P19-40 (20 nm) membrane module.
Figure A1.14: Experiment A3
Mathematically predicted feed and composite permeate absorbance values, ICUMSA colour values and brix values as functions of water recovery, for the ultrafiltration of Johnson sweetwater using the Membralox 1P19-40 (20 nm) membrane module.
Figure A1.15: Experiment A3
Mathematically predicted % colour passing the membrane and % sugar recovered, composite permeate grade, and relative permeate quality as functions of water recovery, for the ultrafiltration of Johnson sweetwater using the Membralox 1P19-40 (20 nm) membrane module.
A1.2.2.4 Experiment A4:
The Ultrafiltration of Johnson Sweetwater using the Modified Membralox 1P19-40 (20 nm) Membrane Module a with Dynamic, Dual-layer Zirconium(iv)oxide/Polyacrylic-acid Membrane

Table A1.11: Experiment A4
Point feed variables and permeate flux values for the ultrafiltration of Johnson sweetwater using the modified Membralox 1P19-40 (20 nm) membrane module with dual-layer dynamic membrane.
Date: 13/07/1993 to 16/07/1993

<table>
<thead>
<tr>
<th>Sample Time (h)</th>
<th>Feed Temperature (°C)</th>
<th>Pressure (kPa)</th>
<th>Linear Flow Rate (ms)</th>
<th>pH</th>
<th>Permeate Flux (L/m²h)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>75</td>
<td>400</td>
<td>1,9</td>
<td>8,08</td>
<td>30</td>
</tr>
<tr>
<td>25</td>
<td>77</td>
<td>400</td>
<td>1,9</td>
<td>7,58</td>
<td>12</td>
</tr>
<tr>
<td>48</td>
<td>82</td>
<td>400</td>
<td>1,9</td>
<td>8,03</td>
<td>8</td>
</tr>
<tr>
<td>68</td>
<td>80</td>
<td>400</td>
<td>1,9</td>
<td>8,25</td>
<td>8</td>
</tr>
<tr>
<td>92</td>
<td>70</td>
<td>400</td>
<td>1,9</td>
<td>7,95</td>
<td>5</td>
</tr>
</tbody>
</table>

Table A1.12: Experiment A4
Point brix retention, absorbance retention and ICUMSA colour retention values for the ultrafiltration of Johnson sweetwater using the modified Membralox 1P19-40 (20 nm) membrane module with dual-layer dynamic membrane.
Date: 13/07/1993 to 16/07/1993

<table>
<thead>
<tr>
<th>Sample Time (h)</th>
<th>°Brix</th>
<th>Absorbance</th>
<th>ICUMSA Colour</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Feed</td>
<td>Perm</td>
<td>Ret (%)</td>
</tr>
<tr>
<td>1</td>
<td>6,6</td>
<td>6,0</td>
<td>9,0</td>
</tr>
<tr>
<td>25</td>
<td>6,6</td>
<td>6,6</td>
<td>0,0</td>
</tr>
<tr>
<td>48</td>
<td>5,8</td>
<td>4,6</td>
<td>18,9</td>
</tr>
<tr>
<td>68</td>
<td>3,9</td>
<td>3,9</td>
<td>0,0</td>
</tr>
<tr>
<td>92</td>
<td>8,0</td>
<td>6,8</td>
<td>15,0</td>
</tr>
</tbody>
</table>

Note: Ret = retention, Perm = permeate
Figure A1.16: Experiment A4
Point feed and permeate variables for the ultrafiltration of Johnson sweetwater using the modified Membralox 1P19-40 (20 nm) membrane module with dual-layer dynamic membrane.
Figure A1.17: Experiment A4
Point feed and permeate brix values, absorbance values and ICUMSA colour values for the ultrafiltration of Johnson sweetwater using the modified Membralox 1P19-40 (20 nm) membrane module with dual-layer dynamic membrane.
Figure A1.18: Experiment A4

Point brix retention, absorbance retention and ICUMSA colour retention values for the ultrafiltration of Johnson sweetwater using the modified Membralox 1P19-40 (20 nm) membrane module with dual-layer dynamic membrane.
Figure A1.19: Experiment A4

Mathematically predicted feed and composite permeate absorbance values, ICUMSA colour values and brix values as functions of water recovery, for the ultrafiltration of Johnson sweetwater using the modified Membralox 1P19-40 (20 nm) membrane module with dual-layer dynamic membrane.
Figure A1.20: Experiment A4
Mathematically predicted % colour passing and % sugar recovered, composite permeate grade, and relative permeate quality as functions of water recovery, for the ultrafiltration of Johnson sweetwater using the modified Membralox 1P19-40 (20 nm) membrane module with dual-layer dynamic membrane.
### A1.2.2.5 Experiment A5:

The Ultrafiltration of Johnson Sweetwater using the M5 Micro-Carbosep (10 000 dalton cut-off) Membrane Module

**Table A1.13 : Experiment A5**

Point feed variables and permeate flux values for the ultrafiltration of Johnson sweetwater using the M5 Micro-Carbosep 60 (10 000 dalton cut-off) membrane module.

**Date : 14/06/1993 to 15/06/1993**

<table>
<thead>
<tr>
<th>Sample Time (h)</th>
<th>Feed Temperature (°C)</th>
<th>Pressure (kPa)</th>
<th>Linear Flow Rate (m/s)</th>
<th>pH</th>
<th>Permeate Flux (ℓ/m²·h)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>75</td>
<td>400</td>
<td>6,9</td>
<td>7,58</td>
<td>186</td>
</tr>
<tr>
<td>8</td>
<td>75</td>
<td>400</td>
<td>6,9</td>
<td>7,40</td>
<td>70</td>
</tr>
<tr>
<td>18</td>
<td>80</td>
<td>400</td>
<td>6,9</td>
<td>7,37</td>
<td>30</td>
</tr>
<tr>
<td>22</td>
<td>80</td>
<td>400</td>
<td>6,9</td>
<td>7,55</td>
<td>15</td>
</tr>
</tbody>
</table>

**Table A1.14 : Experiment A5**

Point brix retention, absorbance retention and ICUMSA colour retention values for the ultrafiltration of Johnson sweetwater using the M5 Micro-Carbosep 60 (10 000 dalton cut-off) membrane module.

**Date : 14/06/1993 to 15/06/1993**

<table>
<thead>
<tr>
<th>Sample Time (h)</th>
<th>°Brix Feed Perm Ret (%)</th>
<th>Absorbance Feed Perm Ret (%)</th>
<th>ICUMSA Colour Feed Perm Ret (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>6,6 6,6 0,0</td>
<td>0,172 0,075 56,4</td>
<td>2 544 1 109 56,4</td>
</tr>
<tr>
<td>8</td>
<td>6,6 6,0 9,0</td>
<td>0,234 0,123 47,0</td>
<td>3 409 1 988 41,7</td>
</tr>
<tr>
<td>18</td>
<td>8,4 7,8 7,0</td>
<td>0,175 0,107 38,8</td>
<td>1 995 1 298 34,9</td>
</tr>
<tr>
<td>22</td>
<td>4,8 4,6 4,0</td>
<td>0,089 0,047 48,4</td>
<td>1 825 963 47,2</td>
</tr>
</tbody>
</table>

**Note :** Ret = retention, Perm = permeate
Figure A1.21: Experiment A5
Point feed and permeate variables for the ultrafiltration of Johnson sweetwater using the M5 Micro-Carbosep 60 (10,000 dalton cut-off) membrane module.
Figure A1.22: Experiment A5

Point feed and permeate brix values, absorbance values and ICUMSA colour values for the ultrafiltration of Johnson sweetwater using the M5 Micro-Carbsep 60 (10 000 dalton cut-off) membrane module.
Figure A1.23 : Experiment A5
Point brix retention, absorbance retention and ICUMSA colour retention values for the ultrafiltration of Johnson sweetwater using the M5 Micro-Carbosep 60 (10 000 dalton cut-off) membrane module.
Figure A1.24: Experiment A5

Mathematically predicted feed and composite permeate absorbance values, ICUMSA colour values and brix values as functions of water recovery, for the ultrafiltration of Johnson sweetwater using the M5 Micro-Carbosep 60 (10 000 dalton cut-off) membrane module.
Figure A1.25: Experiment A5
Mathematically predicted % colour passing the membrane and % sugar recovered, composite permeate grade and relative permeate quality as functions of water recovery, for the ultrafiltration of Johnson sweetwater using the M5 Micro-Carbosep 60 (10,000 dalton cut-off) membrane module.
A1.3 Experiment Series B:
The Ultrafiltration of H1 Refined Sugar, Affinated H1 Refined Sugar, Affination Wash Liquor and Raw VHP Sugar - using the CeraMem LMDA-20-P1 Membrane Module

A1.3.1 The Aim of Experiment Series B

The aim of Experiment Series B was to assess the ability of the CeraMem LMDA-20-P1 ultrafiltration membrane to retain colour in solutions of H1 refined sugar, affinated H1 refined sugar, affination wash liquor and VHP sugar. The above sugars are described in Chapter 4.5.2.

The ultrafiltration runs were performed under conditions of zero water recovery, with the permeate and retentate streams being returned to the feed tank.

The refined sugar ultrafiltration rig was used for the ultrafiltration runs. The rig is described in Chapter 3.2.2 while the experimental procedure is described in Appendix A2.5.

A1.3.2 Experimental Results

The results of the ultrafiltration of the various sugar solutions are presented in Table A1.15 to A1.18.

Note: abs = absorbance, Colour = ICUMSA colour

<table>
<thead>
<tr>
<th>Table A1.15: Experiment B1</th>
</tr>
</thead>
<tbody>
<tr>
<td>Results of the ultrafiltration of H1 refined sugar at three concentrations under conditions of zero water recovery.</td>
</tr>
<tr>
<td>Date = 19/07/1993</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th></th>
<th>Low Brix (About 10°Brix)</th>
<th>Medium Brix (About 25°Brix)</th>
<th>High Brix (About 50°Brix)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Brix</td>
<td>Abs</td>
<td>Colour</td>
</tr>
<tr>
<td>Feed</td>
<td>9,6</td>
<td>0,029</td>
<td>58</td>
</tr>
<tr>
<td>Permeate</td>
<td>9,5</td>
<td>0,020</td>
<td>41</td>
</tr>
<tr>
<td>Retention (%)</td>
<td>1,0</td>
<td>31,0</td>
<td>29,3</td>
</tr>
</tbody>
</table>
### Table A1.16: Experiment B2
Results of the ultrafiltration of Affinated H1 refined sugar at three concentrations under conditions of zero water recovery.
Date = 20/07/1993

<table>
<thead>
<tr>
<th></th>
<th>Low Brix (About 10°Brix)</th>
<th>Medium Brix (About 25°Brix)</th>
<th>High Brix (About 50°Brix)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Brix</td>
<td>Abs</td>
<td>Colour</td>
</tr>
<tr>
<td>Feed</td>
<td>9,8</td>
<td>0,020</td>
<td>39</td>
</tr>
<tr>
<td>Permeate</td>
<td>9,7</td>
<td>0,010</td>
<td>20</td>
</tr>
<tr>
<td>Retention (%)</td>
<td>1,0</td>
<td>50,0</td>
<td>48,7</td>
</tr>
</tbody>
</table>

### Table A1.17: Experiment B3
Results of the ultrafiltration of Affination Wash Liquor of H1 refined sugar at two concentrations under conditions of zero water recovery.
Date = 21/07/1993

<table>
<thead>
<tr>
<th></th>
<th>Low Brix (About 10°Brix)</th>
<th>Medium Brix (About 25°Brix)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Brix</td>
<td>Abs</td>
</tr>
<tr>
<td>Feed</td>
<td>9,1</td>
<td>0,047</td>
</tr>
<tr>
<td>Permeate</td>
<td>8,9</td>
<td>0,018</td>
</tr>
<tr>
<td>Retention (%)</td>
<td>2,2</td>
<td>61,7</td>
</tr>
</tbody>
</table>

### Table A1.18: Experiment B4
Results of the ultrafiltration of raw VHP sugar at three sugar concentrations under conditions of zero water recovery.
Date = 22/07/1993

<table>
<thead>
<tr>
<th></th>
<th>Low Brix (About 10°Brix)</th>
<th>Medium Brix (About 25°Brix)</th>
<th>High Brix (About 50°Brix)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Brix</td>
<td>Abs</td>
<td>Colour</td>
</tr>
<tr>
<td>Feed</td>
<td>9,2</td>
<td>0,732</td>
<td>7688</td>
</tr>
<tr>
<td>Permeate</td>
<td>8,9</td>
<td>0,356</td>
<td>3870</td>
</tr>
<tr>
<td>Retention (%)</td>
<td>3,3</td>
<td>51,4</td>
<td>49,7</td>
</tr>
</tbody>
</table>
Low Brix = about 10 °brix  Medium brix = about 25 °brix  High brix = about 50 °brix

**Figure A1.26 : Experiment Series B**

Point ICUMSA colour retention, absorbance retention and brix retention values for the ultrafiltration of H1 refined sugar, affinated H1 refined sugar, affination wash liquor and VHP sugar, under conditions of zero water recovery.
Figure A1.27: Experiment Series B

Point permeate flux values for the ultrafiltration of H1 refined sugar, affinated H1 refined sugar, affination wash liquor and VHP sugar, under conditions of zero water recovery.

Low Brix = about 10 °brix  Medium brix = about 25 °brix  High brix = about 50 °brix
A1.4 Experiment Series C: The Ultrafiltration of H1 Refined Sugar and Affinated H1 Refined Sugar Under Conditions of High Water Recovery - using the CeraMem LMDA-20-P1 Membrane Module

A1.4.1 The Aim of Experiment Series C

The aim of Experiment Series C was to assess the ability of the CeraMem LMDA-20-P1 membrane module to retain ICUMSA colour in solutions of H1 refined sugar and affinated H1 refined sugar, under conditions of high water recovery. This was to observe the effect of the increased concentration of the retained high molecular weight solute molecules on the retention characteristics of the membrane.

The procedure for the experiment is described in Appendix A2.6. The refined sugar ultrafiltration rig was used to prevent excessive heating of the sugar solutions. The rig is described in Chapter 3.2.2.

A1.4.2 Experimental Results

<table>
<thead>
<tr>
<th>WR (%)</th>
<th>Time (min)</th>
<th>Flux (L/m²h)</th>
<th>°Brix</th>
<th>Absorbance</th>
<th>ICUMSA Colour</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td>Feed</td>
<td>Perm</td>
<td>Ret (%)</td>
</tr>
<tr>
<td>0.0</td>
<td>0</td>
<td>125</td>
<td>10.4</td>
<td>10.1</td>
<td>2.9</td>
</tr>
<tr>
<td>23.7</td>
<td>33</td>
<td>117</td>
<td>10.5</td>
<td>10.2</td>
<td>2.9</td>
</tr>
<tr>
<td>50.0</td>
<td>72</td>
<td>113</td>
<td>10.7</td>
<td>10.3</td>
<td>3.7</td>
</tr>
<tr>
<td>64.5</td>
<td>95</td>
<td>107</td>
<td>10.7</td>
<td>10.5</td>
<td>1.9</td>
</tr>
<tr>
<td>75.0</td>
<td>112</td>
<td>103</td>
<td>10.9</td>
<td>10.5</td>
<td>3.7</td>
</tr>
<tr>
<td>86.8</td>
<td>132</td>
<td>81</td>
<td>11.2</td>
<td>10.8</td>
<td>3.6</td>
</tr>
</tbody>
</table>

Note: Ret = retention, WR = water recovery, Perm = permeate

Table A1.19: Experiment C1
Point feed and permeate brix, absorbance and ICUMSA colour values as functions of water recovery for the high water recovery ultrafiltration of H1 refined sugar.
Date = 17/08/1993
Table A.1.20: Experiment C1
Composite feed and composite permeate values of brix and ICUMSA colour, as functions of water recovery, for the high water recovery ultrafiltration of H1 refined sugar.
(Mathematically predicted composite feed and composite permeate values, based on zero water recovery retentions, are presented in brackets)
Date = 17/08/1993

<table>
<thead>
<tr>
<th>WR (%)</th>
<th>Time (min)</th>
<th>Flux (dm³/h)</th>
<th>Composite Brix</th>
<th></th>
<th>Composite Colour</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td>Feed Permeate</td>
<td>Feed Permeate</td>
<td></td>
</tr>
<tr>
<td>0,0</td>
<td>0</td>
<td>125</td>
<td>10,4 (10,4)</td>
<td>10,1 (10,1)</td>
<td>61 (61)</td>
</tr>
<tr>
<td>23,7</td>
<td>33</td>
<td>117</td>
<td>10,5 (10,5)</td>
<td>60 (71)</td>
<td>(29)</td>
</tr>
<tr>
<td>50,0</td>
<td>72</td>
<td>113</td>
<td>10,7 (10,6)</td>
<td>10,3 (10,2)</td>
<td>83 (90)</td>
</tr>
<tr>
<td>64,5</td>
<td>95</td>
<td>107</td>
<td>10,7 (10,7)</td>
<td>10,2 (10,2)</td>
<td>108 (108)</td>
</tr>
<tr>
<td>75,0</td>
<td>112</td>
<td>103</td>
<td>10,9 (10,8)</td>
<td>10,3 (10,3)</td>
<td>129 (132)</td>
</tr>
<tr>
<td>86,8</td>
<td>132</td>
<td>81</td>
<td>11,2 (11,0)</td>
<td>10,4 (10,3)</td>
<td>158 (191)</td>
</tr>
</tbody>
</table>
Figure A1.28: Experiment C1

Point feed, point permeate and composite permeate values of brix and ICUMSA colour for the high water recovery ultrafiltration of H1 refined sugar.
Table A1.21 : Experiment C2

Point feed and permeate brix, absorbance and ICUMSA colour values as functions of water recovery for the high water recovery ultrafiltration of affinated H1 refined sugar.

Date = 18/08/1993

<table>
<thead>
<tr>
<th>WR (%)</th>
<th>Time (min)</th>
<th>Flux (l/m²h)</th>
<th>°Brix</th>
<th>Absorbance</th>
<th>ICUMSA Colour</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td>Feed</td>
<td>Perm</td>
<td>Ret (%)</td>
</tr>
<tr>
<td>0,0</td>
<td>0</td>
<td>123</td>
<td>9,8</td>
<td>9,6</td>
<td>2,0</td>
</tr>
<tr>
<td>23,7</td>
<td>35</td>
<td>115</td>
<td>9,9</td>
<td>9,6</td>
<td>3,0</td>
</tr>
<tr>
<td>50,0</td>
<td>75</td>
<td>112</td>
<td>9,9</td>
<td>9,6</td>
<td>3,0</td>
</tr>
<tr>
<td>64,5</td>
<td>98</td>
<td>103</td>
<td>10,0</td>
<td>9,7</td>
<td>3,0</td>
</tr>
<tr>
<td>75,0</td>
<td>117</td>
<td>100</td>
<td>10,2</td>
<td>10,0</td>
<td>2,0</td>
</tr>
<tr>
<td>86,8</td>
<td>135</td>
<td>80</td>
<td>10,5</td>
<td>10,2</td>
<td>2,9</td>
</tr>
</tbody>
</table>

Note : Ret = retention, WR = water recovery, Perm = permeate

Table A1.22 : Experiment C2

Composite feed and composite permeate values of brix and ICUMSA colour, as functions of water recovery, for the high water recovery ultrafiltration of affinated H1 refined sugar.

(Mathematically predicted composite feed and composite permeate values, based on zero water recovery retentions, are presented in brackets)

Date = 18/08/1993

<table>
<thead>
<tr>
<th>WR (%)</th>
<th>Time (min)</th>
<th>Flux (l/m²h)</th>
<th>Composite °Brix</th>
<th>Composite Colour</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td>Feed</td>
<td>Permeate</td>
</tr>
<tr>
<td>0,0</td>
<td>0</td>
<td>123</td>
<td>9,8</td>
<td>(9,8)</td>
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<tr>
<td></td>
<td></td>
<td></td>
<td>39</td>
<td>(40)</td>
</tr>
<tr>
<td>23,7</td>
<td>35</td>
<td>115</td>
<td>9,9</td>
<td>(9,9)</td>
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<tr>
<td></td>
<td></td>
<td></td>
<td>45</td>
<td>(46)</td>
</tr>
<tr>
<td>50,0</td>
<td>75</td>
<td>112</td>
<td>9,9</td>
<td>(9,9)</td>
</tr>
<tr>
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<td></td>
<td></td>
<td>57</td>
<td>(57)</td>
</tr>
<tr>
<td>64,5</td>
<td>98</td>
<td>103</td>
<td>10</td>
<td>(10,0)</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>67</td>
<td>(67)</td>
</tr>
<tr>
<td>75,0</td>
<td>117</td>
<td>100</td>
<td>10,2</td>
<td>(10,1)</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>79</td>
<td>(80)</td>
</tr>
<tr>
<td>86,8</td>
<td>135</td>
<td>80</td>
<td>10,5</td>
<td>(10,2)</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>93</td>
<td>(111)</td>
</tr>
</tbody>
</table>
Figure A1.29: Experiment C2
Point feed, point permeate and composite permeate values of brix and ICUMSA colour for the high water recovery ultrafiltration of affinated H1 refined sugar.
A1.5 Experiment D:
The Ultrafiltration of Johnson Sweetwater Under
Conditions of High Water Recovery using the CeraMem
LMDA-20-P1 Membrane Module

A1.5.1 The Aim of Experiment D

The aim of Experiment D was to assess the ability of the CeraMem LMDA-20-P1 membrane module to retain ICUMSA colour and brix from Johnson sweetwater under conditions of high water recovery.

A1.5.2 Experimental Results

<table>
<thead>
<tr>
<th>WR (%)</th>
<th>Time (min)</th>
<th>Flux (Dm(^{-3})h)</th>
<th>°Brix Feed</th>
<th>Perm</th>
<th>Ret (%)</th>
<th>Absorbance Feed</th>
<th>Perm</th>
<th>Ret (%)</th>
<th>ICUMSA Colour Feed</th>
<th>Perm</th>
<th>Ret (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0,0</td>
<td>0</td>
<td>128</td>
<td>11,3</td>
<td>11,1</td>
<td>1,7</td>
<td>0,341</td>
<td>0,216</td>
<td>36,7</td>
<td>2,892</td>
<td>1,867</td>
<td>35,4</td>
</tr>
<tr>
<td>23,7</td>
<td>40</td>
<td>104</td>
<td>11,4</td>
<td>11,2</td>
<td>1,8</td>
<td>0,368</td>
<td>0,231</td>
<td>37,2</td>
<td>3,092</td>
<td>1,997</td>
<td>35,4</td>
</tr>
<tr>
<td>50,0</td>
<td>90</td>
<td>93</td>
<td>11,7</td>
<td>11,4</td>
<td>2,6</td>
<td>0,434</td>
<td>0,268</td>
<td>38,2</td>
<td>3,549</td>
<td>2,252</td>
<td>36,5</td>
</tr>
<tr>
<td>64,5</td>
<td>112</td>
<td>86</td>
<td>11,8</td>
<td>11,7</td>
<td>1,7</td>
<td>0,442</td>
<td>0,283</td>
<td>35,9</td>
<td>3,582</td>
<td>2,314</td>
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<td>81</td>
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<td>12,3</td>
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<td>0,325</td>
<td>45,7</td>
<td>4,562</td>
<td>2,522</td>
<td>44,7</td>
</tr>
<tr>
<td>82,9</td>
<td>160</td>
<td>60</td>
<td>13,8</td>
<td>13,5</td>
<td>2,2</td>
<td>0,621</td>
<td>0,384</td>
<td>38,2</td>
<td>4,269</td>
<td>2,700</td>
<td>36,7</td>
</tr>
</tbody>
</table>

Note: Ret = retention, WR = water recovery, Perm = permeate
Table A1.24: Experiment D

Composite feed and composite permeate values of brix and ICUMSA colour, as functions of water recovery, for the high water recovery ultrafiltration of Johnson Sweetwater.

(Mathematically predicted composite feed and composite permeate values, based on zero water recovery retentions, are presented in brackets)

Date = 25/09/1993

<table>
<thead>
<tr>
<th>WR (%)</th>
<th>Time (min)</th>
<th>Flux (g/m² h)</th>
<th>Composite °Brix</th>
<th>Composite ICUMSA Colour</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td>Feed</td>
<td>Permeate</td>
</tr>
<tr>
<td>0,0</td>
<td>0</td>
<td>128</td>
<td>11,3 (11,3)</td>
<td>11,1 (11,1)</td>
</tr>
<tr>
<td>23,7</td>
<td>40</td>
<td>104</td>
<td>11,4 (11,4)</td>
<td>(11,1)</td>
</tr>
<tr>
<td>50,0</td>
<td>90</td>
<td>93</td>
<td>11,7 (11,4)</td>
<td>11,2 (11,2)</td>
</tr>
<tr>
<td>64,5</td>
<td>112</td>
<td>86</td>
<td>11,8 (11,5)</td>
<td>(11,2)</td>
</tr>
<tr>
<td>75,0</td>
<td>136</td>
<td>81</td>
<td>12,5 (11,6)</td>
<td>(11,2)</td>
</tr>
<tr>
<td>82,9</td>
<td>160</td>
<td>60</td>
<td>13,8 (11,7)</td>
<td>11,5 (11,2)</td>
</tr>
</tbody>
</table>
Figure A1.30: Experiment D
Point feed, point permeate and composite permeate values of brix and ICUMSA colour for the high water recovery ultrafiltration of Johnson
A1.6 Experiment Series E:
Johnson Sweetwater Feed and Permeate Colour Transfer Analyses

A1.6.1 The Aim of Experiment Series E

The aim of Experiment Series E was to assess the difference in colour transfer, from solution to sugar crystals, for the Johnson sweetwater feed and corresponding ultrafiltration permeate. The colour transfer results were aimed at indicating whether the ultrafiltration of Johnson sweetwater retains those colour molecules which are preferentially included in the final sugar crystal.

The experimental procedure is described in Appendix A2.8.
### A1.6.2 Experimental Results

#### A1.6.2.1 The Collection of Composite Johnson Sweetwater Feed and Corresponding Ultrafiltration Permeate Samples

<table>
<thead>
<tr>
<th>Time (min)</th>
<th>T (°C)</th>
<th>P (kPa)</th>
<th>V (l/min)</th>
<th>u (m/s)</th>
<th>pH</th>
<th>°Brix</th>
<th>Abs</th>
<th>Colour</th>
<th>Flux (l/m²)h</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>74</td>
<td>400</td>
<td>26,8</td>
<td>1,8</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>40</td>
<td>74</td>
<td>400</td>
<td>26,8</td>
<td>1,8</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>200</td>
</tr>
<tr>
<td>60</td>
<td>72</td>
<td>400</td>
<td>26,8</td>
<td>1,8</td>
<td></td>
<td>Feed</td>
<td>7,49</td>
<td>5,4</td>
<td>0,194</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>Permeate</td>
<td>8,09</td>
<td>5,3</td>
<td>0,102</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>Ret (%)</td>
<td>1,0</td>
<td></td>
<td>47,0</td>
</tr>
<tr>
<td>120</td>
<td>72</td>
<td>400</td>
<td>26,8</td>
<td>1,8</td>
<td></td>
<td>Feed</td>
<td>8,37</td>
<td>9,1</td>
<td>0,273</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>Permeate</td>
<td>7,55</td>
<td>8,4</td>
<td>0,230</td>
</tr>
<tr>
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<td></td>
<td>Ret (%)</td>
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<td>15,0</td>
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<tr>
<td>150</td>
<td>72</td>
<td>400</td>
<td>26,8</td>
<td>1,8</td>
<td></td>
<td>Feed</td>
<td>7,75</td>
<td>10,5</td>
<td>0,325</td>
</tr>
<tr>
<td>180</td>
<td>72</td>
<td>400</td>
<td>26,8</td>
<td>1,8</td>
<td></td>
<td>Permeate</td>
<td>8,03</td>
<td>10,5</td>
<td>0,259</td>
</tr>
<tr>
<td></td>
<td></td>
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<td></td>
<td></td>
<td></td>
<td>Ret (%)</td>
<td>0,0</td>
<td></td>
<td>20,0</td>
</tr>
<tr>
<td>260</td>
<td>72</td>
<td>400</td>
<td>26,8</td>
<td>1,8</td>
<td></td>
<td>Feed</td>
<td>8,03</td>
<td>10,5</td>
<td>0,342</td>
</tr>
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<td></td>
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<td></td>
<td>Permeate</td>
<td>7,73</td>
<td>10,1</td>
<td>0,227</td>
</tr>
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<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>Ret (%)</td>
<td>3,0</td>
<td></td>
<td>33,0</td>
</tr>
<tr>
<td>Composite 36 l Samples</td>
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<td></td>
<td></td>
<td></td>
<td></td>
<td>Feed</td>
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<td>9,1</td>
<td>0,274</td>
</tr>
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<td></td>
<td></td>
<td></td>
<td></td>
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<td></td>
<td>Permeate</td>
<td>8,00</td>
<td>8,7</td>
<td>0,172</td>
</tr>
<tr>
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<td></td>
<td></td>
<td></td>
<td>Ret (%)</td>
<td>4,0</td>
<td></td>
<td>37,0</td>
</tr>
</tbody>
</table>

**Note:** Ret = retention, Abs = absorbance
## Table A1.26: Experiment E2

Feed conditions and experimentally determined values of pH, brix, absorbance and ICUMSA colour for the ultrafiltration of Johnson sweet water to collect composite 36ℓ feed and corresponding permeate samples.

**Date = 15/09/1993**

<table>
<thead>
<tr>
<th>Time (min)</th>
<th>T (°C)</th>
<th>P (kPa)</th>
<th>V (ℓ/min)</th>
<th>u (m/s)</th>
<th>pH</th>
<th>°Brix</th>
<th>Abs</th>
<th>Colour</th>
<th>Flux (ℓ/m²h)</th>
</tr>
</thead>
<tbody>
<tr>
<td>5</td>
<td>70</td>
<td>400</td>
<td>27,0</td>
<td>1,9</td>
<td>Feed</td>
<td>7,00</td>
<td>16,1</td>
<td>0,282</td>
<td>1,646</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>Permeate</td>
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<td>15,7</td>
<td>0,218</td>
<td>1,307</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>Ret (%)</td>
<td>2,0</td>
<td>22,0</td>
<td>2,0</td>
<td>2,0</td>
</tr>
<tr>
<td>30</td>
<td>77</td>
<td>400</td>
<td>27,0</td>
<td>1,9</td>
<td>Feed</td>
<td>7,50</td>
<td>12,0</td>
<td>0,260</td>
<td>2,126</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>Permeate</td>
<td>7,55</td>
<td>12,0</td>
<td>0,180</td>
<td>1,449</td>
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<td></td>
<td>Ret (%)</td>
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<tr>
<td>60</td>
<td>80</td>
<td>400</td>
<td>27,0</td>
<td>1,9</td>
<td>Feed</td>
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<td>9,4</td>
<td>0,244</td>
<td>2,506</td>
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<td></td>
<td></td>
<td></td>
<td>Permeate</td>
<td>7,14</td>
<td>9,2</td>
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<td>1,817</td>
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<td></td>
<td></td>
<td></td>
<td>Ret (%)</td>
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<td>29,0</td>
<td>2,0</td>
<td>27,0</td>
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<tr>
<td>90</td>
<td>80</td>
<td>400</td>
<td>26,8</td>
<td>1,8</td>
<td>Feed</td>
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<td>9,3</td>
<td>0,263</td>
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<td></td>
<td>Ret (%)</td>
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<td>20,0</td>
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<td>11,9</td>
<td>0,263</td>
<td>2,210</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>Permeate</td>
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<td>10,9</td>
<td>0,200</td>
<td>1,744</td>
</tr>
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<td></td>
<td></td>
<td></td>
<td>Ret (%)</td>
<td>8,0</td>
<td>24,0</td>
<td>8,0</td>
<td>21,0</td>
</tr>
</tbody>
</table>

**Note:** Ret = retention, Abs = absorbance
Table A1.27: Experiment E3
Feed conditions and experimentally determined values of pH, brix, absorbance and ICUMSA colour for the ultrafiltration of Johnson sweetwater to collect composite 36 € feed and corresponding permeate samples.
Date = 29/09/1993

<table>
<thead>
<tr>
<th>Time (min)</th>
<th>T (°C)</th>
<th>P (kPa)</th>
<th>V (ℓ/min)</th>
<th>u (m/s)</th>
<th>pH</th>
<th>°Brix</th>
<th>Abs</th>
<th>Colour</th>
<th>Flux (ℓ/m³h)</th>
</tr>
</thead>
<tbody>
<tr>
<td>5</td>
<td>75</td>
<td>400</td>
<td>27,0</td>
<td>1,9</td>
<td>Feed 7,60</td>
<td>11,3</td>
<td>0,449</td>
<td>3 773</td>
<td>184</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>Permeate 7,50</td>
<td>10,8</td>
<td>0,302</td>
<td>2 659</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>Ret (%) 4,0</td>
<td>32,0</td>
<td>29,0</td>
<td></td>
<td></td>
</tr>
<tr>
<td>60</td>
<td>75</td>
<td>400</td>
<td>27,0</td>
<td>1,9</td>
<td>Feed 7,70</td>
<td>11,2</td>
<td>0,567</td>
<td>4 808</td>
<td>176</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>Permeate 7,70</td>
<td>10,8</td>
<td>0,377</td>
<td>3 352</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>Ret (%) 3,0</td>
<td>33,0</td>
<td>30,0</td>
<td></td>
<td></td>
</tr>
<tr>
<td>120</td>
<td>75</td>
<td>400</td>
<td>27,0</td>
<td>1,9</td>
<td>Feed 7,60</td>
<td>12,0</td>
<td>0,622</td>
<td>4 910</td>
<td>180</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>Permeate 7,50</td>
<td>11,7</td>
<td>0,421</td>
<td>3 538</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>Ret (%) 2,0</td>
<td>32,0</td>
<td>27,0</td>
<td></td>
<td></td>
</tr>
<tr>
<td>180</td>
<td>75</td>
<td>400</td>
<td>26,8</td>
<td>1,8</td>
<td>Feed 7,40</td>
<td>12,4</td>
<td>0,572</td>
<td>4 401</td>
<td>114</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>Permeate 7,60</td>
<td>11,9</td>
<td>0,434</td>
<td>3 487</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>Ret (%) 4,0</td>
<td>24,0</td>
<td>20,0</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Composite 36 € Samples

|          |        |         |           |         | Feed 7,70 | 11,9 | 0,512 | 4 302 |     |
|          |        |         |           |         | Permeate 7,60 | 10,9 | 0,369 | 3 249 |     |
|          |        |         |           |         | Ret (%) 8,0 | 27,0 | 24,0 |       |     |

Note: Ret = retention, Abs = absorbance
### A1.6.2.2 Brix Mass Balances

#### Table A1.28: Experiment E1
Brix mass balances at various stages of the colour transfer experiment.

<table>
<thead>
<tr>
<th></th>
<th>Feed</th>
<th>Permeate</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mass solution collected</td>
<td>39,6 kg</td>
<td>38,8 kg</td>
</tr>
<tr>
<td>Original 6 brix</td>
<td>9,1</td>
<td>8,7</td>
</tr>
<tr>
<td>Original mass brix</td>
<td>3,6 kg</td>
<td>3,4 kg</td>
</tr>
<tr>
<td>Original mass water</td>
<td>36,0 kg</td>
<td>35,4 kg</td>
</tr>
<tr>
<td>Mass 1* boiling sugar added to solution</td>
<td>18,0 kg</td>
<td>18,0 kg</td>
</tr>
<tr>
<td>Mass brix following sugar addition (brixing)</td>
<td>21,6 kg</td>
<td>21,4 kg</td>
</tr>
<tr>
<td>6 Brix following sugar addition (brixing)</td>
<td>37,5</td>
<td>37,6</td>
</tr>
<tr>
<td>Mass water required to be evaporated to achieve desired brix of 60</td>
<td>21,6 kg</td>
<td>21,2 kg</td>
</tr>
<tr>
<td>Mass concentrate following evaporation</td>
<td>30,0 kg</td>
<td>30,0 kg</td>
</tr>
<tr>
<td>6 Brix concentrate following evaporation</td>
<td>64,0</td>
<td>60,0</td>
</tr>
<tr>
<td>Mass brix following evaporation</td>
<td>19,2 kg</td>
<td>18,0 kg</td>
</tr>
<tr>
<td>Mass water following evaporation</td>
<td>10,8 kg</td>
<td>12,0 kg</td>
</tr>
<tr>
<td>Mass water evaporated</td>
<td>25,2 kg</td>
<td>23,4 kg</td>
</tr>
</tbody>
</table>

#### Table A1.29: Experiment E2
Brix mass balances at various stages of the colour transfer experiment.

<table>
<thead>
<tr>
<th></th>
<th>Feed</th>
<th>Permeate</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mass solution collected</td>
<td>39,4 kg</td>
<td>39,3 kg</td>
</tr>
<tr>
<td>Original 6 brix</td>
<td>11,9</td>
<td>10,9</td>
</tr>
<tr>
<td>Original mass brix</td>
<td>4,7 kg</td>
<td>4,3 kg</td>
</tr>
<tr>
<td>Original mass water</td>
<td>34,7 kg</td>
<td>35,1 kg</td>
</tr>
<tr>
<td>Mass 1* boiling sugar added to solution</td>
<td>12,0 kg</td>
<td>12,0 kg</td>
</tr>
<tr>
<td>Mass brix following sugar addition (brixing)</td>
<td>16,7 kg</td>
<td>16,3 kg</td>
</tr>
<tr>
<td>6 Brix following sugar addition (brixing)</td>
<td>32,5</td>
<td>31,7</td>
</tr>
<tr>
<td>Mass water required to be evaporated to achieve desired brix of 60</td>
<td>23,6 kg</td>
<td>24,2 kg</td>
</tr>
<tr>
<td>Mass concentrate following evaporation</td>
<td>20,6 kg</td>
<td>20,0 kg</td>
</tr>
<tr>
<td>6 Brix concentrate following evaporation</td>
<td>59,0</td>
<td>55,3</td>
</tr>
<tr>
<td>Mass brix following evaporation</td>
<td>12,2 kg</td>
<td>11,1 kg</td>
</tr>
<tr>
<td>Mass water following evaporation</td>
<td>8,4 kg</td>
<td>8,9 kg</td>
</tr>
<tr>
<td>Mass water evaporated</td>
<td>26,3 kg</td>
<td>26,2 kg</td>
</tr>
</tbody>
</table>
### Table A1.30: Experiment E3

**Brix mass balances at various stages of the colour transfer experiment.**

<table>
<thead>
<tr>
<th></th>
<th>Feed</th>
<th>Permeate</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mass solution collected</td>
<td>39.4 kg</td>
<td>39.4 kg</td>
</tr>
<tr>
<td>Original °brix</td>
<td>11.9</td>
<td>10.9</td>
</tr>
<tr>
<td>Original mass brix</td>
<td>4.7 kg</td>
<td>4.3 kg</td>
</tr>
<tr>
<td>Original mass water</td>
<td>34.7 kg</td>
<td>35.1 kg</td>
</tr>
<tr>
<td>Mass 1° boiling sugar added to solution</td>
<td>12.0 kg</td>
<td>12.0 kg</td>
</tr>
<tr>
<td>Mass brix following sugar addition (brixing)</td>
<td>16.7 kg</td>
<td>16.3 kg</td>
</tr>
<tr>
<td>°Brix following sugar addition (brixing)</td>
<td>32.5</td>
<td>31.7</td>
</tr>
<tr>
<td>Mass water required to be evaporated to achieve desired brix of about 60</td>
<td>23.6 kg</td>
<td>24.2 kg</td>
</tr>
<tr>
<td>Mass concentrate following evaporation</td>
<td>23.0 kg</td>
<td>23.0 kg</td>
</tr>
<tr>
<td>°Brix concentrate following evaporation</td>
<td>61.0</td>
<td>61.0</td>
</tr>
<tr>
<td>Mass brix following evaporation</td>
<td>14.0 kg</td>
<td>14.0 kg</td>
</tr>
<tr>
<td>Mass water following evaporation</td>
<td>9.0 kg</td>
<td>9.0 kg</td>
</tr>
<tr>
<td>Mass water evaporated</td>
<td>25.7 kg</td>
<td>26.1 kg</td>
</tr>
</tbody>
</table>

### A1.6.2.3 Solution and Crystal Colour, for the Johnson Sweetwater Feed and Permeate, at Various Stages of the Colour Transfer Experiment

### Table A1.31: Experiment E1

**ICUMSA Colour values of the Johnson sweetwater feed and corresponding ultrafiltration permeate solutions and crystals at various stages of the colour transfer experiment.**

<table>
<thead>
<tr>
<th>Solution Type</th>
<th>Brix</th>
<th>Absorbance</th>
<th>ICUMSA Colour</th>
<th>% Colour Difference</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Feed</td>
<td>Perm</td>
<td>Feed</td>
<td>Perm</td>
</tr>
<tr>
<td>Original solution</td>
<td>9.1</td>
<td>8.7</td>
<td>0.274</td>
<td>0.172</td>
</tr>
<tr>
<td>Post brixing solution</td>
<td>4.0</td>
<td>4.0</td>
<td>0.113</td>
<td>0.069</td>
</tr>
<tr>
<td>Post evaporation solution</td>
<td>6.0</td>
<td>10.0</td>
<td>0.168</td>
<td>0.174</td>
</tr>
<tr>
<td>Pan sugar</td>
<td>30.3</td>
<td>30.3</td>
<td>0.042</td>
<td>0.031</td>
</tr>
<tr>
<td>Affinited pan sugar</td>
<td>30.0</td>
<td>30.2</td>
<td>0.029</td>
<td>0.022</td>
</tr>
<tr>
<td>Brixing sugar</td>
<td>30.1</td>
<td></td>
<td>0.034</td>
<td></td>
</tr>
<tr>
<td>Affinited brixing sugar</td>
<td>30.0</td>
<td></td>
<td>0.022</td>
<td></td>
</tr>
</tbody>
</table>
Table A1.32: Experiment E2
ICUMSA Colour values of the Johnson sweetwater feed and corresponding ultrafiltration permeate solutions and crystals at various stages of the colour transfer experiment.

<table>
<thead>
<tr>
<th>Solution Type</th>
<th>Brix</th>
<th>Absorbance</th>
<th>ICUMSA Colour</th>
<th>% Colour Difference</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Feed Perm</td>
<td>Feed Perm</td>
<td>Feed Perm</td>
<td></td>
</tr>
<tr>
<td>Original solution</td>
<td>11,4 11,0</td>
<td>0,263 0,200</td>
<td>2 210 1 744</td>
<td>21</td>
</tr>
<tr>
<td>Post brixing solution</td>
<td>8,4  9,7</td>
<td>0,271 0,231</td>
<td>626 460</td>
<td>27</td>
</tr>
<tr>
<td>Post evaporation solution</td>
<td>10,4 10,5</td>
<td>0,368 0,286</td>
<td>681 524</td>
<td>23</td>
</tr>
<tr>
<td>Pan sugar</td>
<td>30,8 30,7</td>
<td>0,071 0,049</td>
<td>41 28</td>
<td>32</td>
</tr>
<tr>
<td>Affinated pan sugar</td>
<td>31,1 31,9</td>
<td>0,046 0,034</td>
<td>26 19</td>
<td>27</td>
</tr>
<tr>
<td>Brixing sugar</td>
<td>31,1</td>
<td>0,048</td>
<td></td>
<td>27</td>
</tr>
<tr>
<td>Affinated brixing sugar</td>
<td>31,1</td>
<td>0,027</td>
<td></td>
<td>15</td>
</tr>
</tbody>
</table>

Table A1.33: Experiment E3
ICUMSA Colour values of the Johnson sweetwater feed and corresponding ultrafiltration permeate solutions and crystals at various stages of the colour transfer experiment.

<table>
<thead>
<tr>
<th>Solution Type</th>
<th>Brix</th>
<th>Absorbance</th>
<th>ICUMSA Colour</th>
<th>% Colour Difference</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Feed Perm</td>
<td>Feed Perm</td>
<td>Feed Perm</td>
<td></td>
</tr>
<tr>
<td>Original solution</td>
<td>11,9 10,9</td>
<td>0,512 0,369</td>
<td>4 302 3 249</td>
<td>24</td>
</tr>
<tr>
<td>Post brixing solution</td>
<td>10,7 12,1</td>
<td>0,624 0,513</td>
<td>1 122 811</td>
<td>28</td>
</tr>
<tr>
<td>Post evaporation solution</td>
<td>20,6 21,0</td>
<td>1,256 1,013</td>
<td>1 126 890</td>
<td>21</td>
</tr>
<tr>
<td>Pan sugar</td>
<td>30,8 30,1</td>
<td>0,072 0,050</td>
<td>41 28</td>
<td>32</td>
</tr>
<tr>
<td>Affinated pan sugar</td>
<td>31,1 31,4</td>
<td>0,055 0,049</td>
<td>31 25</td>
<td>19</td>
</tr>
<tr>
<td>Brixing sugar</td>
<td>31,3</td>
<td>0,060</td>
<td></td>
<td>34</td>
</tr>
<tr>
<td>Affinated brixing sugar</td>
<td>31,1</td>
<td>0,027</td>
<td></td>
<td>15</td>
</tr>
</tbody>
</table>

A1.6.2.4 Experiment E4
The Evaporation and Re-crystallisation of a First Boiling Sugar Liquor

Experiment E4 was performed to determine whether the evaporation and boiling of a sugar solution using the SMRI pilot evaporator and crystallisation pan resulted in any significant colour formation.

The procedure involved the dissolving of 16.7 kg first boiling sugar in 34.7 kg water. The mass of sugar and water were the same as those for Experiment E2 and E3. The solution was then evaporated and boiled to produce affinated and unaffinated sugar crystals according to the procedure in Appendix A2.8.2.
The results are presented in Table A1.34.

<table>
<thead>
<tr>
<th>Solution Type</th>
<th>Brix</th>
<th>Absorbance</th>
<th>ICUMSA Colour</th>
</tr>
</thead>
<tbody>
<tr>
<td>Original first boiling sugar solution</td>
<td>30.4</td>
<td>0.031</td>
<td>30</td>
</tr>
<tr>
<td>Affinated first boiling sugar</td>
<td>30.0</td>
<td>0.035</td>
<td>21</td>
</tr>
<tr>
<td>Post evaporation solution</td>
<td>17.4</td>
<td>0.046</td>
<td>147</td>
</tr>
<tr>
<td>Pan sugar</td>
<td>30.0</td>
<td>0.033</td>
<td>20</td>
</tr>
<tr>
<td>Affinated pan sugar</td>
<td>30.2</td>
<td>0.026</td>
<td>15</td>
</tr>
</tbody>
</table>
Appendix 2

Experimental Procedures
A2.1 Procedure for ICUMSA Colour Determination

ICUMSA colour is a measure of the amount of colour contained in a sugar solution. It is determined according to the procedure specified by the International Commission for Uniform Methods of Sugar Analysis (ICUMSA). The procedure is as follows:

(i) For highly coloured solutions such as Johnson sweetwater, a filter pad made up of 4 g Kieselguhr on Whatman No. 5 paper was prepared in a 60 mm diameter Buchner funnel. The solution was then filtered through this, under vacuum, and collected in a Buchner flask.

For refined sugar colour determination, the crystals were first dissolved in de-ionised water to form a sugar solution of concentration between 30 and 50 °brix. This solution was then filtered through a 0.45 μm membrane.

(ii) The filtered solution was transferred to a 50 mL beaker and placed on a magnetic stirrer.

(iii) The pH value of the solution was measured using a pH meter. The solution pH was then adjusted to a value of 7.00 using hydrochloric acid or sodium hydroxide, depending on its original pH.

(iv) The refractometer brix was measured and the corresponding concentration of total solids (g/cm³) was looked up in tables in SASTA [1985]. The refractometer is described in Section 3.5.2.

(v) The absorbance of the solution was measured, using a spectrophotometer, at a wavelength of 420 nm. The spectrophotometer is described in Section 3.5.1.

(vi) The ICUMSA colour of the solution was then calculated according to equation A2.1:

\[
\text{ICUMSA Colour} = \frac{\text{Absorbance (at 420 nm)} \times 10000}{\text{Concentration Total Solids (g/cm}^3\text{)} \times \text{Cell Length (mm)}}
\]  

(A2.1)

A2.2 Procedure for the Determination of Membrane Pure Water Permeability

The aim of determining the pure water permeability (PWP) of a particular membrane was to be able to assess the degree of fouling of that membrane, following its exposure to a sugar solution, relative to its original PWP when first purchased. The original pure water permeability values of the new membranes were determined prior to exposing them to any sugar solution or process fluid.
Following exposure to sugar solutions, the PWP of a particular membrane was measured and compared with its original PWP. The difference between the value of the PWP of a particular membrane and its original PWP is a measure of the degree of fouling of that membrane.

A2.2.1 Stepwise Experimental Procedure

(i) The membrane module was installed in the membrane cleaning rig (Figure A2.1). The membrane cleaning rig is described in Section 3.2.1.

(ii) The feed tank was filled with reverse osmosis permeate water which was then heated to and maintained at 40 °C for all pure water permeability determinations. A Eurotherm controller was used to control the temperature by switching on and off, a 2 kW feed tank immersion heater in the feed tank.

(iii) The pump was switched on and the control valves in the bypass and retentate return lines were adjusted to achieve a linear flow rate of 1.5 m/s through the membrane module, at the desired
trans-membrane pressure. The rig was run under conditions of zero water recovery, with the permeate and retentate being returned to the feed tank.

(iv) The rate of flow of permeate through the membrane was measured, using a measuring cylinder and stopwatch, at the permeate sample port. The permeate flux rate was determined by dividing the permeate flow rate by the particular membrane surface area. This constitutes the pure water permeability of the membrane at the particular operating conditions.

(v) Pure water permeabilities were determined at 300, 400 and 500 kPa.

A2.3 Membrane Cleaning Procedures

A2.3.1 The CeraMem Membrane Modules

(i) The particular CeraMem membrane module was installed in the membrane cleaning rig (Figure A2.1) and the system thoroughly flushed with reverse osmosis permeate water and drained. The membrane cleaning rig is described in Section 3.2.1.

(ii) Membrane pure water permeability was determined according to the procedure in Appendix A2.2..

(iii) A cleaning solution consisting of 500 mg/l sodium hypochlorite (14.3 m/l household bleach with 3.5 % (m/m) chloride) and 5 m/l hydrogen peroxide (40 % v/v), dissolved in reverse osmosis permeate water, was prepared in the feed tank.

(iv) The cleaning solution was heated to and maintained at 70 °C using the feed tank immersion heater and Eurotherm temperature controller arrangement.

(v) Following heating, the solution was circulated at 9 l/min (0.6 m/s) at a trans-membrane pressure below 50 kPa. To avoid permanent back-pressurisation at the downstream end of the membrane module, the permeate valve was kept open during cleaning.

(vi) The rig was run under zero water recovery conditions with the permeate and retentate being returned to the feed tank.

(vii) The cleaning time was dependent on the nature of the foulants and the extent of the membrane fouling.
(viii) The cleaning solution was drained from the system and the membrane module allowed to cool down to room temperature.

(ix) Following cooling, the system was flushed using reverse osmosis permeate water to remove any residual cleaning solution.

(x) Membrane pure water permeability was determined, according to the procedure in Appendix A2.2, to assess the effectiveness of the clean for the restoration of original membrane pure water permeability.

(xi) The above procedure was repeated until original pure water permeability of the membrane had been restored.

### A2.3.2 The Membralox Membrane Module

(i) The Membralox membrane module was installed in the membrane cleaning rig (Figure A2.1) and the system flushed thoroughly with reverse osmosis permeate water and drained. The membrane cleaning rig is described in Section 3.2.1.

(ii) Membrane pure water permeability was determined according to the procedure in Appendix A2.2.

(iii) The cleaning rig was run with a 20 g/l sodium hydroxide and 10 m/dl hydrogen peroxide (40 % v/v) solution. The system temperature was maintained at 70 °C using the 2 kW feed tank heater and Eurotherm temperature controller. Trans-membrane pressure was kept below 50 kPa.

(iv) The system was run under zero water recovery conditions with the permeate and retentate being returned to the feed tank.

(v) Following the clean, the system was allowed to cool to room temperature before being flushed with reverse osmosis permeate water. Membrane pure water permeability was determined according to the procedure in Appendix A2.2.

(vi) The rig was then cleaned using a 2 % (v/v) nitric acid solution (36.4 m/dl of 55 % (v/v) nitric acid), at 70 °C.

(vii) Following the clean, the membrane was allowed to cool down to room temperature. The system was then flushed with reverse osmosis permeate water and pure water permeability determined according to the procedure in Appendix A2.2.
(viii) The cleaning times for the above two solutions were dependent on the nature of the foulants and the extent of the membrane fouling.

(ix) The above procedure was repeated until the original pure water permeability had been restored.

A2.3.3 The Carbosep Membrane Module

The procedure for cleaning the Carbosep membrane module was the same as that for the Membralox membrane module (Appendix A2.3.2).

A2.4 Experiment Series A:
The Ultrafiltration of Johnson Sweetwater

A2.4.1 The Aim of Experiment Series A

The aim of Experiment Series A was to assess the ability of the various inorganic membranes, listed below, to retain colour in Johnson sweetwater. The membranes used were the CeraMem LMDA-20-P1, CeraMem LMA-0005-P, Membralox 1P19-40 (20 nm nominal pore size) and the M5 Micro-Carbosep 60 (10 000 dalton cut-off) modules.

The series of experiments were performed using the refinery ultrafiltration rig (Figure A2.2) which is described in Section 3.2.3.
A2.4.2 Stepwise Experimental Procedure

Figure A2.2: Flow diagram of the refinery ultrafiltration rig.

(i) The particular membrane module was heated to about 75 °C in a controlled hot water bath. This was to prevent thermal shock on exposure of the membrane module to the hot Johnson sweetwater, which is characteristically at a temperature between 70 and 80 °C.

(ii) The hot module was then installed in the refinery ultrafiltration rig (Figure A2.2). The rig is described in Section 3.2.3.

(iii) The membrane isolation valve was closed and the sweetwater purge valve opened. The ultrafiltration-rig booster pump was switched on and any residual Johnson sweetwater in the system purged to the sump - thereby bypassing the membrane module.

(iv) Once the temperature of the system became steady, the membrane isolation valve was opened and the purge valve closed allowing flow through the membrane module. The permeate valve was opened to allow permeate to flow to the sump.

(v) The back pressure valve was adjusted to achieve the desired trans-membrane pressure.
(vi) Feed and permeate samples were taken periodically from the feed and permeate sample ports. Permeate flux was determined by measuring the rate of flow of permeate using a measuring cylinder and a stopwatch. The feed flow rate was determined using a 25 l bucket and stopwatch.

(vii) The samples were then analysed for brix and ICUMSA colour.

(viii) Brix and ICUMSA colour retention values were calculated from the above data.

(ix) Following the experimental run, the membrane module was removed from the refinery ultrafiltration rig and installed in the membrane cleaning rig (Section 3.2.1). Membrane pure water permeability was determined according to the procedure in Appendix A2.2.

(x) The particular membrane module was cleaned according to the procedure in Appendix A2.3.

A2.5 Experiment Series B: 
The Ultrafiltration of H1 Refined Sugar, Affinated H1 Refined Sugar, Affination Wash Liquor and Raw VHP Sugar - using the CeraMem LMDA-20-P1 Membrane Module

A2.5.1 The Aim of Experiment Series B

The aim of Experiment Series B was to assess the ability of the CeraMem LMDA-20-P1 ultrafiltration membrane to retain colour in solutions of H1 refined sugar, affinated H1 refined sugar, affination wash liquor and VHP sugar.

The above sugars are described in Section 4.5.2.

The series of experiments were performed using the refined sugar ultrafiltration rig (Figure A2.3).
A2.5.2 Stepwise Experimental Procedure

(i) The CeraMem LMDA-20-P1 membrane module was installed in the refined sugar ultrafiltration rig (Figure A2.3) described in Section 3.2.2.

(ii) The refined sugar ultrafiltration rig was cleaned using a solution of 2 % (v/v) nitric acid in reverse osmosis permeate water, followed by a mixture of 500 mg/l sodium hypochlorite and 5 ml/l hydrogen peroxide (40 % v/v) in reverse osmosis permeate water. The membrane module was bypassed during the rig cleaning operation due to its sensitivity to acid conditions.

Following each chemical clean, the rig was rinsed thoroughly with reverse osmosis permeate water. A background colour reading was taken by measuring the absorbance of the reverse osmosis permeate water in the system after running for a sufficient period of time (about 15 min). The background colour following each clean was found to be negligible (less than 0.002 absorbance units).

Figure A2.3: Flow diagram of the refined sugar ultrafiltration rig.
Care was taken to ensure that neutral to slightly alkaline conditions prevailed in the rig prior to exposing the acid sensitive CeraMem ceramic membrane to the sugar solutions.

(iii) A volume of 10 ℓ reverse osmosis permeate water was added to the feed tank and heated to 40 °C using a stainless steel heating coil connected to a hot water tank. Temperature was maintained by switching on and off, the pump in the hot water circuit. The hot water tank was maintained at 60 °C using a 2 kW immersion heater and Eurotherm temperature controller.

(iv) Once the feed water had reached 40 °C, membrane pure water permeability was determined according to the procedure in Appendix A2.2.

(v) With the pump off, the required mass of sugar was added to the feed tank and allowed to dissolve. The sugar solutions are described in Section 4.5.2. The required sugar masses for the selected concentrations are listed in (viii) below. The pump was then started and the control valves, in the bypass and retentate return lines, adjusted to give the following operating conditions:

- Feed temperature: 40 °C
- Trans-membrane pressure: 400 kPa
- Feed volumetric flow rate: 21 ℓ/min
- Feed linear flow rate: 1.5 m/s

The rig was run under zero water recovery conditions with the permeate and retentate being returned to the feed tank.

(vi) The sugar solution was circulated for 30 min whereafter point feed and permeate samples were taken for brix and ICUMSA colour analysis. A permeate flux reading was also taken using a measuring cylinder and a stopwatch.

(vii) The pump was switched off and an additional mass of the same sugar added to the feed tank to increase feed concentration to the next desired brix value. The sugar was allowed to dissolve in the feed tank prior to being pumped through the membrane system following (iv), (v) and (vi) above.

(viii) The above procedure was duplicated for the three sugar concentrations below:

- Low concentration (about 10 °brix): Mass sugar = 1 110 g, Volume water = about 10 ℓ
- Medium concentration (about 25 °brix): Mass sugar = 3 333 g
High concentration (about 50 °brix)

\[
\begin{align*}
\text{Volume water} & = \text{about 10 } \ell \\
\text{Mass sugar} & = 10000 \text{ g} \\
\text{Volume water} & = \text{about 10 } \ell 
\end{align*}
\]

(ix) Following the final experimental run at high concentration, the solution was drained and the system rinsed using reverse osmosis permeate water.

(x) Membrane pure water permeability was determined according to the procedure in Appendix A2.2.

(xi) The feed and permeate samples were analysed for brix and ICUMSA colour.

(xii) The fouled CeraMem LMDA-20-P1 membrane was cleaned according to the procedure in Appendix A2.3.1.

(xiii) The above experimental procedure was followed for the experiments on H1 refined sugar, affinated H1 refined sugar, affination wash liquor and raw VHP sugar.

The only exception was in the case of the affination wash liquor. Being a liquid, the concentrated affination wash liquor had to be added to the feed tank in specific volumes to bring the feed solution to the desired concentration (brix). There was only sufficient affination wash liquor to perform runs at low and medium concentrations.

A2.6 Experiment Series C:
The Ultrafiltration of H1 Refined Sugar and Affinated H1 Refined Sugar Under Conditions of High Water Recovery - using the CeraMem LMDA-20-P1 Membrane Module

A2.6.1 The Aim of Experiment Series C

The aim of Experiment Series C was to assess the ability of the CeraMem LMDA-20-P1 membrane module to retain ICUMSA colour and brix in solutions of H1 refined sugar and affinated H1 refined sugar, under conditions of high water recovery. This was to observe the effect of the increased concentration of the retained high molecular weight solute molecules on the retention characteristics of the membrane.

The sugar solutions are described in Section 4.5.2.
A2.6.2 Stepwise Experimental Procedure

(i) The CeraMem LMDA-20-P1 membrane module was installed in the refined sugar ultrafiltration rig (Figure A2.3) described in Section 3.2.2.

(ii) The refined sugar ultrafiltration rig was cleaned using a solution of 2% (v/v) nitric acid in reverse osmosis permeate water, followed by a mixture of 500 mg/l sodium hypochlorite and 5 ml/l hydrogen peroxide (40% v/v) in reverse osmosis permeate water. The membrane module was bypassed during the rig cleaning operation due to its sensitivity to acid conditions.

Following each chemical clean, the rig was rinsed thoroughly with reverse osmosis permeate water. A background colour reading was taken by measuring the absorbance of the reverse osmosis permeate water in the system after running for a sufficient period of time (about 15 min). The background colour following each clean was found to be negligible (less than 0.002 absorbance units).

Care was taken to ensure that neutral to slightly alkaline conditions prevailed in the rig prior to exposing the acid sensitive CeraMem ceramic membrane to the sugar solutions.

(iii) A volume of 38 l reverse osmosis permeate water was added to the feed tank and heated to 40 °C using a stainless steel heating coil connected to a hot water tank. The temperature was controlled by switching on and off, the pump in the hot water circuit. The hot water tank was maintained at 60 °C using a 2 kW immersion heater and Eurotherm temperature controller.

(iv) Once the feed water had reached 40 °C, membrane pure water permeability was determined according to the procedure in Appendix A2.2.

(v) With the pump off, 4 500 g of the particular sugar was added to the feed tank and allowed to dissove. The pump was then started and the control valves, in the bypass and retentate return lines, adjusted to give the following operating conditions:

| Feed temperature | 40 °C |
| Trans-membrane pressure | 400 kPa |
| Feed volumetric flow rate | 21 l/min |
| Feed linear flow rate | 1.5 m/s |

(vi) The sugar solution was circulated for 30 min at zero water recovery, with the permeate and retentate being returned to the feed tank. This was to allow a state of equilibrium to be achieved...
at the above operating conditions. Permeate flux readings were taken periodically to observe the state of the membrane system.

(vii) Once the membrane had attained equilibrium (after 30 min), the permeate flow was directed to a separate permeate collection tank to allow the retained species to concentrate and so that composite permeate samples could be taken for brix and ICUMSA colour analysis.

(viii) Point feed and permeate samples were taken at water recovery values of 0; 23,7; 50,0; 64,5; 75,0 and 86,8 %. These values corresponded to permeate volumes of 0,0; 9,0; 19,0; 24,5; 28,5; and 33,0 l respectively. Permeate flux readings were also taken by measuring the rate of flow of permeate using a measuring cylinder and a stopwatch.

(ix) Composite permeate samples were taken at water recoveries of 50 % (19 l) and 86,8 % (33 l).

(x) After attaining the maximum water recovery (86,8 %), the solution was drained and the system flushed using reverse osmosis permeate water.

(xi) Membrane pure water permeability was determined according to the procedure in Appendix A2.2.

(xii) The point feed, point permeate and composite permeate samples were analysed for brix and ICUMSA colour.

(xiii) The fouled membrane was cleaned according to the procedure in Appendix A2.3.1.

(xiv) The above experimental procedure was followed for the H1 refined sugar ultrafiltration run and for the affinated H1 refined sugar ultrafiltration run.

A2.7 Experiment D:
The Ultrafiltration of Johnson Sweetwater Under Conditions of High Water Recovery - using the CeraMem LMDA-20-P1 Membrane Module

A2.7.1 The Aim of Experiment D

The aim of Experiment D was to assess the ability of the CeraMem LMDA-20-P1 membrane to retain ICUMSA colour and brix in Johnson sweetwater under conditions of high water recovery.
A2.7.2 Stepwise Experimental Procedure

(i) The CeraMem LMDA-20-P1 membrane module was installed in the refined sugar ultrafiltration rig (Figure A2.3) described in Section 3.2.2.

(ii) The ultrafiltration rig was cleaned using a solution of 2% (v/v) nitric acid in reverse osmosis permeate water, followed by a mixture of 500 mg/L sodium hypochlorite and 5 mg/L hydrogen peroxide (40% v/v) in reverse osmosis permeate water. The membrane module was bypassed during the rig cleaning operation due to its sensitivity to acid conditions.

Following each chemical clean, the rig was rinsed thoroughly with reverse osmosis permeate water. A background colour reading was taken by measuring the absorbance of the reverse osmosis permeate water in the system after running for a sufficient period of time (about 15 min). The background colour following each clean was found to be negligible (less than 0.002 absorbance units).

Care was taken to ensure that neutral to slightly alkaline conditions prevailed in the rig prior to exposing the acid sensitive CeraMem ceramic membrane to the Johnson sweetwater solution.

(iii) Membrane pure water permeability was determined according to the procedure in Appendix A2.2.

(iv) A volume of 38 l hot Johnson sweetwater was added to the feed tank and maintained at 75 °C using a stainless steel heating coil connected to a hot water tank. Temperature was controlled by switching on and off, a pump in the hot water circuit. The hot water tank was maintained at 90 °C using a 2 kW immersion heater and Eurotherm temperature controller.

(v) The pump was started and the control valves, in the bypass and retentate return lines, adjusted to give the following operating conditions:

- Feed temperature : 75 °C
- Trans-membrane pressure : 400 kPa
- Feed volumetric flow rate : 21 l/min
- Feed linear flow rate : 1.5 m/s

(vi) The Johnson sweetwater was circulated for 30 min at zero water recovery, with the permeate and retentate being returned to the feed tank. This was to allow a state of equilibrium to be achieved.
at the above operating conditions. Permeate flux readings were taken periodically to observe the state of the membrane system.

(vii) Once the membrane had attained equilibrium (after 30 min), the permeate flow was directed to a separate permeate collection tank to allow the retained species to concentrate and so that composite permeate samples could be taken for brix and ICUMSA colour analysis.

(viii) Point feed and permeate samples were taken at water recovery values of 0; 23.7; 50.0; 64.5; 75.0 and 82.9 %. These values corresponded to permeate volumes of 0.0; 9.0; 19.0; 24.5; 28.5; and 31.5 ℓ respectively. Permeate flux readings were also taken by measuring the rate of flow of permeate using a measuring cylinder and a stopwatch.

(ix) Composite permeate samples were taken at water recoveries of 50 % (19 ℓ) and 82.9 % (31.5 ℓ).

(x) After attaining the maximum water recovery (82.9 %), the Johnson sweetwater was drained and the system flushed using reverse osmosis permeate water.

(xi) Membrane pure water permeability was determined according to the procedure in Appendix A2.2.

(xii) The point feed, point permeate and composite permeate samples were analysed for brix and ICUMSA colour.

(xiii) The fouled membrane was cleaned according to the procedure in Appendix A2.3.1.

A2.8 Experiment Series E: Johnson Sweetwater Feed and Permeate Colour Transfer Analyses

A2.8.1 The Aim of Experiment Series E

The aim of Experiment Series E was to assess the difference in colour transfer, from solution to sugar crystals, for the Johnson sweetwater feed and corresponding ultrafiltration permeate. The colour transfer results were aimed at indicating whether the ultrafiltration of Johnson sweetwater retains those colour molecules which are preferentially included in the final sugar crystal.
A2.8.2 Stepwise Experimental Procedure

(i) The CeraMem LMDA-20-P1 membrane module was heated to about 75 °C in a controlled hot water bath. This was to prevent thermal shock on exposure of the membrane module to the hot Johnson sweetwater feed, which is characteristically at a temperature between 70 and 80 °C.

(ii) The hot module was then installed in the refinery ultrafiltration rig, described in Section 3.2.3.

(iii) The membrane isolation valve was closed and the sweetwater purge valve opened. The ultrafiltration-rig booster pump was switched on and any residual Johnson sweetwater in the system purged to the sump - bypassing the membrane module.

(iv) Once the temperature of the system became steady, the membrane isolation valve was opened and the purge valve closed allowing flow through the membrane module. The permeate valve was opened to allow permeate to flow to the sump.

(v) The back pressure valve was adjusted to achieve the desired trans-membrane pressure of 400 kPa.

(vi) The system was left to run for 15 min with permeate being directed to the sump. This was to allow a state of equilibrium to be achieved.

(vii) Following this, the continuous collection of feed and permeate samples was commenced.

(viii) The continuous feed sample port used to collect feed at the same rate as the permeate. The permeate flow rate from the permeate sample port was measured periodically and the control valve in the continuous feed sample port adjusted manually to achieve an equivalent feed flow rate. Feed and permeate solutions were collected continuously and at the same rate to ensure that the samples were representative. This was necessary due to the varying nature of the Johnson sweetwater feed.

(ix) Batches of 36 l of Johnson sweetwater feed and ultrafiltration permeate were collected for subsequent brixing, pilot evaporation, pilot-pan boiling and crystal colour analysis at the SMRI.

(x) The composite feed and permeate samples were analysed for brix and ICUMSA colour to determine the required quantity of brixing sugar for the particular experiment.

(xi) The two samples were brixed up (concentrated) by the addition of equivalent amounts of first boiling sugar from Hulett Refineries. First boiling sugar comprises sugar from the first crop of
crystals produced in the refinery pans and represents the purest sugar produced by the refinery. The solution and brixing sugar were thoroughly mixed to ensure that all the sugar had dissolved prior to the sample being stored in a cold room, below 4 °C, in preparation for pilot evaporation.

For a full boiling, 18 kg sugar was added to the feed and permeate Johnson sweetwater solutions, while for a half boiling 12 kg sugar was added.

(xii) A sample of the concentrated solution was taken prior to evaporation.

(xiii) The respective Johnson sweetwater feed or ultrafiltration permeate solution was then heated to about 70 °C, in the SMRI pilot-clarifier tank, using steam coils (steam pressure = 0.4 MPa(g)). It was then transferred to the evaporator feed tank.

(xiv) The evaporator was run until the required mass of water, to produce a concentrate brix of about 60, had been evaporated from the feed solution and collected in the two condensate collection tanks. The evaporation procedure is described in Appendix A2.8.3.

(xv) The concentrated solution was transferred from the evaporator syrup receiver tank to a sealed container and stored in a cold room overnight (below 4 °C).

(xvi) The solution was preheated to 60 °C, using a small immersion heater, prior to being boiled in the pilot crystallisation pan. The boiling procedure is described in Appendix A2.8.4.

(xvii) Following boiling, the massecuite was struck from the pan and centrifuged, without cooling, in a Martin Christ laboratory centrifuge to separate the crystals from the molasses. The crystals were then washed using an equal mass of saturated H1 sugar solution, centrifuged to separate the washed crystals and allowed to dry.

(xviii) A portion of the sugar was affinated according to the ICUMSA (International Commission for Uniform Methods of Sugar Analysis) cane sugar method:

A sample of 300 g of the pilot-pan sugar crystals was mixed with 600 g saturated H1 refined sugar solution. The magma was stirred for 15 min whereafter it was filtered, under a vacuum, through a sintered glass funnel. The crystals were then added to 300 g saturated H1 refined sugar solution, mixed and filtered as above. Following this, the crystals were mixed with 600 ml of a 95 % (v/v) methanol solution which was saturated with H1 sugar. This was mixed and filtered to separate the crystals. The crystals were then mixed with 300 ml of a 100 % (v/v) methanol solution which was saturated with H1 sugar. The mixture was stirred and filtered using a sintered glass funnel to recover the affinated sugar crystals.
This affination step was important due to the fact that the mother-liquor is much more highly coloured than the crystal. Thus small amounts of mother-liquor left on the crystal could cause large errors in colour analysis.

(xix) The sugar crystals were analysed for sugar colour and affinated sugar colour (crystal colour) respectively according to the procedure in Appendix A2.1.

A2.8.3 Procedure for the Operation of the SMRI Pilot Evaporator

The evaporator is described in Section 3.3.

(i) The Johnson sweetwater feed or ultrafiltration permeate solution was heated to about 70 °C in the clarifier vessel using steam coils (steam pressure was 0.4 MPa) prior to being transferred to the evaporator feed tank.

(ii) The evaporator first effect feed valve and second effect feed valve were closed prior to switching on the vacuum pump.
(iii) The vacuum in the first effect vessel was allowed to reach 50 kPa prior to opening the first effect feed valve and turning on the level controller allowing feed solution to begin filling the evaporator calandria.

(iv) Once the feed solution had reached the required level in the glass column, the four heating elements were switched on and the first effect feed valve closed.

(v) Following the onset of boiling, the second effect feed valve was opened slightly to allow solution to enter the second effect evaporator tubes.

(vi) The first effect feed valve was opened and adjusted to maintain a constant desired level in the glass column. Care was taken to prevent boiling level becoming too high and causing liquid entrainment in the vapour outlet.

(vii) The flow rate to the second effect was controlled, using the second effect feed valve, to prevent boiling above the vertical tubes. This was to avoid entrainment and liquid carry-over to the separator. The boiling was observed in the sight glass viewing mirror at the top of the stainless steel vessel.

(viii) Once evaporator feed was exhausted, the first effect feed valve was closed and the heaters and level controller switched off. Boiling was allowed to cease prior to releasing the vacuum.

(ix) The vacuum collection tanks were disconnected and drained. The amount of water collected in the two condensate tanks was measured and recorded. The concentrate from the syrup receiver tank was transferred to a scaled container, weighed and stored in a cold storage room. A concentrate sample was taken for brix and ICUMSA colour analysis.

(x) To clean the evaporator, both calandria vessels were drained and the system run, according to the above procedure, using water as the feed.
A2.8.4 Procedure for the Operation of the SMRI Pilot Crystallisation Pan

Figure A2.5: Flow diagram of the SMRI pilot crystallisation pan.

(i) The cooling water to the condenser was turned on and the vacuum pump started.

(ii) The pan was fed with an initial batch of 10.5 kg feed solution by drawing it up under vacuum. This was sufficient to just cover the heating element.

(iii) The pan heater and stirrer were both switched on, as well as the heater for the water used in the boiling point elevation measurement.

(iv) The remainder of the feed solution was maintained at 60 °C, in a bucket, using an immersion heater and stirrer.
(v) The solution in the pan was allowed to boil, with the variables being monitored on the computer, until the boiling point elevation value reached 8.0 °C.

(vi) The pan was then seeded with 750 g of H11 superfine sugar crystals from Hulett Refineries. H11 superfine crystals have a size distribution between 150 and 355 μm. The H11 sugar was sieved through a 350 μm sieve and collected on a 125 μm sieve prior to seeding.

(vii) Following seeding, the feed valve was opened and the feed flow rate adjusted to maintain the conductivity reading on the computer at about 40 (units are arbitrary).

(viii) Once all the feed solution had been fed into the pan, the feed valve was closed and the massecuite allowed to brix up.

(ix) When the torque reading on the computer reached a value between 160 and 170 (units are arbitrary), the pan was shut down and the massecuite struck from the vessel.

(x) The crystals were separated from the massecuite in a Martin Christ laboratory centrifuge. The sugar crystals were removed from the basket and mixed with an equivalent mass of saturated H1 refined sugar solution to form a magma. The magma was mixed by hand before being centrifuged again to remove the washed crystals. These were then allowed to air dry on a clean sheet of paper.

A2.9 The formation of a Dynamic, Dual-layer, Hydrous Zirconium(iv)oxide/Polyacrylic-acid Membrane on the 0.02 μm Membralox Membrane Module

The procedure for the formation of the dynamic membrane was obtained from the report by Cawdron and Neytzel-de Wilde [1986].

A2.9.1 Preparation of Zirconium(iv)nitrato from Zirconyl Carbonate

(i) A mass of 65 g (or 43 mL) fuming nitric acid (95 %) was mixed with 6 mL distilled water.

(ii) A mass of 123 g zirconyl carbonate was then added to the nitric acid with vigorous stirring.

(iii) If necessary (due to suspended undissolved matter), the solution may be filter through a glass fibre filter while still hot.

The solution was then diluted to a 10 % zirconium(iv)nitrato solution assuming that all of the
zirconyl carbonate had dissolved. This is not analytically correct, but for the purpose of generating a dynamic membrane was adequate.

The correct analytical method for the synthesis of chemically pure zirconium nitrate is continued below.

(iv) The solution should be allowed to cool and crystallise over two days. Stirring, to induce complete crystallisation, is required on the third day.

(v) After the mass appears to have "set", stir thoroughly and filter through a glass fibre filter. Apply vacuum until the mass on the filter appears dry.

(vi) The zirconium content of the zirconium(IV)nitrate prepared by the above procedure will be about 22 % (m/m) on a wet basis.

A2.9.1.1 Analysis of the Zirconium(IV)nitrate Solution

(i) Excess ammonium chloride was added to a sample of zirconium(IV)nitrate and the solution stirred.

(ii) The resulting zirconium chloride precipitate was filtered off and washed with de-ionised water.

(iii) The precipitate was calcined in a furnace at a temperature of 900 °C. The zirconium chloride was converted to zirconium oxide.

(iv) The zirconium oxide product was weighed.

(v) The zirconium content in the zirconium(IV)nitrate solution was determined by the following method:

\[
\text{Molar mass zirconium oxide} = 123.22 \text{ g/mol} \\
\text{Molar mass zirconium} = 91.22 \text{ g/mol} \\
\text{Mass zirconium in zirconium(IV)nitrate} = \frac{91.22}{123.22} \times \text{mass zirconium oxide}
\]
A2.9.2  Stepwise Procedure

(i)  A solution containing 0.05% sodium nitrate (4 250 mg/l sodium nitrate) in 20 l reverse osmosis permeate water, was prepared in the membrane cleaning rig feed tank. The membrane cleaning rig is described in Section 3.2.1. The function of the sodium nitrate was purely to measure retention based on differences in feed and permeate conductivity.

(ii) The pH value of the above solution was reduced to to 4.0 using nitric acid.

(iii) A 50 ml volume of 10% zirconium(iv)nitrate solution was added to the feed water (pH dropped to a value of about 2.7).

(iv) The pH value was then adjusted to 3.2 using sodium hydroxide (1 M).

(v) The solution was circulated for 1 h at ambient temperature and at trans-membrane pressure of 500 kPa. Permeate and retentate were returned to the feed tank.

(vi) As the hydrous oxide deposited on the membrane surface, the flux decreased and the sodium nitrate retention (based on conductivity) increased.

(vii) Once the desired sodium nitrate retention value was reached, the excess zirconium was flushed from the system using reverse osmosis permeate water adjusted to a pH value of 4.0.

(viii) Following this, a solution containing 5 to 10 ml Acrysol A3 (manufactured by Supacryl) and 4 250 mg/l sodium nitrate in 20 l reverse osmosis permeate water was prepared at a pH value of 4.0.

(ix) The pH value of the solution was adjusted to 2.0 using nitric acid.

(x) This solution was circulated for 30 min at ambient temperature and a trans-membrane pressure of 500 kPa.

(xi) Every 30 min the pH value of the solution was raised, using potassium hydroxide, by 1 unit until a pH value of 7.0 was reached.

(xii) During this period, flux decreased and the sodium nitrate retention (based on conductivity) increased.

(xiii) The procedure was complete when sodium nitrate retention ceased to increase.
Appendix 3

Ceramic Membrane Specifications
Supplied by the Membrane Manufacturers
A3.1 CeraMem® Separations:
Membrane Specifications for the Series LM
Laboratory-scale Membrane Modules

CeraMem's approach to the manufacture of ceramic membrane modules involves the application of specific microfiltration and ultrafiltration membranes to high surface area honeycomb monolith structures. These ceramic honeycomb monoliths are produced in high quantities by Corning Inc. and others, to serve the high volume automotive catalytic converter market. CeraMem take advantage of a relatively inexpensive membrane support material which has the added benefit of providing high membrane surface area in a compact design.

The series LM membrane modules are laboratory-scale, cross-flow, ceramic membrane products which combine the advantages of thermal, chemical and structural durability with a compact and economical design. These compact, 33 mm (1.3 in) diameter by 330 mm (13 in) length, membrane modules are ideally suited for laboratory evaluations or small process flows. CeraMem Separations offer membrane modules containing 2 mm or 4 mm feed channels to accommodate a variety of process or effluent streams.

The series LMA and LMDA modules each contain sixty 2 mm feed channels, having a total membrane surface area of 0.1584 m², whereas the Series LMC modules contain twelve 4 mm feed channels and have a total membrane surface area of 0.065 m². Membranes are available in a range of standard microfiltration and ultrafiltration modules with pore sizes ranging from 0.005 to 0.5 μm. The most recently developed membrane modules have a hydrozirconium(iv)oxide retention layer sintered onto the filtration surface of one of the standard membrane modules.

Each module contains parallel flow channels into which feed material is introduced. Material which passes through the membrane enters the cell walls of the monolith support, flows radially through the monolith skin, then exists as filtrate. Material retained by the membrane exits the module at the downstream end.
A3.1.1 The Module Construction

Each cylindrical monolith support contains a large number of passageways which extend from the inlet end face to the outlet end face. In the industrial-scale modules, CeraMem modifies the monolith by converting some of the passageways to filtrate conduits. This eliminates the flow limiting resistance of the porous support. One or more membrane layers are applied and sintered onto the monolith passageway walls to form a stable, strongly-bonded ceramic membrane. Materials used for the different membranes are α-alumina, zirconium and γ-alumina.

Following application of the specific membrane to the honeycomb monolith support, stainless steel end rings are attached using a polymeric adhesive, or alternatively, ceramic end rings are attached using an inorganic cement. The monolith is recessed from the end ring faces to allow for an internal O-ring seal when installed within the LH module housing.

Modules constructed using polymeric adhesives for attaching the end rings have a maximum operating temperature limit of 130 °C. For modules with end rings attached using inorganic cement, the maximum operating temperature is limited by the housing O-ring/gasket material.

Recommended maximum trans-membrane pressure differential for the series LM modules is 700 kPa. For long term operation, these modules can be applied over a pH range of 2 to 12. For short term cleaning cycles, solutions of slightly higher or lower pH may be employed.
A3.1.2 The Module LH Housing

CeraMem provides housings fabricated from 316L stainless steel. The housing end fittings are grooved to accept an O-ring for positive seal to the internal surface.

A3.1.3 Series LM Module Types

A3.1.3.1 The LMDA-20-P1 Ceramic Ultrafiltration Module

The LMDA-20-P1 membrane consists of a dynamic, hydrous zirconium(IV) oxide membrane formed over CeraMem Separations' standard 0.01 μm zirconium oxide ultrafiltration membrane. The hydrous layer is sintered onto the ceramic support. The module measures 33 mm (1.3 in) in diameter by 330 mm (13 in) in length and has a feed channel width of 2 mm.

Based on retention experiments performed by CeraMem, using polymers of known molecular weight, the nominal molecular weight cut-off for the LMDA membrane has been determined to be between 10,000 and 15,000 daltons.

A3.1.3.2 The LMA-0005-P Ceramic Ultrafiltration Module

The LMA-0005-P module consists of a sintered γ-alumina membrane of 0.005 μm nominal pore size. The module measures 33 mm in diameter by 33 mm in length and has a feed channel size of 2 mm.

A3.1.4 Recommended Operating Conditions

CeraMem has established the following limitations on operating conditions and handling in order to provide a conservative safety margin. CeraMem is expected to broaden these as more experience is gained.

- Maximum operating temperature : 130 °C (series LMDA)
  Limited by inorganic cement (series LMA)
- Maximum operating pressure : 700 kPa (series LMDA and series LMA)
- pH operating range : pH 5 to 12 (series LMA and LMDA)

- Thermal shocks and negative pressure differentials should be avoided.
• Touching of the membrane surface should be avoided.

• The preferred feed circulation flow rate is from about 20 to 45 l/min. This corresponds to a preferred cross-flow velocity of 1.5 to 4.0 m/s.

• Process feed materials should be filtered, before processing, to remove any fibrous matter which could collect at the module inlet and coarse abrasive solids which could abrade the leading edge of the membrane module. Screening with a 200 mesh screen or pre-filtration using a bag filter (100 μm) is recommended.

A3.1.5 Recommended Cleaning Procedures

CeraMem recommends the use of a warm, mildly alkaline, sodium hypochlorite solution for cleaning of its LMDA membranes. The use of ultrafiltered water, with prior softening if from a hard water source, is preferred for make up of cleaning solutions, system flushing and flux measurement.

The following procedures have been used successfully for restoration of flux.

A3.1.5.1 Procedure for the CeraMem Module LMA-0005-P

(i) Flush the system thoroughly with purified water and drain.

(ii) Prepare a cleaning solution consisting of 200 mg/l to 500 mg/l sodium hypochlorite and 0.2 % (m/m) detergent dissolved in purified water. Adjust pH to a value between 8.0 and 8.5. (CeraMem routinely uses household bleach with a concentration of 5.25 % sodium hypochlorite, and Alconox detergent).

(iii) Heat cleaning solution to between 54 and 66 °C and circulate at about 15 l/min. Cleaning time will be dependent on cleaning solution temperature and nature of foulants. Experience with specific process streams will determine the optimum conditions.

Except for intermittent purging, permeate flow should be shut off during cleaning to eliminate trans-membrane pressure drop. Also, while CeraMem has intentionally subjected the membrane modules to repetitive thermal shock between 93 and 4.5 °C, with no adverse effects, this should be avoided.

(iv) Drain the cleaning solution from system, then flush with hot, purified water to remove residual cleaning solution.
(v) Circulate fresh, hot sanitising solution consisting of 150 mg/l sodium hypochlorite dissolved in purified water for approximately 15 min. This solution may be left in the system during shutdown. Flush with fresh water prior to next process run.

A3.1.5.2 Procedure for the CeraMem LMMDA-20-P1 Module

(i) Flush the system thoroughly with warm purified water (50 °C) and drain.

(ii) Prepare a cleaning solution consisting of 500 mg/l sodium hypochlorite dissolved in purified water. For certain foulants, addition of surfactants may prove beneficial.

(iii) Heat the cleaning solution to about 50 °C and circulate at about 12 l/min at a trans-membrane pressure not exceeding 50 kPa. Cleaning time will depend on the cleaning solution temperature and nature of foulants. Experience with specific process streams will determine the optimum conditions.

Too avoid permanent back-pressurisation at the downstream end of the LMMDA membrane module, the permeate valve should be open during cleaning.

(iv) Drain the cleaning solution from the system, then flush with hot, purified water to remove residual cleaning solution. When not in use, the membrane must remain wetted.

A3.2 Societe des Ceramiques Techniques: Specifications for Membralox® Ceramic Filtration Media

The application of cross-flow filtration under extreme conditions of pressure, temperature and pH led to the development of ceramic membranes which associate a well defined texture and overall sturdiness.

A3.2.1 The Membralox Support

The support of the membrane is composed of α-alumina, with a macroporous texture, which couples high permeability with strength. The support configuration can be tubular or multi-tubular (multi-channel).

The multi-channel support consists of a porous block containing a number of parallel channels, the inner surfaces of which are covered by a membrane. The suspension or solution to be filtered flows in each channel, along the membrane, then permeates through the membrane and the support material and comes out the lateral external surface. Due to the very high permeability of the support material, the
pressure drop caused by the filtrate flow through the support is generally quite negligible when compared with the pressure drop across the membrane.

The multi-channel design presents several important advantages:

- Sturdiness, since the filter element acts as a thick bar of support material.
- A small diameter channel design, obtained without any loss of sturdiness, and with the derived advantages of low re-circulation flow in the filtration loop, low energy consumption and low dead volume.
- High compactness for a given membrane surface area.

![Diagram of Membrane Module](image)

**Figure A3.2: Cross-section of the Membralox membrane module.**

### A3.2.2 The Membrane

The membrane is composed of one or several layers of porous ceramic with a well defined texture. These layers are bonded to each other and to the support, in a monolithic way, by very strong ceramic bonds obtained by a sintering operation. Different types of layers are available.

Membralox distinguish two main classes of membranes:

- Microfiltration membranes with pore sizes ranging from 12 to 0.2 μm.
Ultrafiltration membranes with pore sizes ranging from 0.1 to 0.004 μm

A3.2.3 The Module and Housing

Ceramic elements are assembled alone or in parallel, with shrouds easy to assemble in a plant. They comprise:

- One stainless steel (316L) housing.
- The ceramic element.
- A gasket ensuring the connection.

The module used in this investigation is designated as the type 1P19-40, having one filter element with 19 channels, a length of 869 mm and a filtration area of 0.2075 m².

A3.2.4 Recommended Cleaning and Regeneration Procedures

A3.2.4.1 Defouling by Backpulsing

The very high strength of ceramic materials and the intimate bonding between membrane and support allow cleaning by back-pulsing. Back-pulsing involves the application of a counter-pressure, on the filtrate or permeate side, that pushes a controlled amount of permeate back through the membrane.

In most cross-flow filtration cases the permeate flux is limited by the layer of particles or colloids deposited on the surface of the membrane rather than by the resistance to flow through the membrane itself. Back-pressure pulses cause a reverse flow of permeate through the membrane, lifting the layer of deposited material which is then carried away by the bulk cross-flow fluid. Short and frequent back-pressure pulses maintain high permeate flux rates by destroying the flux limiting layer, enabling full exploitation of the higher permeability of ceramic membranes. This technique is one of the key advantages of ceramic membranes.

A3.2.4.2 Procedure for Cleaning By Chemicals

(i) Wash with a sodium hypochlorite solution having 200 to 300 mg/l free chlorine for 10 min at 20 °C and at a pH value greater than 10.
(ii) Water rinse for 10 min at room temperature.

(iii) Wash with 2% (m/m) sodium hydroxide for 20 min at 70 °C (trans-membrane pressure drop must remain below 100 kPa).

(iv) Water rinse for 10 min at room temperature.

(v) Wash with 2% (m/m) nitric acid for 20 min at 70 °C.

(vi) Water rinse for 10 min at room temperature.

Depending on the type of fouling material, use of the same chemicals in a different order may give better results.

A3.3 Rhone-Poulenc/Tech Sep: Specifications for Micro-Carboset® Inorganic Ultrafiltration Membranes

Carboset third-generation mineral membranes are designed and manufactured by Tech Sep, a subsidiary of the Rhone-Poulenc Group. The patented design of their membranes consists of a layer of zirconium oxide on a porous carbon support.

The series Micro-Carboset 60 comprises tubular ultrafiltration and microfiltration modules, specially designed for processing small quantities of fluid. They are multipurpose, easily adaptable and compact, and are particularly suitable for feasibility studies and laboratory research.

A3.3.1 The Membrane

The membrane consists of a zirconium(IV)oxide/titanium(IV)oxide (ZrO₂/TiO₂) retention layer sintered onto a carbon support. The carbon support has an internal diameter of 6 mm, a length of 600 mm and a filtration area of 0.01131 m².
A3.3.2 Recommended Operating Conditions

- The maximum operating temperature is 300 °C.

- The maximum operating pressure is 1 500 kPa. This figure may be lower depending on the type of membrane and/or the fluid being filtered. The membrane will maintain its efficiency at extremely high viscosity levels and under high pressures owing to its rigid inorganic structure.

- The membranes are impervious to the action of solvents and oxidising agents.

- The membranes do not age and may be stored dry.

- The membranes are unaffected by micro-organisms.

- Permissible concentration is set at 20 to 40 % (m/m) suspended solids depending on the solution to be processed. This figure might be higher if the stainless steel turbulence promoter rod is not used.

- Re-circulation flow rates are typically 42 to 83 \( \ell/h \) or 1.2 to 2.4 m/s. Different re-circulation flow rates may be necessary, depending on the product or the process requirements.

A3.3.3 Recommended Cleaning Procedure

(i) Depressurise the fluid being processed and empty the module.

(ii) Rinse with demineralised water until the rinsing water runs clear.
(iii) Circulate decimolar sodium hydroxide (5 to 10 g/l) for 30 min. If the colour changes, a fresh solution should be used until the fluid remains colourless for 30 min.

A detergent or acid solution may be used instead of sodium hydroxide, but in this case the cleaning cycle may take several hours.

(iv) Depressurise and empty the cleaning solution from the system.

(v) Rinse with demineralised water and check that the water flow rate (pure water permeability) of the membrane is at least 95% of the initial flow rate.

Note: If the water flow rate (pure water permeability) does not return to normal, the cleaning procedure should be modified to include additional steps, e.g. stage (ii), followed by stage (iii), followed by stage (ii), followed by cleaning with a detergent, followed by stage (ii), one or more times.

**A3.3.4 Recommended Alternative Cleaning Fluids**

(i) Molar sodium hydroxide at 80 °C for 30 min.

(ii) Decimolar sodium hydroxide at 25 °C for 24 hours.

(iii) 0.1% sodium hypochlorite at 60 °C for 30 min.

(iv) 100% ethyl alcohol at 25 °C for 30 min.

(v) Decimolar nitric acid at 80 °C for 30 min.

(vi) Molar phosphoric acid at 80 °C for 30 min.

(vii) Molar sulphuric acid at 80 °C for 30 min.
Appendix 4

List of Ceramic Membrane Manufacturers
<table>
<thead>
<tr>
<th>Manufacturer</th>
<th>Trade Name</th>
<th>Membrane Material</th>
<th>Support Material</th>
<th>Membrane Pore Diameter</th>
<th>Geometry of Membrane Element</th>
<th>Tube or Channel Inside Diameter (mm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Alcan/Anotec</td>
<td>Anopore*</td>
<td>$\text{Al}_2\text{O}_3$</td>
<td>$\text{Al}_2\text{O}_3$</td>
<td>20 nm; 0.1 μm; 0.2 μm</td>
<td>Plate</td>
<td></td>
</tr>
<tr>
<td>Aloea/SCT</td>
<td>Membralox*</td>
<td>$\text{ZrO}_2$, $\text{Al}_2\text{O}_3$</td>
<td>$\text{Al}_2\text{O}_3$, $\text{Al}_2\text{O}_3$</td>
<td>20 to 100 nm; 0.2 to 5 μm</td>
<td>Monolith tube</td>
<td>4 and 6</td>
</tr>
<tr>
<td>Asahi Glass</td>
<td>Glass</td>
<td>None</td>
<td>None</td>
<td>8 nm to 10 μm</td>
<td>Tube and Plate</td>
<td>3 and 10</td>
</tr>
<tr>
<td>Ceran-Filtre</td>
<td>FITA MM</td>
<td>$\text{SiC}$</td>
<td>None</td>
<td>0.1 to 8 μm</td>
<td>Monolith</td>
<td>25</td>
</tr>
<tr>
<td>CeraMem</td>
<td></td>
<td>Ceramics</td>
<td>Cordierite</td>
<td>0.05 to 0.5 μm</td>
<td>Honeycomb monolith</td>
<td>2 and 4</td>
</tr>
<tr>
<td>Du Port/CARRE</td>
<td></td>
<td>$\text{Zr(OH)}_4$</td>
<td>SS</td>
<td>0.2 to 0.5 μm</td>
<td>Tube</td>
<td>about 2</td>
</tr>
<tr>
<td>Du Port</td>
<td>PRD-80</td>
<td>$\text{Al}_2\text{O}_3$; Multicrystalline</td>
<td>Cordierite</td>
<td>none</td>
<td>Tube</td>
<td>0.5 to 2.0</td>
</tr>
<tr>
<td>Fairey</td>
<td>Strata-Pore*</td>
<td>Ceramics</td>
<td>SS</td>
<td>1 to 10 μm; 0.2 to 1 mm</td>
<td>Tube/Plate</td>
<td>10</td>
</tr>
<tr>
<td>Fuji Filters</td>
<td></td>
<td>SS</td>
<td>None</td>
<td>4 to 90 nm; 0.25 to 1.2 μm</td>
<td>Tube</td>
<td></td>
</tr>
<tr>
<td>Gaston County</td>
<td>Ucarsim*</td>
<td>$\text{ZrO}_2$</td>
<td>C</td>
<td>4 nm</td>
<td>Tube</td>
<td>6</td>
</tr>
<tr>
<td>Industrial Ceramics</td>
<td></td>
<td>$\text{Al}_2\text{O}_3$</td>
<td>$\text{Al}_2\text{O}_3$</td>
<td>0.1 to 0.5 mm</td>
<td>Tube</td>
<td>8</td>
</tr>
<tr>
<td>Hoogeveld</td>
<td></td>
<td>$\text{Ni}, \text{Ag}, \text{Ni}$, etc.</td>
<td>None</td>
<td>Greater than 0.5 μm</td>
<td>Tube</td>
<td>3,2 to 19</td>
</tr>
<tr>
<td>Mott</td>
<td></td>
<td>$\text{Al}_2\text{O}_3$</td>
<td>$\text{Al}_2\text{O}_3$</td>
<td>0.2 to 5 μm</td>
<td>Tube</td>
<td>7 and 22</td>
</tr>
<tr>
<td>NGK</td>
<td>Cefit*UF</td>
<td>$\text{Al}_2\text{O}_3$</td>
<td>$\text{Al}_2\text{O}_3$</td>
<td>0.2 to 1.0 μm; 6 μm symmetric</td>
<td>Monolith tube</td>
<td>3</td>
</tr>
<tr>
<td>Norton</td>
<td>Ceraflo*</td>
<td>$\text{Al}_2\text{O}_3$</td>
<td>$\text{Al}_2\text{O}_3$</td>
<td>0.2 to 5 μm; 0.1 μm</td>
<td>Tube/Plate</td>
<td></td>
</tr>
<tr>
<td>Osmomias</td>
<td>Hytrex*</td>
<td>Ag</td>
<td>None</td>
<td>0.2 to 5 μm; 0.1 μm</td>
<td>Tube/Plate</td>
<td></td>
</tr>
<tr>
<td>Pall</td>
<td></td>
<td>SS, Ni, etc.</td>
<td>None</td>
<td>Greater than 0.5 μm</td>
<td>Tube</td>
<td>60 and 64</td>
</tr>
<tr>
<td>Rhone-Poulenc/SFEC</td>
<td>Carbosim*</td>
<td>$\text{ZrO}_2$</td>
<td>C</td>
<td>4 nm; 0.08 to 0.14 μm</td>
<td>Tube</td>
<td>6</td>
</tr>
<tr>
<td>Schott Glass</td>
<td></td>
<td>Glass</td>
<td>None</td>
<td>10 nm and 0.1 μm</td>
<td>Tube</td>
<td>5 to 15</td>
</tr>
<tr>
<td>TDK</td>
<td>Dynaceram*</td>
<td>$\text{ZrO}_2$</td>
<td>$\text{Al}_2\text{O}_3$</td>
<td>10 nm</td>
<td>Tube</td>
<td>about 5</td>
</tr>
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</table>
### Table A4.2: Addresses of inorganic membrane manufacturers [Bhave (1991)].

<table>
<thead>
<tr>
<th>Manufacturer</th>
<th>Trade Name</th>
<th>Address</th>
</tr>
</thead>
<tbody>
<tr>
<td>Alcan/Anotec</td>
<td>Anopore®</td>
<td>Anotec Separations Ltd., Wildmire Road, Banbury, Oxford, OX16 7RU, UK.</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Anotec Separations, 126 East 54th Street, New York, NY 10022, USA.</td>
</tr>
<tr>
<td>Alcoa/SCT</td>
<td>Membralox®</td>
<td>Société Ceramiques Techniques, Unité de Bazeit B.P. 113, 65000, Tarbes,</td>
</tr>
<tr>
<td></td>
<td></td>
<td>France. Alcoa Separations Technology Inc., 181 Thorn Hill Road, Warren</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Dale, PA 15086, USA.</td>
</tr>
<tr>
<td>Asahi Glass</td>
<td></td>
<td>2-1-2 Marumouchi, Chiyoda-ku, Tokyo 100, Japan.</td>
</tr>
<tr>
<td></td>
<td></td>
<td>1185 Avenue of the Americas, 20th Floor, New York, NY 10036, USA.</td>
</tr>
<tr>
<td>CeraMem</td>
<td></td>
<td>CeraMem Corporation, 12 Clematis Avenue, Waltham, MA 02154, USA.</td>
</tr>
<tr>
<td>Du Pont/CARRE</td>
<td></td>
<td>Du Pont Separation Systems, Glasgow, Wilmington, DE 19898, USA.</td>
</tr>
<tr>
<td>Du Pont</td>
<td>PRD-80</td>
<td>Du Pont Separation Systems, Glasgow, Wilmington, DE 19898, USA.</td>
</tr>
<tr>
<td>Fairey</td>
<td>Strata-Pore® Microfilrex</td>
<td>Fairey Industrial Ceramics Ltd., Filleybrooks Stone, Staffs, ST15 5PU, UK.</td>
</tr>
<tr>
<td>Fuji Filters</td>
<td></td>
<td>Fuji Filter Co. Ltd., 2-4 Nihonbashi-Muramachi, Chuo-ku, Tokyo 103,</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Japan.</td>
</tr>
<tr>
<td>Gaston County</td>
<td>Ucarsep®</td>
<td>Gaston County Filtration Systems, P.O. Box 308, Stanley, NC 28164, USA.</td>
</tr>
<tr>
<td>Filtration Systems</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Hoogovens Industrial</td>
<td></td>
<td>Hoogovens Industrial Ceramics BV, Postbus 10 003, 1970 CA Emmen, The</td>
</tr>
<tr>
<td>Ceramics</td>
<td></td>
<td>Netherlands.</td>
</tr>
<tr>
<td>Imaea/CTI</td>
<td></td>
<td>Imaea, B.P. 94, 34830 Clermont, Uherault, France.</td>
</tr>
<tr>
<td></td>
<td></td>
<td>CTI, B.P. 12, 36508 Bezancourt, France.</td>
</tr>
<tr>
<td>Kubota</td>
<td></td>
<td>Kubota Ltd., 1-4-47 Shikitani-Higashi Naniwa-ku, Osaka 556, Japan.</td>
</tr>
<tr>
<td>Mott</td>
<td></td>
<td>Mott Metallurgical Corporation, Farmington Industrial Park, Farmington,</td>
</tr>
<tr>
<td></td>
<td></td>
<td>CT 06032, USA.</td>
</tr>
<tr>
<td>NGK</td>
<td></td>
<td>NGK Insulators Ltd., Shin Maru Building 1-5-1, Maizuru Chiyodo-ku,</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Tokyo 100, Japan.</td>
</tr>
<tr>
<td>Norton</td>
<td>Cerazlo®</td>
<td>Norton Company, 1 New Bond Street, Worcester, MA 01606, USA.</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Millipore Corporation, Ashby Road, Bedford, MA 01730, USA.</td>
</tr>
<tr>
<td>Osmonics</td>
<td>Hytrex®</td>
<td>Osmonics Inc., 5951 Clearwater Drive, Minnetonka, MN 55343, USA.</td>
</tr>
<tr>
<td></td>
<td>Ceratex®</td>
<td></td>
</tr>
<tr>
<td>Pall</td>
<td></td>
<td>Pall Porous Metal Filters, Courtland, NY 13045, USA.</td>
</tr>
<tr>
<td>Rhone-Poulenc/SPEC</td>
<td>Carbosep®</td>
<td>Boîte Postale No. 231, 84500, Bollene, France.</td>
</tr>
<tr>
<td>Schott Glass</td>
<td></td>
<td>Schott Glaswerke, Postfach 2480, D-6500, Mainz 1, Germany.</td>
</tr>
</tbody>
</table>
Appendix 5

Johnson Sweetwater Characteristics
Figure A5.1: Johnson sweetwater average ICUMSA colour and average brix calculated using weekly average quality control data from April 1991 to October 1993.