

# SYNTHESIS REPORT

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TITLE :

MINERALE NANOFILTRATION MEMBRANES FOR CANE SUGAR REFINING  
PROCESS (NANOSUP)

PROJECT

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## 3. ABSTRACT

Sol-gel processing has been used to fabricate zirconia nanofiltration membranes for application in sugar refining. Two routes were investigated : aqueous processing by AEA (Sol-Gel 2) and alcohol processing by Tech-Sep (Sol-Gel1) Light scattering was used for particle size determination in zirconia sols that were converted to gel and oxide powders. The latter were characterised for pore *size* distribution, surface area and crystalline phase to give information on the possible pore size distribution in membranes made from similar sols. Selected sols were converted to oxide coatings on 7-channel and 19-channel Kerasep ultrafiltration supports, 2 cm in diameter with lengths up to 85.6 cm; the most frequently used supports had a 15 KD molecular weight cut-off. Laboratory-scale trials on model solutes (bromocresol green, vitamin B<sub>12</sub>, sodium chloride, sucrose and a dextran with a molecular weight of 10000) showed that the zirconia coatings behaved as nanofiltration membranes. Pilot-plant trials were made on 85.6 cm lengths for sodium chloride recovery from ion-exchange effluent produced in a refinery. Impurities to be removed by nanofiltration were characterized by HPLC, GPC, ionic chromatography and <sup>1</sup>H and <sup>13</sup>C-NMR by Polytech. These results lead to the required "fingerprint" of the impurity profile.

Pilot plant trials showed that sol-gel, zirconia membranes could recover brines from ion-exchange effluent with targeted specification for flux and colours rejection. For melter liquor, ceramic membranes do not fit the flux objectives in spite of good results of decolourisation.

## 4. INTRODUCTION

Chemical processes are used to purify raw cane sugar liquors and the overall aim of these methods is to remove polymeric species (molecular weight < 3000) that are responsible for decoloration of the sugar liquor. Thus the primary purification stage uses carbonatation while filtration through activated carbon beds and ion-exchange resins are secondary purification stages.

There are increasing requirements, economic and environmental, for alternative purification techniques for sugar liquors. Nanofiltration membranes (1) with a pore size around 2 nm have potential use for refining sugar liquors. This pore size falls between those found in ultrafiltration and reverse dialysis membranes. Zirconia is the material of choice because, in use, the membranes are cleaned at high pH to remove adherent deposits and the insolubility of  $ZrO_2$  makes this ceramic a desirable choice for application in the food industry. Sol-gel processing is a widely used technique for preparation of ceramic materials as powders and coatings (2,3). It can be used to prepare a nanofiltration membrane as a coating on a ceramic support, for example, an ultrafiltration membrane. The purpose of this study was to evaluate sol-gel processing as a route to nanofiltration membranes for use in sugar refining to remove coloured compounds.

TLPT, as the end-user has determined the performance characteristics of the membrane in the refining process. Uses of nanofiltration membranes were investigated on melter liquor, molasses desugarisation and brine recovery applications.

Cane sugar contains numerous impurities of organic (including carbohydrates) and inorganic nature. The colorants in sugarcane are not only naturally occurring plant pigments, associated nitrogen and polysaccharide-based impurities and precursors, but are also compounds produced during the processing operation. The colorant fraction in brine solutions is also highly heterogeneous and is composed mainly of impurities produced during the processing operation. Unlike sugarcane colorants, the naturally occurring compounds are not present. Most of the work on the elucidation of the structure of specific colorants has been carried on low molecular weight compounds. These substances account only for a small portion of the colorant fraction and, although they can survive at trace levels even in granulated sugar, are likely to be transformed into more complex species by further reaction.

The coloured impurities found in cane sugar can be classified as (a) naturally occurring pigments such as chlorophylls, xanthophylls, carotens and anthocyanins, (b) nitrogen-containing compounds formed by the reaction of reducing sugars with amino acids and (c) polyphenols.

Colours are formed in the processing of sugar as a consequence of heating, atmospheric oxygen, chemicals (alkaline), and contaminant iron from the equipment used. These coloured compounds are produced by thermal decomposition (caramel) alkaline decomposition and specifically Maillard reaction. Unlike colorants from caramel, alkaline degradation products contain a high proportion by weight of colorless compounds which are not easily adsorbed by the carbon. Melanoidins are mostly coloured and easily adsorbed.

Colorants in the higher molecular weight range (up to 50,000). Raw cane sugar contains about 0.1 to 0.2% polysaccharides.

Starch in a normal sugar cane juice reaches the amount of 50 ppm. Although insoluble in cold water, starch is solubilised by heating and liming and passes into the clarified juice having the tendency to be incorporated into the raw sugar crystals. An (-glucan, named sarkaran and a gluconoarabinogalactan were also isolated by alcohol precipitation from fresh cane juice. Dextrans are polysaccharides associated with sugar cane but not considered to be present in healthy cane. They are produced by bacteria like *Leuconostoc mesenteroides* and *Leuconostoc dextranicum* in damaged sugar cane, or during sugar manufacture under conditions of poor housekeeping. Dextrans, which are glucan with  $\alpha$ -(1,6) linkages and  $\alpha$ -(1,4) and  $\mu$ -(1,3) linkages at the branch points, are soluble in water and have high molecular weight (100,000-10,000,000). As for the other polysaccharides, the presence of dextrans in *cane* juice and in raw sugar has its greatest effect on the viscosity and hence the filterability of those materials. Carbonatation and phosphatation as well as decolourisation of feed liquor by bone char, granular or powdered carbon and ion exchange resins were reported to be ineffective for an efficient removal of dextrans.

## 5. TECHNICAL DESCRIPTION

### 5.1 Aqueous SOI gel

#### 5.1.1 *Sol-gel* processing

Sol-gel processing is a wet chemical technique for preparation of ceramics as powders and coatings (2,3). One sol-gel process involves (2) preparation of aqueous colloidal dispersions (sols) that are dehydrated to gels in the form of powders or coatings; gels are then calcined to oxide. For coatings, the substrate can be dipped into the sol and the liquid layer on it, after removal from the sol, is dried to a gel coating. Another sol-gel process (2,3) involves hydrolysis of alcoholic solutions of metal-organic compounds such as metal alkoxides. Hydrolysis produces an oxide powder precipitate or polymeric colloidal species in solution. Sol-gel processing has been used for fabrication of zirconia nanofiltration membranes (4-6). Thus controlled hydrolysis of zirconium tertiary amyloxyde (4) yielded a  $ZrO_2$  SOI containing particles < 5 nm in diameter that was cast to an unsupported membrane. Chemical durability of  $ZrO_2$  membranes was claimed (5) to be enhanced when they contained the tetragonal rather than monoclinic phase. Sols made by peptisation of amorphous hydrous zirconia were used (6) for depositing a nanofiltration layer on a microporous support (pore diameter 1-10  $\mu$ m). Membranes have been made by direct fabrication from a polymeric hydrolyses alkoxide solution (7), for example, unsupported silica (8) but this method has not been reported for zirconia membranes.

### 5.1.2. *Aqueous sol preparation and characterisation*

Zirconia sols were prepared by AEA (9) by dissolving zirconium carbonate (MEL Chemicals Ltd) in nitric acid. Representative as-prepared sol properties were (i)  $300 \text{ g l}^{-1}$  oxide,  $\text{NO}_3:\text{ZrO}_2$  mole ratio 1.0:1 (NM001) and (ii)  $218 \text{ g l}^{-1}$  oxide,  $\text{NO}_3:\text{ZrO}_2$  ratio 1.5:1 (NM066). Some sols were prepared by replacing nitric with acetic acid. Sols were filtered, for example, through a  $0.1 \mu\text{m}$  disposable filter (Anotop Plus) in order to remove micron-sized particulate before characterisation for particle size by photon correlation spectroscopy (PCS). The latter was carried out with a Malvern PCS 4700 photon correlation spectrometer system incorporating a 256-channel K-7032 computing correlator and equipped with a Spectra-Physics Stablite 124B He-Ne laser. The effect of ageing selected sols on particle size was monitored by PCS.

### 5.1.3 *Sol $\rightarrow$ gel $\rightarrow$ oxide powder*

Gel powders obtained by drying nitrate-stabilised  $\text{ZrO}_2$  sols and oxide powders made by calcination at  $4000 \text{ C}$  were characterised to give information on the possible pore size distribution in membranes made from similar sols. Gel powders were characterised by thermogravimetric analysis to determine the minimum temperature for decomposition to oxide. Oxide powders were characterised by use of a Micromeritics Digisorb 2600 module.

### 5.1.4 *Membrane supports*

In most cases 7-channel and 19-channel 15 KD ultrafiltration membranes were used as supports for the nanofiltration layer. These supports had an outer diameter of 2 cm, a channel diameter of 2 mm and length up to 85.6 cm.

### 5.1.5 *Fabrication of nanofiltration membranes*

Selected sols were used for membrane fabrication, in particular, aged sols with particle sizes larger than in as-prepared sols. For example, a sol with a  $\text{NO}_3:\text{ZrO}_2$  ratio of 0.9:1, a single peak in the mass distribution at 10.7 nm and a z-average mean size of 13.4 nm was used in conjunction with sol additives. Channels in the ultrafiltration supports were filled simultaneously with dilute sol containing typically  $10 \text{ g l}^{-1}$  of oxide after which liquid was allowed to drain from the channels. Coated supports were then dried and calcined at  $4000 \text{ C}$  to produce a zirconia coating.

### 5.1.6 Evaluation of nanofiltration membranes

A membrane test rig that was constructed at AEA Technology incorporated a Micro Kerasep module and an Alfa Laval SSP rotary lube pump. Coated Kerasep tubes up to 40 cm in length could be tested on the rig and some were also evaluated by Tech-Sep using model solutes, thus bromocresol green, vitamin B<sub>12</sub>, sucrose, a dextran (molecular weight 10000) and sodium chloride. Pilot-scale trials on lengths of 85.6 cm were made by Tate & Lyle Process Technology in order to determine sodium chloride recovery from ion-exchange effluent.

Tetragonal zirconia is a preferred phase due to its chemical durability (5). Complete nitrogen adsorption isotherms were Type IV indicating mesoporous solids (10). BET surface areas of oxide powders were in the range 9-165 m<sup>2</sup> g<sup>-1</sup>. Variation of differential volume with pore diameter indicated pore size distributions centred around 5 nm for oxide derived from NM 066. Thus results from photon correlation spectroscopy and pore size measurements indicated that if membranes had a similar pore structure to the oxide powder they would correspond to nanofiltration membranes.

Representative results from membrane evaluation are summarised here. For a coated 7-channel 15 KD substrate (length 20 cm) a transmembrane pressure of 10 bar with an associated linear flow rate of 1.75 m s<sup>-1</sup> produced a permeate flux of 20 l/h/m<sup>2</sup>/bar and a 2970 sucrose retention.

## 5.2 Alcohol sol-gel 2

### 5.2.1 *Sol-gel processing*

The method used to prepare SOIS of zirconia precursors is called Polymerization of Molecular Units (PMU).

It consists in controlling exactly the hydrolysis of Zirconium Propoxide in propanol by the use of a complexing ligand. This control permits to obtain, after calcination at 400° C, nanoparticles of tetragonal ZrO<sub>2</sub> characterized by a specific surface equal to 11.6 m<sup>2</sup>/g. The method of preparation is well reproducible and the method of Sol's preparation did not evolve during the period January 93- June 94.

We have just checked that we were able to modify phase stability of ZrO<sub>2</sub>, by the addition of 15% of a Magnesium alcoxide to the Zirconium Propoxide. In this case, Sols lead to obtain nanoparticles of cubic ZrO<sub>2</sub>. And for the same conditions of calcination, this ZrO<sub>2</sub> is characterized by a very high specific surface :96.8 m<sup>2</sup>/g.

### 5.2..2 Selection of the support

Carbosep and Kerasep ultrafiltration membrane were tested as support. 5 membranes were tested. Their characteristics are summarized in the table 1.

Table 1: Characteristics of Carbosep and Kerasep membranes used as support of Zirconia layer

| Type of membrane | Configuration   | Water permeability<br>(l/h/m <sup>2</sup> /4 bars) | cut-off<br>(Retention of Dextrane) |
|------------------|---|--|------------------------------------|
| Carbosep M5      | Carbon tube<br>+ ZrO <sub>2</sub> UF layer  | 200  | 10 KD                              |
| Carbosep M9      |   | 800  | 300 KD                             |
| Kerasep 15 KD    | Al <sub>2</sub> O <sub>3</sub> / TiO <sub>2</sub><br>monolith (7 channels)<br>+ ZrO <sub>2</sub> UF layer | 800  | 15 KD                              |
| Kerasep 300 KD   |   | 2000   | 300 KD                             |
| Kerasep 150 KD   |   | 1200   | 150 KD                             |

Initial coating trials were carried out on 20 cm length of support.

It is easier to coat Carbosep support because of its configuration. But Scanning Electron Microscopy indicated that stresses occurring during drying provide a stripping of the UF+NF layer: the adhesion between Carbon support and ZrO<sub>2</sub> UF layer is not enough strong. So we concluded that Carbosep membranes are not adapted.

Coating trials on Kerasep membranes 300 and 150 KD provide membranes characterized by a very high water flux (400 l/h/m<sup>2</sup>/4 bars) and a very low retention of Saccharose (<5%). This is typically due to defects on the nanofiltration layer. Tese defects can be easily detected by Scanning Electron Microscopy.

The microscopy also explains the source of defects : the 300 and 150 KD layer rugosity is too high for a 1 µm nanofiltration layer.

So we concluded that the Kerasep 300 and 150 KD membranes are not well suitable supports for the Sol-Gel Zirconia membrane.

Coating trials realized on Kerasep 15 KD also provide nanofiltration membranes characterized by bad Selectivity performances and high fluxes (see table 2).

Table 2: Filtration performances

|   | NaCl | Na <sub>2</sub> SO <sub>4</sub> | Saccharose | Bromocresol Green | Vitamin B12 |
|---|------|---------------------------------|------------|-------------------|-------------|
| Permeat flux<br>(l/h/m <sup>2</sup> /10 bars) |      |                                 | 80         |                   | 72          |
| Retention rate                                | 8%   | 10%                             | 10%        | 60%               | 26%         |

Water permeability is 200 l/h/m<sup>2</sup>/5 bars, with a linear variation versus pressure.

These results are due to defects on the nanofiltration layer. But in this case, the origin of defects is not the rugosity of the ultrafiltration layer. Kerasep 15 KD shows a good potential as membrane support but we have to improve the quality of the nanofiltration layer by studying the conditions of coating.

### 5.2.3 Coating

We have optimized the experimental conditions of coating (L=20 cm) with the following objectives :

- Increasing the selectivity of the membrane by suppression of defects.
- Permeability as high as possible (control of the layer thickness).

### 5.2.4 Realization and conception of laboratory pilot

Tech-Sep has designed and built a nanofiltration laboratory pilot. Its design provides the following advantages :

Easily interchangeable configuration for working with several types of membranes (spirally wound, Carbosep L = 20 to 120 cm, Kerasep L = 20 to 120 cm).

- Adjustable flow speed.
- Adjustable filtration pressure from 5 to 30 bars.
- Operating in open or closed loop.
- Reduced internal volumes.

## 5.3 Impurities and colour characterisation

In order to characterise impurities and colorants in samples of raw sugar solution from TECH-SEP and TATE & LYLE, the general strategy involved the fractionation of the impurities from raw or affinated sugar using dialysis, ethanol precipitation and solvent extraction.



The molecular weight fractionation was achieved by low (FPLC) or high pressure gel permeation chromatography (GPC). The charged impurities were separated by ion-exchange chromatography. The low molecular weight impurities, such as flavonoids, phenolics and sugar degradation products, were identified using reverse phase liquid chromatography, gas chromatography (GC) and anionic exchange chromatography (AEC). Further detailed structural investigation was carried out using ultraviolet (UV) visible, Fourier transform infrared (FTIR), and nuclear magnetic resonance (NMR) spectroscopy.

The hydrophobic nature of the impurities was established using partitioning between water and different water immiscible organic solvents.

A similar strategy was adopted for the characterisation of impurities and colorants of brine solutions. The impurities were fractionated by dialysis, ethanol precipitation and size exclusion chromatography (SEC). They were further separated by ion-exchange chromatography (IEC), reverse phase liquid chromatography (HPLC), and anionic exchange chromatography (AEC).

#### 5.4 Pilot plants

A pilot scale ceramic membrane which is suitable for the recovery of brine from ion exchange resin regeneration effluent has been developed. The trial work has concentrated on the evaluation of several parameters: flux rate, membrane selectivity, chemical and temperature stability, fouling and cleaning characteristics of the membrane, and the optimisation of operating conditions in terms of TMP and crossflow velocity.

Two pilot plants have been used for membrane testing, the first with a capacity of  $1.5\text{m}^3/\text{h}$  at 40 bar and  $5\text{m}^3/\text{h}$  at 5 bar was used for the experimental scale membranes and the second, with a capacity of  $40\text{m}^3/\text{h}$  at 15 bar, was employed for pilot scale membrane evaluation.

## 6. RESULTS

### 6.1 Sol-gel 2 - aqueous process

As-prepared undiluted sols scattered light intensely and the presence of micron-sized particles was confirmed. Scattering by filtered sols was dominated by large particles although they formed a small fraction by mass of the overall population because the scattered light intensity is roughly proportional to the fifth power of the particle size. Small particles which form the main bulk of the sols by mass scattered light weakly. PCS indicated a peak position of 2.2 nm in sol NM 001 and 3.9 nm in sol NM 004 (acetate: zirconia ratio 1.5:1,  $290\text{ g l}^{-1}$  oxide) after passage through a  $0.1\mu\text{m}$  filter.

The latter sol also had a peak position at 40.1 nm corresponding to c 0.170 of particles by mass. Sols exhibited ageing effects with an increase of particle size with time after preparation. It was possible to produce particle sizes up to 30 nm by ageing the sols.

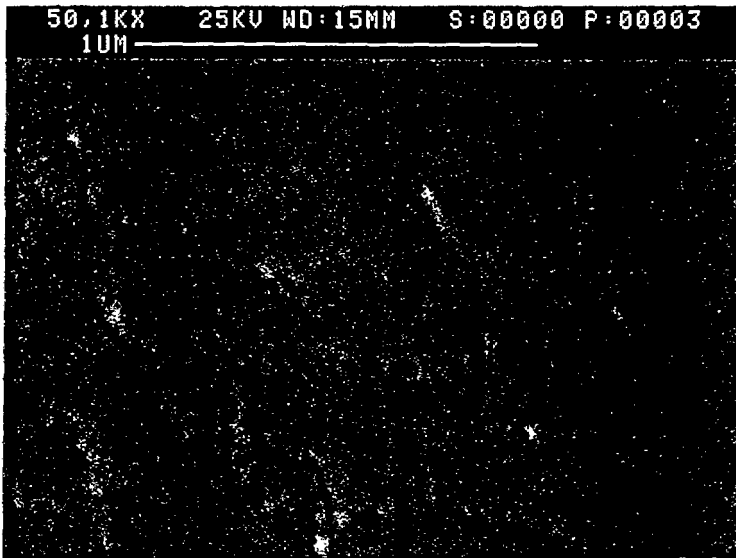
Thermogravimetric analysis showed that gels had decomposed to oxide by 4000 C. X-ray diffraction showed that oxide derived from sol NM 001 produced tetragonal zirconia with a crystallite size from line broadening of 25 nm; a mixed cubic/monoclinic phase with a much smaller crystallite size was obtained from another sol, NM003 (264 g l<sup>-1</sup> oxide, NO<sub>3</sub>:ZrO<sub>2</sub> ratio of 3.0:1).

## 6.2 Alcohol sol-gel processing

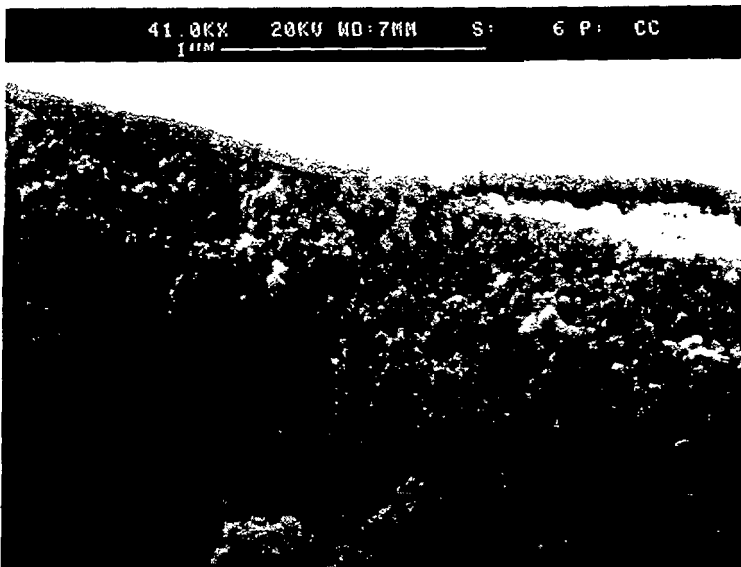
During the project, Tech-Sep succeeded in producing inorganic nanofiltration membranes : the Sol-Gel 1 which permits to obtain ZrO<sub>2</sub> membrane with good performances. The nanofiltration layer obtained is 0,2 μ thickness and the coating is very regular (see figures on the following sheet).

A transmembrane pressure of 10 bar and identical linear flow rate produced 56 % and 78 % rejection for vitamin B<sub>12</sub> and a dextran respectively ; the flux for vitamin B<sub>12</sub> was 24 l/h/m<sup>2</sup>/bar. These results showed that the coated substrate behaved as a nanofiltration membrane.

# *Nanofiltration Sol-Gel Membrane*



*TOP V/EW (Surface)*

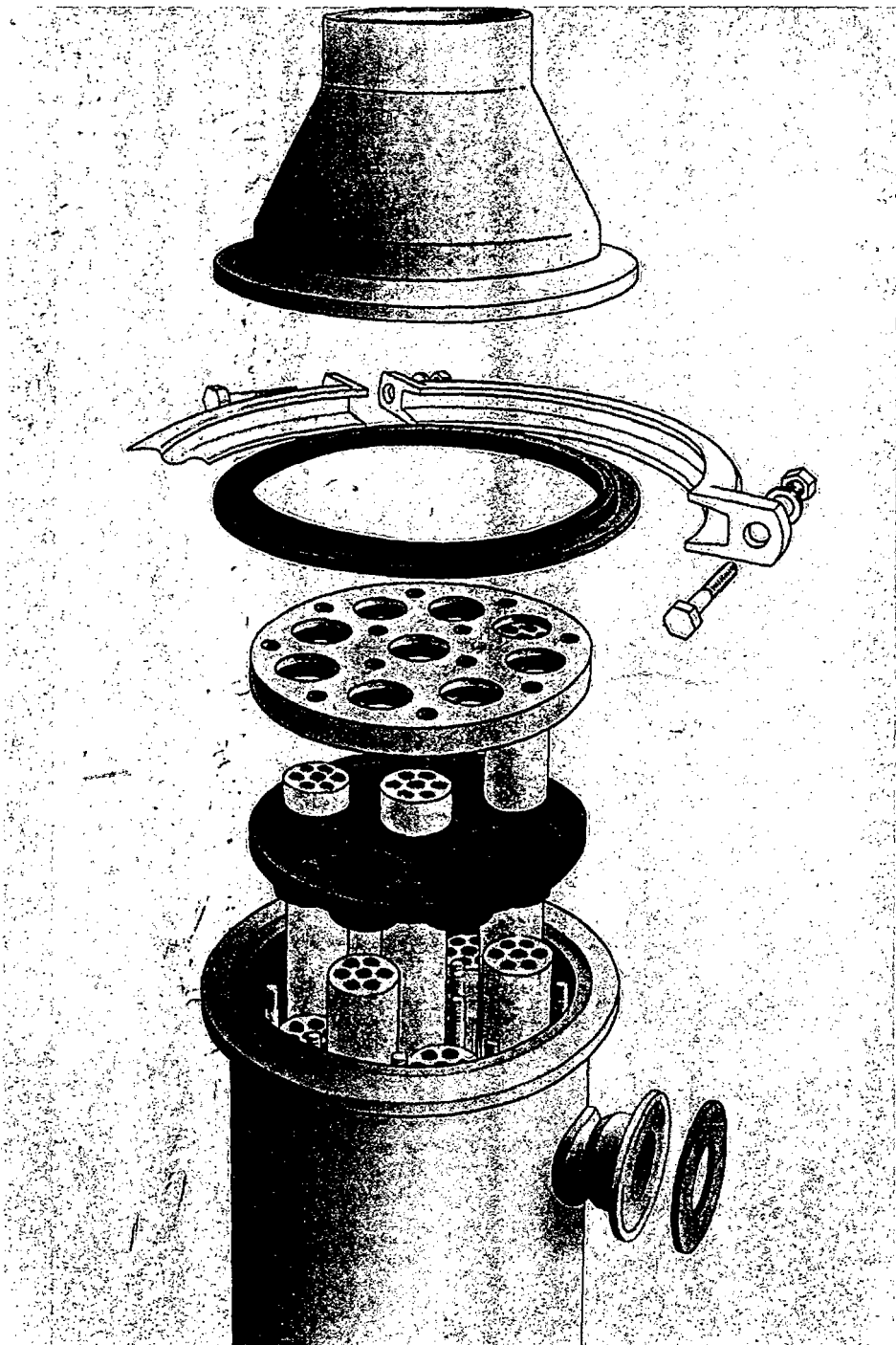


*CROSS SECTION VIEW  
Nanofiltration layer  
thickness. 0,2μ*

By working on the membrane synthesis (selection of the support, composition of the Sol, coating method, firing conditions, . . .), Tech-Sep has improved their fundamental knowledge of the Sol-Gel approach. And consequently nanofiltration characteristics of the membrane have been improved all along the project as shown in table hereafter :

| <b>Date</b> | <b>Water permeability<br/>(l/h/m<sup>2</sup>/5 bars)</b> | <b>Retention of<br/>Saccharose (%)</b> | <b>Retention of<br/>Vitamin B12 (%)</b> |
|-------------|--|--|---|
| June 93     | 200  | 10                                     | 25                                      |
| Dec. 93     | 80   | 20                                     | 65                                      |
| Dec. 94     | 50   | 30 to 40                               |   |
| March 96    | 100  | 30 to 40                               |   |

Moreover, the surface of produced membrane was increased from 0.03 m<sup>2</sup> (laboratory membrane) to 0.12 m<sup>2</sup> (industrial membrane). Tech-Sep has produced, during the last year more than 30 industrial membranes : this step has permitted to assess the reproducibility of membrane manufacturing and to build a nanofiltration pilot module (figure on the following sheet) which has been tested by Tate&Lyle on long term experiments.



### 6.3 Pilot plant trials

TLPT has identified various potential applications of mineral NF membranes in the sugar refining process and has characterised membrane performance for each application.

### 6.4 Impurities characterization

Protocols for the separation of impurities from raw sugar, affinated sugar and brine solutions were established. High molecular and low molecular weight impurities were separated and characterised using HPLC, GPC, ionic chromatography, and  $^1\text{H}$  and  $^{13}\text{C}$ -NMR. These results lead to the required “fingerprint” of the impurity profile.

Twelve samples of retentate and permeate from the ultrafiltration and nanofiltration trials of affinated sugar solutions from Tech-Sep were analysed for sugar and colour retention. The colour retention results were in good agreement with those of the Tech-Sep results. Some variations in the sugar retention data were observed but this could be due to different techniques used in the two Laboratories.

According to thin layer chromatography trials on brine samples, tested on 20cm length TECH-SEP membranes, there was limited selectivity on the separation of various impurities.

Volubility trials in organic solvents revealed that the impurities in brine solutions are charged and not hydrophobic.

A database containing 200 scientific reference literature on impurities present in sugar liquor and brines has been established.

## 7. CONCLUSIONS

Aqueous sol-gel and alcohol processing have been used to prepare zirconia nanofiltration membranes. The membranes rejected model solutes (bromocresol green, vitamin B<sub>12</sub>, dextran) and were evaluated on ion-exchange effluent in pilot-plant trials. Although brine recovery and colour rejection were produced, target performance values were not reached by aqueous sol-gel processing membranes possibly due to flaws in the sol-gel coatings.

For alcoholic sol-gel processing (Tech-Sep) the project has resulted in the development of a pilot scale ceramic NF membrane which is suitable for the recovery of brine from ion exchange resin regeneration effluent.

Protocols ("Fingerprints") for the separation of impurities from raw sugar, affinated sugar and brine solutions have been established.

According to thin layer chromatography trials on brine samples, tested on 20cm length TECH-SEP membranes, there was limited selectivity on the separation of various impurities.

The impurities in brine solutions are charged and not hydrophobic.

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