

Lappeenrannan teknillinen korkeakoulu  
*Lappeenranta University of Technology*

*Niina Laitinen*

***Development of a ceramic membrane filtration equipment  
and its applicability for different wastewaters***

*Dissertation for the degree of Doctor of Science  
(Technology) to be presented with due permission  
for public examination and criticism in the Audi-  
torium of the Student Union House at Lappeen-  
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*”... tahdomme tietoa udella,  
oommepa vanhoja kaljupäitä  
tai nuoria polvet ruvella.  
Täyttää jollain kiinnostavalla  
voisit tämäkin aivon,  
sillä kärpäsenraadot ja nöyhtä valtaa  
äkkiä tyhjän kaivon.  
Siis oppia anna arvokasta,  
unohtunut palauta mieleen,  
parhaasi tee, me teemme myös,  
vaikka välillä menisi pieleen.”*

- J.K. Rowlings (suom. Jaana Kapari)  
Harry Potter ja viisasten kivi

## ABSTRACT

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In this thesis the membrane filtration equipment for plate type ceramic membranes was developed based on filtration results achieved with different kinds of wastewaters. The experiments were mainly made with pulp and board mill wastewaters, but some experiments were also made with a bore well water and a stone cutting mine wastewater. The ceramic membranes used were  $\alpha$ -alumina membranes with a pore size of 100 nm. Some of the membranes were coated with a  $\gamma$ -alumina layer to reduce the membrane pore size to 10 nm, and some of them were modified with different metal oxides in order to change the surface properties of the membranes.

The effects of operation parameters, such as cross-flow velocity, filtration pressure and back-flushing on filtration performance were studied. The measured parameters were the permeate flux, the quality of the permeate, as well as the fouling tendency of the membrane. A dynamic membrane or a cake layer forming on top of the membrane was observed to decrease the flux and increase separation of certain substances, especially at low cross-flow velocities. When the cross-flow velocities were increased the membrane properties became more important. Backflushing could also be used to decrease the thickness of the cake layer and thus it improved the permeate flux. However, backflushing can lead to a reduction of retentions in cases where the cake layer is improving them. The wastewater quality was important for the thickness of the dynamic membrane and the membrane pore size influenced the permeate flux.

In general, the optimization of operation conditions is very important for the successful operation of a membrane filtration system. The filtration equipment with a reasonable range of operational conditions is necessary, especially when different kinds of wastewaters are treated. This should be taken into account already in the development stage of a filtration equipment.

Keywords: ceramic membrane, filtration equipment, equipment development, microfiltration, ultrafiltration, wastewater treatment, pulp and paper industry, drinking water, stone cutting wastewater

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Lappeenranta, September 2002

Niina Laitinen

## LIST OF PUBLICATIONS

The experimental part of this thesis is mainly presented in the following scientific papers. In the text these publications will be referred to by roman numbers. The publications I-V and VII include work that I have carried out by myself with some helpful advice and fruitful discussions with the other co-writers. On the other hand, in publications VI and VIII the actual experiments have been carried out by summer trainees but I have planned and supervised the experiments and written the publications based on the results.

- I Niina Laitinen, Antero Luonsi, Keraamikalvosuodatus kaivoveden arseenin poistossa – case study, *Vesitalous*, (1996) 3, p.38-40
- II Niina Laitinen, Antero Luonsi, Erkki Levänen, Lars Grönroos, Tapio Mäntylä, Marianne Nyström, Modified and unmodified alumina membranes in ultrafiltration of kraft bleachery effluents, *Acta Polytechnica Scandinavica*, (1997) 247, p.4-13
- III Niina Laitinen, Antero Luonsi, Erkki Levänen, Lars Grönroos, Tapio Mäntylä, Marianne Nyström, Modified and unmodified alumina membranes in ultrafiltration of board mill wastewater fractions, *Desalination*, 115 (1998) 1, p.63-70
- IV Niina Laitinen, Erkki Levänen, Antero Luonsi, Tapio Mäntylä, Jari Vilén, Keraamikalvo uusioveden valmistuksessa, *Alueelliset Ympäristöjulkaisut 74*, Pirkanmaan Ympäristökeskus, Tampere 1998, 48 pp.
- V Niina Laitinen, Antero Luonsi, Erkki Levänen, Tapio Mäntylä, Marianne Nyström, Ceramic membranes in pollution control – case studies, *Pollution Prevention and Environmental Risk Reduction, Topical Conference Preprints, The American Institute of Chemical Engineers, Annual Meeting, Miami Beach, FL, November 15-20, 1998*, p.202-214
- VI Niina Laitinen, David Michaud, Christophe Piquet, Nicholas Teillera, Antero Luonsi, Erkki Levänen, Marianne Nyström, Effect of filtration conditions and backflushing on ceramic membrane ultrafiltration of board industry wastewaters, *Separation and Purification Technology*, 24 (2001), p.319-328

- VII Niina Laitinen, Antero Luonsi, Erkki Levänen, Marianne Nyström, Effect of backflushing conditions on ultrafiltration of board industry wastewaters with ceramic membranes, *Separation and Purifications Technology*, 25 (2001), p.323-331
- VIII Niina Laitinen, Maaret Kulovaara, Erkki Levänen, Antero Luonsi, Nicholas Teillera, Marianne Nyström, Ultrafiltration of stone cutting mine wastewater with ceramic membranes –a case study, *Desalination*, 149 (2002) 1-3, p.121-125



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## NOMENCLATURE

$A$	filtration area	$m^2$
$CP$	concentration polarization + reversible fouling	-
$d_a$	width of the flow channel	m
$d_b$	height of the flow channel	m
$d_h$	hydraulic diameter of the duct	m
$f$	friction factor	-
$FR_{1-2}$	flux reduction from $t_1$ to $t_2$	%
$J$	permeate flux	$m^3/(m^2h)$
$J_{end}$	permeate flux at the end of the filtration	$m^3/(m^2h)$
$J_{rel}$	relative flux	-
$J_T$	permeate flux at temperature T	$kg/(m^2h)$
$J_1$	permeate flux at time $t_1$	$m^3/(m^2h)$
$J_2$	permeate flux at time $t_2$	$m^3/(m^2h)$
$J_{25^\circ C}$	permeate flux at $25^\circ C$	$m^3/(m^2h)$
$m$	mass	kg
$PWF_a$	pure water flux after	$m^3/(m^2h)$
$PWF_b$	pure water flux before	$m^3/(m^2h)$
$PWF_c$	pure water flux after cleaning	$m^3/(m^2h)$
$PWF_n$	pure water flux of a new membrane	$m^3/(m^2h)$

$Re$	Reynolds number	-
$t$	filtration time	s
$t_p$	time for permeate collection	s
$T$	temperature	°C
$v$	fluid velocity	m/s
$\Delta$	error	
$\mu$	fluid viscosity	Pa s
$\mu_T$	viscosity of water at temperature T	Pa s
$\mu_{25^\circ\text{C}}$	viscosity of water at 25°C	Pa s
$\rho$	fluid density	kg/m <sup>3</sup>
$\rho_T$	density of water at temperature T	kg/m <sup>3</sup>
$\tau_w$	wall shear stress	Pa

## 1 Introduction

On the membrane market, polymeric membranes are dominating and inorganic membranes are mainly used in special cases, where polymeric membranes cannot be used. In the inorganic membrane markets ceramic membrane materials are dominant, especially alumina membranes which are widely used. Ceramic membranes are especially suitable for processes with high temperatures and harsh chemical environments or for processes where sterilizability of the membrane is important. Because of this, the ceramic membranes have found many applications in the food, beverage, biotechnological and pharmaceutical industries as well as in the petrochemical industry, environmental control, electronic industry, gas separation and other process industries. In 1986, the market of membrane industry worldwide was about \$1 billion. In 1989, the market of inorganic membranes was about \$32 million and of ceramic membranes \$19 million. Nowadays, the worldwide market of the membrane industry is about 10 billion US\$ per year [Anonymous, 2002]. In food, beverage, and biotechnology applications inorganic membranes constitute 12% of the market. The main usage (80%) of inorganic membranes is in the dairy industry. [Hsieh, 1996, p. 5, 185-186, 576-577, 581; Burggraaf and Cot, 1996, p.2-3]

In this thesis a brief discussion on manufacture and modification of ceramic membranes with special attention to alumina membranes is presented. The effect of different operational parameters on performance of the membrane in the area of liquid filtration is discussed and liquid-filtration applications of ceramic membranes are presented in the literature review. In the experimental part the results are presented from the development process of the filtration equipment for a new type of ceramic membrane and the use of this equipment with different types of water is evaluated.

## 2 Ceramic membranes

Typically, porous ceramic membranes are asymmetric with a support thickness of about 1-3 mm. The microfiltration layer is usually 10-30  $\mu\text{m}$  thick and the most common oxides used for the membranes are zirconia ( $\text{ZrO}_2$ ) and alumina ( $\text{Al}_2\text{O}_3$ ). Ultrafiltration membranes are a

few micrometers thick and typical materials are alumina, zirconia, titania ( $\text{TiO}_2$ ) and ceria ( $\text{CeO}_2$ ). Nanofiltration membranes are less than  $1\mu\text{m}$  thick, generally made of zirconia and titania. The support and the microfiltration layer are elaborated by classical ceramic techniques, whereas the sol-gel process is used for ultra- and nanofiltration layers. The ceramic membranes have mostly been made in two main geometries: tubular and flat membranes. [Larbot, 1996, p. 119; Bonekamp, 1996, p.145; Larbot et al., 1993; Guizard et al., 2001]

In this chapter the advantages and disadvantages of ceramic membranes are briefly discussed. The manufacturing processes of tortuous pore membranes are presented with main attention to alumina membranes. Moreover, the possible modification methods are listed with attention to liquid filtration applications. In some cases the precoating of the membrane for example zirconium oxide is used to form a so-called formed-in-place membrane and is considered as a form of membrane modification. However, in this case they are considered as another type of membrane and not a membrane modification and thus they are excluded.

## **2.1 Advantages and disadvantages**

The strengths of ceramic membranes are: (1) high thermal stability, (2) a fine chemical stability and biocompatibility, and (3) good erosion resistance and non-compactability. These properties enable them to be used in more harsh environments than polymeric membranes and it permits more rigorous cleaning procedures, such as stronger cleaning agents, steam sterilization, backflushing, and ultrasonic cleaning. Moreover, the ceramic membranes are less susceptible to microbial attacks and biological degradation and they do not age. In some cases, they show catalytical or electrochemical activity. [Bhave, 1991, p. 26; Hsieh, 1996, p. 8-9; Burggraaf and Cot, 1996, p.3]

The weakness of ceramic membranes arises mainly from the manufacturing process, which makes it difficult to achieve a reproducible final product quality. This along with the intrinsically brittle character of ceramic membranes makes them always more expensive than polymeric membrane systems. Moreover, the price of the membrane system rises substantially with increasing demands on such product properties as porosity, pore size, reproducibility, and reliability. [Burggraaf and Cot, 1996, p.5-9]

## **2.2 Manufacture**

In general, the fabrication process of tortuous pore ceramic membranes involves several stages: at the beginning powder suspensions are formed, in the second stage, porous compacts are formed by packing suspensions into “green” compacts with a certain shape, and in the last stage the green compact is consolidated by heat treatment at high temperature. Reproducibility of the final properties is not easy to obtain due to the polydispersity of the initial powder. [Burggraaf and Cot, 1996, p.4-5]

The manufacture is concerned with macro pores (above 0.1  $\mu\text{m}$  in diameter) for microfiltration, micro pores (ranging from 0.1  $\mu\text{m}$  to 2-3 nm) for ultrafiltration and nano pores (less than 3 nm) for nanofiltration [Larbot et al., 1993]. At the moment there are commercial micro-, ultra- and nanofiltration membranes. Some examples of these ceramic membranes are presented in Table 1. In the following chapters, different steps of the manufacturing process are presented.

### **2.2.1 Slurry preparation**

The main components of slurry used for the fabrication of ceramic membranes are inorganic powder, organic additives and solvent. In the selection of the inorganic powder, important factors are particle size and distribution as well as the shape of the particles. They have an effect on porosity, pore size and pore size distribution of the final product. [Larbot, 1996; Levänen et al., 1994a]

Organic additives, such as binders, plasticizers, lubricants, deflocculants, anti-foaming agents, promoters of porosity, water retention agents, antistatic, chelating, and bactericide agents, are used during the manufacturing process to give the slurry the properties needed. The main requirement for the organic additives is that they must be burnt out without leaving ash and tar. The choice and quantity of organic additives is very important. They have an effect on the slurry properties, which affect the selection of the fabrication method (extrusion, tape casting, dip coating etc.) and the properties of the final product. [Larbot, 1996; Lafarga et al., 1998; Das and Maiti, 1998; Weiguang et al., 1999; Hyun and Kang, 1996; Björkert et al., 1999]

Table 1 Some commercially available ceramic membranes.

Manufacturer	Trade name	Membrane types	Geometries	Pore size / Cut-off	Membrane material	
Hermsdorfer Institut für Technische Keramik		MF		0.1-1.0 $\mu\text{m}$ 0.25 $\mu\text{m}$ , 0.4 $\mu\text{m}$ 0.11 $\mu\text{m}$	$\alpha$ -alumina titania zirconia	
		UF		5, 10, 60 nm 5, 30, 60 nm	$\alpha/\gamma$ -alumina titania	
		NF		3, 5 nm / 2, 6 kg/mol 0.9 nm / 0.45 kg/mol 1.0, 3 nm / 0.60, 1.5 kg/mol	zirconia titania silica	
Rhodia Orelis	Carbosep®	MF	Tubular, multichannel	0.14 $\mu\text{m}$	Support carbon/ Membrane layer zirconia- titania	
		UF		15, 50, 150, 300 kg/mol		
	Kerasep™	MF	Tubular, multichannel	0.1, 0.2, 0.45, 0.8 $\mu\text{m}$	Support monolithic alumina- titania/ Mem- brane layer zirconia or titania	
TAMI Industries	DisRAM INSIDE®	MF	Disk	0.14, 0.20, 0.45, 0.80, 1.40 $\mu\text{m}$		
		UF		8, 15, 50, 150, 300 kg/mol		
		NF		1, 3, 5 kg/mol		
	KéRAM INSIDE®	MF	Plate	0.14, 0.20, 0.45, 0.80, 1.40 $\mu\text{m}$		
		UF		8, 15, 50, 150, 300 kg/mol		
		NF		1, 3, 5 kg/mol		
	CéRAM INSIDE®	MF	Tubular, multichannel	0.14, 0.20, 0.45, 0.80, 1.40 $\mu\text{m}$		Support: alu- mina/titania/ zirconia/ Membrane layer: MF zirconia, UF & NF titania
		UF		8, 15, 50, 150, 300 kg/mol		
		NF		1, 3, 5 kg/mol		
USF (SCT)	Membralox®	MF	Tubular, multichan- nel, mono- lithic	0.1-12 $\mu\text{m}$	$\alpha$ -alumina	
		UF		20-100 nm	zirconia	
		NF		1-5 kg/mol	titania	



The solvent (for example water, organic solvent or their mixture) must dissolve the organic compounds used and it must evaporate. The evaporation characteristics of the solvent have an effect on the drying time of the green compact. [Larbot, 1996]

The preparation process of the slurry depends on the required thickness (paste, slurry, suspension). It can consist of the following steps: mixing, pugging and aging (for paste), milling and ultrasound treatment (for slurry), dispersing (for suspension, e.g. alumina and zirconia). The aggregation of particles in the slurry has an effect on pore size and water permeability of the final product. [Hsieh, 1996, p. 41; Larbot, 1996]

### **2.2.2 The sol-gel process**

The sol-gel process is used for the preparation of functional oxides. The suspension is achieved by synthesizing the solid particles in situ in liquid from organo-metallic precursors (e.g. boehmite and titania sols). There are two main routes through which the sol is prepared:

- (1) The colloidal route, in which a metal salt is mixed with water to form a sol. The sol is coated on a membrane support, where it forms a colloidal gel.
- (2) The polymer route, in which metal-organic precursors are mixed with organic solvent to form a sol, which is then coated on a membrane support, where it forms a polymeric gel.

Organic additives similar to those mentioned in slurry preparation are used in the process mainly for their beneficial effects on the final product quality. The coating is generally made with dip or spin coating and must be carried out at the sol stage. [Guizard, 1996; Larbot, 1996; Benfer et al., 2001]

The sol-gel process is used for example to manufacture  $\gamma$ -alumina membranes with pore diameters of 4-10 nm from a boehmite sol. In this case, polyvinyl alcohol in the boehmite dip solution enhances greatly the reproducibility and decreases the defect level of the final  $\gamma$ -alumina membranes. [Burggraaf, 1996, p.269-270]

The nanofiltration membrane fabrication has a few extra requirements compared to the manufacture of ultra- and microfiltration membranes:

- Individual grains in the sintered ceramic must preserve a size less than 10 nm. This can be enhanced by addition of metal ions, e.g.  $\text{La}^{3+}$ , to limit the pore growth and to suppress phase transformation. [Björkert et al., 1999; Burggraaf, 1996, p.297]
- The aggregation of particles at the sol stage must be prevented. This is achieved by the addition of a peptizing agent.

### 2.2.3 The fabrication process

The most common fabrication processes are extrusion, tape casting, dip and spin coating. From these, extrusion and tape casting are used for support systems, tape casting and dip coating are used for microfiltration membranes and dip and spin coating are used for ultra- and nanofiltration membranes. In the following, the main features of extrusion, tape casting and dip coating are presented:

In extrusion, paste is forced through the opening of a die to form a tubular or multichannel support. The green compact formed is dried at less than 100°C to eliminate water. [Larbot, 1996, p. 123-139]

Tape casting is used for making thin, flat, dense ceramics. The process is limited by the thickness of the films obtained. The green compact is formed from slurry as a result of the relative movement between the doctor blade and the support or carrier. In general, the casting speed varies from 0.1 to 1.5 m/min. After casting, the tape is dried. The dry tape is removed from the support and is very easily handled because of its plastic characteristics. [Larbot, 1996, p. 130-139]

Dip coating is used for multilayer membranes. The permeability of the support system used in dip coating must be higher than that of the membrane layer (at least by a factor of 10) and thus the thickness of each layer must be as thin as possible. There are two different methods of layer formation:

- Capillary colloidal filtration also called slip casting, in which the capillary suction of the substrate drives the particles to the interface, where the dry substrate comes into contact with the dispersion and the pore surface is wetted by the dispersion liquid.

- Film coating, in which the adhering dispersion layer is formed because of the drag force exerted by the substrate during withdrawal from the dispersion.

The critical factors in dip coating are the viscosity of the slip and the coating speed or time. The drying process starts simultaneously with the dip coating, when the substrate gets into contact with the atmosphere that has a relative humidity below 100%. In a multiple step process, after calcination of the first layer, the complete cycle of dipping, drying and calcination is repeated. For example an alumina coating with a median pore size of typically 100 nm can be prepared from a suspension (in water) of commercially available sub micron alumina powder with a mass based median diameter of 500 nm. [Bonekamp, 1996; Burggraaf, 1996, p.267]

As a rule, the thinner the slip is, the more critical the drying step is for the formation of defect free membranes. The drying has also an effect on the formation of the final microstructure. In general, drying is carried out at an intermediate temperature range of 80-350°C and it results in a hybrid organic-inorganic membrane. [Burggraaf, 1996, p.259; Guizard, 1996, p.228]

Firing (calcination and sintering) treatment strengthens the ceramic and helps the membrane to adhere strongly to the porous support. The goal is consolidation of the microstructure by neck-formation. It consists of two stages:

- Combustion of organics (calcination), which is crucial in determining the achievement of a crack-free membrane.
- Sintering of the ceramic by densification and grain growth. For sintering, a temperature below but approaching the melting point of the ceramic is used, e.g. 1100-1400°C for  $\alpha$ -alumina.

Calcination and sintering at relatively low temperature (300-400°C) and for a short time (few hours) do not produce thermally stable membranes. [Larbot, 1996; Bonekamp, 1996]

The temperature profile used for firing is critical especially if the support and membrane materials are different. It has an effect on pore size and the final phase composition. For example the phase transition from  $\gamma$ -alumina to  $\alpha$ -alumina takes place temperatures above 1000°C [Guizard, p.235; Kolari, p.75]. However, addition of other substances such as for example lanthanum oxide or titania can change this temperature. Lanthanum oxide is observed to in-

crease the temperature in which the phase transformation takes place, whereas titania decreases the phase transformation temperature [Björkert et al., 1999]. The pore size can be increased at the cost of decreasing porosity by controlled heating of the membrane in a temperature range of 400-1000°C for most common membrane materials. [Das and Maiti, 1998; Burggraaf, 1996, p.282; Wang et al., 1999; Das and Dutta, 1999; Grönroos et al., 1995; Levänen et al., 1994b; Hsieh, 1996, p.43, 50]

#### **2.2.4 Defects**

Defects are cracks or micro-cracks in the substrate layer, irregularities in surface roughness, pinholes or voids percolating the layer or large percolating pores as a result of the particle packing process. These last defects are not really defects because they are an unavoidable result of the particle size distribution in the slip and random packing. [Bonekamp, 1996, p.178-183]

The size of defects considered to be significant depends on the function of the membrane layer (support for MF, UF or NF). As a rule, defects in a support layer will transfer if they are the same size or thickness as the next layer. [Bonekamp, 1996, p.178-183]

How can the defects be avoided? The essential issue is the optimization of the fabrication process. The careful selection of raw materials for suspension; especially organic additives can have a significant effect on the defect formation. The selection of a suitable, good quality support is important. The significant characteristics of the support are pore size distribution, roughness, homogeneity, and purity of the surface. Care must be taken also in the preparation of the slurry for example sufficient de-aeration should be used. By optimization of the coating process (thickness of the formed layer, no partial gelation in the sol) the number of defects can also be controlled. Most of the defects form during the drying, calcination and sintering processes, when the shrinkage of the membrane layer occurs. Thus, the careful control of these process steps is crucial, especially when the support and membrane layers are made of different materials. However, sintering stress related damage does not occur in  $\alpha$ -alumina coatings on  $\alpha$ -alumina substrates at moderate sintering temperatures (1100-1250°C). Another important issue is a clean working environment: no dust particles or dirt, which can cause problems. [Bonekamp, 1996, p.178-183; Burggraaf, 1996, p.269-270; Guizard, 1996, p.227]

If, however, defects have occurred, a new layer can be applied on top of the defected layer to repair the problem. Chemical vapor deposition (CVD) and other membrane modification techniques may also be useful for repairing defects. [Bonekamp, 1996, p.178-183; Burggraaf, 1996, p.323; Hsieh, 1996, p.80-86]

## **2.3 Membrane modification**

The aim of the modifications is to further decrease the effective pore size [Lin, 1993; Lin and Burggraaf, 1993], and/or to change the chemical nature of the surface [Halfpenny et al., 2000; Ida et al., 1998; Dafinov et al., 2001a; Randon et al., 1995]. Material can be deposited on the membrane from either gases or liquids. In gas/vapor phase modifications, functional groups, e.g. hydroxyl groups, on the surface of the membrane act as reactive sites for modification with chemical agents such as silanes. Silanes can have many different tail groups, which make them ideal for tailoring the membrane properties. In liquid phase modifications, the membrane is dipped into a solution or sol and the modification layer is formed through either adsorption or impregnation. Depending on the wanted modification further treatment with drying and sintering might be necessary. [Bhave, 1991, p.55; Hsieh, 1996, p.81-85]

### **2.3.1 UV irradiation**

A new type of modification method tested with silica is the irradiation of the membrane surface with a UV laser. The radiation causes dehydroxylation of the surface (Figure 1) with a final-stage hydroxyl concentration similar to those obtained through thermal treatment at 1000°C and thus increases significantly the hydrophobicity of the surface. However, the dehydroxylation of a silica surface by UV irradiation is rapid and surfaces treated more than two years ago show that chemical change remains even long term. The advantage of the irradiation treatment over thermal treatment is that it is surface and spatially specific. [Halfpenny et al., 2000]

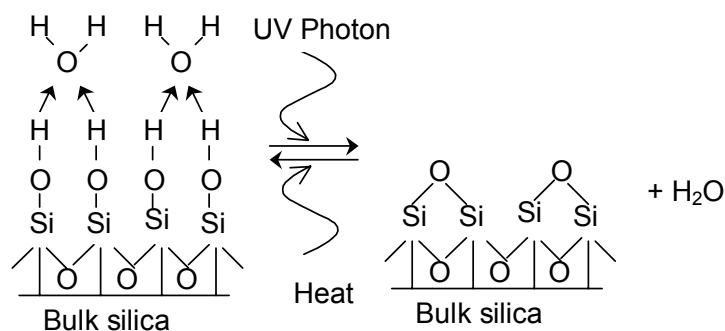


Figure 1 Dehydroxylation of silica surface. [Halfpenny et al., 2000]

### 2.3.2 Gas/vapor phase modifications

Gas/vapor phase modifications have been used to achieve ceramic deposits on ceramic membrane. At least, titania, alumina, and yttria-stabilized zirconia have been used for modifications with this method [Huang et al., 1999; Ott et al. 1997; Lin and Burggraaf, 1993]. The chemical vapor deposition can be used progressively to decrease the pore size of the membrane and the reduction achieved depends on the number of modification layers applied. In some cases, the deposit characteristics are location dependent. For example Huang et al. [1999] used this technique to obtain a titania coating on alumina discs. Titania is an interesting coating material since it has photo catalytic abilities, which might be useful for instance in wastewater treatment. Huang et al. [1999] found in their study that the modification could decrease the pore size of the substrate from 1-2  $\mu\text{m}$  to 64 nm. Moreover, a deposition temperature of about 300°C was found to be beneficial: the deposit had a rock-like packing and good adhesivity to the substrate.

Gas/vapor phase modification of the surface through silanization of the surface, has been utilized to immobilize enzymes on the surface of the membrane. The immobilized enzymes include glucoamylase [Ida et al., 1998; Ida et al., 2000a; Ida et al., 2000b], invertase, and  $\beta$ -fructofuranosidase [Nakajima et al., 1990]. The enzyme is connected to the aminopropyl groups of the silanized surface by glutaraldehyde cross linkage. For example, the enzyme activity of glucoamylase after immobilization was 27% of that of the free enzyme [Ida et al., 2000b], but on the other hand the immobilized enzyme showed greater stability than the free enzyme [Ida et al., 2000a]. The silanized surface has also been used to form the biotin-streptavidin affinity system [Tover et al., 1998]. In this case, biotin was covalently bonded to

amino groups of the silanized surface and then streptavidin molecules were immobilized on the biotin-functionalized membrane.

### 2.3.3 Liquid phase modifications

Liquid modifications, impregnation and adsorption, have been used to introduce ceramic, metallic, and enzyme immobilized modification on ceramic membranes. The ceramic modifications introduced through impregnation include magnesia, silica, alumina, and vanadium oxide [Bhave, 1991, p.55-57; Hsieh, 1996, p.81-85].

Alcohols have been used for the modifications to introduce hydrophobic character on the membrane and decrease the water permeability of  $\gamma$ -alumina membranes [Dafinov et al., 2001a]. The alcohol modification did not change the isoelectric point of the membrane. The ethanol-modified surface was stable in acidic conditions, as experiments with both hydrochloric and nitric acids showed. However, the modification could be removed by heat treatment at 250°C. Also acids, e.g. phosphoric and alkyl phosphonic acids can be used to change the surface characteristics (hydrophobicity, polarity) [Randon et al., 1995].

Enzymes and polymers can also be immobilized to the membranes through impregnation. For example  $\beta$ -cyclodextrin [Krieg et al., 2000] and pectinase [Szaniawski and Spencer, 1997] have been immobilized in this way. The immobilization of enzyme on ceramic membranes combines the strength and inertness of an inorganic support with the specific properties of the enzyme or polymer. For example a  $\beta$ -cyclodextrin polymer can separate enantiomers from each other.

### 2.3.4 Metal modifications

The metal modifications are applied on ceramics mainly to introduce catalytic activity on the membrane. For example palladium [Kim and Lin, 2000], which is one of the most common metals used, can be introduced into the membrane pores through impregnation. Also, palladium and copper or palladium and tin [Daub et al., 1999] have been inserted into the pore structure of ceramic membranes through impregnation and chemical vapor deposition. This kind of membrane can be used for denitrification of drinking water. The membrane acts in this case as a hydrogen diffuser.

### 2.3.5 Polymer coatings

The modification of ceramic membranes with polymers and organic-inorganic composite membranes forms its own group. Polymers that have been used include sulfonated polysulfone [Matsumoto et al., 1999a], poly (vinyl pyrrolidone) [Castro et al., 2000; Faibish and Cohen, 2001a; Faibish and Cohen, 2001b], poly (ethylene imide) [Lucas et al., 1998b; Lucas et al., 1998a], and poly (vinyl imidazole) [Chaufer et al., 1991; Chaufer et al., 1990; Mille-sime et al., 1995; Blainpain-Avet et al., 2000]. The aim in these polymeric coatings has been to introduce certain charges on the membrane surface, to change the pore size or to screen certain groups from the ceramic surface.

Matsumoto et al. [1999a] coated a ceramic support with sulfonated polysulfone to obtain negatively charged membranes that could repel vitamin B<sub>12</sub> and proteins, such as BSA. Chaufer et al. [1991] used poly (vinyl imidazole) to change the surface properties of the membranes in such a way that the membrane repels tetracycline and thus makes it possible to concentrate it. This is possible when the membrane is used in a pH-range, where the organic solute acts as a co-ion and thus does not affect the stability of the solute.

In some cases, these modifications can show properties that are dependent on shear and pressure conditions used in filtration. For example the hydraulic permeability of poly (vinyl pyrrolidone) -modified silica membranes increased with increasing pressure due to the decrease in the thickness of the grafted polymer layer with increasing pore-wall shear rate [Castro et al., 2000]. This behavior could be used to control the separation properties by changing the hydrodynamic conditions in the membrane pores. However, the successful application of the polymer surface that would have the flow-induced deformation requires optimization of the modification process. If the chain density in the modification layer is too high, deformation is not possible.

Faibish and Cohen [2001a, 2001b] used poly (vinyl pyrrolidone) modification on zirconia membranes to prevent irreversible fouling of the membranes. Since the main reason for the fouling in their case was the adsorption of anionic surfactant on hydroxyl groups and negatively charged groups on a zirconia surface they used poly (vinyl pyrrolidone) to screen them and thus decreased the fouling of the membranes. Moreover, they found that a polymer coat-



ing decreased the number of defects in the membrane and thus improved the retention of oil droplets.

## **2.4 Conclusions of ceramic membranes**

In general the manufacturing process of ceramic membranes includes the following steps: preparation of a suspension from ceramic powder with necessary additives, the packing of the suspension into “green” compacts with certain shape and consolidation of these green compacts by heat treatment. These steps are included in both the manufacturing of a ceramic support as well as for the manufacturing of the final membrane layers. In order to obtain good quality membranes the manufacturing process of the membranes should be optimized. With this optimization at least part of the weaknesses of the ceramic membranes can be avoided. However, since the optimization process is not an easy one it is always difficult to achieve reproducible final product quality. This is often considered as a weakness of ceramic membranes and is one of the reasons why the ceramic membranes are much more expensive than the polymeric ones. Moreover, the ceramic membranes are brittle. However, the ceramic membranes have strengths that overcome their weaknesses and these are good thermal, chemical and mechanical stability, biocompatibility, non-compactability, good resistance to microbial attacks and biological degradation.

Different kinds of modifications have been applied to ceramic membranes either to change the pore size or the surface properties of the membranes. Usually, the modifications have been initiated by:

- A need to achieve specific separation properties, which the ceramic membranes do not have as such
- A need to decrease irreversible fouling of the ceramic membranes with certain substances
- A need to introduce the membrane certain properties that can be controlled for example by changing operation conditions

### **3 Filtration performance**

The parameters that influence the filtration performance are the feed solution, membrane, and filtration conditions [Bhave, 1991, p.131]. Three main classes of phenomena concerning solvent and solute transport during membrane filtration are polarization, internal mass transport and fouling [Guizard and Rios, 1996, p. 569; Merin and Daufin, 1990]. They can be affected by changing the following parameters: hydrodynamics, mass transfer kinetics and thermodynamic equilibrium. Differences between inorganic and traditional organic elements mainly result from the structure and intrinsic properties of the materials [Bhave, 1991]. Flow in ceramic membranes occurs through intergranular spaces within the top layer, porous sublayers, and support, while in polymeric membranes it develops through the continuous network of openings from one face to the other. Moreover, metal oxides present electric charges and thus surface phenomena of ceramic materials are more strongly dependent on pH and ionic strength of solutions than those of polymeric materials are and this can lead to interactions.

In the following chapters, the parameters having an influence on the filtration performance and ways of making them more favorable are presented.

#### **3.1 Feed properties**

From the feed properties such factors as concentration, polydispersity, state of agglomeration, viscosity, charge, and presence of gases are important [Ousman and Bennasar, 1995; Matsumoto et al., 1988; Pouliot et al., 1995; McDonogh et al., 1998; Bhave, 1991, p.131]. In most ultra- and microfiltration cases, the smallest particle size present in the feed is very important for the selection of membrane pore size. The feed properties can be changed by pretreatments such as pH adjustment, thermal treatment, addition of chemicals, and pre-filtration. The pH adjustment [Börgardts et al., 1998] and thermal treatment can decrease the precipitation of certain substances and thus the fouling of the membrane. Chemicals can be added to the feed to increase the particle size through aggregation, and the retention of specific substances can be enhanced through micellation or complexation [Alami-Younssi et al., 1994]. The salt concentration of the feed and the valency of the salt present can also be important [Porter and Zhuang, 1996; Elzo et al., 1998; Ricq et al., 1999]. Feed concentration and particle size of the feed can be affected by prefiltration.

In general, the more complex the feed solution is the more difficult it is to find the important factors and the more likely the membranes are fouled. Increased feed concentration usually causes lower filtration flux due to thicker polarization and fouling layers.

### 3.2 Membrane properties

Membrane material and structure, especially pore size and characteristics of the membrane surface and support structure (thickness, porosity, wettability, zeta potential, surface and chemical properties) have an influence on the permeate flux and retention properties as well as on the fouling tendency. The ceramic membranes show in water amphoteric behavior (Figure 2) [Guizard and Rios, 1996] and thus their surface charge is pH dependent. Occurrence of a neutral and charged surface is due to the formation of metal aquo complexes at the oxide-solution interface. This behavior has an effect on permeate flux and fouling tendencies [Dumon and Barnier, 1992; Elzo et al., 1998; Ricq et al., 1999] as well as on retention [Porter and Zhuang, 1996]. In some cases the amphoteric nature of ceramic membranes can lead to preferential adsorption of a particular component and thus improve the retentions [Hsieh, 1996, p.123].

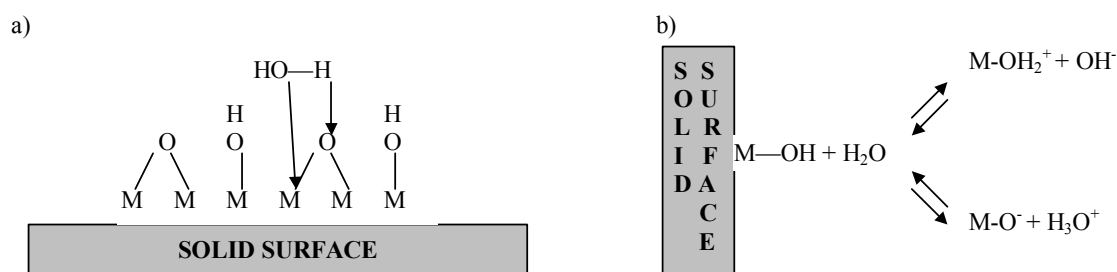


Figure 2 Mechanism of charged surface formation. a) Aquo complex formation. b) Amphoteric behavior of metal oxides. [Guizard and Rios, 1996, p.585]

In general, ceramic membranes have a composite structure, which is used to increase the permeability for small pore size membranes by decreasing the overall hydraulic resistance [Bhave, 1991, p.69]. Other important membrane properties are pore geometry (tortuosity) [Bhave, 1991, p.83], pore size, pore size distribution, and porosity [Bhave, 1991, p.131-132]. An increase in the pore size generally leads to an increase in the permeability and a decrease

in retentions, but it also leads to an increase in polarization and fouling [Ousman and Bennasar, 1995; Matsumoto et al., 1988; Ahn et al., 1998]. In most cases there is an optimal pore size, which depends on the nature of the feed and on the filtration conditions used. Recently, different membrane morphologies have also been found important, especially when backflow techniques are used [Ho and Zydney, 1999; Gan, 2001]

### **3.3 Filtration conditions**

From the parameters identifying the filtration conditions, pressure, cross-flow velocity, temperature, and percentage of recovery are the most important. Moreover, the permeate flux can be enhanced by using different methods such as backflow techniques, feed pulsation, two-phase flow, rotation of filter elements etc. Methods to reduce fouling can be classified, as presented by Guizard and Rios [Guizard and Rios, 1996], as (i) chemical cleaning methods, (ii) physical methods such as backflushing and the use of turbulence promoters, and (iii) hydrodynamic methods related to module design.

#### **3.3.1 Pressure, flow velocity, temperature, pH**

The permeate flow rate depends directly on the applied transmembrane pressure for a given surface area under otherwise uniform conditions [Bhave, 1991, p.135-136]. In Figure 3 the general behavior of the filtration flux with pressure is presented. The flux of the pure water is linearly pressure dependent. When the feed solution is more complex and contains also other substances, the flux behavior is more complex. At the beginning the flux increases linearly until the critical flux is achieved. Then the flux increase slows down until the limiting flux is achieved. Above the limiting flux, an increase in pressure does not have any positive effect on the flux; on the contrary it can lead to a decrease in flux due to the compaction of the fouling layers. In general, increasing flux leads to an increase in polarization and fouling, which limits the flux. [Ousman and Bennasar, 1995; Poirier et al., 1984; Matsumoto et al., 1988; Gésan-Guiziou et al., 1999; Pouliot et al., 1995; Huisman et al., 1998; Conrad and Lee, 1998; Ahn et al., 1998]

The generally recommended cross-flow velocity in micro- and ultrafiltration is 2-8 m/s [Cheryan, 1986]. An increase in velocity usually results in an increase in flux and it also increases the

critical flux [Ousman and Bennasar, 1995; Poirier et al., 1984; Matsumoto et al., 1988; Pouliot et al., 1995; Li et al., 1998; Bhave, 1991, p.134-135; Börgardts et al., 1998; Ahn et al., 1998]

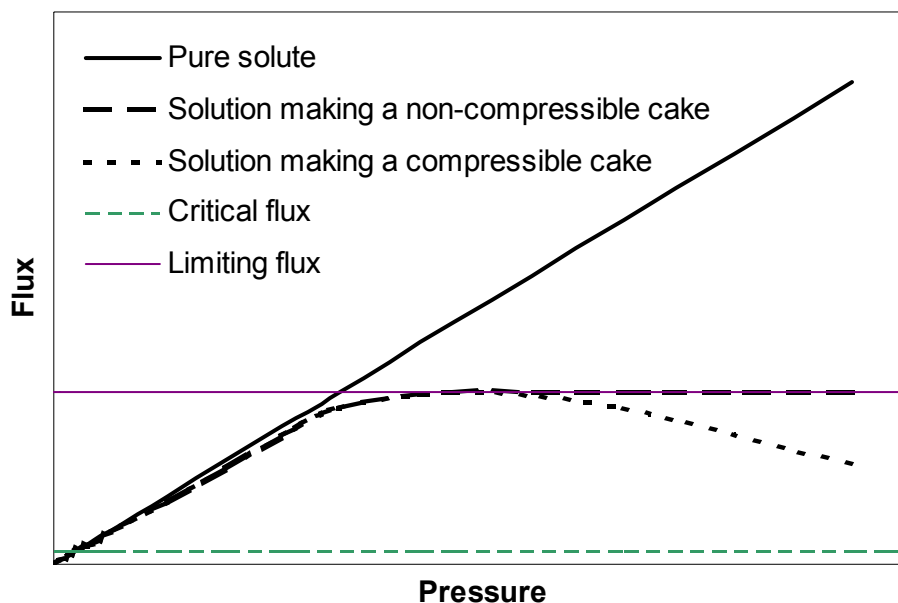


Figure 3 General behavior of filtration flux vs. pressure.

The effect of temperature and pH is partly presented already in the feed properties paragraph. However, it should be added that in general, flux increases with increasing temperature due to a decrease in viscosity and/or due to an increase in solubility of suspended solids [Bhave, 1991, p.136; Poirier et al., 1984]. The exception is the presence of calcium and magnesium salts that might precipitate when temperature is increased. This problem can be avoided at least in some cases through feed pretreatment. Temperature can also have an effect on the surface charge of the membrane [Mustafa et al., 1998]. The pH can have a significant influence on the permeation rate especially around the isoelectric point of certain colloids where they tend to destabilize and precipitate [Bhave, 1991, p.136-137]. It also has an effect because of the changes in surface charge of the membrane either due to the amphoteric nature of the ceramic surface or due to the specific adsorption of species as presented earlier [Elzo et al., 1998; Ricq et al., 1999].

The wall shear stress, which represents the forces applied by the fluid flowing tangentially along the membrane element, is also important. There exists a critical ratio for the flux/wall

shear stress above, which irreversible cake formation begins and the membrane starts to foul. [Gésan-Guiziou et al., 1999; Huisman et al., 1999; Boyaval et al., 1996; Le Berre and Daufin, 1996]

### **3.3.2 Backflow techniques**

Backflow techniques, such as backwashing, backflushing, and pulsing, can increase the permeate flux, if it is limited by the formation of a cake layer, by removing the formed layer from time to time [Jaffrin et al., 1990; Sondhi and Bhave, 2001; Nipkow et al., 1989; Park et al., 1997; Mugnier et al., 2000; Gan et al., 1997; Ho and Zydney, 1999; Börgardts et al., 1998]. It has a similar effect to that of high cross-flow velocity and thus if a high enough cross-flow velocity is used backflushing does not improve the flux any more.

Backflushing can increase solute transmission through removal of the fouling layer [Levesley and Hoare, 1999], but it can also decrease retentions if the cake layer is acting as a secondary membrane and retaining substances.

### **3.3.3 Other flux enhancement methods**

A number of other methods for flux enhancement have also been used and they include feed pulsation [Jaffrin et al., 1994; Gan et al., 1997; Ho and Zydney, 1999; Hadzimajlovic and Bertram, 1998; Gupta et al., 1992; Gupta et al., 1993; Blainpain-Avet et al., 1999], two-phase flow [Mercier-Bonin et al., 2000; Cheng et al., 1999], rotating and vibrating filters [Viadero et al., 1999], electric and ultrasonic fields during filtration [Sabri et al., 1997], hydraulic enhancements such as for example inserts, baffles and stamped membranes [Broussous et al., 2001]. Their positive effect on flux is very much dependent on other filtration parameters and should be evaluated case by case.

## **3.4 Conclusions of filtration performance**

The effects of the feed properties, the membrane properties, and the filtration conditions are obviously very important for the success of a membrane filtration process. Important feed properties are chemical composition, concentration, polydispersity, state of agglomeration, viscosity, charge, and presence of gases. Membrane properties that have an effect on the fil-

tration process are the membrane material and its characteristics as well as the structure of the membrane and the support. The important factors describing the filtration conditions are pressure, cross-flow velocity, wall shear stress, temperature, pH, and percentage of recovery. The filtration performance is almost always a question of optimization and balancing between the separation desired and the permeate flux needed for the process to be economically interesting. A well chosen feed pretreatment, a proper selection of membrane in relation to the feed properties, and an optimization of filtration conditions can help a lot in preventing membrane fouling, improving permeate flux, and enhancing the separation required. The permeate flux can also be enhanced by using specific methods such as for example backflushing.

#### **4 Liquid-phase separation applications**

Most of the commercial applications for ceramic membranes are either for micro- or ultrafiltration. However, recently also ceramic nanofiltration membranes have been developed. Microfiltration is mostly applied in cases where liquid streams contain particulates, and ultrafiltration is used when smaller molecules are removed. Separation is achieved mainly by a sieving mechanism. Nanofiltration is a possible option when separation of dissolved ions is desired, but a total rejection of all ions is not necessary. The separation is based on sieving and charge effects of the membranes.

The first large-scale commercial success of ceramic membranes has been in the food and beverage industries. However, significant applications are found also in other areas, such as biotechnology, pharmaceutical, petrochemical, and other process industries as well as in environmental control. The major advantages of ceramic membranes in the area of food and beverages are their resistance to alkaline cleaning solutions, their stability in steam sterilization, better capability to withstand higher operating pressures, and a consistent pore size. In cross-flow microfiltration applications, the major advantage of the ceramic membranes has been the possibility to use uniform transmembrane pressure (UTP), which for example in dairy industry has enabled high fluxes and low fouling. In biotechnology and pharmaceutical applications [Shackleton, 1987], the biocompatibility of the membranes is important. The thermal and chemical stability of ceramic membranes is a major advantage in petrochemical, textile,

pulp and paper processing as well as in the treatment of metal cleaners. However, in all these application areas the ceramic membranes have to compete with the polymeric membranes which are becoming more and more stable and which have an advantage of much lower prices. The use of ceramic membranes can only be justified in cases, where they give much better performance, or in cases, where there are no suitable polymeric membranes available. The following sections will give more information on applications or possible application areas of ceramic membranes. [Hsieh, 1996, p.185]

## **4.1 Food processing**

The market share of inorganic membranes in the food and dairy industry is about 10% [Bhave, 1991, p.209]. The main applications can be roughly divided into concentration of soluble molecules and suspended solids and clarification by removing suspended solids. As already mentioned, the main usage of inorganic membranes is in the dairy industry, in which the key to success has been the invention of UTP (uniform transmembrane pressure) mode [Sandblom, 1974]. In UTP mode the permeate and the feed flow are carried out in parallel and in the same direction, which means that the pressure drop in the permeate channel will arise in the flow direction. In this way the transmembrane pressure is maintained constant along the entire filter area. Some studies have also been made concerning the usage of inorganic membranes for the concentration of other vegetable and animal proteins as well as for the processing of starch and sugar.

### **4.1.1 Dairy industry**

The first industrial-scale food application of inorganic membranes was the concentration of whey proteins reported in 1980. In recent years, inorganic membranes have been widely used for microfiltration of milk and whey and for ultrafiltration in high viscosity fluid applications (e.g. highly concentrated milk). [Hsieh, 1996, p.186-187; Merin and Daufin, 1990]

The applications in the dairy industry can be divided into bacteria removal, concentration of milk and milk products plus concentration of whey proteins [Cueille et al., 1990]. Typical flux values and protein retention for ZrO<sub>2</sub>-based membranes in the concentration of dairy products are given in Table 2. The major factor limiting the use of membrane technology is



fouling, which in the dairy industry is mainly caused by proteins, lipids and calcium salts [Merin and Daufin, 1990; Vetier et al., 1988]. The fouling can be decreased to some extent by pretreating the feed streams. Some examples of pretreatments are preclarification and demineralization. Moreover, optimization of operating conditions [Van der Horst et al., 1994; Kulozik and Kessler, 1990; Gésan-Guiziou et al., 1999; Pafylas et al., 1996; Marshall et al., 1996] and different flux enhancement methods such as backshock [Guerra et al., 1997] can decrease fouling. However, if fouling despite all efforts occurs, then membrane cleaning [Daufin et al., 1991a; Daufin et al., 1991b; Trägårdh, 1989; Daufin et al., 1992; Trägårdh, 1994; Cabero et al., 1999] is very important.

Table 2 Typical fluxes and protein retention for a MEMBRALOX ZrO<sub>2</sub>-based membrane with 100 nm pores (multi channel with 4 mm diameter channels) in the concentration of dairy products. J = flux in l/(m<sup>2</sup>h), R = protein retention in %. [Gillot et al., 1990]

	CONCENTRATION FACTOR									
	1.2		2		4		10		15	
	J	R	J	R	J	R	J	R	J	R
Reconstituted skim milk	146	99.4	95	99.4	17	99.4				
Pasteurized skim milk	150	99.2	92	99.1	29	99.0				
Pasteurized whole milk	138	99.0	94	99.0	18	99.0				
Raw whole milk	138	99.0	99	99.0	20	99.0				
Soft whey – pH 6.2					130		90	98.0	75	
Acid whey – pH 4.5					85	98.0	63	99.0	51	99.0
Lactic curd – pH 4.3	216	98.0	140	97.0	95	97.0				

The removal of bacteria from milk by microfiltration is based on the fact that bacteria are typically larger than 0.2 µm. At the same time the bacteria are removed so are the fats because the size of fat globules is usually from 0.1 to 2 µm. The best-known commercial method for bacteria removal from milk is the Bactocatch process by Alfa-Laval [Holm et al., 1986]. The principle of the Bactocatch process is microfiltration of milk with a uniform transmembrane pressure, which helps to decrease fouling. It is used for the production of low fat (0.5 w-%) and medium fat (1 w-%) milk. The bacteria removal efficiency of the process is greater than 99% and fluxes over 700 l/(m<sup>2</sup>h) at 50°C have been achieved with Membralox® membranes [Bonneau et al., 1991; Cheryan and Alvarez, 1995, p. 435-439]. An industrial process using this technology is operated in Villefranche, Lyon, and is producing 2000 l/day of fresh milk [Drioli and Romano, 2001].

Some experiments have also been made to remove bacteria from cheese brine. An experiment made with ceramic Membralox® membranes, with a 0.8 µm pore size, prove that bacteria removal of over 99% and an average permeate flux of 600 l/(m<sup>2</sup>h) can be achieved. [Pedersen, 1992, p. 46-47]

Raw milk, pasteurized whole and pasteurized skimmed milk as well as acidified milk can be concentrated. The purpose of the concentration of raw or pasteurized whole milk is to prepare a liquid pre-cheese material with high protein content (higher than 20-22%). Ceramic membranes are used for ultrafiltration due to the high viscosity of the concentrates. Moreover, the better stability and easier cleanability of ceramic membranes make them a more attractive choice than polymeric membranes. [Hsieh, p.188-189; Thoraval, 2000; Vadi and Rizvi, 2001]

The concentration of pasteurized skimmed milk, also called milk protein standardization, is designed to maintain a constant protein level in milk all year around. Microfiltration with α-alumina and zirconia membranes with a pore diameter of 0.1 to 0.7 µm is used in commercial production. In fact, milk protein standardization is one of the major commercial successes of inorganic membranes in the food industry. [Hsieh, 1996, p.190-191; Van der Horst et al., 1994]

Some experiments have also been made to concentrate some of the milk proteins. Surel and Flamelart [1991] have microfiltered sodium caseinate in order to extract beta caseinate. Lucas et al. [1998b] studied the fractionation of negatively charged proteins from whey protein concentrates at pH 7 and Chaufer et al. [1991] have studied the extraction of lactalbumin from whey proteins with modified ceramic membranes.

In production of whey protein concentrates, inorganic membrane filtration can be used at different stages of the process [Hsieh, 1996, p.193-194]. Figure 4 presents the process scheme of whey protein concentrate production. Microfiltration membranes are utilized to remove residual fats and phospholipids. This improves the quality of the feed to the subsequent ultrafiltration step and decreases the fouling during ultrafiltration. Ultra- and diafiltration are used for producing whey protein concentrates of high purity (70-95%). The ultrafiltration of whey has been practiced since the early 1970s.

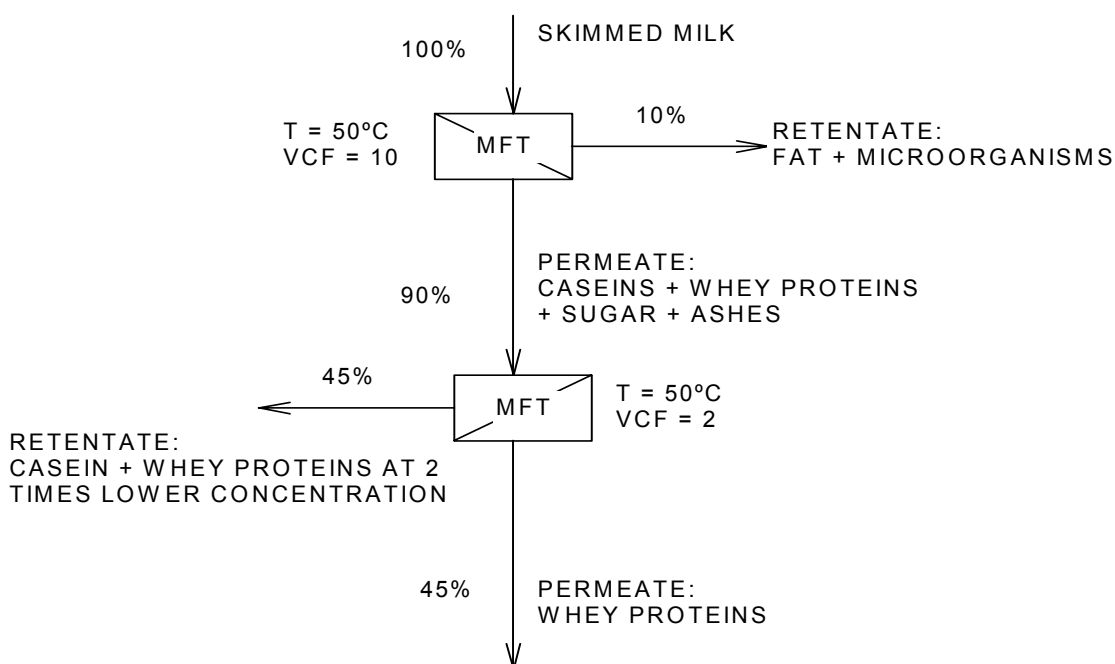


Figure 4 Process scheme of whey protein concentrate production. [Bonneau et al., 1991]

Gésan et al. [1991] have reported working conditions and performance of an industrial micro-filtration plant used for de-fatting rennet casein whey. Numerous studies concerning the filtration of whey proteins have been published and the main interest in the reported whey filtration studies has been on fouling phenomena and its understanding [Gésan et al., 1994; Gésan et al., 1993; Pouliot et al., 1994; Daufin et al., 1991c; Pouliot et al., 1995; Aimar et al., 1988; Taddei et al., 1989; Labbe et al., 1990; Daufin et al., 1991d; Daufin et al., 1991b; Cueille et al., 1990; Vallejo et al., 2001; Ricq et al., 1996].

#### 4.1.2 Protein concentration

The other major area for inorganic membranes in food processing is protein recovery and concentration. The protein solutions studied include fish and egg proteins, animal blood, soymilk, and gelatin solutions [Bhave, 1991, p. 247-248; Hsieh, 1996, p. 195-198; Cueille et al., 1990].

Watanabe et al. [Watanabe et al., 1989] have studied the processing of wastewaters in the fishing industry. They have filtered the wastewaters with dynamic membranes composed of

the water-soluble protein on a porous ceramic support. The dynamic membranes can recover essentially 100% of the protein. Porous ceramic supports were used because they have better resistance to chemicals and heat during cleaning than polymeric supports. [Hsieh, 1996, p. 195]

Jaouen, Bothorel and Quéméneur [1990] reported in their overview on membrane processes in the fishing industry and aqua cultural farming that the only industrial application in France is an IMECA unit equipped with ceramic SCT membranes, which is used in the treatment of fish wastewaters for the clarification of enzymatic hydrolysate juice.

Today's tendency is more towards extraction and preparation of substances with added value, which can be further used in other industries. For this purpose Matsumoto, Sudoh and Suzuki [1999b] have studied the separation of bonito extract with modified ceramic membranes. They achieved extraction of the taste compounds of bonito extract from putrefaction ingredients, which makes it possible to produce high-grade seasoning.

Zirconia membranes have been used to separate and concentrate egg white proteins from yolk. Depending on the cut-off of the membrane the protein solids can be increased from 11-12% to 32-35% with 20 kg/mol zirconia membranes or from 24% to 40-50%, with 70 kg/mol zirconia membranes. [Hsieh, 1996, p.198; Bhave, 1991, p.247; Cueille et al., 1990]

Slaughterhouse wastes contain substantial amounts of protein. Blood and wastewater could be concentrated by ultrafiltration [Belhocine et al., 1998]. Ceramic membrane ultrafiltration followed by drying has been used for processing blood plasma to powder products. [Hsieh, 1996, p.198; Cueille et al., 1990; Lewis, 1996, p.127]

Another important animal product is gelatin. Microfiltration can be used for the purification of gelatin by removing dirt, coagulated proteins, fats, and other particulated material. Ultrafiltration can be used for further concentration and improvement of the gelling properties of the gelatin [Lewis, 1996, p.127; Grandison and Finnigan, 1996, p. 150; Scott, 1995, p.238; Short, 1988]. The electro-ultrafiltration studies [Rios and Freund, 1991; Rios et al., 1988] for concentrating gelatin have proved that the application of an electric field improves the flux and protein rejections.

Soybeans are the most important source of vegetable proteins. Ultrafiltration is utilized for the concentration of soymilk proteins as well as for the removal of oligosaccharides. On an industrial scale, zirconia membranes have been used for concentrating. [Bhave, 1996, p.247-248; Hsieh, 1996, p.198; Cueille et al., 1990; Berry and Nguyen, 1988]

#### **4.1.3 Other food processing applications**

Other applications of ceramic membranes in the food industry can be found in sugar, starch, and soy sauce [Hagasewa et al., 1991] processing. In addition, there is a membrane plant to separate grease and particles in soup manufacture [Horgnies, 1994] as well as a plant to extract substances of low molar mass from algae [Jaouen et al., 1990]. These low molar mass extractable substances are easily assimilable to the human organism and they are used in dietetics-cosmetology. The membrane plant consists of a ceramic ultrafiltration step for the separation of insoluble and macromolecular compounds and a reverse osmosis step for concentrating.

In the sugar industry, the following streams have been considered for membrane separation [Trägårdh and Gekas, 1988]:

- The clarification of raw juice [Bubník et al., 2000; Nene et al., 2000]
- The treatment of thick juice
- The treatment of molasses
- The treatment of raw sugar [Nene et al., 2000].

The advantage of using ceramic membranes for the treatment of thick juice and raw sugar is arising from the fact that these fluids have a high viscosity, which increases with the increasing concentration and decreases with an increase of temperature. Moreover, these process streams have much smaller volumes to be treated than the raw juice. However, most of the studies have concentrated on raw juice, since in that case the advantages achieved with membrane filtration compared to traditional processes (e.g. centrifugation) are more evident. Bolduan and Latz [2000] presented a case in which centrifugation, which was used to remove pulp from juice, was replaced by microfiltration with ceramic membranes in order to improve

the product quality and diminish product losses. The microfiltration improved the glucose quality and that combined with optimization of the other process steps led to an overall reduction of product losses by approximately 7%. The fouling of the membranes is a problem also in the sugar industry and some studies concerning fouling [Khayat et al., 1997] and flux enhancement [Jacob and Jaffrin, 2000] have been published.

Starch hydrolysates and dextrose syrups produced with acid, acid-enzyme, or enzyme-enzyme catalyzed processes need to be clarified. Microfiltration can be used for clarification. However, impurities in feed can cause significant flux loss. Singh and Cheryan [1997] have studied the effect of operation parameters on fouling of microfiltration membranes. They [Singh and Cheryan, 1998] also presented an economic analysis for a ceramic membrane microfiltration system for corn starch hydrolysate. They showed that for clarification of 113.6 m<sup>3</sup>/h of corn starch hydrolysate the annual operation cost of a microfiltration plant would be 0.52 million USD compared to 1.8 million USD for a rotary vacuum precoat filter. The total capital cost for the membrane plant would be 2.08 million USD, which means that with an annual saving of 1.3 million USD, the payback period would be 1.6 years. Thoraval [2000] has presented an example of an ultrafiltration plant used for clarification of starch hydrolysate, in which the replacement of the old ceramic membranes with a new type of ceramic membrane increased the permeate flux by 35%.

## **4.2 Beverages and drinking water**

In recent years, the next largest application of inorganic membranes has been filtration of alcoholic and non-alcoholic beverages and drinking water. In the beverage industry, filtration is used for clarification. The filtration aims at the removal of suspended particles, precipitates and microorganisms. [Hsieh, 1996, p.200; Siskens, 1996, p.629]

### **4.2.1 Potable water**

Ceramic-membrane-based filtration systems have been used for the production of potable water since 1984 [Pouët et al., 1991] and at the beginning of 1991 in France existed already 15 installations working with ceramic membranes. In the production of potable water the membrane filtrations are mainly used for the removal of suspended solids, precipitates caused by water hardness and/or salts, turbidity, and microorganisms (algae, bacteria, fungi) [Siskens,

1996]. In karstic groundwaters [Bourdon et al., 1989] the main problem is turbidity, the level of which may increase substantially during certain periods (rainfalls, snow melting). In surface waters the filtration is used to remove organic substances and microorganisms [Bodzek and Konieczny, 1998; Drozd and Schwartzbrod, 1997; Moulin et al., 1991] and in springs and bore wells to remove iron and other inorganic substances [Tazi Pain et al., 1990].

Microfiltration with ceramic membranes is applied, since the ceramic membranes are not subject to abrasion and bacterial contamination as easily as organic membranes [Duclert and Rumeau, 1990]. Moreover, they can maintain their retention and flow properties with time. A pore size of 0.2  $\mu\text{m}$  has been found to be sufficient in most cases. It is preferable to work with filtration pressures of 1 to 2 bars and crossflow velocities of 1-2 m/s. Backflushing can be used to reduce fouling of the membranes. Most of the existing microfiltration applications use coagulation as a pretreatment to reduce membrane fouling and improve the retention of colloids. Yuasa [1998] has studied coagulation-microfiltration and adsorption-ultrafiltration of river and lake waters with ceramic and polymeric membranes. Moulin, Bourbigot and Faivre [1991] reported the use of ozonation-coagulation for the potabilization of surface waters. The permeate fluxes reported for potable water production [Gillot et al., 1990; Bourdon et al., 1989; Bodzek and Konieczny, 1998; Tazi Pain et al., 1990; Bauer et al., 1991] have been around 800-1000 l/(m<sup>2</sup>h).

In the last few years, research on ceramic nanofiltration membranes has come to the stage where their applications in processes has started to be studied. Alami-Younssi et al. [1995] have suggested that nanofiltration with ceramic membranes could be used for the removal of nitrate ions in soft drinking water. However, the low permeate flux of nanofiltration membranes has been a constraint for industrial applications.

#### **4.2.2 Juices**

Fruit juice clarification is one of the earliest liquid-filtration applications of ceramic membranes [Gillot et al., 1990]. For example Membralox® membranes are used in industrial plants in Germany, France, Eastern Europe and the USA. The success of membrane filtration has been based on the fact that traditional clarification of fruit juices has been time-consuming and labor-intensive. Thus, membrane filtration can simplify the production proc-

ess, decrease the operation and energy costs as well as shorten the processing time. In Figure 5 traditional and UF production processes for apple juice are compared. The clarification of apple juice [Cueille et al., 1990; Gillot et al., 1990] is probably the most common application, but applications for citrus juice [Cueille et al., 1990; Gillot et al., 1990] also exist and clarifications of pineapple juice [de Carvalho et al., 1998] and apricot puree [Hart et al., 1989] have been studied.

Capanelli et al. [1994] have compared polymeric and ceramic membranes in the clarification of orange and lemon juices. They achieved higher permeate fluxes with the ceramic membranes at a lower Reynolds number than with the polymeric membranes and thus concluded that ceramic membranes might have greater energy efficiency for industrial applications.

The main reason for the membrane fouling during clarification of fruit juices is pectins. The pectins can be removed by enzyme pre-treatment of the feed [Alvarez et al., 1998]. Szaniawski and Spencer [1991; 1996; 1997] have studied the filtration of citrus and apple pectin solutions and the use of immobilized pectinase for flux improvement. Gupta et al. [Jaffrin et al., 1990; Gupta et al., 1992; Gupta et al., 1993] have studied the use of backflushing as well as pressure and flow pulsation of the inlet flow as a means to increase the permeate flux in microfiltration of apple juice. Enzyme treatment is mainly used in combination with microfiltration whereas backpulsing is important when the use of enzymes are avoided due to their potential side effects on health [Bolduan and Latz, 2000]. The combination of enzyme treatment and ceramic membrane microfiltration with an absorber can be used also for citrus fruit juices.



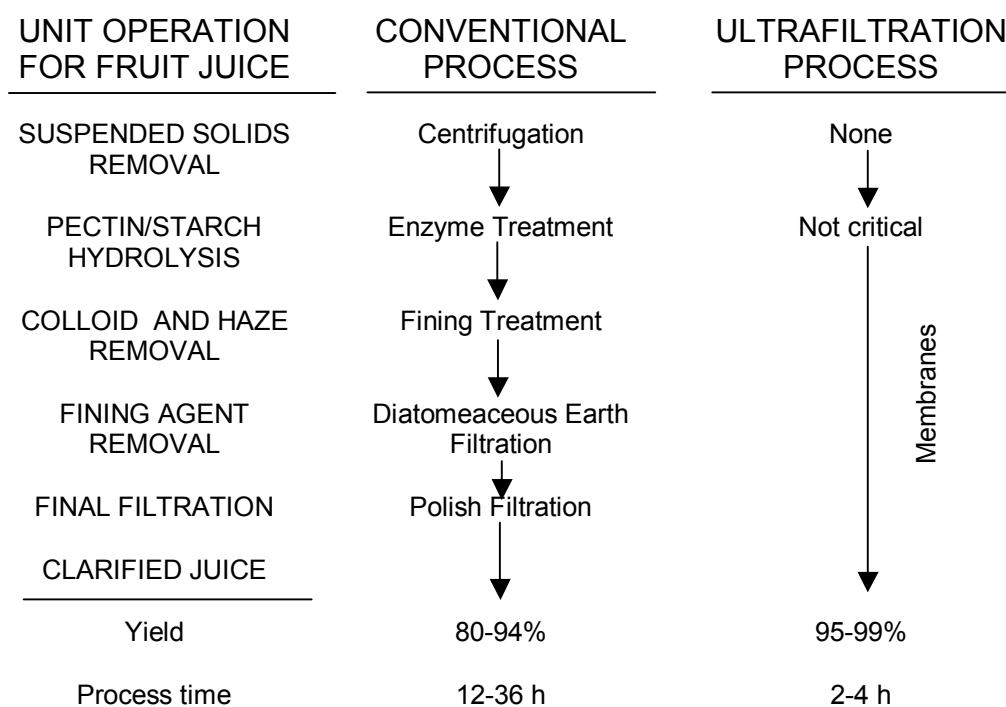


Figure 5 Manufacture of apple juice by a traditional and an ultrafiltration process. [Cheryan and Alvarez, 1995, p.447]

#### 4.2.3 Alcoholic beverages

In the area of alcoholic beverages, ceramic membranes are used for the clarification and sterilization of the final products. Ceramic membrane applications exist at least for the filtration of wine and beer [Cueille et al., 1990; Gillot et al., 1990] as well as for sake and vinegar [Hagasewa et al., 1991]. Some experiments have also been made on the filtration of cider [Finnigan and Skudder, 1989], vinegar [Güell and López, 2001] and fortified wines [Navrotsky et al., 1991; Avakiants and Balinov, 1991].

Walla and Donhauser [1990] have estimated that in the 1990s the amount of kieselgur needed for the world beer production of approximately 97 million m<sup>3</sup> has been circa 130 000 to 140 000 t/year. By membrane filtration the amount of waste generated and chemicals used during the production can be considerably decreased. Finnigan et al. [1989] have presented that a brewery producing 165 000 m<sup>3</sup> of beer per year could achieve potential savings of 600 000 £ (in year 1989) by using ceramic membrane filtration for unrefined beer. In the savings they only took into account the savings from decreased chemical consumption, improved

yield and decreased amount of effluent. The use of membrane filtration instead of a conventional process is advantageous also since membrane filtration produces a sterile product and further sterilization is not necessary.

Membrane filtration is mainly used in two areas: in beer clarification and in the recovery of tank bottoms. For Membralox® membranes these applications for example have existed since 1988 [Gillot et al., 1990]. Some research has also been made on beer recovery from spent yeast [Meunier, 1990; Schlenker, 1998]. Also in beer filtration the membrane fouling is a problem and thus a number of studies concerning membrane fouling [Gan et al., 1997; Blainpain-Avet et al., 2000; Fillaudeau and Carrère, 2002] and cleaning [Gan et al., 1999] as well as flux enhancement [Kuiper et al., 1998; Blainpain-Avet et al., 1999; Gan, 2001; Stopka et al., 2000] has been published.

As in breweries also in wineries membrane filtration can be used to replace clarification, stabilization, and sterilization steps. The ceramic Membralox® membranes are for example used to further concentrate tank bottoms or centrifuge concentrates [Gillot et al., 1990]. Békéssy-Molnar [2000] filtered Hungarian red and white wines using ceramic membranes and Urkiaga et al. [2000] have used ceramic microfiltration membranes for the clarification of Rioja Alvesa red wine. They both found that filtration with ceramic membranes did not cause changes in organoleptic qualities of the wines. Moreover, some of the studies have been published concerning fouling [Poirier et al., 1984; Belleville et al., 1991] and flux enhancement [Jaffrin et al., 1994] in clarification and stabilization of wines.

### ***4.3 Biotechnology and pharmaceutical applications***

In biotechnology and in pharmaceutical applications, the main interest has been on the filtration of fermentation broths. However, sometimes it is difficult to discern the biotechnology applications from applications in other more established industries like for example the dairy industry or from environmental applications such as wastewater treatment processes. Moreover in biotechnology, membrane bioreactors are often used for enzymatic and microbial conversion.

In biotechnology, ceramic membranes have been used for primary extraction, purification, and concentration of biomass, antibiotics, vitamins, amino acids, organic acids, enzymes, biopolymers, and biopesticides [Cueille et al., 1990]. There are also applications in the treatment of vaccines, recombinant proteins, cell cultures, and monoclonal antibodies as well as in continuous fermentation.

#### 4.3.1 Fermentation broths

Rudd [1998] presented a case study from the cosmetics industry in which a fermenter broth containing extra-cellular product, bacterial cells and cell debris was filtered to produce a clear and sterile permeate for further processing. In this case, tubular ceramic membranes with a pore size of 100 nm replaced the polymeric hollow fiber membranes. The ceramic membrane system diminished the time used for processing of the product, increased the yield by 8%, and saved in membrane replacement costs.

Some filtration studies of different bacterial cultures have been reported by Mourot et al. [1989], Fane et al. [1990], Hodgson and Fane [1991], Boyaval et al. [1996], Hodgson et al. [1993], and Cardis and Papathanasiou [1997]. Boyaval and Corre [1987] and Blanc and Goma [1989] have studied the production of propionic acid with *Propionibacterium acidi-propionici* using ceramic membrane ultrafiltration for cell recycle. Boyaval and Corre [1987] achieved a volumetric productivity of 14.3 g/l/h and Blanc and Goma [1989] achieved a volumetric productivity of 5 g/l/h for the propionic acid and that of 3.2 g/l/h for the biomass. Boyaval et al. [1987] have studied continuous lactic acid fermentation of sweet whey permeate with ceramic membrane ultrafiltration for cell recycle. Börgardts et al. [1998] have used an integrated bio-process for the simultaneous production of lactic acid and dairy sewage treatment.

Cowieson and Gallagher [1991] evaluated the use of Ceramesh filters for filtration of lysed yeast. They achieved a concentration of 18% total solids, before the permeate flux began to decline. Cheryan and Bogush [1994], Lafforgue et al. [1987], and Chang and his group [Park et al., 1997; Zhang et al., 1998; Park et al., 1999; Lee et al., 2000] have used ceramic membranes to process ethanol fermentation broths. The goal has been to improve the fermenter productivity to the higher cell densities and continuous removal of product. Chun and Rogers [1988] have done the same for the ethanol/sorbitol process.

Haarstrick et al. [1990] have studied microfiltration in the separation of fungal cells and the purification of the produced polysaccharide. They concluded that cross-flow microfiltration could be an alternative to conventional separation including purification processes and suggested that a diafiltration mode should be used in order to avoid the problems arising from the high viscosity of the broths.

#### **4.3.2 Other biotechnology and pharmaceutical applications**

Adikane et al. [1999] have used a ceramic microfiltration membrane to optimize penicillin G recovery from fermentation broth. They achieved 41% reduction in processing time by optimizing the cross-flow velocity from 1.3 m/s to 3.8 m/s. Moreover, they showed that the operating fluxes could be regenerated and a 98% recovery of penicillin G could be obtained over 12 cycles. Harris et al. [1988] evaluated the use of ceramic microfilters in the continuous production of  $\beta$ -lactam. They found that microfiltration could be used without any negative effects to filter the *Streptomyces olivaceus* fermentation broth and thus enable the continuous production of antibiotics under sterile conditions. Chaufer et al. [1991] have studied the use of modified ceramic membranes for the concentration of tetracycline.

Nipkow et al. [1989] have used ceramic microfiltration for cell recycle in a pilot system for continuous thermo-anaerobic production of exo- $\beta$ -amylase. The filtration rates were 20-60 l/(m<sup>2</sup>h) and the productivity of  $\beta$ -amylase and the concentration of biomass were increased 11- and 12-fold, respectively.

Conrad and Lee [1998] have studied microfiltration for the recovery of a water-soluble, chiral compound of therapeutic interest from a bioconversion broth of whole cells and soybean oil. They found that it was possible to use microfiltration to harvest an aqueous product stream from the oil-water bioconversion broth.

### **4.4 Environmental applications**

The increasing concern for the environment and tighter legislation on emissions are increasing the applications of ceramic membranes. Environmental applications can be roughly divided into wastewaters from various sources, as well as oily wastes and sludges.

#### 4.4.1 Wastewater applications

Ceramic membranes can be used to decrease the wastewater volumes and for the recovery of valuable substances from the wastewaters. Some of the food processing wastewaters, mainly those containing proteins, have already been presented previously in the chapter Protein concentration. However, in the following chapters some other wastewaters from the food processing industry as well as wastewaters from the agriculture are presented. The process industry wastewaters from the chemical, textile, and pulp and paper industry are discussed as well as wastewaters from the nuclear industry.

##### 4.4.1.1 Food processing and agriculture

According to Thoraval [2000] there are at least two industrial nanofiltration plants for brine recovery from ion exchange resin regeneration effluents in cane sugar refineries. The objectives for the plants are a flux rate of over 50 l/(m<sup>2</sup>h), a color retention of over 90% and a NaCl retention of less than 10%.

Scott and Smith [1997] have used a ceramic membrane coupled to a bioreactor to provide both aeration and filtration in ice-cream factory wastewater remediation. The 0.2 µm membrane provided good aeration and kept the permeate quality good. The suspended solids in the permeate were below 50 mg/l, despite an input of 1510-3800 mg/l. COD and BOD reductions were 97% and 98%, respectively. Scott et al. [1998] showed the effectiveness of the system in developing a microflora capable of treating a high strength wastewater despite the apparent nutrient limitations.

Lee and his research group [Chang et al., 1994; Kim et al., 1997; Yoon et al., 1999; Kim et al., 1999] as well as Cheryan and Bogush [1994] have studied the treatment of stillages, a waste from alcohol-distilleries. Cheryan and Bogush [1994] studied the possibility to use membrane filtration to replace centrifuges and to provide a clarified thin stillage for recycle and a higher solids level for evaporators. Lee and his group have studied both the recycling of the stillages back to the cooking phase of ethanol production [Kim et al., 1997; Kim et al., 1999] as well as the further treatment of membrane filtered stillage waste in an anaerobic digester [Chang et al., 1994; Yoon et al., 1999].

Reimann and Yeo [1997] have studied the use of organic and inorganic membranes for different wastewaters from agriculture. The wastewaters they studied included wash water of potatoes and carrots, pig and cattle slurry and wastewater from a milking plant. The ceramic membranes gave the highest permeate flux and COD retentions.

#### ***4.4.1.2 Petrochemical industry***

The wastewater applications in the petrochemical industry include the treatment of acidic and alkaline process wastewaters from a vinyl chloride monomer manufacturing facility. Lahier and Goodboy [1993] have shown that the high content of heavy metals from acidic wastewater can be removed by using two-stage membrane filtration with ceramic membranes. As a pre-treatment the pH of the wastewater was adjusted from 0.7 to 12. In the first filtration stage, the precipitated metal hydroxides were separated from the water and in the second filtration stage the filtered metals were concentrated to 17-20 weight-%. The water recoveries from the filtrations were 80% and 99.5%.

Lahier and Goodboy [1993] have also shown that an alkaline waste stream containing 1,2-dichloroethane, water, and calcium/iron hydroxides can be treated with ceramic membranes. The emulsified 1,2-dichloroethane can create problems during the manufacture of a vinyl chloride monomer. However, the filtration with ceramic membranes produced water that was free of emulsified 1,2-dichloroethane and solids.

#### ***4.4.1.3 Pulp and paper industry***

In pulp and paper industry the main interest in studying the possible applications of ceramic membranes has been in bleach plant effluent treatments [Jönsson, 1987, 1989; Jönsson and Petterson, 1988; Afonso and de Pinho, 1990; Afonso and de Pinho, 1991; de Pinho et al., 1995] and lignosulfonate recovery [Barnier et al., 1987; Gagnon et al., 1989]. Some studies exist also concerning spent sulfite liquor [Gaddis et al., 1991], black liquor [Dafinov et al., 2001b; Romero et al., 2001], white water [Sabri et al., 1997; Barnier et al., 1993], bark press filtrate [Sabri et al., 1997], and coating color effluents [Barnier et al., 1993]. Moreover, Imasaka et al. [1989] have studied the ceramic membrane filtration of methane fermentation broth of the evaporator condensate discharged from a kraft pulp mill.

From bleach plant effluents the main interest has been on the alkaline, E<sub>1</sub> stage and the acidic, C stage effluents. The fluxes achieved with these wastewater streams alone have been fairly high, for example Jönsson and Petterson [1988] achieved a permeate flux of 550 l/(m<sup>2</sup>h) for the E<sub>1</sub> stage effluent and a 1300 l/(m<sup>2</sup>h) flux for the C stage effluent. However, with combined total effluent the results were much worse. De Pinho et al. [1995] have made economic calculations for the nanofiltration of E<sub>1</sub> stage effluent and they found that it was technoeconomically feasible to use nanofiltration to purify the E<sub>1</sub> bleaching effluent.

Barnier et al. [1987] have concluded after 2000 hours of operation on an industrial scale that utilization of ceramic membranes for the separation and purification of lignosulfonates shows considerable potential at high temperature and high pressure.

Gaddis et al. [1991] have reported the results achieved in one of the Abitibi-Price's newsprint mills using sulfonated chemimechanical pulp (SCMP). They showed that the ultrafiltration permeate of the SCMP spent liquor was satisfactory for continuous recycling. The pulp produced with recycling had better strength properties than when recycling was not used. Moreover, toxic discharges were reduced, waste management became more effective, and the need for maintenance was reduced.

#### **4.4.1.4 Municipal wastewater**

In arid areas, the scarcity of water has brought up an issue of the reuse of municipal wastewater. For example, in Tenerife the water requirements exceed the water resources of the island. Thus, in 1993 a project focused on the reuse of the wastewater from the wastewater treatment plant to irrigate the banana and tomato crops was started. Vera et al. [1997] have made a study on the microfiltration of the secondary clarified suspension. They found that the microfiltration membrane, the pore size of which was 0.14 μm, was a total barrier for suspended solids, total coliform, fecal coliform, and fecal streptococci. This fact together with the reductions of turbidity, COD and phosphorus made the microfiltered water perfectly adapted to irrigation. A critical flux of 100 l/(m<sup>2</sup>h) was achieved at 1bar pressure and 3 m/s cross-flow velocity.

Ahn et al. [1998] have studied the possibility of applying ceramic membranes to treat the wastewater from hotel buildings for reuse in secondary purposes, such as toilet flushing. They

found that microfiltration using membranes with a pore size of 0.1  $\mu\text{m}$  was enough to produce a permeate the quality of which satisfied the guidelines set by the Korean Ministry of Environment for the reuse of wastewater for secondary applications.

#### **4.4.1.5 Other wastewater applications**

In the textile industry, ceramic membranes have been used for the recovery of polyvinyl alcohol [Porter, 1998] and dyestuff [Cueille et al., 1990]. The first polyvinyl alcohol recovery system was installed to JP Stevens manufacturing plant in Clemson, South Carolina, United States in 1973 and it is still in operation. The ceramic membranes used in the application were UCARSEP membranes, which have a zirconium oxide coating on porous carbon tubes. The pore size of the used membranes was 0.5  $\mu\text{m}$ . The filtration system operated at 80-90°C and a flow rate of 100-200 l/min and a pressure of over 7 atm. The lifetime of the membranes has been approximately 10 years. Besides recovering the polyvinyl alcohol for reuse, the membrane filtration reduced significantly the pollution discharges. The payback time for the filtration system was approximately one year.

In the nuclear industry, ceramic membranes have been studied for the treatment of radioactive waste streams. AEA Technology [Anonymous, 1989] in England has done excessive pilot plant studies with ceramic membranes and the results have shown that, for a low-level radioactive general site waste, good alpha and beta/gamma removal can be achieved. The process has also proved to be both reliable and flexible.

#### **4.4.2 Oily wastes**

Oily wastes include oil-water emulsions as well as waste oils. The use of membranes to treat oil-water emulsions is increasing, especially in applications where the value of recovered material is high or in applications where the savings from the reduced waste volumes are high. In 1998, according to Cheryan and Rajagopalan [1998] there existed 75 commercial applications with inorganic/ceramic membranes for treatment of oily wastewaters. The sources for the oily wastes are: (1) alkaline and acid cleaners used in metal industries and industrial laundries, (2) floor washes in all industries, (3) machine coolants in metal and machining industries, (4) vegetable and animal fats, in food, chemical, textile and leather industries, and (5) petroleum oils in petrochemical and oil industry and from tanker washes.



#### **4.4.2.1 Metal and machining industry**

Benito et al. [2001] have ultrafiltered emulsified cutting oils used in metalworking processes. They found that coagulation/flocculation pretreatment with ultrafiltration decreased the oil level below 5 mg/l, which is the discharge standard for EU countries. The pretreatment improved the permeate flux up to 300% when membranes with a pore size of 100 nm were used. Moreover, complete membrane regeneration was achieved by cleaning the membrane with a caustic detergent solution in distilled water.

Yüksel et al. [1990] have treated cooling lubricant-water –emulsions with chemical breaking of emulsions followed by ultra- or microfiltration with ceramic membranes. They concluded that the combined process produced a wastewater of an excellent quality and the process also drastically decreased the oil phase to be disposed of. Moreover, the cost comparison showed that the costs of the conventional process were between 30% and 100% higher than those of the combined process.

#### **4.4.2.2 Industrial laundries**

Menjeaud [1991] has studied the microfiltration of a wastewater produced by an industrial laundry. The washing water flow from an industrial laundry was 7 m<sup>3</sup>/h for 8 h/day. The water had a temperature of 60°C, a pH from 10 to 11, and an average COD of 100 000 mg/l. It contained organic fibers, several solvents, hydrocarbons, suspended solids etc. Microfiltration produced a permeate, which still contained the washing agents and which could be reused as an efficient washing solution, and a concentrate, where the volumetric concentration was high enough to transform it into a combustible.

#### **4.4.2.3 Petrochemical and oil industry**

Zaidi et al. [1992] have given a review of the use of micro/ultrafiltration membranes for the removal of oil and suspended solids from oilfield brines. They reported that by the year 1992 nearly 100 pilot scale studies had been made with ceramic membrane systems on onshore and offshore oilfield brines, and two commercial installations already existed. One of the full-scale installations was at Marathon Oil's EI-349B platform in the Gulf of Mexico and the other was the Petro-Canada Resources' Valhalla Field, in Alberta, Canada. Both of the installations had a design capacity of 1000 m<sup>3</sup>/d, the pore size of the membranes was 0.8 µm, the permeate was used for reinjection and FeCl<sub>3</sub> was used for pretreatment. The feed for Marathon Oil's application was a slip-

stream from the precipitator effluent and that for the Petro-Canada Resources' was 5% from heater water and 95% from groundwater.

Lahiere and Goodboy [1993] have used ceramic membranes to separate the aromatic oils from the wastewater of a linear alkyl benzene plant. The wastewater they studied contained 15-500 ppm of aromatic and paraffinic oils (measured by a Freon-extraction method), solids, and dirt. The components included linear alkyl benzene, dialkyl benzene, paraffins (C<sub>10</sub>-C<sub>16</sub>), and acid-soluble oil. Microfiltration with ceramic membranes reduced the oil and grease levels to less than 5 ppm and its performance was unaffected by fluctuations in the feed.

Elmaleh and Ghaffor [1996] have studied the use of ceramic ultrafiltration membranes for upgrading the oil refinery effluents with a synthetic emulsion containing Iranian crude oil and biological solids sampled from an activated sludge plant. They found that ultrafiltration produced an effluent free of hydrocarbons and suspended solids at all operating conditions.

#### **4.4.2.4 Waste oils**

Higgins et al. [1994] have ultrafiltered waste lubricating oils with ceramic membranes. They found that the flux stability during filtration was dependent on the surface chemistry of the membrane and that the dependence of the flux on temperature corresponded to the dependence of the oil viscosity on temperature. Membrane fouling was accelerated at temperatures above 250°C due to thermal decomposition. The permeates produced were clean enough for combustion. According to Porter [1990] there is one plant in Europe, where the spent lubricating oil is treated with inorganic membranes. The spent oil is pretreated with thermal shock and centrifugation at 180°C followed by ultrafiltration, in which a stable flux of 1000-2000 l/(m<sup>2</sup> d) is achieved over six months without cleaning.

Gourgouillon et al. [2000] have used ceramic membrane filtration assisted with pressurized CO<sub>2</sub> to treat motor oils. The concentration run carried out at 120°C made it possible to regenerate 96% in mass of the used oil and to separate a majority of the metals in a black, extremely viscous gum.

#### **4.4.2.5 Other oily wastes**

Ennouri et al. [2000] have presented a study on treatment of a tannery wastewater with a hybrid process combining a biological reactor and microfiltration. They achieved a constant flux

of 100 l/(m<sup>2</sup>h) at a temperature of 25°C, a flow velocity of 3 m/s, and a transmembrane pressure of 1.5 bar. The COD level in the processed water achieved with microfiltration was 50% lower than that achieved by using biological treatment alone. Moreover, the permeate obtained was totally free from bacteria and suspended solids.

Murton and White [2000] have reported the use of ceramic microfiltration membranes for the treatment of oily wastewater from ships bilges. Microfiltration with 0.2 µm pore size membranes is based on the formation of an oil-in water -emulsion by shear mixing within the membrane system prior to separation. The oil content in the permeate was consistently below 15 ppm of free oil in water, which is the maximum limit for discharge to the sea, and stable operations were achieved at oil levels of up to 45% oil in water.

#### **4.4.3 Activated sludge**

Xing et al. [2000] have studied the use of a bioreactor combined with ceramic ultrafiltration membranes for the reclamation of urban wastewater. According to their results, the treated water could be reused directly for municipal purposes, such as toilet flushing and car washing, and after softening treatment for industrial purposes such as cooling supply and process water. Moreover, some studies [Defrance and Jaffrin, 1999a; Tardieu et al., 1999; Defrance and Jaffrin, 1999b; Tardieu et al., 1998] concerning the fouling with activated sludge have been published.

#### **4.5 Other applications**

Guizard et al. [1994] have studied the ultrafiltration of asphaltenes from a Basrah crude oil and Lai and Smith [2001] have used microfiltration for removal of asphaltenes from Cold Lake heavy oil. Guizard et al. [1994] focused in their study on finding possible membrane materials and operation conditions for the separation of asphaltenes. From the investigated membrane materials, only zirconia/carbon membranes exhibited a weak interaction with asphaltenes. At low filtration pressures, there was a direct relationship between the asphaltene rejection and pore size, whereas at high pressures the separation was operated by an asphaltene dynamic layer, which was formed as a result of the combined effect of surface velocity and transmembrane pressure.

#### ***4.6 Conclusions of liquid filtration applications***

The ceramic membranes have found their applications especially in the areas where the advantages of the ceramic membranes can be exploited. These areas are for example food and beverage processing, drinking water treatment, biotechnology, and pharmaceuticals in which the steam sterilizability of the membranes is very important. In food and beverage processing as well as in drinking water treatment, good chemical stability of the ceramics is appreciated since it makes it possible to use more rigorous cleaning agents. In biotechnology, the biocompatibility of ceramic membranes is important as well as their resistance to microbial attack and biological degradation. In environmental applications, wastewater treatment, treatment of oily wastes and sludges, the advantages of the ceramic membranes are more dependent on the process in which they are used and thus for example good thermal and chemical stability of the membranes can be the factors that have made it beneficial to use ceramic membranes. The use of ceramic membranes in environmental applications is justified when valuable substances can be recovered from the wastes or when the volume of problematic wastes can be decreased significantly. Moreover, it is advantageous to use ceramic membranes for viscous fluids, since they are more stable at high pressures and it is also possible to use higher filtration temperatures with them.

## **Experimental**

In this thesis, new ceramic membranes developed by Tampere University of Technology were used for filtration of mainly pulp and board mill wastewaters, but some experiments were also made with a bore well water and a stone cutting mine wastewater. The ceramic membranes used were  $\alpha$ -alumina membranes with a pore size of 100 nm. Some of the membranes were coated with a  $\gamma$ -alumina layer to reduce the membrane pore size to 10 nm and some of them were modified with different metal oxides in order to change the surface properties of the membranes.

### **5 Aim of the work**

The aim of this work was to develop the membrane filtration equipment for new ceramic membranes produced in Finland and to find possible filtration applications for them. The effect of different metal oxide modifications to enhance the separation properties was also studied.

### **6 Materials and methods**

In this section, membranes, their manufacturing process, modifications, and characteristics; the wastewaters and their characteristics; as well as the development of the membrane filtration equipment are presented. Moreover, an overview of the used filtration procedure is given.

#### **6.1 Membranes**

The membranes used were plate type membranes with a filtering layer on both sides of the membrane (Figure 6). In the following sections, the manufacturing process and the modification of the membranes and their characteristics are briefly presented.



Figure 6 A photograph of the type of ceramic membrane used.

### 6.1.1 Manufacture and modifications of membranes

The plate membrane supports were manufactured by Outokumpu Mintec and Ensto Ceramics Oy and they were originally made for vacuum filtrations. The separating membrane layers were made on the top of the supports by the Institute of Materials Sciences in Tampere University of Technology. The membranes were multilayer membranes consisting of a coarse support structure and macro porous filtration layers on both sides of the supporting plate. On the top of the macro porous layers was the micro porous filtration membrane, the surface properties of which were changed by coating the pore walls with different metal oxides. The shape and the strength of the membrane were determined by the ceramic support plate (Figure 6). The plate was approximately 165 mm long, 116 mm wide, and 25 mm thick. The support material was mainly alumina. The microstructure was formed from alumina particles a few micrometers in size, which were bonded to each other with glass. The pore size of the support was approximately 1  $\mu\text{m}$  and its water permeability was a little over 1  $\text{m}^3/\text{m}^2$  at 1 bar pressure during one hour according to the manufacturer. [IV]

The membrane supports were cleaned, by soaking them in dilute nitric acid (pH 3). After soaking, the supports were rinsed and dried at 85°C for 12 h. Then the supports, except for the first set of membranes, were fired at 800°C for 2 hours. The membrane layer was slip casted on both sides of the cleaned supports. [IV]

The membrane layer was manufactured from pure  $\alpha$ -alumina (Alcoa 16 SG, Alcoa Industrial Chemicals Europe, Bad Homburg, Germany, purity of 99.97%), of which the average particle size was 0.5  $\mu\text{m}$ , by dispersing it in water with nitric acid or with ammonium polyacrylate.

The solids concentration in the water-based slip was kept fairly low, in order to make the membrane layer as thin as possible. A 2 weight-% poly(vinyl acetate)-based binder was used to improve the strength properties, when ammonium polyacrylate was used as the dispersing agent. When nitric acid was used as the dispersing agent, poly(vinyl alcohol) was used as the binder. Both of the used dispersing agent/binder combinations gave similar membrane properties. After making the slip, the supports were dipped into the slip and capillary suction arranged the particles in layers. Then the membranes were dried for 24 hours after which they were sintered at 1200°C for 3 hours. The details of the manufacturing process have been presented by Levänen and Mäntylä [2002]. [IV; Levänen et al., 2000; Levänen et al., 2001]

$\gamma$ -alumina membranes were made from boehmite ( $\text{AlOOH}$ ) powder, the average particle size of which was 60 nm, by dispersing it in water. The solids content in the sol was 1.5 weight-% and poly(vinyl alcohol) was used as the binder. The water was acidified with nitric acid prior to dispersion of the boehmite powder in order to ensure proper dispersal. The sol was dip coated on top of the  $\alpha$ -alumina membrane by a similar process as used for the  $\alpha$ -alumina membrane on top of the support. Dipping was done twice and the dipping time was 66 s. The membranes were dried first at room temperature over night and then at 100-200°C and sintering was made at 700°C for 3 h. The details and the optimization of the manufacture of the  $\gamma$ -alumina membranes have been described in the licentiate thesis of Mika Kolari [1997].

Some of the  $\alpha$ -alumina membranes were modified in order to change the charge and the energy of the surface. The modifications were made with titania, magnesia, and silica. Titania modification was made with sol-gel –synthesis from tetraisopropylortotitanate. The membranes were dipped in a dilute sol for about 5 seconds after which they were dried at room temperature for 12 hours. Then the membranes were calcined at 500°C for 3 h. The magnesia modification was made by impregnating the magnesium nitrate solution into the membrane. After drying at room temperature, the membranes were calcined at 900°C for 3 h in order to achieve magnesia. The silica modification was made by impregnating silane on a hydrated alumina surface. The modification was dried at 180°C for 2 h, after which the excess silane was rinsed off with toluene. Finally, the silane was oxidized to silica at 575°C for 3 h. [IV; Levänen, 2002]

After manufacture and modifications, the sides of the membrane were sealed and a tube for permeate collection was installed. A filtration experiment was made also with the ceramic membrane support and another one with the polymeric membrane (Nadir® C30, Hoechst), which was glued on a ceramic support. [IV]

### 6.1.2 Characteristics of the membranes used

The pore size of the formed  $\alpha$ -alumina membrane was approximately 100 nm and the porosity approximately 40% [Levänen and Mäntylä, 2002]. The pore size of the formed  $\gamma$ -alumina layer was approximately 10 nm and the porosity approximately 60% for  $\gamma$ -alumina [Kolari, 1997]. The modifications showed that the treatment with titania sol resulted in amorphous titania and impregnation with magnesium nitrate resulted in spinel,  $MgO \cdot Al_2O_3$ , when calcined at 900°C. All these membranes in this work have been considered as ultrafiltration membranes although the 100 nm membranes are nowadays usually categorized as microfiltration membranes. [IV]

Table 3 Pure water permeabilities of new membranes.

	$\alpha$ -alumina	Magnesia-modified alumina	Titania-modified alumina	Silica-modified alumina	$\gamma$ -alumina
Range of permeabilities, $l/(m^2 \text{ h bar})$	77-689 <sup>*)</sup>	231-415	259-434	245	37-53
Average permeability $\pm$ standard deviation, $l/(m^2 \text{ h bar})$					
RO/IO water	476 $\pm$ 130	415	294 $\pm$ 46	245	41 $\pm$ 7
Tap water	393 $\pm$ 72	257 $\pm$ 24	357 $\pm$ 54		
Number of observations					
RO/IO water	11	1	4	1	5
Tap water	5	4	5		

<sup>\*)</sup>The flux value of 77  $l/(m^2 \text{ h bar})$  was excluded when the average permeabilities were counted.

The filtration area of the membranes varied from 328 to 387  $cm^2$ , the average filtration area was 368  $cm^2$  and the observed thickness of the membrane layer varied approximately from 30



to 80  $\mu\text{m}$ . The pure water permeabilities of the new membranes are presented in Table 3. However, the extremely low pure water permeability of 77  $\text{l}/(\text{m}^2 \text{ h bar})$  in the case of the unmodified  $\alpha$ -alumina membrane indicates manufacturing problems, which have resulted in membrane properties significantly different from what is normal for this pore size (smaller porosity or pore size).

The pure water permeabilities were affected by the quality of the water used for the measurement. Since large amounts of reverse osmosis treated or ion-exchange water was not always available, tap water was used in the second and third equipment versions in most experiments for the measurement of the pure water flux and it usually resulted in lower pure water fluxes (Table 3). The differences in pure water permeabilities achieved with deionized water and with tap water could be more than 150  $\text{l}/(\text{m}^2 \text{ h bar})$  in favor of deionized water as measurements of Beyer [2000] for the magnesia-modified alumina membrane showed. However, in case of the titania-modified membranes the pure water permeabilities achieved with the tap water were higher than those achieved with the reverse osmosis treated water, which was quite unexpected. When comparing only the pure water permeabilities measured with tap water (Table 3), the permeability of magnesia-modified membrane was significantly lower than that of unmodified and titania-modified membranes, which indicates that the magnesia modification had probably slightly decreased the pore size of the membrane. When the comparison is made with the pure water permeabilities measured with the reverse osmosis treated water, also the permeability of the titania-modified membrane is slightly lower than that of the unmodified membrane, which would indicate that also the titania modification had decreased the pore size.

Contact angles and surface energies of the membranes were measured with the so-called drop method [Adamson, 1976], in which the liquid (water, methylene iodide) is dropped on the surface to be analyzed. From the drop profile, the contact angle is measured and from the contact angles, the surface energy and its components are determined. The contact angle was  $16^\circ$  for  $\alpha$ -alumina,  $14^\circ$  for titania, and  $10^\circ$  for a magnesia surface. However, the surface energies and the surface energy components of the different membrane modifications were similar, which is partly due to the limitation of the measurement methods used. [IV]

The amount of modification material on the membrane was calculated from the change in weight of the membrane. At the same time with the membranes some pieces for testing were manufactured and the amount of modification as well as the crystal phases were analyzed from these test pieces. The amount of modification substance was measured with electron dispersion spectroscopy (EDS) and the crystal phases were measured with x-ray diffraction. The calculated amount of modification substances varied from 3.0 to 4.0 weight-% for titania and magnesia and for the silica modified membrane it was 16.7 weight-%. The much higher amount of silica in the membranes is explained by a thinner (only 43 $\mu$ m) membrane layer. The analysis of test pieces gave 1.8 weight-% of titania and 5.3 weight-% magnesia. The crystal phases observed were  $\alpha$ -alumina for the unmodified and the titania-modified membranes, and  $\alpha$ -alumina and spinel,  $\text{Al}_2\text{O}_3\cdot\text{MgO}$ , for the magnesia-modified membranes. The lower weight-% of titania measured with EDS could indicate that the titania sol had penetrated deeper into the membrane structure. Moreover, the titania is in an amorphous form after calcination, which explains why only  $\alpha$ -alumina is observed. The behavior of magnesia seems to be different from that of titania: the higher weight-% measured with EDS seems to indicate that the magnesia is enriched on the surface of the membrane. The formation of spinel indicates that the calcination was made at a too high temperature and at least a part of the magnesia had reacted with alumina to form spinel. [IV; Levänen, 2002]

## **6.2 Waters and wastewaters**

The waters and wastewaters studied were chosen from different potential application areas. The bore well water is an example of water purification, where the ground water is contaminated by geogenic arsenic. The Finnish Ministry of Social Affairs and Health has set the limit for arsenic content in household water to 10  $\mu\text{g/l}$  [Sosiaali- ja terveystieteiden ministeriö, 1994]. In certain areas of Finland high arsenic contents in bore well waters have been measured where there are high arsenic contents in the fine fraction of moraine [Kurtio, 1995; Koljonen, 1992]. For example in the Tampere region a number of bore wells with significantly higher arsenic contents have been found. This is a problem especially in rural areas where people are dependent on their own wells. The drinking water studied in I was from a 25 m deep household bore well in the Tampere region and at the time the experiments were made the household was totally dependent on their own well. The aim of this study was to use ceramic membranes

for arsenic removal and in this case the advantage of ceramics would be their steam sterilizability. [I]

The pulp and paper industry is one of the most important industries in Finland. For a long time the closure of the pulp and paper mill water systems and the decrease of the water consumption have been important issues. The membrane processes have brought a new option for the development of closed water systems. For that reason a number of board and pulp mill effluents were studied.

In pulp mills, the bleach plant is producing most of the wastewaters. Since most of the mills are nowadays using the counter current principle the wastewaters from the end of the process are recycled back. One of the major sources of outgoing effluent is the first alkaline bleaching step. The high pH and temperatures of 50-60°C imply that ceramic membranes could be useful. Some studies concerning the use of ceramic membranes for the treatment of this effluent have been published [Jönsson, 1987; Jönsson and Petterson, 1988; Afonso and de Pinho, 1990; Afonso and de Pinho, 1991; de Pinho et al., 1995]. Some industrial applications using polymeric membranes [Okamoto et al., 1985; Haagensen, 1982] have also appeared. The pulp mill wastewater fractions studied include alkaline effluents, E<sub>1</sub> and E<sub>2</sub>, from the first and second caustic extraction stages and acidic effluents, D<sub>0</sub> and D<sub>1</sub>, from the first and second chlorine dioxide bleaching stages and mixtures of these effluents. The wastewaters came from a Finnish kraft pulp mill, which uses both soft and hardwood. The bleaching sequence of the mill is ODE<sub>o</sub>DE<sub>p</sub>D (o = oxygen, p = peroxide) and effluents from different bleaching stages are recycled counter currently. The effluents in this study were taken from a softwood run, with pine as raw material. [III]

The board mill wastewaters studied were from two Finnish board mills. The wastewaters from these particular board mills were chosen since they are producing boards for packing material. The material is used for food, cosmetics and cigarettes and thus the demands for recycled water are high. Especially critical is the odor and taste properties of the recycled water. At the same time both of the mills are having another product, for which the water quality demands are not as high. One of the mills manufactures graphic products and the other manufactures wallpaper base. One of the mills was a special case also because its ability to further treat the wastewaters is limited by the space; for example a biological wastewater treatment plant

would need too much space. For that reason membrane filtration might be an option. Since the demands for the recycled water were high, the waters to be treated were chosen from the end of the process after effluent treatment. The improvement of the water quality for recycling was studied. The wastewater fractions studied included flotation treated circulation wastewater, clarified coating color wastewater, clear filtrate from the disk filter and biologically treated total effluent. [II, IV, VI, VII]

Stone cutting wastewater is an environmental issue. The stone cutting wastewater was from an open stone cutting mine in Kuru circa 50 km north from Tampere. The mine is producing granite stones. As the shape of the mine is like a basin, it receives both rainwater and runoff from the surroundings. The water contains both organic material and inorganic slurry from the cutting process. This water is pumped to an adjacent ditch along which it flows to the receiving lake. The very fine fraction of solids, which settles poorly, reduces the water quality in the lake. The settling is not an option for the treatment of this water since a long retention time would be needed and thus a very large basin area. [VIII]

The analysis methods used for the characterization of the waters are presented in Table 4.

### **6.2.1 Characteristics of the waters**

The wastewaters studied are roughly divided into three different groups: board mill wastewaters, pulp mill wastewaters and others. The general characteristics of these are presented in Table 5.

The board industry wastewaters [III, IV, VI, VII] were neutral with a broad range of suspended solids content (from 2.8 to 210 mg/l). The conductivities of board industry wastewaters varied from 80 to 170 mS/m, turbidities from 1.4 to 111 NTU, color from 20 to 400 mg Pt/l, COD<sub>Cr</sub> from 60 to 650 mg/l, and the iron content from 0.03 to 0.61 mg/l.

Table 4 Analytical methods used.

Item	Method / Instrument	Standard
pH	MeterLab PHM 220 Lab pH Meter	SFS 3021
Conductivity	MeterLab CDM 210 Conductometer	SFS-EN 27888
Turbidity	Hach Ratio Turbidimeter	Abolished standard SFS-EN 27027
Color	Comparative method	SFS-EN ISO 7887
Chemical oxygen demand (COD <sub>Cr</sub> )	Oxidation with dichromate. Hach COD Reactor	SFS 5504
Chemical oxygen demand (COD <sub>Mn</sub> )	Oxidation with manganese. Hach COD Reactor	SFS 3036
Total organic carbon (TOC)		SFS-EN 1484
Dissolved organic carbon (DOC)		SFS-EN 1484
Biological oxygen demand (BOD <sub>7</sub> )	Dilution method	SFS-EN 1899-1, SFS-EN 1899-2
Suspended solids (SS)	Filtration with Whatman GF/A, drying at 105°C	SFS-EN 872
Suspended solids (SS)	Filtration with Whatman GF/C, drying at 105°C	SFS-EN 872
Suspended solids (SS)	Filtration with Nuclepore 0.45 µm, drying at 105°C	SFS-EN 872
Suspended solids (SS)	Filtration with Gelman 0.4 µm, drying at 105°C	SFS-EN 872
Total solids (TS)	Drying at 105°C	SFS 3008
Inorganic matter, fixed solids (FS)	Incineration at 550°C	SFS 3008
Organic matter, volatile solids (VS)	Calculated from the difference between TS and FS	SFS 3008
Lignin	Nitrosomethod	[Barnes et al., 1963]
Absorbance 280 nm	UV-spectrophotometer	[Böttger and Krause, 1980]
Absorbance 400 nm	UV-spectrophotometer	
Sodium	Atomic absorption spectrophotometry	SFS 3017, SFS 3044
Calcium	Atomic absorption spectrophotometry	SFS 3018, SFS 3044
Magnesium	Atomic absorption spectrophotometry	SFS 3018, SFS 3044
Iron	Photometric determination	SFS 3028
Manganese	Photometric determination	SFS 3033
Arsenic	Atomic absorption spectrophotometry	SFS 5074, SFS 5502, SFS 5503
Aluminum	Atomic absorption spectrophotometry	SFS 5074, SFS 5502, SFS 5503
Sulfate	Nephelometric method	SFS 5738
Chloride	Mercury nitrate titration	SFS 3006
Total nitrogen	Modified Kjeldahl method	SFS 5505
Total nitrogen	Method using oxidative digestion with peroxodisulfate (FIA-Method)	Abolished standard SFS 3031
Phosphate phosphorus	Photometric determination	Abolished standard SFS 3025
Total phosphorus	Decomposition with peroxodisulfate	SFS 3026

Table 5 General characteristics of the studied waters and wastewaters.

		pH (-)	Conduc- tivity (mS/m)	Turbidity (NTU)	Sus- pended solids (mg/l)	COD <sub>Cr</sub> (mg/l)	Total solids (mg/l)	Iron (mg/l)
Board mill wastewaters	Flotation treated	6.3 ± 0.12	98 ± 11	2.7 ± 1.6	6.3 ± 3.6	250 ± 55	990 ± 8	0.16 ± 0.02
	Clarified coating color	6.7 ± 0.07	163 ± 3	8 ± 7	14 ± 7			0.48 ± 0.09
	Clear filtrate	6.2 ± 0.10	133 ± 1	18.7 ± 1.3	23 ± 3	650 ± 0		0.07 ± 0.06
	Biologically treated	7.7 ± 0.18	139 ± 12	29 ± 31	43 ± 54	117 ± 58	1140 ± 110	0.17 ± 0.15
Pulp mill wastewaters	E <sub>2</sub>	10.5	218	46		700	1780	
	D <sub>1</sub>	7.8 <sup>2)</sup>	410	23		750	3320	
	E <sub>2</sub> :D <sub>1</sub>	7.9	240	45		740	2070	
	E <sub>1</sub>	9.9 ± 0.7	490 ± 50	37 ± 20	17 ± 8	2800 ± 600	5300 ± 700	0.66 ± 0.36
	E <sub>1</sub> :D <sub>0</sub> (2:1)	6.3 ± 0.06	470 ± 20	19.5 ± 0.8	29 ± 4	2000 ± 140	4450 ± 160	0.47 ± 0.08
	E <sub>1</sub> :D <sub>0</sub> (1:2)	4.4 ± 0.05	487 ± 3	30 ± 2	45 ± 14	1950 ± 70	4400 ± 80	0.51 ± 0
Bore well water		7.2 ± 0.7	37 ± 0.1					0.11 ± 0.02
Stone cutting wastewater		6.8 ± 0.1	10 ± 0.8	370 ± 24	450 ± 40 <sup>1)</sup>	27 ± 4	540 ± 40	18 ± 1

<sup>1)</sup> Analyzed with GF/C.

<sup>2)</sup> pH adjusted with NaOH solution.

Pulp industry wastewaters [II] were either acidic (pH ca. 2.5) or alkaline (pH 9-10) depending on which bleaching stage they came from. E<sub>1</sub> effluent had high conductivities from 460 to 590 mS/m and D<sub>0</sub> even higher, approximately 700 mS/m. The color as well as the COD<sub>Cr</sub> were extremely high for the bleach plant effluents, circa 4000 mg Pt/l and 2200-3800 mg/l in E<sub>1</sub> effluent. However, the turbidity and the suspended solids were not that high, 20-33 NTU and 8-22 mg/l in E<sub>1</sub> effluent. The pulp mill wastewaters were also mixed with each other and the pH was adjusted with sodium hydroxide and sulfuric acid.

The wastewater from the stone cutting mine [VIII] was neutral and it had very low conductivity, COD<sub>Cr</sub> and total solids content compared to the pulp and paper industry wastewaters. However, the turbidity, suspended solids, and iron contents were much higher than those in the pulp and board industry wastewaters. The high iron content originated from the geological

surroundings. The average iron content in granite is 2.0% and in moraine in areas in which granite is the main rock 3.2% [Koljonen, 1992].

The bore well water [I] was “clean” compared to the wastewaters, the only problem was that it had an arsenic content 25 times higher than the limit (10 µg/l) set for household water by The Finnish Ministry of Social Affairs and Health [Sosiaali- ja terveystieteiden ministeriö, 1994].

### **6.3 Filtration equipment**

The filtration equipment was developed throughout the years to meet the demands for higher cross-flow velocity and thus lower fouling of the membranes. The wideness of the membrane and the structure of the membrane module set demands for a high pumping capacity. The membrane module and different equipment versions used are described in the following sections.

#### **6.3.1 Membrane module**

The membrane module was manufactured from polyethylene by the workshop of Tampere University of Technology. The module cross-section is presented in Figure 7. Different plate inserts could be attached to the flow channel and thus the cross-sectional area of the flow channel was adjusted. The height of the flow channel could be adjusted with inserts from less than 1 mm to a maximum of ca. 10 mm. The height of the flow channel depended also on the thickness of the membrane: with thicker membranes the height of the upper flow channel was smaller. With the first attachment bolts, the cross-sectional area of the upper flow channel in the module was larger than that in the lower part of the module as can be seen in Figure 8. However, the bolts were changed for the second equipment version so that the size difference in upper and lower flow channels was smaller. With baffles the height of the flow channel varied from approximately 2.6 to 6 mm. The baffles were added to the module to increase the turbulence, which they did according to visual observations on fouling deposits on the membrane surface after filtration experiments. The membrane surface had lighter color in places, where the baffles existed than in places where the flow channel was higher.

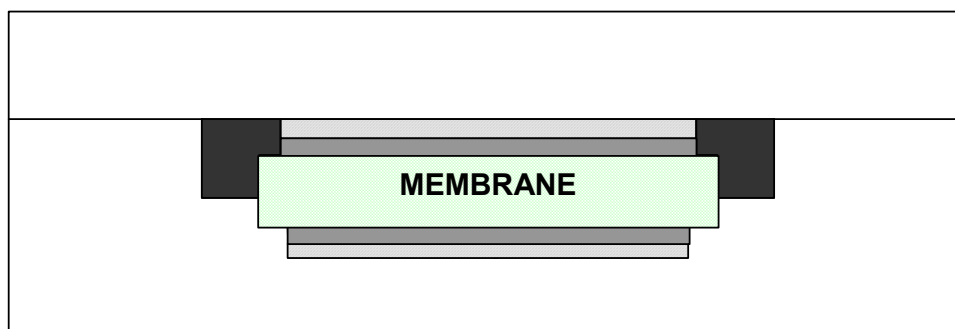


Figure 7 A schematic cross-section of the membrane module.

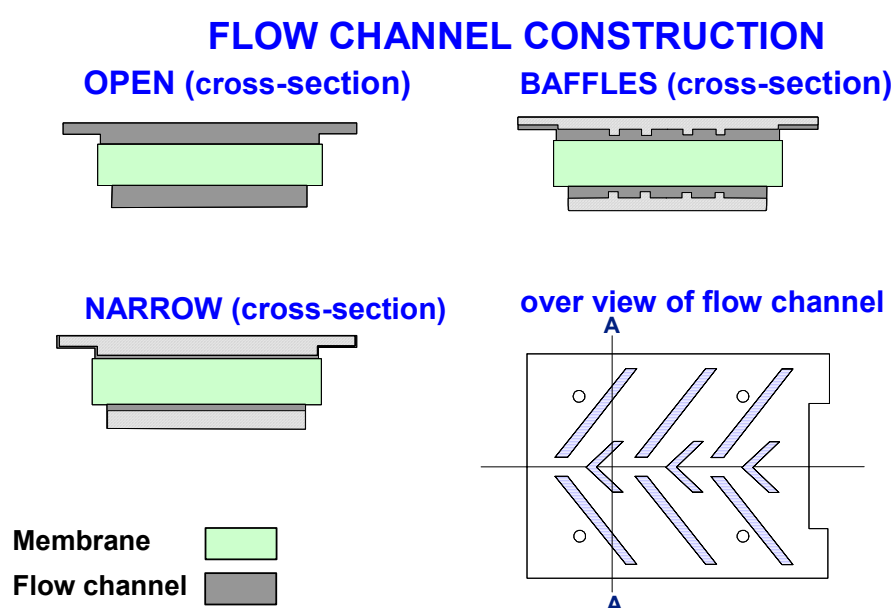


Figure 8 Different flow channel constructions used in the equipment version I.

### 6.3.2 Equipment version I

The equipment first used in the studies was a Laboratory Unit for micro-, ultra- and nanofiltration made by Oy Metalcity Ab Ltd (Figure 9). The equipment was designed for batch filtration of 20-30 l at filtration pressures of 1-15 bar, temperatures of 20-100°C, a pH range 3-12, and a permeate flow less than 120 l/h. The equipment had two centrifugal pumps P1 (Grundfos CRN2-180 A-P-G-AUUE85800008) and P2 (Grundfos CRN2-40 A-P-G-AUUE 3X220-240/380-415V 85800). The temperature in the equipment was controlled by a heat exchanger. Pressure was measured with STIKO/SECUTHERM POX (0-25 bar) manometers and flow



with a KLK-4CA flow meter from Kytölä Oy. The feed tank and the pipelines were manufactured from AISI 316. The equipment had the possibility for backwashing. The membrane module was connected to the equipment with food quality poly(vinyl chloride) pipes reinforced with woven polyester (Arianna TA/L, Industrie Plastiche Lombarde, Italy), which could withstand pressures of up to 12 bar at 20°C. [Anonymous, 1994]

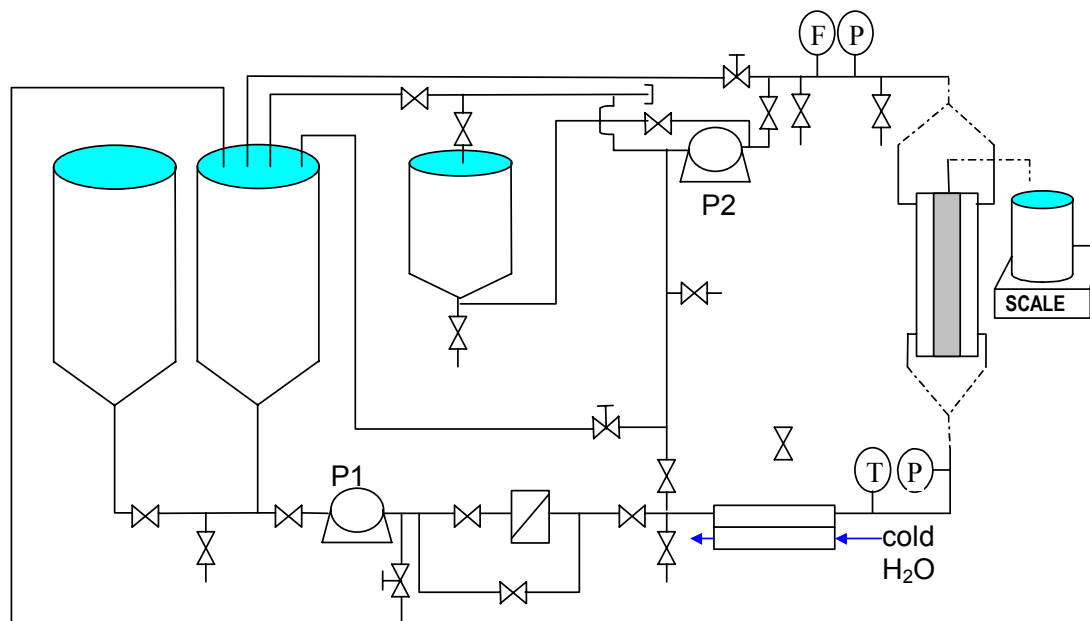


Figure 9 Equipment version I, Metalcity pilot. Solid line metal pipes, dashed line plastic pipes. [I, II, III]

### 6.3.3 Equipment version II

The low crossflow velocity and complicated construction of the filtration system, which made it difficult to clean and drain the first equipment, made it necessary to simplify it. Version II (PREC pilot I) was made in order to remove some of the hydraulic resistances of the previous equipment and to improve its cleanability. The new equipment (Figure 10) had a feed tank of approximately 189 l, with an effective capacity of circa 120 l. The pumps in the new equipment were the same as in version I. The plate heat exchanger type 10407621 from Alfa-Laval (Alfa Laval, 1995, Thermal Ab, Ronneby, Sweden) was used for temperature control. The feed tank, the pump holder and the return flow pipes were made from AISI 316. Other pipelines were food quality poly(vinyl chloride) reinforced with woven polyester (Arianna TA/L,

Industrie Plastiche Lombarde, Italy) and could withstand pressures of up to 12 bars. The polymeric pipes could be changed to new ones when ever necessary.

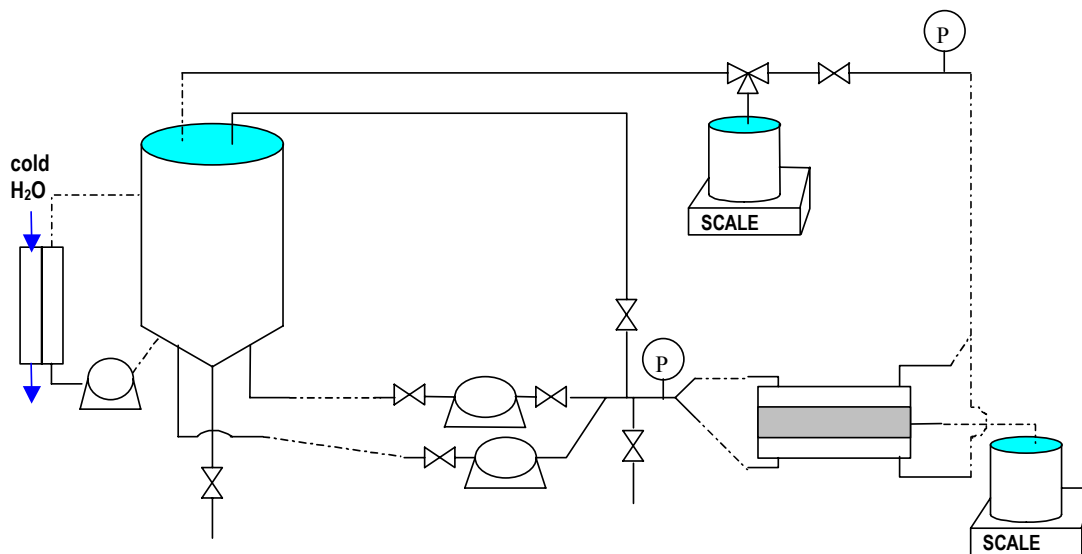


Figure 10 Equipment version II, PREC pilot I. Solid line metal pipes, dashed line plastic pipes.[IV]

### 6.3.4 Equipment version III

In order to be able to achieve higher cross-flow velocities in the membrane module and to improve the filtration flux a new, centrifugal pump (flow rate of 42-109 m<sup>3</sup>/h, maximum head of 62 m, power intake of 18.5 kW and rotation speed of 2900 rpm) was installed in equipment version III (PREC pilot II, Figure 11). Due to the more effective pump, the pipe material was changed to food quality polyurethane, which is reinforced with poly(vinyl chloride) (Nettuno SE, Industrie Plastiche Lombarde, Italy), and could withstand operation pressures of up to 5 bar. Moreover, the backflushing system, comprised of computer controlled valves and pressurized air, connected to the permeate pipe. The backflush was achieved by forcing the permeate, that was in the permeate pipe, to flow in the reversed direction with the aid of pressurized air.

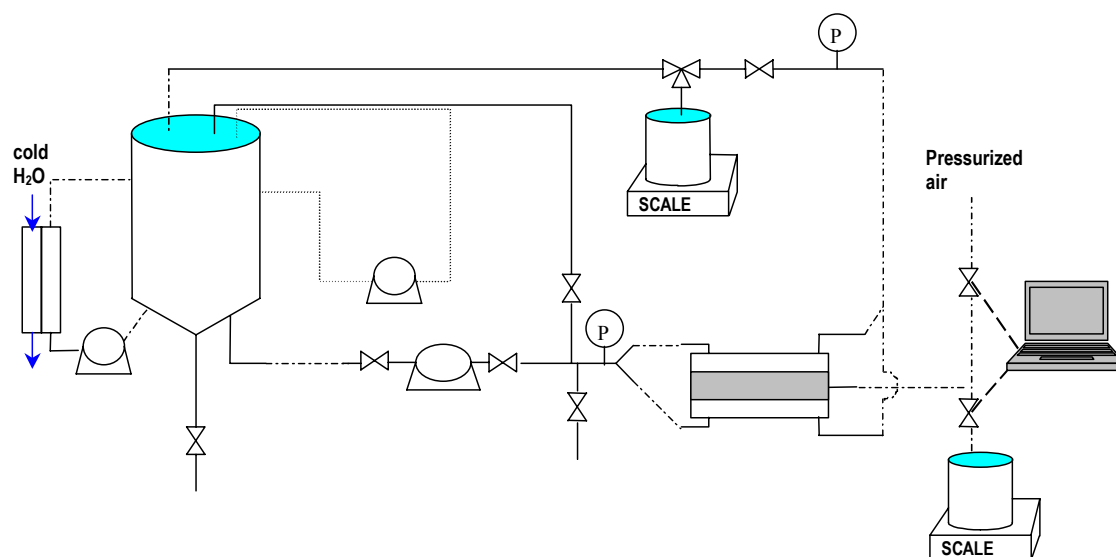


Figure 11 Equipment version III, PREC pilot II. Solid line (—) metal pipes, dashed line(- -) plastic pipes, dashed line (···) optional level control loop, dashed line (---) computer controls. [V, VI, VII]

### 6.3.5 Cross-rotational (CR) filter

Some experiments for comparison of the PREC pilot I used here with the ceramic membranes were made with a commercially available membrane filter for polymeric membranes. The equipment used in these studies was the CR-filter developed by ABB Flootek, sold nowadays by Metso PaperChem Oy. The laboratory pilot used was the CR 250, in which two polymeric membranes can be tested at the same time. The filtration pressure used in the experiments was 0.8-1.0 bar, usually 0.8 bar, and the circumferential velocity of the rotor blade was 0-11 m/s, usually approximately 10 m/s [IV]. The polymeric membrane used for the comparison was the C30, made of regenerated cellulose, which had already proven its applicability with pulp and paper industry wastewaters [Sutela, 1997].

## 6.4 Experimental procedure – general

In the first filtration experiments the membranes were not stabilized since, according to literature, the purpose of the stabilization was to prevent the variations caused by the compaction of the membranes under pressure. Since ceramic membranes are more solid structures than

polymeric ones, the pressure difference over the membrane does not cause compaction and thus it was thought unnecessary to stabilize the membranes. However, as it turned out the pure water fluxes of the ceramic membranes are far from stable. The stability of the pure water flux is dependent on the filtration pressure used, the quality of the water used for measurement of the flux, the membrane material and the pore size of the membrane. For example, the pure water flux of the  $\gamma$ -alumina membranes (pore size 10 nm) measured at 2 bar pressure was stable after 1.5 hours of filtration and the pure water flux of 100 nm membranes measured at 0.8 bar with ion-exchange water was usually stable after 3.5 hours of filtration, whereas the pure water flux of silica-modified membrane (pore size 100 nm) measured with ion-exchange water at 1.3 bar was not stable even after 7 hours of filtration. The flux change during filtration of pure water varied from a 7.5% increase in flux to a 51% decrease in flux compared to the pure water flux at the beginning of filtration. Usually the first water flux value was measured either after 3 or 5 min of filtration. A higher flux at the beginning and a longer stabilization time usually resulted in a larger change. A higher flux change was also observed when tap water and ion-exchange water were used. The instability of the flux can be caused by several factors:

- Air entrapped inside the membrane and its slow removal could result in a lower pure water flux at the beginning.
- Loose ceramic powder and other inorganic manufacturing residuals can lead also to a lower pure water flux and can even plug the pores when backflushing is used.
- Hydration of the ceramic surface.
- The quality of the water used for stabilization: even a small amount of certain substances can decrease the pure water flux

In equipment version I, after the first experiments all new membranes were characterized by filtering reverse osmosis treated water through the membrane at filtration pressures of 1, 2, 3 and 4 bar for 10 min. Then the membranes were stabilized at a pressure of 2 bar for 1 to 2 hours.

In the second and third equipment versions only the pure water flux at a certain pressure, usually at 1 bar, was measured for 2 hours. The water used for the measurements was tap water

or ion-exchange water. The reason for the usage of tap water as pure water was that a large amount of ion-exchange water was not available. When tap water was used a yellowish or brownish layer, which could be removed by wiping the membrane with a cloth, was observed to form on the membrane surface.

The general experimental procedure was the following:

1. measurement of the pure water flux before filtration
2. filtration experiment
3. rinsing of the equipment and the membrane
4. measurement of the pure water flux after the filtration experiment

If the membrane was used again it was cleaned and the pure water flux after cleaning was measured.

The following cleaning methods were tested during the experiments: nitric acid, sodium hydroxide, commercial cleaning agents (Tend, Ultrasil 10), ultrasonic treatment, wiping with cloth, soaking etc. The ultrasonic treatment was efficient, but if it was used for too long it destroyed the membrane. Pinholes were observed in the membrane surface after 5 and 10 min of treatment. The nitric acid cleaning and wiping were used since they seemed to be the best ones. The wiping removed the cake layer formed on the top of the membrane and it had a visible effect on the color of the membrane surface. However, the experiments were not systematic and conclusions made based on them are not certain. In most cases, simple cleaning with nitric acid and wiping of the membrane with cloth under water was used, since it did not require too much time and it could remove part of the membrane fouling.

## **7 Theoretical calculations**

The permeate fluxes measured have been calculated to 25°C, by using the temperature correction for the viscosity and density. Usually the filtration temperature was 25±3°C. But in the case of the bore well water filtration, the experiments were started at a temperature of 14-16°C and the temperature increased during the filtration test to close to 25°C. Also in 24h experiments the temperature changed more than 6°C. It was assumed that the viscosity and den-

sity of the permeate would be considered the same as those of pure water. The correction was made as follows:

$$J_{25^{\circ}\text{C}} = \left( \frac{J_T}{\rho_T} \right) \cdot \frac{\mu_T}{\mu_{25^{\circ}\text{C}}} \quad (1)$$

where  $J_{25^{\circ}\text{C}}$  [ $\text{m}^3/(\text{m}^2\text{h})$ ] is the permeate flux at  $25^{\circ}\text{C}$ ,  $J_T$  [ $\text{kg}/(\text{m}^2\text{h})$ ] is the measured permeate flux at temperature  $T$  [ $^{\circ}\text{C}$ ],  $\rho_T$  [ $\text{kg}/\text{m}^3$ ] is the density of water at temperature  $T$ ,  $\mu_T$  [ $\text{Pa s}$ ] is the viscosity of water at temperature  $T$  and  $\mu_{25^{\circ}\text{C}}$  [ $\text{Pa s}$ ] is the viscosity of water at  $25^{\circ}\text{C}$ . The correct temperature dependence of the viscosity of water can be presented as follows [Bingham, 1922]:

$$\mu_T = \frac{100}{2.1482 \cdot [(T + 8.435) + \sqrt{(8078.4 + (T + 8.435)^2}] - 120} \quad (2)$$

The temperature dependence of the density of water can be presented as follows [Kell, 1975]:

$$\rho_T = \frac{999.83952 + 16.945176 \cdot T - 7.9870401 \cdot 10^{-3} \cdot T^2 - 46.170461 \cdot 10^{-6} \cdot T^3 + 105.56302 \cdot 10^{-9} \cdot T^4 - 280.54253 \cdot 10^{-12} \cdot T^5}{1 + 16.87985 \cdot 10^{-3} \cdot T} \quad (3)$$

Relative flux is the permeate flux divided by the pure water flux before the filtration and it can be calculated as follows:

$$J_{rel} = \frac{J}{PWF_b} \quad (4)$$

where  $J_{rel}$  is relative flux,  $J$  is the permeate flux and  $PWF_b$  is the pure water flux before the experiment.

The flux reduction describes how much the flux has changed in a certain time. It can be calculated between any two filtration times as follows:

$$FR_{t_1-t_2} = \left( 1 - \frac{J_2}{J_1} \right) \cdot 100\% \quad (5)$$

where  $FR_{1-2}$  is the flux reduction from  $t_1$  to  $t_2$ ,  $t$  is the filtration time,  $J_1$  is the permeate flux at time  $t_1$  and  $J_2$  is the permeate flux at time  $t_2$ . Reduction of the pure water flux is calculated similarly by replacing  $J_1$  with the pure water flux before and  $J_2$  with pure water flux after the filtration experiment.

In Figure 12 the typical behavior of pure water fluxes and permeate flux as a function of time as well as the fraction of concentration polarization, reversible, irreversible fouling and membrane poisoning are presented.

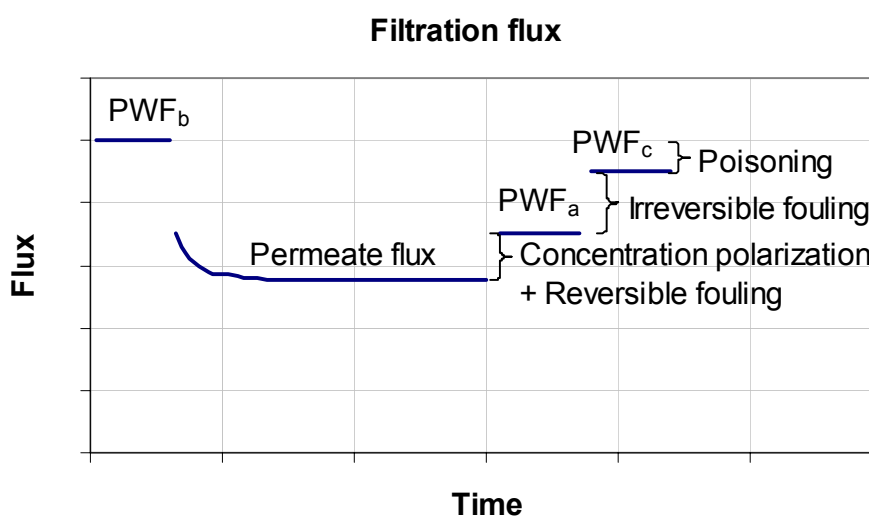


Figure 12 Pure water fluxes (PWF), permeate flux and different flux reductions. Indexes:  $b$  = before,  $a$  = after,  $c$  = after cleaning.

The concentration polarization and reversible fouling (CP) is the fraction of the flux reduction, which can be removed just by rinsing the membrane. It was calculated as follows

$$CP = \frac{PWF_a - J_{end}}{PWF_b - J_{end}} \quad (6)$$

where  $PWF$  is pure water flux,  $J_{end}$  is permeate flux at the end of the filtration, index  $b$  is before and index  $a$  is after. The irreversible fouling is the fraction which can be removed by nitric acid cleaning and membrane poisoning is the fraction which remains after cleaning with nitric acid and is responsible for the continuous reduction of the pure water flux. The irreversible fouling and membrane poisoning were calculated as follows

$$\text{Irreversible fouling} = \frac{PWF_c - PWF_a}{PWF_b - J_{end}} \quad (7)$$

$$\text{Poisoning} = \frac{PWF_b - PWF_c}{PWF_b - J_{end}} \quad (8)$$

where index c means after cleaning.

## 8 Results from filtration experiments with equipment version I

The wastewaters filtered with equipment version I were bore well water, flotation treated wastewater and clarified coating color wastewater from the board industry, E<sub>1</sub>, E<sub>2</sub>, and D<sub>1</sub> effluents and mixtures of E<sub>1</sub> and D<sub>0</sub> as well as E<sub>2</sub> and D<sub>1</sub> effluents from the bleach plant. The average permeate fluxes achieved with these waters are presented in Figure 13.

The bore well water, which was very “clean” compared to the board mill and bleach plant effluents, gave a flux of approximately 340 l/(m<sup>2</sup>h) with the unmodified α-alumina membrane, whereas the fluxes achieved with the board mill effluents were all below 165 l/(m<sup>2</sup>h) with the 100 nm membranes and those achieved with bleach plant effluents were 61 l/(m<sup>2</sup>h) or less with the 100 nm membranes. With the γ-alumina membrane, the pore size was 10 nm, the fluxes were lower, as expected, but the trend of lower fluxes with dirtier water was similar to those with the 100 nm membranes. Moreover, the retentions achieved with the 10 nm membranes were only slightly higher than those achieved with the 100 nm membranes. Since the fluxes achieved with the 100 nm membranes were much higher, it seemed unnecessary to use 10 nm membranes for these applications. Besides, the low corrosion resistance of γ-alumina restricts the use of them at pHs between 3 and 9 [Hofman-Züter, 1995; Schaep et al., 1999; Van Gestel et al., 1999].



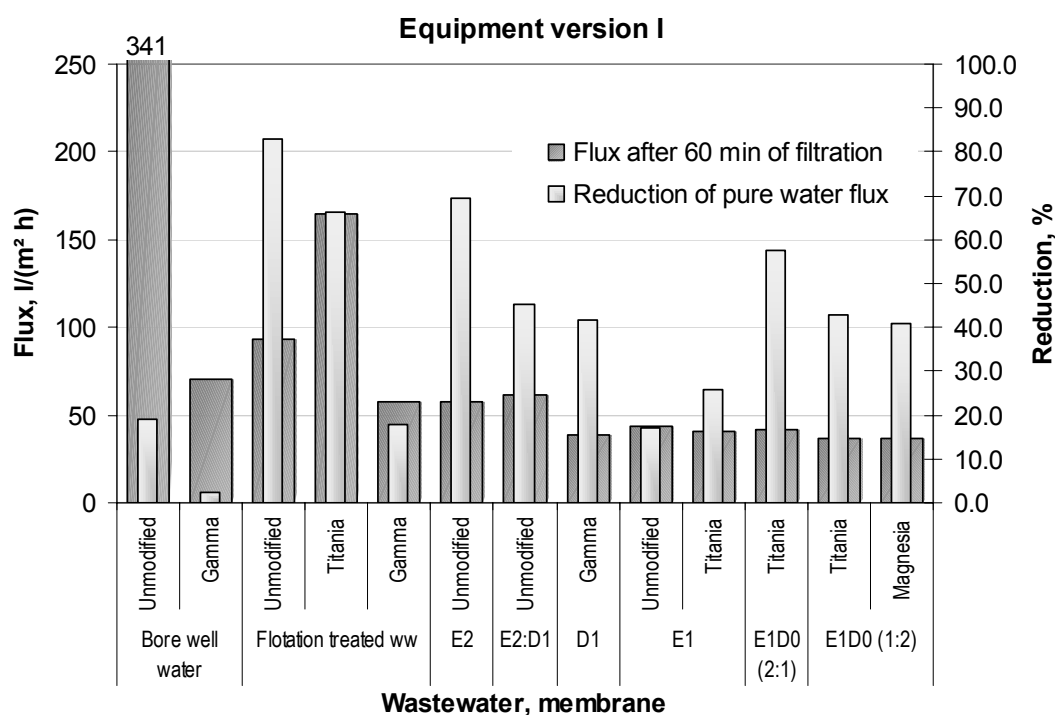
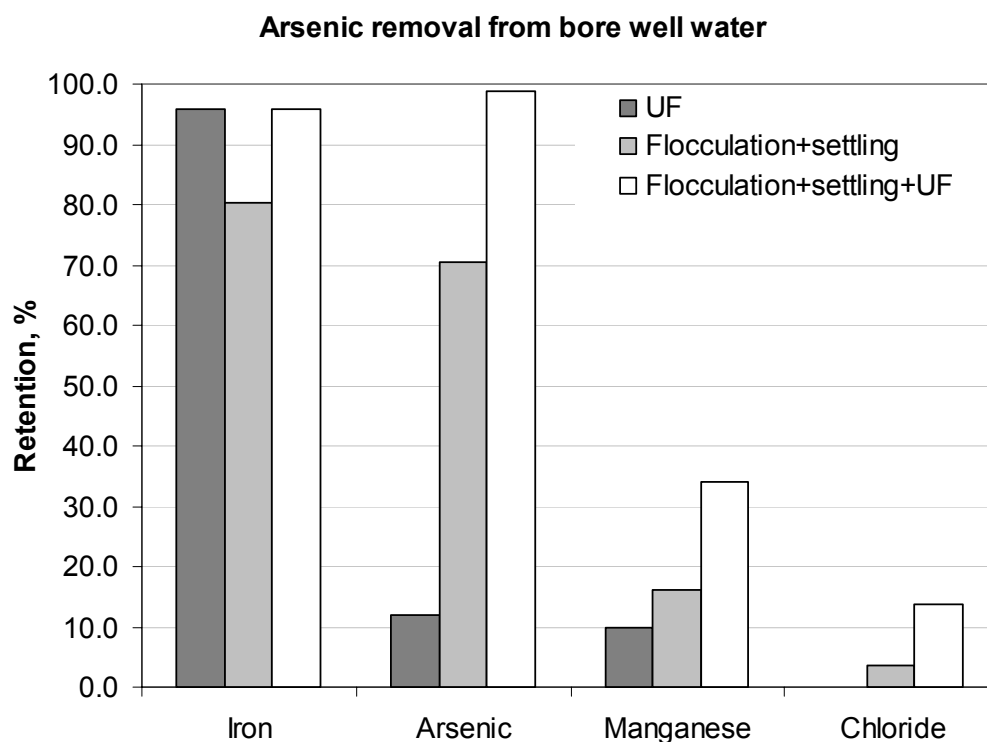


Figure 13 Permeate fluxes achieved with the different waters/wastewaters and different alumina membranes in equipment version I. The filtration pressure was 2 bar, the cross-flow velocities varied from 0.13 to 1.6 m/s, the filtration temperature was approximately 25°C and the filtration times varied from 60 to 120 min. The pore size of the  $\gamma$ -alumina membrane was 10 nm, whereas the pore size of the other membranes was 100 nm.

### 8.1 Arsenic removal from bore well water

The arsenic in groundwater is posing a possible health risk. In countries, such as for example Taiwan and Bangladesh, where the arsenic content in water is high, the diseases related to arsenic poisoning are very common [Pontius et al., 1994; Karim, 2000]. The arsenic in water has two different oxidation stages: arsenic (II) and arsenic (V), but it can also be found as oxo-substances and organic arsenic. In cases, where the arsenic is found in ground water due to geological reasons, arsenic (III) and arsenic (V) are usually the only species of concern [Jekel, 1994, p.121]. The abundance of different oxidation stages is related to the oxidation level: at a high oxidation level (redox potential and  $\text{pH} > 8$ ) arsenic (V) is more abundant whereas at low oxidation levels (redox potential and  $\text{pH} < 8$ ) arsenic (III) would be dominant [Mok and Wai, 1994, p.101]. From these oxidation stages arsenic (III) is more difficult to remove and can be removed to a very low level only after oxidation. The pentavalent form of

arsenic can be removed by ion-exchange, reverse osmosis and electrodialysis [Kartinen and Martin, 1995]. As such, neither one of these arsenic forms can be retained by ultrafiltration membranes as our experiments showed (Figure 14) [I].



*Figure 14 Retentions of different substances from bore well water with ultrafiltration (UF), flocculation+settling, and flocculation+settling+ultrafiltration. The filtration pressure was 2.0 bar and the cross-flow velocity 0.13 m/s. Unmodified  $\alpha$ -alumina membrane (pore size 100 nm) was used for the ultrafiltration. [I]*

Pre-treatment of the feed water to flocculate arsenic was necessary. Lime softening, alum and iron coagulation as well as a combination of iron and manganese removal are used for the precipitation of arsenic [Kartinen and Martin, 1995]. Ferric coagulants have been found to be more efficient than alum for arsenic removal, especially when arsenic is in the trivalent form or the pH is higher than 7.5 [Harper and Kingham, 1992; Edwards, 1994]. Above pH 8 the formation of soluble coagulant metal residuals is prevented. Recently, also hydrous oxides of rare earth metals have been used for the adsorption of arsenic [Takunaga et al., 1997; Raichur and Panvekar, 2002]. Brandhuber and Amy [1998] have studied different filtration methods for arsenic removal from drinking water. They also used combined ferric chloride coagulation - microfiltration treatment for arsenate removal. They found that arsenic removal increased

with increasing coagulant dosage and decreased with increasing pH in the pH range 6 to 9. pH 8.1 was found to be at a limit above which arsenic removal was significantly decreased. Gullledge and O'Connor [1973] found that arsenic removal increased with increasing dosage of aluminum and ferric hydroxides, but in their case the critical pH was 8.0, in which the arsenic removal was reduced.

In this study the aluminum sulfate was chosen as a precipitation chemical since it is the most common drinking water treatment chemical in Finnish water treatment facilities. The experiment with flocculation pre-treatment showed that with a combined treatment arsenic levels lower than 5 µg/l, which was the detection limit of the determination method, could be achieved and moreover, the concentrations of the flocculation agents in the permeate were lower than the limits set for those substances in household water [Sosiaali- ja terveystieteiden ministeriö, 1994] (Figure 14).

It can be concluded that, the good flux values achieved with the bore well water were accompanied with low reductions of pure water flux. Both of the factors indicate that the water was clean and suitable for filtration with the used membrane. The aim, arsenic removal, was achieved only when feed water was pre-treated with aluminum sulfate, which flocculated the arsenic. The resulting aluminum and sulfate contents in the permeate were below the limits set for household water [Sosiaali- ja terveystieteiden ministeriö, 1994].

## **8.2 Board mill effluents**

The flotation treated wastewater consisted of waters from the board machines and waters from chemithermo-mechanical pulping. The mill had a flotation treatment and the clean fraction of the water was taken from that for the filtration. Mänttari et al. [1998] have studied the use of microflotated and screened water in nanofiltration, but they did a few experiments also with micro- and ultrafiltration membranes. The effluent they used in their studies had a much higher COD content, 1550 mg/l, and a slightly higher content of inorganic matter and conductivity, 1000 mg/l and 160 mS/m, than the water in this study [III].

In the case of the flotation treated board mill wastewater, the permeate fluxes achieved varied from 58 l/(m<sup>2</sup>h) to 164 l/(m<sup>2</sup>h), the titania-modified membrane having the higher flux (Figure 13).

These fluxes are of the same magnitude as those that Mänttari et al. [1998] achieved in their studies with polymeric membranes. The retentions of COD and inorganic matter in this study [III] were somewhat lower than those Mänttari et al. [1998] had achieved with micro-and ultrafiltration membranes in their experiments, but then also the contents in the feed were lower in this case. The feed in this study [III] had a much lower COD<sub>Cr</sub> content than their permeate, and the content of inorganics in the feed in this research was close to their permeate content after microfiltration. Since the water qualities were so different it is understandable that the retentions are different.

The permeate flux achieved with the modified membrane was about 60 l/(m<sup>2</sup>h) higher than that of the unmodified membrane. The reasons for the observed differences in fluxes with different types of membranes could have resulted from the membrane modification, the different quality of the wastewaters or differences in the flow conditions in the membrane cell. The measurement made from the feed water did not show any significant differences in the quality, although the operational situation at the mill was different when the samples were taken. Thus, it is more likely that differences are either due to the membrane modification or due to the changed flow channel configuration. With the modified membrane the filtration experiments were made with the baffled flow channel, whereas with the unmodified membrane an open configuration was used.

The effect of differences in flow conditions was studied by repeating the experiments with the unmodified and titania-modified membrane with the same water using both flow channel constructions for both of the membranes. The results from these experiments are shown in Figure 15. The unmodified membrane could not be cleaned after the first filtration experiment and the pure water flux as well as the permeate flux were much smaller than those of the titania-modified membrane. The reduction of the permeate flux after 5 min of filtration compared to the pure water flux before was always much higher with the alumina membrane. This could indicate that it adsorbs substances from the water more eagerly and thus is not suitable for the filtration of the flotation treated board mill wastewater. This is also supported by the total fouling results, which are described by FR(PWF<sub>n</sub>-PWF<sub>a</sub>), and by the fact that it could not be cleaned after the first filtration experiment. Even after four filtration experiments the total fouling of the modified membrane was lower than that of the unmodified membrane. [III]

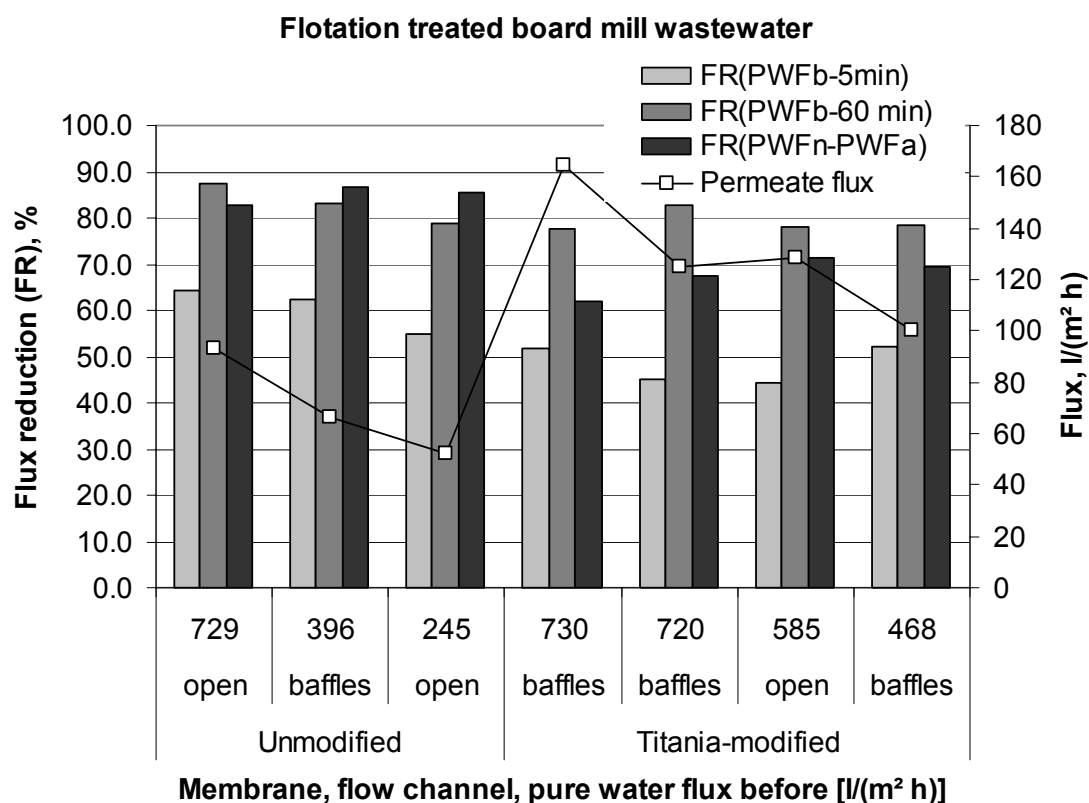


Figure 15 Permeate fluxes and different flux reductions with flotation treated board mill effluent in ultrafiltration with unmodified and titania-modified alumina membranes. The filtration pressure was 2 bar and the cross-flow velocity with an open flow channel was 0.13 m/s and with baffles it varied from 0.13 to 1.6 m/s. The filtration temperature was approximately 25°C. Abbreviations: FR = flux reduction, PWF = pure water flux, b = before, n = new membrane, a = after. E.g. FR(PWFb-5min) = flux reduction from the pure water flux before the filtration experiment to permeate flux at 5 min.

The average feed and permeate quality in the filtration experiments with the flotation treated wastewater is presented in Table 6. As can be seen from the table, the suspended solids and turbidity were retained effectively and the retention of color was in all cases nearly 60%. The substances that were mainly in a soluble form, for instance total solids, inorganic and organic matter, COD<sub>Cr</sub>, iron, and manganese, had very low retentions.

Table 6 Average feed and permeate quality in ultrafiltration experiments with flotation treated wastewater and clarified coating color wastewater from a Finnish board mill.

	Flotation treated wastewater		Coating color wastewater	
	Feed	Permeate	Feed	Permeate
pH, -	6.3 ± 0.12	6.6 ± 0.14	6.8	7.0
Suspended solids, mg/l	6.3 ± 3.6	0.8 ± 0.6	20	0.2
Turbidity, NTU	2.7 ± 1.6	0.14 ± 0.06	16	0.17
Conductivity, mS/m	98 ± 11	94 ± 10	161	151
Color, mg Pt/l	24 ± 2	10 ± 0		
COD <sub>Cr</sub> , mg/l	250 ± 55	230 ± 50	180	150
Total solids, mg/l	990 ± 8	940 ± 20		
Inorganic matter, mg/l	730 ± 8	690 ± 20		
Organic matter, mg/l	260 ± 5	250 ± 7		
Iron, mg/l	0.16 ± 0.02	0.17 ± 0.08	0.48	0.045
Manganese, mg/l	1.04 ± 0.14	0.94 ± 0.12		

The coating color wastewater is one of the paper mill wastewaters usually treated by membrane filtration [Anonymous, 1997; Paatero et al., 1999]. Usually, in these cases the aim is to restore the expensive components of the coating paste and reuse them. The permeate can be reused in the paste preparation. In our case the clarified coating color wastewater was further treated with membrane filtration. The coating color wastewater was filtered only with a  $\gamma$ -alumina membrane. The permeate flux achieved was 58 l/(m<sup>2</sup>h), which was exactly the same as that achieved with the flotation treated wastewater. The feed and permeate quality are presented in Table 6. The retention of iron was significantly higher for the coating color wastewater than that for the flotation treated wastewater. This indicates that the iron in the coating color wastewater was in particles or bonded to bigger molecules, which then could be retained by the membrane, whereas the iron in the flotation treated wastewater was in a dissolved form.

### 8.3 Pulp mill effluents

The bleach plant effluents are the most studied wastewater fractions for recycling. This is quite understandable since the bleach plant is the major source of wastewater in a modern kraft pulp mill. In an elemental chlorine free (ECF) kraft mill more than half of the entire mills organic load comes from the bleaching section, and from this organic load over 50% is

originally from the first alkaline extraction stage. Both ultra- and nanofiltration have been studied for the recycling of these bleach plant effluents. Ultrafiltration can reduce color, COD<sub>Cr</sub> and absorbable organic halides (AOX) significantly. Retentions of 67-99.7% for color and 45-95% for COD<sub>Cr</sub> from E<sub>1</sub> effluent have been reported [Jönsson, 1987]. For AOX the reported retentions for E<sub>1</sub> effluent have been 53-89% [Jönsson, 1989; Boman et al., 1991]. With nanofiltration smaller organic substances and part of the multivalent ions can be removed. For nanofiltration 100% retention of color and total organic carbon, and over 90% retention of organochlorinated compounds from E<sub>1</sub> effluent have been reported [Rosa and de Pinho, 1995]. Recently, also ceramic nanofiltration membranes for treatment of bleach plant effluents have been developed [Tomani and Seisto, 1999].

With the pulp mill wastewaters and especially with the E<sub>1</sub> effluent, which have high concentrations of total solids and ionic compounds (measured by conductivity), all membrane modifications showed similar fluxes (approximately 30 l/(m<sup>2</sup>h), Figure 13) and retentions. The fluxes achieved were similar to those achieved by Afonso and de Pinho [1990] in their studies with ultrafiltration Carbosep membranes at low, 0.65 m/s, cross-flow velocity. From their studies the importance of cross-flow velocity can be seen: when the cross-flow velocity was increased to 1.76 m/s, the permeate flux increased to approximately 90 l/(m<sup>2</sup>h) at 2 bar. The color removal we achieved was 56-59% and the TOC removal was 43-44%. These are close to those achieved by Afonso and de Pinho [1990]. However, the retentions of total solids (15-25%) reported here were the same or better than those Afonso and de Pinho had achieved. The retentions of iron, manganese and magnesium in our experiments were 70-83%, 89-94% and 57-60%, respectively. Jönsson [1993] has reported similar retentions for magnesium, but the retentions she achieved for iron were slightly lower than those achieved in this study.

With the E<sub>1</sub> effluent the titania-modified membrane had a slightly higher reduction of the pure water flux compared to that of the unmodified membranes, which could indicate that the unmodified membrane would be a better option for these waters. Moreover, the mixture of E<sub>1</sub>:D<sub>0</sub> effluent showed slightly lower fluxes and higher reductions of pure water fluxes. Jönsson and Petterson [1988] obtained similar results in their study with the effluent from the C stage. The C stage effluent contained, according to the studies of Jönsson and Petterson [1988], substances, which are soluble only at very low pH and when the pH is increased these substances adsorb onto the membrane. The D stage effluent is probably quite similar to the C stage efflu-

ent. The increase in suspended solids concentration and especially the fact that the concentration of suspended solids is much higher in the concentrate than in the feed indicated that the mixing of these liquors caused some kind of precipitation and that the precipitation is probably happening during the filtration process. The fouling might be decreased if a separate mixing step is added before the filtration, but this was not tested since it seemed that mixing did not bring out any benefits. However, the increased fouling and decreased retentions indicate that the separate treatment of the alkaline and acidic effluents would be more reasonable. This for example Bryant et al. [1995] have concluded in their work.

#### ***8.4 Conclusions from the filtration experiments with equipment version I***

In the membrane filtration experiments above, the thickness of the boundary layer was important since the concentration gradient forming was one of the factors determining the separation efficiency of the membrane. Even though, the Reynolds numbers achieved with the highest cross-flow velocities indicated that the flow in the module was turbulent or at least changing from laminar to turbulent, the boundary layer on the membrane surface was too thick. A thick boundary layer acts as a secondary membrane and causes the separation of large molecules to increase due to the steric hindrance of the molecules. Moreover, it also increased the resistance of the permeate flow and thus decreased flux. It seems that with the pulp wastewaters the flow achieved with equipment version I was not high enough and the retention and flux values achieved were mainly determined by the dynamic membrane formed by the substances in the wastewater [II, V]. However, in the case of the board mill wastewaters the dynamic membrane formed by the substances in the wastewater was not as thick and some differences in different membrane modifications could be seen. With the flotation treated board mill wastewater it seemed that the titania-modified membrane worked better than the unmodified membrane [III, V]. It gave higher fluxes and was more easily cleaned after filtration.

As a conclusion from the filtration experiments with equipment version I, it seems that arsenic removal from the bore well water, when a flocculation pre-treatment of arsenic is used, might be one possible application for ceramic membranes. The possibility to sterilize the membranes, high permeate fluxes, and arsenic removal using flocculation are indicating this.



However, further research is needed to confirm the long-term stability of the flux and the arsenic removal. For the flotation treated board mill effluent a moderate flux was achieved and the titania-modified membrane was found to be better than the unmodified one. However, the fouling of both the membrane types studied was high and since the waters did not have any specific features of interest with respect to ceramic membranes they were not considered for further study. For the pulp industry wastewaters, low flux values were achieved since a dynamic membrane, which determined both the separation and the permeation, was formed. It was not possible to obtain cross-flow velocities high enough to diminish this dynamic membrane and improvements in the equipment were needed. However, since the fouling of the membranes with the  $E_1$  effluent was fairly low, it was chosen as the reference water to be studied in the second equipment version.

## 9 Results from filtration experiments with equipment version II

The wastewaters filtered with equipment version II were an  $E_1$  effluent from a kraft pulp mill bleach plant and two new board mill effluents, a clear filtrate from a board mill disk filter and a biologically treated board mill total effluent (Table 5). The average permeate fluxes achieved with these wastewaters are presented in Figure 16.

The permeate flux achieved with  $E_1$  effluent at 1 bar pressure after an hour of filtration (94 l/(m<sup>2</sup>h)) was almost twice that achieved in the previous equipment version. The retentions achieved were slightly lower than those achieved in equipment version I, but then also the concentrations in the feed were somewhat higher. Thus, it seemed that the improvements made were beneficial: flux increased and the retentions remained similar. However, the long term stability of the permeate flux requires further study. Since the membrane used in the experiment had been used earlier for the filtration of  $E_1:D_0$  (2:1) effluent it was already fouled and its pure water flux reduction was much lower than that of a new membrane. However, it seemed that  $E_1$  effluent was not causing very much fouling, especially when the membrane was already fouled.

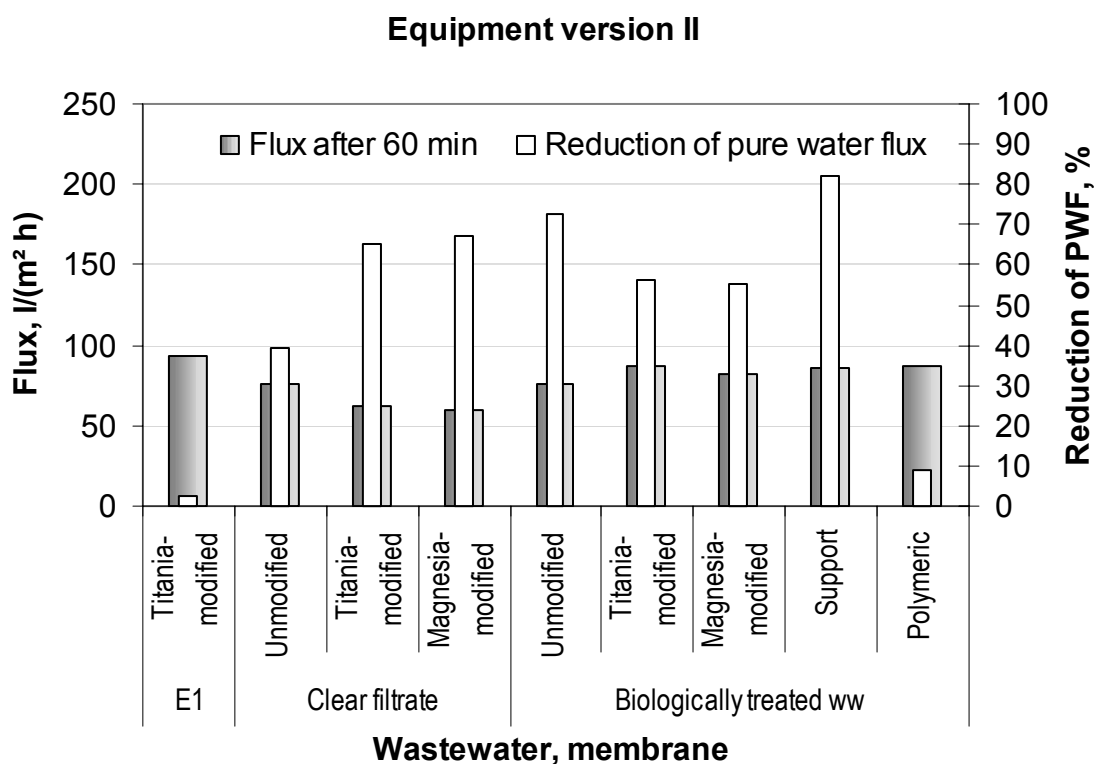


Figure 16 Permeate fluxes achieved with the different wastewaters (Table 5) and alumina membranes in equipment version II. The filtration pressure was 1 bar and the cross-flow velocity approximately 1 m/s, the filtration temperature approximately 25°C and the filtration time from 60 to 120 min. Polymeric corresponds to a polymeric membrane (Nadir® C30, Hoechst), which was glued on a ceramic support.

## 9.1 Board mill effluents

The permeate fluxes achieved after 2 hours of filtration with the board mill wastewaters varied from 57 to 76 l/(m<sup>2</sup>h) depending on the wastewater type and the membrane modification [IV]. In the following sections filtration results for the clear filtrate from a disk filter as well as those for the biologically treated board mill total effluent are presented and discussed.

### 9.1.1 Clear filtrate

The clear filtrate from the disk filter is one of the water fractions that could be recycled as such at least to some extent inside the paper and board mills. Membrane filtration of the clear filtrate is however necessary, if it is to be used in high-pressure showers where the solids still left in the clear filtrate can cause plugging of the nozzles and thus disturb production. More-

over, when considering a closed water system, it is necessary to limit the build up of dissolved and colloidal substances since they may affect the quality of the final product or cause problems in the production process. Membrane filtration of clear filtrate has been studied for example by Nuortila-Jokinen [1997] and some full-scale applications using polymeric membranes exist [Anonymous, 1997; Sutela, 1997].

With clear filtrate, the magnesia-modified membrane (Figure 16) gave the lowest flux, 60 l/(m<sup>2</sup>h), and the unmodified membrane gave the highest, 76 l/(m<sup>2</sup>h). The pure water flux of the unmodified membrane was approximately 175 l/(m<sup>2</sup>h) higher than that of the magnesia-modified membrane and 120 l/(m<sup>2</sup>h) higher than that of the titania-modified membrane. It seems that the higher fluxes achieved with the unmodified membrane were possible to retain at least for two hours [IV]. Since the reductions of pure water fluxes were higher with the modified-membranes, it could indicate that the unmodified membrane would be a better choice in the case of the clear filtrate. The fluxes achieved were good if they are compared to those that Nuortila-Jokinen and Nyström [1996] achieved in a PCI module, which had filtration conditions close to those used in this study [IV]. However, if the comparison is made to the CR filter in which the flow is enhanced by a rotor, and the cross-flow velocities are around 10-12 m/s, the fluxes achieved in this study were low.

All the membrane modifications showed quite similar retentions. Approximately 98% or more of the suspended solids and colloidal substances (measured by turbidity), 81% or more of the substances absorbed at a wavelength of 400 nm, 60 % of color, and 23 % of COD<sub>Cr</sub> were retained. The permeate had a turbidity and a suspended solids content comparable to the chemically treated water used at the mill as fresh water, but the COD<sub>Cr</sub> and the conductivity were significantly higher. It means that it might be possible to reuse the water, but in the long run it would probably lead to problems in the process since the COD<sub>Cr</sub> and the ionic compound levels inside the mill would increase. However, there is not a definite knowledge on the minimum water quality required for the paper or board manufacture. Usually the mills are not ready to take any risks of production break-ups so they prefer using higher quality water when ever possible.

### 9.1.2 Biologically treated board mill total effluent

The biologically treated board mill total effluent is actually the wastewater fraction, which is discharged to the river. Since the raw water used in the mill is usually taken from the same river, it would be more sensible to reuse the already treated water in the mill. However, the biologically treated water has a much higher turbidity, suspended solids and color concentration than for example the clear filtrate (Table 5). On the other hand, the concentrations of substances absorbed at a wavelength of 280 nm and  $\text{COD}_{\text{Cr}}$  are lower than those in the clear filtrate.

In the case of the biologically treated board mill total effluent, all fluxes were quite similar (Figure 16). The unmodified membrane gave the lowest flux, 76 l/(m<sup>2</sup>h), and the titania-modified and polymeric membrane gave the highest, 87 l/(m<sup>2</sup>h). The polymeric membrane glued on ceramic support in the PREC pilot had approximately 100 l/(m<sup>2</sup>h) lower pure water flux than the unglued membrane in the CR pilot. However, it was more or less similar to the pure water fluxes of the modified ceramic membranes, which were slightly lower than the pure water flux of the unmodified membrane. Neither a change in membrane material from ceramic to polymeric nor an increase in the membrane pores from 100 nm to 1250 nm showed any significant difference. Thus, it seemed that the biologically treated wastewater, even though it was taken after the clarification step, contained so much suspended and total solids that a dynamic membrane was formed on top of the membrane and this dynamic membrane was the one determining the flux and the retention properties. However, the differences between the membrane materials and the pore sizes can be seen in the reductions of the pure water fluxes. The polymeric membrane had a very low reduction in the pure water flux whereas the ceramic membrane support, the pore size of which was 1250 nm, showed the highest reduction. The polymeric membrane, C30 has already proven its applicability for pulp and paper industry wastewaters. For example, the Metsä-Serla Kirkniemi paper mill is using these membranes for the treatment of the white water in the fine paper and in the newspaper mill. The fluxes measured in the fine paper mill have been over 300 l/(m<sup>2</sup>h) [Sutela, 1997].

In this study [IV], the permeate fluxes achieved after two hours of filtration with the polymeric membrane in a CR filter were around 215-230 l/(m<sup>2</sup>h) compared to 76 l/(m<sup>2</sup>h) achieved in the PREC pilot [IV]. Moreover, the importance of shear forces could be seen in the CR fil-

ter in which the flux was strongly dependent on the rotation speed of the rotor (Figure 17). When the rotation speed of the rotor was decreased stepwise from over 1000 to 0 the permeate flux decreased from approximately 300 l/(m<sup>2</sup>h) to 100 l/(m<sup>2</sup>h). Moreover, when the rotor speed was increased back to over 1000 the fluxes achieved were lower than the ones achieved during the decreasing steps. These results showed the importance of the high shear forces in limiting the thickness of the dynamic cake and pointed out that it was necessary to further improve the PREC pilot towards even higher cross-flow velocities.

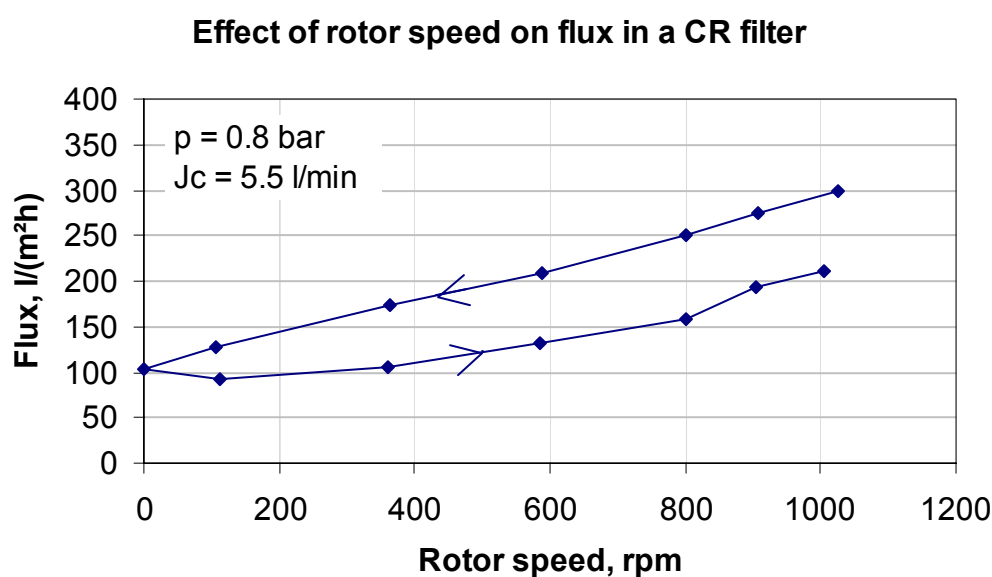


Figure 17 The effect of the rotor speed on permeate flux in ultrafiltration of biologically treated board mill wastewater with a CR250 filter. The filtration pressure was 0.8 bar and the concentrate flow ( $J_c$ ) 5.5 l/min.

The retentions achieved with the CR filter were slightly lower than those achieved in the PREC pilot and the permeate collected from the CR filter had a slightly higher concentration than the permeate collected from the PREC pilot [IV]. This was probably due to the fact, that the dynamic membrane formed on top of the membrane in the PREC pilot was thicker and thus enhanced the separation of different substances.

## **9.2 Conclusions from the filtration experiments with equipment version II**

The improved permeate flux achieved with the E<sub>1</sub> effluent showed that the changes made in the equipment were appropriate. In the case of the board mill effluents and especially with the clear filtrate the unmodified membrane had higher permeate fluxes and lower pure water flux reductions than the modified membranes, which could indicate that it would be more suitable for that type of water. In the case of the biologically treated board mill effluent, neither the membrane material nor the membrane pore size had an effect on the permeate flux or the retentions. It seemed that due to the low cross-flow velocity a dynamic membrane was formed on top of the membrane and it was determining the permeation and separation properties. The importance of the shear forces was obvious, as the experiments with the CR filter showed, and it was necessary to develop the PREC pilot in a way so that even higher cross-flow velocities could be achieved.

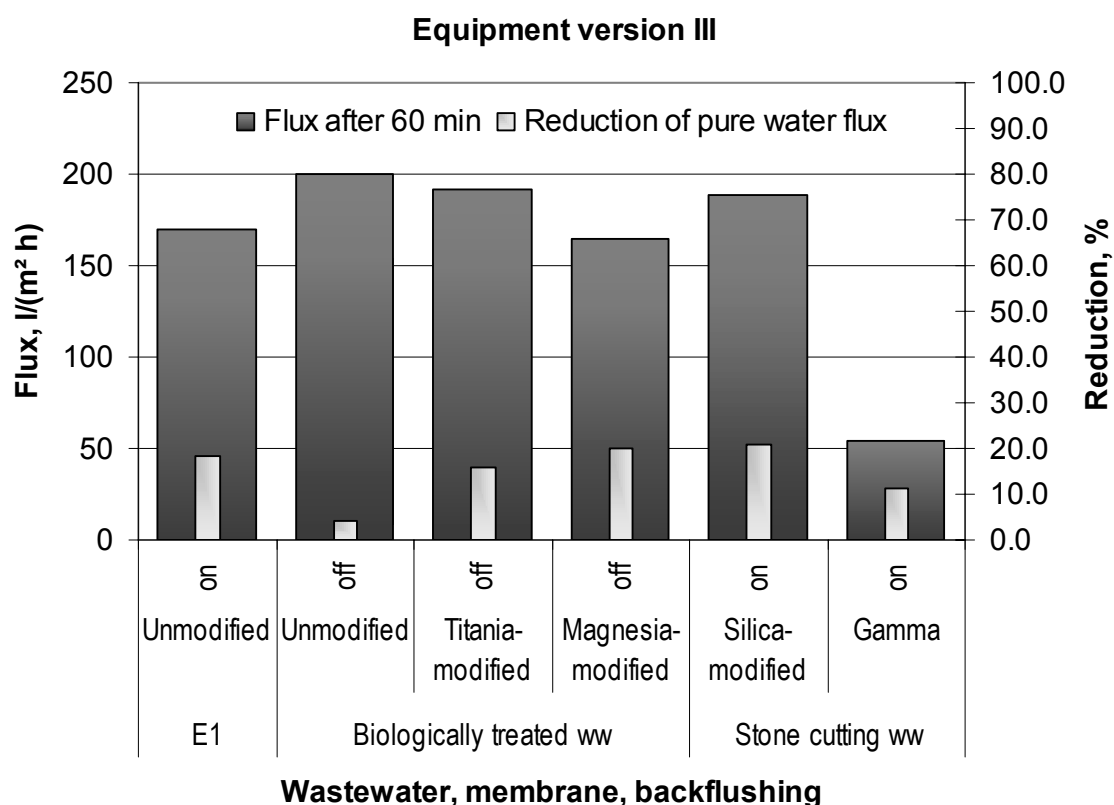
## **10 Results from filtration experiments with equipment version III**

Since the results with the biologically treated board mill effluent showed that the dynamic membrane was still forming on top of the membrane and determining the separation efficiency, a new more powerful pump was installed to equipment version III. Moreover, a back-flushing system was established. In the filtration experiments with equipment version III, the effect of the operating conditions as well as backflushing and backflushing conditions on the permeate flux were studied [VI, VII]. Transmembrane pressures of 0.8 to 1.8 bar and cross-flow velocities of approximately 2.5 to 9 m/s were used.

The wastewaters filtered with equipment version III, were an E<sub>1</sub> effluent from a bleach plant, a biologically treated board mill total effluent and a wastewater from an open stone cutting mine. The average permeate fluxes achieved with these waters at filtration pressures of 1.2 to 1.5 bar and cross-flow velocities of 4.5 to 6.3 m/s are presented in Figure 18.

In the filtration experiments with the E<sub>1</sub> effluent and those with the stone cutting wastewater backflushing was used, whereas the experiments with the biologically treated wastewater

were made without backflushing. The permeate fluxes achieved with the 100 nm membranes were from 157 l/(m<sup>2</sup>h) to 199 l/(m<sup>2</sup>h). The lowest permeate flux was achieved with the E<sub>1</sub> effluent whereas the highest was achieved with the stone cutting wastewater. These two wastewaters are very different from each other (Table 5 in Chapter 6.1.2). The E<sub>1</sub> effluent has a high conductivity and total solids content whereas the contents of suspended solids and turbidity are low compared to the stone cutting wastewater. The biologically treated wastewater is somewhere between these two in characteristics. The reductions in pure water fluxes were quite low, 4-23% compared to in the previous equipment versions, except for the E<sub>1</sub> effluent for which the reduction in pure water flux was similar to those achieved in equipment version I.



*Figure 18* Permeate fluxes and reductions of pure water fluxes achieved in equipment version III with different wastewaters and membranes. Operating conditions: filtration pressure from 1.2 to 1.5 bar, cross-flow velocity from 4.5 to 6.3 m/s and temperature 25 °C. With E<sub>1</sub> effluent and stone cutting effluent backflushing of 1 s every 60 s was used. The total filtration time was 25 h for the E<sub>1</sub> effluent, 2-24 h for the stone cutting wastewater and 2 h for the biologically treated wastewater. The  $\gamma$ -alumina membrane had an average pore size of 10 nm, whereas the other membranes had an average pore size of 100 nm.

## 10.1 $E_1$ effluent

Filtration experiments of 5 h to 24 h were made with the  $E_1$  effluent. The permeate fluxes achieved in 24 h filtration experiments are presented in Figure 19. The fluxes achieved at the end of the filtrations varied from approximately 80 l/(m<sup>2</sup>h) to 177 l/(m<sup>2</sup>h). These values show that for the membranes studied it was possible to achieve fluxes similar to those for the ceramic nanofiltration membranes as reported by Tomani and Seisto [1999]. In the first filtration experiment the pressure was adjusted only at the beginning of the experiment and not after that. The pressure decreased significantly towards the end of the filtration. Moreover, the cross-flow velocity was only measured at the beginning of the experiment and not after that. It is likely that the cross-flow velocity decreased as the pressure decreased.

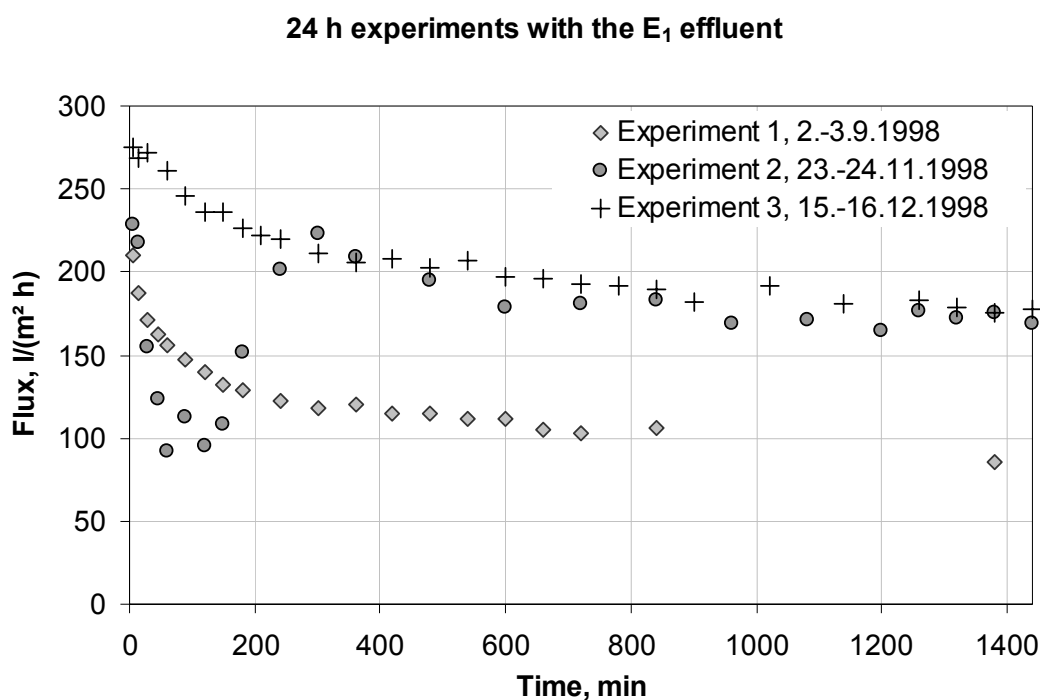


Figure 19 Permeate fluxes achieved with unmodified alumina membrane in ultrafiltration of  $E_1$  effluent. The filtration pressure was 1.6-1.3 bar in experiment 1 and 1.5 bar in experiments 2 and 3. The cross-flow velocity was approximately 6 m/s. Backflushing of 1 s every 60 s was made at a 4 bar pressure.

The permeate fluxes achieved with a pressure of 1.5 bar were 100 l/(m<sup>2</sup>h) higher than those achieved with a 1.3 bar pressure. This higher flux can be partly explained by the higher filtration pressure, but probably it is partly also due to the different feed water characteristics. The



feed waters used in the experiments had slightly different characteristics depending on the time they were sampled. The first set of E<sub>1</sub> effluent was taken in August 1998 and the second set was taken in November-December 1998. The average qualities of the feed water in these two cases are presented in Table 7. It seems that the feed water quality had an effect on flux: The flux achieved in the cases where the suspended solids and iron content in the feed water (feed I) was lower, but the conductivity, color, COD<sub>Cr</sub>, BOD<sub>7</sub>, total solids, fixed solids, volatile solids and phosphorus content were higher, resulted in 100 l/(m<sup>2</sup>h) or lower fluxes than the cases in which the feed water (feed II) quality was the opposite. [Niskanen, 1998]

Table 7 Characteristics of E<sub>1</sub> effluent used in ultrafiltration experiments and that of the permeate achieved with equipment version III. The filtration pressure was 1.6-1.3 bar for feed I and 1.5 bar for feed II. The cross-flow velocity was approximately 6 m/s. Back-flushing of 1 s every 60 s was made at a 4 bar pressure. The average filtration temperature was from 26-30°C.

	Feed I (August 1998)	Permeate I (August 1998)	Feed II (November- December 1998)	Permeate II (November- December 1998)
pH, -	9.3	9.2	10.5	10.5
Suspended solids, mg/l	9.2	1.3	21	1.5
Turbidity, NTU	26	0.98	60	0.97
Conductivity, mS/m	580	580	454	438
Color, mg Pt/l	5630	2750	3850	2000
COD <sub>Cr</sub> , mg/l	3700	2350	2670	1530
BOD <sub>7</sub> , mg/l	765	655	580	503
Total solids, mg/l	6200	5450	5120	4150
Fixed solids, mg/l	3570	3570	3170	2680
Volatile solids, mg/l	2640	1880	1950	1470
Iron, mg/l	0.59	0.16	1.01	0.17
Total nitrogen, mg/l	2.8	1.9	1.7	1.2
Total phosphorus, mg/l	0.58	0.35	0.34	0.24

The retentions achieved with equipment version III seemed to be slightly lower than those achieved with equipment version I. This is partly explained by a higher concentration of substances in the feed and partly by the dynamic membrane, which probably enhanced the separations in equipment version I. The permeate quality achieved is presented in Table 7.

## 10.2 Biologically treated wastewater

A number of studies were made with the biologically treated wastewater. The experiment made included the evaluation of the effect of the operating conditions and backflushing on flux and fouling as well as long-term experiments and comparison of different membrane modifications. In this section the results from the long-term experiments are presented whereas the operating conditions and backflushing are presented in chapter 10.4 and a comparison of different membrane modifications in chapter 12.

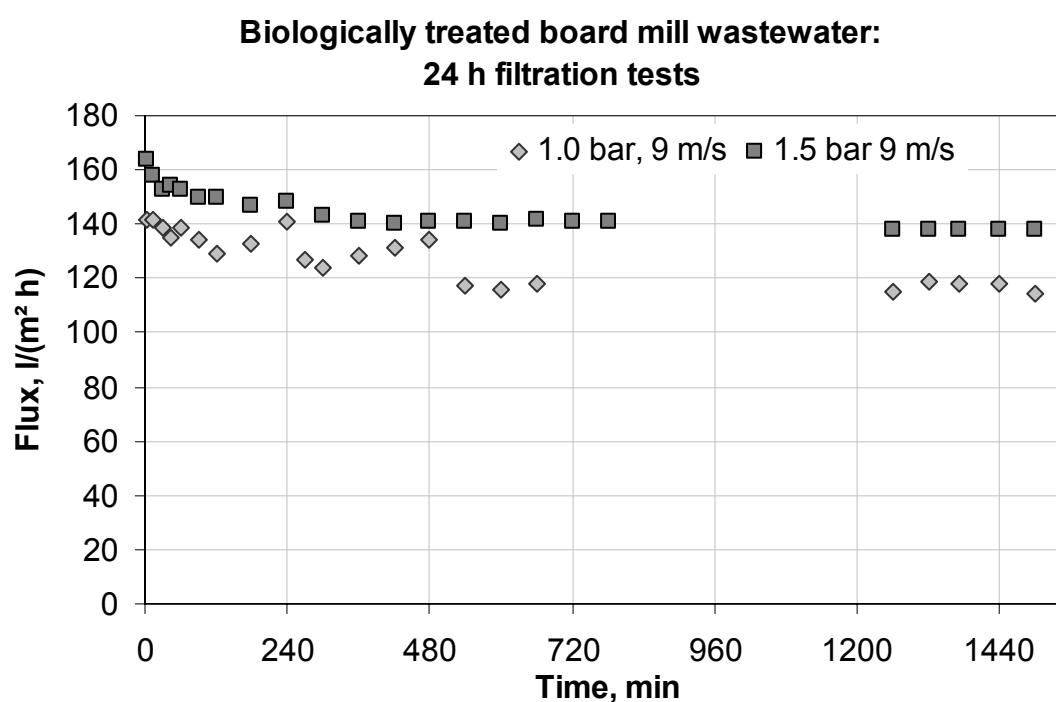


Figure 20 The permeate flux achieved with the biologically treated board mill total effluent in 24 h filtration experiments with a magnesia-modified alumina membrane in the equipment version III.

The permeate fluxes achieved after 24 h of filtration varied from 114 to 139 l/(m<sup>2</sup>h) as can be seen in Figure 20. All long-term filtration experiments were made with the same magnesia-modified membrane. The reduction in pure water flux was higher for the experiment with the higher filtration pressure, since a higher pressure forces more substances into the membrane and those substances cannot be removed with a simple rinsing. The retentions achieved in these long-term experiments were also good. Suspended solids and turbidity had retentions

over 96%. Moreover, iron and manganese had retentions over 60%, usually over 85%, and BOD<sub>7</sub> had retentions over 56%. In some cases, also total phosphorus had retentions over 88%. The permeate achieved was neutral, almost free of suspended solids and had a very low turbidity. The average characteristics of the permeate are presented in Table 8.

Table 8 Characteristics of the permeate achieved in 24-25 h filtration of biologically treated board mill effluent with a magnesia-modified alumina membrane.

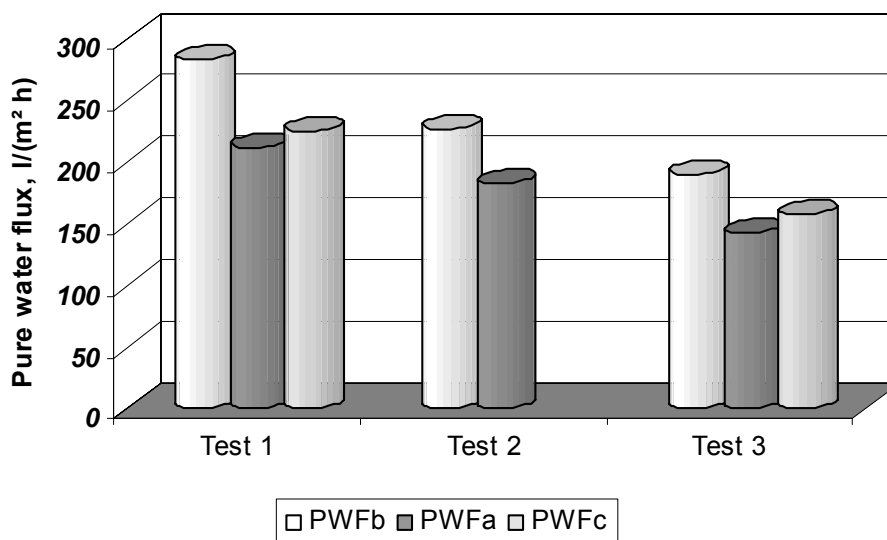
Analysis	Permeate, average (range)	Analysis	Permeate, average (range)
pH, -	8.5 (8.4-8.6)	Abs. 400 nm	0.071 (0.065-0.075)
Suspended solids, mg/l	0.9 (0.4-1.6)	Total solids, mg/l	1010 (1000-1040)
Turbidity, NTU	0.6 (0.3-0.8)	Fixed solids, mg/l	880 (850-900)
Conductivity, mS/m	131 (130-131)	Volatile solids, mg/l	140 (120-150)
Color, mg Pt/l	60 (50-70)	Iron, mg/l	0.020 (0.013-0.024)
COD <sub>Cr</sub> , mg/l	82 (80-85)	Manganese, mg/l	0.011 (0.005-0.016)
BOD <sub>7</sub> , mg/l	6 (3-10)	Total phosphorus, mg/l	0.076 (0.013-0.20)
Abs. 280 nm	0.36 (0.35-0.37)	Total nitrogen, mg/l	3.6 (2.9-4.0)

### 10.3 Stone cutting wastewater

The wastewaters produced in mining industries cannot always be discharged to the rivers and lakes as such [Bodzek, 2000]. They can contain high amounts of particles, heavy metals, salts etc, which can cause problems in the receiving waters and in the worst case destroy even the water flora and fauna. In open stone cutting mines, the slurry produced during the cutting process has a very small particle size and it settles poorly. This kind of wastewater causes problems in the receiving water by increasing turbidity and resulting in a muddier lake bottom when the slurry finally settles down.

The permeate fluxes achieved with the stone cutting wastewater stabilized very slowly [VIII]. Even after 24 h of filtration the flux (130 l/(m<sup>2</sup>h)) was decreasing, whereas the flux achieved with the biologically treated board mill total effluent remained more or less at the same level, 140 l/(m<sup>2</sup>h), after 9 hours of filtration [Piquet et al., 1998]. The comparison of pure water fluxes in Figure 21 show that the pure water flux is decreasing continuously. The reductions of pure water fluxes were 19-25% without any cleaning agents and 16-21% with nitric acid

treatment. The effect of nitric acid cleaning was minimal, which means that either most of the fouling was irreversible or that the cleaning method used was insufficient.



*Figure 21 Pure water fluxes in ultrafiltration experiments with the stone cutting mine wastewater. The membrane was a silica-modified alumina membrane (pore size 100 nm). The filtration pressure was 1.1 bar, the crossflow velocity 4.5 m/s, and the temperature 20°C. During experiments backflushing with permeate was made for 1 s every 60 s. The filtration time in test 1 was 2 h, in test 2 4 h and in test 3 24 h. Abbreviations: PWF = pure water flux, b = before, a = after, c = after cleaning.*

The reason for the fairly high and continuous fouling of the silica-modified alumina membrane could be the larger pore size, which enabled the small particles in the feed to penetrate inside the pores of the membrane and block them. Backflushing and high crossflow were able to remove the particles which were on top of the membrane or very close to the surface of the membrane, but not the particles that were deeper inside the membrane pores, as the lower fouling of the unmodified  $\gamma$ -alumina membrane shows. Bertram et al. [1993] have concluded in their study with dilute silica suspension that backpulsing can remove the particles forming the cake layer and those lying in the superficial membrane pores, but not those deeper inside the membrane structure. It could also be possible that the chosen silica-modification is unsuitable for this kind of wastewater. The unmodified membrane should be used in experiments in the future with this water in order to see, whether the reason was the modification. Moreover, the optimization of the operating parameters might decrease fouling and should be investigated.

The permeate flux achieved with the  $\gamma$ -alumina membrane with a pore size of 10 nm was slightly higher (57 l/(m<sup>2</sup>h)) without backflushing than that with backflushing (54 l/(m<sup>2</sup>h)). The backflushing was not beneficial in this case since the permeate flux was so low and the amount of permeate used for the backflushing was higher than that gained from the increase in flux. The flux with the wastewater was only 7-12% lower than the pure water flux measured before the experiment. Moreover, the reduction of the pure water flux was 12% and after nitric acid cleaning only 8%, which are very low values compared to those achieved with the 100 nm membranes.

Both of the membranes removed all suspended solids and turbidity, almost all iron, total phosphorus and color, and approximately 90% of total solids and manganese. The permeate quality compared to the water quality in the receiving lake was the same when the suspended solids and turbidity were in question. The permeate had always a lower color and iron content and in some cases also a lower phosphorus content. The nitrogen content in the permeate was slightly higher (0.3-0.6 mg/l) than in the lake. Thus, the permeate is well suited for discharge to the lake.

#### ***10.4 Operating conditions and backflushing***

At first, the filtration equipment was developed in a direction in which the cross-flow velocities in the membrane module could be increased. The cross-flow velocity necessary for the agreeable permeate fluxes was found to be over 2 m/s, which could be achieved in equipment version III. The operating conditions, especially filtration pressure and cross-flow velocity, were found to be important; by increasing the pressure and cross-flow velocity the permeate flux could be increased (Figure 22). With higher cross-flow velocities, the limiting flux was higher than with the lower cross-flow velocities and thus higher fluxes could be achieved with higher pressures. Afonso and de Pinho [1990] achieved similar results with E<sub>1</sub> effluent. In the case of the filtration pressure, there probably exists a limiting flux above which an increase in pressure does not increase the permeate flux any more. However, in the experimental pressure range it is not yet achieved, although with the lower cross-flow velocity it is quite near.

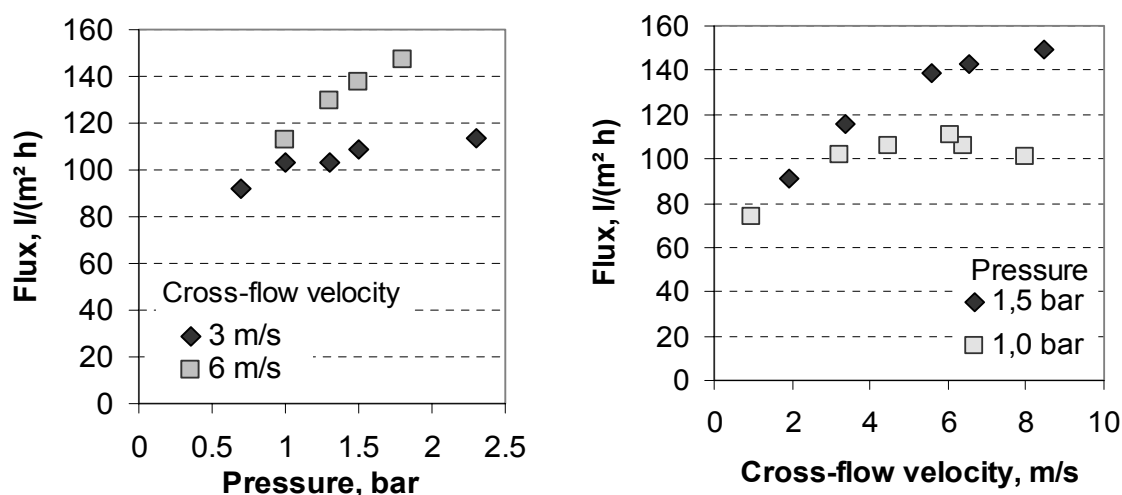


Figure 22 Effect of transmembrane pressure and cross-flow velocity on permeate flux with biologically treated board mill wastewater in microfiltration with a magnesia modified alumina membrane (M19B).

With a 1.0 bar pressure, a cross-flow velocity of 3.5 m/s is enough to limit the cake layer formation in such a way that an increase in cross-flow velocity does not have any additional effect on flux. Whereas, with a 1.5 bar pressure even the highest cross-flow velocity increased the flux. However, the increase at higher cross-flow velocities was not as large as with the lower cross-flow velocities. This indicated that eventually a limiting flux is reached, above which an increase in cross-flow velocity will not improve the flux any more.

Backflushing was used to improve filtration flux and to reduce fouling of the membranes. Good results were achieved in cases where a cake layer was formed on top of the membrane (Figure 23), but with tighter membranes the benefits achieved by cake removal were lost in the amount of permeate used for backflushing. The highest flux difference, over 54 l/(m<sup>2</sup>h), was achieved when backflushing was used in the first experiment and the experiment without backflushing was made after it, as was the case with the unmodified alumina membrane S3A. The benefits achieved by the backflushing were diminished when several experiments with and without backflushing were made one after another as the results achieved with the magnesia-modified membrane M20B showed. The results presented in Figure 23 are from the fifth (without backflushing) and the sixth (with backflushing) filtration experiments and the improvement in flux due to backflushing was only 5 l/(m<sup>2</sup>h). [VI; VIII].

The optimization of backflushing parameters for the biologically treated board mill wastewater [VII] showed that the backflushing time was the most important factor and the backflushing frequency was the second most important. The optimum for the biologically treated wastewater was found to be one second every two minutes with a 4 bar backflushing pressure. The effect of backflushing parameters on permeate quality was not as obvious, but it seemed that for example turbidity was retained better when the backflushing frequency, pulse length and pressure were decreased, which is understandable if part of the retention is based on the secondary membrane.

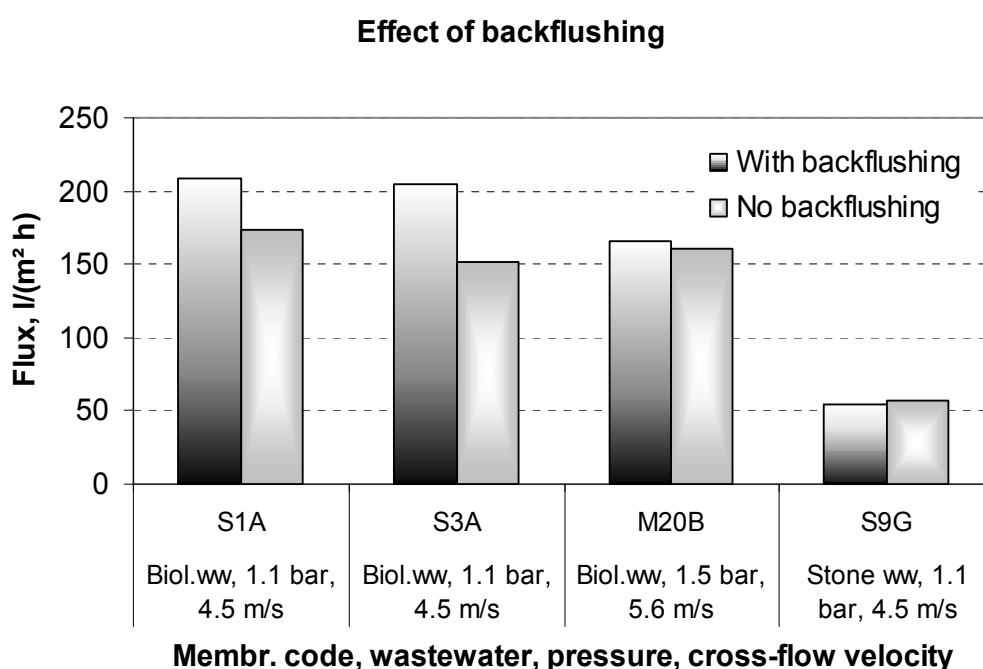


Figure 23 Effect of backflushing on flux in the filtration of biologically treated board mill wastewater (biol.ww) and stone cutting wastewater (stone ww). Membrane codes: S1A and S3A  $\alpha$ -alumina membranes (pore size 100 nm), M20B magnesia-modified  $\alpha$ -alumina membrane (pore size 100 nm), S9G  $\gamma$ -alumina membrane (pore size 10 nm). [VI; VIII]

### 10.5 Conclusions from the filtration experiments with equipment version III

The high cross-flow velocity improved significantly the permeate fluxes. A cross-flow velocity of 3 m/s or higher was found necessary to achieve reasonable fluxes. With higher pressures, higher cross-flow velocities were needed. Moreover, in cases where the flux was lim-

ited by the formation of a cake layer, the backflushing was found to be an effective way to enhance the flux. The effect of backflushing parameters was studied with the biologically treated board mill wastewater. The results obtained proved that the pulse length was the most important factor and the backflushing frequency the second most important factor in determining the flux. It was also observed that if the retention of substances was enhanced by the dynamic membrane or cake layer, better retentions were achieved when the backflushing frequency, pulse length and backflushing pressure were decreased.

Long term experiments, 24-25 h, showed that it was possible to obtain permeate fluxes from approximately 60 l/(m<sup>2</sup>h) to nearly 140 l/(m<sup>2</sup>h) depending on the type of wastewater filtered and the filtration pressure used. These values can be considered reasonably good. Moreover, the filtration experiments with the stone cutting wastewater showed that a high solids concentration in the feed is not a problem for the filter.

The removal of different substances was slightly lower than in the equipment versions I and II, which was expected since in those earlier equipment versions the dynamic membrane formed on top of the membrane was also participating in the separation of substances and enhanced it. From all the studied wastewaters, turbidity and suspended solids were retained fairly well and the permeate had a suspended solids content of 0.4-1.6 mg/l and a turbidity of 0.3-1.0 NTU.

## **11 Comparison of equipment versions**

In the filtration experiments with equipment version I, a transmembrane pressure of 2 bar and cross-flow velocities of 0.13-1.7 m/s were used. With the membrane module used the maximum cross-flow velocity was approximately 1.7 m/s with a flow channel height of approximately 1.6-1.9 mm, in which case the Reynolds numbers were approximately 6000 in the lower part of the module and 7200 in the upper part of the module. In the filtration experiments with equipment version II, a transmembrane pressure of 1 bar and a cross-flow velocity of approximately 1 m/s were used. Due to the problems with pump over heating, no inserts were used in the membrane module and thus the maximum cross-flow velocity achieved with equipment version II was approximately 1.1 m/s, in which case the Reynolds numbers were



approximately 23300 in the lower part of the module and 24300 in the upper part of the module. In equipment version III transmembrane pressures of 0.8 to 1.8 bar and cross-flow velocities of approximately 2.5 to 9 m/s were used. With a cross-flow velocity of 9 m/s and a flow channel height of approximately 2 mm, the Reynolds numbers were approximately 42200 to 48000.

According to Coulson and Richardson [1990], in a tubular pipe the flow would in this case be turbulent. The Reynolds number (Re) has been calculated as follows:

$$\text{Re} = \frac{\rho d_h v}{\mu} \quad (9)$$

where  $\rho$  is fluid density,  $d_h$  is the hydraulic diameter of the duct,  $v$  is the fluid velocity and  $\mu$  is the fluid viscosity. For turbulent flow in a duct of non-circular cross-section, the hydraulic mean diameter can be used. It is defined as four times the cross-sectional area divided by the wetted perimeter and in the case of a rectangular cross-section it is calculated as follows:

$$d_h = \frac{4d_a d_b}{2(d_a + d_b)} \quad (10)$$

where  $d_a$  is the width of the flow channel and  $d_b$  is the height of the flow channel. In a duct the flow is said to be streamline, when the Reynolds number is below 2000. In the area between 2000 and 4000 the flow is rapidly changing from streamline to turbulent. However, if a turbulent flow passes into a pipe in which the Reynolds number is below 2000, the flow will change to streamline at some distance from the point of entry. On the other hand, if the flow is initially streamline and the pipe diameter is gradually increased so that the Reynolds number exceeds 2000, the streamline flow will persist. Unstable streamline flows have been obtained in this manner at Reynolds numbers as high as 40000. However, it is not as much the question of whether the flow in the membrane module is turbulent or streamline, but how thick the streamline layers are. Since even when the turbulent flow exits there is a streamline boundary layer on top of the membrane and its thickness is the limiting factor. The theoretical development of an achievable Reynolds numbers in different equipment and membrane module versions is presented in Figure 24. With thinner flow channels higher cross-flow velocities can be achieved.

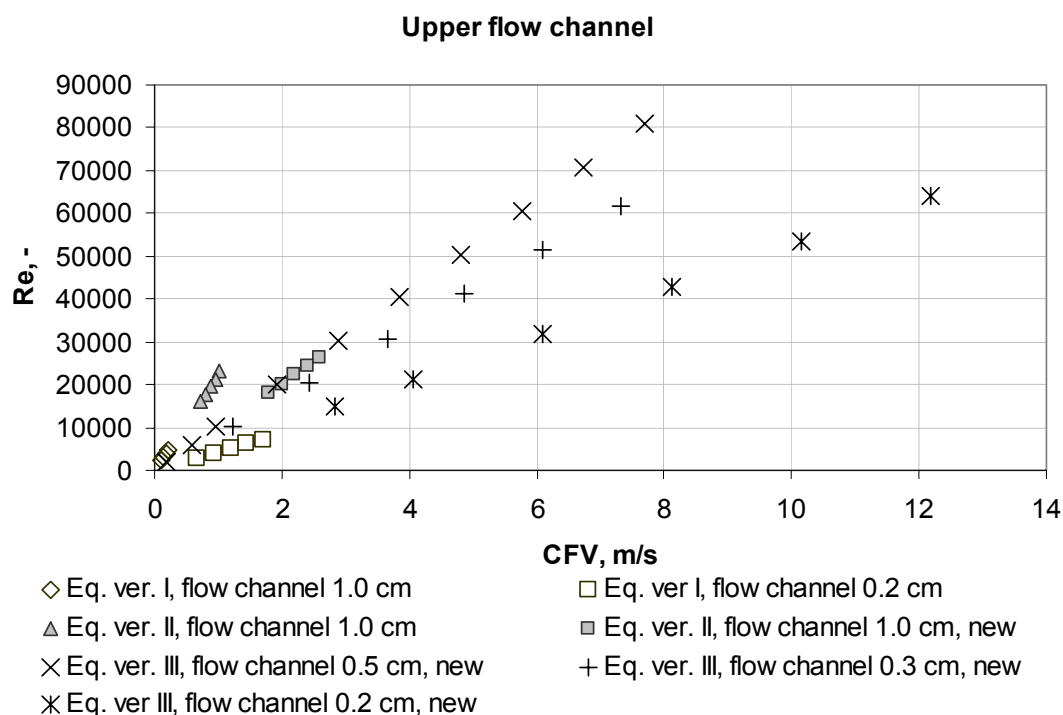
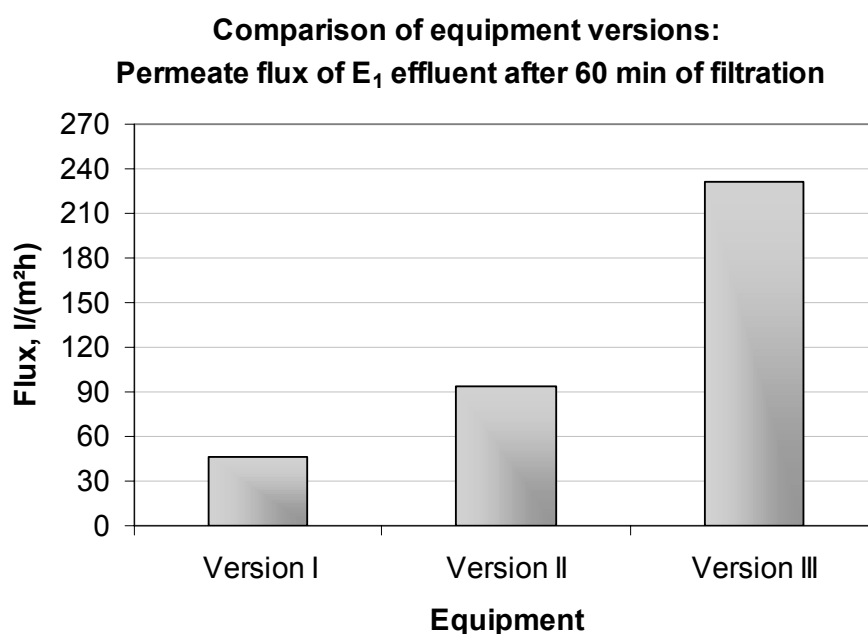


Figure 24 Reynolds numbers ( $Re$ ) versus cross-flow velocities ( $CFV$ ) achieved in different equipment and membrane module versions with different flow channel heights.

The first filtration experiments with pulp and board mill wastewaters proved that cross-flow velocities high enough to avoid cake filtration could not be achieved with the first equipment used [II, III]. It was obvious that at very low cross-flow velocities a dynamic membrane was formed on top of the membrane and its properties were determining both the permeate flux and the retentions of different substances. The effect of membrane materials and membrane modifications were secondary in these cases. Moreover, equipment version I proved to be very difficult to clean properly between experiments. Thus, the filtration equipment was further developed in order to be able to evaluate the actual behavior of the membrane. Equipment version II had also too low cross-flow velocities at least for the biologically treated board mill wastewater and the possible effects of membrane modifications could not be observed [IV]. Actually, even the polymeric membrane, which in a different kind of filtration apparatus gave good fluxes, showed similar flux and retention properties in equipment version II as the ceramic membranes. With equipment version III [VI] high enough cross-flow velocities could be achieved and some small differences with the membrane modifications could be observed.

In Figure 25 are presented the permeate fluxes achieved with the E<sub>1</sub> effluent in different equipment versions. As it shows, the permeate fluxes achieved with the E<sub>1</sub> effluent increased when moving from equipment version I to equipment version II and from equipment version II to equipment version III. The differences in flux values are so significant that they are not caused by the variations of the feed water quality, but more likely are due to the improved filtration conditions.



*Figure 25 Comparison of filtration performance of different equipment versions for filtration of E<sub>1</sub> effluent from a kraft mill bleach plant. Operating conditions: the filtration pressure was 2 bar in equipment versions I, 1 bar in equipment version II and 1.5 bar in equipment version III, the cross-flow velocity was 0.9 m/s in equipment version I, 1.1 m/s in equipment version II, and 5.9 m/s in equipment version III. Backflushing of 1 s every 60 s at 4 bar pressure was used in equipment version III.*

Wall shear stress ( $\tau_w$ ) can be used for the evaluation of the filtration conditions on the membrane surface. It can be calculated as follows [Coulson and Richardson, 1990, p.53]:

$$\tau_w = f \cdot \rho \cdot v^2 \quad (11)$$

where  $f$  is the friction factor. For smooth pipes when the Reynolds number is between 2500 and 100000 the friction factor can be estimated from Blasius equation [Coulson and Richardson, 1990, p.53]:

$$f = 0.0386 \cdot \text{Re}^{-0.25} \quad (12)$$

When wall shear stresses were calculated by using equations (11) and (12) the values achieved for the experiments made in equipment version I were from 0.1 to 12 Pa, in equipment version II from 2 to 3 Pa, and in equipment version III from 13 to 213 Pa depending on the cross-flow velocity used. The pure water densities and viscosities were used in the equations since the measured values for the used wastewaters were not available. Because of this the calculated values are probably underestimated. The low wall shear stress values in equipment versions I and II explain the flux behavior, as with lower wall shear stress values lower fluxes are achieved. Moreover, the limiting flux values are lower. Gésan-Guiziou et al. [1999] and Samuelsson et al. [1997] have achieved similar results with skim milk; the permeate flux and limiting flux values for the skim milk were lower with lower wall shear stress values. Gaucher et al. [2000] have determined the local average wall shear stress values for a Reynolds number of 5500 to be from approximately 0.5 to 4 Pa at different positions on a plate.

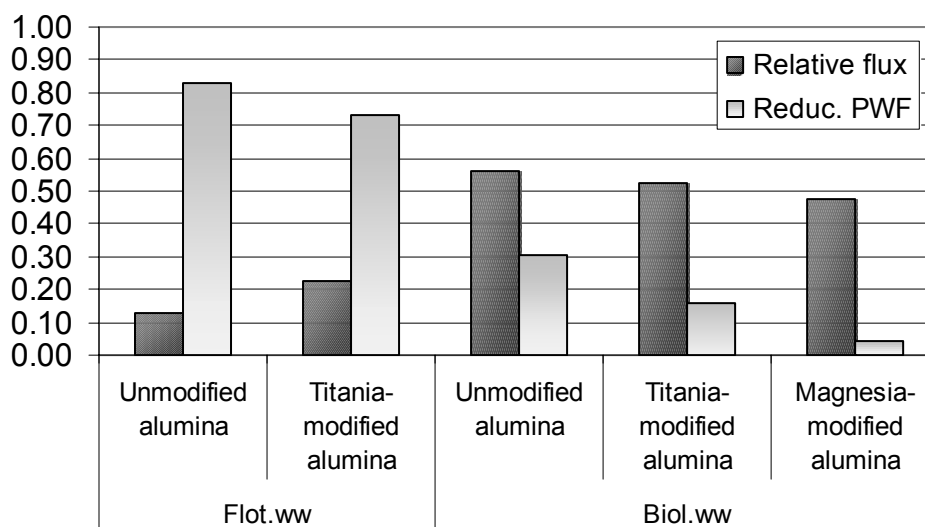
## 12 Comparison of membrane modifications

In cases where the dynamic membrane that formed on the membrane surface was not too thick the effect of membrane modifications on permeate flux could be seen (Figure 26).

In the case of the flotation treated board mill effluent, the titania-modified membrane seemed to be better than the unmodified membrane; whereas in the case of the biologically treated board mill total effluent, the unmodified membrane gave the best relative flux (Eq.(3) in Chapter 7). The differences in pure water flux reductions can be explained by the use of the different equipment versions and with the shorter rinsing time used in the experiments with the flotation treated board mill total effluent. [III; V; VII] The reasons why some of the modifications work better than the others is still uncertain since the characterizations of the membranes did not show any significant differences between the titania-modified and the unmodi-

fied membrane. Magnesia-modified membrane seemed to have a slightly smaller pore size due to the modification as the pure water fluxes of the new membranes indicated.

### Effect of membrane modification



*Figure 26* Effect of membrane modification on relative flux and reduction of pure water flux (PWF) with flotation treated (flot.ww) and biologically treated (biol.ww) board mill total effluent. The flot.ww was filtered with equipment version I (filtration pressure 2 bar, cross-flow velocity 0.13-1.0 m/s, temperature ca. 25°C) and the biol.ww was filtered with equipment version III (filtration pressure 1.5 bar, cross-flow velocity 6 m/s, filtration temperature ca. 25°C). Pure water fluxes in equipment version I were measured with reverse osmosis treated tap water and in equipment version III with untreated tap water.

## 13 Membrane fouling and foulant analysis

Some of the membranes used in equipment versions I and II were taken for analysis after the filtration experiments. Scanning electron microscopy (SEM) was used for the visual observation of fouling. Moreover, energy dispersive spectrometry (EDS) and electron spectroscopy for chemical analysis (ESCA) were used for analyzing foulants from the surfaces. The SEM pictures of clean and fouled membranes are presented in Figure 27.

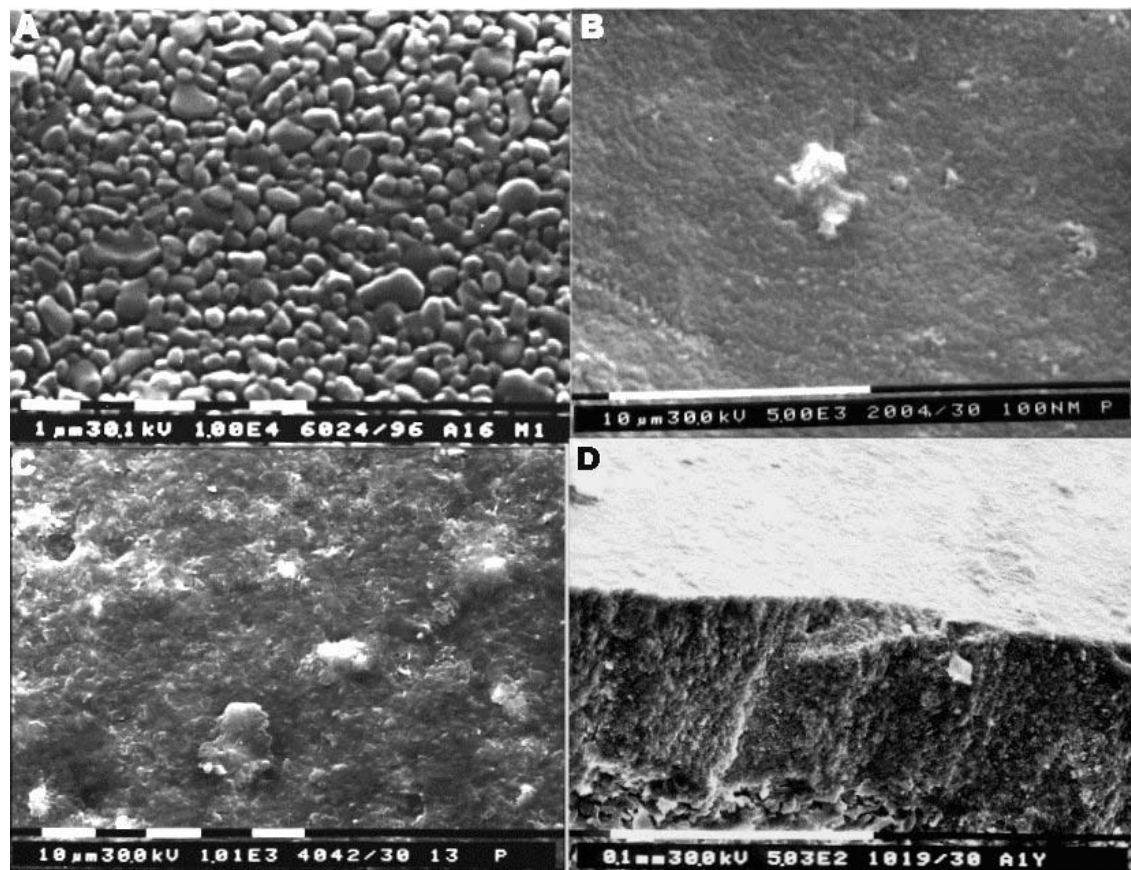


Figure 27 SEM images of A) surface of clean  $\alpha$ -alumina membrane, B) membrane used in arsenic removal, C) membrane used in filtration of  $E_2$  effluent and D) cross-section of membrane used in filtration of  $E_1$  effluent

The surface of the used membranes was covered with dirt and the original membrane surface could not be seen in the case of the membrane used for the treatment of the bleach plant effluent (Figure 27 C). The membrane used in arsenic removal was not as much covered with dirt but also there the original membrane surface could not be seen clearly (Figure 27 B). From the cross-section of the membrane used for the treatment of the bleach plant effluent it can be seen that dirt particles were piled-up on the surface of the membrane.

The EDS analysis of the surface of the membrane used in arsenic removal showed that the main components, aluminum excluded, were silicon, iron and arsenic. In dirty areas of the membrane the iron and the arsenic contents were higher than on the membrane surface overall. The dirt particles contained also sulfur. The silicon on the membrane surface can be leached from the supporting membrane in which alumina particles were bonded to each other with glass.

The ESCA analysis on the membrane used for the filtration of E<sub>2</sub>-effluent showed that the main components on the surface of the membrane were carbon, oxygen, silicon, nitrogen, magnesium and aluminum, respectively. Magnesium, iron, silicone and calcium were the main components of the fouling layer when analyzed with EDS. Agglomerates observed on the surface of the membrane contained mainly calcium, silicon, magnesium, iron and chlorine. If we compare the solubilities of some inorganic compounds containing these elements and select from them those that are insoluble or only slightly soluble in water and could be found from these waste waters we get the following list of possible foulants: calcium- and magnesium carbonate, different kinds of calcium, magnesium and iron silicates, calcium and magnesium oxalate, and some calcium and magnesium salts of carboxylic acids.

Dorica [1986] and Dorica et al. [1986] found in their studies with pulp mill effluents that the membrane deposits contained mainly magnesium, calcium and carbonate ions. From LWC-paper mill white water the deposit on the membrane surface contained also sodium soaps of carboxylic acids, esters of wood extractives and lignous substances [Laitinen, 1995]. As a conclusion, all of the substances listed above are possible as foulants and more studies have to be made in order to specify the foulants more precisely.

The EDS analysis of the board mill clear filtrate and the biologically treated board mill total effluent showed that the main components on the membrane surface, aluminum and metal oxides used for the membrane modification excluded, were silicon and iron. In the case of the clear filtrate also calcium, sodium, sulfur, and chloride were observed on all membranes and potassium on the unmodified membrane. While with the biologically treated wastewater, chloride and potassium were observed only on the unmodified membrane. Calcium was not observed on the titania-modified membrane and sodium was not observed on the magnesia-modified membrane. It was also noted that silicon, calcium, iron and sulfur were concentrated on the membrane surface whereas the sodium and potassium were observed also in the cross-section of the membrane.

## 14 Error estimation for the permeate flux

The error for the measured permeate flux can be estimated using the differential of the flux equation:

$$\Delta J = \frac{\Delta m}{A \cdot t_p \cdot \rho(T)} + \frac{m \cdot \Delta A}{A^2 \cdot t_p \cdot \rho(T)} + \frac{m \cdot \Delta t_p}{A \cdot t_p^2 \cdot \rho(T)} + \frac{m \cdot \Delta \rho(T)}{A \cdot t_p \cdot (\rho(T))^2} \quad (13)$$

In the equation  $\Delta$  means error,  $J$  is the permeate flux,  $m$  is the mass of permeate,  $A$  is the filtration area,  $t_p$  is the permeate collection time and  $\rho(T)$  is the fluid density, which is a function of temperature  $T$ .

The temperature error at the measurement point was estimated to be at the most 1°C, which was the accuracy of the thermometer used. Thus, if the measured temperature was around 30°C, the density error was 0.00030 kg/l. The error for the mass measurement was estimated to be 0.1 g and for the time measurement 5 s. The error in the measurement of the filtration area was estimated to be 0.2 cm<sup>2</sup>. However, the variation in membrane area due to manufacturing was larger than this and the standard deviation of the membrane area was 15 cm<sup>2</sup>, when all the used membranes were compared.

The pressure measurement error was estimated to be 0.2 bar. However, in some cases it could have been even 0.5 bar, especially in equipment version III in which the bigger pump caused more vibrations and thus also the needle of the manometer was vibrating more. The cross-flow velocity error varied from one equipment version to another. In equipment version I, when the cross-flow velocity was 0.13 m/s the variation was 0.006 m/s and for a cross-flow velocity of 1.2 m/s it was 0.06 m/s. In equipment version II, the measured variation in cross-flow velocity was in most cases 0.10 m/s, but in one case when there were problems in adjusting the pressure the variation in cross-flow velocity was 0.5 m/s. The error in cross-flow velocity in equipment version III was estimated to be  $\pm 0.5$  m/s, but it might have been even higher due to the robustness of the measurement process.

The estimated errors for the permeate flux calculated using equation (1) depended on how large the flux was. If the permeate was collected for two minutes the error was 4.3%, but when the time was extended to three minutes the error was only 3.0%. This means that for



example if the amount of permeate collected was 100 g (over 3 min) the permeate flux at 25°C would be 54 l/(m<sup>2</sup>h) and the flux error would be 2 l/(m<sup>2</sup>h). If the amount collected was increased to 400 g (over 2 min) the permeate flux would be 327 l/(m<sup>2</sup>h) and the flux error would be 14 l/(m<sup>2</sup>h).

Most of the values presented in this work were results from single experiments, since the availability of the membranes was limited and it was not possible to use a new membrane for each experiment. The cleaning of the membranes between experiments was not always efficient and thus using the same membrane gave results that were not comparable. Moreover, working with real industrial effluents meant that the quality of the wastewater changed from batch to batch. Thus it was nearly impossible to estimate statistical parameters such as standard deviation and average flux for the results. However, there were some results where the same membrane and same operating conditions for the same kind of wastewater were used. Most of these results were achieved with equipment version III and with a biologically treated board mill wastewater. In the best cases four experiments were available for comparison but in most cases only two. The standard deviations of the permeate fluxes measured after 60 min of filtration, for these different experiments, were found to be  $\leq 10\%$  in the cases where the membrane was not cleaned. This was considered to be satisfactory, especially since it included at least some of the variations existing in the wastewater quality and the variations originating from the operator. If the membrane was cleaned in between experiments the deviation was larger.

It can be concluded that the error estimated from the differential of the permeate flux was 4.3% in most cases. Statistical estimation of the results was pointless since in most cases the results were for single experiments and therefore there were simply not enough reproducible results available for use in evaluating the statistics.

## **15 Summary and conclusions**

As the literature review showed the manufacturing process of ceramic membranes includes: the preparation of a suspension from ceramic powder with necessary additives, the packing of the suspension into green compacts, and consolidation of these green compacts by heat treat-

ment. It is also obvious that the optimization of this process is not that easy and the reproducibility of the final product is one of the weaknesses of ceramic membranes and one of the reasons why they are always more expensive than polymeric membranes. However, ceramic membranes have advantages that overcome their weaknesses.

The literature review also showed that the effect of the feed properties, the membrane properties, and the filtration conditions are obviously very important for the success of a membrane filtration process. Since the filtration performance is almost always a question of optimization and balancing between the separation desired and the permeate flux required, a well chosen feed pre-treatment, a proper selection of membrane in relation to the feed properties, and optimization of filtration conditions are extremely important.

According to literature, ceramic membranes are applied especially in the areas where the advantages of them can be exploited. In food and beverage processing steam sterilizability and good chemical stability of the ceramics are appreciated. In biotechnology and pharmaceutical industry steam sterilizability and the biocompatibility of ceramic membranes are important as well as their resistance to microbial attack and biological degradation. In environmental applications, the advantages of the ceramic membranes are more dependent on the process in which they are used. Thus, good thermal and chemical stability of the membranes are often the factors that have made it beneficial to use ceramic membranes. The use of ceramic membranes in environmental applications is justified when valuable substances can be recovered from the wastes or when the volume of problematic wastes can be decreased significantly.

The experimental work showed the importance of the operating parameters such as filtration pressure and cross-flow velocity. The thickness of the boundary layer on the membrane surface is important since the concentration gradient is one of the factors determining the separation efficiency of the membrane. Even though, the Reynolds numbers achieved with the highest cross-flow velocities in equipment version I indicated, that the flow in the module was turbulent or at least changing from laminar to turbulent, the boundary layer on the membrane surface was too thick. It seemed that the cross-flow velocity was more important than the Reynolds number in describing the thickness of the boundary layer, which acts as a secondary membrane. This secondary membrane can increase the separation of large molecules but it also increases the resistance to permeate flow and thus decreases flux.

Equipment version I, even though it worked well for the bore well water, had limited abilities to treat board and pulp mill effluents. Especially, with the pulp mill wastewaters the flow achieved with equipment version I was not high enough and the retention and the flux values achieved were mainly determined by the dynamic membrane [II, V]. Even though, the improvements made to equipment version II were beneficial and better fluxes were achieved with the E<sub>1</sub> effluent without significant reductions in retentions. In the case of the biologically treated board mill total effluent [IV] a dynamic membrane, which determined both the retentions and flux, was formed. The comparative study with a CR filter and polymeric membranes proved that it was necessary to achieve even higher cross-flow velocities. In equipment version III operational conditions good enough for the treatment of different kinds of wastewaters could be achieved.

A cross-flow velocity of 3 m/s or higher was found necessary to achieve reasonable fluxes with wastewaters. With higher pressures, higher cross-flow velocities were needed. Moreover, in cases where the flux was limited by the formation of a cake layer, backflushing was found to be a good way to enhance the flux. The effect of the backflushing parameters was studied with the biologically treated board mill wastewater. The results obtained proved that the pulse length and the backflushing frequency were the most important factors in determining the flux. It was also observed that if the retention of substances was enhanced by a dynamic membrane or a cake layer, better retentions were achieved when the backflushing frequency, pulse length and backflushing pressure were decreased.

In cases where the dynamic membrane formed on the membrane surface was not too thick, some differences between different membrane modifications could be seen. The  $\gamma$ -alumina membrane gave always the lowest flux around 40-68 l/(m<sup>2</sup>h), which was due to a much smaller pore size (10 nm) compared to the other membranes (100 nm). The fouling of the  $\gamma$ -alumina membranes was also low. With the flotation treated board mill wastewater it seemed that the titania-modified membrane worked better than the unmodified membrane [III, V] and in the case of the clear filtrate the unmodified membrane had higher permeate fluxes and lower pure water flux reductions than the modified membranes [IV]. In case of the biologically treated wastewater, the unmodified membrane gave the highest flux, but then also the reduction of the pure water flux was the highest. The reasons why some of the modifications worked better than others, are still uncertain since the characterizations made on the mem-

branes did not show any differences between the titania-modified and the unmodified membranes.

Long term experiments, 24-25 h, showed that it was possible to obtain permeate fluxes from approximately 60 l/(m<sup>2</sup>h) to nearly 140 l/(m<sup>2</sup>h) depending on the type of wastewater filtered and the filtration pressure used. These values can be considered reasonably good. Moreover, the filtration experiments with the stone cutting wastewater showed that a high solids concentration in the feed is not a problem for the filter.

The removal of different substances was slightly lower in equipment version III than in the equipment versions I and II, which is quite understandable since in those earlier equipment versions the dynamic membrane formed on top of the membrane was also participating in the separation of substances. From all the studied wastewaters, turbidity and suspended solids were retained almost totally. Moreover, color and some inorganic substances, as for example iron, had good retentions in cases, where they existed as bigger molecules and not in a dissolved form.

From all the waters and wastewaters studied it could be said, that the membranes studied were suitable for arsenic removal from bore well water if flocculation was used as a pre-treatment as well as for the treatment of the stone cutting wastewater. The fluxes achieved in short-term experiments for the bore well water were promising, however the long-term stability of the process should be checked. In the case of the stone cutting wastewater, the flux achieved after 24 h was quite good, but it showed a declining trend. For both of these cases the optimization of operation conditions should be considered.

With the bleach plant effluents fluxes of nearly 100 l/(m<sup>2</sup>h) could be achieved for at least 24 hours. The suspended solids as well as the turbidity were almost totally retained, but the dissolved substances were not. If the goal is to have a closed water circuit, the dissolved substances would most likely cause problems in production. Thus further treatment of the permeate, with for example nanofiltration, would be necessary. The biologically treated board mill effluent showed also fluxes of 150 l/(m<sup>2</sup>h) for 24 hours, but also in this case only suspended solids and turbidity were retained almost totally. The amount of dissolved solids in the permeate remained high. The water might have some use in places where the quality demands are not so high. The membrane separation improved the quality of the water leaving from the

wastewater treatment plant by decreasing the nutrient load slightly and by ensuring a very low suspended solids and turbidity level even in cases where the operation of the activated sludge plant was disturbed.

It can be concluded, that the membranes studied have shown that it is possible to have reasonable fluxes even with dirty waters such as pulp and board mill effluents. The importance of operating parameters such as transmembrane pressure and cross-flow velocity are more significant as the water gets dirtier. These parameters should be optimized for each of the wastewaters separately. The backflushing was found to be an effective way to improve the permeate flux in cases where the permeate flow was restricted by the cake layer formed on top of the membrane. If the retention of the substances is enhanced by the dynamic membrane formed on top of the membrane, backflushing can reduce retentions. In these cases, an optimum between the flux and retentions should be found.

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## **17 Appendices**

I-VIII Publications