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Arne Lindbråthen[a]; David Ryan Grainger[a]; May-Britt Hägg[a]
[a] Department of Chemical Engineering, Norwegian University of Science and Technology, Trondheim, Norway

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Membranes for Purification of Chlorine in the Chlor-Alkali Industry: A Viable Option

Arne Lindbråthen, David Ryan Grainger, and May-Britt Hägg
Department of Chemical Engineering, Norwegian University of Science and Technology, Trondheim, Norway

Abstract: Polydimethylsiloxane, surface-modified glass, unmodified glass, and hollow-fiber were evaluated as membrane materials for chlorine beneficiation. The purification of industrial grade chlorine and the recovery of chlorine from a tail gas in a chlor-alkali process were considered. Polydimethylsiloxane (at low temperature) appeared to be a suitable material for both cases. The cost of separation was €0.04/kg Cl_2 recovered for Case 1 and €0.07/kg Cl_2 for Case 2. The selectivity of the surface-modified glass is lower and complex, expensive configurations were required. Glass hollow fibers achieved the purity specifications but low permeabilities necessitate large modules.

Keywords: Membranes, chlorine, gas separation, industry, chlor-alkali

INTRODUCTION

Chlorine as a reagent is widespread in a variety of industrial processes including water purification, various chemicals, plastics, and magnesium production. The worldwide production capacity of chlorine in 1998 was approximately 48 million tons per year (1). In 2003, 55% of European chemical industry turnover was underpinned by the chlor-alkali sector (2).

In many of these processes, chlorine purification or recovery is needed. Currently these are in the form of energy intensive processes, such as

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Address correspondence to May-Britt Hägg, NTNU, Department of Chemical Engineering, Norwegian University of Science and Technology, NTNU, Trondheim, Norway. E-mail: may-britt.hagg@chemeng.ntnu.no

cryogenic distillation and solvent-based absorption (1). Membrane gas separation, however, potentially has several advantages compared to conventional unit operations, including less energy consumption and being environmentally-friendly since no solvents are needed or emitted.

A comprehensive search for a well-suited and stable membrane for chlorine gas separation from inert gases started more than ten years ago at MEMFO, an R&D group at the Norwegian University of Science and Technology. Over the years several types of membrane materials have been tested. These include Teflon®, Viton®, carbon membranes, Poly(dimethylsiloxane) (PDMS), surface-modified glass membranes, glass hollow fibers and Matrimid®.

Also, under current development in the group are mixed matrix membranes consisting of Hyflon® and glass or fumed silica, in an attempt to combine durability and performance. However, this paper presents results for materials that have undergone more extensive testing.

The purpose of the current study was to investigate the feasibility of applying chlorine-resistant membranes in chlorine gas purification in general. The separation performance and durability of these materials have been reported by Hägg (3–5), Eikeland et al. (6) and Lindbråthen and Hägg (7). Based on the findings of these works, three of the tested materials (PDMS, surface-modified glass capillaries and unmodified glass hollow fiber) were chosen as the basis. The simulations were performed using an in-house membrane model integrated into the process simulation package Aspen Hysys®.

DESCRIPTION OF THE MEMBRANE SIMULATION TOOL

The membrane model, which consists of a system of coupled non-linear ordinary differential equations, is solved by dividing the membrane into N perfectly mixed stages (successive stages method) and following a procedure of successive approximation to converge the permeate-side component flows. The model was validated against models and experimental data published in literature. The membrane modules are integrated within the Hysys flowsheet and are capable of simulating the separation of any number of components in a co-, counter- or cross-flow configuration. A sweep stream may be fed to the permeate side and the Joule-Thompson cooling effect inherent in membrane separation is also calculated. The simulator calculates transport based on partial pressures rather than fugacities, but this is not believed to introduce any significant error in the moderate pressure range presented in this study. The simulation tool allows a quick assessment of membrane units in different configurations as well as the optimization of area and pressure arrangements.

BASE CASE PROCESSES

The design goal in this study was to achieve significant beneficiation of waste chlorine streams while optimising the energy and capital requirements. In order to cover a broad range of processes two different cases are simulated; one with a stream rich in chlorine (~97 vol%) and one lean in chlorine (~44 vol%). Details about the streams in Cases 1 and 2 are given in Table 1.

Case 1 is a more academic example involving the purification of a relatively pure industrial chlorine stream to gas cylinder purity. The reason for using this example is to exemplify how the different membranes perform in this concentration range.

Case 2 is an example from the Chlor-Alkali industry, where chlorine and caustic soda are produced from brine. The product stream from the electrolysers also includes hydrogen, nitrogen, oxygen and carbon dioxide. Most of the chlorine produced in these processes is recovered by liquefaction (1, 8, 9), but not all chlorine can be recovered. Some remains with the waste gases in what is known as a tail gas. The chlorine in this tail gas must be removed before the gas can be released into the environment. Currently, there are several methods which can be used and they are classified according to two classes: reactive methods, which convert the residue chlorine into a valuable product (like sodium hypochlorite or hydrogen chloride) and separative methods, which concentrate and recover the chlorine. The latter is often done using adsorption (1), but chlorine-resistant membranes may offer an alternative.

Table 1. Properties for the streams that need purification

	Case 1	Case 2
Temperature [°C]	30	From −30°C to 20
Feed flow, tons/h	16	16
Composition [mol%]	97.8 [Cl_2], 1.5 [O_2], 0.7 [N_2]	44.2 [Cl_2], 27.9 [O_2], 16.8 [N_2], 1.8 [H_2], 9.3 [CO_2]
Feed pressure (to membrane section) [bar]	1.06	1–16
Assumed product destination	Bottled high purity gas	Chlorination reactor, VCM plant
Delivery pressure [bar]	8.5	6.5
Purity of product [mol%]	≥99.8	98
Recovery (total chlorine) [%]	≥95	≥90

The composition of the tail gas depends on the extent of the liquefaction, amongst other process variables. In Case 2, the authors chose compositions that are typically found in a 95% liquefaction process (1, 9).

The required recovery and purification stated in Table 1 will depend on the final use of the chlorine. For Case 1 the feed is already relatively pure and the recovery should therefore be high. In Case 2 there are two possibilities: the scale-up of an existing process with an already installed chlorine tail gas removal unit, or the design of a completely new process.

SEPARATION BY MEMBRANES

Gases are transported through membranes due to a driving force, which is usually in the form of a fugacity difference across the membrane. The gas flux through a membrane is given by Eq. (1).

$$dQ_i = dA \cdot \frac{P_i}{l}(\phi_{i,f} \cdot p_{i,f} - \phi_{i,p} \cdot p_{i,p}) \tag{1}$$

where dQ_i (m^3/h) is the volumetric flow rate of component i through the membrane in an area increment, P (m^3(STP) m/(m^2 bar h)) is the permeability of component i in the membrane, dA (m^2) is an area increment, l (m) is the thickness of the membrane, p is the partial pressure of i, and subscripts f and p refer to the feed and permeate sides, respectively. ϕ is the fugacity coefficient of i. It was assumed in this study that the gases behave ideally and the fugacity coefficients are equal to 1 and hence the driving force is due to the partial pressure difference.

If the sorption-diffusion model is assumed, then permeability is defined as the product of the diffusivity (D) and the sorption (S) of the component in the material; the importance of these two factors will vary depending on the type of material.

$$P_i = D_i \cdot S_i \tag{2}$$

The permselectivity of the membrane for the transport of one component over another is the ratio of the permeabilities:

$$\alpha = \frac{P_i}{P_j} = \frac{D_i \cdot S_i}{D_j \cdot S_j} \tag{3}$$

Gases permeate through PDMS according to the sorption-diffusion mechanism. In porous membranes, the transport mechanisms include selective surface diffusion (surface-modified glass), molecular sieving (glass hollow fiber), Knudsen diffusion and bulk flow, although Eqs. (1)–(3) are still applicable. More information on these can be found in (10, 11).

The glasses can be drawn or processed as fibers. PDMS would most likely be produced as a composite membrane for flat sheets in a spiral-wound module.

The pressure difference is crucial in a membrane process, since it is inversely proportional to the required membrane area. However, an increased pressure difference may yield an economic penalty, since it will require additional compressors. Increasing the feed pressure to permeate pressure ratio increases the permeate purity of the component with the highest permeability (12).

The Membranes

For a material to be suitable to be used as a membrane, three requirements must be satisfied:

1) The material must be stable over time
2) The material must be easy to form into a membrane
3) The material must have sufficient permeability and selectivity

The first requirement is especially challenging with respect to chlorine exposure. The third requirement requires simulations for verification, which is the scope of this work.

POLYDIMETHYLSILOXANE (PDMS)

PDMS is a rubbery material and retains rubbery properties even at very low temperatures (glass transition temperature (Tg) is -123°C). Generally, the most condensable gas, here chlorine, is the fastest permeating compound in rubbery polymers. As Hägg (3) and Eikeland et al. (6) have demonstrated, PDMS has an excellent permeability and selectivity for the use in chlorine separation. Eikeland et al. (6) gives the details on the synthesis and cross-linking of the PDMS.

However, the durability of PDMS when exposed to chlorine gas is strongly dependent on three factors:

1) The presence of iron(III) chloride (6): Iron(III) chloride seems to catalyze the degradation of PDMS, most likely by acting as a catalyst for the substitution of a hydrogen (or methyl group) by chlorine in the PDMS. This is believed to lead to an increase in the glass transition temperature (Tg), yielding a more brittle material and thus losing material performance.
2) The curing method chosen (6). Commercially available PDMS polymers are not very chlorine-stable. However, the stability can be significantly improved by choosing the proper curing method. A "normal" PDMS

will be severely degraded after approximately three hours chlorine gas exposure, even at 30°C and 1 bar, whereas a properly crosslinked PDMS membrane was observed within the current study to withstand at least 50 days exposure at identical conditions.

3) The chlorine exposure temperature: Material degradation is usually associated with a chemical change in the material and, as in most chemical reactions, the reaction rate is proportional to the temperature. Thus, a lower process temperature results in slower degradation.

In the case of PDMS, the higher sorption of chlorine relative to the other gases is the dominating factor in the selectivity equation (3). Permeabilities are presented in Table 2.

Surface-modified Glass Membranes

Microporous glass membranes are synthesized from a borosilicate glass that is phase separated and acid leached (13). As reported by Lindbråthen and Hägg (7), surface-modified glass membranes (Fig. 1), produced and modified according to Kuraoka et al. (14), can be made quite chlorine stable if the proper modifying compound is chosen. A perfluorinated silane (heptadeca-fluoro-1,1,2,2-tetrahydrodecyl-dimethylchlorosilane) was found to give the best stability and permselectivity combination. The membrane was proven to be stable after months of exposure (the permselectivity actually improved).

Table 2. Membrane properties for chosen materials

	PDMS	Surface mod. glass	Glass hollow fiber
Chlorine permeability $[\mathrm{m^3(STP)\cdot m/(m^2\cdot bar\cdot h)}]$	$1.36\cdot 10^{-5}$	$2.01\cdot 10^{-5}$	$1.18\cdot 10^{-11}$
Oxygen permeability $[\mathrm{m^3(STP)\cdot m/(m^2\cdot bar\cdot h)}]$	$7.33\cdot 10^{-7}$	$5.15\cdot 10^{-6}$	$1\cdot 10^{-9}$
Nitrogen permeability $[\mathrm{m^3(STP)\cdot m/(m^2\cdot bar\cdot h)}]$	$3.42\cdot 10^{-7}$	$4.29\cdot 10^{-6}$	$5.89\cdot 10^{-10}$
Hydrogen permeability $[\mathrm{m^3(STP)\cdot m/(m^2\cdot bar\cdot h)}]$	$8.97\cdot 10^{-7}$	$1.11\cdot 10^{-5}$	$2.65\cdot 10^{-8}$
Carbon dioxide permeability $[\mathrm{m^3(STP)\cdot m/(m^2\cdot bar\cdot h)}]$	$3.91\cdot 10^{-6}$	$1.19\cdot 10^{-5}$	$2.18\cdot 10^{-10}$*
Membrane thickness [μm]	7 (on support, flat)	30 (Capillary)	10 (Fibre)
Membrane replacement factor [1/year]	1	0.5	0.2
Membrane module cost $[\$/\mathrm{m^2}]$	20	100	35

*Value estimated using molecular dimensions.

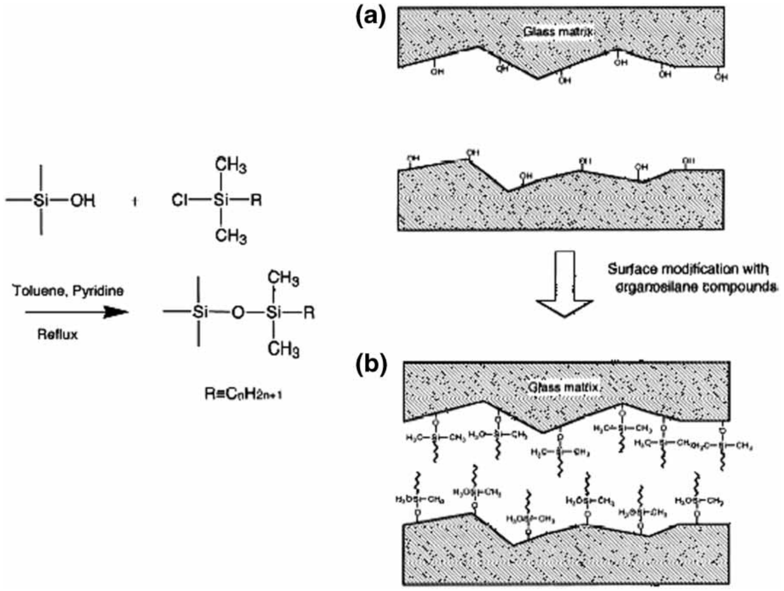

Figure 1. Surface modification of glass pores (14).

The surface-modified glass transports the chlorine according to a selective surface diffusion mechanism (15). In this model the more condensable gases accumulate on the glass surface as a two dimensional liquid. These can slide over the surface, providing a more selective transport mode compared to Knudsen diffusion.

The major disadvantage with the glass is its brittleness, so restrictions may be imposed on the operating conditions. The cost of the surface modifying compound is also very high.

Glass Hollow Fibers

Glass hollow fibers are produced differently to the surface-modified glass capillaries, since no explicit phase separation is performed. The fibers are spun directly from the melt, with only slight phase separation as the glass is cooled. When this glass is acid leached, a molecular sieve membrane is obtained (16). A molecular sieve material discriminates between molecules according their size and shape, thus the glass hollow fiber retains chlorine. The gas permeabilities are low (Table 2).

Membrane Properties

Table 2 summarizes the measured properties for the chosen materials and in the membrane thickness row, the most probable module configuration is also indicated. Permeabilities were measured using the fixed volume-varying pressure set-up, which is the system of choice when handling poisonous and corrosive gases such as chlorine because they are contained within the system. In this method, a gas is applied on the high pressure side, the permeate side initially evacuated to less than 1 mbar, and then isolated. The pressure increase with time on the permeate side is logged. The permeability is calculated from the steady state pressure gradient (dp/dt) on the permeate side of the membrane.

A MKS Instrument type 626A (0-10 mbar) pressure transducer was used to measure the permeate pressure. The accuracy of this transducer is 0.15% of the measured value. On the high-pressure side, a MKS Instrument (type 121A(0-5000 mbar)) pressure transducer was used with an accuracy of 0.5% of measured value. The "background leakage rate" was also taken into account.

The packing density for a membrane module is determined by the configuration. A hollow fiber module may contain up to 30,000 m^2 (membrane surface)/m^3 (module volume) whereas a spiral wounded module typically has a packing density of about 300 m^2/m^3 (10). A capillary module typically has a packing density of 600–1200 m^2/m^3.

The membrane replacement factors given in Table 2 are rough estimates and will be a function of many process variables, such as temperature and the presence of trace components or particulates that are harmful to the membrane material.

For the membrane module cost, it has been estimated that simple polymers may be produced for 20 $\$/m^2$ (17) and this was assumed to be the case for PDMS. For the surface-modified glass and the glass hollow fibre, estimating the module cost is more difficult. The cost of a glass hollow fiber module is estimated to be three times the material cost quoted by Schott AG (Germany). The most uncertainty is in the module cost for the surface-modified glass. The surface-modifying compound will contribute a significant portion of the total cost, but a commercial-scale quote is not yet available. Therefore, the typical cost of an equal amount of Teflon® (polytetrafluoroethylene) has been used as an estimation of the cost of the surface modifying component. The uncertainty of these estimates is discussed in Results and Discussion.

As Table 2 reveals, the PDMS seems to be a better over-all solution for chlorine gas separation than the surface-modified glass membrane. However, both materials are simulated because of the uncertainty surrounding the durability of the materials (particularly PDMS) at the process conditions.

Cost Estimation

To be able to distinguish which membrane performs the best in a given case, the capital and operating costs for the given process were estimated.

Because many configurations were evaluated, indicative capital and operating costs were first calculated based only on the membrane and compressors. Remaining equipment items such as heat exchangers would have contributed only a small fraction of the cost. The operating cost included the electric power consumption, chlorine loss, module replacement, capital charge, maintenance, and insurance (see Table 3). The optimal configuration in each case was later costed in more detail using Aspen Icarus$^{\mathrm{TM}}$.

The membrane installation cost, $C_{\mathrm{mem,ins}}$ is estimated as the product of the membrane area [m^2], the membrane module cost [\$/m^2] and the installation factor. The compressor installation cost, $C_{\mathrm{comp,ins}}$, was estimated using Equation (4), which was derived from a figure presented in Peters and Timmerhaus (20).

$$C_{\mathrm{comp,ins}} = 912 \cdot \left(W_{\mathrm{comp}}\right)^{0.9315} \cdot f_m \cdot f_i \cdot f_{\mathrm{inst}} \tag{4}$$

Where W_{comp} is the compressor duty [kW], f_m is the material of construction factor (i.e. 1 for carbon steel and 2.5 for stainless steel), $f_i =$ inflation factor (2003 is the base) estimated to 1.03 (for 2006).

The annual chlorine waste cost is the cost that arises because the membrane process will not be able to recover 100% of the chlorine. This is significant in Case 1 because a ready-for-market product is used as the feed, but is neglected in Case 2, where the tail gas is considered a waste stream.

$$C_{Cl\_waste} = (100 - \mathrm{R})/100 \cdot \mathrm{F} \cdot (\text{annual run time}) \cdot (\text{chlorine value}) \tag{5}$$

Where R is the percentage of chlorine recovered and F is the feed size [tons/h].

Table 3. Cost estimation assumptions (18)

Factor	
Installation factor for purchased equipment	4
Annual operating time	8000 hours
Fixed costs	
Capital charge	15% of installed capital cost
Module replacement frequency	According to material durability
Maintenance	2% of installed capital cost, excluding module replacement
Insurance	1% of installed capital cost
Variable cost	
Electrical power	€0.035/kW h (19)
Chlorine value	
98 Vol% Cl_2	\$300/ton
99.8 Vol% Cl_2 (bottled)	\$47, 000/ton[a]
\$:€ euro exchange rate	1.28

[a] Budget quote from AGA AS (Oslo, Norway).

RESULTS AND DISCUSSION

An optimization study was done in which the number of membrane stages, configuration, and process pressures were varied for each material and both base cases. The goal was to optimize the cost and energy consumption of the case. Initial screening was done using simplified economics (as discussed in Cost Estimation), whereas the optimum case was costed using Aspen Icarus^{TM} 12.0 and with a full equipment list.

Case 1 – Purification of Industrial Grade Chlorine

It was generally difficult to achieve 95% recovery of chlorine at 99.8 mol% purity with the permselectivities of the membranes under investigation. The membrane inlet temperature was kept constant at 30°C in all simulations.

PDMS

As a screening of the process, the following simulation variables were chosen for cross-linked PDMS.

Feed pressures from 3 to 7 bar with 2 bar increments
Permeate pressures of 0.1, 0.75, and 1.4 bar

It was found that one membrane stage could achieve the specifications (see configuration presented in Fig. 2).

The pressure ratio ($P_{feed}/P_{permeate}$) dictated whether or not 99.8 mol% chlorine could be achieved at 95% recovery. It can be seen in Fig. 3 that a ratio of at least 30 was required.

Since PDMS is a standard commercial membrane material, the material costs are relatively low for this polymer. It was found that the compressors contributed about 99% of the capital cost. Fixing the pressure ratio at 30 and varying the feed pressure yielded the cost curve shown in Fig. 4.

The permeate pressure decreases accordingly as the feed pressure decreases, since the pressure ratio is fixed. Pressure drops in the interstage coolers become more significant and so the energy consumed by the compressors increases.

The most cost-effective alternative was to apply 6 bar on the feed side of the membrane and 0.2 bar on the permeate side, which leads to a membrane area of 0.03 $m^2/(kg\ Cl_2\ recovered/h)$. In this case, with a feed flow of 16 tons/h, a membrane area of only 440 m^2 is needed. Detailed costing revealed a separation cost of €0.036/kg of purified chlorine. The main uncertainty in this estimate was the material durability. However, the extent

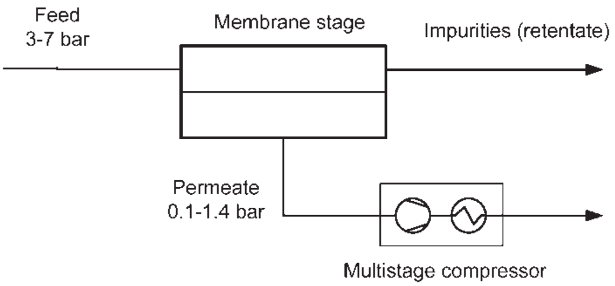

Figure 2. PDMS process (Case 1).

of membrane life time was seen to have little effect on the separation cost (Fig. 5), as the cost of the compressors is the dominant factor.

Surface-modified Glass

The separation was harder to perform using a surface-modified glass membrane, since the selectivities for chlorine over the other gases are lower than for PDMS. Figure 6 presents the results of the process screening.

The values in Fig. 6 are calculated with an infinite pressure ratio, as this leads to the maximum purity that any module may possibly achieve. Figure 6 reveals that the separation cannot be fulfilled to the desired chlorine specifications using one module or even two modules with inter-stage recompression.

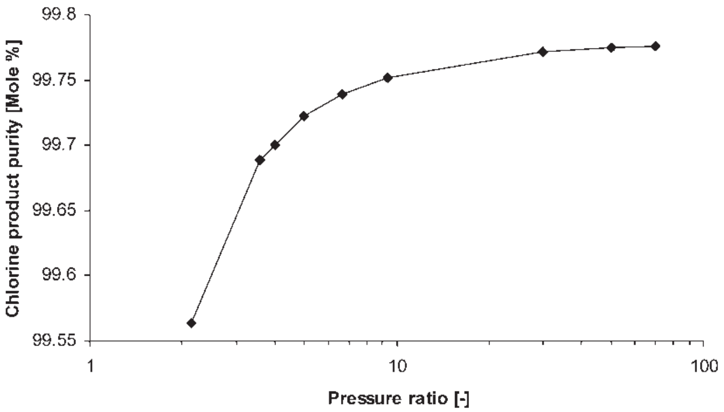

Figure 3. Variation of chlorine product purity with pressure ratio. Feed concentration of chlorine is 97.84 mol%, recovery is 95% (PDMS).

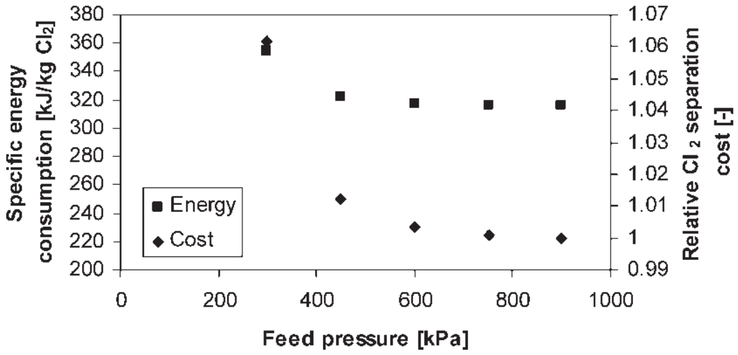

Figure 4. Effect of feed pressure on separation cost and energy consumption per kilogram chlorine produced. Pressure ratio ($P_{feed}/P_{permeate}$) is 30. Costs relative to case for which pressure is 900 kPa (€0.024/kg Cl_2) (PDMS).

The increase in product purity gained by introducing an intermediate recompression stage (Fig. 7) is relatively limited, so many recompression stages will be necessary to achieve the chlorine purity spec of 99.8 mol%.

The economic feasibility of such a staged process is limited, and was not pursued further.

Glass Hollow Fiber

With glass hollow fibers, the critical separation is between chlorine, which will be retained on the feed side according to the molecular sieving mechanism, and oxygen, which is the next slowest permeating component

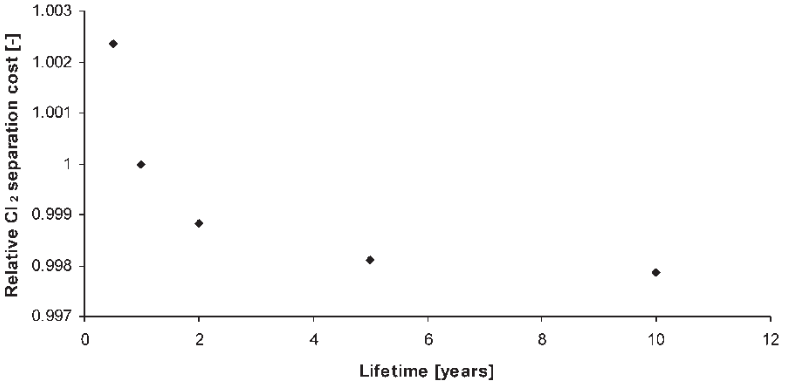

Figure 5. Effect of membrane lifetime on Cl_2 separation cost. Base case for which assumed lifetime is 1 year taken as reference cost (PDMS).

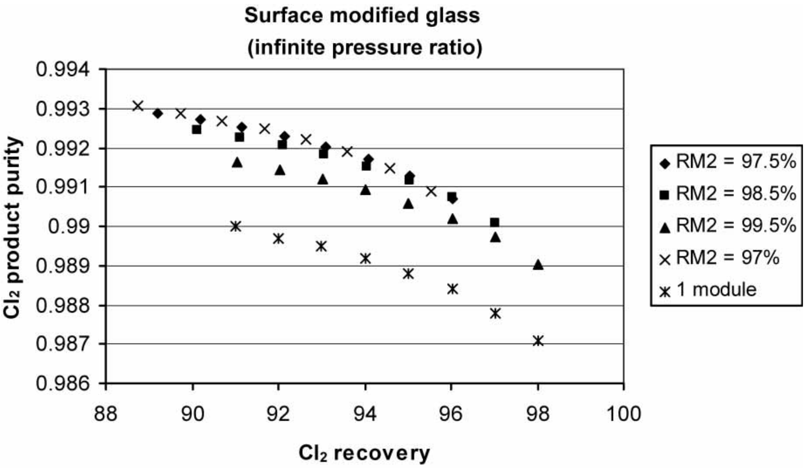

Figure 6. Chlorine product purity for surface-modified glass as a function of the chlorine recovery, for 1 or 2 modules ("RM2" = recovery in 2nd module, 1st module recovery set to 99%).

(refer to Table 2). The flowsheet for this membrane separation is the same as shown in Fig. 2 for PDMS, but the purified chlorine produce will be retained on the feed side (retentate stream) due to molecular sieving, while the impurities will permeate through.

As the oxygen permeability is low, the dominating economic factor will be the size of the membrane unit. To minimize the required area, the maximum feasible pressure difference was used in the design; in this case, 8 bar on the feed side and 0.02 bar on the permeate side. The chlorine saturation pressure of 8.3 bar at 27°C placed an upper limit on feed pressure and the low permeate pressure was required to meet the chlorine purity specification. It can be seen in Fig. 8 that this is achieved at approximately 95% recovery of the feed chlorine.

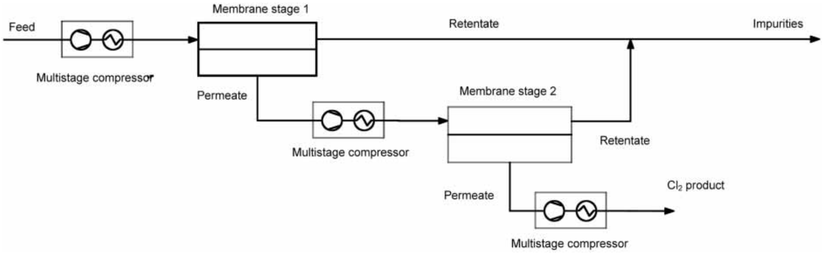

Figure 7. Surface-modified glass process (Case 1).

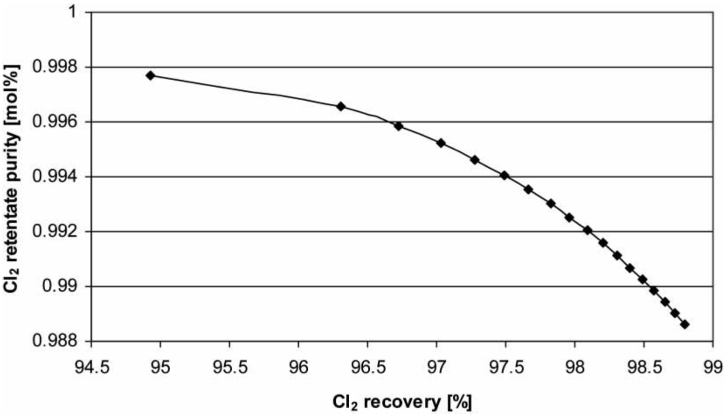

Figure 8. Chlorine product purity as a function of recovery. Feed pressure 8 bar, permeate pressure 0.02 bar (glass hollow fiber).

The large membrane area required, however, results in high separation costs (refer to Fig. 9), making the process unattractive.

Approximately 99% of the capital cost in this case was the membrane modules.

Case 2 – Recovery of Chlorine from Tail Gas

In the production of chlorine from sodium chloride, vapor from the electrolyzers is compressed and cooled to recover up to 95% of the chlorine in a primary liquefaction step. The uncondensed stream from this step is assumed to be at 1–16 bar (abs) (1) and 44 mol% Cl_2 (9) providing a reasonable Cl_2 vapour pressure and opportunity for membrane recovery (see Table 4). This

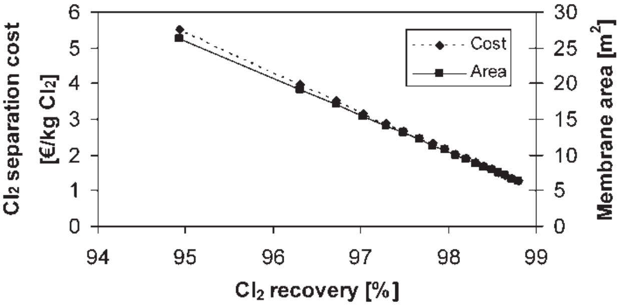

Figure 9. Chlorine separation cost and membrane area as a function of recovery. Feed pressure 8 bar, permeate pressure 0.02 bar (glass hollow fiber).

Table 4. Possible states of tail gas from liquefaction

Liquefaction pressure, MPa	0.1	0.3	0.8	1.6
Liquefaction temperature, °C	−42	−17	14	40

membrane step would replace the secondary and tertiary liquefaction stages often used for tail gas beneficiation (1).

The design target in the study was to recover at least 90% of the chlorine at a purity of 98% or greater. It was assumed that the unrecovered Cl_2 after membrane separation that was routed to the NaOCl production had the same value as in the sniff gas stream.

PDMS

With PDMS, chlorine is the fastest permeating compound. It was found that a single membrane stage was insufficient to increase the Cl_2 purity from 44 to 98 mol% and still recover 90% of the chlorine. Adding stages in a cascade, in which the permeate from the previous stage was processed in the following stage, allowed the purity but not the recovery specification to be achieved. Thus, a two-stage configuration was chosen with a recycle of the retentate of the second stage, which consists of concentrated chlorine, to the feed of the first (see Fig. 10).

The effect of recycling concentrated chlorine is to raise the chlorine concentration profiles in stages 1 and 2. This will increase the average partial pressures of the chlorine on the feed sides and the final product can be removed at the required purity. Higher recoveries can be obtained by increasing the recycle size, which is achieved by increasing the area of the first membrane stage. There is a trade-off between the degree of recovery and the size of the recycle compressor and

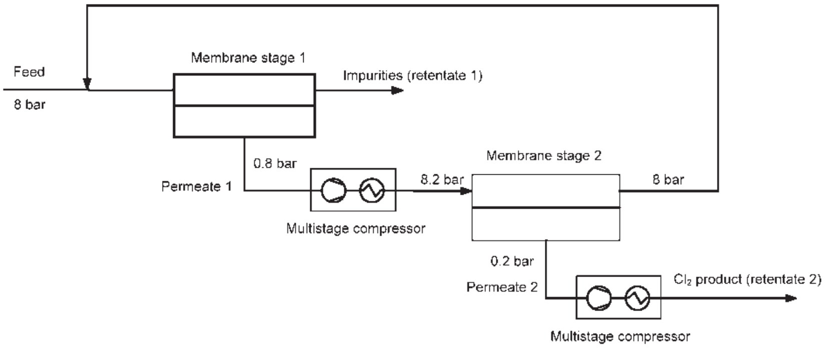

Figure 10. PDMS process (case 2).

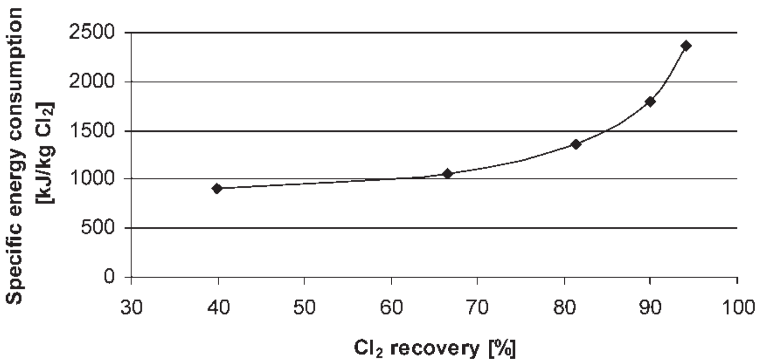

Figure 11. Energy consumption as a function of recovery, 98 mol% purity. Feed pressure = 8 bar, permeate pressure stage 1 = 0.8 bar (PDMS).

membrane modules. This relationship is shown in Fig. 11, for the case where the permeate pressure in the first stage is 0.8 bar.

The cost to separate the chlorine, which incorporates the capital charge for the unit, the yearly replacement costs of the modules and power consumption, also rises exponentially with increasing recovery, as seen in Fig. 12.

The process is also sensitive to the permeate pressure of the first stage and the pressure of the feed to the cycle (see Fig. 13).

Increasing the pressure of the feed to the process decreases the membrane area and increases the purity of the recycle, allowing the recycle to be smaller. Decreasing the permeate pressure of the first stage also increases the recycle chlorine concentration, resulting in a smaller recycle to achieve the same separation performance. However, a lower permeate pressure increases the ΔP over the recycle compressor. These factors combine to produce a minimum

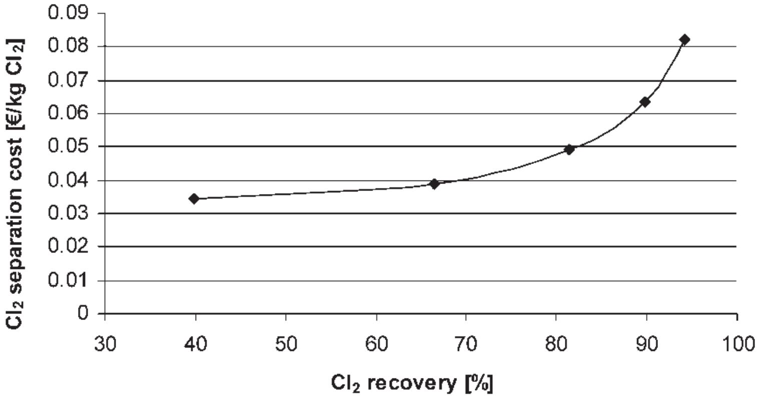

Figure 12. Specific cost of Cl_2 separation as a function of recovery, 98 mol% purity. Feed pressure = 8 bar, permeate pressure stage 1 = 0.8 bar (PDMS).

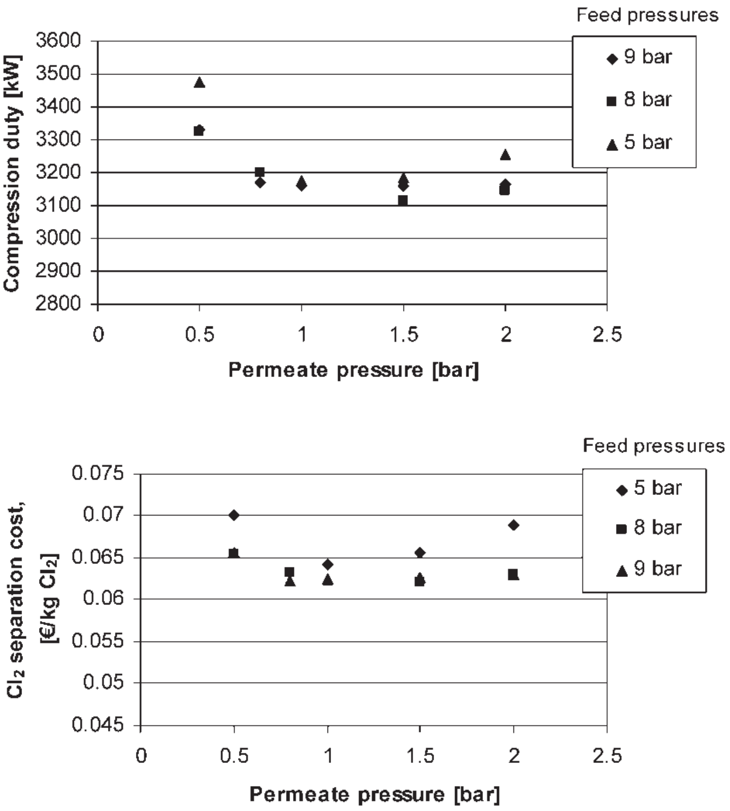

Figure 13. Variation of compression duty and separation cost with permeate pressure (PDMS).

energy consumption at about 1.5 bar. The cost per unit of chlorine produced graph exhibits a minimum at approximately 0.8 bar.

The optimal feed pressure in this case was 8 bar. Increasing the pressure to 9 bar showed little benefit and increases the likelihood that chlorine condenses over the membrane, while a lower pressure than 8 bar resulted in a significantly larger recycle. At these conditions, the cost of separating 90% of the chlorine was estimated to be roughly €0.07/kg Cl_2 produced.

It was assumed for the results presented in Table 5 that the PDMS membranes operate for 1 year without significant deterioration in performance. This assumption was tested and it was seen that the cost of separation is insensitive to the membrane lifetime (Fig. 14).

Surface-modified Glass

In this membrane, the chlorine will permeate according to selective surface diffusion, whereas the impurities are retained on the feed side. Due to the

Table 5. Process results for the PDMS optimal case

	Stage 1	Stage 2
Membrane area, m^2	3000	140
Compression duty, kW_e	2800	180

lower selectivity of the modified glass membranes ($\alpha_{Cl_2/N_2} = 5.7$), a two stage process was unable to achieve 98% Cl_2 purity at 90% recovery. Four stages in cascade were required; each with the retentate recycles to the previous stage (Fig. 15). This meant that both the total membrane area and compression duty of the complex arrangement were prohibitively larger than in the PDMS case. The selectivity must be increased, to make this membrane a viable option. This may be done by more careful pore tailoring of the glass.

In total, approximately 50 000 m^2 of membrane area and 33 MW_e of compression power were required. The cost of recovering 90% of the Cl_2 was estimated to be €19.4/kg Cl_2 produced.

Glass Hollow Fiber

The glass hollow-fiber membrane used in this study retains the larger chlorine molecules according to molecular sieving and allows the H_2, CO_2, O_2 and N_2 to permeate (see Fig. 16).

Due to the high selectivity of the membrane ($\alpha_{N_2/Cl_2} = 50$), it is possible to recover approximately 87% of the chlorine at 98% purity in the first stage. The second stage is used to recover the remaining three percent of the chlorine from a slipstream of the permeate from the first stage. The Cl_2 is retained at a value close to the feed pressure. The process requires less energy than the

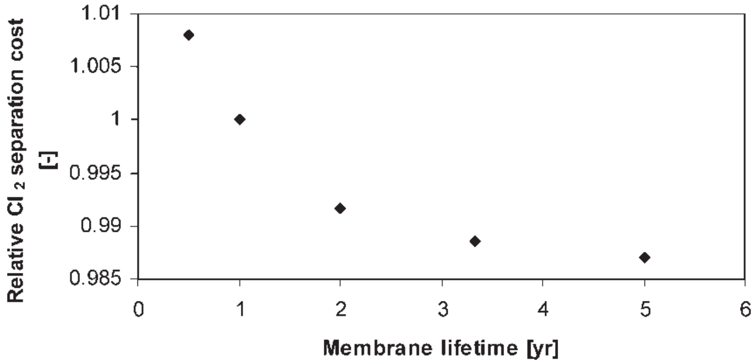

Figure 14. Effect of membrane lifetime on Cl_2 separation cost. Base case where assumed lifetime is 1 year taken as reference cost (PDMS).

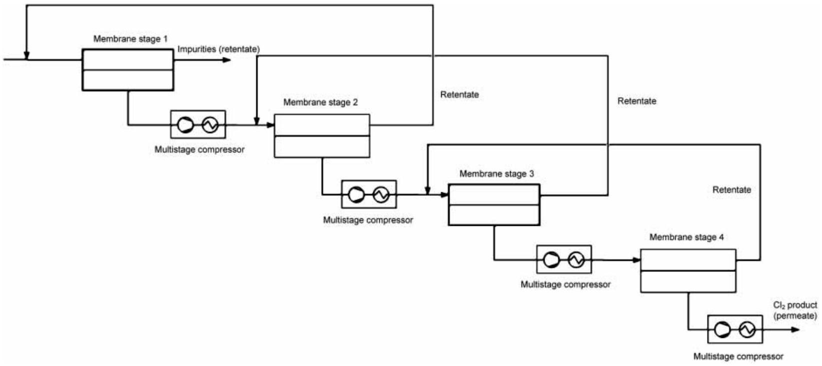

Figure 15. Surface modified glass process (Case 2).

previous cases, due to the absence of a recycle, but is challenged by the low permeability and high cost of the membrane modules.

The design variables in this case include the feed pressure and the first and the second stage permeate pressures. Since the membrane contributes most of the cost of the process, it is desirable to maximize the driving force and decrease the membrane area. The highest available pressure in this study, 16 bar, was used, although the feed temperature needed to be raised to 55°C to prevent chlorine condensation. This should not influence the permeances in a negative way since the separation mechanism in this case is molecular sieving. The permeances were measured at 30°C.

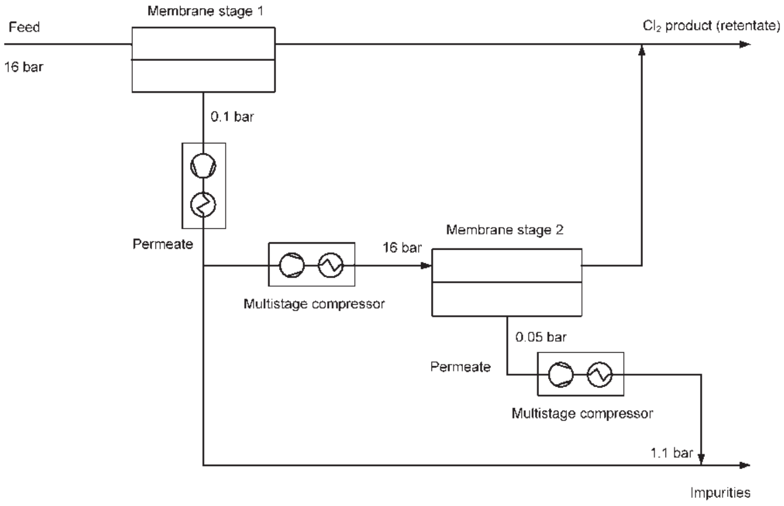

Figure 16. Glass follow-fiber process (Case 2).

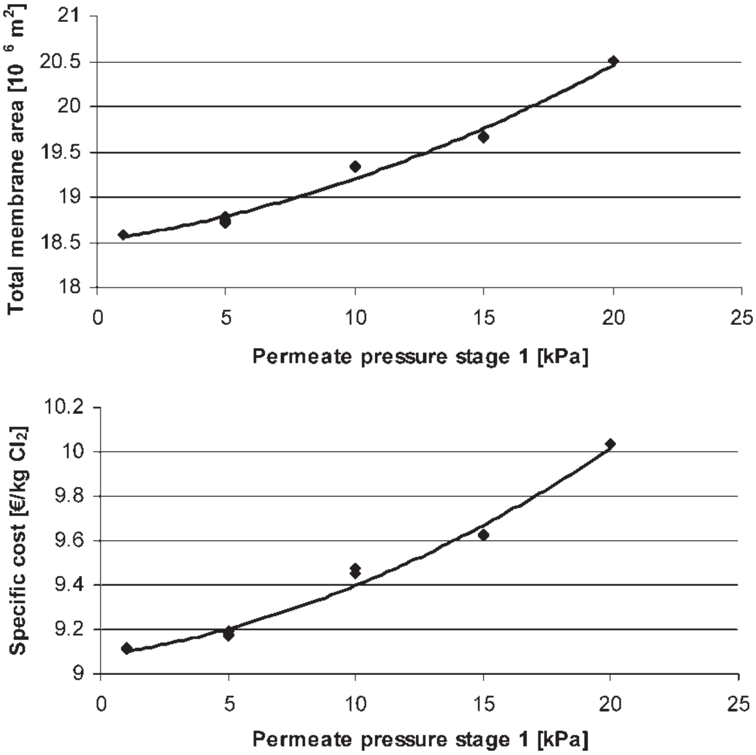

Figure 17. Variation of membrane area and separation cost with permeate pressure in stage 1, 90% recovery of Cl_2 (glass hollow fiber).

It was observed that the total required membrane area (and hence Cl_2 separation cost) is strongly sensitive to the permeate pressure in the first stage, but largely insensitive to the permeate pressure of the second stage (Fig. 17). This is because

1) the first membrane is responsible for most of the recovery and has a larger area and
2) a lower permeate pressure results in a sharper separation of Cl_2—allowing a higher recovery in the first stage at the required purity.

Thus, the second stage can be smaller when the permeate pressure of the first stage is lower. Permeate pressures of 0.1 and 0.05 bar were chosen for stages 1 and 2, respectively.

The cost of separating the chlorine was estimated to be €9.3/kg Cl_2 produced.

Membrane Module Price Uncertainty

As discussed in the section on membrane properties, there is a large uncertainty in the price of the modules. Simulations and costing have shown PDMS to be the most attractive material. The economics of PDMS application in Cases 1 and 2 are dominated by the compressors and variations in module price have little influence on the separation cost. A 100% increase in the module price results in a 1.5% increase in the estimated separation cost for Case 2. The increase in Case 1 is negligible due to the small membrane area. In order for glass fibers to compete with PDMS, the cost of the membrane module must be reduced to \$0.01/m^2.

CONCLUSIONS

The purpose of this paper was to evaluate the application of membranes in chlorine separation. In doing so, the laboratory performance of four materials has been transferred to process simulations and an economic evaluation conducted.

PDMS appeared to be suitable for both cases, although there is still uncertainty about the long-term durability of the material, even for the specially cross-linked PDMS. Nevertheless, the life time sensitivity analysis showed that replacing the modules every 6 months increases the cost of separation by only 3% and 7% in Cases 1 and 2, respectively. The cost of separation was €0.04/kg Cl_2 for Case 1 and €0.07/kg Cl_2 for Case 2. Compared with the added value of the products, this process appears attractive. The selectivity of the surface modified glass is lower than PDMS and as a result, complex, expensive configurations were required to achieve the chlorine purity specifications. Glass hollow fibers could achieve the purity specifications but suffer from low permeabilities, making the modules extremely large. The high cost of the bottled chlorine (€36/kg) makes the €5/kg separation cost appear attractive, but this separation cost is still significantly higher than for the PDMS case.

This work has highlighted the need for durable membranes with even higher productivity. Future work on membranes for chlorine separation will focus on mixed matrix materials, which hopefully will achieve better productivity.

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