Desalination Using Porous Glass Tube Coated with Thin Cellulose Acetate

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1. Introduction

Saline water conversion has world wide interest. Many techniques of saline water conversion have been developed. These are;

- i) distillation process by atomic energy, solar energy,
- ii) electrodialysis,
- iii) ion exchange,
- iv) reverse osmosis, etc.

Although each of these techniques has its own advantages, the reverse osmosis technique is very unique and the major attractions of this process are its simplicity and relatively low energy consumption. This technique was successfully developed by water conversion groups of University of California at Los Angeles and the largest plant reported to date has been a 50,000 gal/day unit, constructed in San Diego, California¹⁾.

The principal of reverse osmosis is schematically illustrated in Fig. 1. The solvent passes through the membrane, but solute cannot pass at start (Fig. 1-1), and the solvent continues passing through the water column and solution column reaches the osmotic pressure (Fig. 1-2). The osmotic pressure for water-sea water interface is about 350 psi (about 24 atm). If one applies a pressure greater than the osmotic pressure to the solution, fresh water is pushed out through the membrane to the direction of arrows, which is called reverse osmosis (Fig. 1-3).

This phenomenon has been known for a long time but Breton and Reid²⁾, and Loeb and Sourirajan^{3),4)}, respectively reported the practical application of reverse osmosis to sea water conversion.

At present there have been many discussions of mechanism of salt and water transport through the membrane under pressure.

One group explains the mechanism on simple microscopic models⁵⁾, and the other group utilized irreversible thermodynamics⁶⁾ to explain the pheno-

menon, and even now the mechanisms are not clearly explained. As an example of simple interpretation the authors introduce "preferential sorption-capillary flow mechanism" proposed by Sourirajan⁷⁾. He mentioned that according to Langmuir⁸⁾ there is a mono-molecular layer of pure water at the air-aqueous sodium chloride interface, which will be represented by surface tension equation of Gibbs⁹⁾. Sourirajan illustrated a microscopic model as shown in Fig. 2. The thickness of the pure water layer t can be calculated by the following equation,

Fig. 1. Principle of reverse osmosis. (A) pure water, (B) NaCl solution. The direction of arrows shows the transport of water molecules through membrane.
(1): start
(2): equilibrium
(3): reverse osmosis

Fig. 2. Microscopic model of interface between solution and solid under reverse osmosis pressure.

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$$t = \frac{-1000 \alpha}{2 RT} \cdot \frac{d\sigma}{d(\alpha c)} \dots \dots \dots (1)$$

Where σ is interfacial tension, α is the activity coefficient of sodium chloride in solution, c is the molarity of solution, R is gas constant, T is absolute temperature. The equation indicates that the thickness of pure water depends on

- i) concentration of the solution,
- ii) temperature, and
- iii) nature of the interface, in other words interaction among water, solute and solid.

The basic idea of the purification of sea water by reverse osmosis is that by applying pressure greater than the osmotic pressure to the solution pure water layer (t) is pushed through the pore of the membrane. This process is schematically illustrated in Fig. 3. The maximum diameter of the pore is twice the thickness of pure water layer, because of the pore diameter is greater than the $2t$, the bulk solution would be pushed out through the pore together with pure water. The model introduced here is not always accepted, but is good enough for the present discussion. Many researchers have investigated new porous membranes which may be organic or inorganic for reverse osmosis. Loeb and Sourirajan¹⁰⁾ successfully found that cellulose acetate cured at 80~90°C has a very good salt rejection properties. The cellulose acetate film indicates salt rejection of more than 90%.

Krause et al.¹¹⁾ reported that Vycor porous glass

can indeed filter sodium chloride solution under pressure. They controlled the pH of the solution and also changed the surface properties of porous glass, that is, modified the pore surface charge and therefore salt rejection properties. Their results indicate that by changing pH of solution from 6 to 10 the rejection increased from 5 to 35 percent, and by adding 0.05 mol ThCl₄ to 0.03 mol in NaCl the salt rejection increased from 5 to 63%. The thorium adsorption on the surface of pore might convert the porous glass to anion-exchange membrane.

The merits of porous glass over organic polymer membrane are as follows:

- i) great mechanical strength, thus the desalination apparatus is simplified. The present reverse osmosis unit using cellulose acetate has complicated structures to hold the high pressure;
- ii) the pore of porous glass does not easily collapse under high pressure and it permits long-term operation. On the other hand, the organic polymer membrane is densified under high pressure, which slows down the permeability of the membrane;
- iii) chemical stability is excellent, and porous glass is especially strong for low pH solution, but the organic membrane hydrolyzes unless the pH of solution is controlled.

Thus porous glass has higher potential for good and economical salt rejection membrane.

In the present paper we report some results of desalination experiment using a porous glass tubing coated with cellulose acetate film, which can be referred to be "composite porous glass tubing".

2. Experimental

Porous glass tube (60 cm long, O.D. 8 mm, wall thickness 1 mm) was coated with cellulose acetate to change the nature of the interface, in other words, interaction among water, solute and solid. The tube was prepared by Corning Glass Work. The solution of cellulose acetate was prepared by mixing the following compositions in weight percent¹²⁾.

cellulose acetate	23%
formanide	27%
acetone	50%

After complete mixing the above chemicals at a room temperature, we put the tube into the solution of cellulose acetate and took out the tube after 15 minutes dipping. The composite porous glass tube was left overnight for curing the cellulose acetate at a room temperature. The cellulose acetate film adhered firmly on the surface of the tube. The one end of the composite tube was sealed with plastic resin and the tube was set in desalination apparatus

Fig. 3. Apparatus of desalination experiment using composite porous glass tube. The outer surface of the porous glass tube is coated with thin film of cured cellulose acetate.

as shown in Fig. 3. We poured hot water (ca. 60°C) into the apparatus to cure the cellulose acetate for 3 hours. After drainage of the hot water from the apparatus, we left the apparatus overnight for cooling down to a room temperature and then started desalination experiment. The concentration of NaCl solution, operation pressure were varied. Salt rejection was monitored by measuring the electrical resistance of desalinated water.

3. Results and Discussions

The results of the desalination experiment are shown in Table 1. The salt rejection depends on the concentration of NaCl solution and operation pressure. The flux of the porous glass or composite porous glass after 24 hours operation are tabulated in Table 2.

These results indicate that;

- 1) salt rejection of composite porous glass tube is better than that of porous glass only at the concentrations of NaCl solution between 0.25 wt% and 0.05 wt%.
- 2) We can obtain better salt rejection in the case of
 - a) lower salt concentration, and
 - b) higher operation pressure up to 300 psi.

Based on the "preferential sorption-capillary flow mechanism", we consider that one of the reason why cellulose acetate has good salt rejection is better nature of interface, in other words, better interaction among water, solute and solid. Thus the thickness of pure water t in equation (1) is greater.

Therefore, by putting thin film of cellulose acetate on the surface of porous glass tube, the thickness of pure water t of the composite porous tube might become greater by changing σ and α of the composite porous tube. Some of pores of porous glass may be filled with cellulose acetate and it lowers the flux of the composite porous tube in desalination experiment. This is indicated in Table 2.

However, many pores might not be filled with cellulose acetate, and very near to the pores there might be cellulose acetate which will have effect on the increasing thickness of pure water t . This might be one of the reason why we can obtain better salt rejection for composite porous glass tube. Another reason is that cellulose acetate film works as salt rejection membrane and the porous glass is only the membrane supporter. In this case it is natural that we'll get better salt rejection comparable to the good salt rejection of cellulose acetate only, but the salt rejections in Table 1 indicate lower values. Therefore, the salt rejection obtained in the present work might be caused by overlapping effects of different works of cellulose acetate film around the pores of porous glass tube.

Two stage desalination have been proposed by

Table 1. Salt rejection in desalination experiments using porous glass tube and composite porous glass tube coated with cellulose acetate.

No.	Solution wt%	Pressure psi	Salt rejection (%)	
			porous glass	composite porous glass
1	0.25 NaCl	84	8(av. of 3 runs*)	22(av. of 7 runs*)
2	0.05 NaCl	84	51.2(av. of 4 runs*)	64.1(av. of 3 runs*)
3	0.05 NaCl	300	74(one run*)	94(one run*)

* One run means 24 hours operation.

Table 2. Flux of porous glass tube and composite porous glass tube coated with cellulose acetate after 24 hours desalination operation.

Materials	Flux $\frac{\text{cm}^3}{\text{cm}^2 \text{ h atom}}$
Porous glass only	1.20×10^{-3}
Composite porous glass	2.8×10^{-4}

Manjikian¹³⁾ based on the calculation of cost of desalination operation. This process is composed of two desalination apparatuses, one is for desalinating higher salt solution to lower salt solution, and the other is for further desalination of the lower salt solution into almost pure water. The results shown in Table 1 and 2 indicate that, although the flux of the composite porous glass is less satisfactory, the salt rejection of the composite porous glass tube is better than that of porous glass tube. We obtained good salt rejection at lower salt concentration and higher operation pressure. Therefore, considering the many merits of porous glass over the organic membrane, the composite porous glass tube can be used for the second stage of desalination in the two stage desalination process.

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薄膜セルロースアセテートを被覆した多孔質ガラス管による塩水の脱塩

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多孔質ガラスの逆浸透圧法による塩水の脱塩率を高める目的で、コーニング社製多孔質ガラス管の外側の面に薄いセルロースアセテート膜をコーティングし、この複合多孔質ガラス管の脱塩作用を調べた。この結果、同一圧力、塩水濃度において複合多孔質ガラス管は多孔質ガラス管のみの場合よりも高い脱塩率が得られた。これは複合多孔質ガラス管と塩水との界面の水分子層の厚みが

多孔質ガラス管と塩水との界面のそれよりも厚くなった為と思われる。脱塩率は、1) 0.25 wt% から 0.05 wt% 塩水濃度範囲内で低い塩水濃度のほうが高くなり、2) 300 psi までの加圧条件で圧力が高くなると高くなる。この複合多孔質ガラス管は2段階海水脱塩法における低濃度塩水の純水化に使用され得ると思われる。

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Selective Growth of NbO Whisker

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1. Introduction

In the system Nb-O, various compounds have been reported as follows, NbO, NbO₂, Nb₂O₅, Nb₁₂O₂₇, and so on. Among these compounds Nb₂O₅ and NbO₂ are the most stable and familiar. The less common niobium monoxide (m.p. 1945°C, cubic) has been prepared by oxidation of niobium metal with low pressure of oxygen^{1)~4)}, by precipitation from a solid solution of Nb-O^{5),6)}, and by a partial reduction of niobium dioxide with hydrogen or magnesium^{7),8)}. Reed and Fahey⁹⁾ obtained NbO single crystal by means of crystal pulling from a melt at 2000°C in a tantalum crucible, and Schaefer and Hueesker^{10),11)} by the chemical transport using iodine as a transport agent. Chemical transport method requires rather long reaction times. No papers have been published, however, on the preparation of a single crystal of niobium monoxide by chemical vapor deposition in gas flow. Therefore, it is of great use to develop a simple technique to

afford a pure crystal for a few hours from vapor phase in order to study its physical properties.

The main purpose of this investigation consists in seeking for the growth condition of NbO single crystal and studying on its morphology.

2. Experimental

2.1 Materials

Commercial niobium foil (99.9%) and liquefied chlorine were used without further purification. Argon was purified by passing over titanium sponge kept at 800°C, and hydrogen was also refined by passing through active copper nets heated at ca. 400°C, conc. sulfuric acid, and phosphorus pentoxide, successively. Niobium pentachloride was prepared *in situ* (*vide infra*).

2.2 Preparation of NbO

An apparatus used in this experiment is shown in Fig. 1. A quartz tube (1) (9 mm in O.D. and 100 mm in length), to which SiC heater was inserted,