

## REGENERATION OF DEACTIVATED POROUS CERAMIC MEMBRANES

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(Received 18 April 1994 • accepted 20 July 1994)

**Abstract**—Because of the pore structure change and blocking of the ceramic membrane pores, deactivation of ceramic membranes occurred after repeated use. A pore blocking mechanism has been observed from the SEM study that in the first stage of deactivation, the membrane pore sizes became smaller due to the accumulation of the unrecovered chemicals, and the pore neck parts were closed and/or blocked. Finally, the pore structures changed to the broken piece of long and thin elliptical shapes. Two regeneration methods were explored and tested in attempts to recover useful activity for the deactivated membranes. Relatively fresh membranes, including intermediately used membranes, can recover fluxes as much as 70 percent of fresh membrane flux by chemical treatments such as acetone-acid treatment, while the severely deactivated membranes were partially regenerated by an oxidation method followed by the acetone and acid treatment.

**Key words:** *Regeneration, Ceramic Membrane, Deactivation, Oxidation*

### INTRODUCTION

Disposal of hazardous wastes is a significant industrial waste problem. Rising disposal costs and more stringent environmental regulations for waste water are extending some conventional treatment methods to their technological and economical limits. The predominant method of treatment of waste streams is the precipitation of metal ions in the form of hydroxides or carbonates [1, 2], which results in a sludge that is dumped at hazardous waste sites. Other recovery methods recently evaluated include evaporation, electrolyte metal recovery, reverse osmosis [3], ion exchange [4], membrane separation [5], and solvent extraction.

Recently, the applicability of ceramic membranes have been evaluated for the waste water treatment in many industries. They exhibit excellent chemical, thermal, and pressure reliability and long lifetimes to a wide variety of practical conditions. Neither creep nor deformation occurs during cooling and high permeabilities can be achieved. Accordingly, ceramic membranes show promise for treatment of waste water in industries, especially for the microfiltration and reverse osmosis processes, and separation of oil and water in petrochemical process.

A major operation parameter for the practical application is the useful life of ceramic membranes. Deactivation characteristics have a significant impact on module performance and economics. Short-term deactivation could result from several factors: concentration polarization, gel formation, precipitation, biological fouling, and surface pore blockage from adsorption of the trace solids in the waste streams. Long-term deactivation may be attributed to internal blocking of pores due to polymer formation by chemical reactions after long time contacting with waste streams or destruction or dissolution of pore structure due to successive and severe regeneration procedures. Long-term deactivation may permanently damage the membranes to the extent that the ceramic membranes can not be used for useful operations. In other words, this type

of deactivation may either be irreversible or reversible following severe regeneration procedures. In particular, development of effective regeneration techniques of ceramic membranes deactivated by the organic materials is important, since the small amount of organics present in the waste streams to be treated can affect the ceramic membrane performances after a long time operation, and ceramic membranes are also frequently used for the separation process of water (aqueous phase) and organics from the waste water streams.

In this study, deactivation phenomena of ceramic membranes is discussed, and two regeneration techniques are evaluated for possible reuse of these deactivated ceramic membranes: (i) chemical treatments, such as acetone flushing or acetone and sulfuric acid flushing, and (ii) oxidation. Chemical treatments for regeneration of the membranes was assumed to leach any residual organics and complexed chemicals from the pores. In the latter regeneration method, chemical treatment was followed by oxidation to remove any residual materials which remained in the membrane after chemical treatments.

### EXPERIMENTS

The rotating diffusion cell (RDC) technique was employed to obtain overall mass transfer rates across the ceramic membranes. Fig. 1 shows the apparatus, in which ceramic membranes were contacted to either side with the copper solution and distilled water. Instantaneous monitoring of the internal or external fluid was accomplished with an on-line UV-visible spectrophotometer (Perkin Elmer: Model 559). Also, a pH unit controller (Brinkman: Impulsomat 614, Dosimat 665, pH meter 632) permitted maintenance of constant pH during the flux experiments. The system was isothermally controlled using a thermostatic circulation bath. A nitrogen gas purge prevented oxidation of the solutions, and a controller was used to maintain constant rotational speed. For the oxidation of ceramic membranes, an apparatus shown in Fig.

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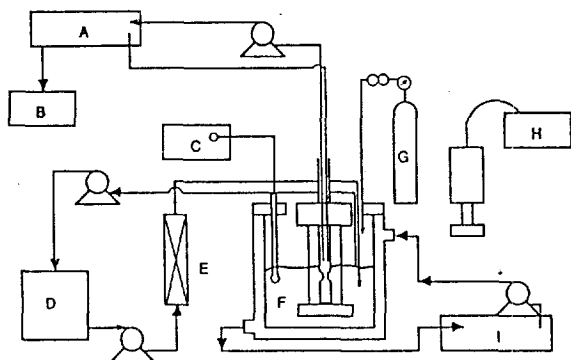


Fig. 1. Schematic of experimental apparatus.

- |                             |                       |
|-----------------------------|-----------------------|
| A: UV-Vis spectrophotometer | F: RDC                |
| B: Recorder                 | G: Nitrogen gas purge |
| C: pH meter                 | H: Motor & control    |
| D: Feed Reservoir           | I: Water bath         |
| E: Flowmeter                |                       |

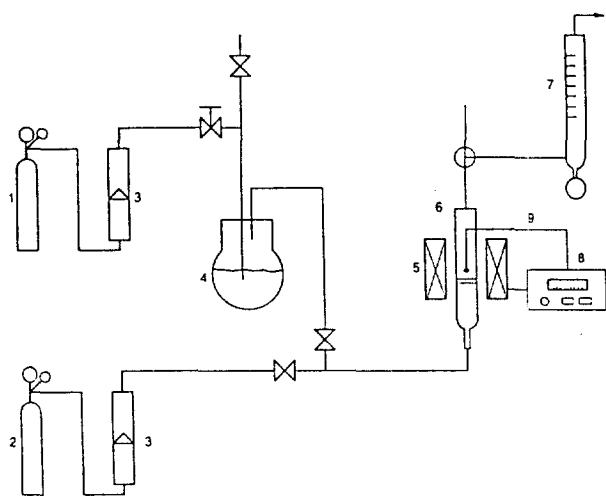


Fig. 2. Apparatus for regeneration of deactivated ceramic membranes.

- |                       |                                      |
|-----------------------|--------------------------------------|
| 1: Gas 1              | 6: Reactor for membrane regeneration |
| 2: Gas 2              | 7: Bubble flowmeter                  |
| 3: Flowmeter          | 8: Temperature controller            |
| 4: Vaporization flask | 9: Thermocouple                      |
| 5: Heating block      |                                      |

2 was used with an air flow rate of 60 cm<sup>3</sup>/min at the setting temperature.

The dilute metal ion aqueous phase consisted of a copper sulfate solution having concentration of 0.03 gmol/l. The solutions were prepared from copper sulfate powder (Fisher). For the simulation of ceramic membranes deactivated by organics, the pores of membranes were impregnated with an organic acid of high molecular weight. In the experiments, the organic acid of 2-hydroxy-5-nonylacetophenone oxime (Henkel Co.) was used for the impregnating chemicals. The ceramic membranes were selected from commercially available products (P55: Coors Ceramic Co.). They were composed of 63%  $\alpha$ -alumina, 31% silica, and approximately 1% of Fe<sub>2</sub>O<sub>3</sub>, TiO<sub>2</sub> and KO<sub>2</sub> with average pore size of 49–55  $\mu$ m and porosity of 41.7%. The thickness and diameter of ceramic membrane disks are 2 mm and 2.54 cm, respectively. De-

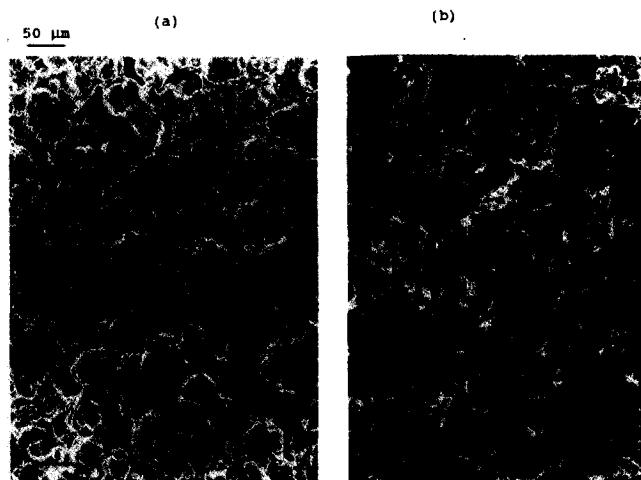


Fig. 3. Photographs of Scanning Electron Microscopy (SEM) pictures of (a) membrane surface and (b) cross-section of membrane of P55D (severely deactivated membrane).

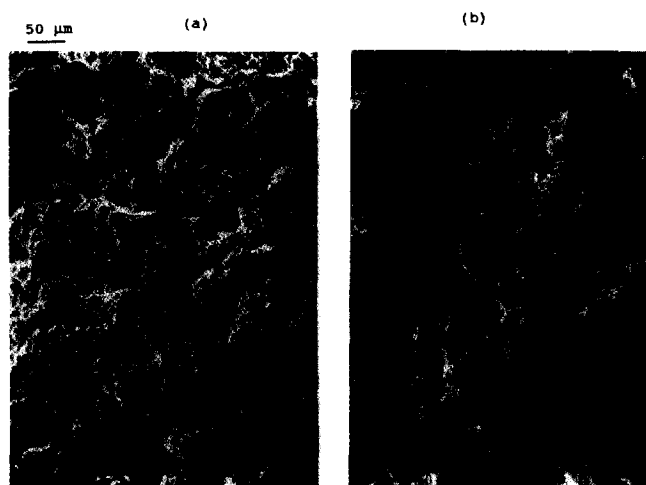


Fig. 4. Photographs of Scanning Electron Microscopy (SEM) pictures of (a) membrane surface and (b) cross-section of membrane of P55G (intermediately deactivated membrane).

tails of experimental procedures were presented elsewhere [6].

## RESULTS AND DISCUSSIONS

Membranes investigated are classified into three groups, which are (i) severely deactivated membranes of P55B, P55C, and P55D, (ii) intermediately deactivated membranes and are labeled of P55F and P55G, and (iii) fresh membranes of P55E and P55H. Figs. 3–5 are scanning electron microscopic (SEM) pictures of the membranes used in this study. In Figs. 3–5, (a) and (b) represent the membrane pictures of surface and cross section, respectively. Pore structures of the fresh membranes (P55H) are close to circular shapes, while pore shapes of the intermediately deactivated membranes (P55G) are long elliptical shapes.

Several possible factors may have contributed to the membrane deactivation, including the repeated contact of the membrane with the chemicals used in this study.

Two regeneration methods were used in an attempt to regen-

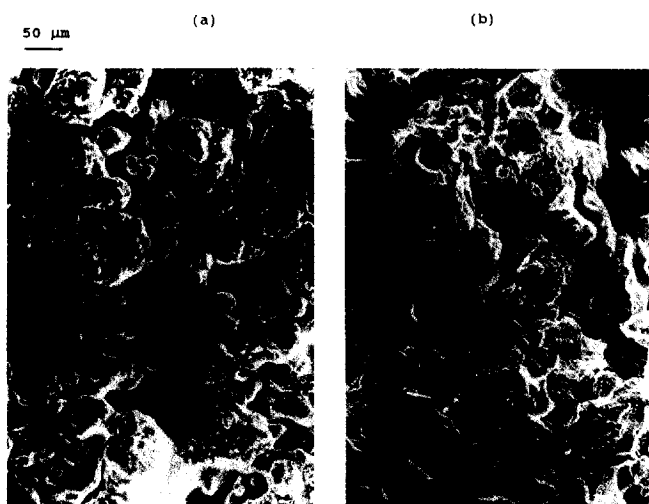


Fig. 5. Photographs of Scanning Electron Microscopy (SEM) pictures of (a) membrane surface and (b) cross-section of membrane of P55H (fresh membrane).

erate the deactivated ceramic membranes: the acetone and acid treatment and the oxidation method. After applying the regeneration technique and reimpregnating the membranes, flux experiments were executed to investigate the feasibility of these regeneration techniques. In the experiments, copper ion transport through the membrane were studied experimentally. Diffusional copper ion flux experiments were executed to determine the overall mass transfer coefficients for the copper ion transport through the membranes. In these experiments, the feed copper solution used was 0.03 gmol/l at pH 3.0, the strip solution was 1.5 gmol/l sulfuric acid, and the membranes were impregnated with the distilled water. The fluxes ( $J$ ) were calculated from the strip-side solution concentration measurements by UV-visible spectrophotometry. The overall mass transfer coefficients,  $K_w$ , were determined by

$$K_w = \frac{J}{(C_M^F - C_M^S)} \quad (1)$$

where  $C_M^F$  and  $C_M^S$  are the copper concentrations in the feed and strip solution, respectively.

### 1. Acid-Treatment

The effectiveness of the acid treatment method to regenerate the deactivated ceramic membranes is examined. This leaching technique was employed using acetone and 1.5 gmol/l sulfuric acid solution. In this treatment, there was the additional use of 1.5 gmol/l sulfuric acid for immersing the membranes, after they first were immersed in acetone. In addition to the acetone back-flushing, the membranes were also backflushed with this acid solution. This procedure was employed because the organic acid used can be dissolved in acetone. This dissolution leads to the decrease of the viscosity of the organic materials inside the membrane pores. Back-flushing with vacuum application was expected to withdraw and dissolve the materials trapped in the pores.

Fig. 6 displays the overall mass transfer coefficients,  $K_w$ , after acetone-acid treatment between flux experiments. This figure shows that the overall copper ion diffusional mass transfer coefficients,  $K_w$ , decreased as the extent of use increases for the rotation speed ranges between 60-180 rpm. The average value of the

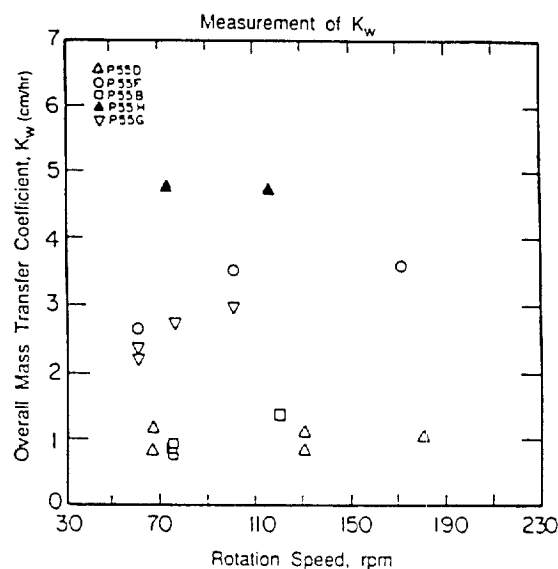


Fig. 6. Effect of the extent of use on the overall mass transfer coefficients for copper ion transport.

P55B, P55D-severely deactivated membranes, P55F, P55G-intermediately deactivated membranes, P55H-(relatively) fresh membrane.

overall copper ion diffusional mass transfer coefficients,  $K_w$ , for the used membranes of P55B and P55D was about 0.96 cm/hr and this value corresponds to about 20 percent of the  $K_w$  value for the fresh membrane of P55H, which was 4.8 cm/hr. For the intermediate used membranes of P55F and P55G, the  $K_w$  range was 2.0-3.5 cm/hr for the different rotation speeds of RDC used in this study, as shown in Fig. 6. The results show that the overall mass transfer coefficients decreased with the extent of deactivation. The pore structure change of the membrane reduces the contact areas to the feed and strip solutions and increases the tortuosity. As a result, the fluxes through the membrane decreased with the repeated use of the membranes, although the acetone and acid treatment were employed to regenerate the activity.

### 2. Oxidation

The second method to regenerate the deactivated membranes was to oxidize the deactivated membranes. The ceramic membrane used in this study has sufficient rigidity and stability at temperature up to 800°C to allow regeneration by an oxidation technique. In this treatment, the deactivated membranes were oxidized after chemical treatment. The oxidation method was presumed to oxidize and remove any residual materials, such as organics and any precipitates remaining after acetone or acid treatment. After the oxidation method were employed, acetone and acid solutions were used to clean up the membrane surface and pores before flux experiments.

Fig. 7 shows the effect of oxidation regeneration method on the  $K_w$  of regenerated membranes. The deactivated membrane of P55D was oxidized at 800°F (426°C) for 15 hours in an air flow of 60 cm<sup>3</sup>/min after acetone treatment. The average value of  $K_w$  of P55D-oxidation in Fig. 7 increased from 1.0 to 2.0 cm/hr at the rotating speed of 130 rpm because of the oxidation regeneration steps. After this membrane has been impregnated with organic acid, it is regenerated again by the acetone-acid treatment, followed by the oxidation at 400°F (204°C) for 24 hours in an

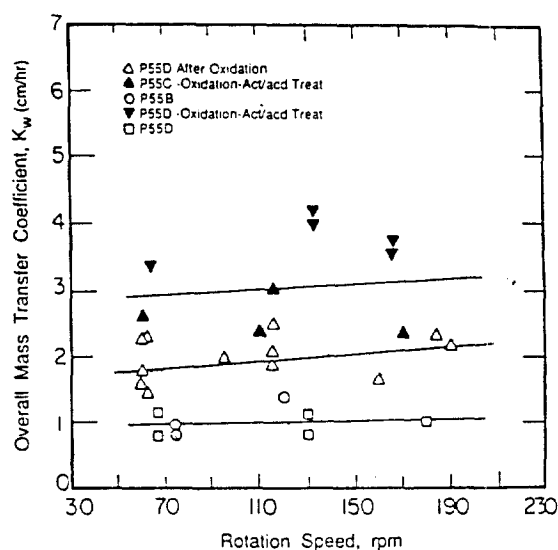


Fig. 7. Effect of oxidation method on the overall mass transfer coefficients for the copper ion transport.

P55B, P55C and P55D are labeled for severely deactivated membranes.

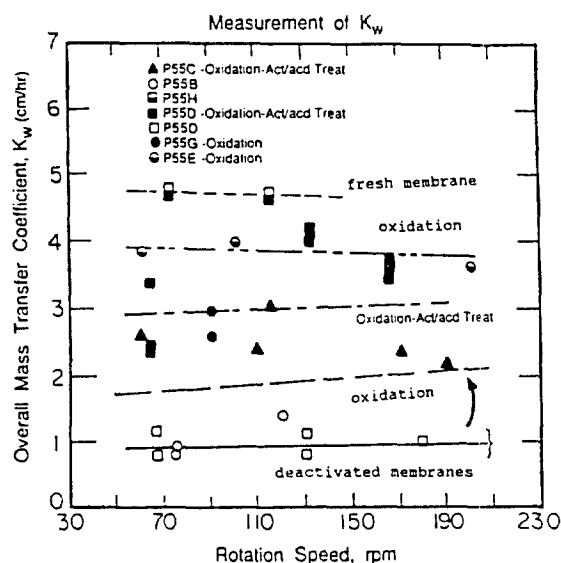


Fig. 8. Effect of the pretreatment before oxidation method on the overall mass transfer coefficients for the copper ion transport.

P55B, P55C, P55D-severely deactivated membranes, P55G-intermediately deactivated membranes, P55H, P55E-(relatively) fresh membrane

air flow of 60 cm<sup>3</sup>/min. The  $K_w$  of this membrane regenerated (designated by P55D-oxidation-Act/Acd and P55C-oxidation-Act/Acd in Fig. 7) increased to 3.0 cm/hr at the rotating speed of 130 rpm.

The results in Fig. 7 show that  $K_w$  values of the deactivated membranes were increased by the oxidation method. These values increase more when the oxidation method was employed after the acetone-acid treatment.

Fig. 8 also shows the effect of the oxidation method on  $K_w$  values for regenerated membranes. The second-line from the top in Fig. 8, designated by oxidation, represents the  $K_w$  values as

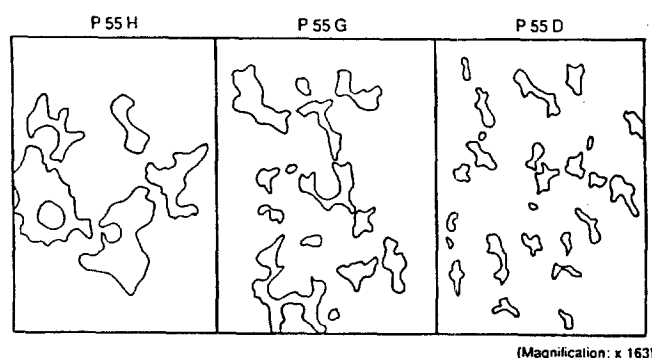


Fig. 9. Trace of apparent pore structure on the membrane surface for the different stages of deactivation.

P55D-severely deactivated membranes, P55G-intermediately deactivated membranes, P55H-(relatively) fresh membrane.

a function of the rotational speed of RDC after acetone treatment followed by oxidation of the fresh membrane of P55E, while second-line from the bottom in the same figure, also designated by oxidation, shows the change of the  $K_w$  values of the deactivated membranes, P55D and P55B. Note that, for clarity, the linear regression results of the P55D after oxidation data are shown in Fig. 8 (the data points are shown in Fig. 7). After oxidation of the fresh membrane of P55E at 300°F (approximately 150°C) for 24 hours in an air flow of 60 cm<sup>3</sup>/min, the average  $K_w$  values decrease from 4.8 for P55H to 4.0 cm/hr for P55E-oxidation, respectively, as shown in Fig. 8. This result implies that the membrane pore morphology of the relatively fresh, but used membranes, was changed by the oxidation method employed (designated by P55E-oxidation). However, in the case of the severely deactivated membranes of P55C and P55D, the average  $K_w$  values were increased about two times from about 1 to 2 cm/hr by this oxidation method, as shown in Fig. 8 (two lines from the bottom). Apparently, the organics of high molecular weight materials blocked in the pores can be oxidized and eventually removed from the pores by this oxidation method.

Furthermore, the oxidation effect on the regeneration becomes greater when the acetone-acid treatment is performed on the deactivated membranes before the oxidation, as shown in Fig. 8. However, the recovered  $K_w$  values of the regenerated membranes were not equal to the original  $K_w$  values of fresh membrane.

A series of experimental results show that the  $K_w$  values of the severely deactivated membranes (P55C and P55D) decreased by about 20 percent compared to fresh membranes (P55H). This deactivation may occur by pore blocking or/and tortuosity increases due to membrane morphology changes. The deactivated membranes could be regenerated by the oxidation and the acetone-acid treatment followed by the oxidation method. The  $K_w$  values of regenerated membranes have about 60 percent of the  $K_w$  for the fresh membranes.

### 3. Observation of Membrane Morphology Change

The experimental results indicated that the fluxes through the ceramic membranes decrease after deactivation occurs. To investigate possible structural reasons for this behavior, a scanning electron microscopic (SEM) study was performed to examine pore morphology changes of the surface and cross section of the membranes used in this study, as shown in Figs. 3-5. Fig. 9 displays a trace of apparent pore structures on the membrane surfaces for the different stages of deactivation. This picture clearly shows

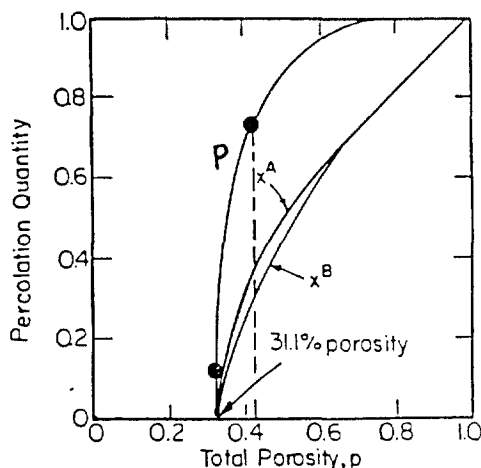


Fig. 10. The percolation quantity versus porosity for a simple cubic network

P: fraction of sample-spanning cluster

$x^A$ : accessible fraction of pores

$x^B$ : fraction of conducting pores

that after repeated use of the membranes for a long time, the pore structures of P55D (severely deactivated membrane) evolved to long and thin elliptical shapes. These results show that in the first stage of deactivation, the membrane pores became smaller due to the accumulation of the unremoved chemicals, and the pore necks were connected and/or blocked by the chelation agents and copper complexes. Finally, the pore structures changed to the broken piece of the long and thin elliptical shapes, as shown in Fig. 9.

It is difficult to remove these materials blocking the pores by a physical method, such as the vacuum suction. Pore blocking materials formed in relatively large pores could be removed by the vacuum suction. The pore blocking materials can be removed to a some extent by chemical treatments, such as acetone treatment and acetone-acid treatment. These methods are shown to be effective in regenerating short-term or intermediately deactivated membranes. It was observed from the SEM pictures that foreign materials at the surface of P55C membrane however are not removed completely after the oxidation step, and a large portion of pores for the deactivated membrane were blocked compared to the fresh membrane pores of P55H. This pore blocking phenomena for the deactivated membrane is expected and can explain the flux decrease after long time and repeated use of membranes. Such a pore structure change of the membrane due to deactivation reduces the contact areas to the feed and strip solutions and increases the tortuosity.

Another indication of physical morphology changes after deactivation is the porosity decrease. The porosity measured by the manufacturer (Coors Co.) decreased from 41.7 percent for the new and fresh membrane to 33.7 percent after repeated use for a long time. Most likely, the observed decrease in flux is related to those membrane porosity changes. A further indication that fluxes may decrease with porosity is given by the theoretical analysis of the percolation quantity [7]. Fig. 10 shows the percolation quantity versus porosity for a simple cubic network. Defined

as an accessible fraction of the pores ( $x^A$  in Fig. 10), the percolation quantity changes drastically with porosity as shown in Fig. 10. This effect is magnified at the percolation threshold of 31.1 percent porosity where, according to theory, there are no accessible pores. This theoretical value is close to the measured porosity of 33.7 percent for membrane P55D. P,  $x^A$  and  $x^B$  in Fig. 10 represent the fraction of the sample-spanning cluster and the fraction of conducting pores which actually participate in transport, respectively. This result demonstrates that porosity management is important to obtain high and stable fluxes for the ceramic membrane system operation.

## SUMMARY AND CONCLUSION

Membrane deactivation occurs due to the pore structure change and blocking of the membrane pores. A pore blocking mechanism has been observed from the SEM study that in the first stage of deactivation, the membrane pore sizes become smaller due to the accumulation of the unremoved chemicals, and the pore neck parts are closed and/or blocked by the chelation agent and copper complexes. Finally, the pore structures change to the broken piece of long and thin elliptical shapes.

The pore structure changes of membranes due to the deactivation reduces the contact areas to the feed and strip solutions and increases tortuosity. As a result, the fluxes through the membranes decrease. For relatively fresh membranes, including intermediate used membranes, loss of flux can be recovered up to 70 percent by acetone-acid treatment. The severely deactivated membranes were regenerated by the oxidation method followed by the acetone and acid treatment. A further study is needed to more effectively regenerate severely deactivated membranes.

## NOMENCLATURES

- $C_M^F$ : copper concentrations in the feed
- $C_M^S$ : copper concentrations in the strip-side solution
- $J$ : flux
- $K_w$ : overall mass transfer coefficients
- $P$ : fraction of sample-spanning cluster
- $x^A$ : accessible fraction of pores
- $x^B$ : fraction of conducting pores

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