CHAPTER V

RESULTS AND DISCUSSIONS

5.1 Characterization of Supported and Intermediated Layers' Properties

The aim of this section was to repeat Sittinun's work in producing supported tubular microfilter. In general, slip casting method is a scientific-art-work, therefore the properties of made tube will be in some different range. After supported tube was produced, the properties of made tubes were compared with Sittinun's tubes.

Table 5.1 Properties of Supported Layer

Properties	**This work**	**Sittinun's work**
Bulk density ; g/cm^3	2.39	2.86
Apparent porosity ; %	38.39	33.00
Water absorption ; %	16.09	12.50
Shrinkage ; %	5.83	9.20
Strength ; MPa	68.10	68.00

As shown in Table 5.1, although there are some different range, but if we stressed in porosity's value which is very important property for filter, we can say that the made tubes were suitable for further sol-gel coating.

Similarly, we analyzed pore size distribution of supported and intermediated layer from Pore Sizer, and morphology of these layers from SEM. The pore size distribution curves and SEM photographs are shown in Figure 5.1 and 5.2, consecutively.

As shown in Figure 5.1, most of pore size in supported and intermediated layer were at 11,000 and 600 A which were closely to Sittinun's work [2].

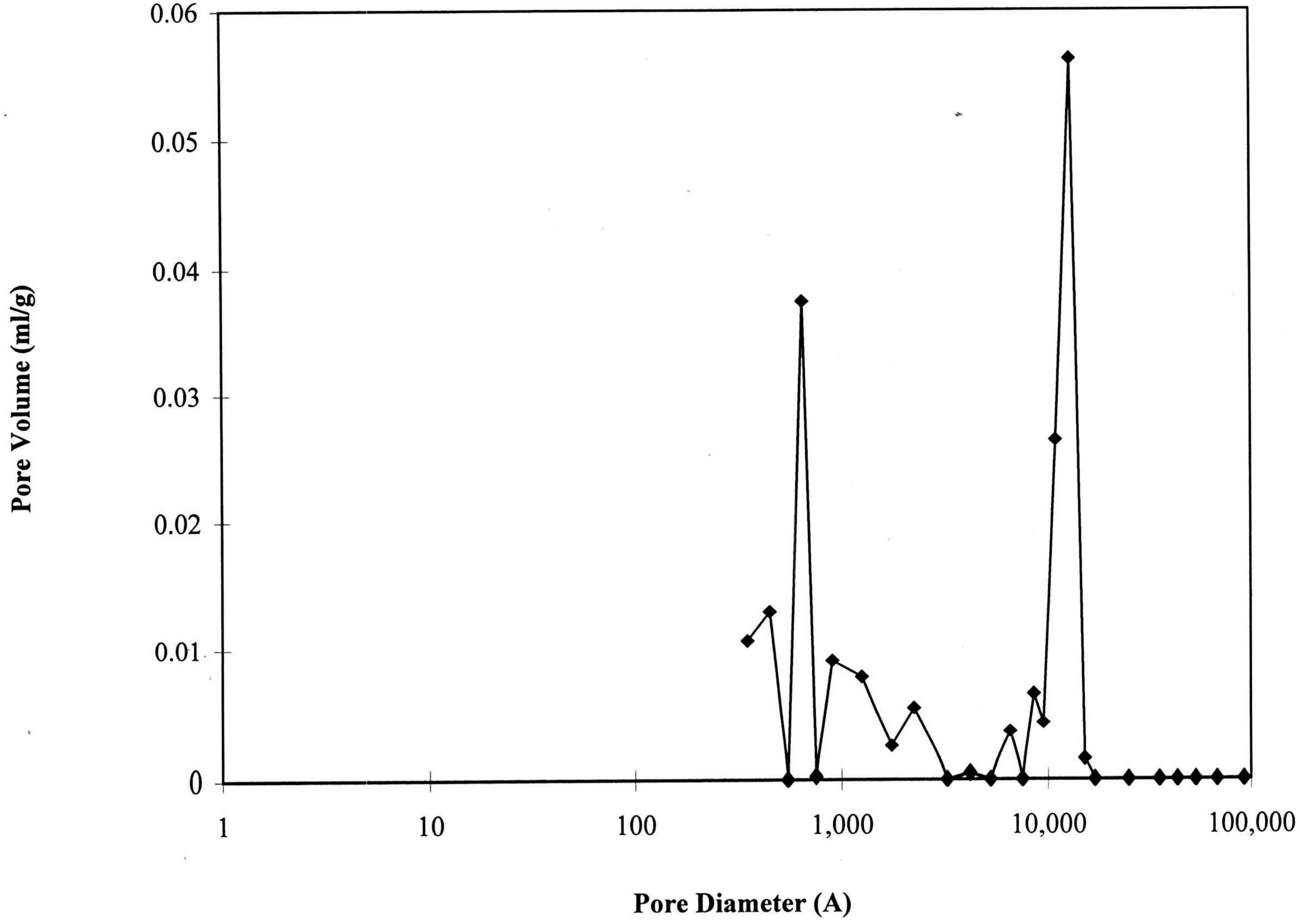
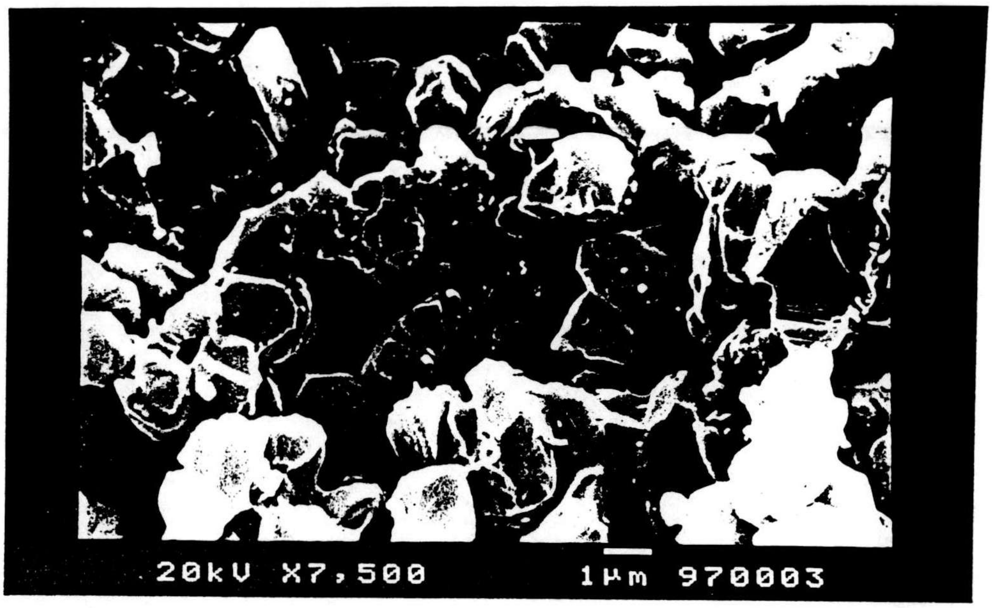
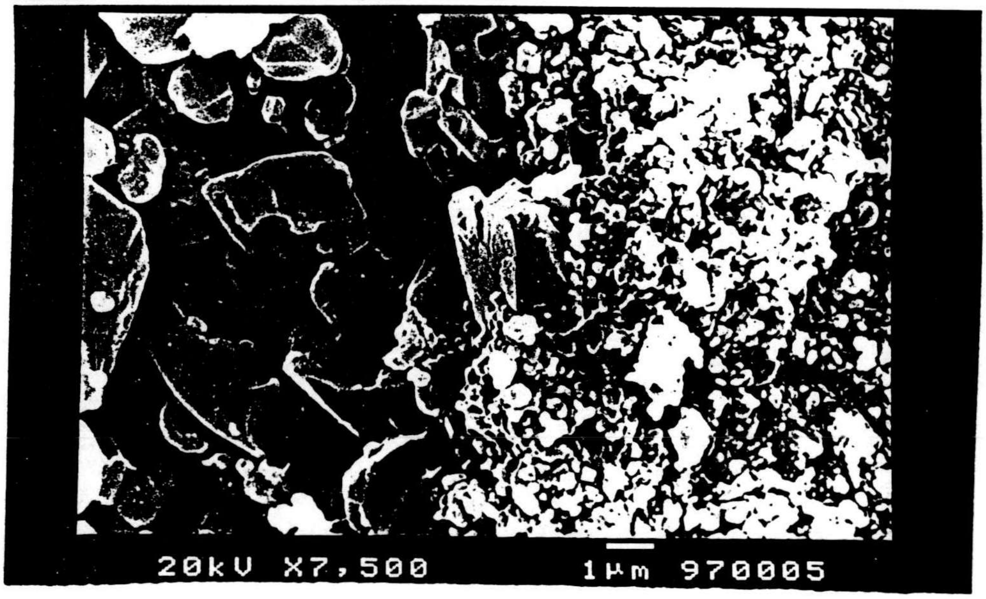


Figure 5.1 Pore Size Distribution of Support and Intermediate



A) Cross-Section of Supported Layer



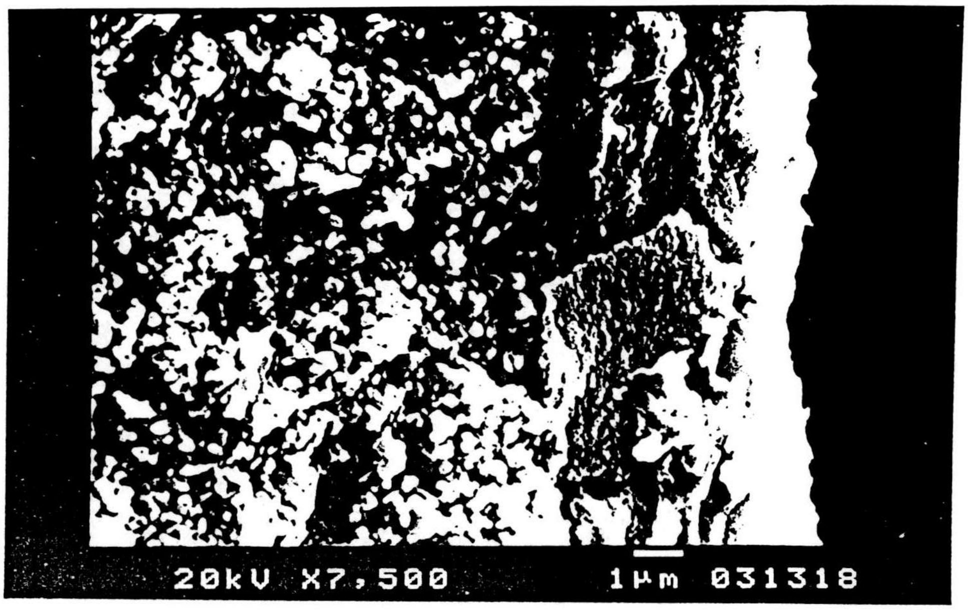
B) Cross-Section of Intermediated Layer

Figure 5.2 SEM Photograph of Supports (A) Cross-Section of Supported Layer and (B) Cross-Section of Intermediated Layer

5.2 The Influence of Acid Concentrations in Sol Solution on Membrane Formation

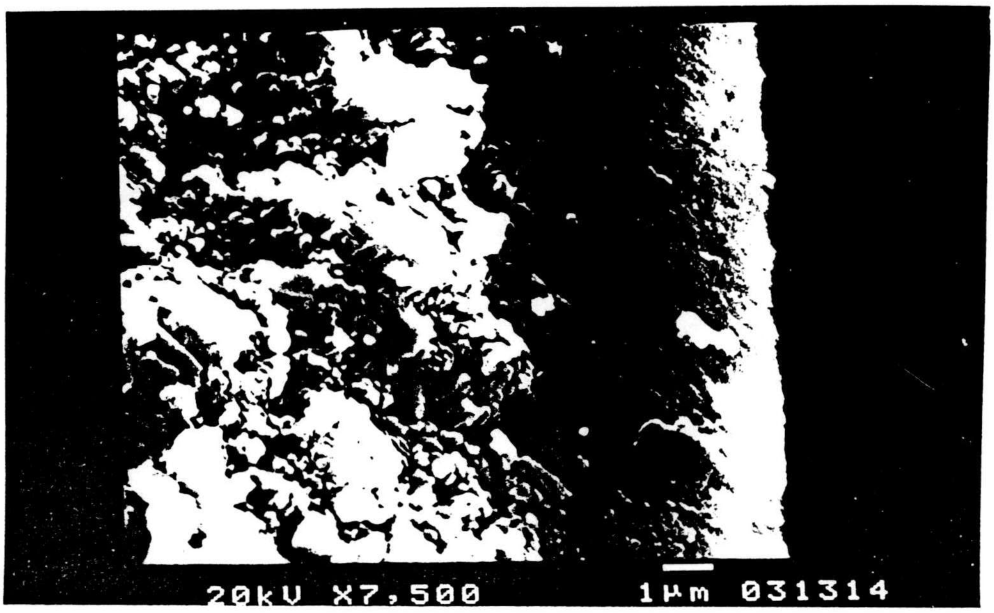
In sol-gel processing, alkoxide was put into water for hydrolysis and acid was added in this solution for peptization the solution to a clear sol. In condition of water in sol solution is excess for complete hydrolysis of alkoxide, then amount of acid addition become the important influence for solution to be a clear sol. In this experiment, we studied effect of acid concentration in sol solution on gel formation. These solutions were containing 0.03, 0.05, 0.07, 0.09, and 0.11 mole of nitric acid per mole of alkoxide, respectively. It appears that all of these sols are clear sols, due to peptization of alkoxide. After that, these sols were coated on the supported tube and calcined at 600 °C for 30 minutes. From SEM photograph, we found that 0.03 and 0.05 mole of HNO_3 afforded the crack gel because of incomplete peptization, which causing a breakdown in gel network during pyrolysis. Otherwise, adding 0.07 to 0.11 mole of HNO_3 were produced gel layer without crack due to complete peptization of alkoxides, as shown in Figure 5.3.

From these results, we can conclude that the suitable concentration of nitric acid in the sol is 0.07 mole per mole of boehmite, because this condition is minimum acid quantity for producing crack-free membrane.

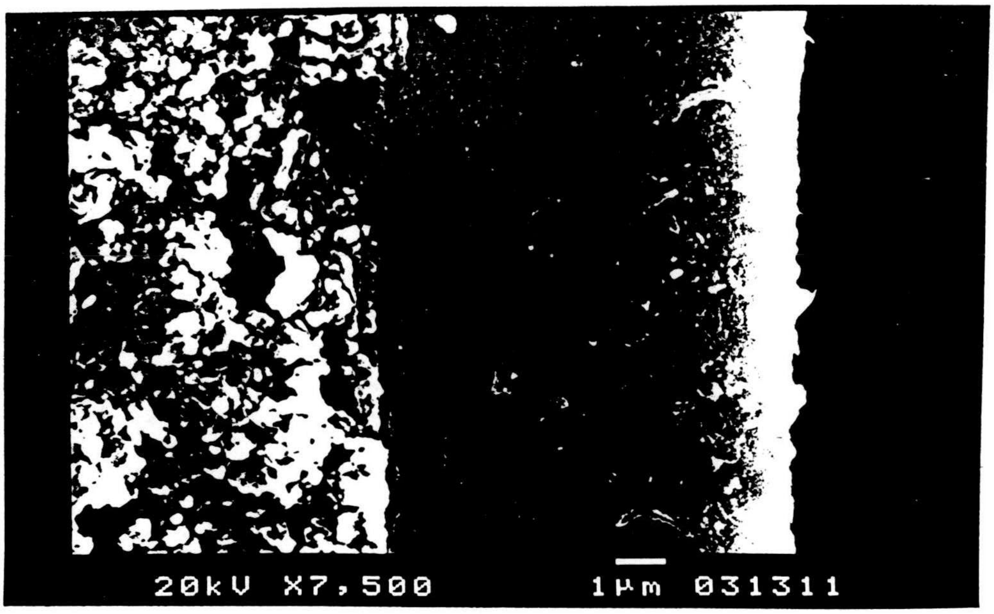


A) 0.03 mole of HNO_3

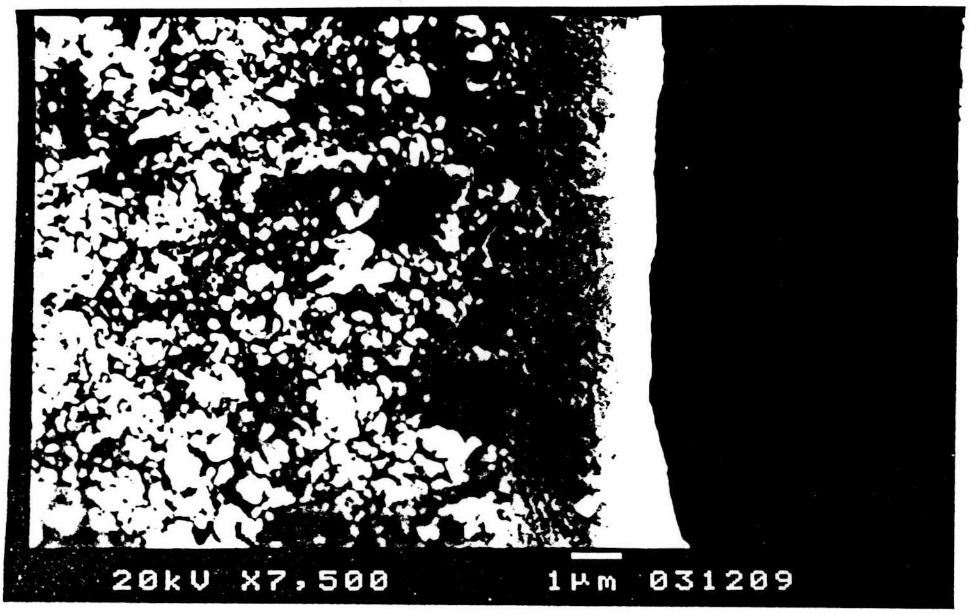
B) 0.05 mole of HNO_3



C) 0.07 mole of HNO_3



D) 0.09 mole of HNO_3



E) 0.11 mole of HNO_3

Figure 5.3 SEM Photograph of Gel Layer at Various Acid Concentration (A) 0.03 (B) 0.05 (C) 0.07 (D) 0.09 and (E) 0.11 mole of HNO_3 per mole of boehmite

5.3 The Effect of Coating Time on the Membrane Thickness

The coating time is the important function of crack-free membrane thickness. So this experiment was studied the effect of coating time on membrane thickness. The made tube was coated with sol at various coating time (10, 20, and 30 seconds) and calcined at 600 °C for 30 minutes. From Figure 5.4, it shows that membrane layer grow as a function of the square root of coating time. From this correlation, we also can take the equation of these:

$$x = 0.4056t^{1/2}$$

where x is the thickness of membrane : μm

t is the coating time : seconds

From Figure 5.5, SEM photographs show that crack-free membrane was obtained from the membrane which coating for 10 seconds, whereas the others were cracking. So we can concluded that the crack-free membranes were obtained from the membranes which have thickness are equal or less than 5 μm.

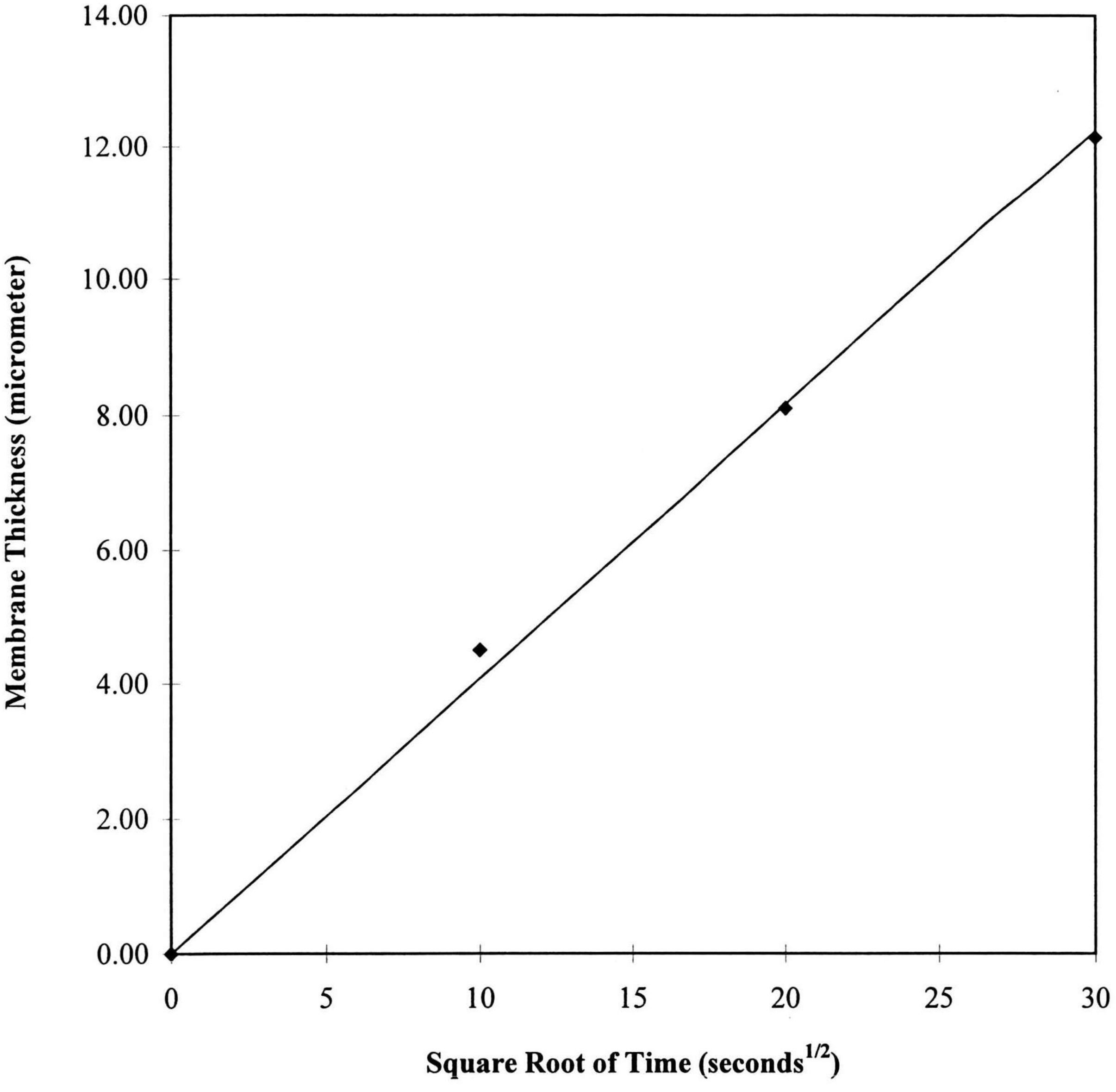
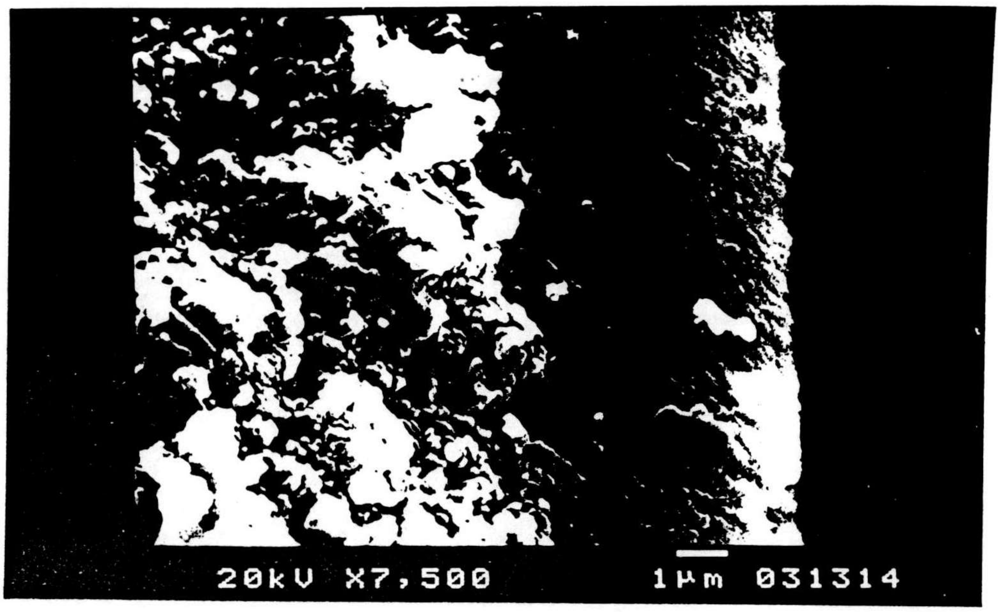
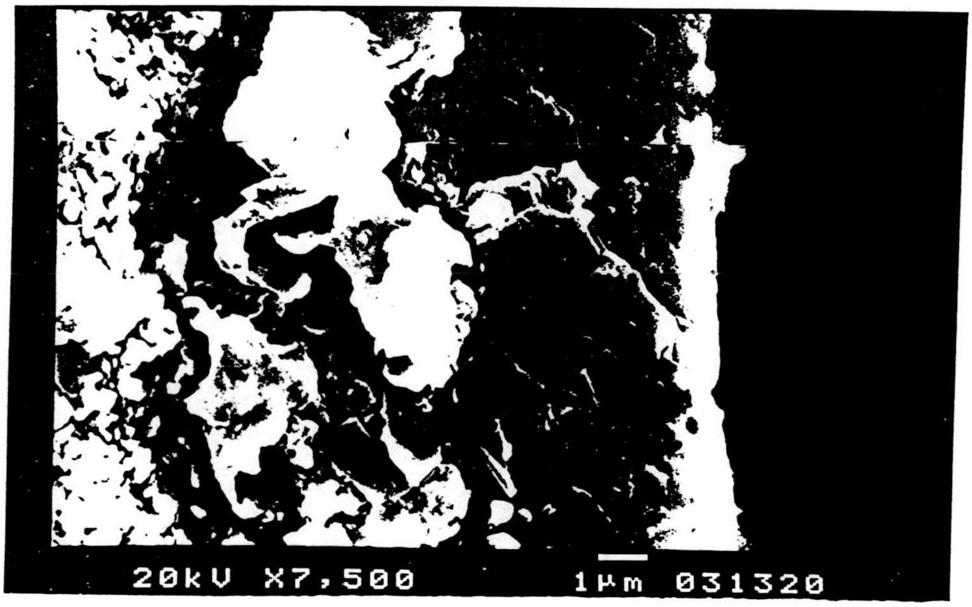


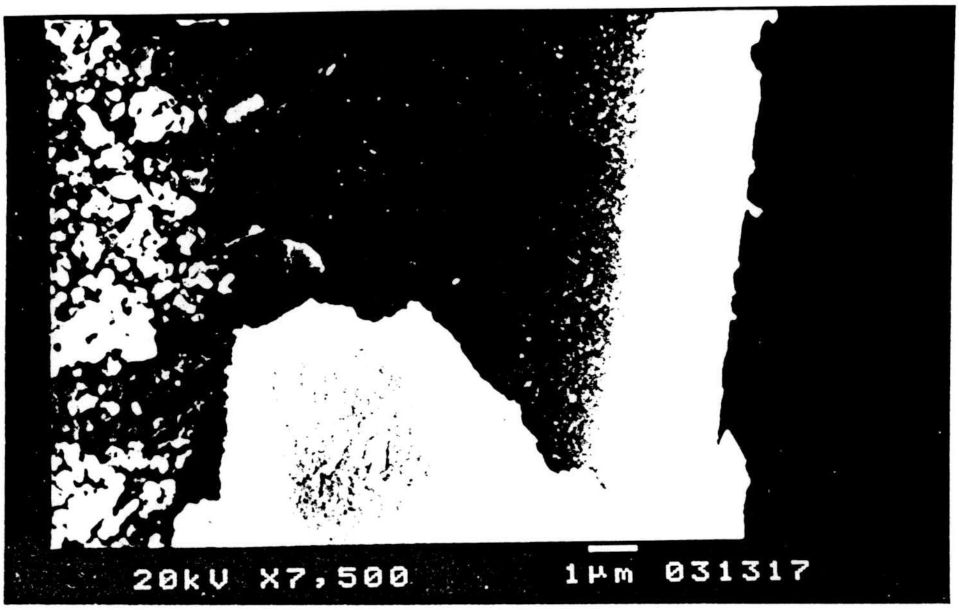
Figure 5.4 Correlation between Membrane Thickness and Coating Time



A) Coating for 10 seconds



B) Coating for 20 seconds



C) Coating for 30 seconds

Figure 5.5 SEM Photograph of Gel Layer at Various Coating Time

(A) 10 seconds, (B) 20 seconds, and (C) 30 seconds

5.4 The Effect of Calcination Temperature on the Microstructure

In this section, the effect of calcination temperature on membrane microstructure was studied for choosing the best temperature that will create suitable γ-alumina filter. The sol was coated on the tubes for 10 second and calcined at various temperature of 300 to 800 °C for 30 minutes. After that, these membranes were measured transition crystal phase by x-ray diffraction (XRD). Figure 5.6 show that the crystal phase of transition temperature at 300 ° C is boehmite phase, and transform to γ-alumina at 400 to 800 °C. (These XRD patterns can be referenced from microfilm of International Centre for Diffraction Data, JCPDS:1980).

Then, these membranes were characterized by BET method for observing microstructure of γ-alumina. Porosity, pore size, and pore volume versus the calcination temperature are shown in figure 5.7. It was found that pore size increased with the increased calcination temperature while porosity was closely constant, whereas pore volume increases up to the maximum value at 600 °C before gradually decreases. As the temperature is increased, there is a dehydration, which causes an irreversible loss in physical surface area and a loss in its surface hydroxyl group, then pore size is increased [26].

Above result can be concluded that a suitable calcination temperature is 600 °C. Because this temperature has the maximum pore volume.

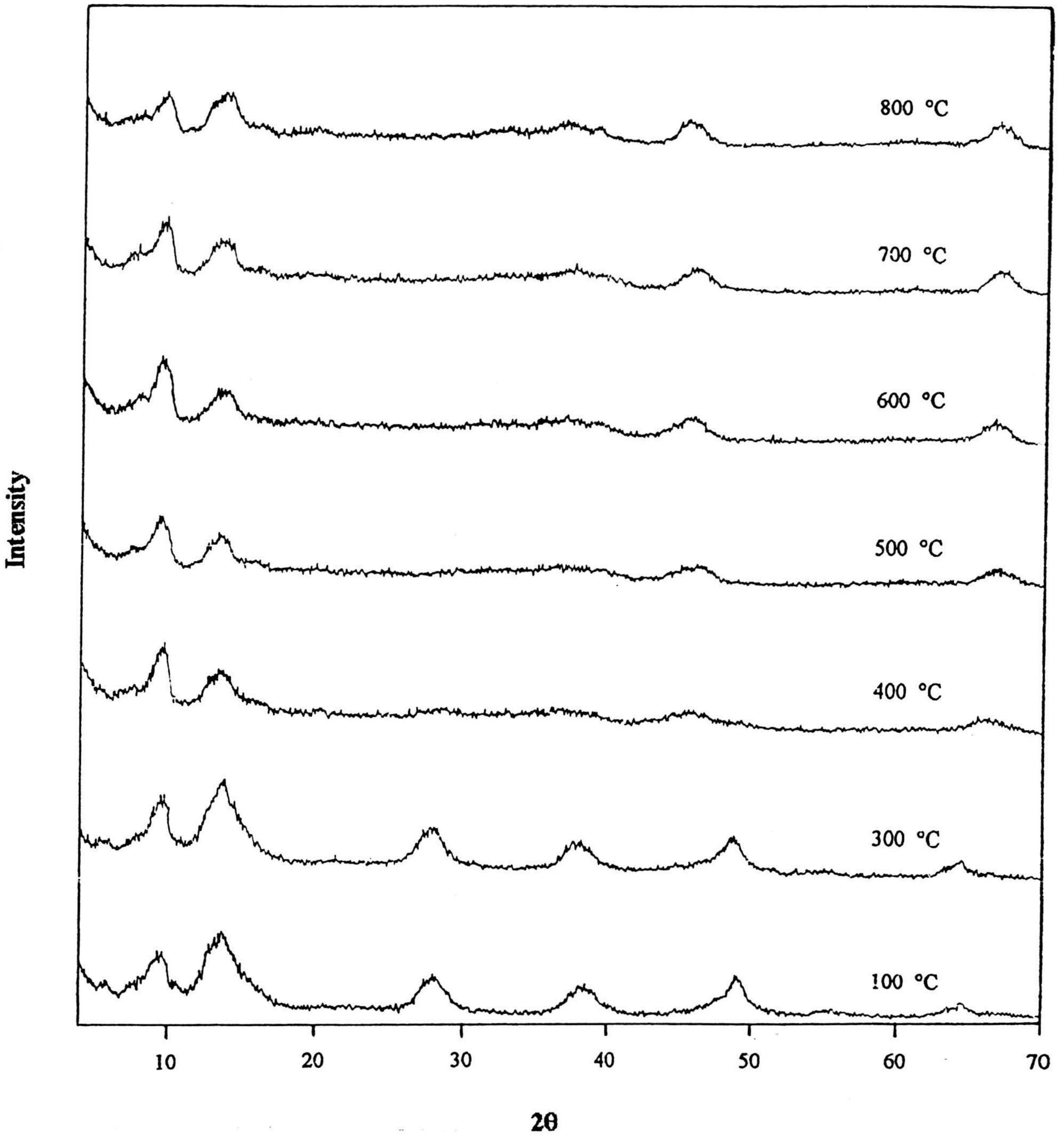


Figure 5.6 X-Ray Diffraction Patterns of Al_2O_3

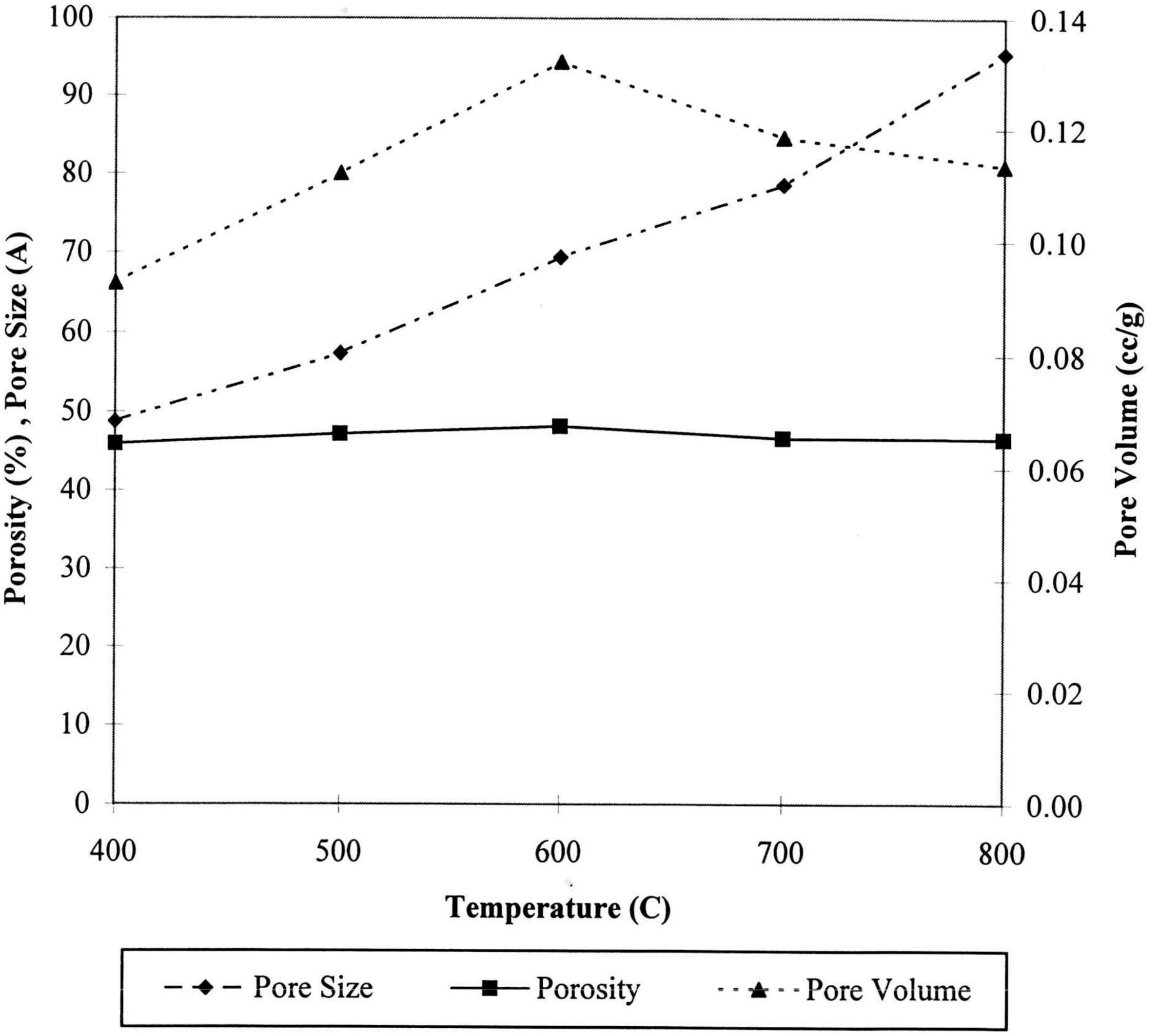


Figure 5.7 Correlation between Porosity, Pore Volume, and Pore Diameter VS. Calcination Temperature

5.5 The Effect of Calcination Time on the Microstructure

In this section, we selected the suitable calcination temperature to study the effect of calcination time on the microstructure of membrane. The experiments were carried out at various calcination time: such as 5, 30, 120, and 240 minutes. From Figure 5.8, pore size is closely constant with the increase of calcination time. The relationship between porosity and calcination time is similarly trend and so does the pore volume.

So, we concluded that the suitable calcination time is 30 minutes, and also observed that calcination time is less effective than calcination temperature.

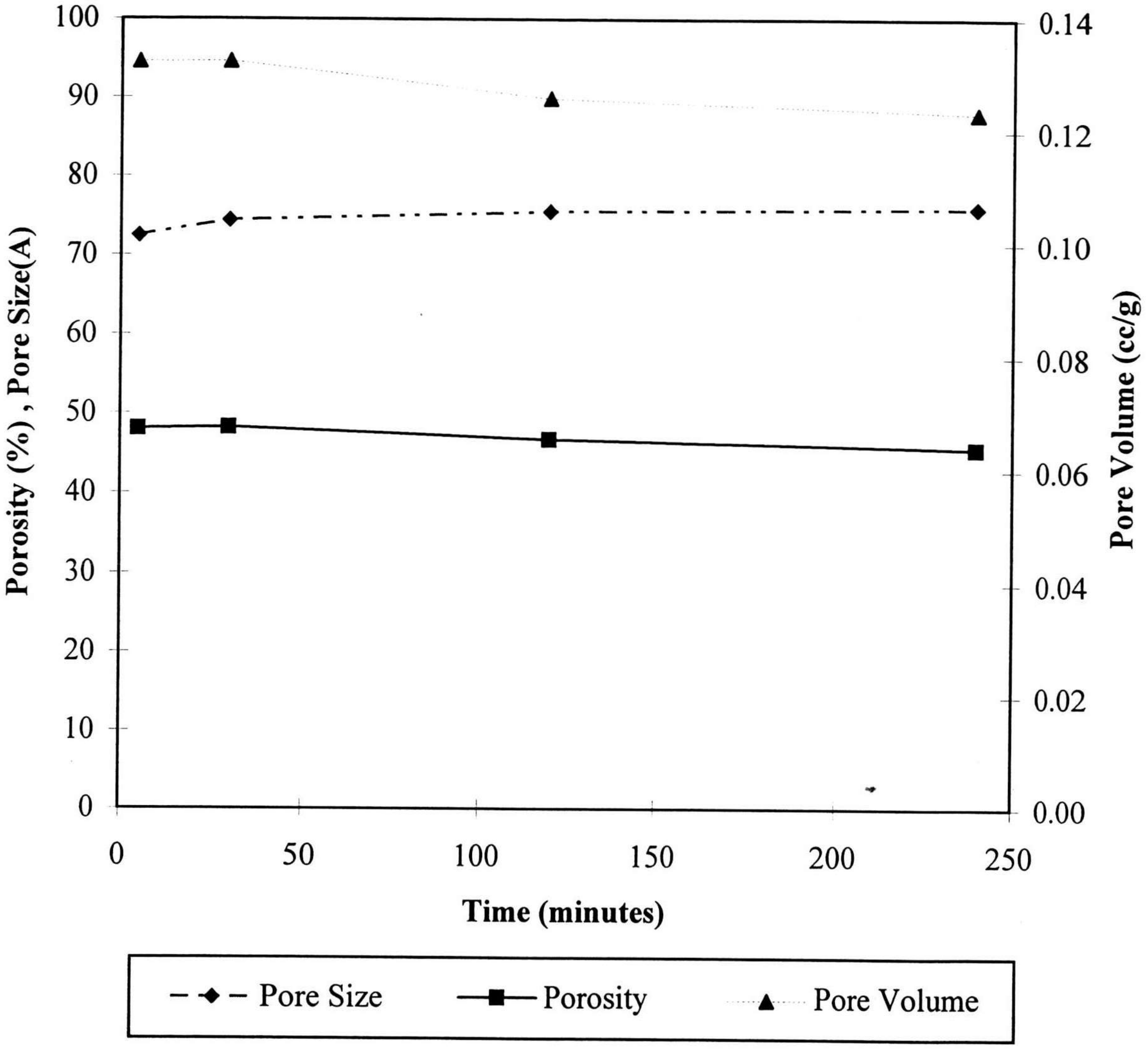


Figure 5.8 Correlation between Porosity, Pore Volume, and Pore Diameter VS. Calcination Time

5.6 Study of Rejection Performance on Home Made Porous Filter

The membranes which is prepared from 0.07 mole of acid per mole of alkoxide in solution, coating time for 10 seconds, and calcination at 600 °C for 30 minutes, were determined their rejection by using 0.2 % wt PVA at transmembrane pressure and recirculation velocity of 0.5 bars and 1.66 m/sec, respectively. For 120 minutes of batch filtration, the rejection was determined as shown in Table 5.2. This result indicates that this membrane has low rejection property even through most of their pore size are small but some of them are having large pore size which effect to the percentage of rejection. Then, the first layers were coated again by the same sol for producing bi-layer membrane under the same condition.

From the experimental result, rejection of bi-layer membrane is higher than of one-layer about 27.24 %, due to percentage of large pore volume (above 1000 A) in the bi-layer membrane is reduced to 36.46 %.

This result implies that the more layer we coated it, the more rejection we obtained.

Table 5.2 Comparison of One and Bi-Layer Membrane Properties

	One-Layer Membrane	Bi-Layer Membrane
Rejection (%)	32.67	44.9
Pore Volume (Above 1000 A) (cm^3/g)	0.0081	0.0051
(%)	1.92	1.22
Maximum Pore Volume (cm^3/g)	0.1321	0.1322
(%)	31.22	31.46
Pore Size (at Maximum Pore Volume) (A)	74.4	73.9
Porosity (%)	48.21	48.04

5.7 Standard Permeation Flux of Distilled Water on Home Made Porous Filter

This section is investigated the filtration of distilled water with home made porous filter, in order to test the properties of filter and use to be standard for confirming the regenerated filter in next usage. Therefore, the value of distilled water permeation flux of clean filter must be equal to the value of standard permeation flux. In this experiment, permeation flux of supported and intermediated layer were determined under recirculation velocity of 1.66 m/sec, transmembrane pressure of 0.3, 0.4, and 0.5 bars, respectively. These results are shown in Figure 5.9. After that, standard permeation flux of bi-layer membrane was determined under transmembrane pressure of 0.3, 0.4, and 0.5 bars and recirculation velocity of 1.66, 1.43, and 1.04 m/sec, respectively. These results are shown in Figure 5.10.

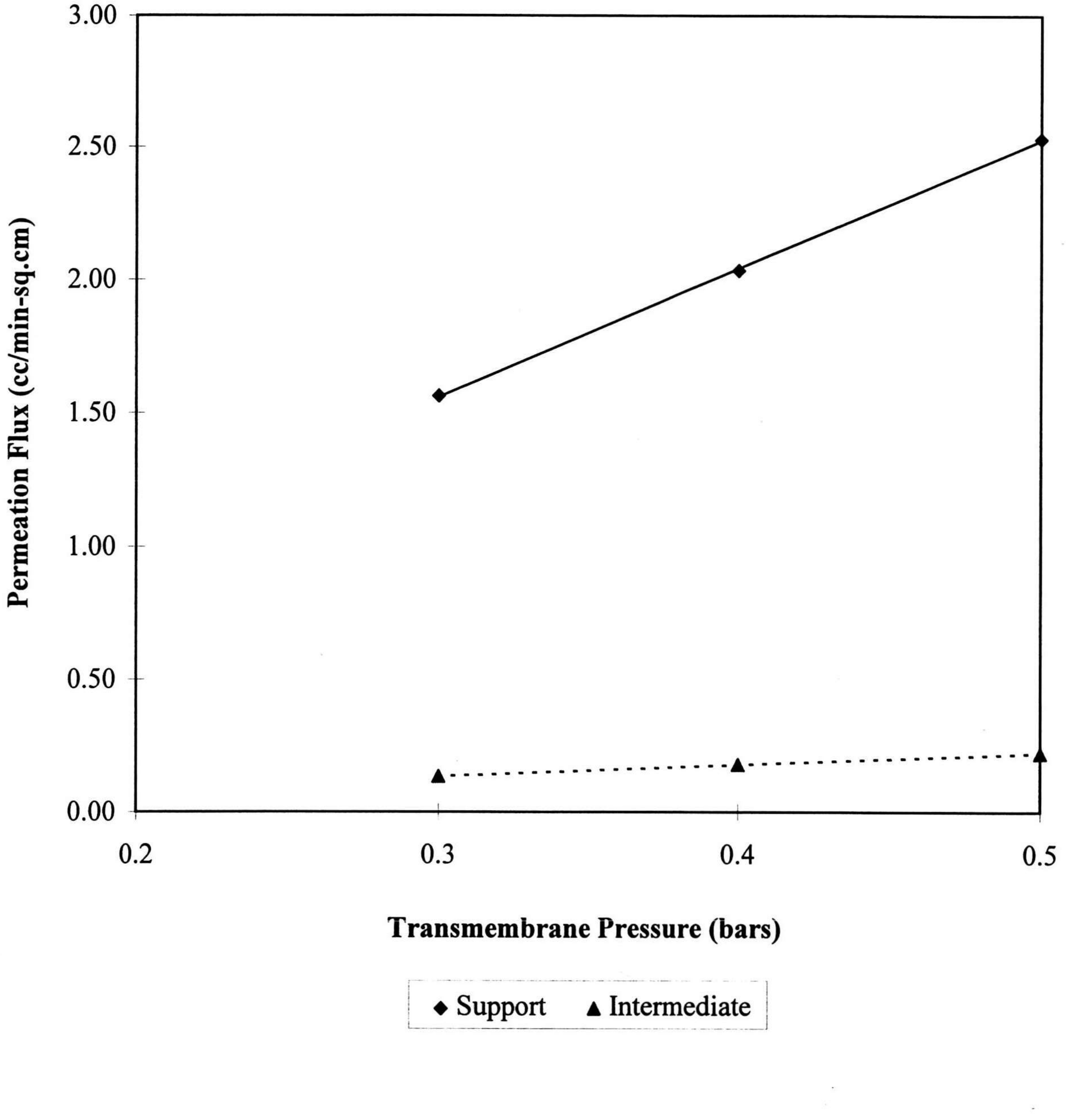


Figure 5.9 Correlation between Permeation Flux of Distilled Water and Transmembrane Pressure on Supported and Intermediated Layer

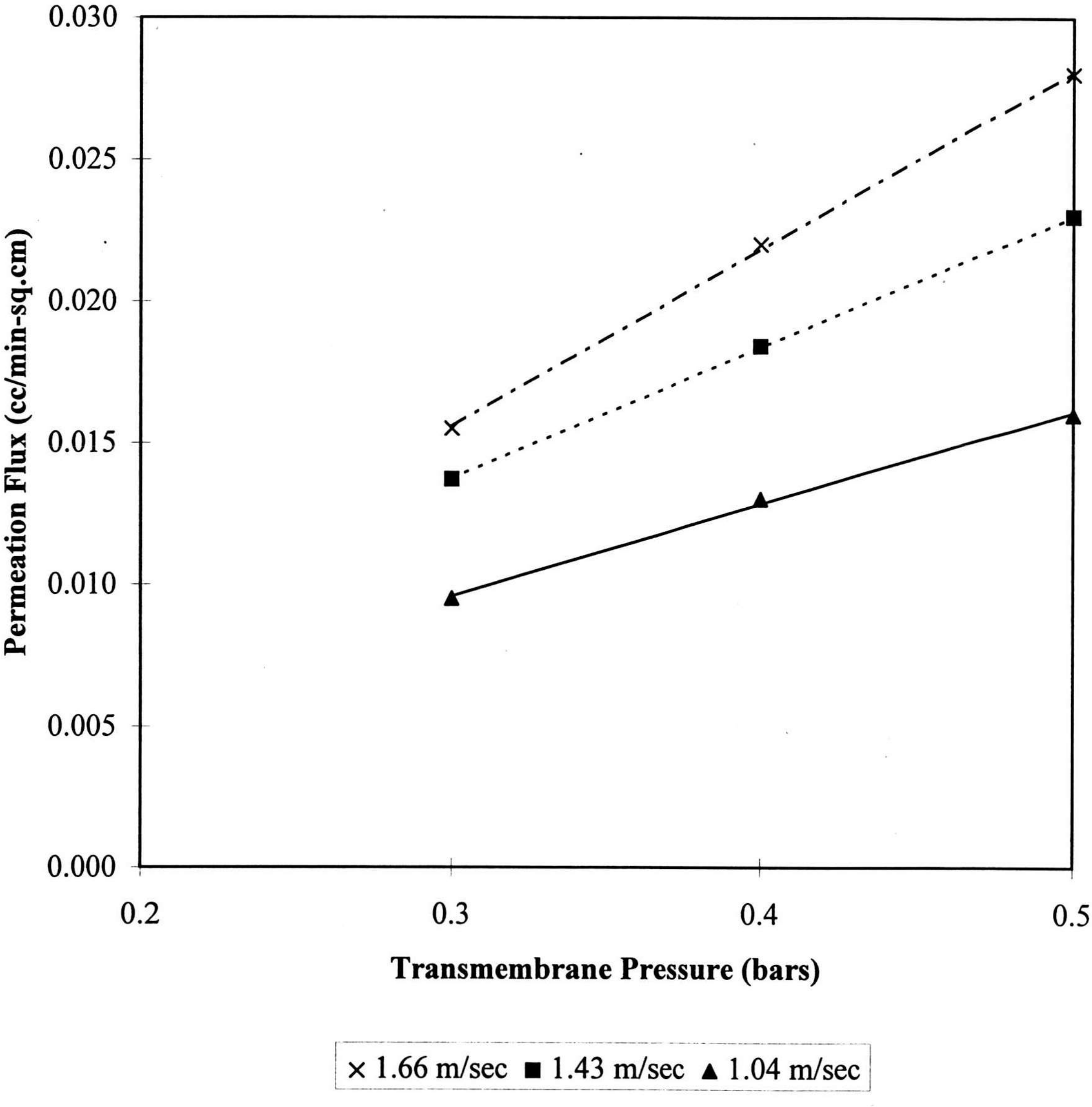


Figure 5.10 Correlation between Permeation Flux of Distilled Water and Transmembrane Pressure on Bi-Layer Membrane

From Figure 5.9 and 5.10, they were found that permeation flux linearly relate to transmembrane pressure due to no particle in the distilled water. Therefore, the value of gel resistance is zero. Then, filtration resistance expressed to permeation flux (equation (3.17)) is the value of membrane resistance only. Because membrane resistance is constant, permeation flux of distilled water is also constant. From these graphs, the value of slope is $1/\mu R_M$.

From results of calculation, membrane resistance of supported layer, intermediated layer, and bi-layer membrane at recirculation velocity of 1.66, 1.43, and 1.04 m/sec, respectively, are $1.23*10^9$, $1.41*10^{10}$, $1.14*10^{11}$, $1.29*10^{11}$, and $1.85*10^{11}$ cm^{-1}, respectively.

5.8 α-Amylase Concentration

In this section, the separation of α-amylase were investigated at various transmembrane pressure (0.3, 0.4, and 0.5 bars) and recirculation velocity (1.66, 1.43, and 1.04 m/sec) by using enzyme solution of 2.4 g/litre. The results are shown in Figure 5.11, 5.12, and 5.13. The observed permeation flux increases with the increase of pressure and recirculation velocity due to high pressure driving force and high shear rate (see Figure 5.14).

Table 5.3 Result of Percent Increasing of Enzyme Concentration at 120 minutes of Filtration

Pressure / Velocity	0.3 bars	0.4 bars	0.5 bars
1.04 m/sec	1.34 %	5.19 %	13.09 %
1.43 m/sec	1.92 %	6.07 %	14.58 %
1.66 m/sec	2.45 %	7.45 %	17.08 %

As shown in Table 5.3, the experimental results indicated that percentage of enzyme concentration increases as pressure and recirculation velocity increase. The rejection of α-amylase enzyme on bi-layer home made filter was also determined at 8 minute intervals for 120 minutes under 0.5 bars and 1.66

m/sec of recirculation velocity (see in Appendix D). It was found that the rejection of α-amylase (67.22 % in average)(see the experimental data in Table D11) is higher than PVA's rejection. By using α-amylase rejection value, the increasing of enzyme concentration in retentate was calculated and compared at different pressure and recirculation velocity of 120 minutes of filtrate.

Above datas in Table 5.3, it can be concluded that in the range of study, home made filter will give the highest concentration at 0.5 bar and recirculation velocity of 1.66 m/sec.

After that, under operating condition at transmembrane pressure 0.5 bar and recirculation velocity 1.66 m/sec, the permeation flux was investigated by varying enzyme concentration (1.2, 1.8, and 2.4 g/litre). The enzyme concentration increases as permeation flux decreases that resulted in decreasing of enzyme concentration. This results are shown in Figure 5.15 and Table 5.4

So we can concluded that the suitable condition for increasing α-amylase enzyme is operated at transmembrane pressure 0.5 bar, recirculation velocity 1.66 m/sec, and enzyme concentration 1.2 g/litre under no denaturalization assumption.

Table 5.4 Comparison of Percent Increasing α-amylase Enzyme at Transmembrane Pressure 0.5 bar, Recirculation Velocity 1.66 m/sec

Enzyme Concentration (g/litre)	Percentage of increasing enzyme (%)
1.2	44.6
1.8	28.4
2.4	17.08

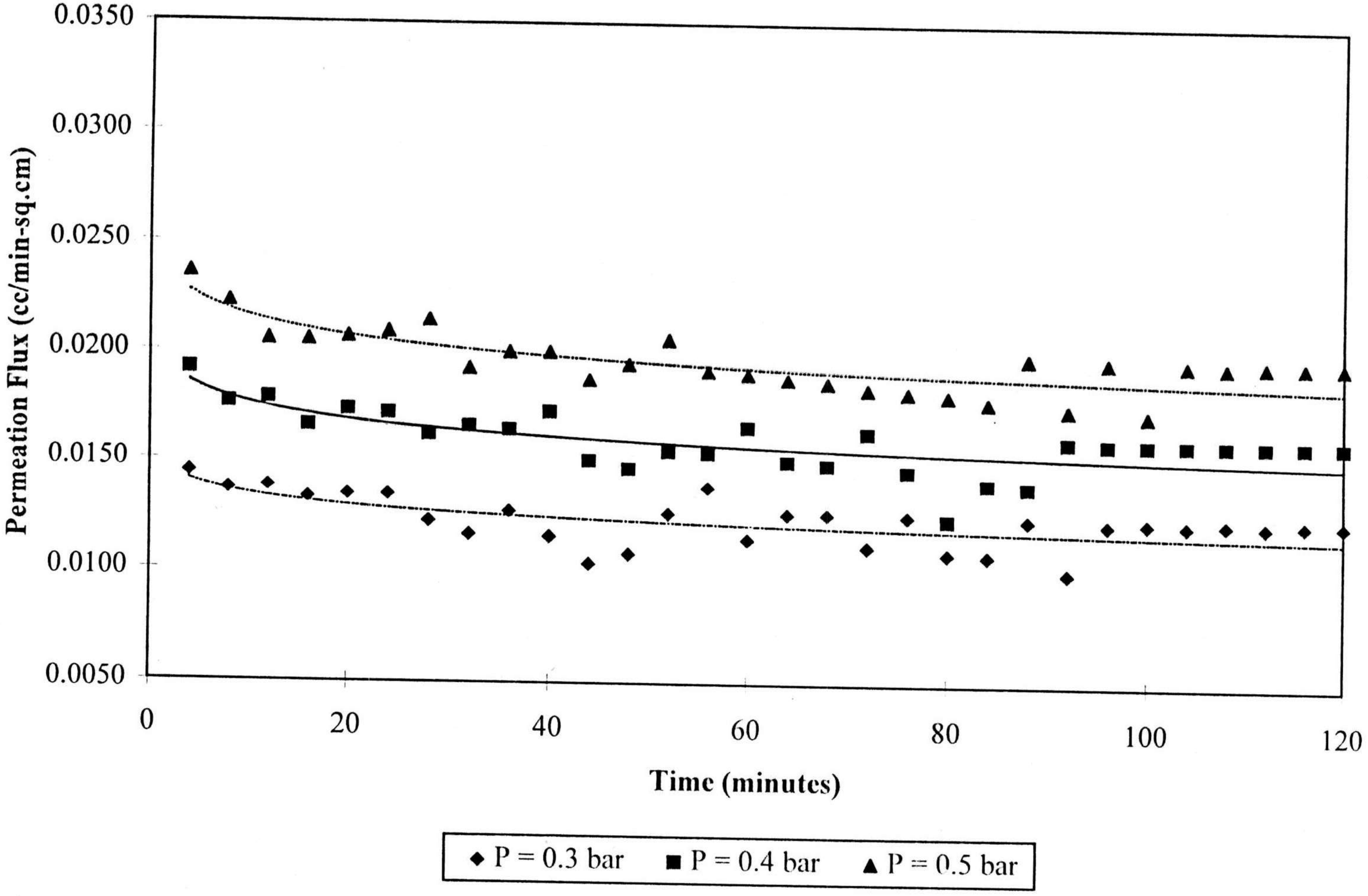


Figure 5.11 Permeation Flux at Enzyme Concentration and Recirculation

Velocity of 2.4 g/litre and 1.66 m/sec

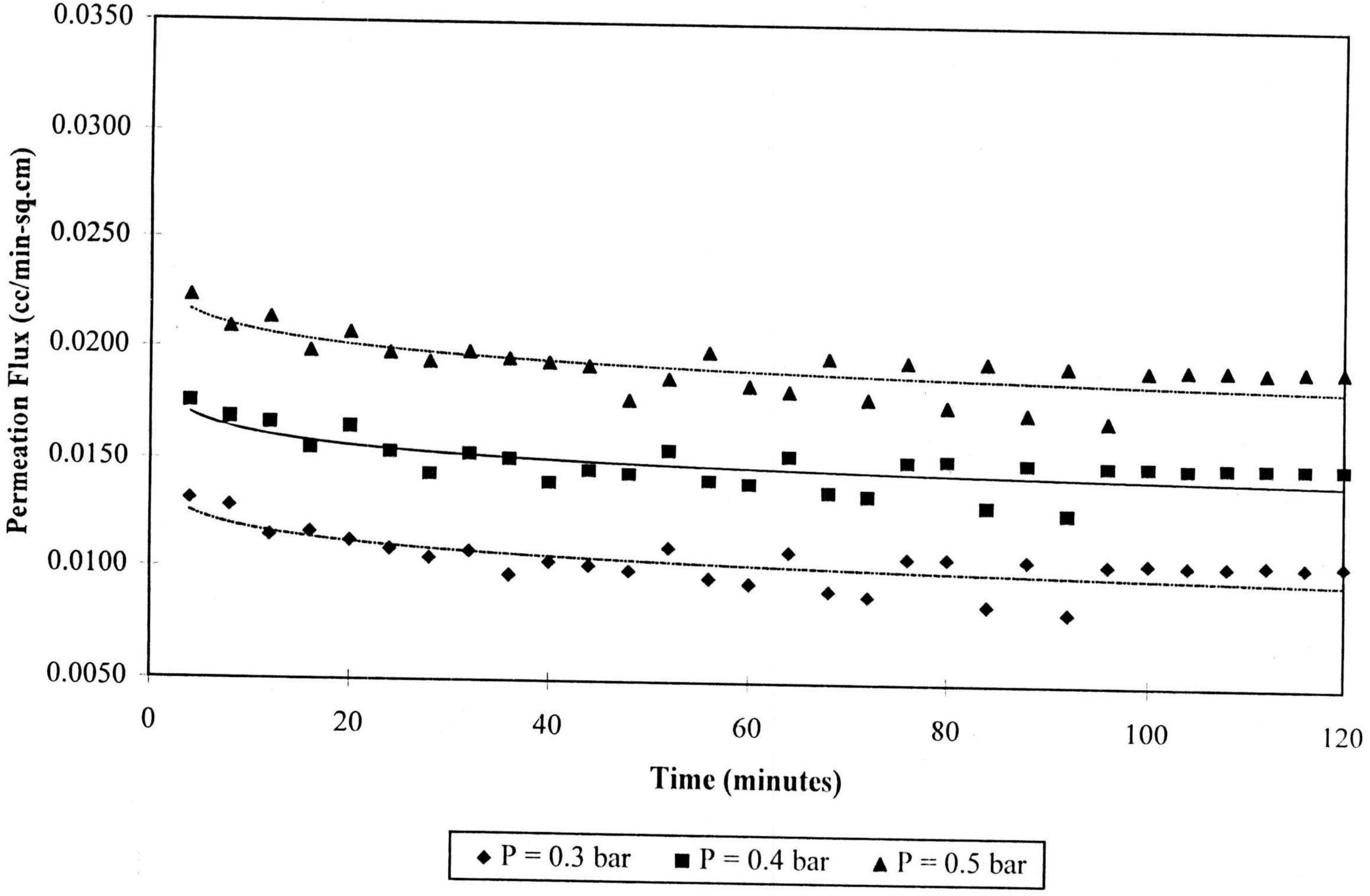


Figure 5.12 Permeation Flux at Enzyme Concentration and Recirculation

Velocity of 2.4 g/litre and 1.43 m/sec

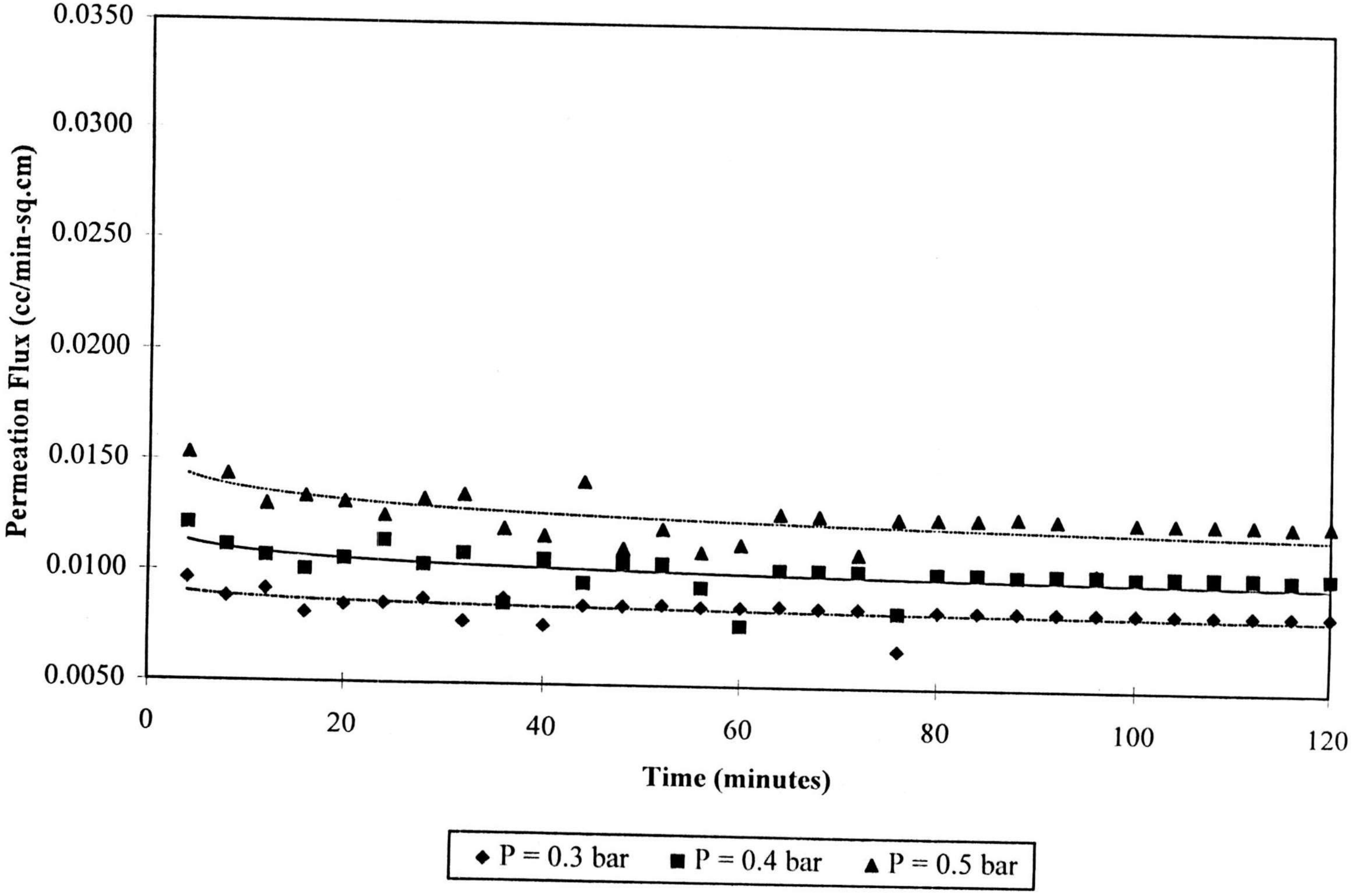


Figure 5.13 Permeation Flux at Enzyme Concentration and Recirculation

Velocity of 2.4 g/litre and 1.04 m/sec

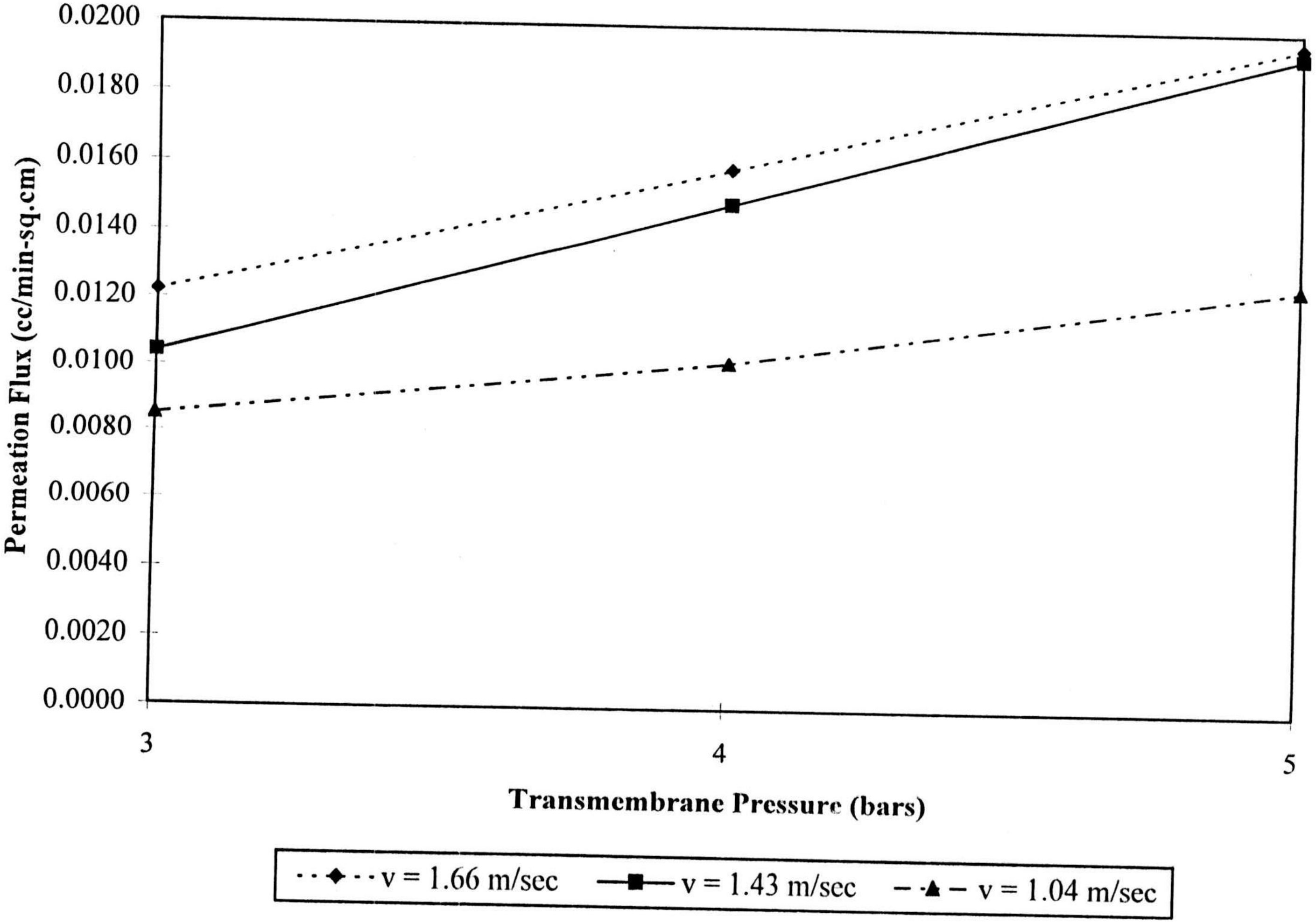


Figure 5.14 Correlation of Transmembrane Pressure and Permeation Flux

at Enzyme Concentration 2.4 g/litre

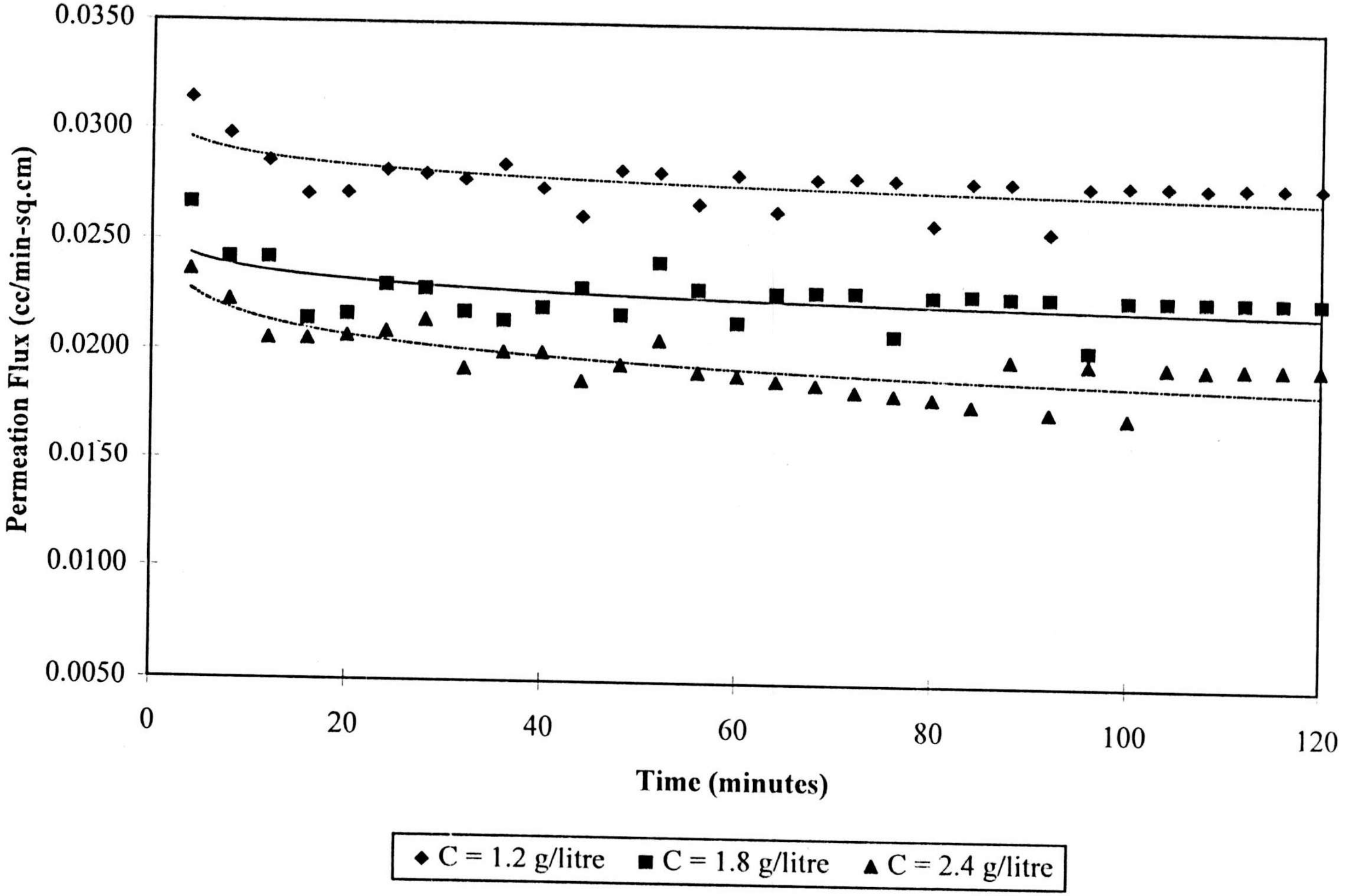


Figure 5.15 Permeation Flux at Transmembrane Pressure and

Recirculation Velocity of 0.5 bar and 1.66 m/sec