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# QUARTERLY PROGRESS REPORT (10/1/96-12/31/96)

**Contract No. DE-FG22-94PC94215**
**Project Title: Conversion of Coal Wastes into Waste-Cleaning Materials**
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**Graduate Student: Hsiao-Lan Chang**

## INTRODUCTION

Besides working on the conversion of fly ash to zeolites, we have been studying the possibility of converting fly ash to mesoporous molecular sieves. Mesoporous materials contain ordered pore structures with pore sizes in the range of 3-10 nm. These mesoporous materials are first synthesized as organic-inorganic biphase composites. After calcination, the organic phase is burned out, the remaining porous inorganic phase contains periodic pores that are either hexagonally arranged (MCM-41) or cubically arranged (MCM-48). Most of the mesoporous molecular sieves made thus far are aluminosilicates or silicates. These mesoporous molecular sieves have been referred to as mesoporous zeolites, i.e., zeolites with larger pore sizes.

It was reported in previous reports that fly ash can participate in the formation of mesoporous materials. However, fly ash has not been converted to mesoporous materials directly. In the last report, we showed that by fusing the fly ash with sodium hydroxide, the yield of zeolites increased significantly. The fusion process increases the amount of silicates and aluminates that are dissolved in the precursor solutions. Therefore, in the last three months, we have been studying the conversion of fly ash into mesoporous materials using the fusion process. As expected, we succeeded in converting fly ash into mesoporous molecular sieves. Due to their uniform molecular pore sizes and large surface areas, the mesoporous materials are very useful materials for a wide range of applications such as molecular sieves, adsorbents, and catalysts. Therefore converting fly ash into mesoporous materials not only eliminates the disposal problem but also turns an otherwise waste material into a useful one. The successful conversion of fly ash into mesoporous molecular sieves broadens the possible application of fly ash.

## EXPERIMENTAL PROCEDURE

The raw materials for the experiments were class F fly ash from Conemiaugh power plant. The chemical composition of the fly ash was analyzed by EDX in SEM. The compositions of the Conemiaugh ash is 49 wt% $SiO_2$, 24 wt% $Al_2O_3$, 22 wt% $Fe_3O_4$ and others. The surfactant used was $C_{16}H_{32}(CH_3)_3NBr$ (cetyl trimethyl ammonium bromide, CTAB). The fusion process began with mixing fly ash with NaOH powder and treating them at 550°C. After fusion, the powder was dissolved in water forming fly ash solutions. The supernatant of the solution was separated from the sediment by centrifugation. This solution is solution I. When the sediment was used again to prepare a second solution and further separating the supernatant from the sediment, this supernatant solution is called solution II. The fly ash solution was aged for one day at room temperature. The surfactant solution was prepared by mixing 10.9 g of surfactant, $C_{16}H_{32}(CH_3)_3NBr$, with 32.7 g distilled water at room temperature. The 25 wt% aqueous surfactant solution was then added to the fly ash solution. After the surfactant were fully dissolved, 7.25 ml of 4.96 N $NH_4OH$ solution was added to the surfactant solution and then diluted by adding 200 ml of distilled water. The pH value of the solutions was typically at 11. The mixture solution with different Si/Al molar ratios were then hydrothermally cured at 10 psi (corresponding to 115°C). Samples were taken at various curing times and were washed with distilled water two times and then centrifuged to collect the powders. The centrifuged sediment was dried in the range of 60-80°C for 12 hours. After grinding, the solid powders were studied with X-ray diffractometer. The powders were calcined at 540°C for 7 hours at 1 °C/min. The calcined powders were studied with X-ray diffraction and BET. The curing solutions were characterized by Atomic Absorption spectroscopy for the ionic concentration of Si, Al, and Fe.

## RESULTS and DISCUSSION

Both solution I and solution II were studied for the formation of mesoporous materials. It was found that solution II can form mesoporous phase earlier than solution I. The XRD patterns of the precipitate from solution I is shown in Fig.1 for 2-day, 4-day, and 7-day curing. The MCM-41 phase was stable against calcination. The XRD patterns in the higher angles region showed a small amount of zeolite P in the precipitates. After 2 days of curing, solution I only contained zeolite P without the formation of MCM-41 phase. MCM-41 phase only appeared after 4 days of curing for solution I. Fig.2 shows the XRD patterns for precipitates obtained from solution II. It can be seen that the intensity of the MCM-41 phase obtained from solution II is generally higher than that from solution I. Furthermore, there is no zeolite P formed from solution II. It is clear that solution II is a better solution for producing MCM-41 phase than solution I. This may be related to the high concentration of NaOH in the solution I. High concentration of NaOH has an adverse effect on the formation of MCM-41 phase. Furthermore, high NaOH concentration in the precursor solutions favored the formation of zeolite P thereby hindered the formation of MCM-41 phase. It should be noted that the fusion of fly ash with NaOH is critical for the formation of mesoporous materials. Previously we have studied the formation of mesoporous materials with fly ash and NaOH solutions and surfactants. No mesoporous materials were found. It was only when we fused fly ash with NaOH that mesoporous materials were formed. Clearly, the much higher concentration of Si and Al species in the solutions of fused fly ash promotes the formation of mesoporous materials.

The nitrogen adsorption isotherms for the MCM-41 phase obtained from solution I is shown in Fig.3. The adsorption isotherm is typical of MCM-41 phase with a surface area of 834 $m^2/g$. The pore size distribution of the MCM-41 phase is shown in Fig.4. It is seen that the pore size is quite uniform with an average pore size of 2.8 nm. From the XRD, we found the d100 spacing to be 3.6 nm which gives a lattice constant of $a=(4/3)^{1/2}\ d_{100}=4.2$ nm. Thereby, the wall of the hexagonally arranged pores has a thickness of 1.4 nm. Similar results were obtained for MCM-41 phase precipitated from solution II. The nitrogen adsorption isotherms for the MCM-41 phase obtained from solution II is shown in Fig.5. The surface area is 978 $m^2/g$. The pore size distribution is shown in Fig.6 and the average pore size is 2.9 nm. The pore wall has a thickness of 1.3 nm. The results of nitrogen adsorption clearly indicate that the mesoporous phase precipitated from fly ash solution is the same as those produced from pure chemicals.

## CONCLUSIONS and FUTURE PLAN

It was shown that mesoporous aluminosilicates can be precipitated from fused fly ash solutions and surfactants. The characteristics of the mesoporous phase were similar to that synthesized with pure chemicals. Even though there are significant amounts of impurities in the fly ash, mesoporous phase still precipitated. Our results indicate that the conditions for mesoporous phase formation is not sensitive to the impurities in the precursor solutions. For the next three months, we will study the conversion of various ashes with varying compositions into mesopoprous molecular sieves. The goal is to show that our conversion method is general and can be applied to a wide variety of coal ashes.

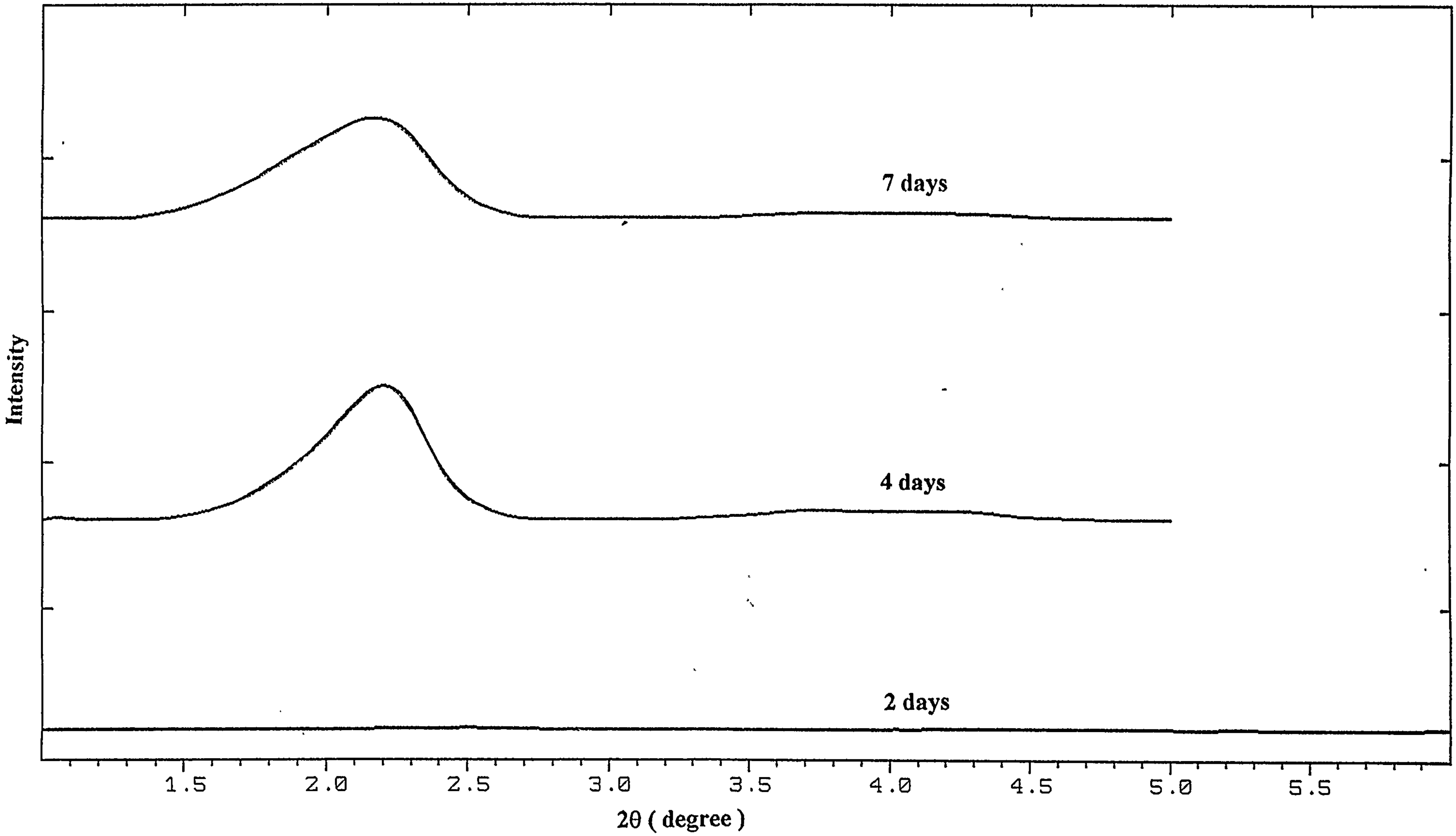

Fig.1(a). X-ray diffraction patterns of precipitates from solution I cured for 2 days, 4 days, and 7 days, in low scattering angles.

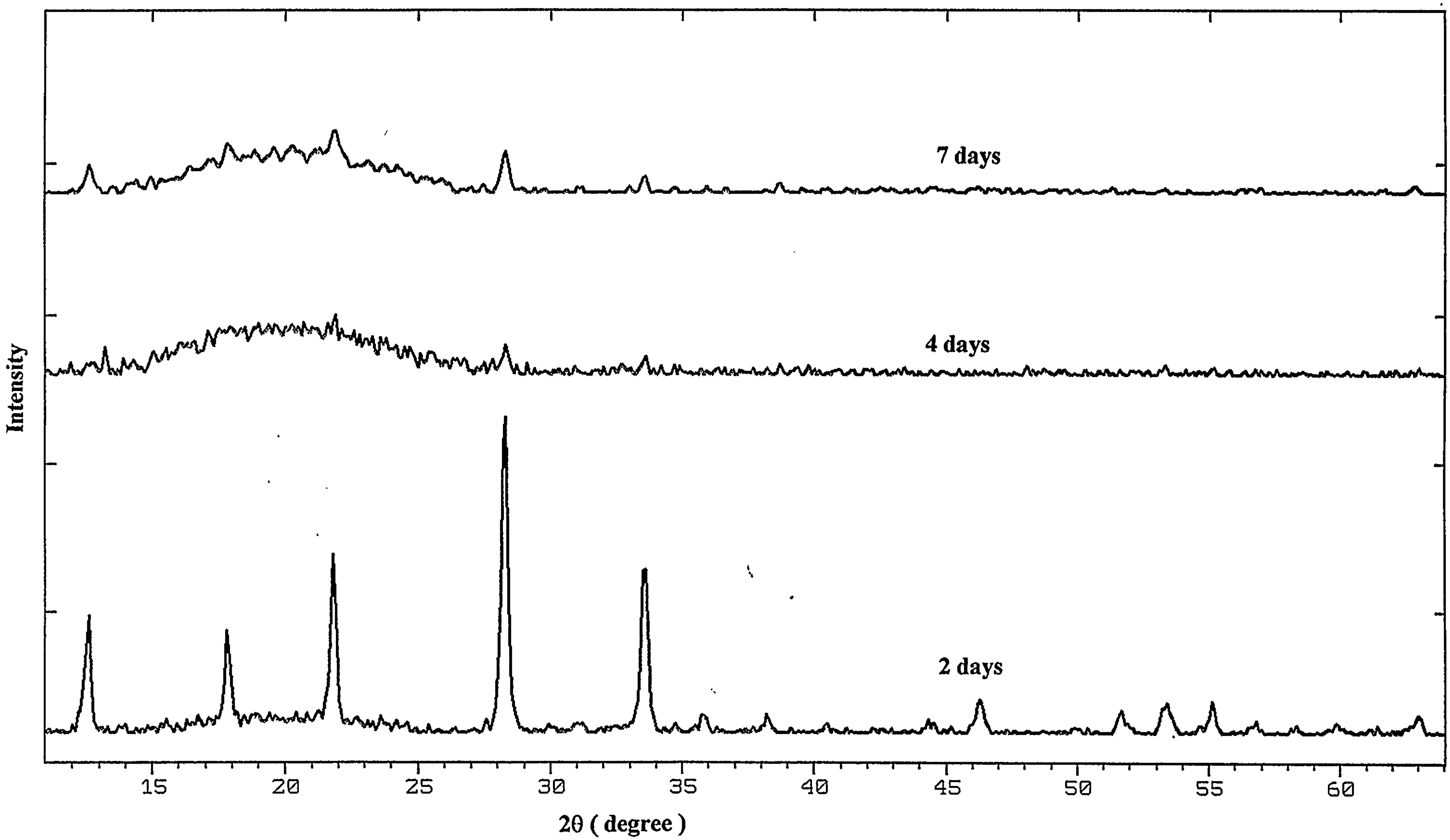

Fig.1(b). X-ray diffraction patterns of precipitates from solution I cured for 2 days, 4 days, and 7 days, in high scattering angles.

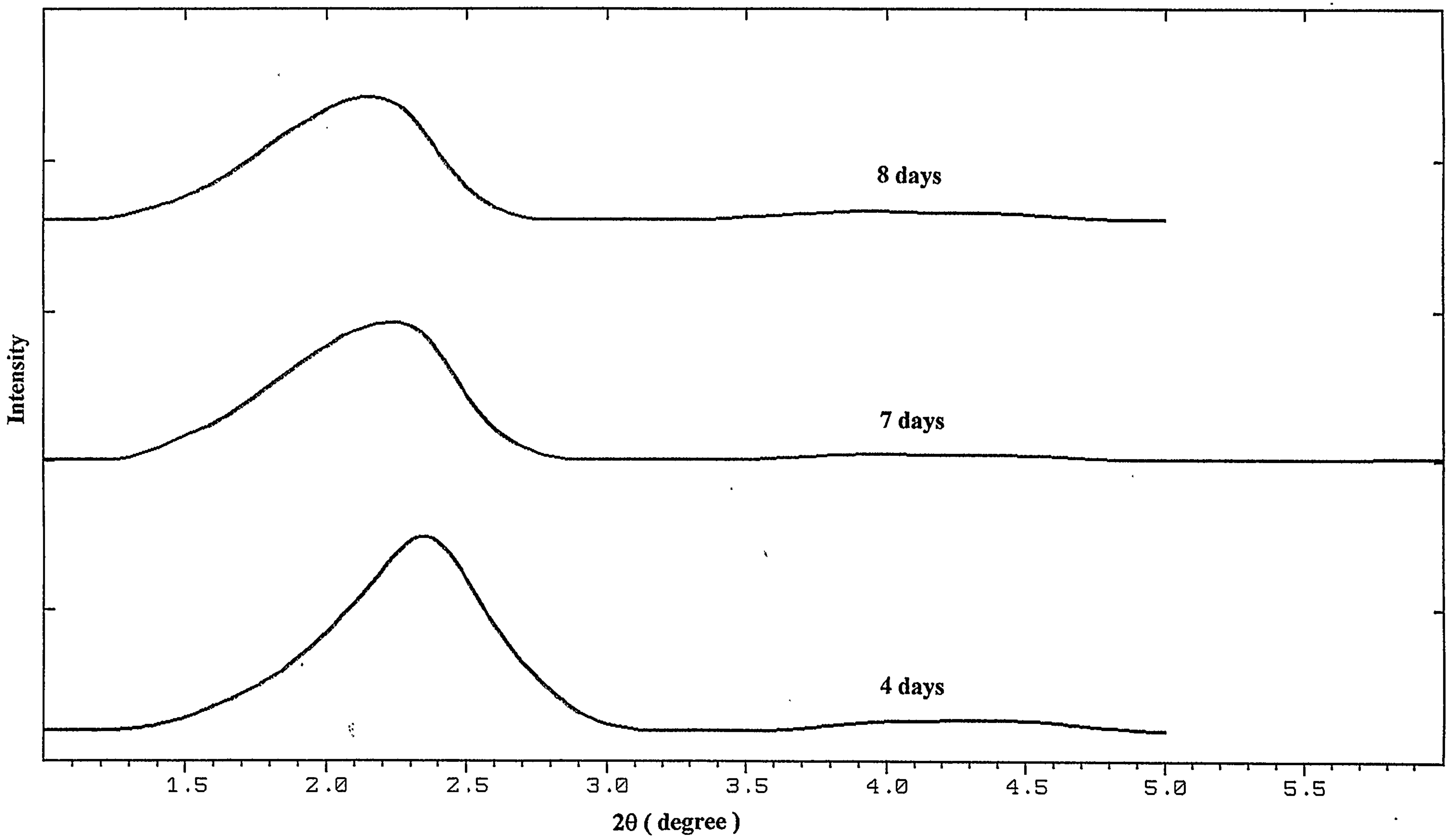

Fig.2(a). X-ray diffraction patterns of precipitates from solution II cured for 4 days, 7 days, and 8 days, in low scattering angles.

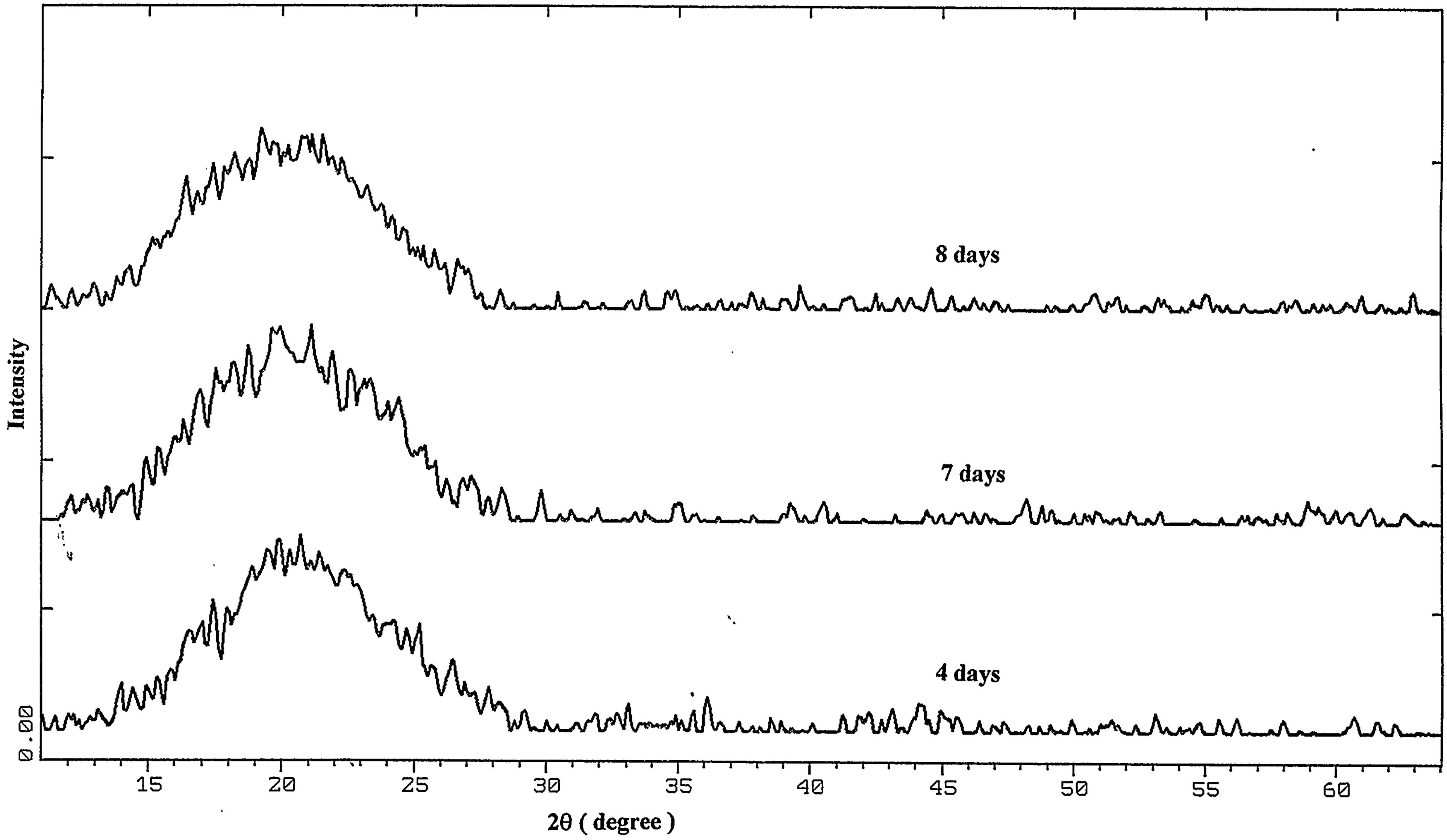

Fig.2(b). X-ray diffraction patterns of precipitates from solution II cured for 4 days, 7 days, and 8 days, in high scattering angles.

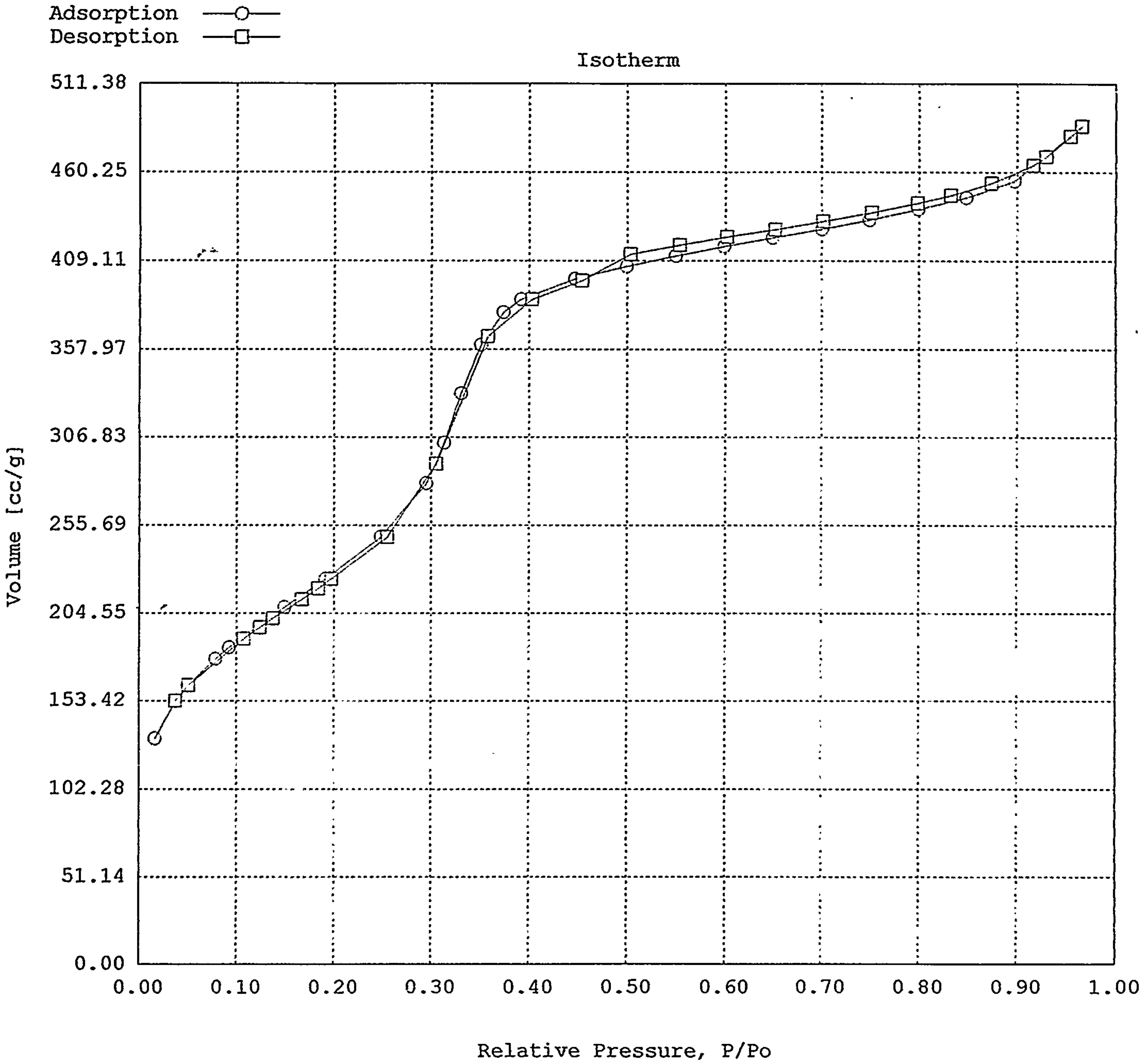

Fig.3. Nitrogen adsorption isotherm for mesoporous molecular sieves obtained from solution I cured for 4 days.

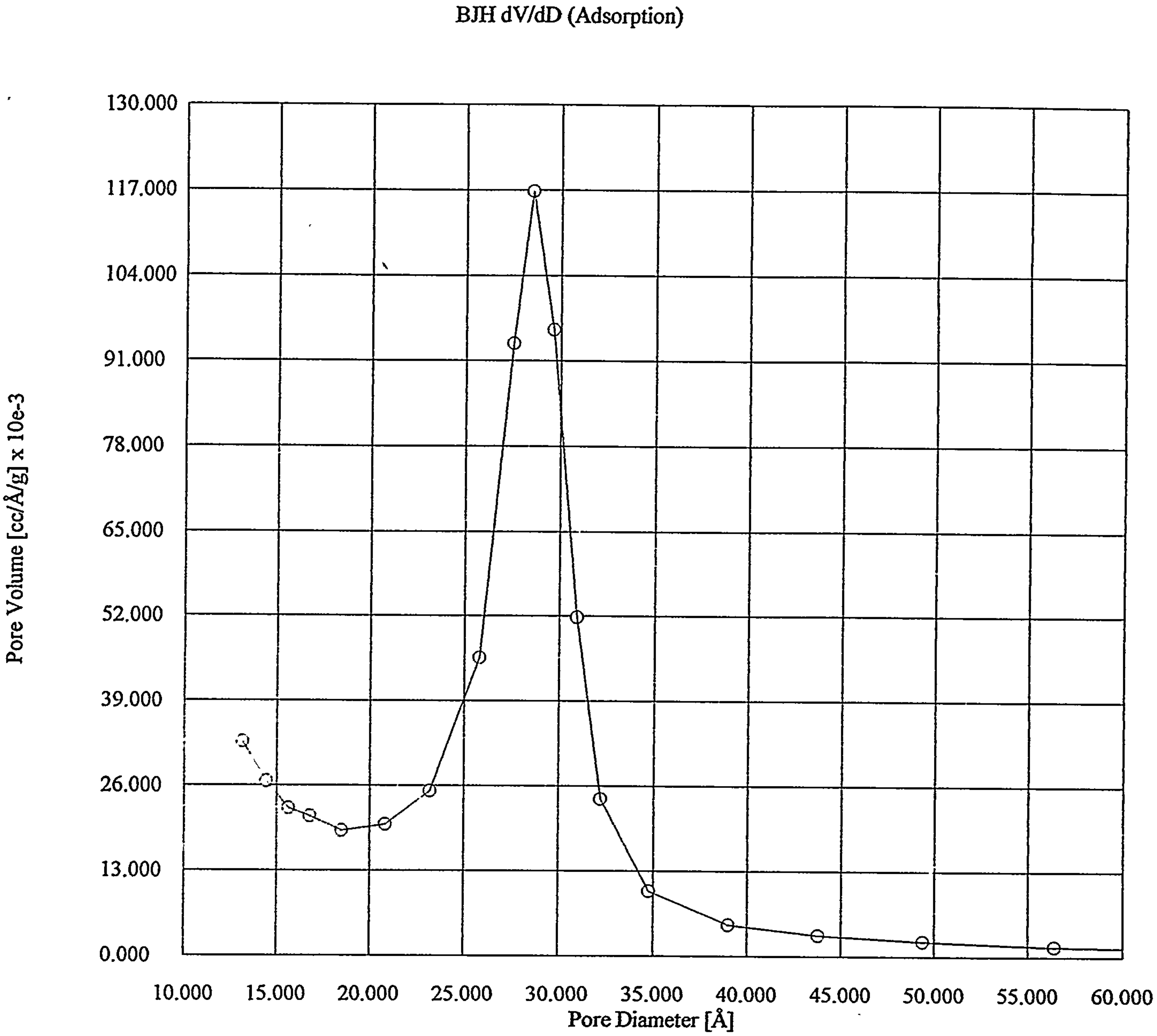

Fig.4. Pore size distribution of mesoporous molecular sieves obtained from solution I cured for 4 days.

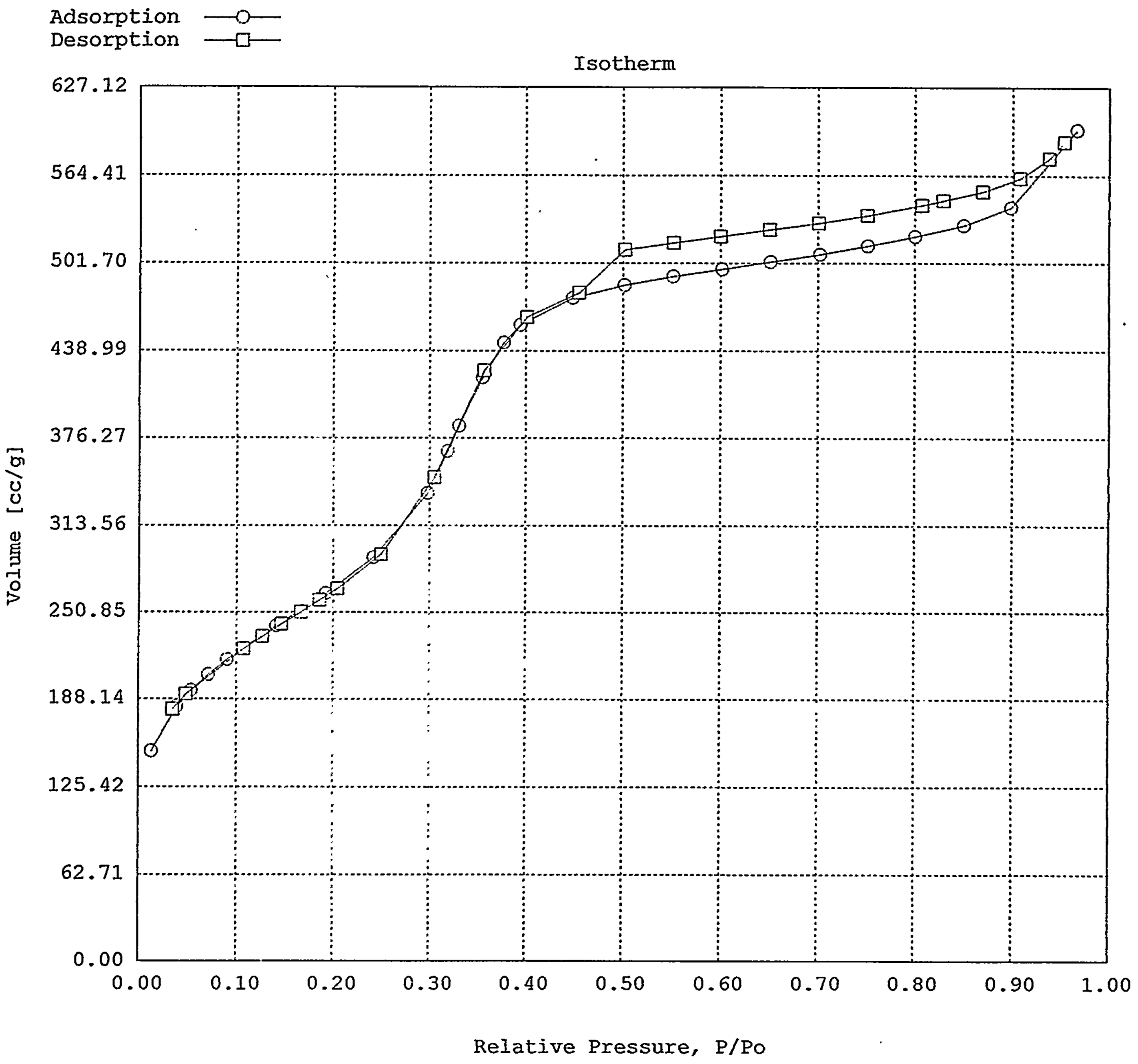

Fig.5. Nitrogen adsorption isotherm for mesoporous molecular sieves obtained from solution II cured for 8 days.

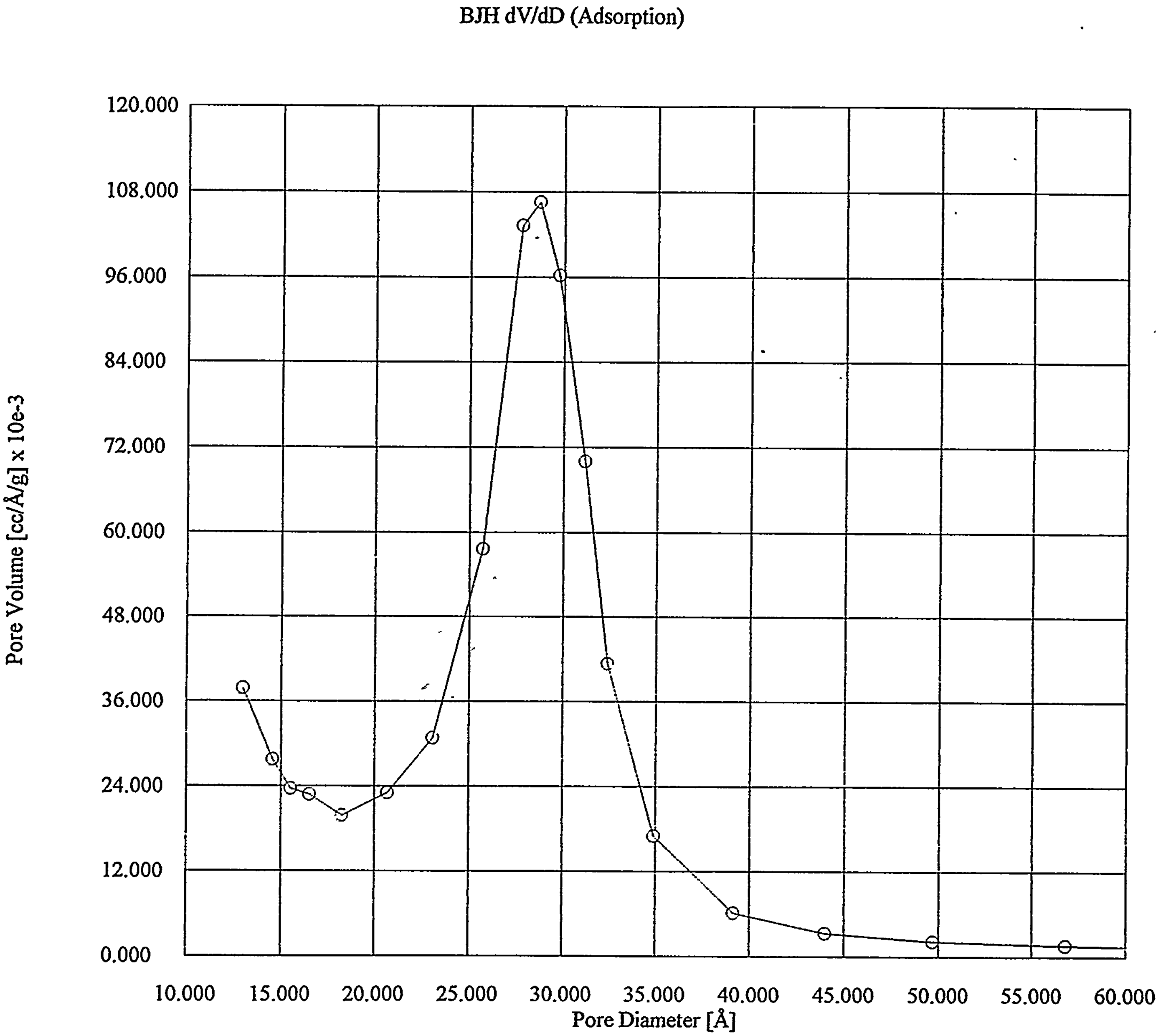

Fig.6. Pore size distribution of mesoporous molecular sieves obtained from solution II cured for 8 days.