DOE/PC/94215--T/2

RECEIVE
AUG 05 1996
OSTI

RECEIVED
USDOE/PETC
96 APR -1 AM 10:55
ACQUISITION & ASSISTANCE

QUARTERLY PROGRESS REPORT (1/1/96-3/31/96)

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

INTRODUCTION

In the model study that was reported in the last Report, we have found that the surfactant/Si molar ratio in the precursor solutions is a determining factor for the formation of the hexagonal mesoporous silicates (MCM-41 phase as designated by Mobil). When the surfactant/Si molar ratio is equal to 0.2, two lamellar phases were found to coexist. However, when the surfactant/Si molar ratio is reduced to 0.15, the MCM-41 phase was formed. Since the fly ash contains a large amount of Si and Al, it is conceivable that when fly ash is added to the model system with surfactant/Si molar ratio equals 0.2, the hexagonal phase may be formed. If this can be demonstrated, it indicates that fly ash can participate in the formation of mesoporous materials and a variety of applications of fly ash can be explored.

EXPERIMENTAL PROCEDURE

The Eddystone fly ash solution was prepared by mixing 24.1 g of fly ash in water with 1.29 g of NaOH. The fly ash solution was aged for two days. 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. After the surfactant solution was added, 31.35 g of sodium silicate sodium silicate (PQ Co., 28.7 wt% SiO_2, 8.9 wt% Na_2O, 62.4 wt% H_2O) was added. The mixture solutions were stirred for 30 minutes at room temperature. 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.

RESULTS and DISCUSSION

The study on the sodium silicate-surfactant precursor solutions with surfactant/Si=0.2 has been reported previously.[1] It was found that no MCM-41 phase was formed. Instead, two lamellar phases were found to coexist. When the 24.1 g of fly ash was added to the sodium silicate-surfactant mixtures, a MCM-41 phase was precipitated. The X-ray diffraction pattern of the precipitates obtained in the fly ash-silicate-surfactant mixtures is shown in Fig.1. Clear diffraction peaks corresponding to (100), (110), and (200) can be identified. After calcination at 540°C for 7 hours, the hexagonal diffraction pattern remains as can be seen in Fig.1. The d_{100}-spacing of the MCM-41 phase decreases from 37.2 A to 33.3 A during calcination. In addition, the diffraction intensity of the (100) peak increases after calcination indicating that more MCM-41 phase was formed during calcination.

It is apparent that fly ash is contributing to the formation of MCM-41 phase since no MCM-41 phase was formed without it. However, it is not clear what chemical component of fly ash is contributing to the formation of MCM-41. The major chemical components of the fly ash are SiO_2,

Al_2O_3, and Fe_3O_4. In the previous report[1] we have shown that when the surfactant/Si molar ratio is reduced to 0.15, MCM-41 phase was precipitated after 4 hours of curing. Therefore, it is possible that the SiO_2 in the fly ash dissolved and contributed to the formation of MCM-41 phase. However, Al_2O_3 can be a contributing factor as well. Chen et al.[2] have found that adding Al species to the silicate-surfactant mixtures, MCM-41 can be formed provided the Si/Al molar ratio is not too small. As a model study, 0.158 g of $Al(OH)_3$ was added to the sodium silicate-surfactant solution without fly ash. It was found that MCM-41 phase was formed after 4 hours of curing. The intensity of the (100) peak is much higher than that of the precipitates from the fly ash-sodium silicate-surfactant mixtures. Therefore, it is also possible that Al_2O_3 component in the fly ash is contributing to the formation MCM-41 phase. No study has been done on the mixtures of iron oxide with sodium silicate-surfactant solutions. So far, using CTAB as the surfactant, only titanium oxide and aluminum oxide have been successfully incorporated in the MCM-41 phase.[3,4] Therefore, we suspect that the iron oxide does not contribute to the formation of MCM-41 very much.

More recently, we studied the effect of fly ash addition to solutions with surfactant/Si molar ratio equals to 0.25 and 0.35. The intent of the study is to to see if we can increase the contribution from fly ash by decreasing the Si content in the original solutions. The results are summarized in Tables 1, 2, 3, and 4. The X-ray diffraction patterns of samples cured at 115°C for various amount of time is shown in Fig.2 and Fig.3 for systems without and with fly ash. The X-ray patterns of both before and after calcination are shown in Fig.2 and Fig.3. It can be seen in Fig.2 that without fly ash, the silicate-surfactant solutions form multiple phases. In Fig.2, the X-ray patterns of the calcined samples show smaller intensity with a broadened peak. The broadened peak does not correspond to a hexagonal phase. In Fig.3, the X-ray patterns of the calcined samples showed higher intensity and the patterns correspond to a hexagonal phase. Therefore, fly ash can participate in the formation of hexagonal phase for solutions with surfactant/Si=0.25. These results indicate that up to surfactant/Si=0.25, fly ash can participate in the formation of MCM-41 phase. However, when surfactant/Si=0.35, no mesoporous materials can be formed with the addition of fly ash. Apparently, certain amount of Si is needed in the precursor solution for the MCM-41 phase to be formed. The contribution from the fly ash is limited.

CONCLUSIONS and FUTURE PLAN

It is shown that fly ash can be used to participate in the formation of mesoporous materials. The dissolution of silicate species changes the surfactant/Si molar ratio in the silicate-surfactant solutions precipitating the MCM-41 phase. The current results demonstrate that fly ash can be used to form mesoporous materials and the impurities in the fly ash is not detrimental to the formation of MCM-41 phase.

Although the MCM-41 phase can be formed with fly ash in the silicate-surfactant solutions, no MCM-41 phase can be made with solutions of surfactant/Si=0.35. Our study so far indicates that fly ash has the potential to be used to form mesoporous materials. However, in order to make further progress, the concentration of silicate and aluminate species in the solutions needs to be controlled. In other words, the chemistry of the fly ash solutions needs to be studied in more detail. In the next few months, we plan to study the effects of using different fly ash solutions for the formation of zeolites as the first step in controlling the chemistry of fly ash solutions. Once we can control the chemical composition of the fly ash, it may be possible to increase the amount of participation of fly ash to the formation of mesoporous materials.

REFERENCES

1. W.-H. Shih, DOE Quarterly Progress Report for 17/1/95-9/30/95
2. C.-Y. Chen, H.-X. Li, and M. E. Davis, *Microporous Materials* **2**, 17 (1993).
3. P. T. Tanev, M. Chibwe, and T. J. Pinnavaia, *Nature*, **368**, 321 (1994).
4. A. Sayari, C. Danumah, and I. L. Moudrakovski, *Chem. Mater.*, **7**[5], 813 (1995).

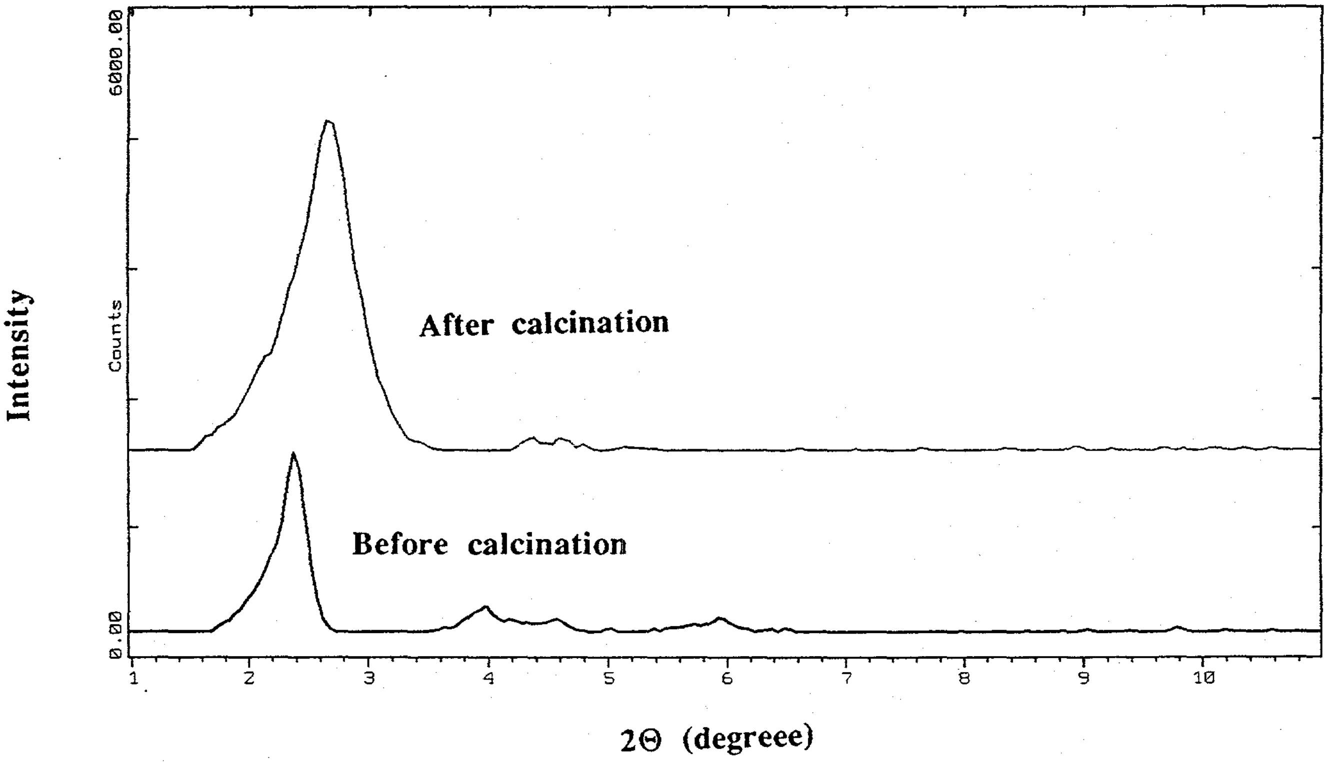

Fig.1. The X-ray diffraction pattern of precipitates of fly ash-sodium silicate-surfactant mixtures with surfactant/Si=0.2, cured at 115°C for 22 hours before and after calcination.

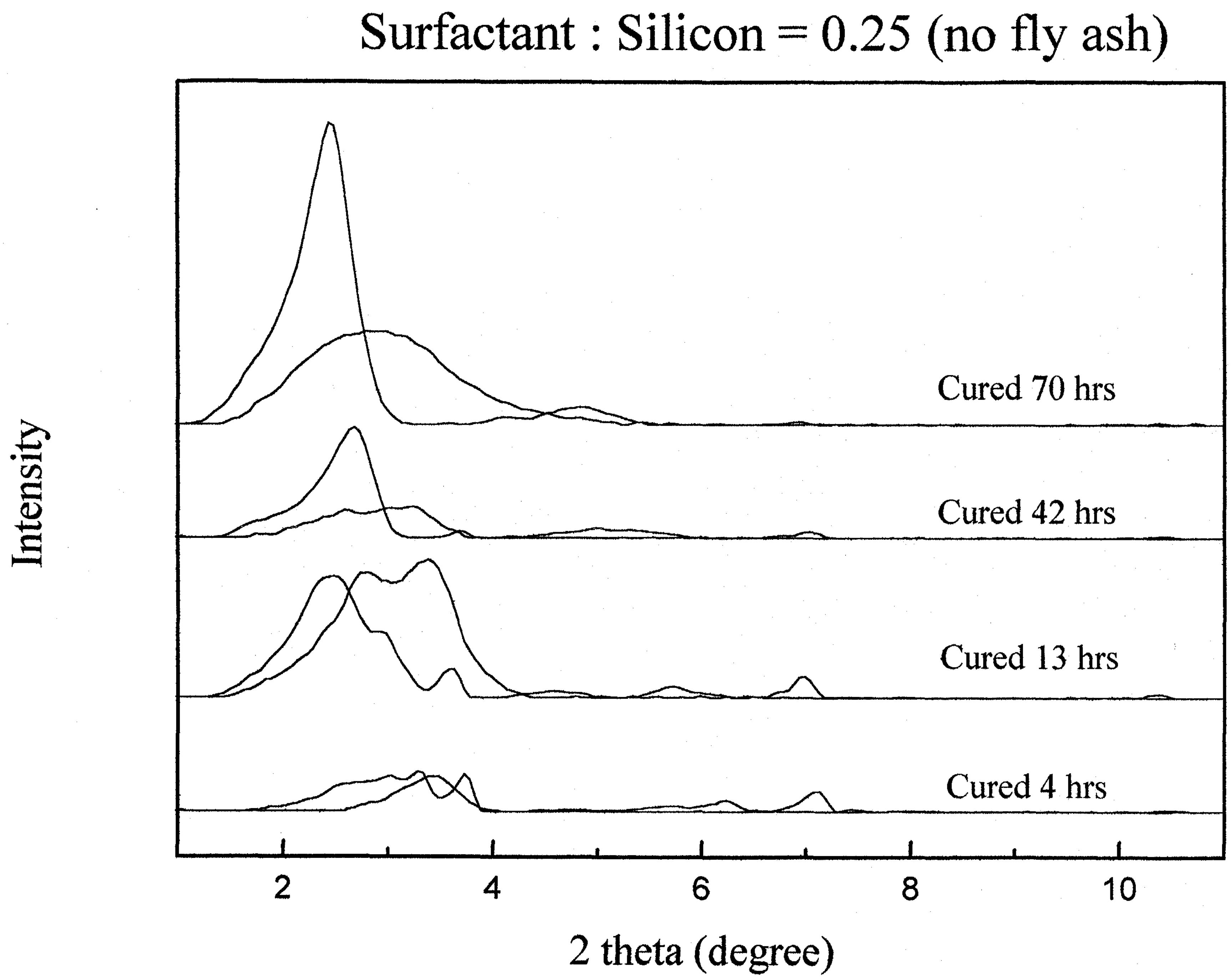

Fig.2. X-ray diffraction patterns of silicates from silicate-surfactant solutions. Both before and after calcination are shown

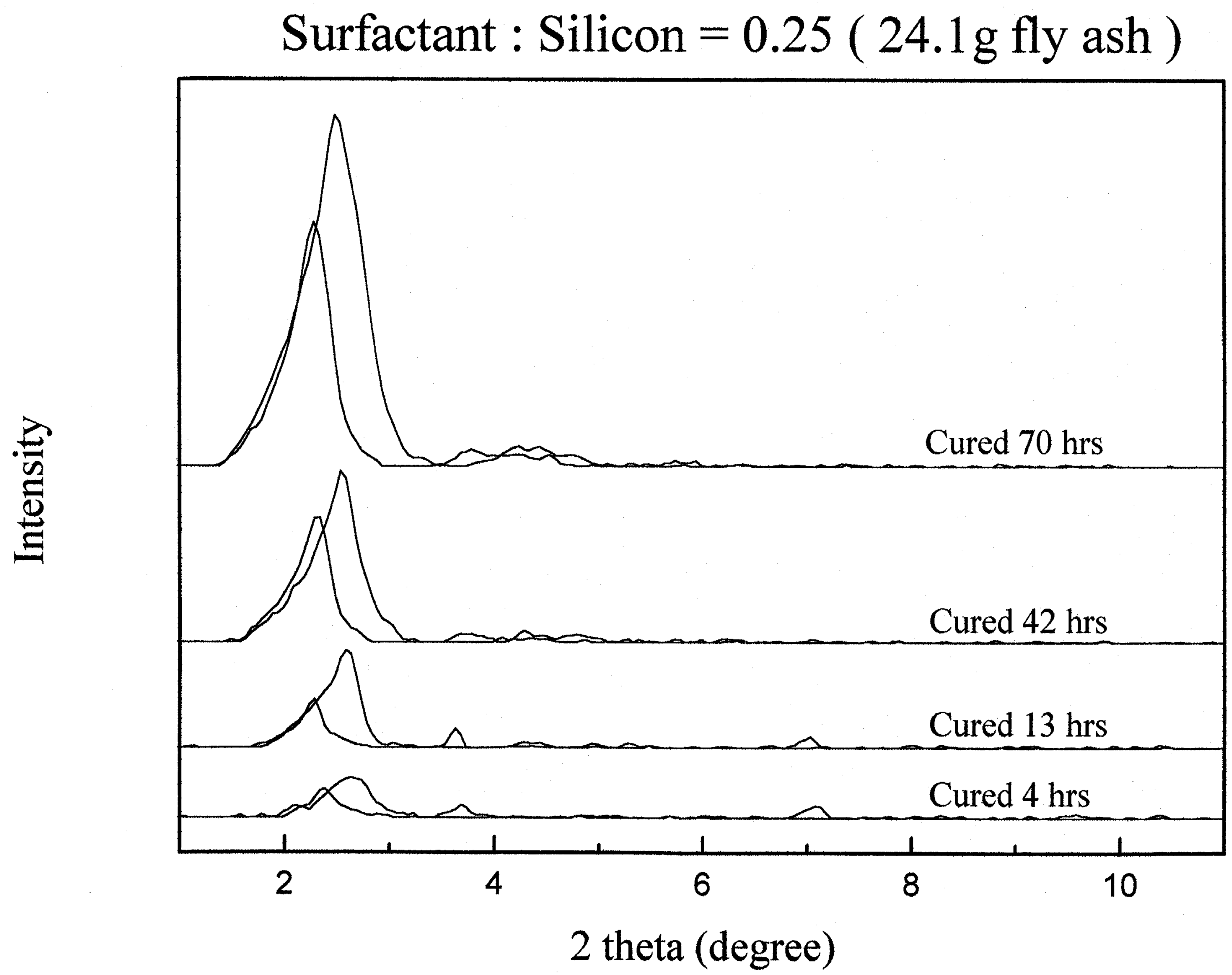

Fig.3. X-ray diffraction patterns of precipitates from ash-silicate-surfactant solutions. Both before and after calcimation are shown

Table(1) The molar ratio of surfactant (10.9 g) to silicon (25.09 g sodium silicate:28.7 wt% SiO_2, 8.9 wt% Na_2O, 62.4 wt% H_2O) = 0.25 and 24.1 g Fly ash, 1.92 g $NaOH_{(s)}$

Curing Temperature (°C)	Curing Time	Results
115	4 hours	Hexagonal phase with d_{100}-spacing = 37.77Å and lamellar phase with d_{100}-spacing = 23.87Å were formed. After calcination at 540°C a peak of d-spacing = 33.51Å existed.
115	13 hours	Hexagonal phase with d_{100}-spacing = 38.93Å and lamellar phase with d_{100}-spacing = 24.33Å were formed. After calcination at 540°C a peak of d-spacing = 34.19Å existed.
115	42 hours	Hexagonal phase with d_{100}-spacing = 38.34Å was formed. After calcination at 540°C a peak of d-spacing = 34.43Å existed.
115	70 hours	Hexagonal phase with d_{100}-spacing = 38.93Å was formed. After calcination at 540°C a peak of d-spacing = 35.64Å existed.

Table(2) The molar ratio of surfactant (10.9 g) to silicon (17.91 g sodium silicate) = 0.35 and 24.1 g Fly ash, 3.77 g $NaOH_{(s)}$

Curing Temperature (°C)	Curing Time	Results
115	4 hours	No peak existed before & after calcined
115	13 hours	No peak existed before & after calcined
115	42 hours	No peak existed before & after calcined
115	70 hours	No peak existed before & after calcined

Table(3) The molar ratio of surfactant (10.9 g) to silicon (25.09 g sodium silicate) = 0.25 and 1.92 g $NaOH_{(s)}$

Curing Temperature (°C)	Curing Time	Results
115	4 hours	Hexagonal phase with d_{100}-spacing = 32.86Å and lamellar phase with d_{100}-spacing = 23.65Å were formed. After calcination at 540°C a peak of d-spacing = 25.69Å existed.
115	13 hours	Hexagonal phase with d_{100}-spacing = 36.15Å and lamellar phase with d_{100}-spacing = 24.33Å were formed. After calcination at 540°C peaks of d-spacing = 32.23Å and 26.35Å existed.
115	42 hours	Hexagonal phase with d_{100}-spacing = 33.08Å and lamellar phase with d_{100}-spacing = 23.98Å were formed. After calcination at 540°C peaks of d-spacing = 33.96Å and 27.35Å existed.
115	70 hours	Hexagonal phase with d_{100}-spacing = 38.15Å was formed. After calcination at 540°C a peak of d-spacing = 31.05Å existed.

Table(4) The molar ratio of surfactant (10.9 g) to silicon (17.91 g sodium silicate) = 0.35 and 3.77 g $NaOH_{(s)}$

Table 4

Curing Temperature (°C)	**Curing Time**	**Results**
115	4 hours	Hexagonal phase with d_{100}-spacing = 46.87Å and lamellar phase with d_{100}-spacing = 24.92Å were formed. After calcination at 540°C a peak of d-spacing = 44.4Å existed.
115	13 hours	Lamellar phase with d_{100}-spacing = 24.69Å was formed. After calcination at 540°C no peak existed.
115	42 hours	Hexagonal phase with d_{100}-spacing = 45.6Å and lamellar phase with d_{100}-spacing = 24.68Å was formed. After calcination at 540°C a peak of d-spacing = 41.15Å existed.
115	70 hours	Hexagonal phase with d_{100}-spacing = 38.63Å and lamellar phase with d_{100}-spacing = 24.81Å were formed. After calcination at 540°C a peak of d-spacing = 34.43Å existed.