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QUARTERLY PROGRESS REPORT (4/1/95-6/30/95)

Contract No. DE-FG22-94PC94215
Project Title: Conversion of Coal Wastes into Waste-Cleaning Materials
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Co-op Student: Jorge Moller

I. INTRODUCTION

In the last three months we have studied the ion exchange behavior of the zeolites converted from fly ash in more detail. In particular, the ion-exchange isotherms of the treated fly ash containing zeolite Y with Cs^+ ions were studied. For comparison, the ion exchange isotherms of synthetic zeolite Y and commercial zeolite A were also studied. These results showed that the background materials in the fly ash do not affect the ion exchange performance of the zeolites that the fly ash contains. It is also found that a higher total ion concentration (Na^+ plus Cs^+) in the solutions results in a higher amount of ions exchanged with the zeolites. The ion exchange of treated fly ash with Co^{2+} ions was studied as well. This part of the research was done by Mr. Jorge Moller who was hired starting April 3 for 6 months as a co-op student.

In an attempt to broaden the applications of fly ash, investigation into the formation of mesoporous materials from fly ash was initiated. Mesoporous materials were discovered three years ago by scientists at Mobil[1] and have been under active research by many researchers since then. Mesoporous materials have large surface areas with variable pore sizes in the range of >20 angstroms. Potential applications of mesoporous materials include catalysts, absorbents, molecular sieves, etc. If mesoporous materials can be converted from fly ash, it will open up another area of applications for fly ash.

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II. EXPERIMENTAL PROCEDURE

II.1 Ion-Exchange Study

The ion exchange behavior was studied with 0.114 N Co^{2+} solutions which were added in small quantity to the test solutions and the Na^+ concentration in the solution was measured using a sodium ion probe. As the Co^{2+} ions exchanges with the Na^+ in the zeolites, the Na^+ concentration in the solution would increase. As the ion-exchange capability of the treated fly ash saturates, the sodium concentration in the solution would saturate. Each 40 ml test solution consisting of 0.7 g synthetic zeolites, treated fly ash, or commercial zeolites was stirred before testing. When cobalt chloride was gradually added into the sample solutions, the sodium concentrations were measured until saturation occurred. The ion exchange capacity of treated fly ash was compared with those of two kinds of pure zeolites: one source of zeolites was provided by UOP Inc. (25 East Algonquin, Des Plaines, IL 60017-5017), the other was made by mixing aluminum hydroxide powders, Ludox silica and sodium hydroxide solution, as described in the previous report.

The second set of experiments was designed to obtain the ion-exchange isotherm. So far this set of experiment was done for Cs^+ ion only. The total concentration of Cs^+ and Na^+ in all solutions were kept constant while the relative amounts of Na^+ and Cs^+ ions were varied. The same amount of treated fly ash was then added to each of these solutions and the Na^+ concentration was measured.

II.2 Fly Ash-Surfactant Solutions

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Fly ash solutions were prepared in both acidic and basic conditions. The acidic solution was prepared by adding 7.2 g fly ash in 18 g of hydrogen chloride solution (1N). The basic solution was prepared by adding 7.2 g fly ash in 18 g of sodium hydroxide solution (2.8 N). Two kinds of surfactants had been used for studying the formation of mesoporous phases from fly ash solution : $C_9H_{19}(CH_3)_3NBr$ and $C_{16}H_{32}(CH_3)_3NBr$. The surfactant solutions were prepared as 25 wt% aqueous solutions.

Three types of fly ash-surfactant mixture solutions were studied:

(a) Basic and acidic fly ash solutions were mixed with the appropriate $C_9H_{19}(CH_3)_3NBr$ or $C_{16}H_{32}(CH_3)_3NBr$ solution. The ratio of surfactant to fly ash was 0.03 mole/7.2 g. One treatment process was to age the mixture solution at room temperature and ambient pressure (~ 1atm) for 2 days and 6 days respectively. The other treatment process was to cure the mixture solution at 80 °C and ambient pressure for 2 days and 6 days respectively. The resulting solid product was washed with water, centrifuged and dried in air at 60 ~ 80 °C. The as-synthesized product was then calcined at 540 °C for 7 h in air. The phase characterization of as-synthesized and calcined products was obtained by X-ray diffractometry with voltage at 40 KV and current of 30 mA. The experimental results were shown in Table(1).

(b) Acidic and basic fly ash solutions were kept at room temperature and ambient pressure for 2 days before the appropriate $C_{16}H_{32}(CH_3)_3NBr$ solution was added. The ratio of surfactant to fly ash was studied at two conditions : 0.025 mole/7.2 g and 0.015 mole/7.2 g. The treatment processes were the same as procedure (a). The as-synthesized and calcined products were characterized by X-ray diffractometer and the results were shown in Table(2),(3).

(c) Acidic and basic fly ash solutions were kept at room temperature and ambient pressure for 3 days and then the $C_{16}H_{32}(CH_3)_3NBr$ solution was added with a ratio of 0.0075 mole/7.2 g of surfactant to fly ash. One treatment process was aging the samples at room temperature and ambient pressure for 2 and 6 days respectively. The other treatment process was curing the samples at 80 °C and ambient pressure for 2 days. The experimental results were shown in Table(4).

III. RESULTS

III.1 Ion-Exchange Study

Fig.1 compares the ion exchange capabilities of zeolites Y with Co^{2+} ions. The treated fly ash containing zeolite Y shows a lower capacity than the synthetic zeolite Y and the commercial UOPY54. The treated fly ash has an efficiency of about 58% relative to the synthetic zeolite Y. The total ion exchange reaction time was about 3 hours. Fig.2 compares the ion exchange behavior of zeolites A with Co^{2+} ions. Although initially the commercial UOP4A shows very little ion exchange with Co^{2+} ions, the ion exchange capability increases significantly after seven days. The ion exchange capacity of treated fly ash is about 40% relative to the synthetic zeolite A after seven days. It is shown in Fig.1 and Fig.2 that zeolite Y has a higher ion exchange capacity than zeolite A. This result is similar to our previous result for the ion exchange with Cs^+ ions.

The ion-exchange isotherm is a plot of Z_M versus X_M where Z_M=equivalent fraction of M ions in the zeolite and X_M is the equivalent fraction of M ions in the solution after ion exchange occurred. Both Z_M and X_M can be calculated from the amount of M ions exchanged and the amount of zeolites in the test solutions. Because the zeolites were in the treated fly ash, an estimate of the amount of zeolites in the treated fly ash is required. By comparing the ion exchange capacity of pure zeolite and the treated fly ash, as shown in the previous report, we obtained an estimate for the amount of zeolite in the treated fly ash to be around 19% for zeolite A and 39% for zeolite Y.

The ion-exchange isotherm of treated fly ash Y with Cs^+ ions at a total Cs^+ and Na^+ concentration of 0.1N is shown in Fig.3. Similarly the ion-exchange isotherm of synthetic zeolite Y with Cs^+ at 0.1 N concentration is shown in Fig.4. Both Fig.3 and Fig.4 show that the ion exchange is a time-dependent phenomenon; the ion exchange at 40 hours is more than that at 20 hours and 5 minutes. The ion exchange isotherm of treated fly ash containing zeolite Y is similar to that of synthetic zeolite Y indicating that the background materials in the fly ash do not affect the ion exchange property of zeolite Y within the fly ash.

Fig.5 and Fig.6 show the ion exchange isotherms of commercial UOP4A with Cs^+ ions at two different total ion concentrations, 0.1N and 0.05N. When the total ion concentration of Cs^+ and Na^+ increases, the amount of ion exchange increases.

III.2 Fly Ash-Surfactant Solutions

Table(1) The ratio of surfactant to fly ash = 0.03 mole/7.2 g

Surfactant Type	**Processing**	**Results**
$C_{16}H_{32}(CH_3)_3NBr$	Aged 2 days at RT	Basic and acidic solution formed lamellar phases. But after calcination at 540 °C, lamellar phases disappeared
	Aged 6 days at RT	Basic and acidic solution formed lamellar phases. But after calcination at 540 °C, lamellar phases disappeared
	Cured 2 days at 80 °C	Basic and acidic solution formed lamellar phases. But after calcination at 540 °C, lamellar phases disappeared
	Cured 6 days at 80 °C	Basic and acidic solution formed lamellar phases. But after calcination at 540 °C, lamellar phases disappeared
$C_9H_{19}(CH_3)_3NBr$	Aged 2 and 6 days at RT	No lamellar phases formed
	Cured 2 and 6 days at 80 °C	No lamellar phases formed

Table(2) The ratio of surfactant to fly ash = 0.025 mole/7.2 g

Surfactant Type	Processing	Results
$C_{16}H_{32}(CH_3)_3NBr$	Aged 2 days at RT	Basic solution formed lamellar phases. But after calcination at 540 °C, lamellar phases disappeared
	Aged 6 days at RT	Basic and acidic solution formed lamellar phases. But after calcination at 540 °C, lamellar phases disappeared
	Cured 2 days at 80 °C	Acidic solution formed lamellar phases. Basic solution formed zeolite P. But after calcination at 540 °C, lamellar phases disappeared and the intensity of zeolite p decreased
	Cured 6 days at 80 °C	Acidic solution formed lamellar phases. But after calcination at 540 °C, lamellar phase disappeared

Table(3) The ratio of surfactant to fly ash = 0.015 mole/7.2 g

Surfactant Type	Processing	Results
$C_{16}H_{32}(CH_3)_3NBr$	Aged 2 days at RT	Basic and acidic solution formed lamellar phases. But after calcination at 540 °C, lamellar phases disappeared
	Aged 6 days at RT	Basic and acidic solution formed lamellar phases. But after calcination at 540 °C, lamellar phases disappeared
	Cured 2 days at 80 °C	Basic and acidic solution formed lamellar phases. But after calcination at 540 °C, lamellar phases disappeared
	Cured 6 days at 80 °C	Basic solution formed lamellar phases. But after calcination at 540 °C, lamellar phase disappeared

Table(4) The ratio of surfactant to fly ash = 0.0075 mole/7.2 g

Surfactant Type	**Processing**	**Results**
$C_{16}H_{32}(CH_3)_3NBr$	Aged 2 days at RT	No lamellar phase formed
	Aged 6 days at RT	Acidic solution formed lamellar phases. But after calcination at 540 °C, lamellar phases disappeared
	Cured 2 days at 80 °C	Basic solution formed zeolite P After calcination at 540 °C, zeolite P still existed

A typical X-ray diffraction pattern of a lamellar phase is shown in Fig.7. The X-ray diffraction patterns of zeolites P before and after calcination are shown in Fig.8.

IV. DISCUSSION

From the ion-exchange results presented above, it was seen that zeolites Y has a higher ion-exchange capacity than that of zeolite A. This observation is true for all the zeolites studied: zeolites converted from the ash, synthetic zeolites and the commercial zeolites. Since zeolite Y has a higher molecular weight than zeolite A, this observation indicates that zeolite Y should be a more efficient ion-exchanger than zeolite A on a per-mole basis. Preliminary SEM study showed that the synthetic zeolites contain small cubic crystallites of 0.5 micron in size. Whereas the commercial zeolites have cubic crystallites with size in the order of 2 micron. The micrographs of treated fly ash show conspicuous fly ash particles but no cubic crystallites can be found. The morphology of zeolites converted from fly ash is less than 0.1 micron. It is speculated that the morphology of converted zeolites may be different from the synthetic one since the converted zeolites may be formed on the fly ash particles. This is likely because the formation of zeolite involves the dissolution of aluminosilicate from fly ash particles. Also, the converted zeolites could be too small, therefore the cubic morphology can not be easily seen in the SEM micrographs. T

V. SUMMARY

The ion exchange study shows that the treated fly ash can ion-exchange with Co2+. The ion exchange capacity of treated fly ash containing zeolite Y is about 58% of that of synthetic zeolite Y and that of treated fly ash containing zeolite A is about 40% of that of synthetic zeolite A. The ion exchange isotherms of treated fly ash containing zeolite Y and synthetic zeolite Y were obtained. The comparison between the ion exchange isotherms of treated fly ash and synthetic zeolites shows that the background materials in the fly ash do not affect the ion exchange performance of zeolites within the fly ash. Ion-exchange isotherms of commercial zeolite UOP4A shows that higher total ion concentration increases the amount of ions exchanged.

The investigation in mesoporous materials found that (1) Only $C_{16}H_{32}(CH_3)_3NBr$ could form mesoporous phase from fly ash solution. The lamellar phase disappeared after calcination at 540 °C, i.e, thermal stability of lamellar phase was lower. (2) When the ratio of surfactant to fly ash increases, the lamellar phase formed in both acidic and basic conditions. When the surfactant/fly ash ratio decreases, zeolites P can form in basic conditions. However, the X-ray intensity of the zeolites P decreases after calcination.

VI. PLAN FOR NEXT QUARTER

The composition of fly ash will be performed to find ways to increase the yield of zeolites. Using cheaper material to form zeolites in fly ash will also be considered. Converting fly ash into mesoporous materials will be continued. The control of the Si/Al ratio seems to be the key to the success of the conversion. Also, the curing temperature will be increased to speed up the formation process.

VII. REFERENCES

1. J. S. Beck, J. C. Vartuli, W. J. Roth, M. E. Leonowicz, C. T. Kresge, K. D. Schmitt, C. T-W. Chu, D. H. Olson, E. W. Sheppard, S. B. McCullen, J. B. Higgins, and J. L. Schlenker, "A New Family of Mesoporous Molecular Sieves Prepared with Liquid Crystal Templates," *J. Am. Chem. Soc.*, **114**, 10834-43 (1992).

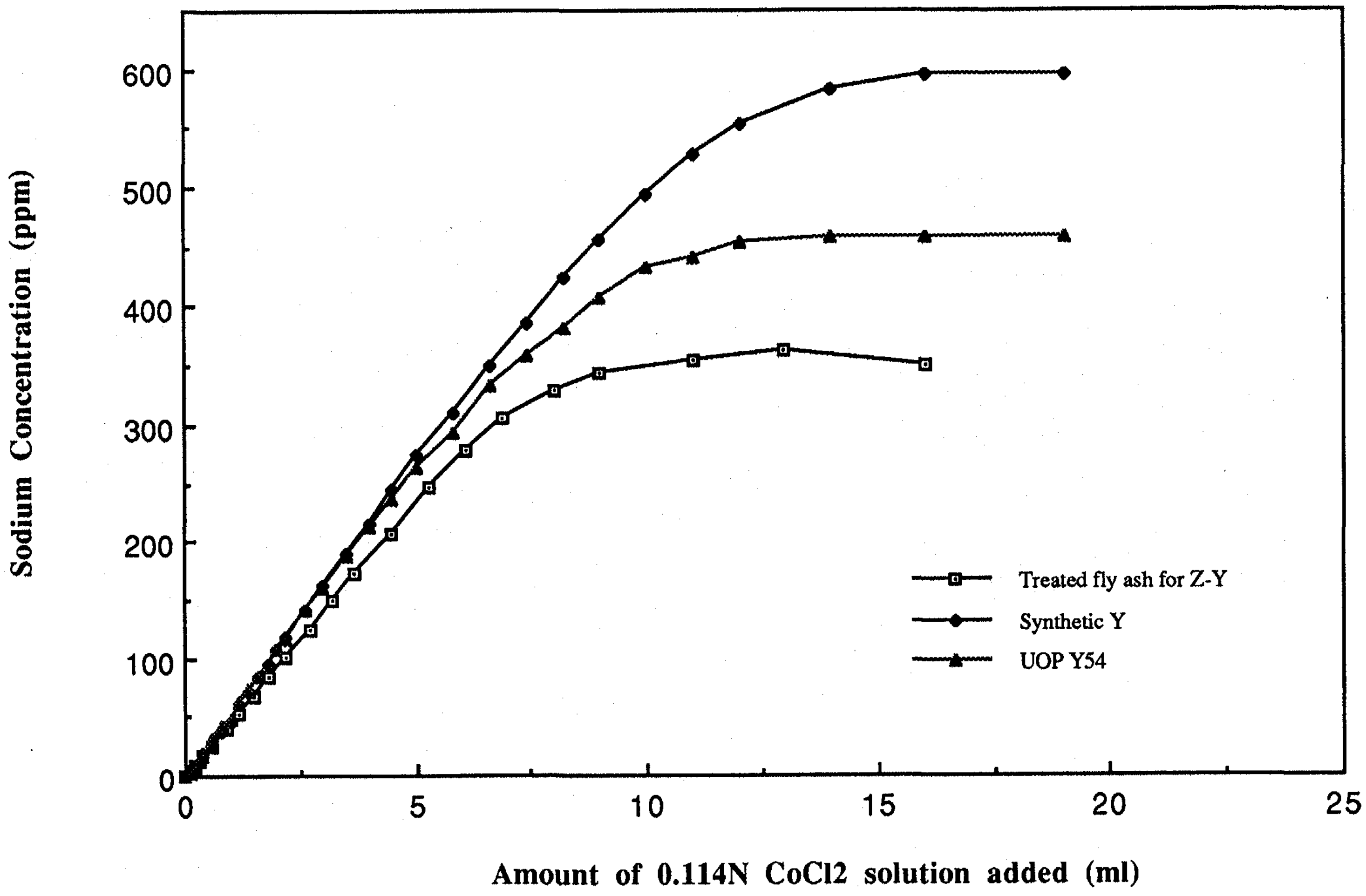


Figure 1. Comparison of ion exchange capabilities among treated fly ash for Zeolite Y, Synthetic Y and UOP Y54.

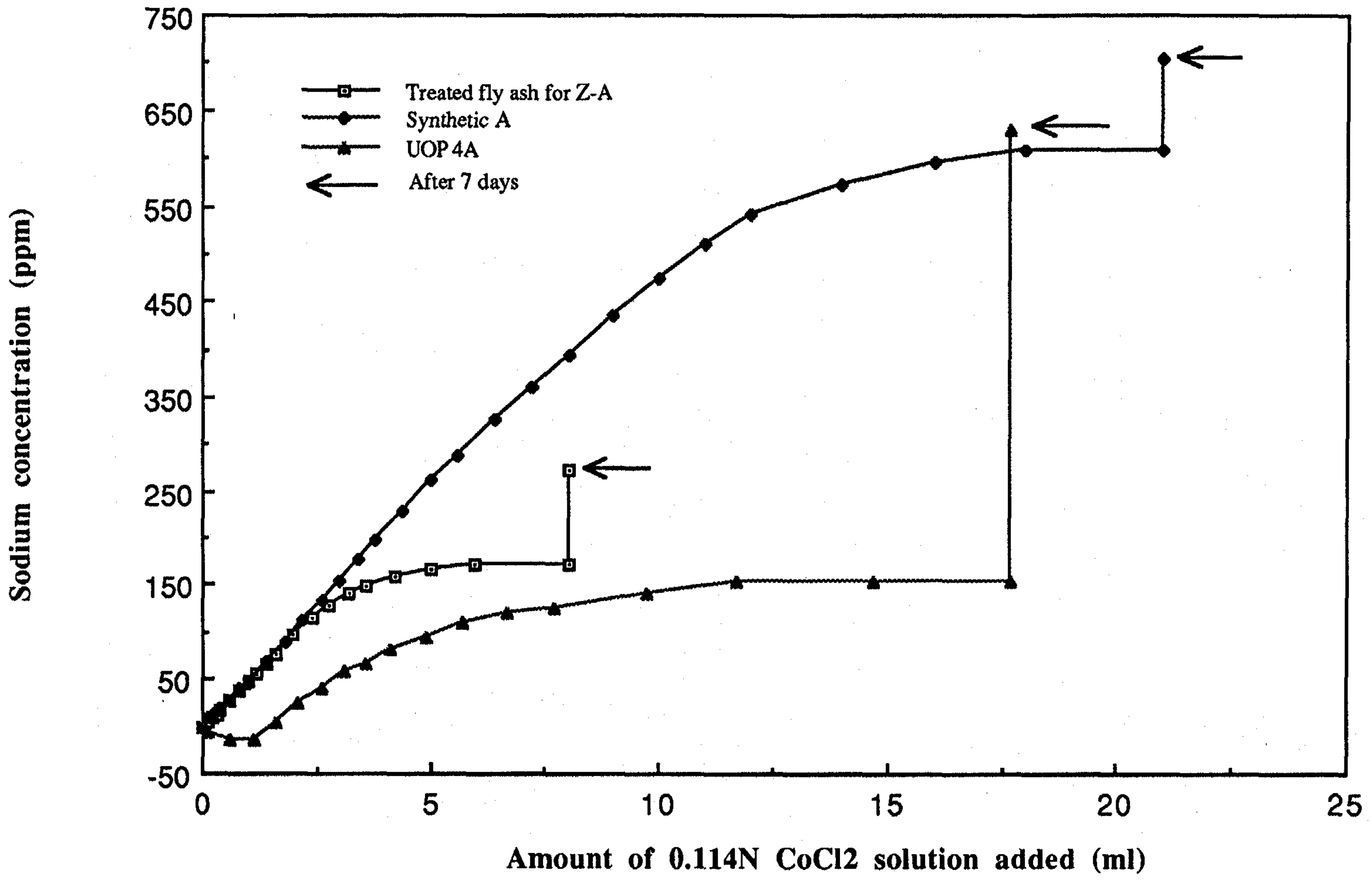


Figure 2. Comparison of ion exchange capabilities among treated fly ash for Zeolite A, Synthetic A and UOP 4A

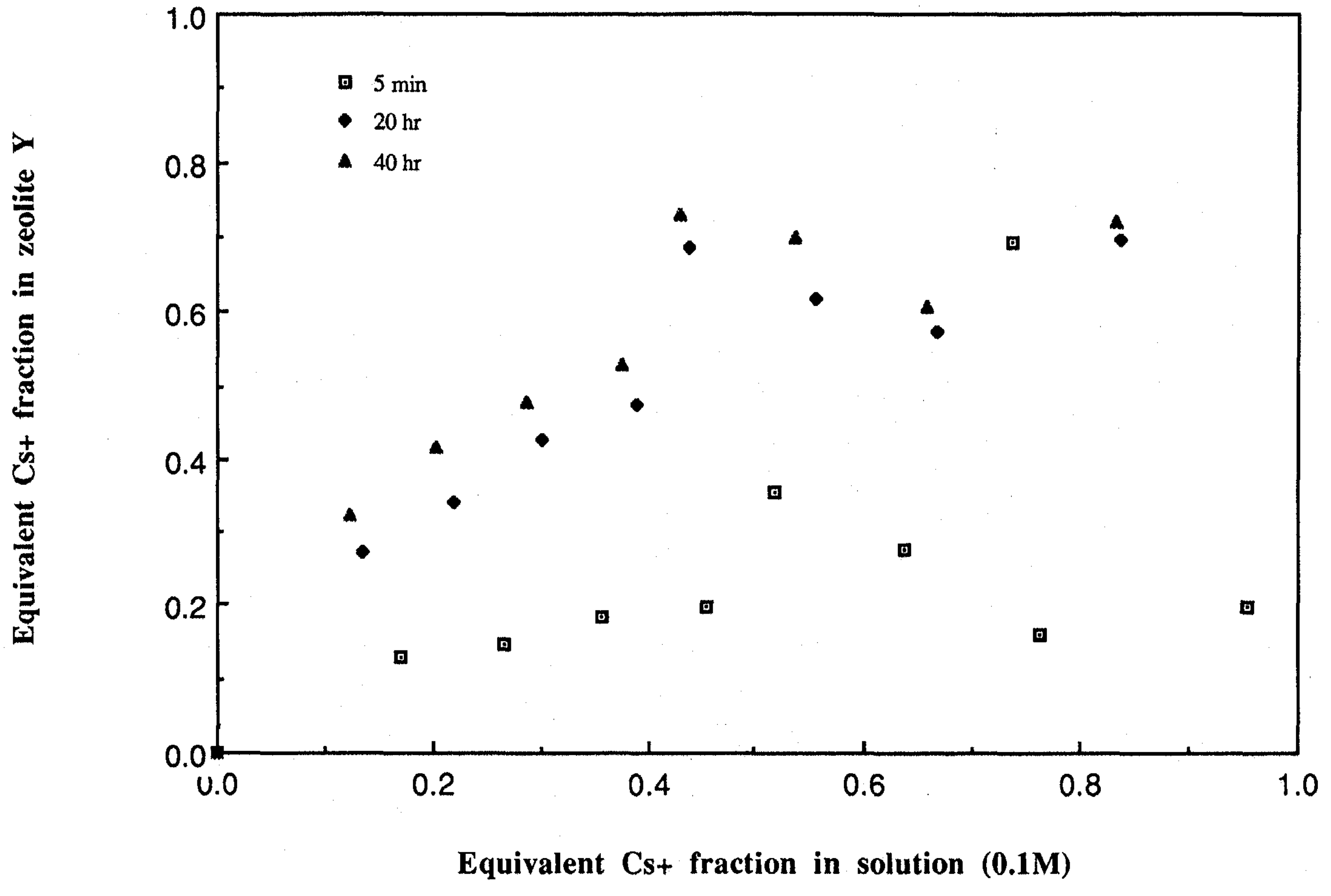


Figure 3. Isotherm for ion exchange of Cs+ in treated fly ash for zeolite Y. Results obtained after 5 minutes, 20 hrs and 40 hrs.

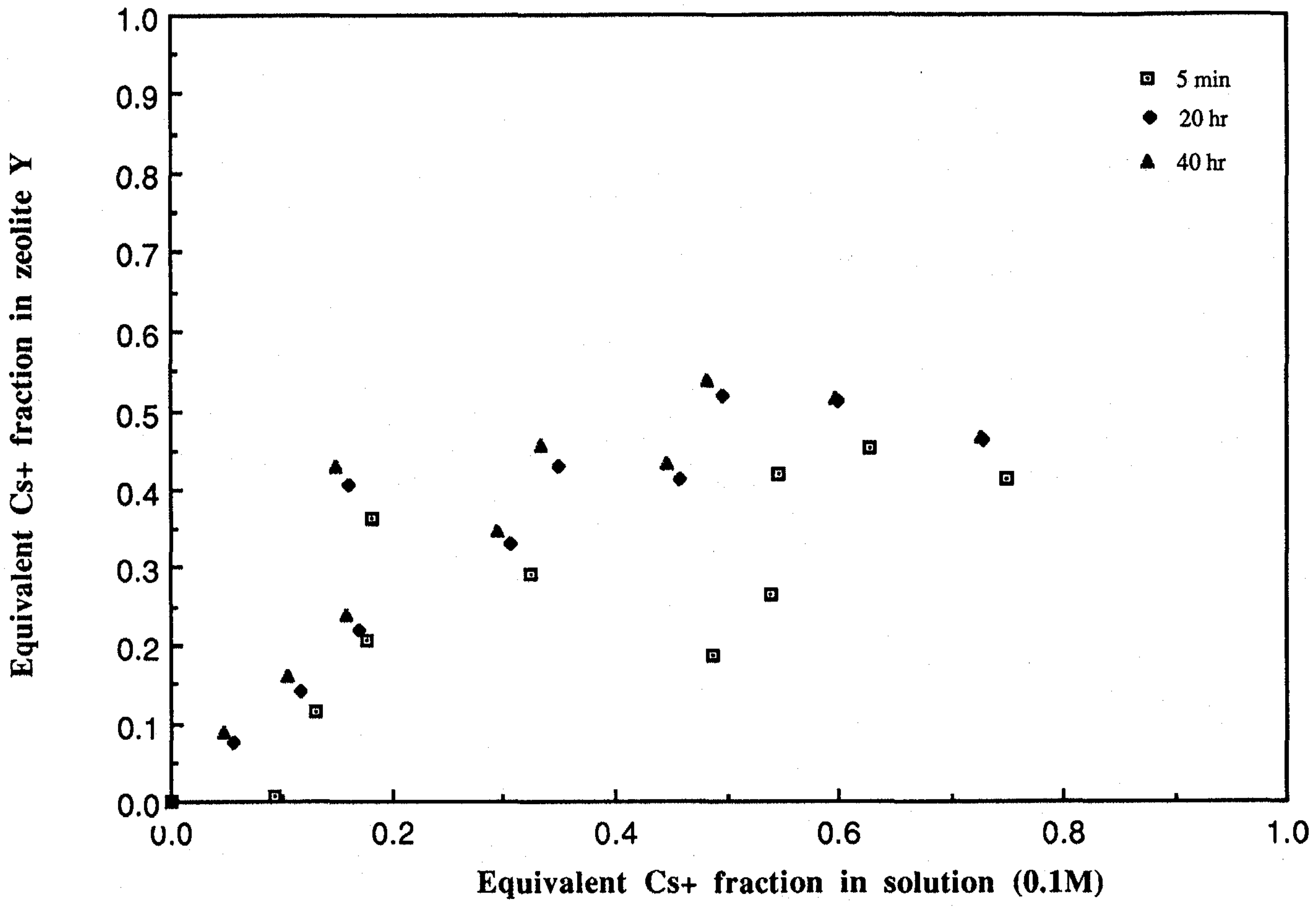


Figure 4. Isotherm for ion exchange of Cs+ in synthetic zeolite Y. Results obtained after 5 minutes, 20 hrs. and 40 hrs.

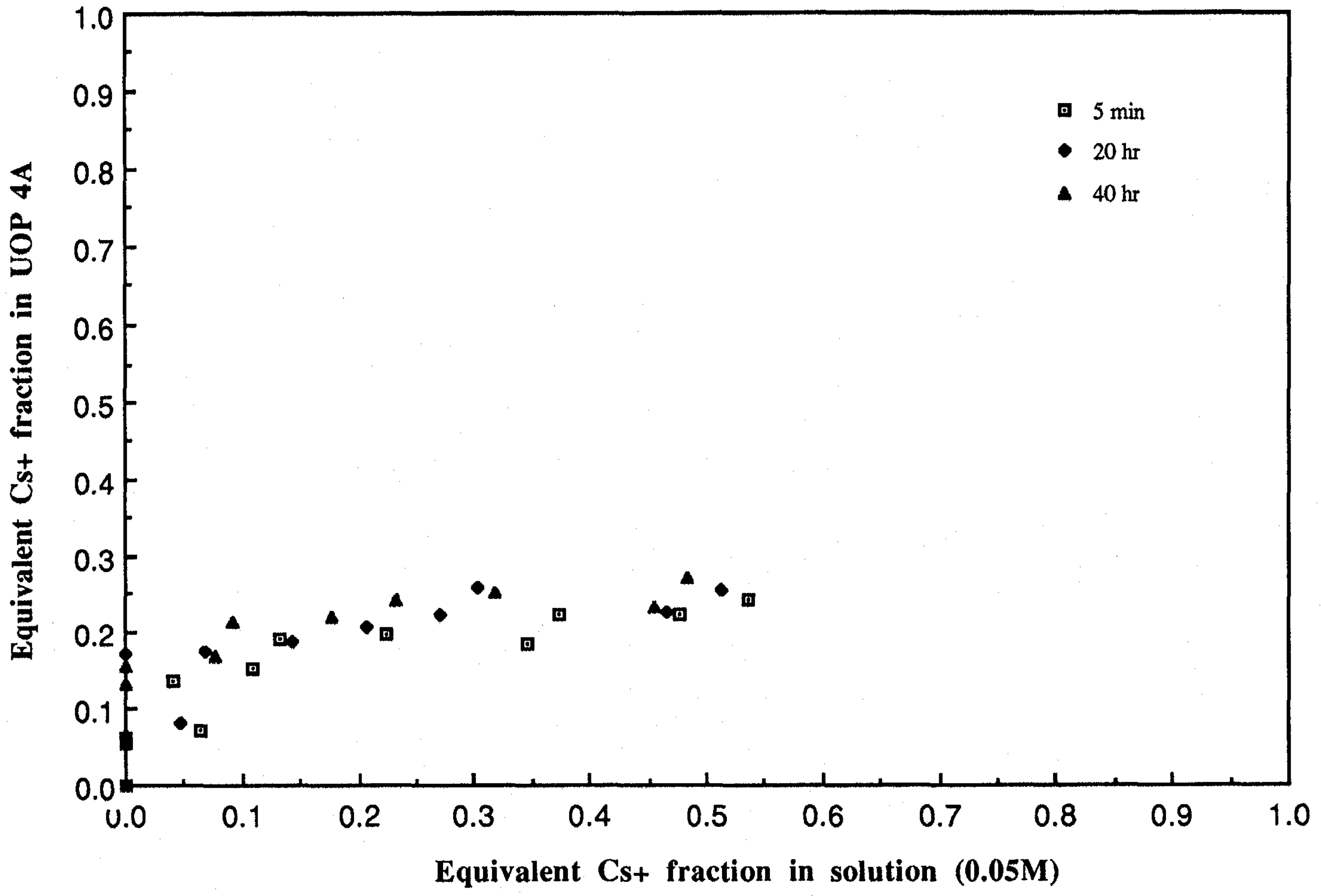


Figure 5. Isotherm for ion exchange of Cs+ in UOP 4A.
Results obtained after 5 minutes, 20 hrs. and 40 hrs.

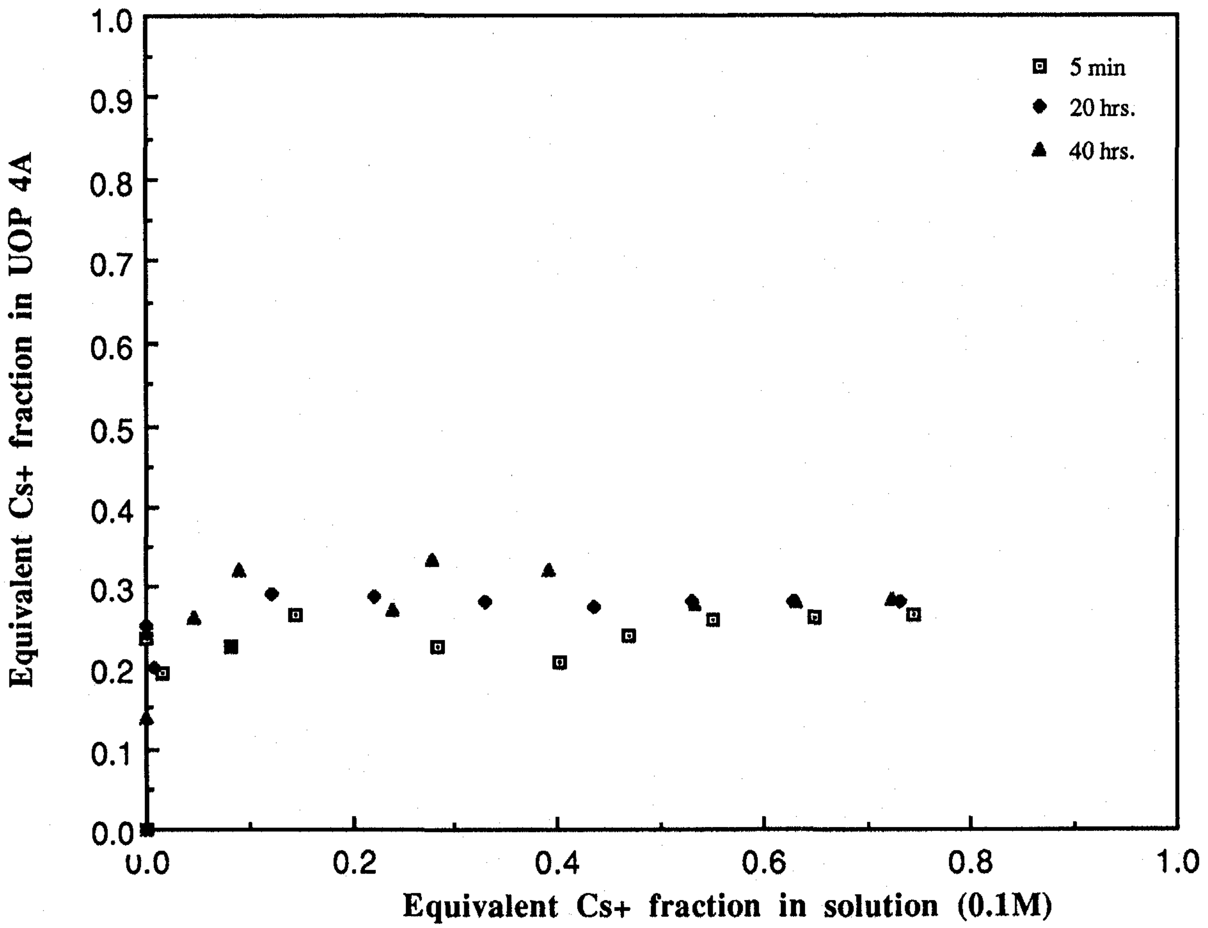
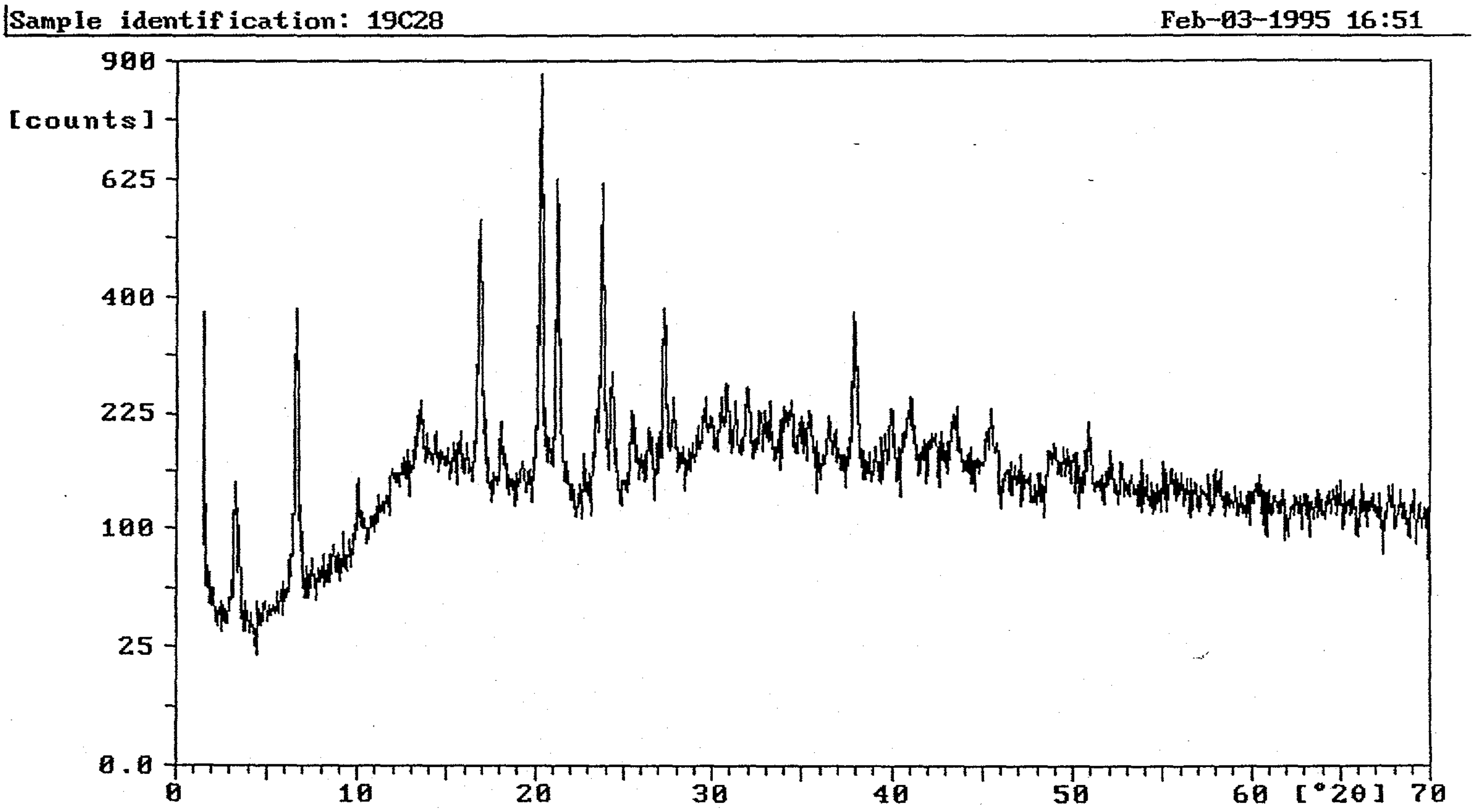
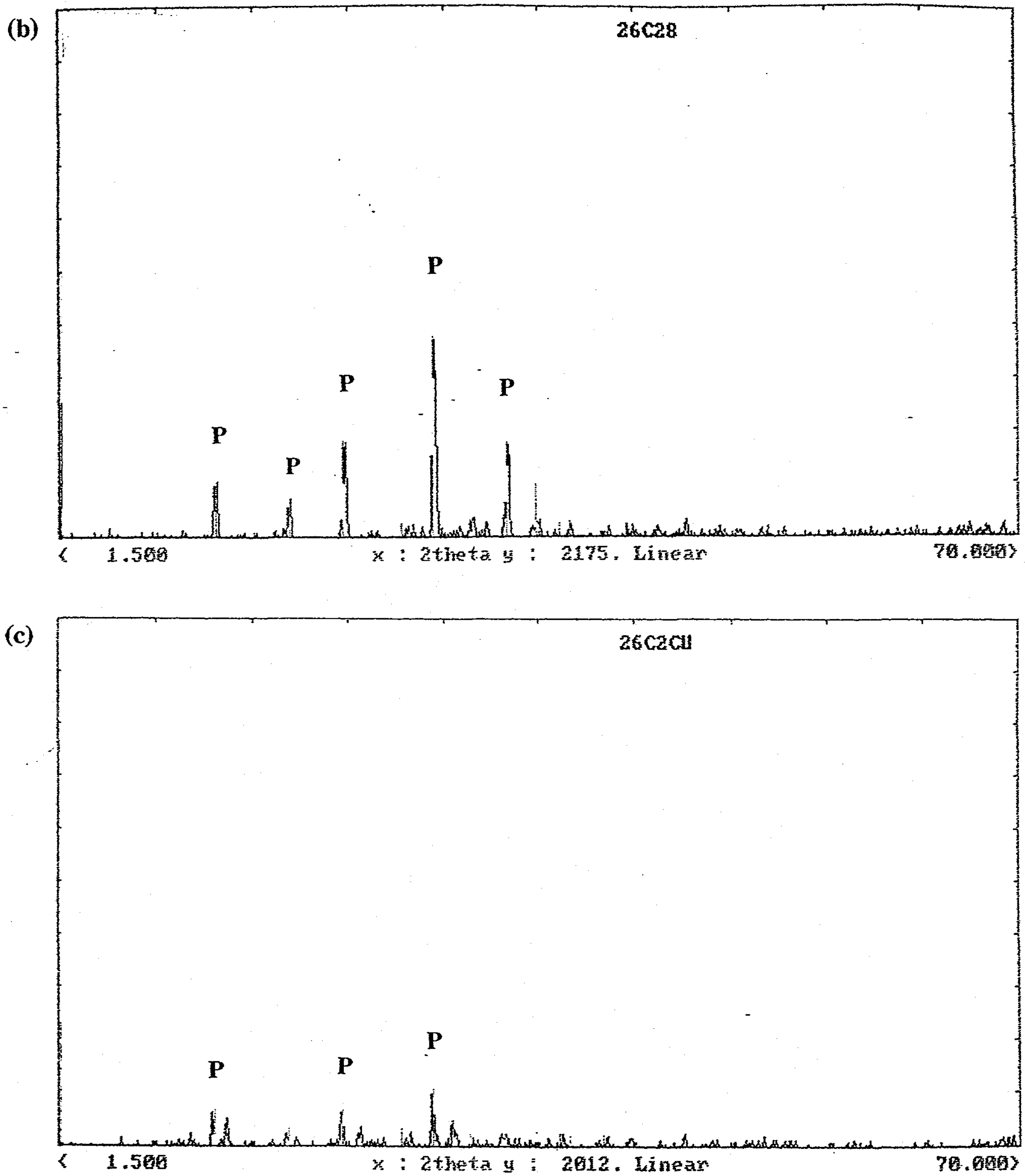


Figure 6. Isotherm for ion exchange of Cs+ in UOP 4A
Results obtained after 5 minutes, 20 hrs. and 40 hrs.



(a) The lamellar phase formed at the ratio of surfactant to fly ash = 0.03 mole/7.2 g, aged 2 days at RT in basic condition



(b) Zeolite P formed at the ratio of surfactant to fly ash = 0.0075 mole/7.2 g, cured 2 days at 80 °C (c) Zeolite P still appeared after calcination at 540 °C

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