DOE/PC/94215--T8

QUARTERLY PROGRESS REPORT (7/1/96-9/30/96)

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

In the last few months we have been working on the conversion of various fly ashes into zeolites. It was reported in the last report that by fusing fly ash with sodium hydroxide, all fly ashes that were studied can be converted into zeolites. Apparently, the fusion between the fly ash and sodium hydroxide produced sodium silicates which dissolve more readily than fly ash itself. The higher concentration of silicates within the solutions enhances the formation of zeolites. In this report, we summarize the results on the ion-exchange behavior of those treated fly ash with Cs^+, Co^{2+} and Cu^{2+} ions as well as the characterization of the concentration of Si, Al, and Na in the curing solutions.

EXPERIMENTAL PROCEDURE

The composition of fly ashes that were studied were described in the previous report. 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, followed by aging and heat treatment for the precipitation of zeolites. The solution of fused powders was heat treated at 60°C. This higher curing temperature increased the formation rate of faujasites. Previously, when curing pure fly ash solution without fusion, only 38°C can be used for the curing. The fusion process allows a higher curing temperature. The curing solutions were characterized by Atomic Absorption spectroscopy for the ionic concentration of Si, Al, and Fe.

The ion exchange behavior was studied with 0.1 N Cs^+, or Co^{2+}, or Cu^{2+}, solutions. Two types of ion exchange experiments were studied. Type I involved preparing a 40 ml 0.1 N test ions solution. Then 0.9 g of treated fly ash was added to the test solution. The Na^+ concentration in the solution was measured using a sodium ion probe. As the test ions exchange with the Na^+ in the zeolites, the Na^+ concentration in the solution would increase. We measured the Na^+ concentration as a function of time to make sure that the test ions have exchanged with sodium ions and reached an equilibrium. As the ion-exchange capability of the treated fly ash saturates, the sodium concentration in the solution would saturate. Type II experiments involved preparing a 40 ml of water containing 0.9 g of treated fly ash. Then 2 ml of 0.1 N test ion solution were added to the treated fly ash solution. Similar to the Type I, the sodium concentration of the solution was then measured as a function of time. Type I experiment corresponds to ion exchange with concentrated solutions of test ions and Type II corresponds to that with dilute solution of test ions.

RESULTS and DISCUSSION

The ion exchange behavior of treated fly ash with Cs^+ ions is shown in Fig.1. Fig.1(a) shows the sodium concentration in the treated fly ash solution as a function of time for Type II experiment and Fig.1(b) that of Type I. When the concentration of the test ion Cs^+ is high, as seen in Fig.1(b), the Conemiaugh ash shows higher amount of ion exchange indicating a higher amount of faujasites were converted with Conemiaugh ash than Goudey and Eddystone. The higher yield of faujasites using Conemiaugh ash is consistent with our earlier XRD results presented in the previous report. However, when the concentration of test ion Cs^+ is low, Goudey and Eddystone ashes showed higher ion exchange capacity than Conemiaugh. The results in Fig.1 indicate that the ion exchange behavior of treated fly ash is strongly affected by the test ion concentration. Zeolite P was

also converted from Goudey ash and its ion exchange capacity is relatively low compared to faujasites.

The ion exchange results with Co^{2+} are shown in Fig.2. The results for Co^{2+} are very similar to that for Cs^+. The better performance of Conemiaugh ash for concentrated test ion solutions is also observed. Similarly, at lower test ion concentrations, Goudey and Eddystone ashes have better performance than Conemiaugh ash. The similarity between Fig.1 and Fig.2 shows that the difference between Fig.1(a) and 1(b), and similarly between Fig.2(a) and Fig.2(b), may be due to the differences in the chemical compositions of the faujasites from different ashes. It is possible that the Si/Al ratio in the faujasites converted from the three ashes are different thereby having different ion exchange behavior with test ion concentration.

Fig.3 shows the ion exchange behavior of converted faujasites with low concentrations of Cu^{2+} ions. The study on the concentrated Cu^{2+} solution was not carried out due to the acidity of the Cu^{2+} solutions resulting in the dissolution of the faujasites. The results in Fig.3 are similar to that in Fig.1(a) and Fig.2(a).

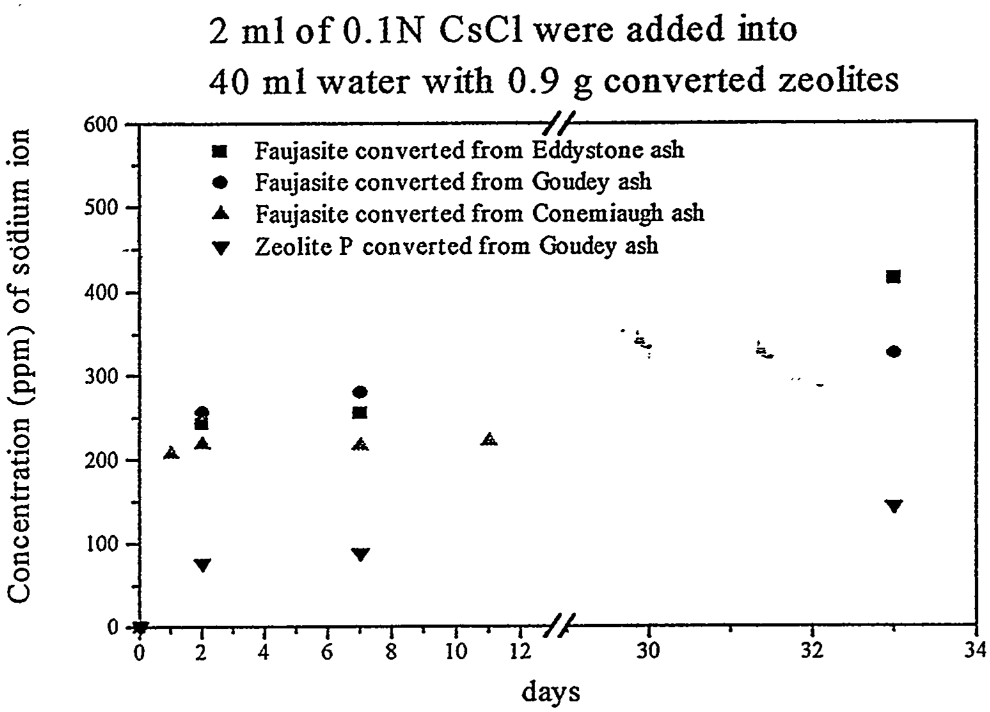
The ionic concentrations of Si, Al, and Na, of the solutions cured at various amount of time are shown in Fig.4, 5, and 6. These results were obtained from Atomic Absorption Spectroscopy. It is seen that Conemiaugh ash has the highest amount of Al at all time. Furthermore, from Fig.5, it is seen that when the concentration of Al saturates, the yield of the faujasites also saturates (the yield result was presented in the previous report). On the other hand, the Si concentration continues to vary after the concentration of Al saturates. Therefore, we believe that Al is the controlling factor in the formation of faujasites in the solution. Once Al ions are used up, no more zeolites can be formed. The higher amount of Al ions in the Conemiaugh ash solutions may explain why Conemiaugh ash has the highest amount of faujasites in the treated fly ash.

We have also investigated the conversion of fly ash to zeolites by using the supernatant of the dissolved fused powder solution. When $Al(OH)_3$ was added to the supernatant, zeolite A can be formed at a curing temperature of 60°C. The XRD pattern of zeolite A is shown in Fig.7. The high intensity of the zeolite A shown in Fig.7 indicates that the amount of zeolite A obtained from the supernatant is much higher than that from the fly ash solutions.

CONCLUSIONS and FUTURE PLAN

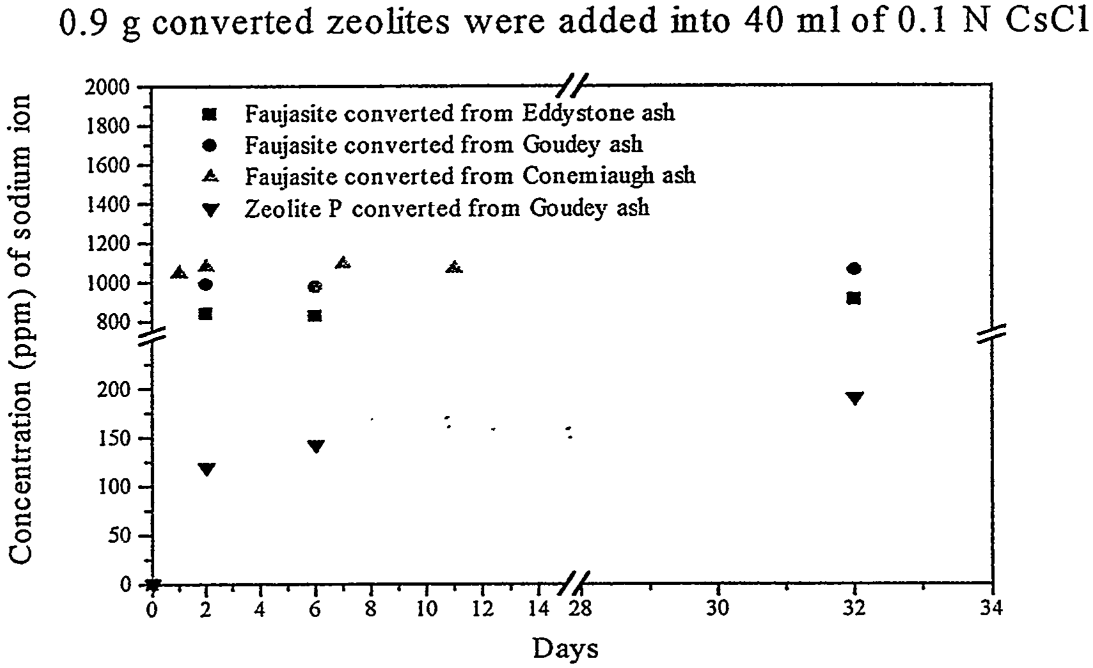
The ion exchange behavior of the faujasites converted from various fly ash by the fusion method is presented. It is shown that the ion exchange behavior at high concentration of test ions is consistent with the XRD results on the yield of faujasites converted. However, at low concentrations of test ions, the trend was reversed. The difference between the ion exchange behavior of treated fly ash with high and low concentrations of test ions is likely due to the different compositions of the faujasites produced from the different ashes. Furthermore, the atomic absorption study on the ionic concentration in the curing solutions showed that Al may be the controlling parameter in the synthesis. Once the Al is consumed, the yield of zeolite saturates.

In the next three months, we will focus our attention to the conversion of carious ashes to mesoporous aluminosilicates. It is expected that due to the higher concentration of silicates in the solution of fused powders, mesoporous materials can be made.



2 ml of 0.1N CsCl were added into 40 ml water with 0.9 g converted zeolites

Fig.1(a)



0.9 g converted zeolites were added into 40 ml of 0.1 N CsCl

Fig.1(b)

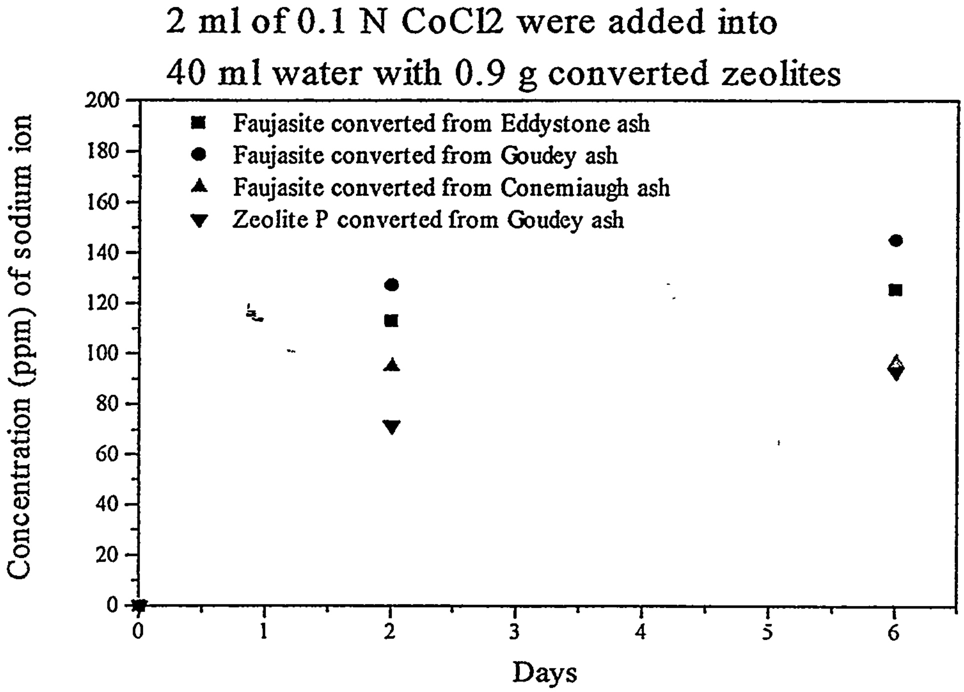

2 ml of 0.1 N CoCl2 were added into 40 ml water with 0.9 g converted zeolites

Fig.2(a)

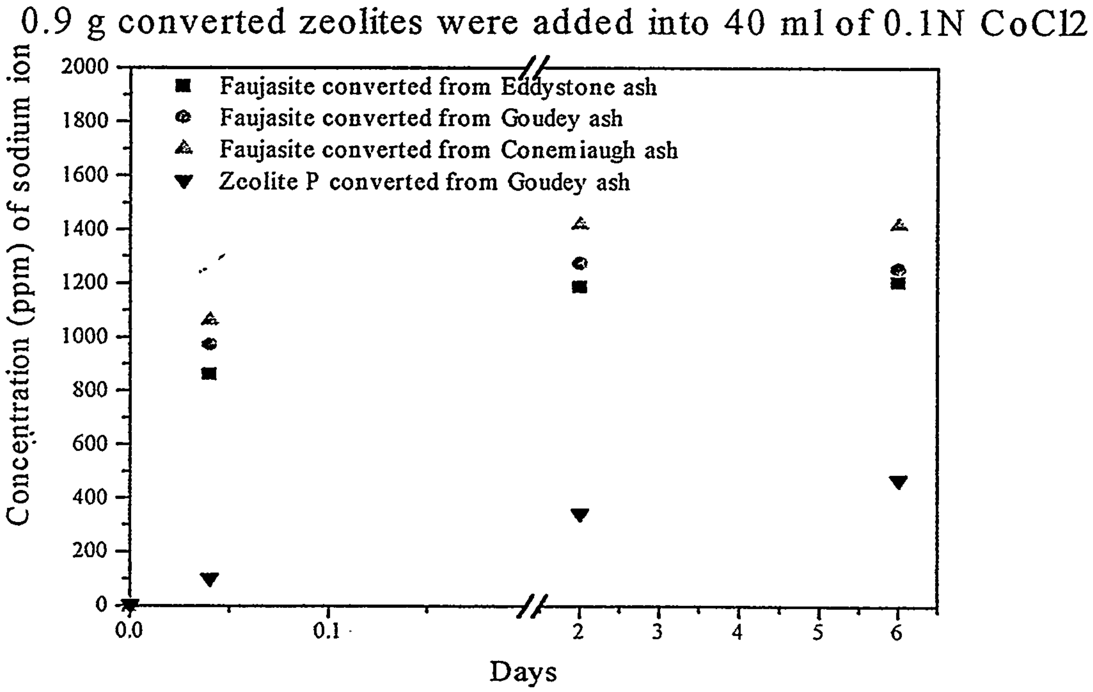

0.9 g converted zeolites were added into 40 ml of 0.1N CoCl2

Fig.2(b)

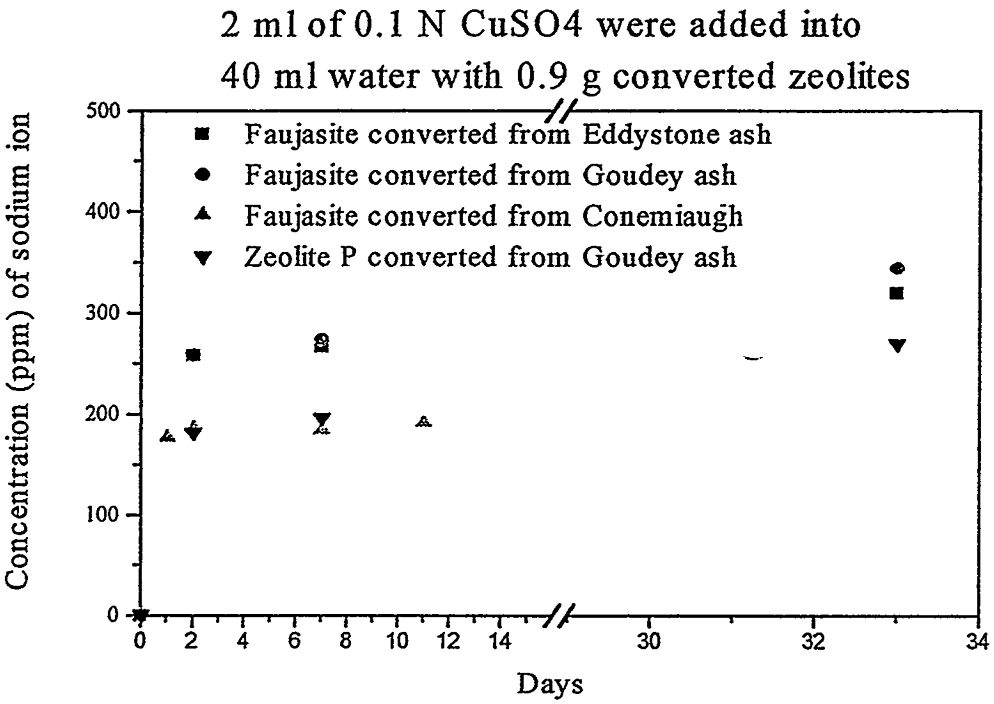

2 ml of 0.1 N CuSO4 were added into
40 ml water with 0.9 g converted zeolites
■ Faujasite converted from Eddystone ash
● Faujasite converted from Goudey ash
▲ Faujasite converted from Conemiaugh
▼ Zeolite P converted from Goudey ash
Concentration (ppm) of sodium ion
500
400
300
200
100
0
0
2
4
6
8
10
12
14
30
32
34
Days

Fig.3

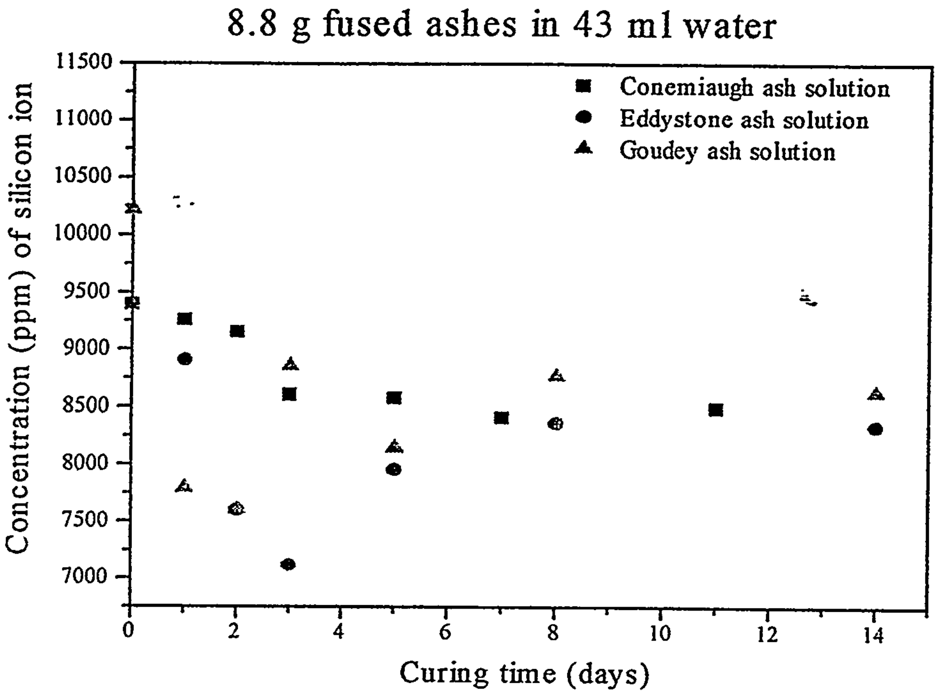

8.8 g fused ashes in 43 ml water
Concentration (ppm) of silicon ion
11500
11000
10500
10000
9500
9000
8500
8000
7500
7000
0
2
4
6
8
10
12
14
Curing time (days)
■ Conemiaugh ash solution
● Eddystone ash solution
▲ Goudey ash solution

Fig.4

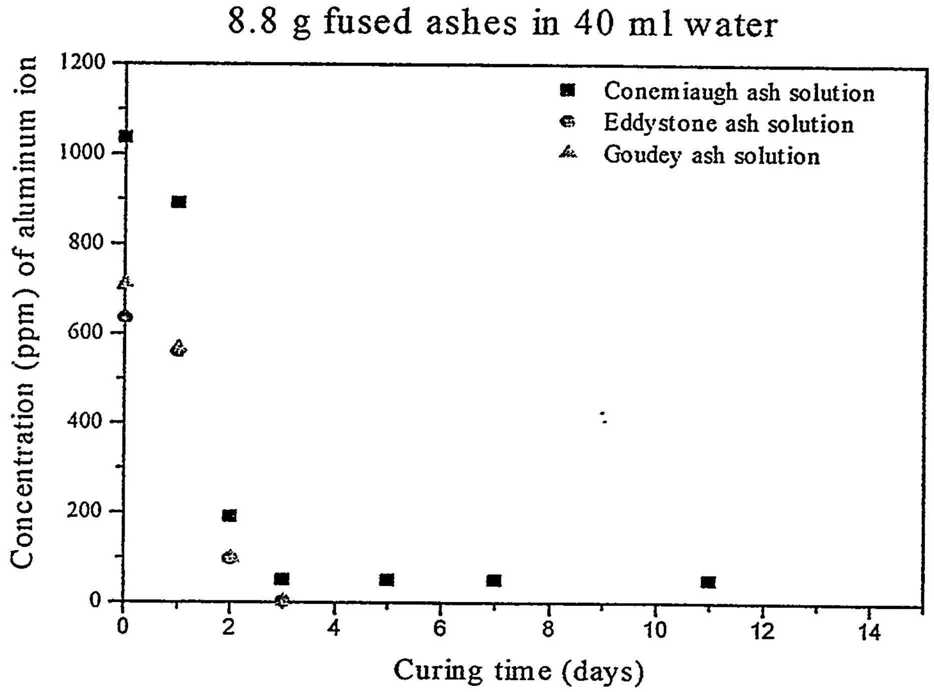

8.8 g fused ashes in 40 ml water
Concentration (ppm) of aluminum ion
1200
1000
800
600
400
200
0
0
2
4
6
8
10
12
14
Curing time (days)
■ Conemiaugh ash solution
● Eddystone ash solution
▲ Goudey ash solution

Fig.5

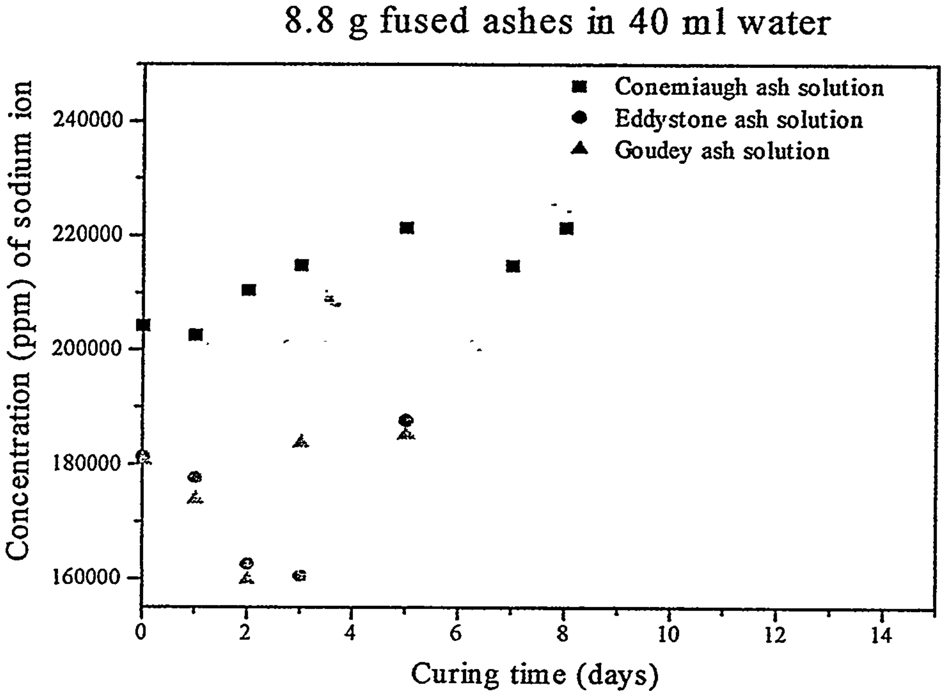
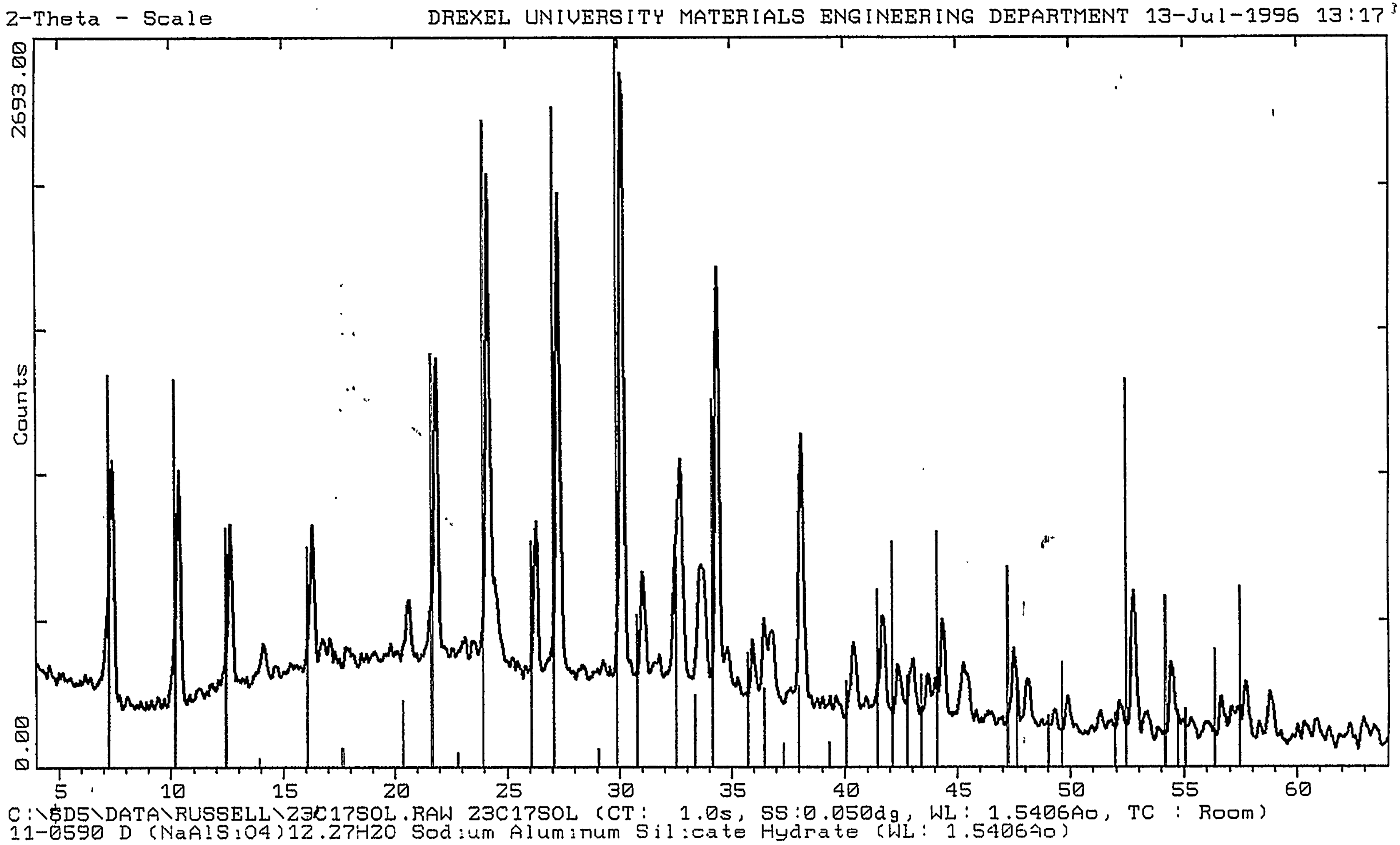
8.8 g fused ashes in 40 ml water
■ Conemiaugh ash solution
● Eddystone ash solution
▲ Goudey ash solution
Concentration (ppm) of sodium ion
240000
220000
200000
180000
160000
0
2
4
6
8
10
12
14
Curing time (days)

Fig.6


2-Theta - Scale
DREXEL UNIVERSITY MATERIALS ENGINEERING DEPARTMENT 13-Jul-1996 13:17
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Counts
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10
15
20
25
30
35
40
45
50
55
60
C:\D5\DATA\RUSSELL\23C17SOL.RAW 23C17SOL (CT: 1.0s, SS:0.050dg, WL: 1.5406Ao, TC : Room)
11-0590 D (NaAlSiO4)12.27H2O Sodium Aluminum Silicate Hydrate (WL: 1.5406Ao)

Fig.7