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# GROWTH OF ZEOLITE CRYSTALS IN THE MICROGRAVITY ENVIRONMENT OF SPACE

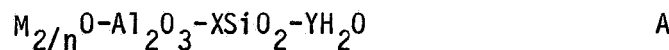
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## 1. Introduction

Zeolites are hydrated, crystalline aluminosilicates with alkali and alkaline earth metals substituted into cation vacancies (Equation A)



They have a uniform internal channel system which makes them ideal for use as catalysts and adsorbents. Presently zeolite materials constitute a 1-2 million dollar/year business. Typically zeolite crystals are 3-8  $\mu m$  along their characteristic dimension (e.g., edge). Larger zeolite crystals are desirable. Large crystals will allow more detail characterization of their complex crystal structures. Also, they will help improve reactor performance, may be used as membrane separators, and they should enhance basic studies in molecular diffusion in zeolites.

Large zeolite crystals have been produced (100-200  $\mu m$ ); however, they have taken restrictively long times to grow. It has been proposed if the rate of nucleation or in some other way the number of nuclei can be lowered, fewer, larger crystals will be formed. The microgravity environment of space may provide an ideal condition to achieve rapid growth of large zeolite crystals (e.g., >100  $\mu m$ ). Since settling crystals are believed to cause secondary nucleation, by limiting crystal movement by suspension in the zero gravity environment, fewer crystals will form, but they will grow larger. The objective of the project is to establish if large zeolite crystals can be formed rapidly in space.

## 2. Experimental Procedure

The experimental procedure for making zeolites is straight forward. An example of this procedure is illustrated in Figure 1. An aqueous Sodium Metasilicate solution is mixed with an aqueous Sodium Aluminate solution which

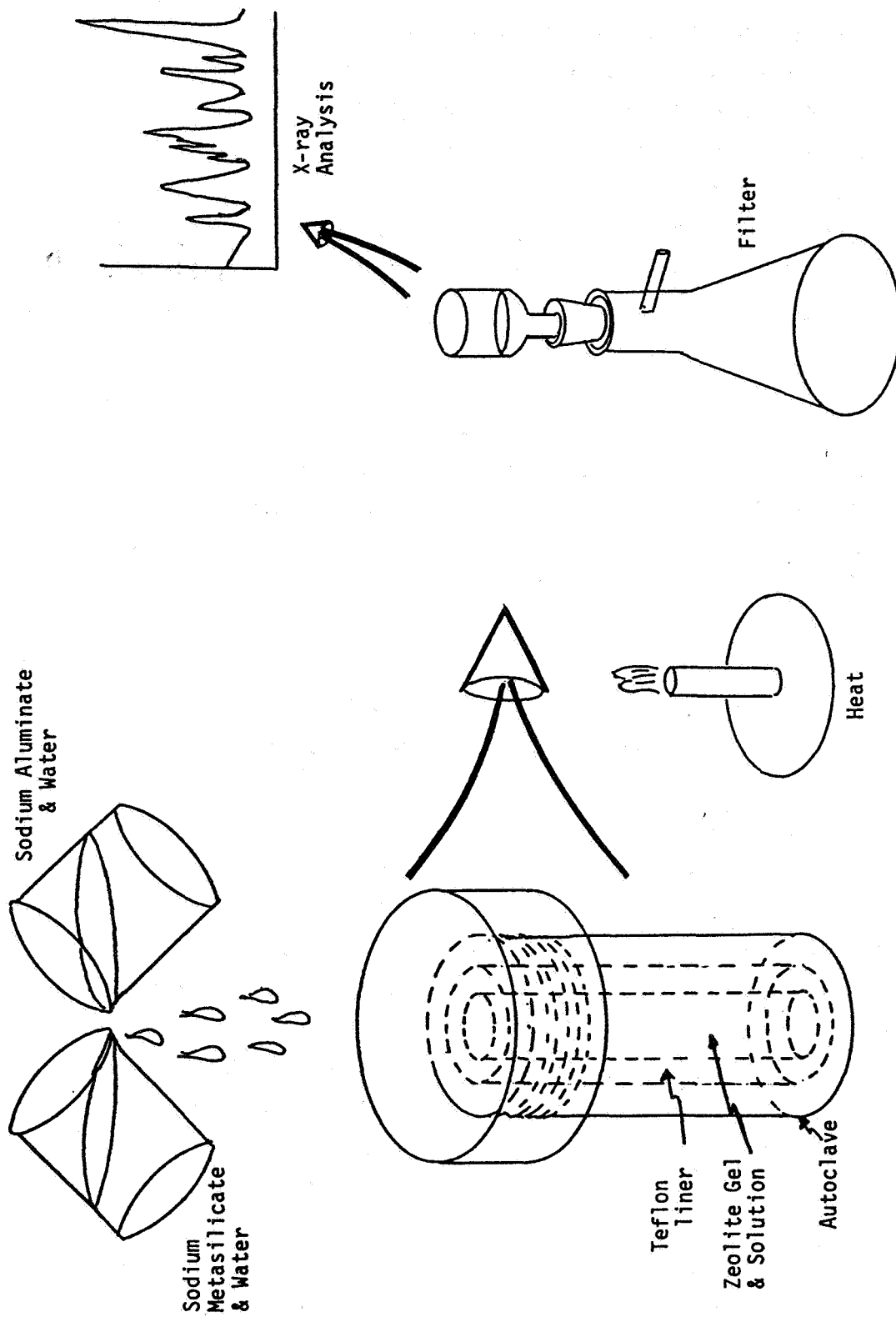


Figure 1. Experimental Procedure

forms a "gel". This gel is poured into a teflon lined stainless steel or aluminum vessel (autoclave). The autoclave is then heated to the desired temperature and held at the temperature for the required time. The resulting mixture is filtered and the crystal structure of the crystals formed are characterized using X-ray diffraction. For the space shuttle, this procedure is only moderately altered. The solutions are premixed and stored in a specially designed autoclave. This system is designed to heat up the reaction vessel rapidly to the desired temperature and maintain the temperature for up to 72 hours. Analysis of the product (crystals) will be performed on return to earth.

### 3. Zeolite Selection and Preliminary Results

There are 44 species of natural zeolites and as many as 150 synthetic zeolites. The initial selection criterion used to determine which zeolite should fly was as follows:

- A. Material of industrial interest
- B. Must achieve at least 40% crystallization within 72 hours
- C. Reaction temperature must not exceed 393K
- D. The "gel" must be unreactive at temperatures below 308K for up to 90 days.
- E. No rapid phase transformations at 393K or on slow cooling

Criteria B-E were the direct or indirect result of NASA requirements. For example, NASA will only guarantee a flight of 72 hours duration. Thus, the experiment must be complete in that time. The internal pressure was not to exceed one atmosphere. This limited the mostly water solution to a maximum temperature of 393K. Since launch delays could be as long as 90 days, the premixed system must not substantially settle or react in that time while at ambient temperature. Also, post flight delays require the typically metastable zeolites not to transform rapidly to a more stable form on cooling. After a detailed literature survey and some experimentation, zeolite A was chosen.

Figure 2 is a plot of percentage crystallization versus reaction time for zeolite A at three temperatures. As shown, at all three temperatures, 100% crystallization is reached in 72 hours. The intermediate temperature of 369K was chosen. At this temperature the system's vapor pressure is less than 1

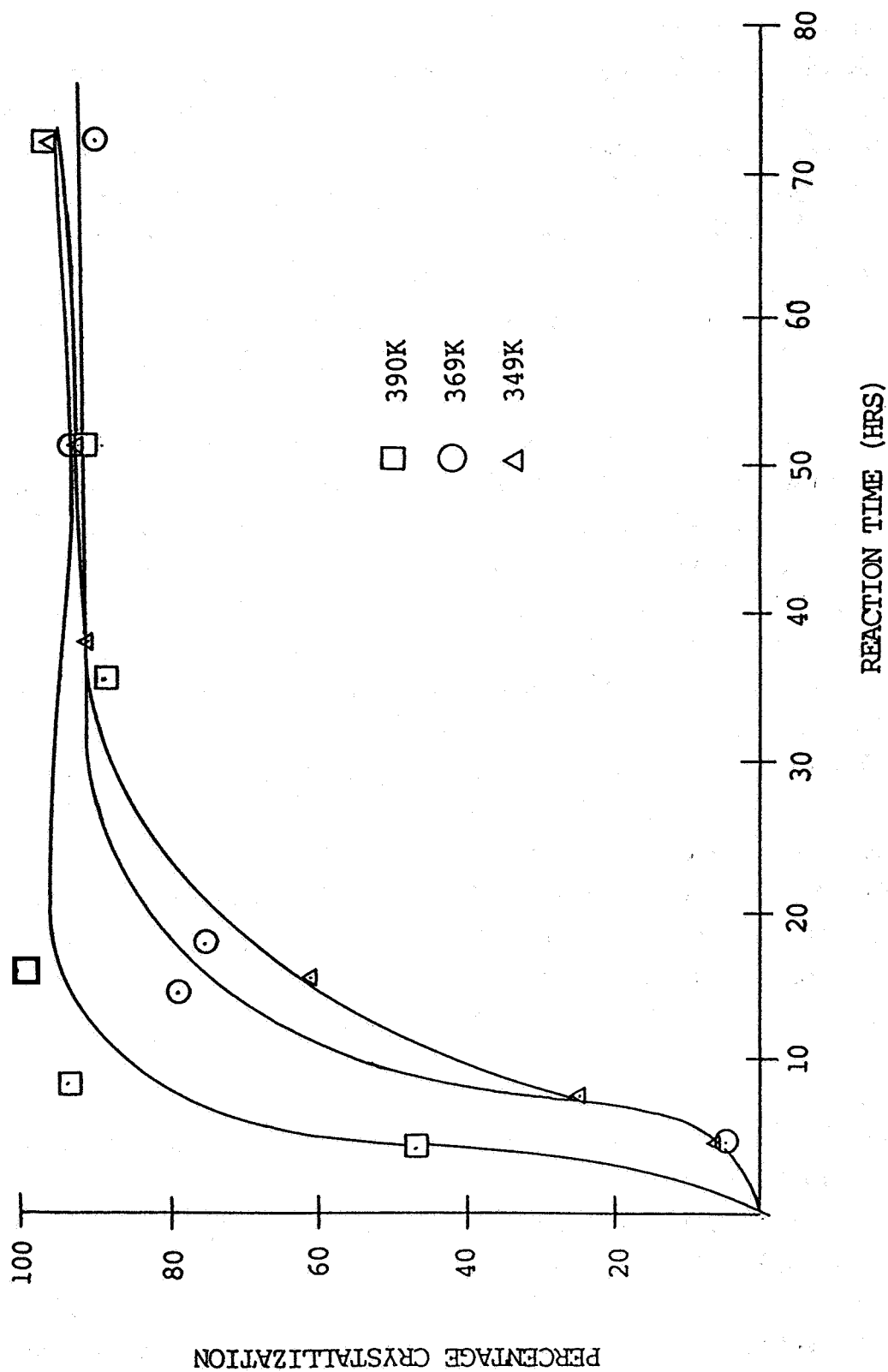


Figure 2. Percentage Crystallization versus Reaction Time for Zeolite A  
(2.05 Na<sub>2</sub>O - Al<sub>2</sub>O<sub>3</sub> - 1.05 SiO<sub>2</sub> - 138 H<sub>2</sub>O)

atmosphere and the reaction rate is still high.

It is known that if one suspends a crystal in solution, it depletes local nutrients and the growth rate is slowed. The effect of this phenomenon was tested on zeolite A by systematically adding more and more water (diluting the reaction mixture). Figure 3 is a plot of crystal size versus the moles  $\text{H}_2\text{O}/\text{moles Al}_2\text{O}_3$  ratio for zeolite A at 369K for 24 hours. As shown, the more dilute the solution, the greater the average and maximum crystal size. The rate is linear for both the average and the maximum crystal sizes, and it is about 1-1.5  $\mu\text{m}/100$  moles  $\text{H}_2\text{O}$ . At the present time, this is not anticipated as a problem.

Figure 4 shows two plots. One illustrates the systematic addition of Triethanolamine (TEA) to zeolite A solutions. This was done to enhance the growth of large zeolites as well as to provide a suspending mixture to help stop settling during the prelaunch phase. As indicated in Figure 4(a), both the maximum and average crystal size were increased by adding TEA up to a TEA/ $\text{H}_2\text{O}$  ratio of  $1.83 \times 10^{-2}$ . After this value crystal size decreased. The reason for the maximum is still under investigation. However, growth is definitely enhanced when settling is hindered. Also, the dark symbols indicate the effect of filtering the initial reactants. Upon filtering, secondary nucleation points are eliminated resulting in fewer larger crystals. Also shown in Figure 4(b) is the effect of a prelaunch delay. A similar set of experiments to those presented in Figure 4(a) was performed. However, these solutions were held at room temperature for 45 days prior to reaction at 369K for 72 hours. As shown settling is hindered but not eliminated. Additional work to improve this performance is presently being done.

#### 4. Conclusions

These results as well as others, not included for the sake of brevity, suggest the following conclusions:

- A. Zeolite A is a viable candidate for testing in space.
- B. Triethanolamine, TEA, helps in the growth of large crystals.
- C. Filtering the reactants helps in the growth of large crystals.
- D. Shelf-life experiments suggest TEA/zeolite A solutions may not be substantially affected by a 90 day delay to launch.
- E. At projected growth rates, zeolite crystals over 100  $\mu\text{m}$  should form.

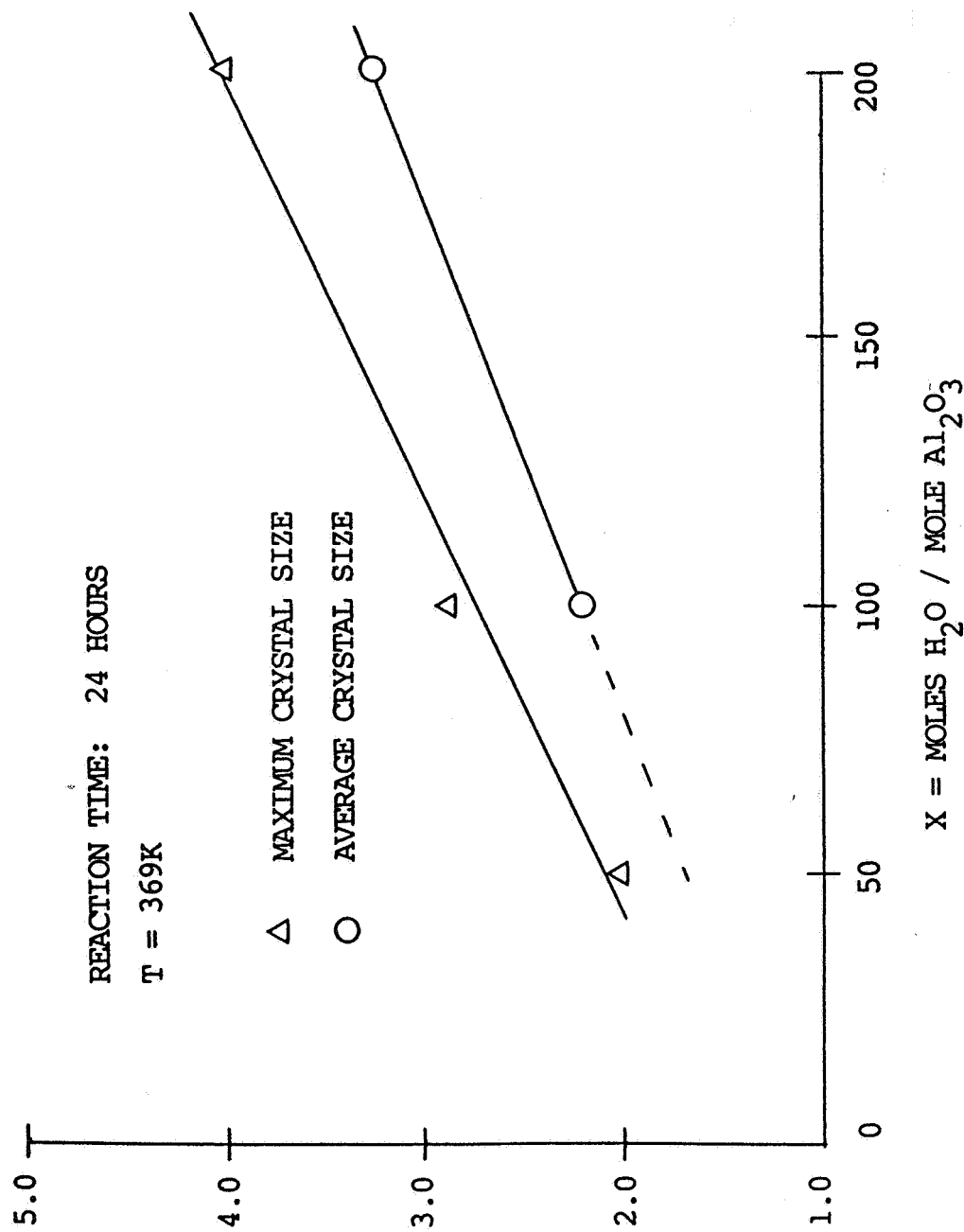
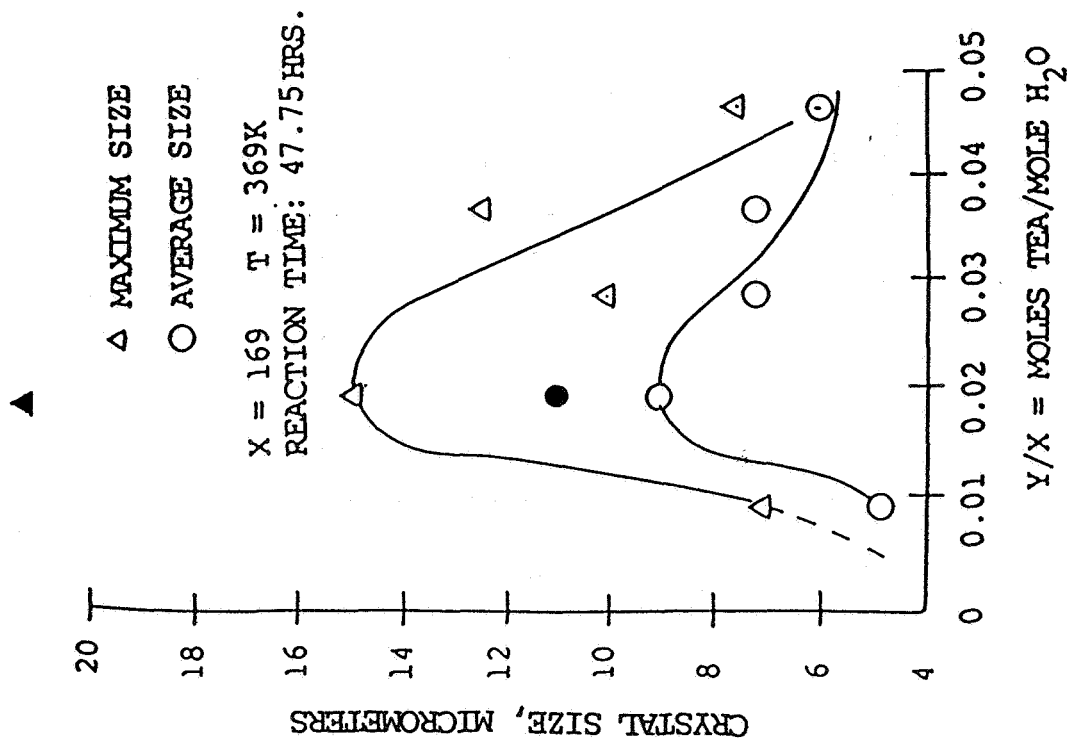
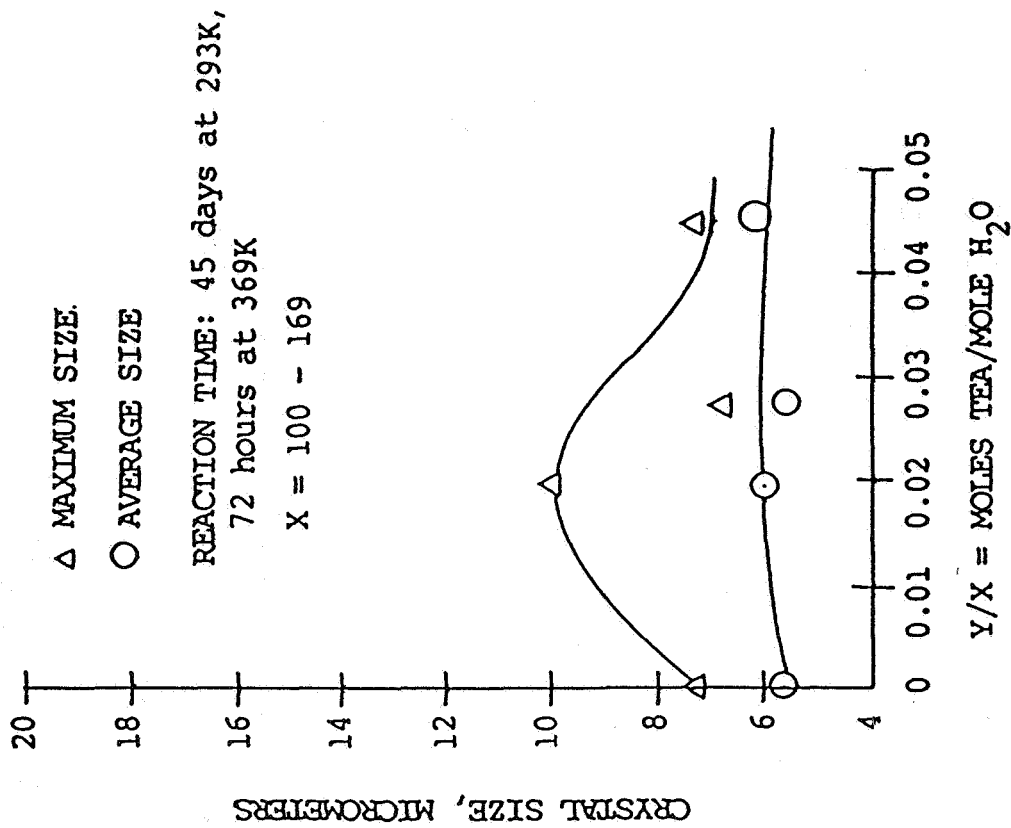


Figure 3. Crystal Size Versus H<sub>2</sub>O/Al<sub>2</sub>O<sub>3</sub> Ratio for Zeolite A  
2.03 Na<sub>2</sub>O - Al<sub>2</sub>O<sub>3</sub> - 1.5 SiO<sub>2</sub> - XH<sub>2</sub>O



a) dark samples represent filtered samples



b) reaction after 45 days at 293K

Figure 4. Systematic Addition of TEA to Zeolite A (2.04 Na<sub>2</sub>O - Al<sub>2</sub>O<sub>3</sub> - 1.04 SiO<sub>2</sub> - xH<sub>2</sub>O - YTEA)

### ACKNOWLEDGEMENT

We gratefully acknowledge the technical and financial help of the MITRE Corporation in this work.