

**MODELLING THE UNSTEADY GROWTH STATE POPULATION  
BALANCE FOR A NONLINEAR GROWTH MODEL  
IN AN MSMPR CRYSTALLIZER**

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**THE UNSTEADY STATE POPULATION BALANCE  
FOR A NONLINEAR GROWTH MODEL IN AN MSMPR CRYSTALLIZER**

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**ABSTRACT**

The precipitation of zirconium and other metal species as hydroxides (hydrous oxides) from simulated nuclear waste process solutions has been investigated as a potential method to reduce radioactive waste volumes. The reaction of ammonium hexafluorozirconate was used to simulate these waste streams. Studies were conducted to investigate the unsteady state response of crystallization in mixed suspension, mixed product removal (MSMPR) crystallizer. Size distributions below 40  $\mu\text{m}$  from laboratory batch and MSMPR data indicate size-dependent growth may be occurring because they may fit the Abegg, Stevens and Larson (ASL) model. However, these distributions also may fit a transient growth model based on the Method of Lines numerical solution to the unsteady state population balance equation. The development of the Method of Lines solution as well as experimental agreement with both models were studied.

## INTRODUCTION

The precipitation of zirconium and other metal species as hydroxides (hydrous oxides) from simulated nuclear waste process solutions has been investigated as a potential method to reduce radioactive waste volumes. Studies were conducted to investigate the unsteady state response of crystallization in a mixed suspension, mixed product removal (MSMPR) crystallizer. The unsteady state population balance equation for a MSMPR crystallizer was manipulated to show the effects of unsteady state behavior.

Since the population balance equation includes both growth rate and number density as dependent variables, an auxiliary relationship between the two is required for solution. By substituting an exponential relationship between the number density, growth rate, and crystal size (corresponding to the steady state, linear growth rate model), the number of dependent variables is reduced to one, the growth rate. This unsteady state, nonlinear partial differential equation in crystal size and time is then converted to a system of coupled ordinary differential equations in time by the Method of Lines. The set of ordinary differential equations was then solved by the Runge-Kutta method. The numerical results indicate that unsteady state behavior may yield number density versus size plots that exhibit "apparent" nonlinear growth rates. The numerical results also predict trends that have been observed in experimental work.

## DEVELOPMENT OF EQUATIONS

The Method of Lines allows the number of independent variables in a partial differential equation to be reduced by one. For example, the population balance partial differential equation is<sup>(1)</sup>

$$\frac{\partial n}{\partial t} + n \frac{\partial G}{\partial L} + G \frac{\partial n}{\partial L} + \frac{n}{\tau} = 0 \quad (1)$$

The population balance equation has two unknowns, growth rate  $G$  and number density  $n$ . There are also two independent variables: size,  $L$  and time,  $t$ . The Method of Lines can reduce this equation from being dependent on growth rate and number density to being dependent only on growth rate.

Another relationship between the growth rate and nucleation must be assumed in order for the population balance equation to be solved. One relationship, often used to express the number density, is the McCabe linear growth model which

assumes that the growth rate is independent of particle size. Thus at steady state, the number density can be expressed by

$$n = n^0 \exp\left(-\frac{L}{G\tau}\right) \quad (2)$$

If the McCabe number density is substituted into the population balance equation and the assumption is made that the growth rate is the only unknown, then two partial differential equations are produced. One partial differential equation is expressed with time as the independent variable

$$\frac{\partial n}{\partial t} = \frac{n}{\tau} \left[ \frac{L}{G^2} \frac{\partial G}{\partial t} - 1 \right] \quad (3)$$

The other partial differential equation is expressed with particle size as the independent variable

$$\frac{\partial n}{\partial L} = \frac{n}{G\tau} \left[ \frac{L}{G} \frac{\partial G}{\partial L} - 1 \right] \quad (4)$$

Substituting these two equations into the population balance equation leads to

$$\frac{\partial G}{\partial t} + \left[ \frac{G^2\tau}{L} + G \right] \frac{\partial G}{\partial L} - \frac{G^2}{L} = 0 \quad (5)$$

rearranging the equation results in:

$$\frac{\partial G}{\partial t} = - \left[ \frac{G^2 \tau}{L} + G \right] \frac{\partial G}{\partial L} + \frac{G^2}{L} \quad (6)$$

A simple first order approximation to the derivative of growth rate with respect to particle size was used to convert the equations from a partial differential equation to a series of ordinary differential equations. The differential of the growth rate with respect to crystal size is

$$\frac{\partial G}{\partial L} = \frac{G_{i+1} - G_i}{h} \quad (7)$$

where h is the step size. The differential of the growth rate with respect to crystal size is substituted into the reduced form of the population balance equation which converts the equation to a series of ordinary differential equations:

$$\frac{\partial G_i}{\partial t} = - \left[ \frac{G_i^2 \tau}{L_i} \right] \left[ \frac{G_{i+1} - G_i}{h} \right] + \frac{G_i^2}{L_i} \quad (8)$$

In order to solve this series of equations an initial condition and a boundary condition (growth rate at a given size and time) are required. Two possibilities were explored batch data was used to calculate the initial growth rates; and the initial growth rates of unity were used for all particle sizes.<sup>(2)</sup>

## DEVELOPMENT OF COMPUTER MODEL

One of the purposes of the computer model was to determine how accurate the numerical methods predicted the crystal behavior of  $Zr(OH)_4$ . Experimental runs were conducted by  $(NH_4)_2ZrF_6$  being precipitated with  $NH_4OH$  in a MSMPR crystallizer. The data from these runs was plotted by  $\ln(N)$ , where N is the cumulative number greater than at a given particle size, versus particle size L. Most of the experimental data indicated that the crystals were behaving in a nonlinear manner. The computer model was designed to determine if the crystal

behavior was nonlinear or if another phenomena was causing the behavior.

A computer program was designed applying the Method of Lines theory to the differential equation software package, TK Solver<sup>(3)</sup>. Short routines were written in conjunction with existing numerical functions from TK Solver's library to solve these equations. Four short routines were developed for the Method of Lines theory. A fourth order Runge Kutta numerical method from the TK Solver library was used to solve the differential equations. The other three routines were to store the differential equations, to set the boundary conditions, and to converted the  $n$ , the number density, to the  $\ln(N)$ .

The initial growth rates were difficult to determine because determination would require knowing the growth rate at time zero. Since the batch data was taken after 1 to 5 minutes in the reactor, determining the initial growth rates from batch data appeared to be the most accurate method. The growth of the crystal seed is given by

$$G = \left( \frac{\partial L}{\partial t} \right)_F \quad (9)$$

This show that, the growth rate is the rate of change of size at a constant value of the crystal size distribution function  $F$ . Thus, if the cumulative size distribution is known at two time intervals,  $t$  apart, the growth rate can be evaluated from the displacement of  $L$  between the curves at a given value of  $F$ .

Size analysis methods are limited to a minimum crystal size below which accurate counts cannot be made. This means that the number of particles per unit volume,  $n$ , is also unknown. However, the analysis will easily give  $N$ , the cumulative number of crystals of all sizes with a size greater than any specified size  $L$ . Thus, the growth rate can then be evaluated as a function of time and crystal size.

Figure 1 presents data from batch crystallization runs having 0.1 M  $(\text{NH}_4)_2\text{ZrF}_6$  precipitated with 0.048 M  $\text{NH}_4\text{OH}$ . Data is reported for samples taken at one minute intervals from one minute to five minutes. From this data it is observed that the number of particles within the crystallizer at any time is approximately constant.

The initial growth rates were determined using batch experimental data. Figure 1 plots the  $\ln(N)$  verses particle size,  $L$ . If the  $\ln(N)$  is held constant between samples taken, the difference in length and time are determined, then equation 9 is used to calculate the initial growth rate.

One problem was that the particle size distribution for batch data did not match the distribution for the MSMPR experimental data. The particle size for the batch data ranged from 0-15 microns, while the experimental MSMPR data ranged from 0-40 microns. In order to conduct effective modeling, a parameter fit for the Abegg, Stevens and Larson (ASL) model of growth rate was conducted to expand the particle size distribution. The statistical software package TableCurve<sup>(4)</sup> was used to fit the parameters to the batch data. The ASL model is

$$G=G_o(1+\gamma L)^b \quad (10)$$

The parameters  $G_o$ ,  $\gamma$ , and  $b$  were determined by fitting the ASL model to a batch data plot of  $\ln(N)$  versus particle size,  $L$ . Once the parameters  $G$ ,  $\gamma$ , and  $b$  were determined, the initial growth rate for any particle size could be calculated.

With the batch data, it was assumed that growth rate is dependent upon particle size. Another assumption is that the growth rate is independent of particle size. Under this assumption the initial growth rates were set at an equal value for all particle sizes.

Other parameters which could be varied in the model were residence time and elapsed time. The different residence times of 10, 60 and 135 minutes were examined. Elapsed time was also varied between 5 - 300 minutes. These parameters were taken from experimental data in order to make the model as accurate as possible.

### ASSESSMENT OF THE MODEL

Figures 2 through 4 are plots of the  $\ln(N)$  versus particle size  $L$  for the computer model using the batch data as the initial growth rate. Figure 2 has a residence time of 10 minutes and an elapsed time of 5.5 minutes. There is no linear behavior present in Figure 2. The top line represents time zero and the bottom line is for 5.5 minutes elapsed. The effect of residence time is seen in the difference between Figures 2 and 3. The same initial growth rates were used for both runs but the residence time was change to 60 minutes in figure 3 with an elapsed time of 8 minutes. Figure 2 at time zero is linear and for the other times it appears to be linear with slight deviations around 5 microns. Figure 4 is similar to Figure 3. The same initial growth rates were used in both figures, only the residence time

was changed to 135 minutes with elapsed time of 4 minutes in Figure 4. The behavior of the crystals appears to be linear with deviations in the small particle sizes.

Although the batch data should be the most accurate, a problem was noted in using this data since the model will only converge at small elapsed times, less than about 8 minutes. This is not representative of the experimental data which had elapsed times ranging from 85 - 300 minutes.

One reason why the model would not converge for longer elapsed times is that the batch initial growth rates were comparatively large. Several plots of the growth rates from the experimental MSMPR runs vs. particle sizes were fitted to the ASL model. The initial growth rates from the continuous data ranged from 0.02 - 0.42 microns/minute which did not correspond with the batch data of 0.75 - 2.45 microns/minute. The growth rates from the batch data were much higher than for the MSMPR data. One reason could be the difference in elapsed time. For the batch data the elapsed time was 0 - 5 minutes but for the MSMPR runs the elapsed times would range from 80 - 200 minutes.

In an attempt to allow the model to converge, for Figures 5 through 13 the initial growth rates of all particles sizes were set to a constant value. These growth rate were determined by examining the experimental data and choosing three representative growth rates for each residence time.

Figures 5 through 7 have a residence time of 10 minutes and an elapsed time of 144 minutes. Figures 5 through 7 look similar to Figure 2, which is the batch data at a residence time of 10 minutes. The growth rate for Figure 5 is 0.3 microns/minute; Figure 6 is 0.4 microns/minute; and Figure 7 is 0.5 micron/minute. Figures 5 through 7 follow the same trend of small particle sizes showing nonlinear behavior but the large particle sizes converge to very small values which are below detectable limits. For Figures 8 through 10 the residence time is 60 minutes and the elapsed time is 320 minutes. Figure 8 has an initial growth rate of 0.03 microns/minute; Figure 9 an initial growth rate of 0.06 microns/minute; and Figure 10 an initial growth rate of 0.09 microns/minute. These graphs have the same trends as the previous graph of nonlinear behavior in the small particles sizes and the larger particles are converging to a value which is too small to determine from the graph. As the growth rate increased, so did the growth of the larger particles sizes. For the Figures 11 through 13 the residence time was 135 minutes and the elapsed time is 80 minutes. Figure 11 had an initial growth rate of 0.3 microns/minute; Figure 12 had an initial growth rate of 0.4 microns/minute; and Figure 13 had an initial growth rate of 0.5 microns/minute. Figures 12-13 are the most similar to experimental data. Both figures have a definite nonlinear curve which is steeper at the smaller particle sizes and which levels out as particle size increases.

## CONCLUSIONS

In conclusion, the Method of Lines model matched the experimental data better when the initial growth rates were independent of particle size and set at an equal value for all particle sizes. There was definite nonlinear behavior displayed in Figures 5 through 13. Figures 11 through 13 were representative of the nonlinear behavior demonstrated with the experimental data.

The batch data was expected to be the most accurate method of determining the initial growth rates, but when it was used in the model the results were not representative of the experimental data. Two reasons why the batch data did not produce representative results are (1) that the initial growth rates were much larger than the experimental data and (2) that the elapsed time of the batch data was much shorter compared to the experimental data.

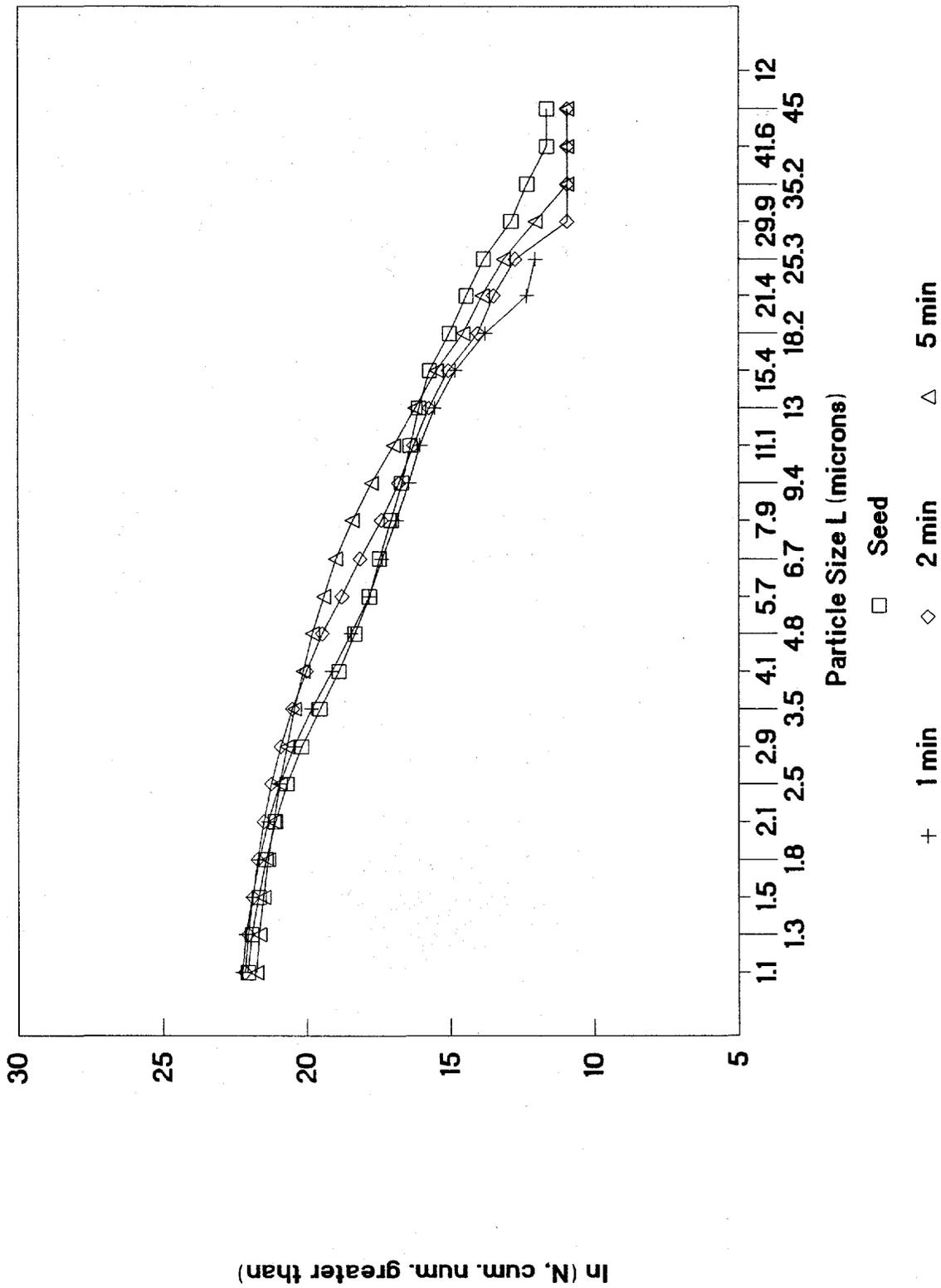
The Method of Lines model predicted the crystal behavior to be nonlinear which matched the behavior of the experimental data. The nonlinear behavior could be caused by unsteady state behavior or by transient growth. It is possible that the nonlinear crystal distribution is caused by unsteady state behavior. Since most studies involve crystals at larger particle sizes, it is difficult to determine if the behavior seen in this study is true unsteady state behavior or a combination of several factors working together.

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3. TK Solver Plus™, Universal Technical Systems, Inc. Rockford, Illinois (1989).
4. TableCurve™, Jandel Scientific, San Rafael, California (1991).

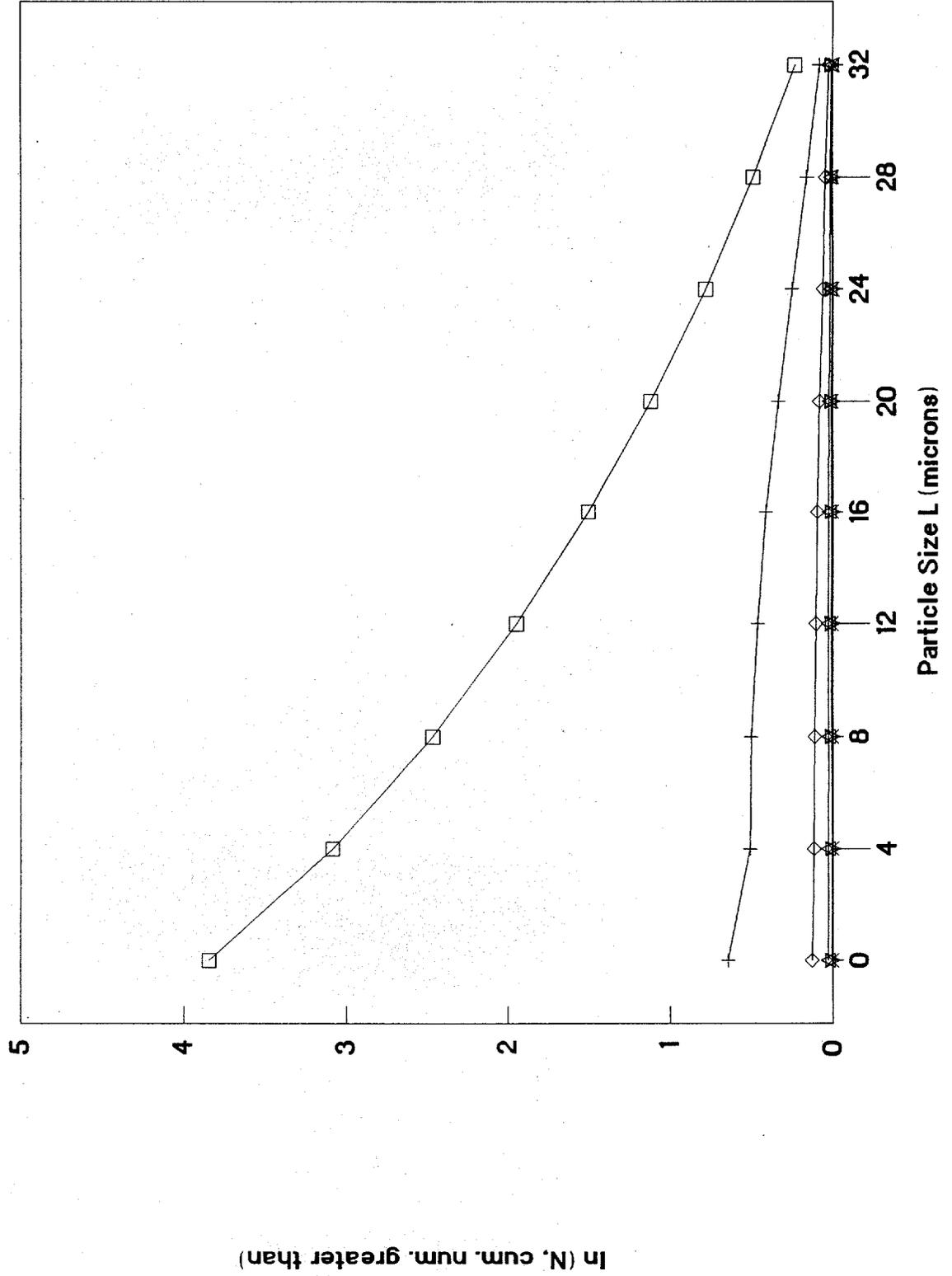
# Figure 1

Seeded Batch, 1 - 5 min elapsed



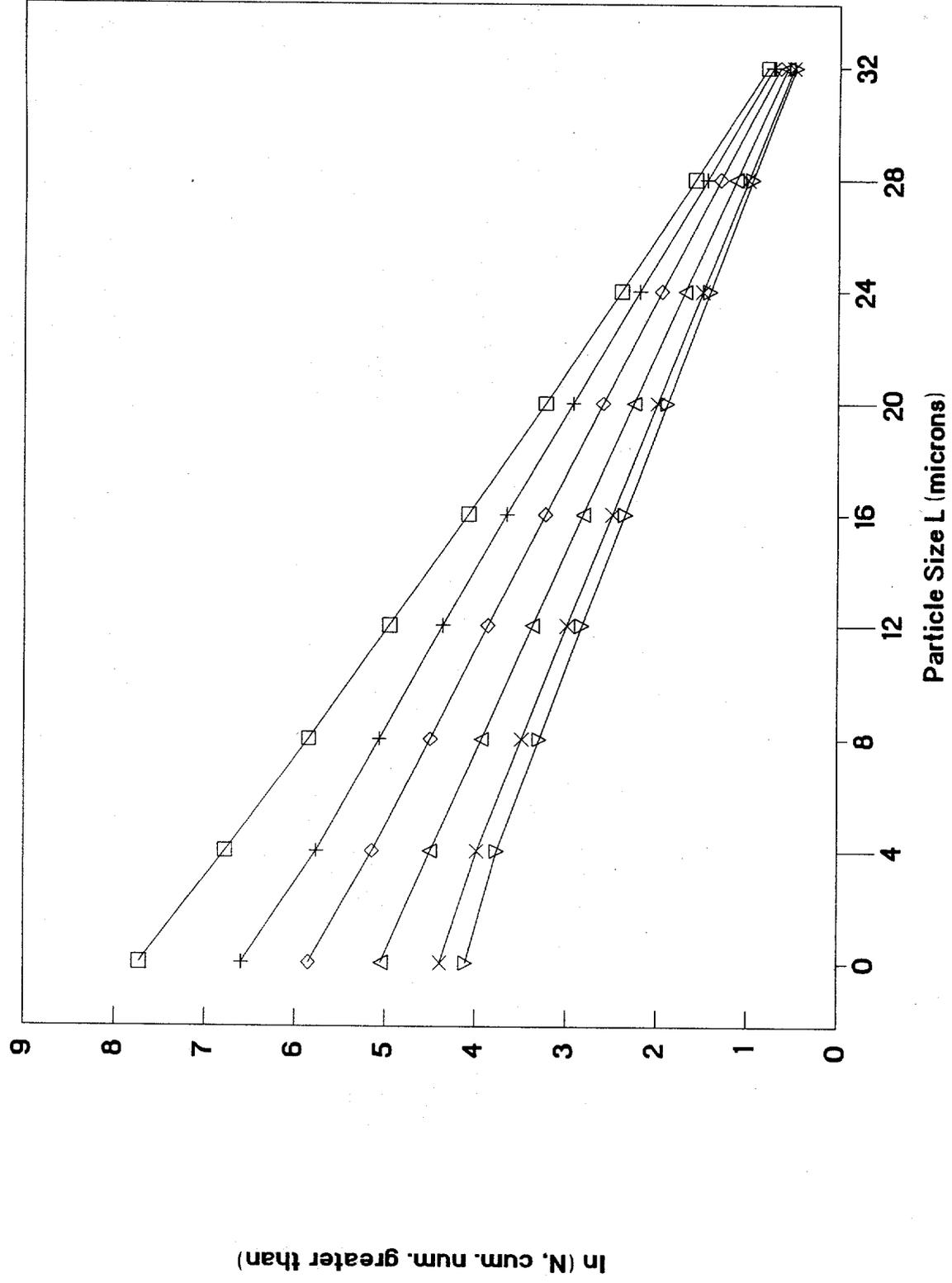
# Figure 2

Res. Time = 10 min., 5.5 min. elapsed



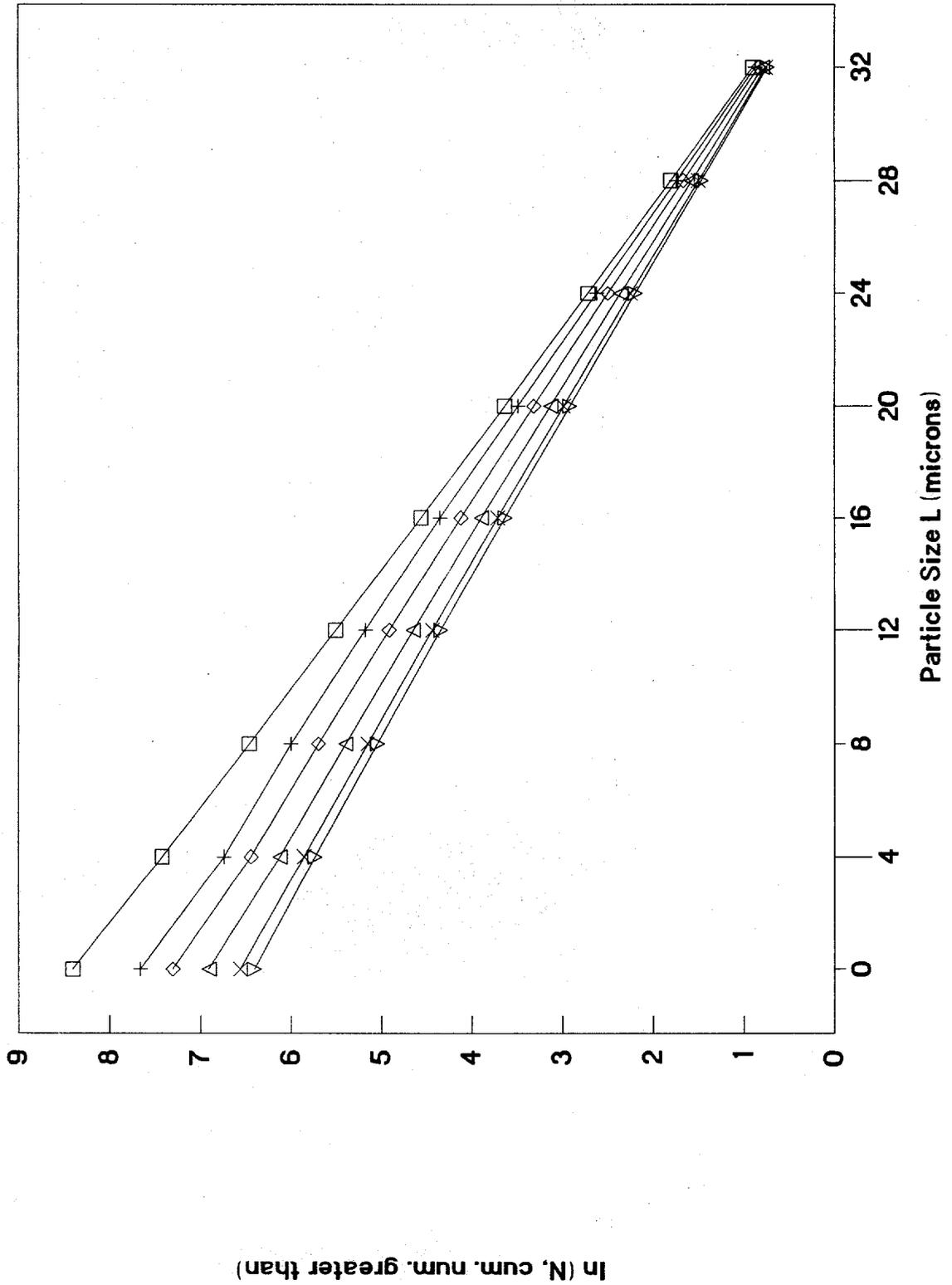
# Figure 3

Res. Time = 60 min., 8 min. elapsed



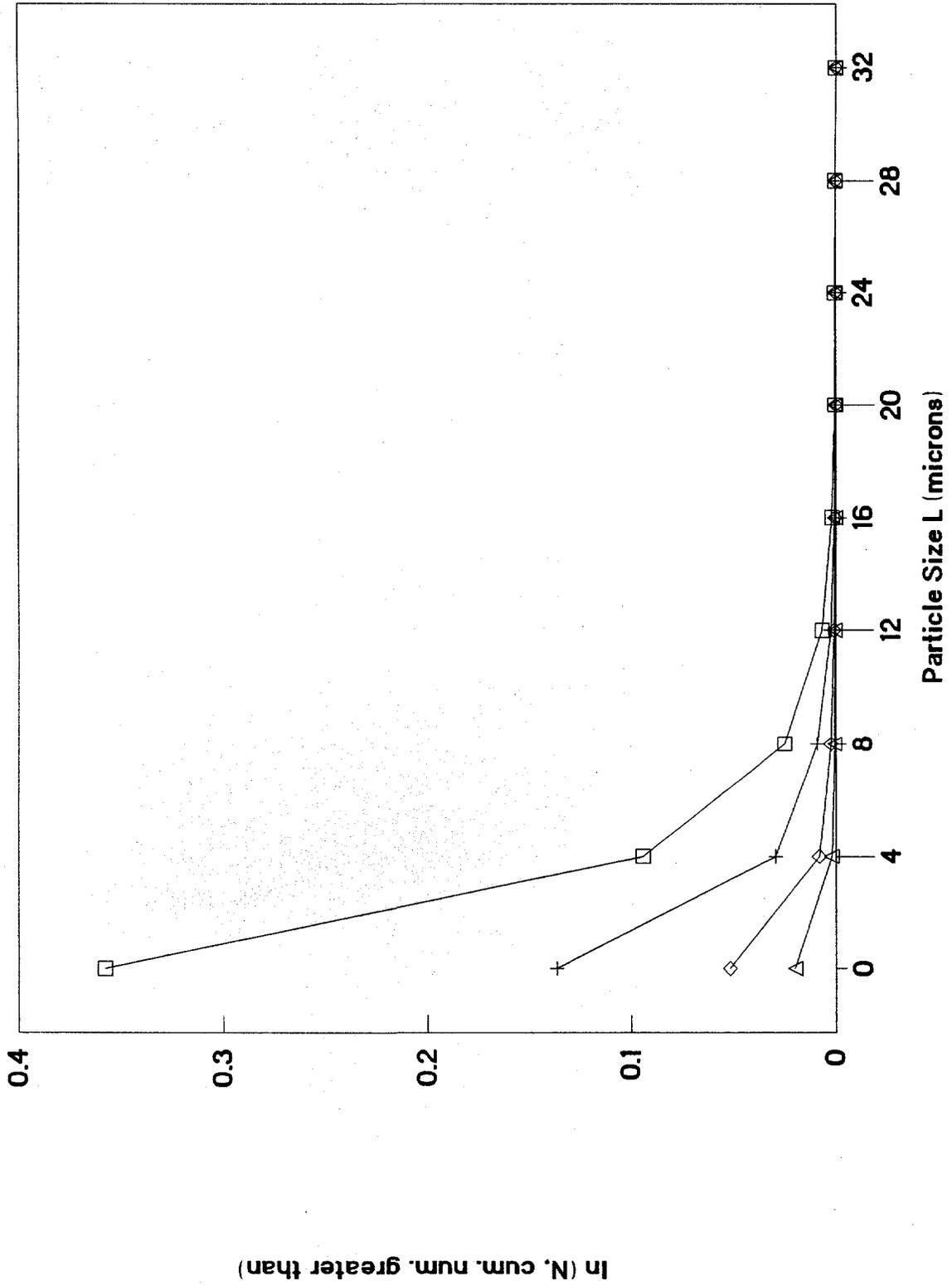
# Figure 4

Res. Time = 135 min., 4 min. elapsed



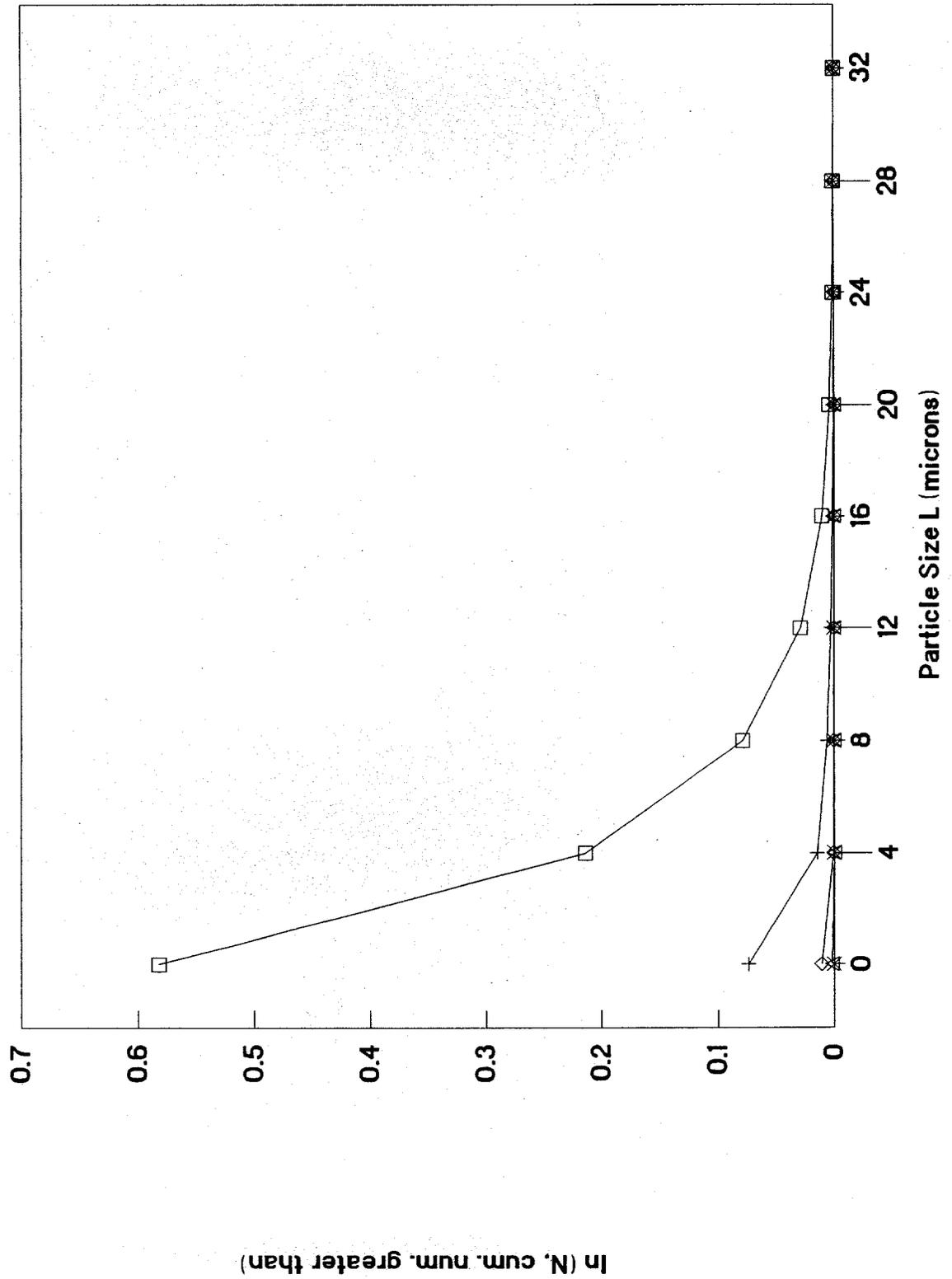
# Figure 5

Res. Time - 10 min., 149 min. elapsed



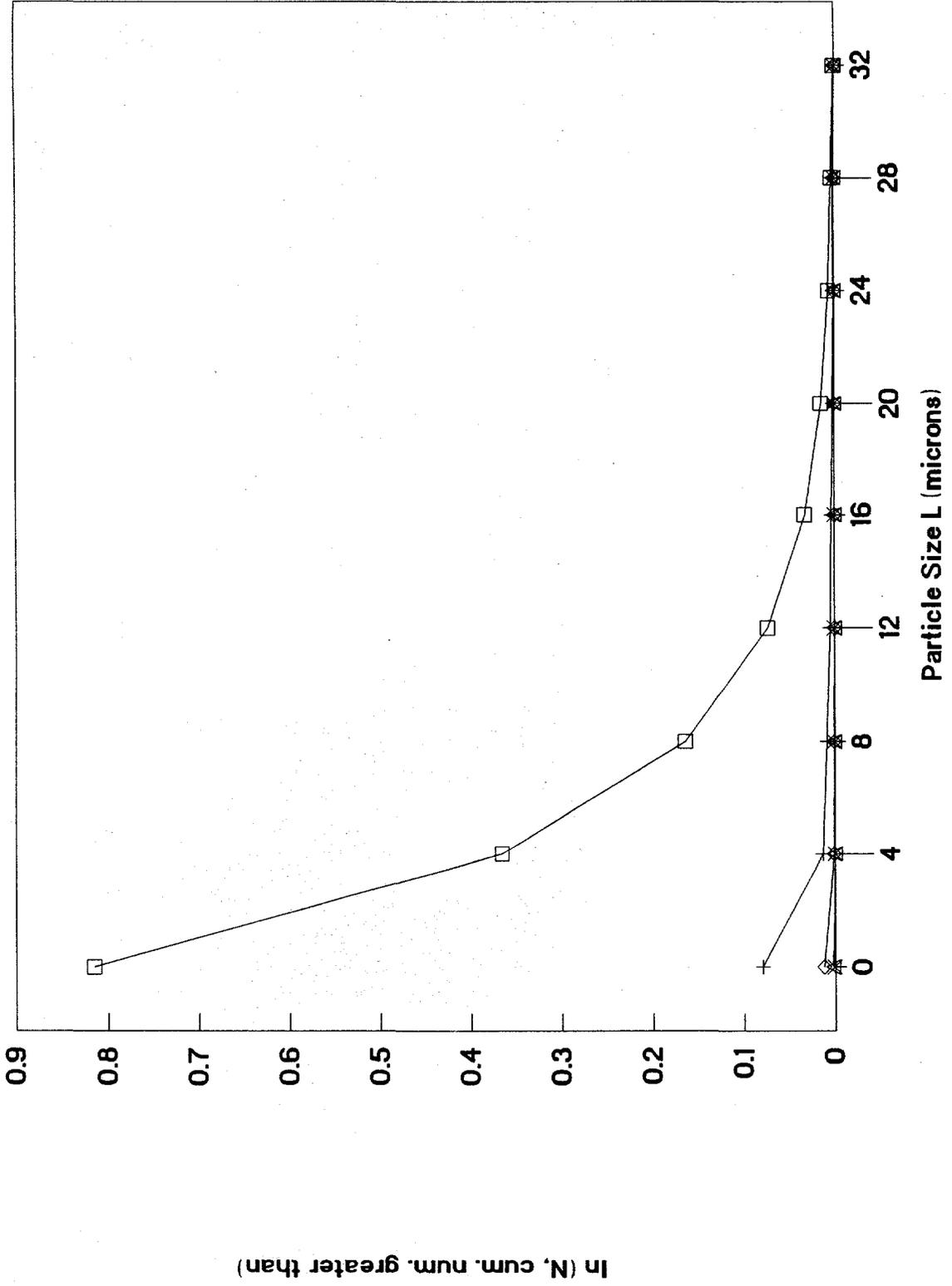
# Figure 6

Res. Time = 10 min., 144 min. elapsed



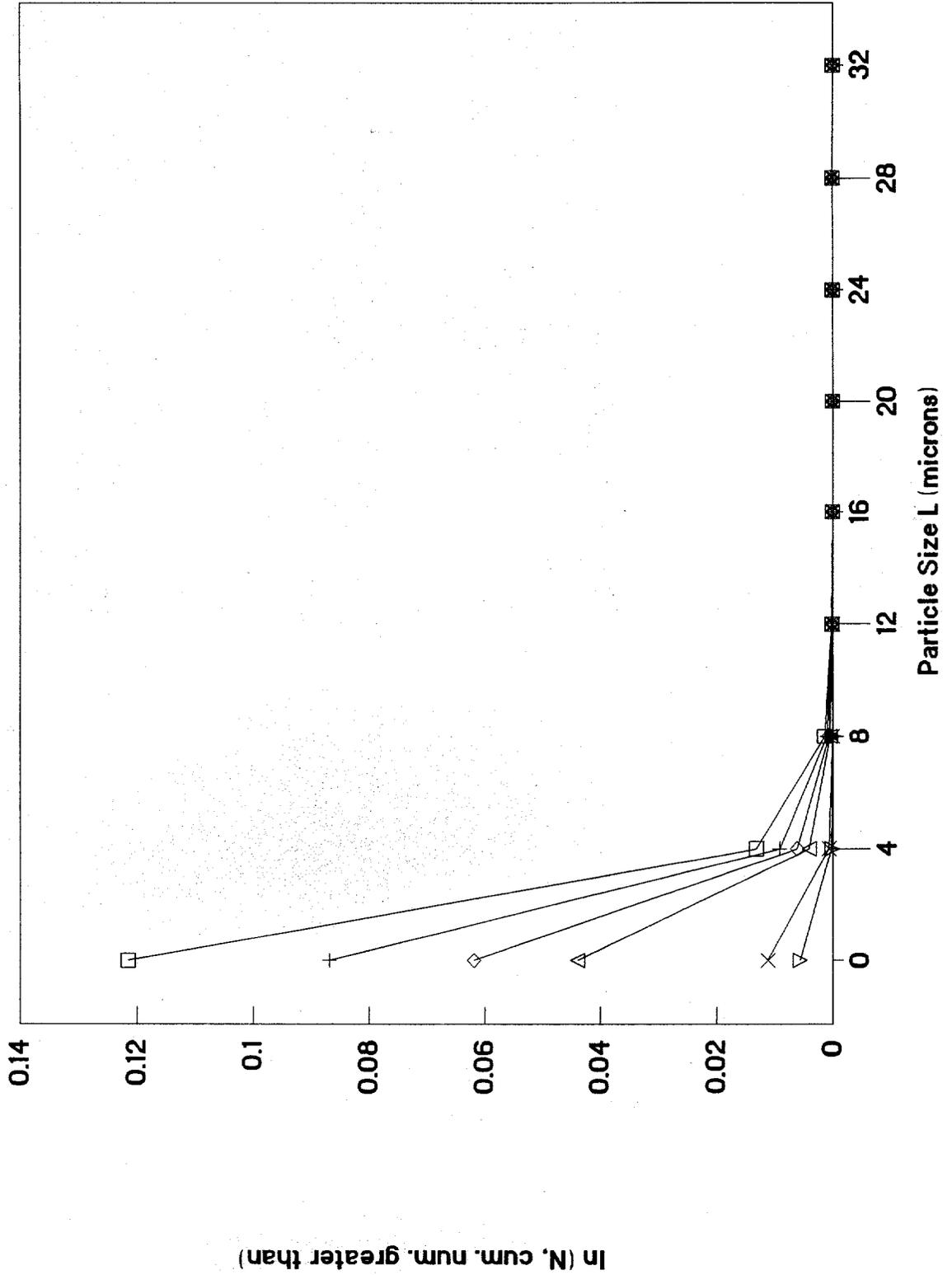
# Figure 7

Res. Time = 10 min., 144 min. elapsed



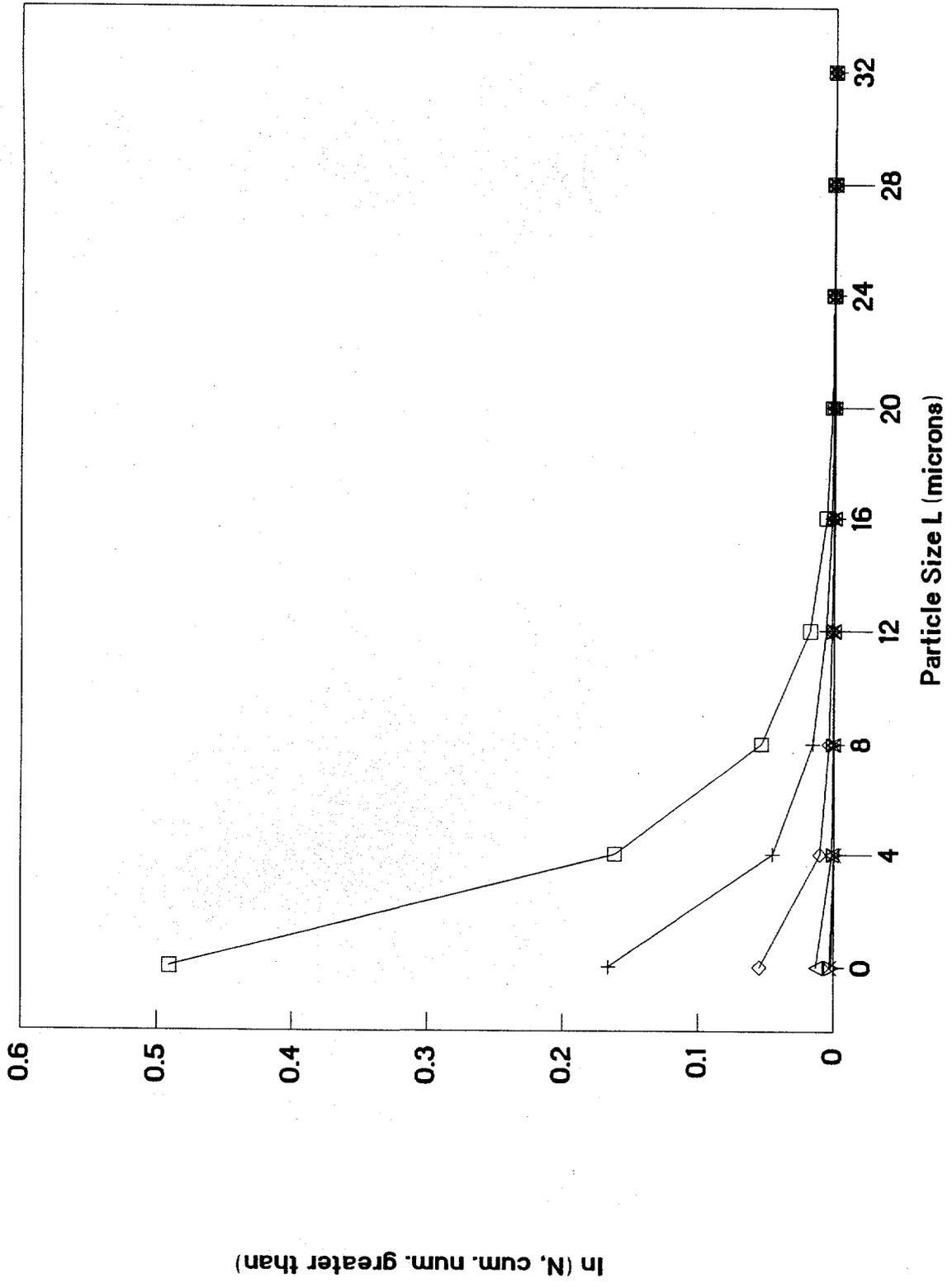
# Figure 8

Res. Time - 60 min., 320 min. elapsed



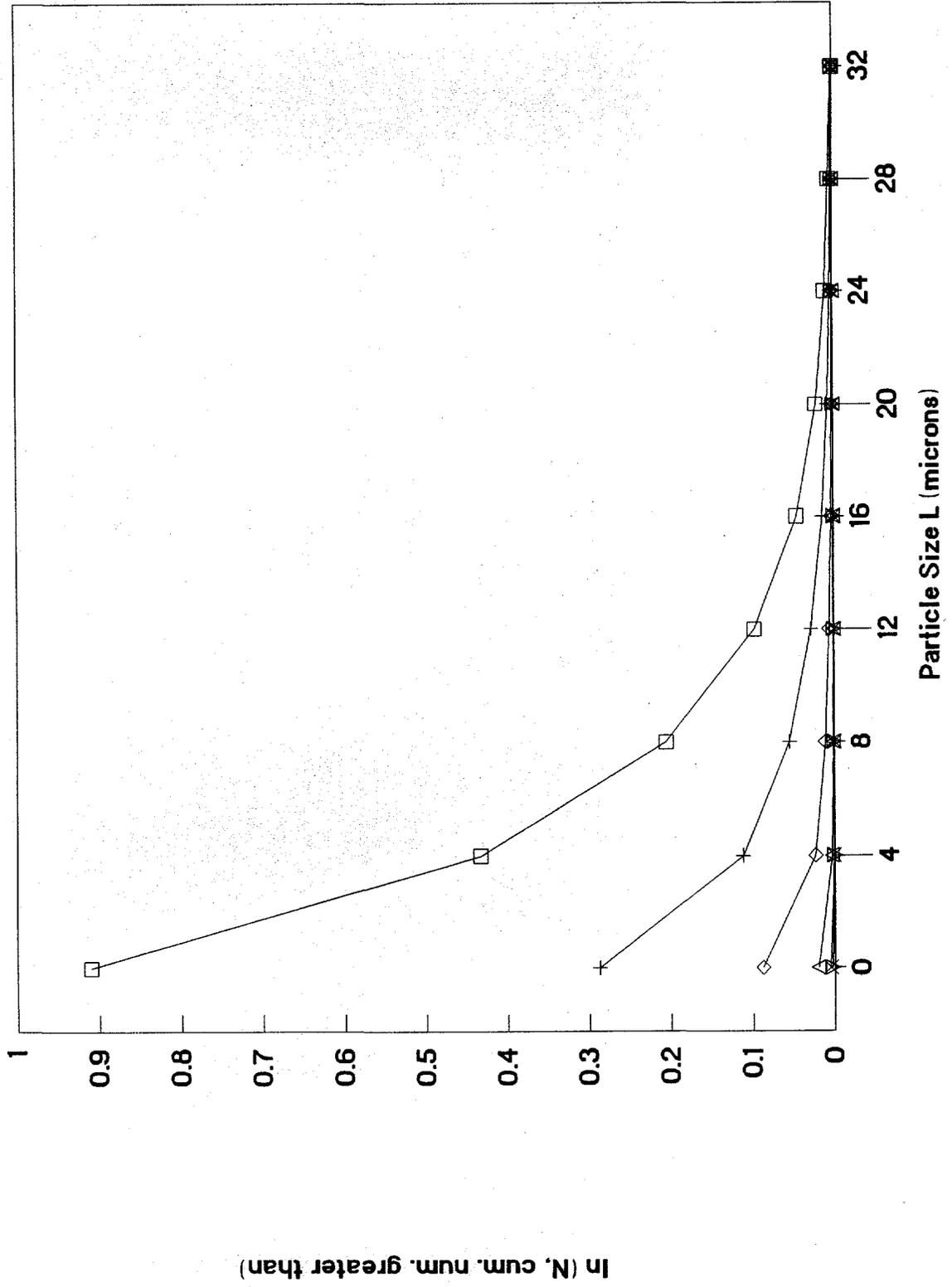
# Figure 9

Res. Time = 60 min., 320 min. elapsed



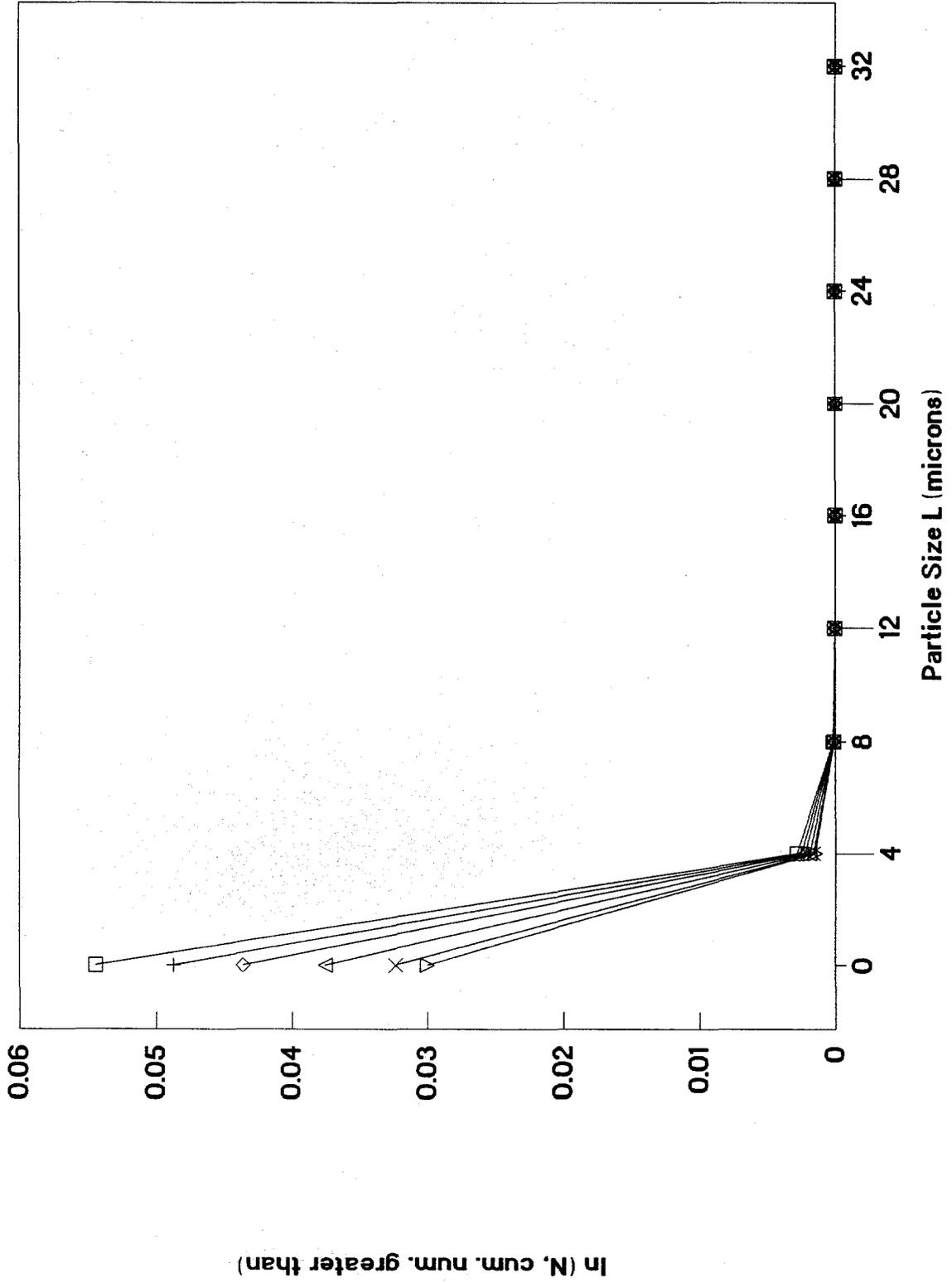
# Figure 10

Res. Time - 60 min., 320 min. elapsed



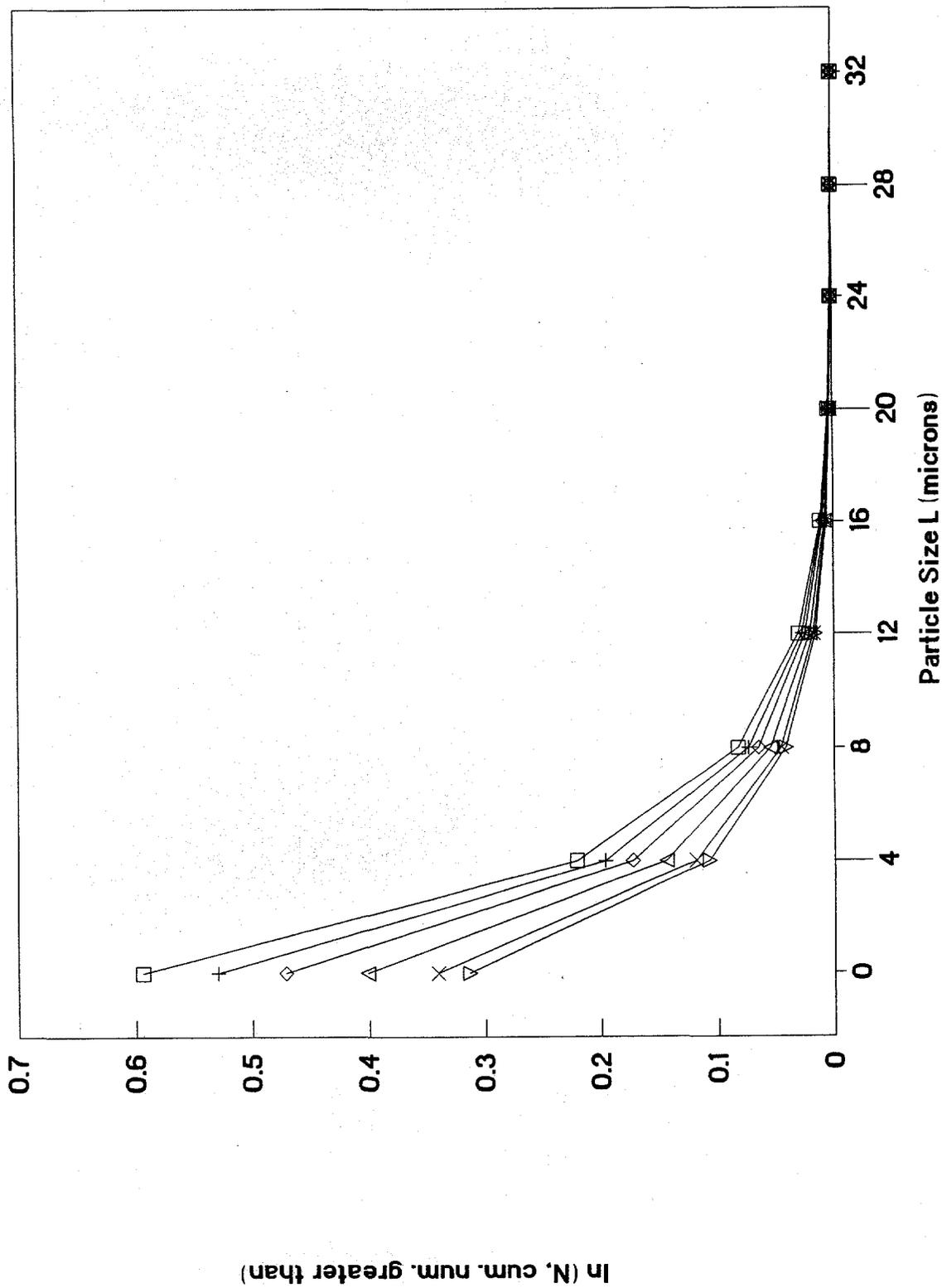
# Figure 11

Res. Time = 135 min., 80 min. elapsed



# Figure 12

Res. Time = 135 min., 80 min. elapsed



# Figure 13

Res. Time = 135 min., 80 min. elapsed

