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INVESTIGATION OF COMBINED SO_2/NO_x REMOVAL BY CERIA SORBENTS

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ABSTRACT

Simultaneous removal of SO_2 and NO_x using a regenerable solid sorbent will constitute an important improvement over the use of separate processes for the removal of these two pollutants from stack gases and possibly eliminate several shortcomings of the individual SO_2 and NO_x removal operations. Recent studies at PETC considered cerium oxide as an alternate sorbent to CuO.

The present study aims to determine the effects of ammonia on the sulfation of the sorbent and to obtain a rate expression for the regeneration of alumina-supported CeO_2 sorbents. In the past quarter the effect of ammonia on sulfation was investigated.

It was found that the presence of ammonia affects the sulfation process unfavorably by forming ammonium sulfate species on the surface which subsequently decompose and cause sulfur loss from the surface. Since formation of surface ammonium sulfates increase the sorbent mass, it is difficult to deduce the magnitude of the sulfur loss from the surface only by thermogravimetric analysis.

I. WORK DONE

A. Introduction

In this quarter of the project, the main focus was on the completion of the experimental program to study the effect of ammonia on sulfation and the evaluation of the data.

B. Experimental Program

The experimental work done in this quarter is summarized below:

- continue with the replicate runs to study the effect of ammonia on sulfation: These replicate runs were performed on fresh sorbent for each run; the particle size of the sorbent is 90-150 μm. The sample size was nominally 3 mg. These runs were repeated because there was the possibility of confounding with the cycling of the sorbent in the previous data.
- start with the experimental program to find the effect of ceria content on sorbent performance.

In the experiments performed under the first item, a sorbent after the following treatment was used: A large amount of ALCOA16-CE4-VI sorbent was placed in a quartz reactor and sulfated under 200 cc/min of standard sulfation gas (SO_2: 3000 ppm, O_2: 3 %, CO_2: 14 %, and N_2 : 82.7 %) at 873 K. Subsequently, the sorbent was regenerated with hydrogen for three hours and then oxidized with 6.6 % oxygen in nitrogen . This pretreatment generated a sorbent characteristic of the sorbent in the second cycle. This approach was adopted because the sorbents showed very reproducible behavior after the first cycle.

C. Data Evaluation

The data from the repeated runs to study the effect of ammonia on the rate of sulfation and sorbent capacity were evaluated by calculation of the initial rate, and the S/Ce ratios as a function of time and conversion during sulfation. As was done previously, the following reaction was assumed to take place during sulfation:

$$2\,CeO_2 + O_2 + 3\,SO_2 \rightarrow Ce_2(SO_4)_3 \qquad (1)$$

The following equations are used to calculate S/Ce and X_s as introduced in the 'July 1994 Progress Report' and used in the 'October 1995 Progress report'.

$$\frac{S}{Ce} = 1.5\frac{\Delta m}{112 n_o} \qquad (2)$$

$$X_s = \frac{\Delta m}{112 n_o} \qquad (3)$$

D. Additional Activities

A batch of fly ash has been obtained from Malcolm-Pirnie and will be used in the next quarter for the evaluation of the effect of fly ash on sulfation. Talks with the engineers at the Malcolm-Pirnie company to evaluate a commercial scale desulfurization system using alumina-supported ceria sorbents has been initiated. The process simulator ASPEN has been purchased ond installed.

II. RESULTS and DISCUSSION

Figures Jan01-Jan07 show the effect of ammonia on the sulfur capacity of the sorbent (as S/Ce ratio) at different temperatures and for different SO_2 partial pressures. Table 1 shows the effect of ammonia on the initial rate of sulfation and sorbent capacity (as S/Ce ratio)

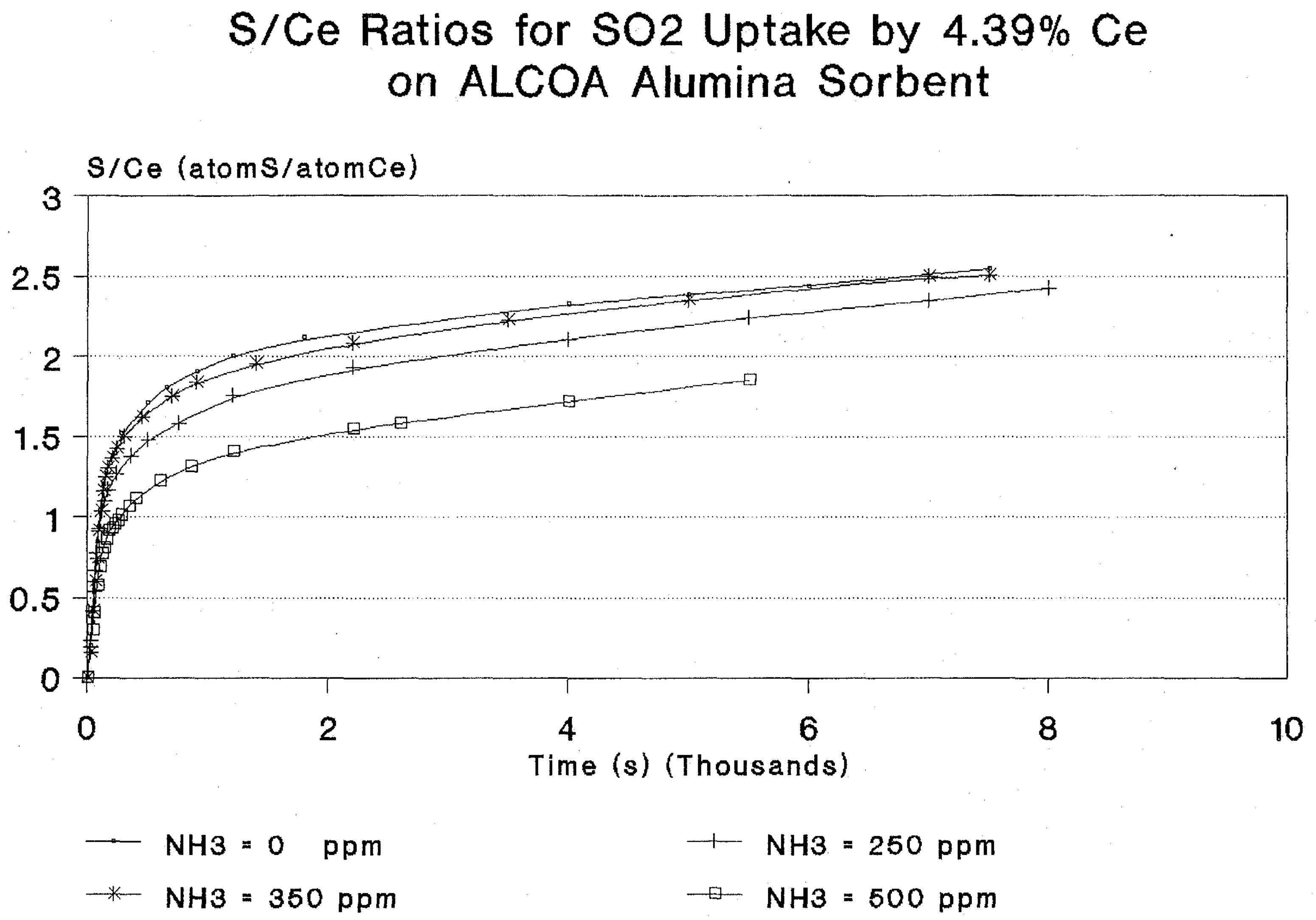


Figure Jan01. Effect of Ammonia
SO2=3000 ppm; T=873 K; 90-150 micron

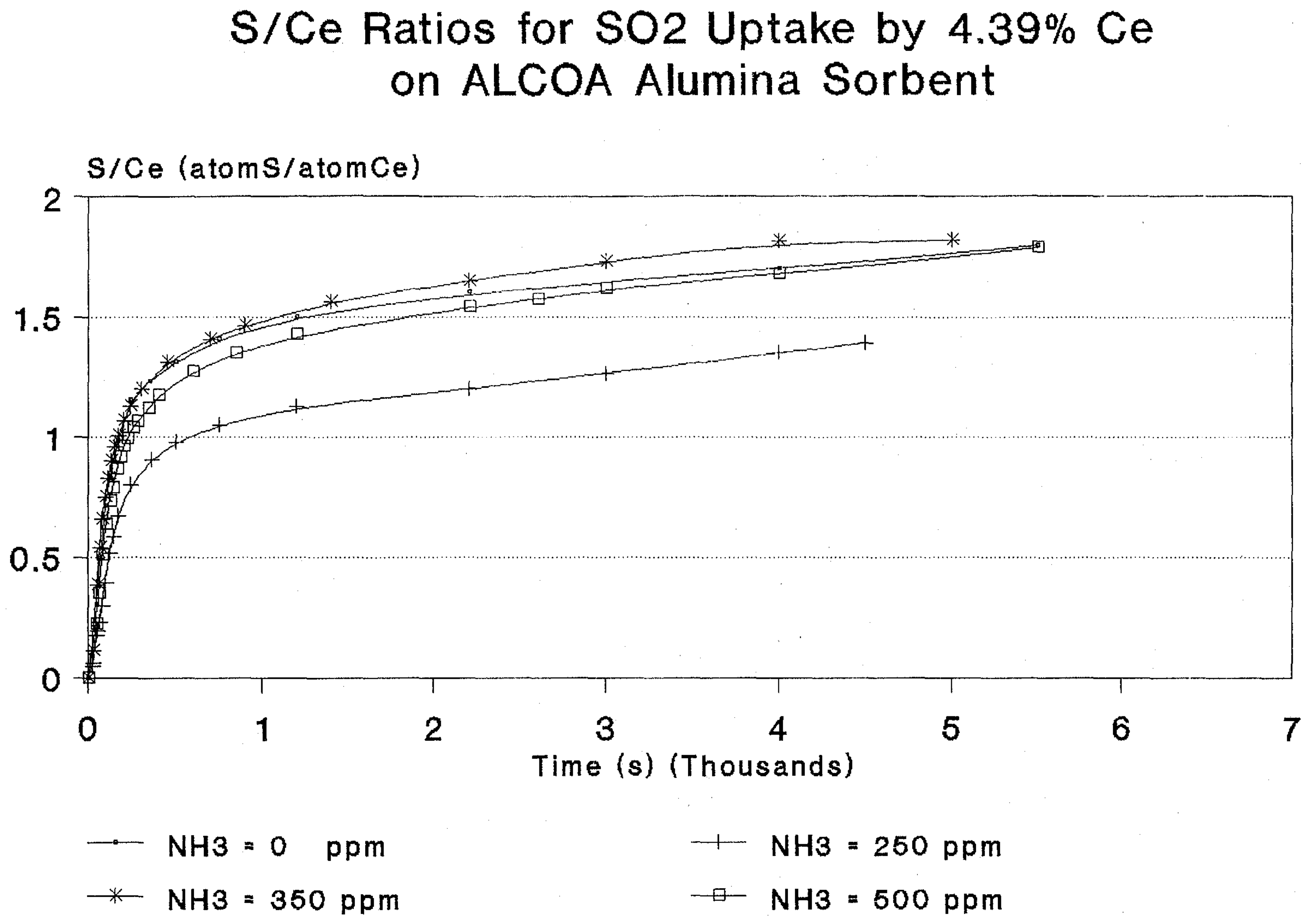


Figure Jan02. Effect of Ammonia
SO2=3000 ppm; T=773 K; 90-150 micron

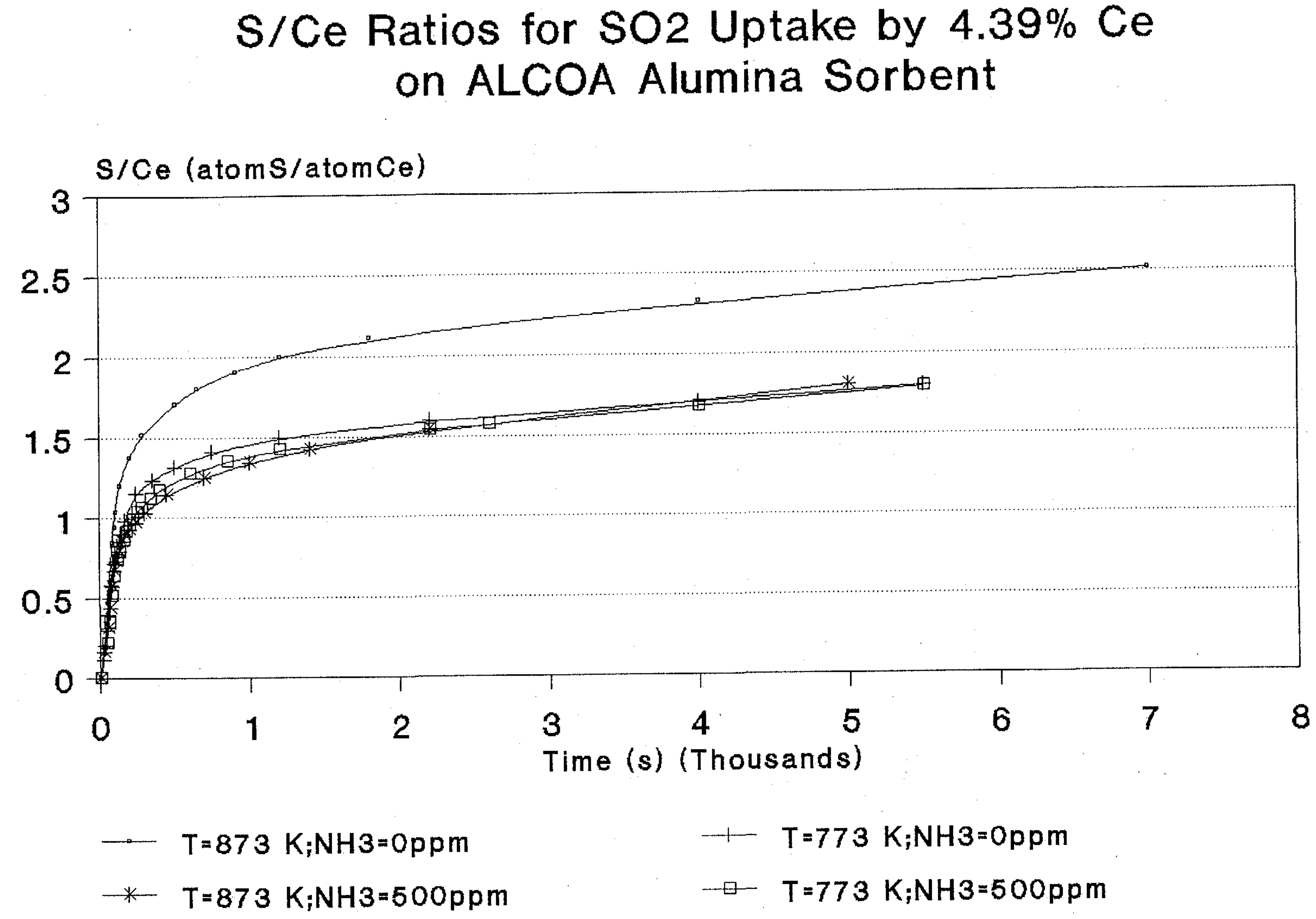


Figure Jan03. Effect of Ammonia
SO2=3000 ppm; 90-150 micron

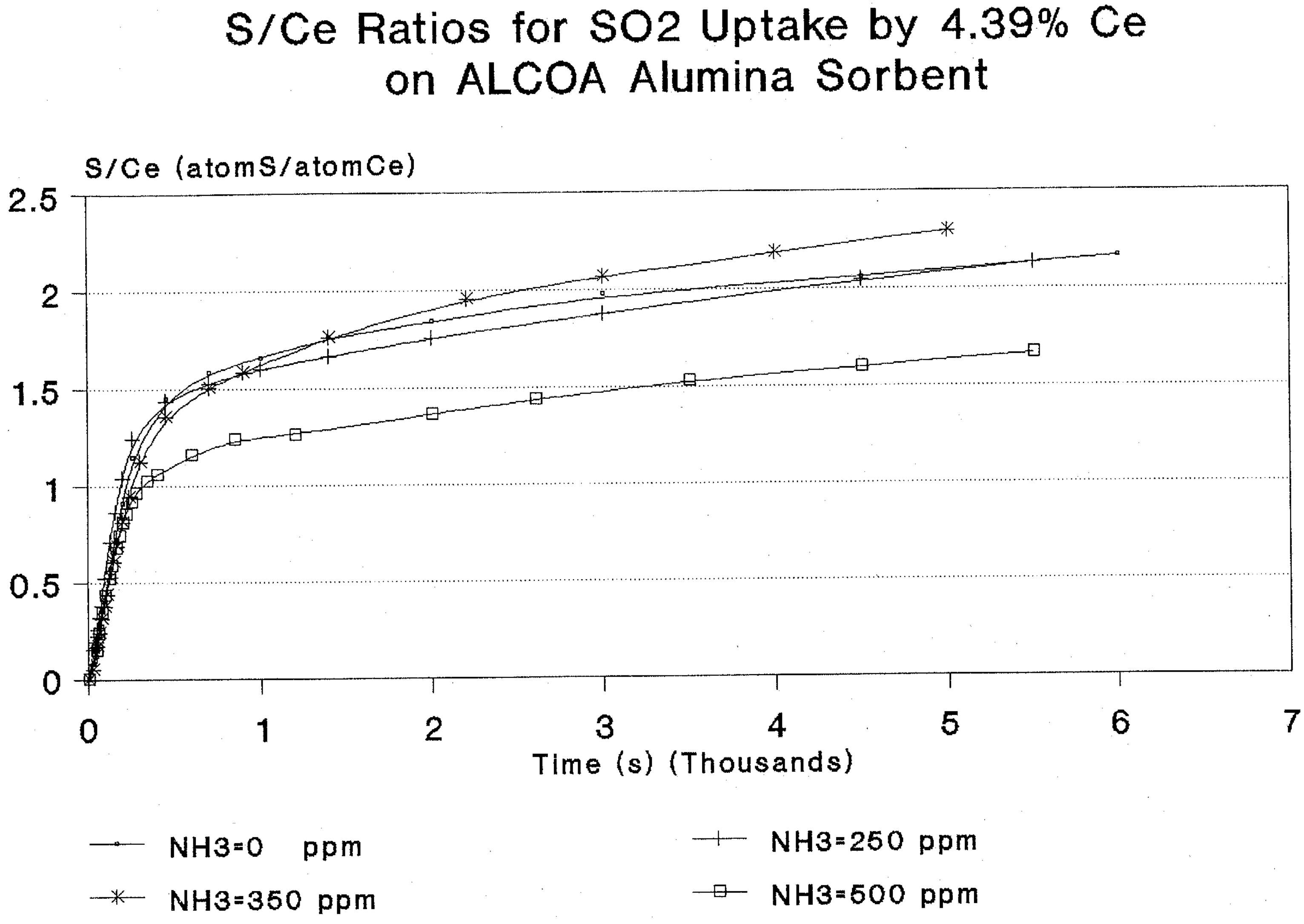


Figure Jan04. Effect of Ammonia
SO2=1500 ppm; T=873 K; 90-150 micron

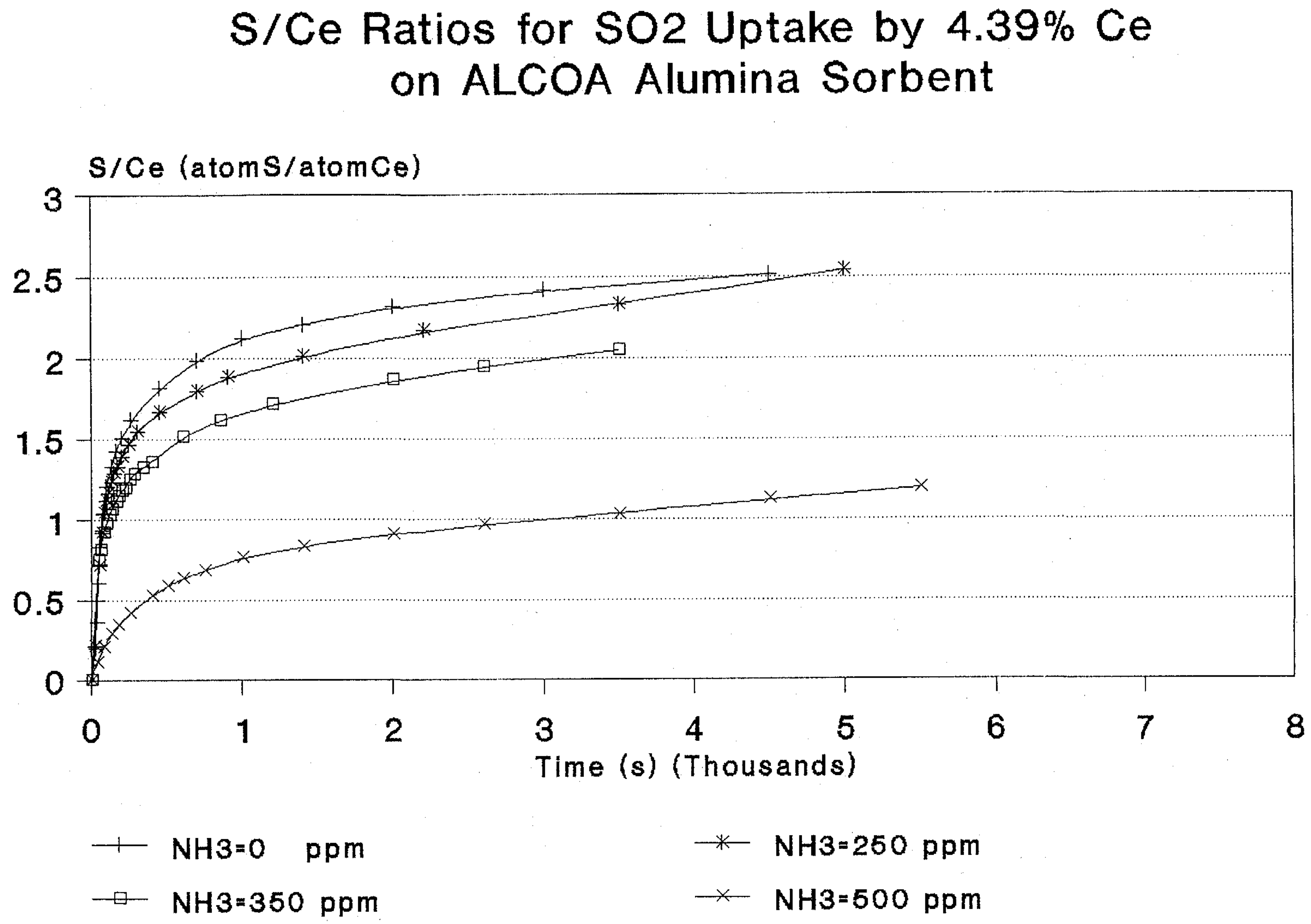
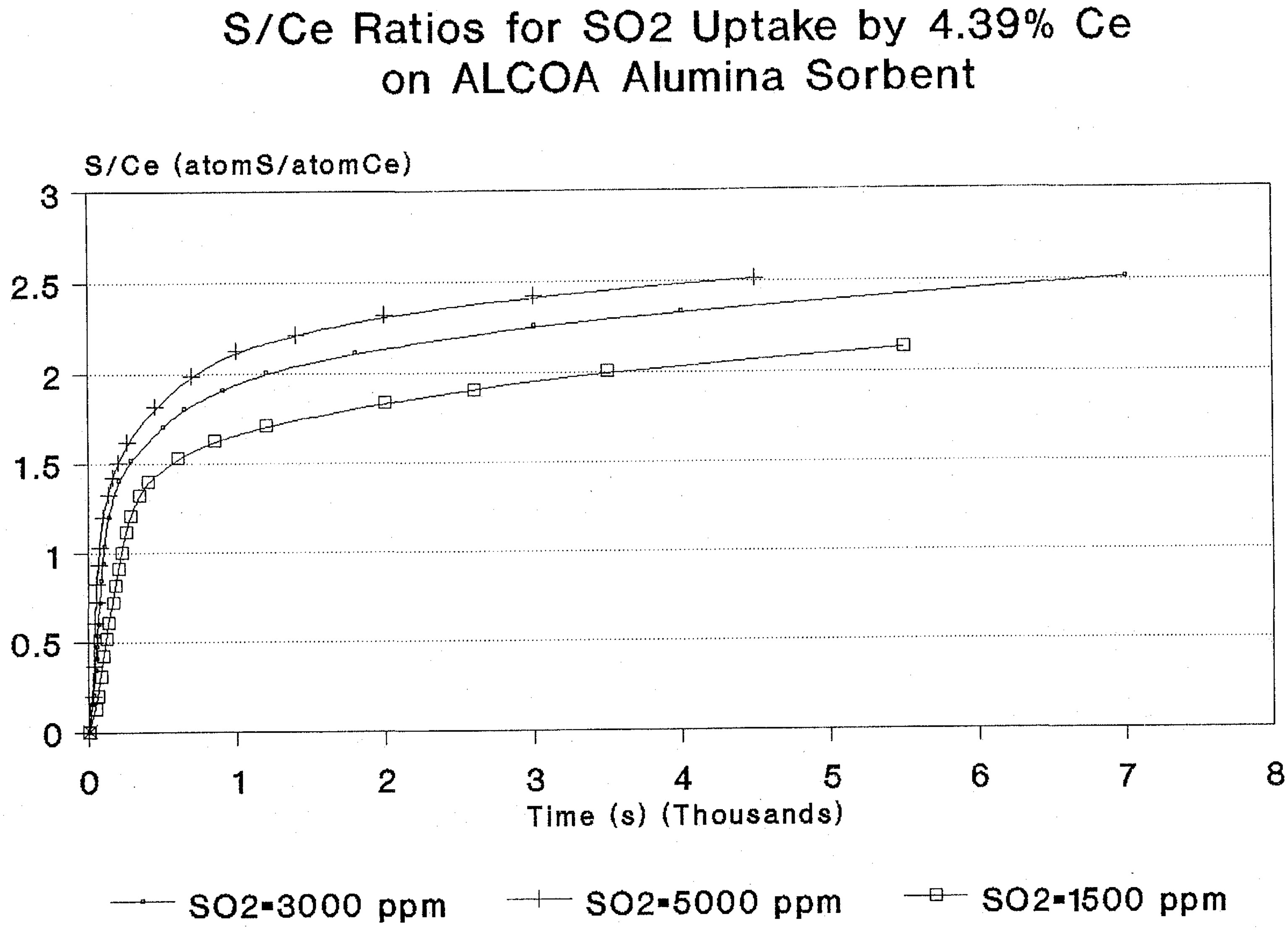
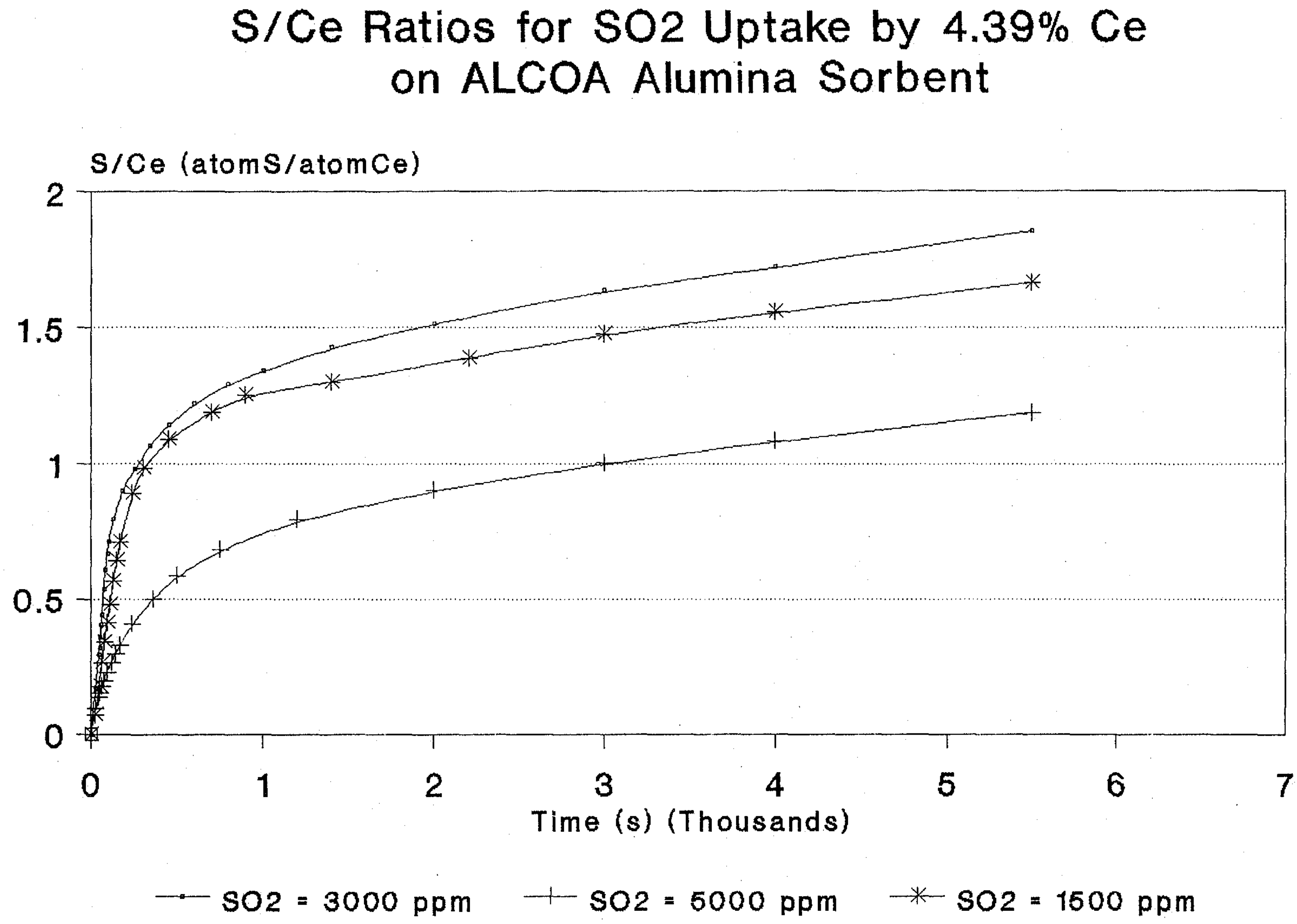


Figure Jan05. Effect of Ammonia
T=873 K; SO2=5000 ppm; 90-150 micron



FigureJan06. Effect of SO2 concentration
T=873 K; no ammonia; 90-150 micron



FigureJan07. Effect of SO2 concentration
T=873 K; NH3=500 ppm; 90-150 micron

after 50 minutes of sulfation.

Table 1. Effect of Ammonia on the Initial Sulfation Rate (R_{SO}) and on S/Ce at 50 minutes for Different Temperatures and p_{SO2}
Sorbent: ALCOA 16-CE4-VI; second cycle

C_{NH3}, ppm	Temperature,K	C_{SO2}, ppm	S/Ce	R_{so}, mol/g.s X 10^{-6}
0	873	1500	1.9734	1.1185
250	873	1500	1.8748	1.1393
350	873	1500	2.0660	0.89343
500	873	1500	1.4761	0.93546
0	873	3000	2.2566	2.4342
250	873	3000	2.0089	2.5009
350	873	3000	2.1742	2.2883
500	873	3000	1.6355	1.6713
0	873	5000	2.4168	5.2772
250	873	5000	2.2748	4.3314
350	873	5000	1.9949	2.7660
500	873	5000	1.0027	3.8794
0	773	3000	1.6589	1.9094
250	773	3000	1.2639	1.0147
350	773	3000	1.7275	2.0587
500	773	3000	1.6146	1.5646

For the data in Table 1, two facts should be noted: The S/Ce values at 50 minutes does not represent the ultimate sorbent capacity under the conditions specified, but is an indication of the overall sulfation rate. This argument is based on theobservation form Figures Jan01 - Jan07 that beyond 50 minutes, S/Ce ratios increase at almost constant rate indicating that the sorbent might end up capturing about 2.5 S atoms per Ce atom if sufficient sulfation time is allowed. Secondly, the comparison of the overall rate indicated by the S/Ce ratio at 50 minutes and the initial rates given in the last column should indicate whether the observed effect of ammonia is on the sulfation kinetics or due to changes in surface area or magnitudes of mass transfer resistances.

With the above considerations the following observations can be made:

- For 1500 ppm and 3000 ppm SO_2 concentrations the effect of ammonia is minimum for 350 ppm ammonia at both 873 and 773 K. Introduction of 500 ppm ammonia results in very significant decrease in the overall rate.
- Same observations can be made for initial rates at 773 K but at 873 K no definite trend can be observed for the effect of ammonia. Considering the lower accuracy of the initial rate data, it may be said that there is no significant effect of ammonia on the initial rates.
- Figures Jan02, Jan04, and Jan05 appear to show a possibility for increasing sulfur capacity in the presence of some ammonia. This observation may be misleading because the S/Ce ratios were determined by assuming all the weight gain during sulfation to be the result of Equation 1. It is possible that some of the weight gain is the result of the formation of ammonium sulfate species on the surface as discussed below.

Several processes may take place when sulfation gases contain some ammonia. Since it has been reported that(1) ceria -based sorbents have high activity and selectivity for catalytic reduction of NO with ammonia at high temperatures (above 773 K), it is expected that some ammonia will chemisorb on the sorbent forming ammonium sulfate species. At the high temperatures under consideration these species are unstable and will decompose giving SO_3 and H_2O, or the sulfates may be reduced by ammonia on the surface to sulfites which may desorb forming SO_2 and H_2O. Ammonia may also be oxidized to N_2 and H_2O or may form some nitrate species on the surface which may further react with ammonia to form nitrogen oxides. The rate of chemisorption of ammonia will depend on the temperature and partial pressure of ammonia. The rates of decomposition of surface species and desorption also depend on temperature. Without any further information about the surface species, adsorption and desorption rates, and reactor effluent compositions, only a tentative explanation of our observations can be proposed.

The apparent increase in the S/Ce ratios, which we will assume to be due to the chemisorption of ammonia and formation of surface ammonium sulfate species, will increase with ammonia partial pressure and decrease with temperature. Rate of decomposition of surface species will increase with the concentration of surface ammonium sulfates and with temperature. Also, larger ammonia partial pressures may enhance reduction of surface sulfates and facilitate the decomposition of surface species. In summary, the increase in the ammonium sulfate species on the surface will increase the apparent S/Ce ratio and the decomposition of these species will result in sulfur loss and decrease the S/Ce ratio. From the observed S/Ce ratios, it appears that at low ammonia partial pressures, the rate of formation of surface ammonia species is faster than their decomposition and hence apparent S/Ce ratios are larger. On the other hand, at higher ammonia partial pressures the decomposition and reduction of surface sulfates become significant and lower S/Ce ratios are observed.

Observations with 5000 ppm SO_2 indicate that at high SO_2 partial pressures, even a small amount of ammonia causes sulfur loss from the surface and there is no apparent increase in the S/Ce ratio with ammonia addition.

FUTURE WORK

In the next quarter, it is planned :

1) to continue with the evaluation of the data generated in the last quarter;

2) to complete the experimental program to study the effect of fly ash on sulfation;

3) to investigate the adsorption and desorption of ammonia on fresh and sulfated sorbents;

4) to determine the dissociation temperature of sulfate species formed;

3) to continue with the modeling of the sulfation and regeneration reactors; and

4) to continue cooperation with the industrial partner on the economic evaluation of the process.

BIBLIOGRAPHY

1. **Longo, T. M. And Cull, N. L.**, "Process for the Removal of SO_2 and No_x from Gaseous Mixtures Containing the Same," U. S. Patent #4251496, 1981.