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INVESTIGATION OF COMBINED SO_2/NO_x REMOVAL BY CERIA SORBENTS

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Table of Contents

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. The sulfation experiments indicated that 100% conversion of ceria could be attained. Activation energy for the sulfation reaction was found to be 19 kJ/mol. The rate of sulfation reaction is first order with respect to SO_2 and solid reactant concentrations. For regeneration with hydrogen, the activation energy and the reaction order with respect to hydrogen was found to be 114 kJ/mol and 0.56, respectively. The ceria sorbent preserved its activity and structural stability after 6 cycles.

The information obtained from these studies will be used to develop models for reactor-regenerator configurations. Subsequently, the SO_2/NO_x removal facility will be integrated into the power production process using a commercial process simulation software.

I. WORK DONE

A. Introduction

In this quarter of the project, the main focus was on the performance of the experimental program for the regeneration of the ceria sorbent by hydrogen and evaluation of the experimental results.

B. Experimental Program

For the regeneration experiments, a large sample of sulfated sorbent was prepared. The ceria sorbent prepared previously (ALCOA16-CE4-VI) was crushed and sieved to the 90-150 µm, 75-90 µm, and <75 µm fractions. The experimental setup was modified by replacing the TGA reactor with a quartz tubular reactor which is of 1.5 cm ID in the middle, and 1 cm ID otherwise. The reactor is fitted with a quartz frit of 20 µm to hold a fixed bed of sorbent. This reactor was loaded with 0.5 g of the 90-150 µm fraction of the ALCOA16-CE4-VI sorbent, which was subsequently sulfated for seven hours with 400 cc/min of a sulfation gas of the following composition: 0.3% SO_2, 3% O_2, 14% CO_2, and 82.7% N_2. Then the reactor was cooled under a nitrogen atmosphere; and the sulfated sorbent was stored to be used for the regeneration experiments.

In the regeneration experiments to be performed in the TGA, it was decided to put some quartz wool into the pan in order to disperse the sulfated sample. However, this caused static in the TGA reactor. Static was eliminated and it was decided to leave the quartz wool in the pan for the regeneration experiments.

Hydrogen was the first regeneration agent to be used. Due to its low molecular weight, buoyancy effects were appreciable in the TGA. Therefore blank tests were run with no sorbent in the pan and thermograms were obtained for these runs in the TGA to be used for the correction of the buoyancy and gas switching effects.

The following procedure was used during the regeneration runs:

3.5 mg of the sulfated sorbent (ALCOA16-CE4-VI) was heated to the regeneration temperature under a nitrogen flow rate of 200 cc/min. After the heat-up period, time was allowed for the desorption of all adsorbed species. After the weight of the sample became reasonably constant, the reactant gases, consisting of hydrogen and nitrogen, were introduced into the TGA reactor by the switching valves. The sulfated sorbent was exposed to the regeneration gases until no further weight changes occurred. When the regeneration was complete, the system was cooled to room temperature under nitrogen flow.

The hydrogen concentration in the regeneration gases and the reaction temperature were the main variables used during the regeneration tests. The hydrogen concentration was varied between 10 and 75% (by mole), while the temperature range was 773 - 873 K.

Thermograms corrected for buoyancy effects were obtained by subtracting the blank runs from the test runs. To do this first both data are lightly smoothed. Then, the times for both runs were matched at the tip of the small flow disturbance peak which occurred when the reactant gases were switched on. The corrected data were then obtained as the difference of the test run and the blank run data. The initial linear portion of the corrected regeneration weight versus time data was used to obtain the initial rate for the run.

C. Data Evaluation

The regeneration data were evaluated using the following stoichiometry:

$$Ce_2(SO_4)_3 + 3H_2 \rightarrow Ce_2O_3 + 3SO_2 + 3H_2O \tag{1}$$

The conversion of $Ce_2(SO_4)_3$ is calculated from the mass data as follows: Cerium to alumina mass ratio in the original sample,

$$\frac{m_{Ce}}{m_{Al_2O_3}} = \frac{w_{Ce}}{1 - w_{Ce}} \tag{2}$$

where w indicates mass fraction. The cerium to alumina mole ratio is

$$\frac{n_{Ce}}{n_{Al_2O_3}} = \left(\frac{m_{Ce}}{m_{Al_2O_3}}\right)\left(\frac{M_{Al_2O_3}}{M_{Ce}}\right) \tag{3}$$

where M indicates the molecular weight. Then the mass of $Ce_2(SO_4)_3$ in the original sulfated sample becomes

$$m_{o,Ce_2(SO_4)_3} = \left(\frac{n_{Ce}}{n_{Al_2O_3}}\right)\left(\frac{m_{Al_2O_3}}{M_{Al_2O_3}}\right)\left(\frac{M_{Ce_2(SO_4)_3}}{2}\right) \tag{4}$$

The initial mass of the sulfated sample, m_o can be written using this relationship.

$$m_o = m_{o,Ce_2(SO_4)_3} + m_{Al_2O_3} = [1 + 2\ (\frac{n_{Al_2O_3}}{n_{Ce}})\ (\frac{M_{Al_2O_3}}{M_{Ce_2(SO_4)_3}})\ ]\ (m_{o,Ce_2(SO_4)_3}) \tag{5}$$

Mass of sample, m, at any time during the reaction will be

$$m = m_o - x\ (\frac{m_{o,Ce_2(SO_4)_3}}{M_{Ce_2(SO_4)_3}})\ (M_{Ce_2(SO_4)_3} - M_{Ce_2O_3}) \tag{6}$$

Therefore, the conversion of $Ce_2(SO_4)_3$ at anytime during regeneration becomes

$$x = \frac{(m_o - m)\ (M_{Ce_2(SO_4)_3})}{(m_{o,Ce_2(SO_4)_3})\ (M_{Ce_2(SO_4)_3} - M_{Ce_2O_3})} \tag{7}$$

Hence,

$$\frac{dx}{dt} = -\frac{(M_{Ce_2(SO_4)_3})}{(m_{o,Ce_2(SO_4)_3})\ (M_{Ce_2(SO_4)_3} - M_{Ce_2O_3})}\ (\frac{dm}{dt}) \tag{8}$$

The rate of the regeneration reaction, r, is written as

$$r = -k\ p_{H_2}^{\ a}\ \ c_{CS}^{\ b} \tag{9}$$

where k is the reaction rate constant and a and b are the reaction orders with respect to hydrogen and cerium sulphate,respectively. The subscript CS indicates $Ce_2(SO_4)_3$. Moles of cerium sulfate present at any time, can be written in terms of conversion

$$n_{Ce_2(SO_4)_4} = (1 - x)\ \ (\frac{m_{o,Ce_2(SO_4)_3}}{M_{Ce_2(SO_4)_3}}) \tag{10}$$

The reaction rate becomes

$$r = \frac{1}{m_o} \frac{dn_{o,Ce_2(SO_4)_3}}{dt} = -\frac{1}{m_o} \frac{m_{o,Ce_2(SO_4)_3}}{M_{Ce_2(SO_4)_3}} \frac{dx}{dt} \tag{11}$$

or , using equation (8)

$$r = \frac{1}{(M_{Ce_2(SO_4)_3} - M_{Ce_2O_3})} \left(\frac{dm}{dt}\right) \tag{12}$$

D. Additional Activities

In addition to the above activities, a presentation entitled 'Investigation of the Regeneration of Ceria Sorbents for Simultaneous SO_2/NO_x Removal' was made at the AIChE Annual Meeting held at San Francisco, CA in November 13-18, 1994, in the symposium Gas Purification-I (paper 246f). A copy of the extended abstract is included in Appendix I.

An abstract entitled 'Investigation of the Effect of Ammonia on Ceria Sorbents During Simultaneous SO_2/NO_x Removal' has been submitted to the Catalysis Society 14th North American Meeting to be held in Snowbird, Utah on June 11-16, 1995. A copy of the abstract is included in Appendix II.

II. RESULTS and DISCUSSION

The results from the regeneration tests are summarized below. Figure 1 shows the Arrhenius plot for the regeneration reaction with 50 % hydrogen (Equation 1). The activation energy is found to be 114 kJ/mol (27 kcal/ mol).

Figure 2 is the log-log plot of initial rate versus hydrogen mole fraction. The spread in data points at high hydrogen concentrations is mainly due to the errors introduced in accounting for the buoyancy effect during data analysis. The reaction order with respect to hydrogen is determined from the slope of this curve as 0.56. This fractional order can be explained by using Langmuir-Hinshelwood kinetics. For dissociative adsorption of hydrogen

$$r = \frac{k_2 p_{H_2}}{[1 + (K_1 p_{H_2})^{1/2}]^2} \tag{13}$$

Equation (13) was linearized as shown in equation (14)

$$\sqrt{\frac{p_{H_2}}{r}} = \sqrt{\frac{K_1}{k_2}} \sqrt{p_{H_2}} + \frac{1}{\sqrt{k_2}} \tag{14}$$

and fitted to initial rate versus hydrogen fraction data using a linear regression software. The correlation coefficient for the fit is 0.95844 and the estimates for K_1 and k_2 are

$K_1 = 9.23$
$k_2 = 1.17$

The conversion versus time data are given in Figure 3. It is apparent that even with a regeneration gas containing 10 % hydrogen 70 % conversion is attained within 10 minutes. Figure 4 shows the effect of temperature on equilibrium conversion. This figure suggests that equilibrium conversion decreases with temperature. At 773 K the rate of reaction becomes so small that the curve for this temperature does not give any indication of equilibrium conversion.

If the reaction rate is first order with respect to the solid reactant conversion will change with time according to equattion (14).

$$-\ln(1 - x) = k_1 t$$

Figure 5 shows a plot of -ln(1-x) versus time. It can be seen from this figure that the reaction is first order with respect to solid reactant up to about 40 % conversion.

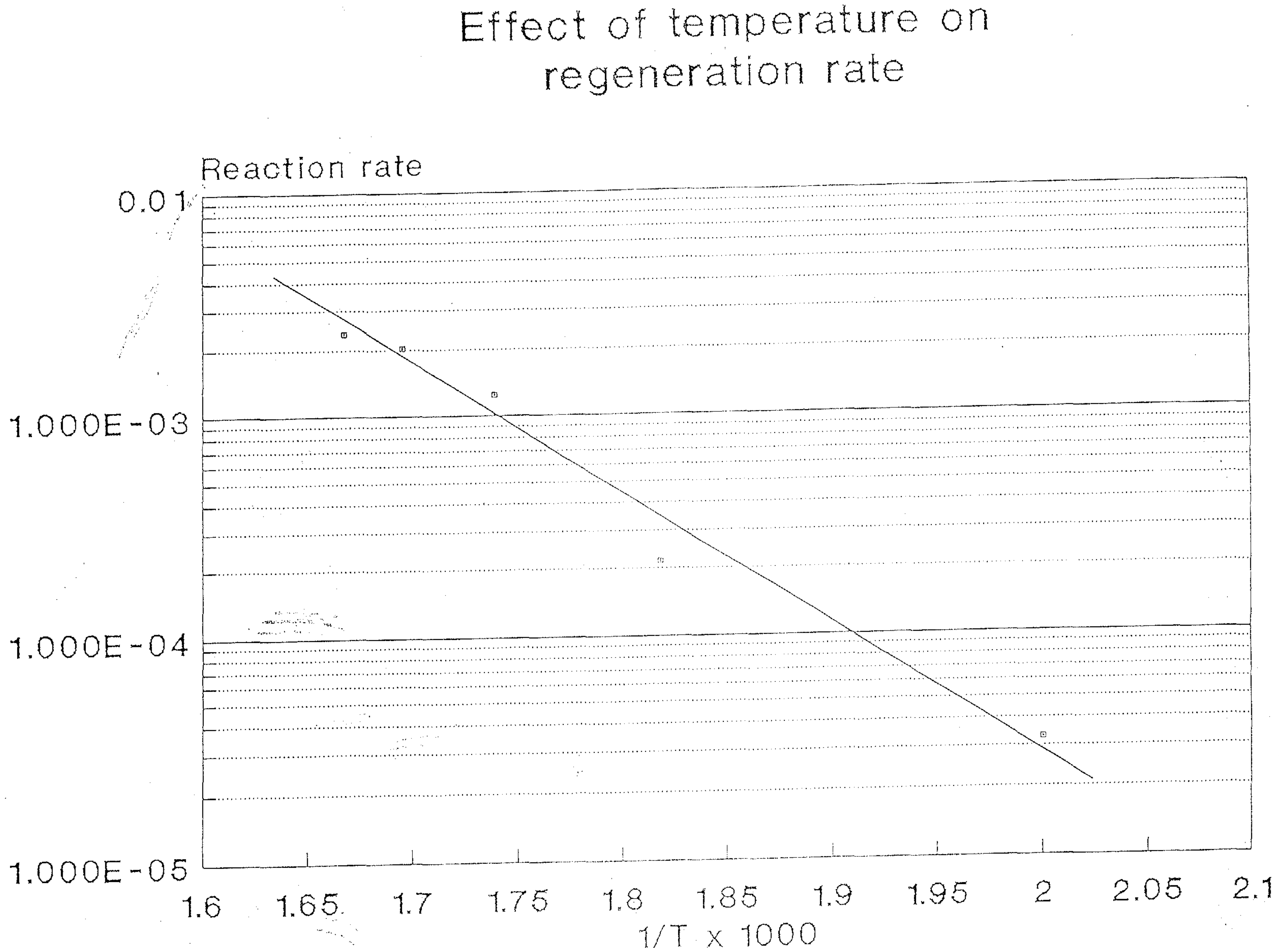

Figure 1. H2 mole fraction = 0.5

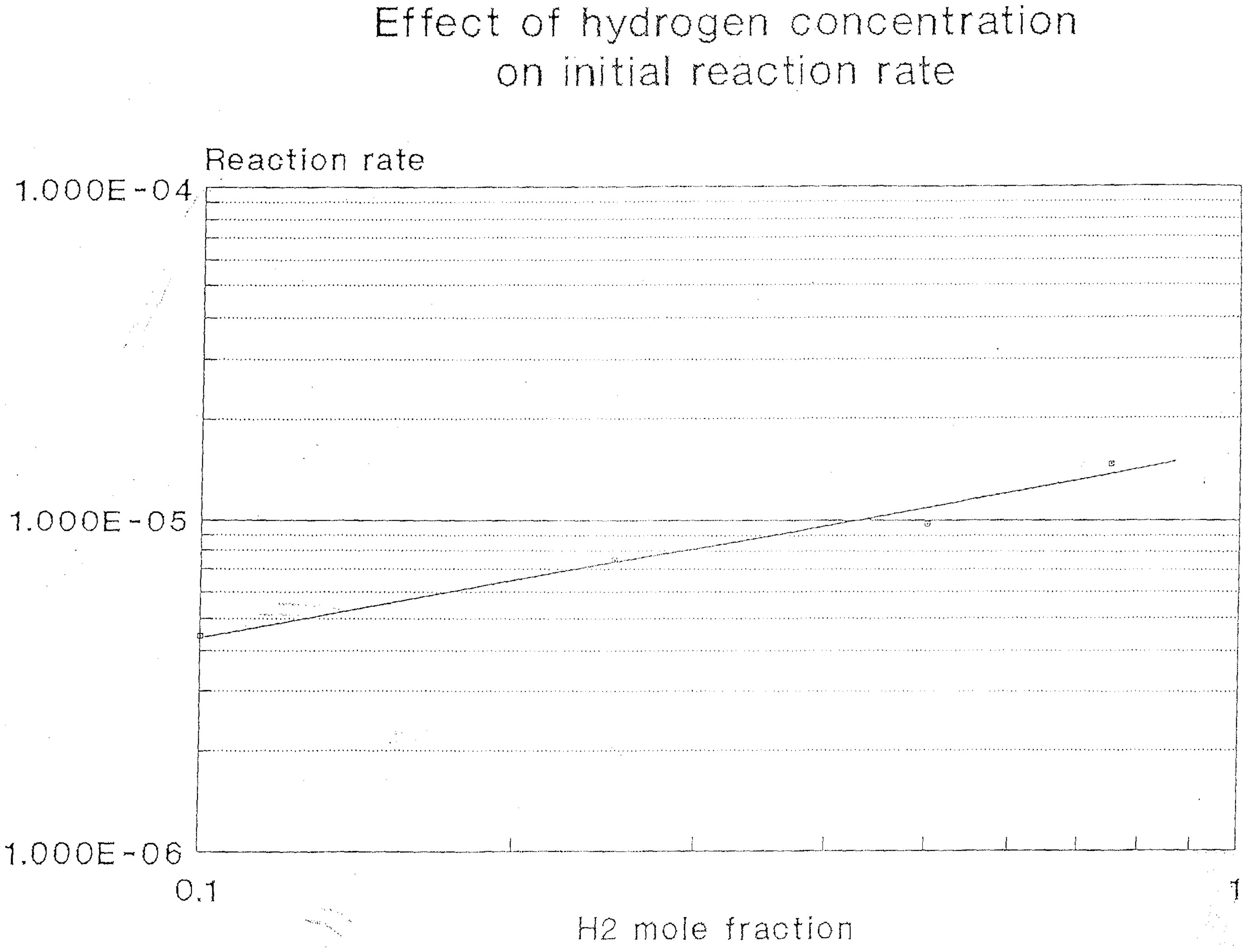

Figure 2. T = 873 K

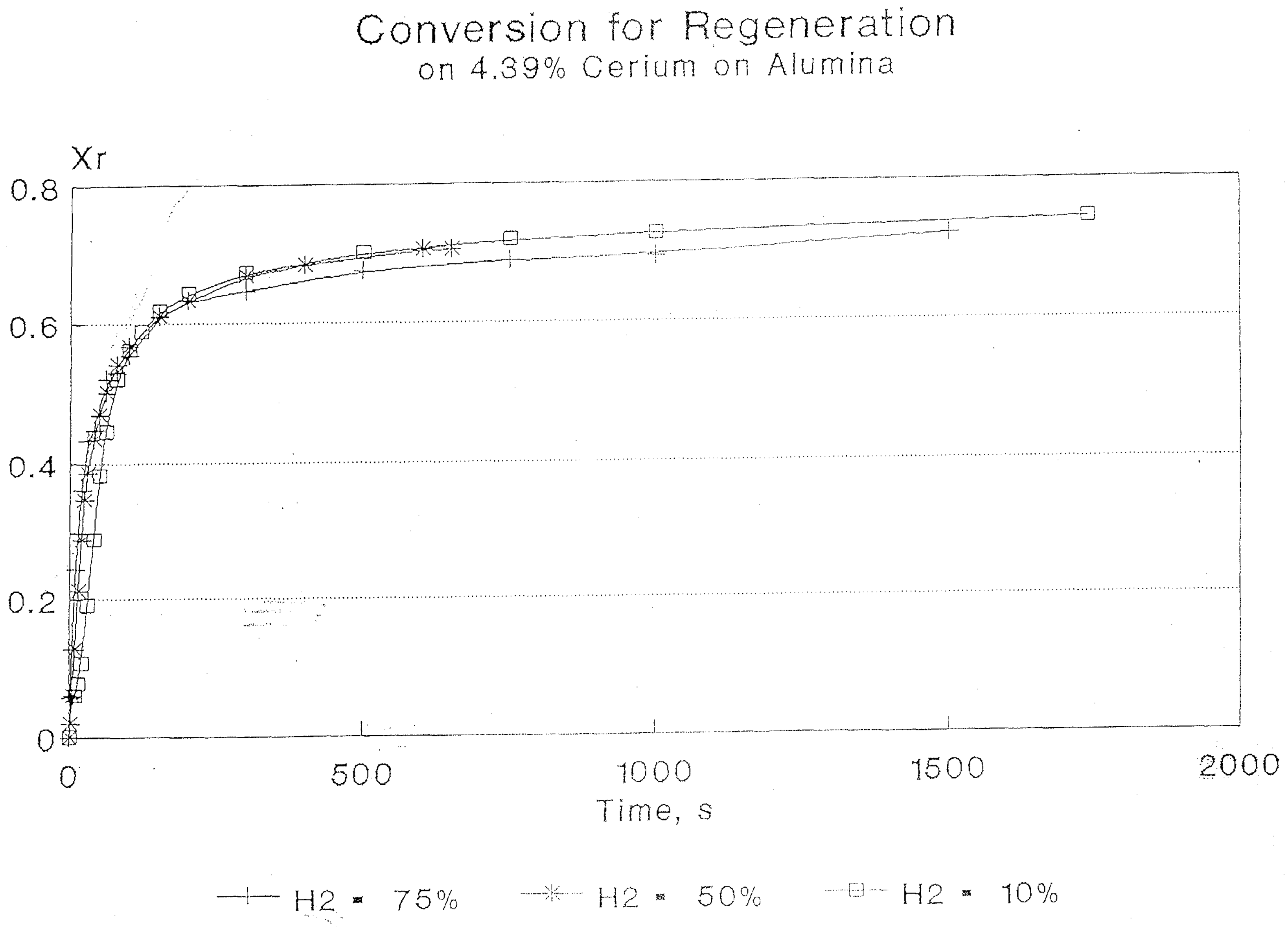

Figure 3. T=873 K

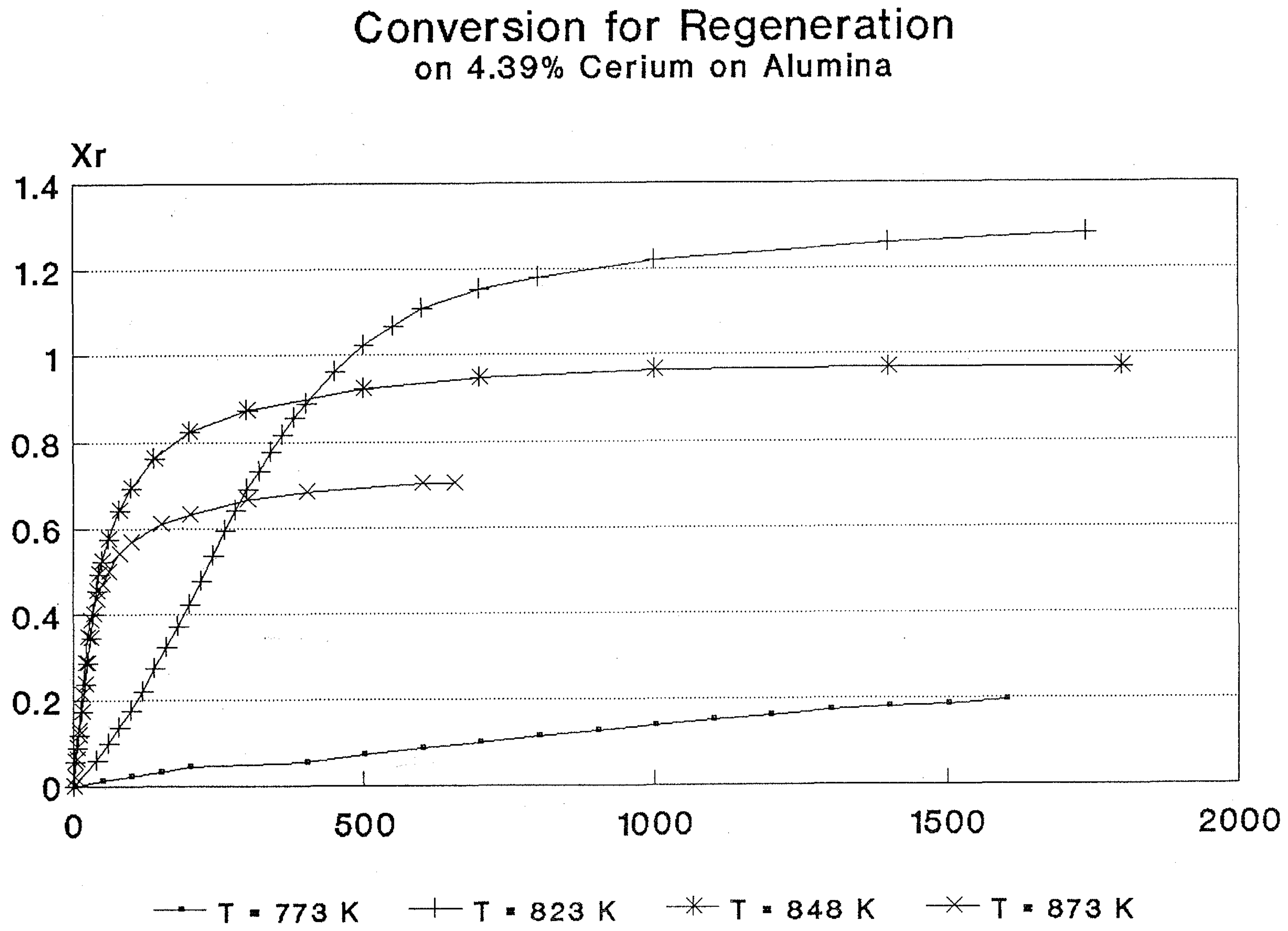

Figure 4. H2= 50%

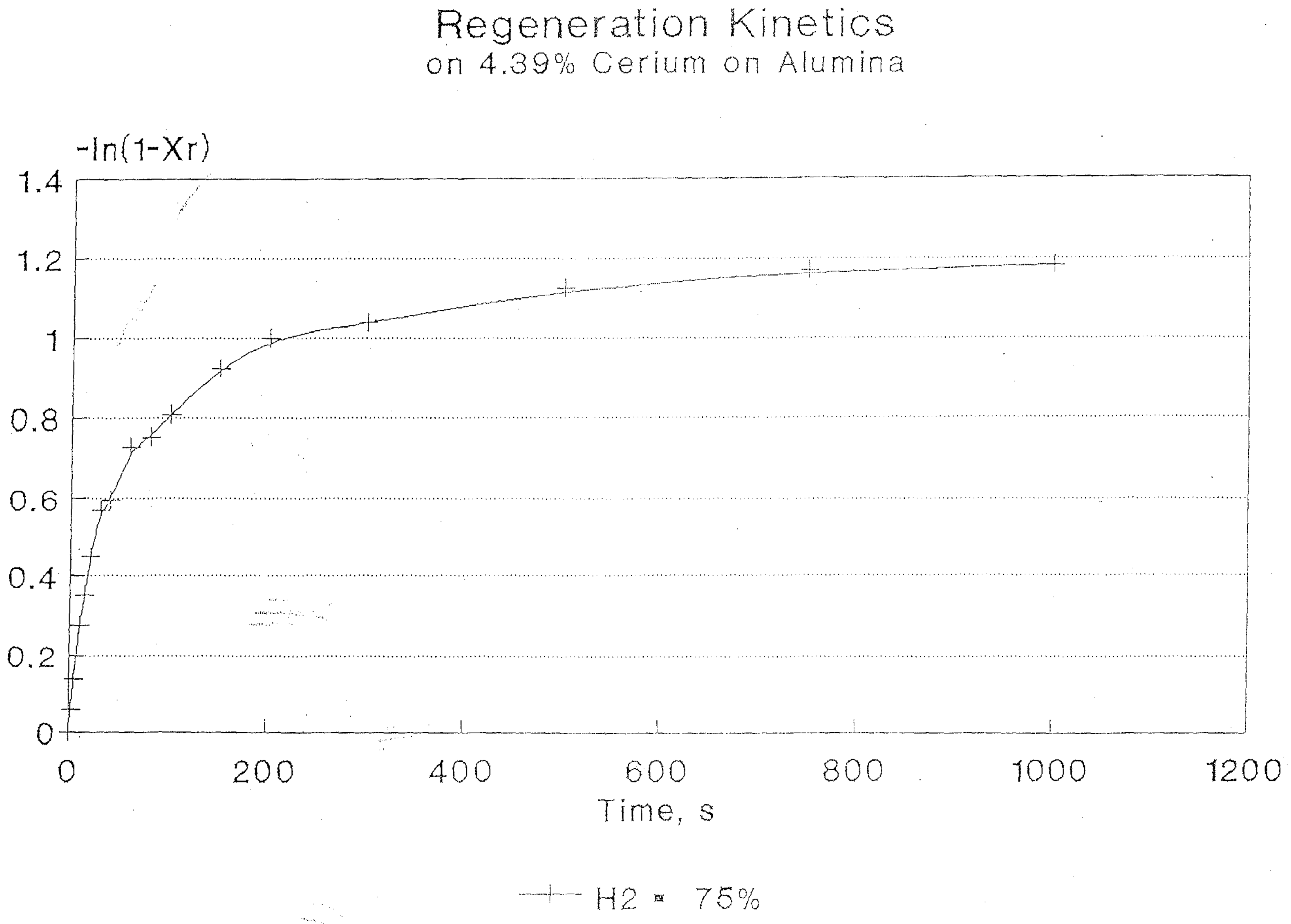

Figure 5. T=873 K

FUTURE WORK

In the next quarter, it is planned :

1) to generate data on the regeneration of the ceria sorbents using methane as the regeneration gas;
2) to evaluate the data generated;
3) to initiate the modeling of the sulfation and regeneration reactors; and
4) to initiate the process development for the industrial application of the method.

APPENDIX I

EXTENDED ABSTRACT

INVESTIGATION OF THE REGENERATION OF CERIA SORBENTS FOR SIMULTANEOUS SO_2/NO_x REMOVAL

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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. This process will allow simple and reliable cleanup of large volumes of stack gases at a competitive cost; produce a concentrated stream of SO_2 which can easily be converted into valuable by-products; be compatible with existing power generation plants; and essentially eliminate the waste materials generated in some other sulfur removal processes. Department of Energy's Pittsburgh Energy Technology Center (PETC) and UOP/Shell have developed processes which both employ copper oxide-based sorbents in different reactor configurations, namely, former uses a regenerative fluidized bed while the latter employs a cyclic fixed bed contactor.

More recent studies at PETC considered cerium oxide as an alternate sorbent to CuO. Ceria improves the resistance of the alumina support to thermal sintering and produces a regeneration off-gas stream that can be easily converted to elemental sulfur. It has a potentially higher sulfur capture capacity than copper. It is readily available at a moderate cost. Although it is more expensive than copper oxide, since the cost of metal oxide is a small fraction of the total sorbent cost, this may not be a significant factor.

The objective of the present research is to determine the effects of fly ash on the sulfation and regeneration of the sorbent; and to obtain a rate expression for the regeneration of alumina-supported CeO_2 sorbents.

Ceria sorbents were prepared by the incipient impregnation of aqueous ceric ammonium nitrate on ALCOA alumina particles (1/16"). These sorbents were then dried overnight at 393 K and calcined in air at 923 K. The prepared sorbents were characterized by measuring their surface area, porosity, pore size distribution, and cerium metal contents. The kinetics of regeneration of these sorbents is being investigated in a thermogravimetric analyzer.

APPENDIX II

INVESTIGATION OF THE EFFECT OF AMMONIA ON CERIA SORBENTS DURING SIMULTANEOUS SO_2/NO_X REMOVAL

by

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The present study aims to determine the effects of ammonia and fly ash on the sulfation of the alumina-supported cerium oxide sorbents. The sorbents were prepared by the incipient impregnation of ALCOA alumina with an aqueous solution of cerium ammonium nitrate; they are subsequently dried and calcined at 923 K under a flowing air stream. Nominal cerium loadings were 4, 8, and 12%. The sorbents were characterized by surface area and porosity measurements, and the determination of the cerium content by A.A. spectrometer. Standard sulfation - regeneration experiments were performed in a thermogravimetric analyzer setup at 873 K; a gas flow rate of 200 cc/minute; a sulfation gas composed of 0.3% SO_2, 3% O_2, 14% CO_2, 4% H_2O, balance N_2; and a regeneration gas composed of H_2 and N_2 whose hydrogen composition was varied.

The preliminary sulfation experiments indicated that 100% conversion of ceria could be attained. The standard sulfation-regeneration was repeated for 6 cycles; the ceria sorbent was found to preserve its activity and structural stability after these 6 cycles; the sulfur capture capacity decreases by about 10% after the first cycle, but the decrease becomes much smaller in further cycling. The regenerated sorbents captured about 2 sulfur atoms for each cerium atom while this ratio is about 2.5 for fresh sorbent. About 250 ppm of ammonia is sufficient to cause about 10-15% reduction in sorbent capacity. Presence of water vapor in the flue gas also reduces the sulfation capacity of the sorbents in the presence of ammonia. The regeneration reaction was found to be of 1/2 order with respect to hydrogen.