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INVESTIGATION OF COMBINED SO<sub>2</sub>/NO<sub>x</sub> REMOVAL  
BY CERIA SORBENTS

MT 92018

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## ABSTRACT

Simultaneous removal of  $\text{SO}_2$  and  $\text{NO}_x$  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  $\text{SO}_2$  and  $\text{NO}_x$  removal operations. Recent studies at PETC considered cerium oxide as an alternate sorbent to  $\text{CuO}$ .

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  $\text{CeO}_2$  sorbents. The sulfation experiments indicated that 100 % conversion of ceria can 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  $\text{SO}_2$  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. In the last quarter regeneration with methane was studied. Since regeneration with methane is more complicated than regeneration with hydrogen, the evaluation of data needs the development of new methods.

The information obtained from these studies will be used to develop models for reactor-regenerator configurations. Subsequently, the  $\text{SO}_2/\text{NO}_x$  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 methane.

### B. Experimental Program

For the regeneration experiments, a large sample of sulfated sorbent had been prepared as mentioned in the previous progress report. In this quarter, regeneration experiments were performed by using methane as the regeneration agent on that sulfated sample.

The following procedure was used during the regeneration runs:

The sulfated sorbent (3.5 mg of 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 methane and nitrogen, were introduced into the TGA reactor by switching the valves. As will be discussed later during the regenerations with methane coke deposition was observed. This resulted in an initial mass decrease followed by a mass increase. The sulfated sorbent was exposed to the regeneration gases until a constant mass increase rate is obtained. After the regeneration was terminated, the system was cooled to room temperature under nitrogen flow.

The methane concentration in the regeneration gases and the reaction temperature were the main variables used during the regeneration tests. The methane concentration was varied between 15 and 45% (by mole), while the temperature range was 873 - 943 K.

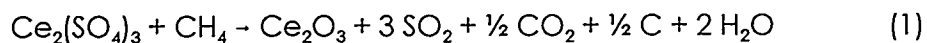
Because the buoyancy effects are smaller for methane mixtures and considering the

error introduced when a thermogram is subtracted from another, a different procedure was used in the evaluation of methane regeneration data. It was observed that the transient flow disturbance and buoyancy effects existed within the first 60 seconds of the thermogram. For this reason, the initial rates were obtained by fitting a straight line to the mass versus time data. Data points were included until the correlation coefficient for the fit fell below 0.9950.

Additional runs were performed to investigate the effect of the regeneration agent, i.e. methane in this case, on the cyclic performance of the sorbent, because the previous runs on cyclic behavior were done using hydrogen during regeneration.

### C. Data Evaluation

The regeneration of alumina-supported ceria has been investigated by Shyu, et al.<sup>1</sup> They report that while below 600 K the formation of nonstoichiometric  $\text{CeO}_{1.83}$  and  $\text{CeO}_{1.72}$  is the most favorable reaction, above 800 K the formation of  $\text{CeAlO}_3$  is a more favorable thermodynamic process. On the other hand, kinetically, reduction to  $\text{CeAlO}_3$  requires temperatures higher than 873 K. According to these results both  $\text{CeO}_x$  and  $\text{CeAlO}_3$  can exist at the temperatures used for regeneration experiments. This makes the interpretation of the regeneration data difficult and the XRD analysis of the reduced sorbents to identify the crystalline species a must. Since we do not yet have the results of these analyses, to find out which reduction product is predominant some regeneration data were analyzed separately using  $\text{Ce}_2\text{O}_3$  and  $\text{CeAlO}_3$  as the reaction products. While the former gave reasonable results the latter indicated conversions over 100 %. Therefore it appears that  $\text{CeAlO}_3$  is probably not present in significant amounts. Therefore, for this report, the regeneration data using methane as the regeneration agent were evaluated using the following stoichiometry:



Elemental carbon is included in the reaction stoichiometry because significant coking of the sorbent was observed both visually and from the TGA results. For proper evaluation of the regeneration data, the mass change due to the reduction of cerium sulfate need to be separated from the mass change due to coke formation. Currently we are in the process of developing a method to accomplish this. Since copper sulfate is reduced to elemental copper during regeneration coking was not observed during the regeneration of copper oxide-based sorbents<sup>2</sup>.

#### D. Additional Activities

In addition to the above activities, a presentation entitled 'Investigation of the Sulfation and Regeneration of Ceria/Alumina Sorbents' was made at the Third Annual Historically Black Colleges and Universities/ Private Sector Energy Research and Development Technology Transfer Symposium held at Atlanta, GA, on April 27-29, 1995. A copy of the abstract is in the Appendix I.

We have also started to work with the engineers at the Malcolm-Pirnie company to evaluate a commercial scale desulfurization system using alumina-supported ceria sorbents.

## II. RESULTS and DISCUSSION

As indicated above, the evaluation of the methane regeneration results is very complicated. For this reason we are still in the process of evaluating the data from the regeneration tests with methane and in this report only the thermograms from some experimental runs are presented in figures 1 to 6.

## FUTURE WORK

In the next quarter, it is planned :

- 1) to evaluate the data generated on the regeneration of the ceria sorbents using methane as the regeneration gas;
- 2) to do additional experiments on the effect of ammonia on sulfation;
- 3) to continue with the modeling of the sulfation and regeneration reactors; and
- 4) to continue with the process development for the industrial application of the method.

## BIBLIOGRAPHY

1. Shyu, J. Z., Weber, W. H., and Gandhi, H. S., "Surface Characterization of Alumina-Supported Ceria", *J. Phys. Chem.* 92, pp. 4964-4970, 1988.
2. Markussen, J. M., Pennline, H. W., and Brodd, C. F., "A Microbalance Study of the Sorbent Regeneration Kinetics in the Copper Oxide Process", presented at the AIChE 1994 Summer National Meeting, Denver, CO, August 14-17, 1994.

## APPENDIX I



Title: Investigation of the Sulfation and Regeneration of Ceria/Alumina Sorbents

Authors: Ateñ Akyurtlu (presenter) and Jale F. Akyurtlu

Affiliation: Hampton University, Department of Engineering

Topic: Power Systems - Environmental Control Technologies for Coal

### ABSTRACT

Simultaneous removal of  $\text{SO}_2$  and  $\text{NO}_x$  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  $\text{SO}_2$  and  $\text{NO}_x$  removal operations. Recent studies at PETC considered cerium oxide as an alternate sorbent to  $\text{CuO}$ .

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  $\text{CeO}_2$  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  $\text{SO}_2$  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.

Investigation of regeneration with methane and the investigation of the effect of ammonia are currently under way.

APPENDIX II

# Thermogram for Regeneration with Methane on 4.39% Cerium on Alumina

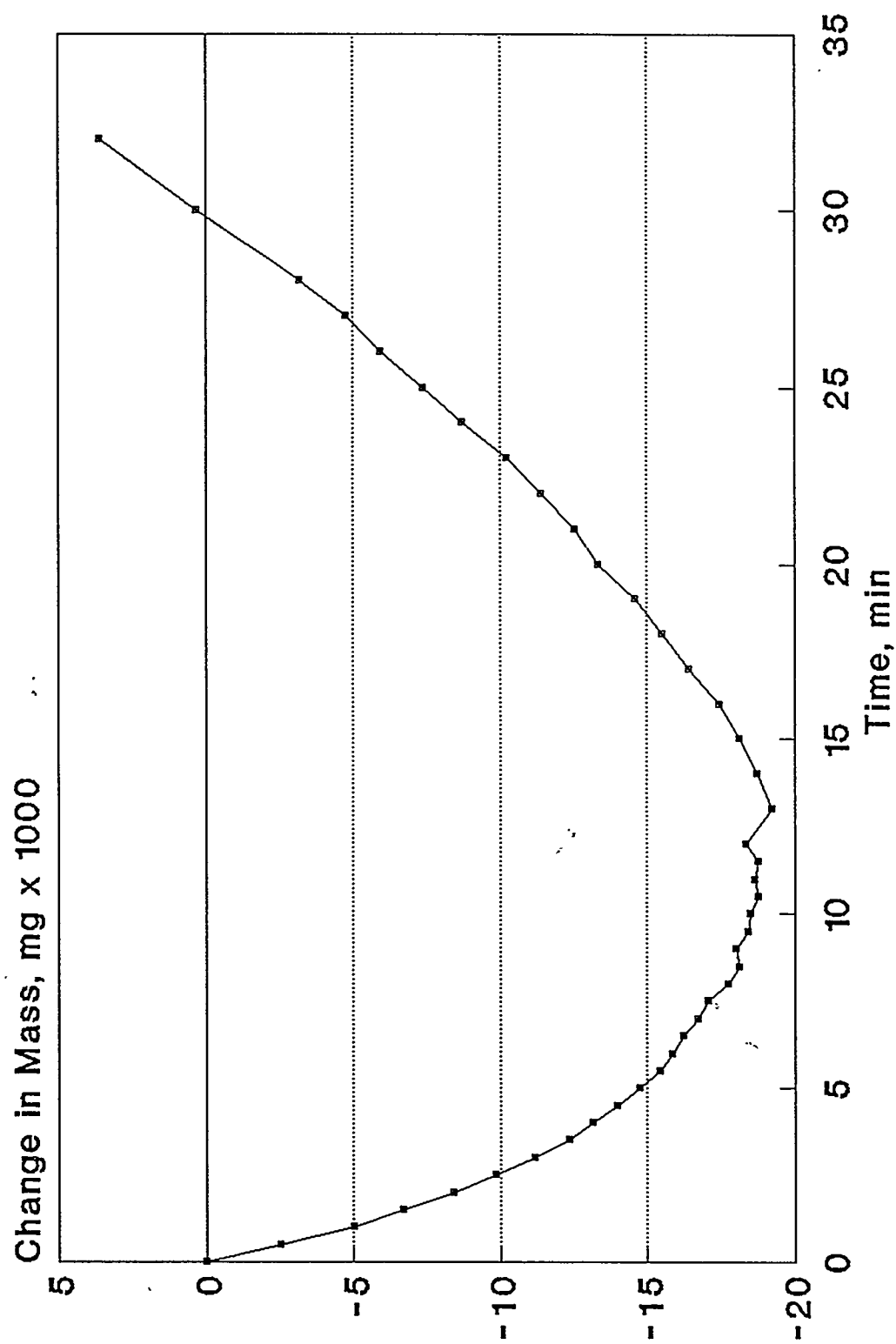


Figure 1. CH<sub>4</sub> 100% , T = 873 K

# Thermogram for Regeneration with Methane on 4.39% Cerium on Alumina

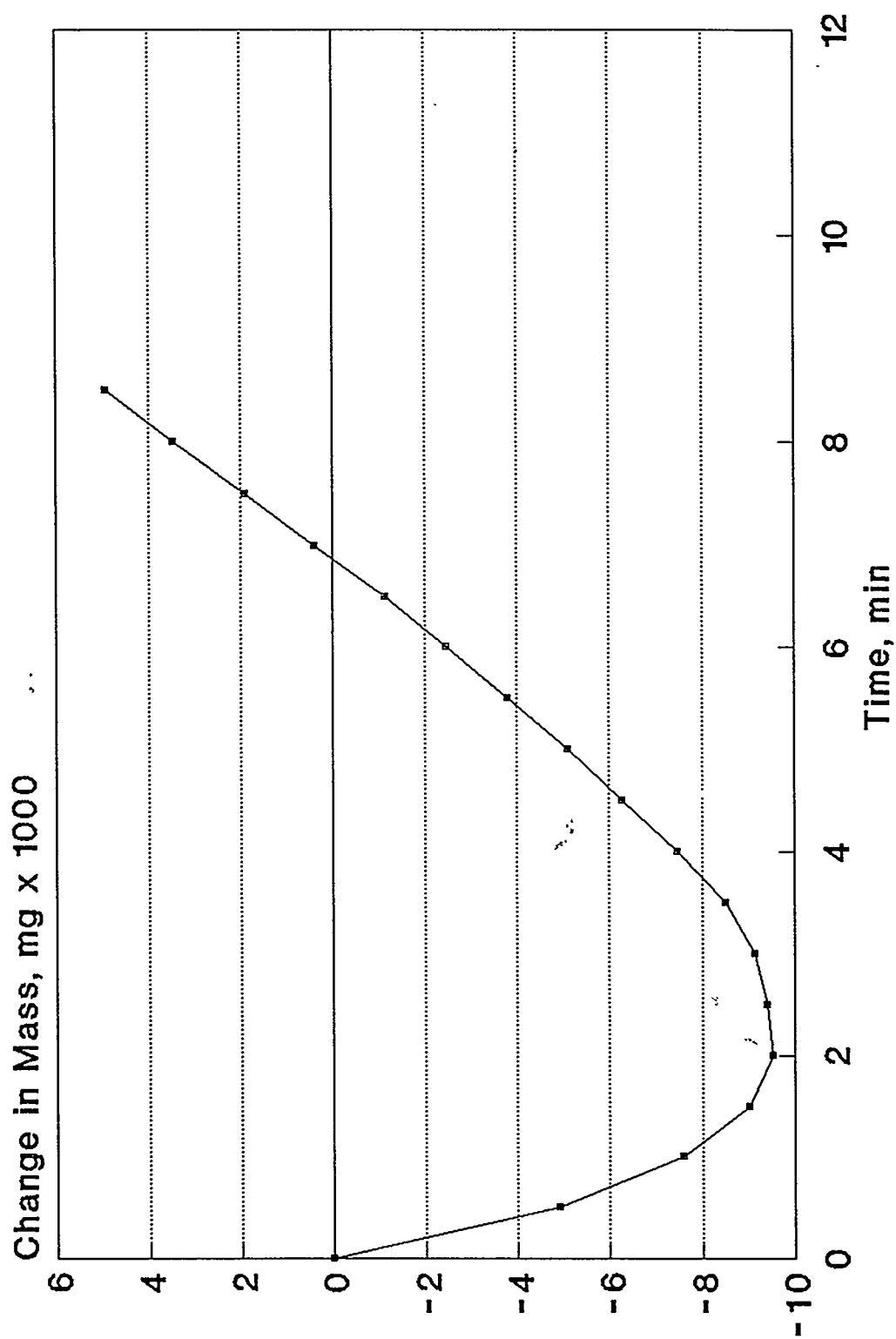


Figure 2.  $\text{CH}_4 = 100\%$ ,  $T = 923 \text{ K}$

# Thermogram for Regeneration with Methane on 4.39% Cerium on Alumina

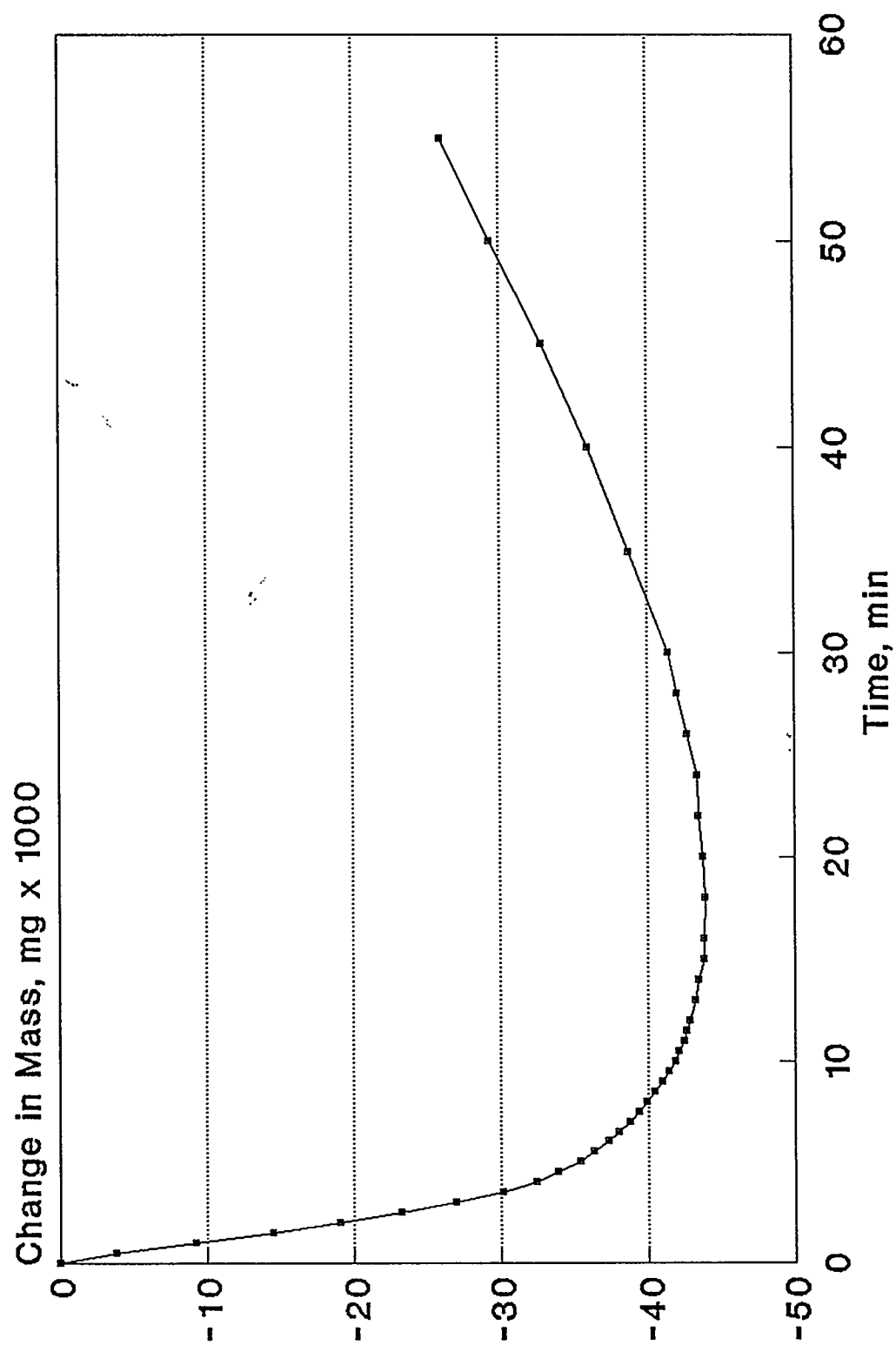


Figure 3. CH<sub>4</sub> 15% , T = 923 K

# Thermogram for Regeneration with Methane on 4.39% Cerium on Alumina

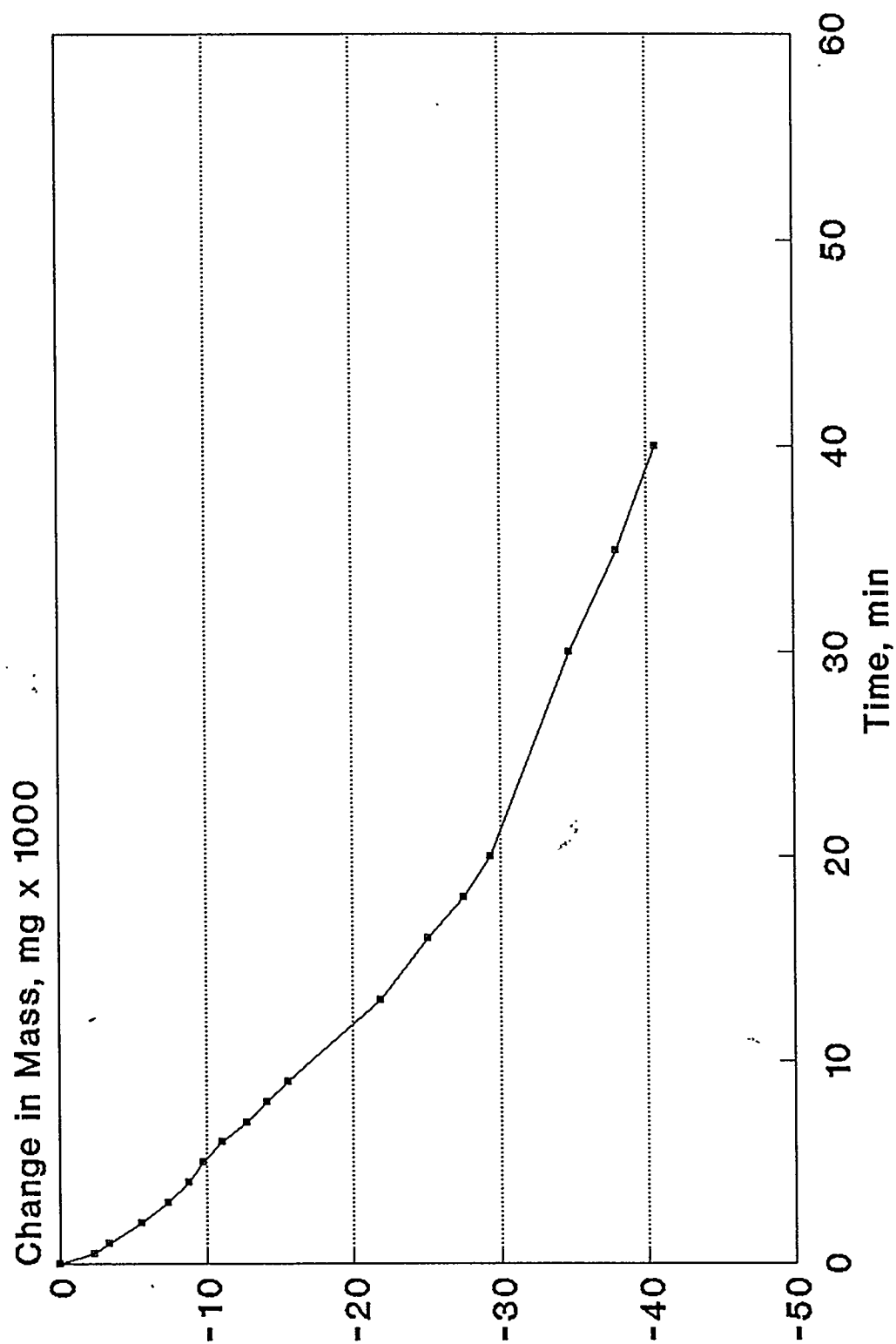


Figure 4. CH<sub>4</sub> 15%, T = 898 K

# Thermogram for Regeneration with Methane on 4.39% Cerium on Alumina

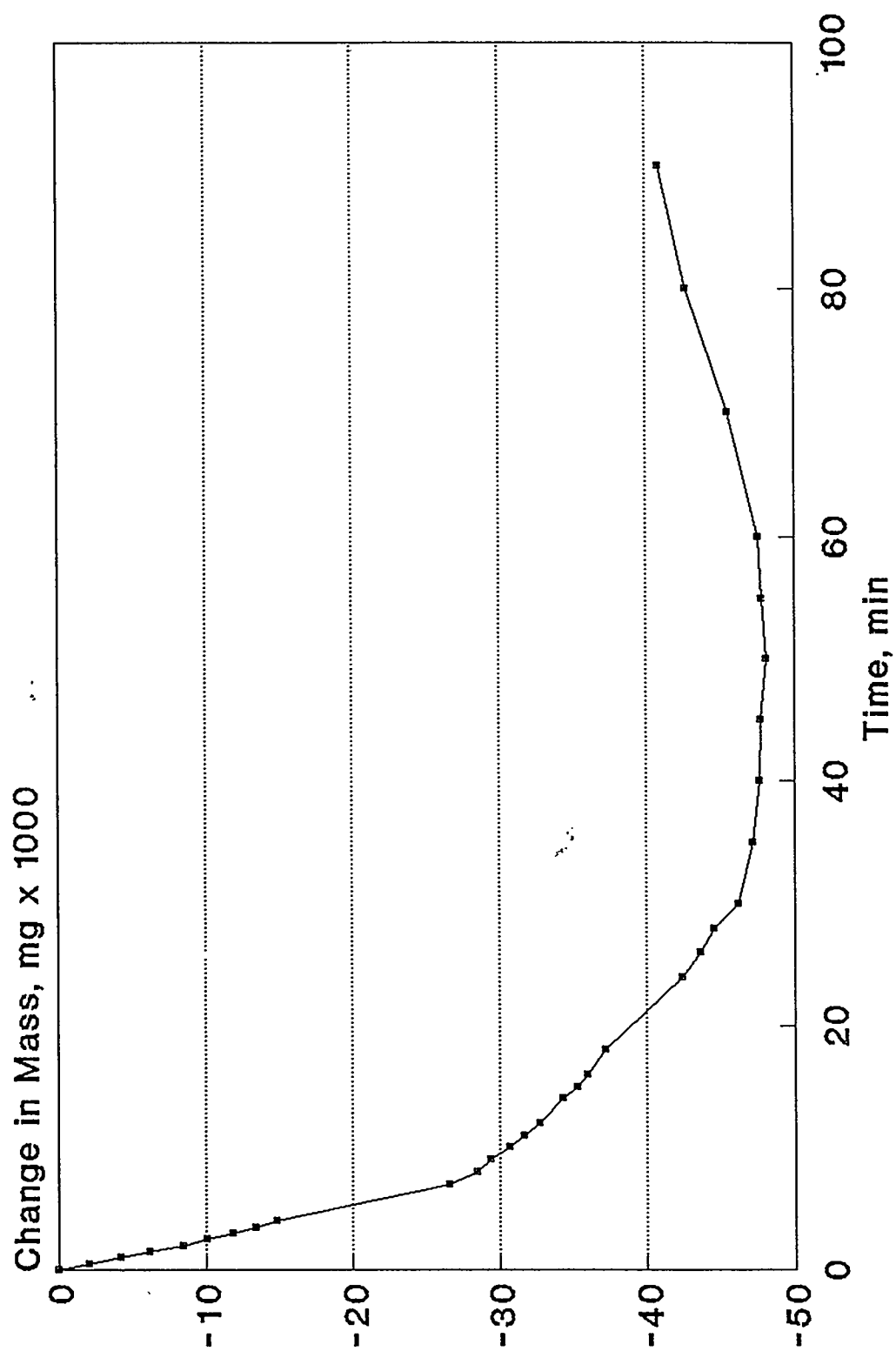


Figure 5. CH<sub>4</sub> 15% , T = 913 K

# Thermogram for Regeneration with Methane on 4.39% Cerium on Alumina

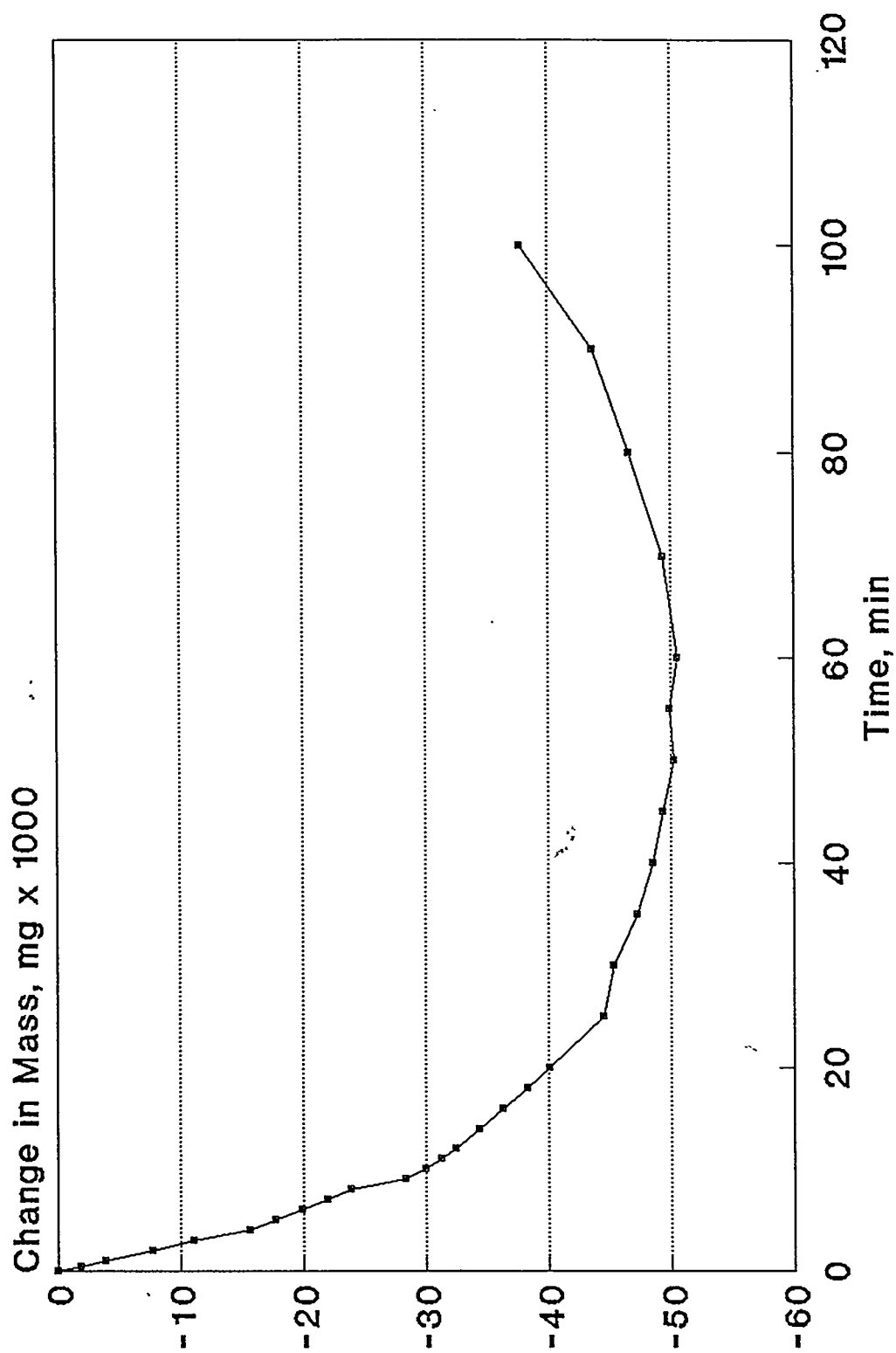


Figure 6.  $\text{CH}_4$  16%,  $T = 933 \text{ K}$