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Investigation of Combined SO₂/NO_x Removal by Ceria Sorbents

**Quarterly Report
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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 cerium content of the sorbent on its performance through four sulfation-regeneration cycles were investigated and the analysis of the economics of a commercial scale ceria process was sub-contracted to TECOGEN.

It was found that all ceria sorbents did not show any capacity loss after the first cycle and, in fact, their performance improved slightly after the third cycle. Increasing cerium loading appears to reduce the S/Ce ratio to about 2 as monolayer coverage is approached. It was found that the sulfation rate for the sorbents containing 9.28% and 7.64% cerium were first order with respect to cerium oxide up to 90% conversion. The sorbents containing 4.39% and 1.59 showed first order kinetics up to only about 40% conversion. The effects of product layer diffusion and gas phase diffusion are currently being considered for these sorbents.

I. WORK DONE

A. Introduction

In this quarter of the project, the main focus was on the determination of the effect of cerium content on the sorbent performance and providing data to the subcontractor for commercial scale evaluation of the ceria process.

B. The Effect of Cerium Content on the Sorbent Performance

To observe the effect of cerium content the following sorbents were used:

- ▶ ALCOA-CE4-IV, cerium loading 1.59% by mass
- ▶ ALCOA-CE4-VI, cerium loading 4.39% by mass
- ▶ ALCOA-CE8-II, cerium loading 7.64% by mass
- ▶ ALCOA-CE12-I, cerium loading 9.28% by mass

The ALCOA16-CE4-VI sorbent has been investigated, and the results have been reported before. The other sorbents were subjected to four cycles of successive sulfation, regeneration, and oxidation. Sulfation was performed 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 and then oxidized with 6.6 % oxygen in nitrogen.

The cyclic behaviors of the sorbents containing 1.59%, 7.64%, and 9.28% cerium by mass are shown in figures 1,2, and 3, respectively. The extremely high S/Ce ratios for the 1.59% Ce containing sorbent is most probably due to an error in the determination of the cerium content of the sorbent, which is expected due to the very low metal concentration. Although the S/Ce ratios for the other sorbents are within the reasonable range we have decided to repeat the metal analyses. Currently we are in the process of locating a different laboratory to do these analyses.

Figure 1. Sulfation-Regeneration Cycles
1.59% Cerium Sorbent

Figure 2. Sulfation-Regeneration Cycles
7.64% Cerium Sorbent

Figure 3. Sulfation-Regeneration Cycles
9.28% Cerium Sorbent

Figures 1, 2, and 3 show that all sorbents show a very stable performance after the first cycle and show an improvement in the sulfur capture capacity after the third cycle. Figure 4 shows the comparison of the second cycles of all the sorbents tested. Disregarding the 1.59% Ce sorbent for the apparent error, it appears that increasing the cerium content of the sorbent decreases the S/Ce ratio probably due to the decrease in the surrounding surface alumina sites as monolayer coverage is approached. These surrounding alumina sites are needed for the formation of aluminum sulfate species and thus regeneration of ceria sites for further sulfur removal. The optimum cerium loading will be determined by the trade off between the higher cerium efficiency at lower loadings and larger sorbent mass needed.

C. Effect of Cerium Content on the Order of Reaction With Respect to the Solid Reactant

It has been observed that with the sorbent containing 4.39% cerium by mass the sulfation reaction was first order with respect to cerium oxide only up to about 40% conversion. The new data obtained for sorbents containing 7.64% and 9.28% cerium indicated that with these sorbents, the dependence of reaction rate on cerium oxide is first order up to about

90% conversion (Figure 5). Since the monolayer coverage corresponds to about 10% for the alumina used as support, it appears that as monolayer coverage is approached the rate of sulfation is controlled by kinetics only. Currently we are using the unreacted core model to check if the deviation from the first order behavior is due to the effect of product layer diffusion resistance for low cerium loadings.

Figure 4. Effect of Cerium Content
on Sorbent Performance

Figure 5. First Order Dependence on
Solid Reactant: 9.28% Cerium Sorbent

D. Evaluation of the Commercial Scale Ceria Process

Our negotiations with Malcolm Pirnie, Inc. Has indicated that the resources allocated by Malcolm Pirnie to this task were not adequate for the successful completion of the task. Therefore we have contacted TECOGEN of Waltham, MA, and asked them if they could modify the software they have developed for the evaluation of the copper oxide sorbent, to accommodate the ceria sorbent. Upon their acceptance we have sent a task order containing the data we have obtained on ceria sorbents (Appendix I). The sulfation rate indicated on the task order was based on initial rate data and was found to be inadequate at longer times. The following updated rate equation was obtained by fitting all the reaction data to a first order reaction equation:

$$\frac{dX_s}{dt} = 1.94 \exp\left(-\frac{2045}{T}\right) y_{SO_2} (1-X_s)$$

where X_s is the fractional conversion of cerium oxide, y_{SO_2} is the mole fraction of SO_2 , T is the temperature in K, and t is the time in seconds. The correlation coefficient for the linear fit of $\ln(1-X_s)$ versus time data is 0.99788 and the standard error of estimate is 0.0614.

E. Additional Activities

The experimental program for the evaluation of the effect of fly ash on sulfation has been started.

FUTURE WORK

In the next quarter, it is planned :

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

- 2) to complete the evaluation of the data generated;
- 3) to investigate the adsorption and desorption of ammonia on fresh and sulfated sorbents;
- 4) to determine the dissociation temperature of sulfate species formed;
- 5) to evaluate the report to be obtained from TECOGEN; and
- 6) to write the final report.

Appendix - 1

Task Order for TECOGEN

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TASKS TO BE PERFORMED BY THE CONSULTANT

The process to be evaluated will be very similar to the COBRA copper oxide process, but it will use a different metal oxide as the sorbent and the sulfation and regeneration reactors will operate at temperatures between 773 K and 873 K. The specific tasks to be performed under this purchase order are stated below. The time available for the completion of these tasks is 5 weeks from the receipt of the purchase order. The information on the specific sorbent to be used is supplied on the attached sheets.

Task 1: Model a cross-flow moving-bed sulfation reactor for the metal oxide sorbent to be specified. For two reactor operating temperatures (823 K, 873 K), and two sorbent sizes (1/16 in, 1/8 in), the following information is needed from the model:

- Size and cost of the reactor.
- Sorbent needed to process a specified gas flow rate.
- Gas exit temperature for adiabatic operation.

Task 2: Model a cross-flow moving-bed regeneration reactor for the metal oxide sorbent to be specified. For the two regenerator operating temperatures specified on the attached sheet, two sorbent sizes (1/16", 1/8"), and two different regeneration gases (methane and hydrogen), the following information is needed from the model:

- Size and cost of the regenerator.
- Gas exit temperature for adiabatic operation.

Task 3: Compare the cost of the process with that of the process using copper oxide sorbent. In the cost comparison the following effects should be considered:

- Effects of the different sulfation and regeneration kinetics on the reactor and regenerator costs.
- Effect of higher operating temperatures on the reactor and regenerator costs.
- Effect of different heats of reactions on the total cost (energy credit from exothermicity). Thermodynamic data for solid species will be supplied if needed.
- Effect of sorbent cost on total cost for three specified cost ratios (ratio of the cost of ceria sorbent to the cost of copper oxide sorbent equal to 1, 1.2, and 1.4).

TECHNICAL INFORMATION

Sorbent: 9% by mass cerium (as CeO_2) on alumina (1/16-in and 1/8-in spheres).

Reactions: Sulfation

$$r_s = 0.205 \exp \left[-\frac{2050}{T} \right] y_{\text{SO}_2} c_0 (1 - X_s)$$

Regeneration with hydrogen

$$r_H = 2420 \exp \left[-\frac{13700}{T} \right] y_H^{0.56} c_0 (1 - X_H)$$

Regeneration with Methane

$$r_M = -346 \exp \left[-\frac{15600}{T} \right] y_M^{0.76} c_0 (1 - X_M)$$

Very fast oxydation (assumed instantaneous) on contact with sulfation gases

In the rate equations r_s is the sulfation rate in moles of Ce_2O reacted per second per gram of sorbent; r_H and r_M are the regeneration rates with hydrogen and methane, respectively in moles of sulfate reacted per second per gram of sorbent; T is the reaction temperature in K; y_s , y_H , and y_M are the mole fractions of SO_2 , H_2 , and CH_4 , respectively; c_0 is the mass fraction of Ce on the sorbent (as prepared); X_s is the fractional conversion of CeO_2 ; and X_H and X_M are the fractional conversion of the sulfate.

Gas Composition: Default with 3000 ppm SO_2

Gas temperature: For sulfation 823 K and 873 K; for regeneration with hydrogen 823 K

TECHNICAL INFORMATION

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Gas Composition: Default with 3000 ppm SO_2

Gas temperature: For sulfation 823 K and 873 K; for regeneration with hydrogen 823 K

and 873 K; for regeneration with methane 873 K and 923 K.

Gas Pressure: Default

Sorbent Size: 1/16" and 1/8"

Maximum Sulfur Capture: 2 sulfur atoms per cerium atom

Maximum Pressure Drop: Default

Maximum Outlet SO₂: Default

Heats of Reaction: Standard heat of reaction for the sulfation of CeO₂:

$$\Delta H_s(298 \text{ K}) = -294.14 \text{ kJ/mol SO}_2$$

Standard heat of reaction for the oxidation of Ce₂O₃

$$\Delta H_o(298 \text{ K}) = -119.46 \text{ kJ/mol SO}_2$$

$$\text{Total heat of reaction for the sulfation step} = \Delta H_s + \Delta H_o$$

Standard heat of reaction for regeneration with hydrogen:

$$\Delta H_H(298 \text{ K}) = 91.16 \text{ kJ/mol SO}_2$$

Standard heat of reaction for regeneration with methane:

$$\Delta H_M(298 \text{ K}) = 258.91 \text{ kJ/mol SO}_2$$