INVESTIGATION OF COMBINED SO₂/NOₓ 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 this quarter runs for methane regeneration were completed. The data obtained were evaluated and interpreted.

When the sulfated sorbent was regenerated with methane coke formation on the sorbent was observed. Treatment of fresh sorbent with methane also resulted in coking. Coke formed on the sorbent disappeared very rapidly after the methane flow was replaced with nitrogen.

The order of the regeneration reaction with respect to methane was estimated as 0.76 and the activation energy of the reaction was estimated as 130 kJ/mol. During repeated sulfation-regeneration cycles the decrease in the sulfur capacity after the first cycle was slightly more when regeneration was done with methane compared to that observed with hydrogen regeneration. In the subsequent 4 cycles, the ceria sorbent preserved its sulfur capacity. The regenerated sorbent was able to capture 1.5 sulfur atoms per cerium atom in less than an hour of sulfation, compared to S/Ce of 2.5 for fresh sorbents and 2 for sorbents regenerated with hydrogen.
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 and the evaluation of the data obtained. A presentation was made at the 11th Coal Preparation, Utilization, and Environmental Control Conference in Pittsburgh by Dr. Jale Akyurtlu.

B. Experimental Program

The experimental work done in this quarter is summarized below:

- Runs to investigate coking on fresh sorbent with methane.
- Runs to determine the effects of CO and SO on regeneration with CH.
- Runs to see the effect of SO on regeneration with H.
- Runs to see the effect of gas composition during heating after sulfation.
- Repeat runs to observe the effect of NH on sulfation.
- Repeat runs to check the temperature and SO concentration dependence of the sulfation reaction.

C. Data Evaluation

All the regeneration data obtained in this and the previous quarter were evaluated and the results are reported in this report. According to these results of Shyu, et al.\(^1\) both CeO\(_x\) and CeAlO\(_3\) can exist at the temperatures used for regeneration experiments. Since we do not yet know which reduction products are present in significant amounts, the regeneration data using methane as the regeneration agent were evaluated using the following stoichiometry:

\[
\text{Ce}_2(\text{SO}_4)_3 + \text{CH}_4 \rightarrow \text{Ce}_2\text{O}_3 + 3 \text{SO}_2 + \frac{1}{2} \text{CO} + 2 \text{H}_2\text{O}
\]  (1)
\[
\text{CH}_4 \rightarrow C + 2 \text{H}_2 \hspace{2cm} (2)
\]
\[
3 \text{C} + 2 \text{Ce}_2\text{O}_3 \rightarrow 4 \text{Ce} + 3 \text{CO}_2 \hspace{2cm} (3)
\]
The initial rate data were evaluated assuming that reaction (1) is the dominant reaction at the start of regeneration. The conversion data were obtained by assuming a constant rate for the second reaction. Thus, to obtain the mass of sorbent at any time, the amount of coke formed (obtained using the constant coking rate) is subtracted from the measured mass.

D. Additional Activities

In addition to the above activities, a presentation entitled "Investigation of Combined \text{SO}_2/\text{NO}_x Removal by Ceria Sorbents: Sulfation and Regeneration Characteristics" was made at the 11th Coal Preparation, Utilization, and Environmental Control Conference in Pittsburgh by Dr. Jale Akyurtlu. A copy of the presentation is included in Appendix I.

II. RESULTS and DISCUSSION

Coking during regeneration with methane: The most significant observation during regeneration with methane is the formation of coke on the sorbent. This is indicated by a minimum in the observed mass during regeneration. If the sorbent was allowed to cool after regeneration under methane atmosphere, it was visually observed that the sorbent was blackened significantly. On the other hand, if the methane was switched off at the end of regeneration and only nitrogen flowed over the sorbent, coke rapidly disappeared as indicated by a very rapid decrease in mass. It was also observed that under these conditions the sorbent regained its off-white color and no blackened areas existed. These observations led us to hypothesize the reaction scheme indicated by equations 1 to 3 which needs to be confirmed by the analysis of the regenerated sorbent.
Thermogram for Regeneration with Methane on 4.39% Cerium on Alumina

Figure 1. CH4= 100% , T = 873 K
Thermogram for Regeneration with Methane on 4.39% Cerium on Alumina

Figure 2. CH4 = 100%, T = 923 K
Thermogram for Regeneration with
Methane on 4.39% Cerium on Alumina

Figure 3. CH4 = 15%, T = 923 K
Figures 1 to 3 show the mass changes during regeneration under different conditions. Comparison of figures 1 and 2 indicate that as temperature increases, the time to reach the minimum mass decreases. Since the minimum in the observed mass is the result of the mass decrease due to reaction 1 and the mass increase due to reaction 2, it can be concluded that the activation energy of the coking reaction (reaction 2) is greater than the activation energy of the regeneration reaction (reaction 1). Similarly, from reactions 2 and 3 it can be concluded that since the time to reach minimum mass increases with decreasing methane partial pressure, the order of the regeneration reaction with respect to methane is positive and is smaller than the order of the coking reaction with respect to methane.

**Effect of regeneration gas composition on regeneration:** Figure 4 shows the conversions for regenerations with different methane concentrations. From this figure it can be seen that the final conversion decreases as the methane concentration increases. This observation can be explained by the faster coverage of the sorbent surface with carbon at higher methane concentrations, thus, preventing the regeneration of increasing amounts of sorbent. On the other hand, since coking is not significant at the start of regeneration, the initial rate of the regeneration reaction increases with increasing methane concentrations. The order of the initial regeneration rate with respect to methane was found to be 0.76.

**Effect of temperature on regeneration:** Assuming an Arrhenius type of temperature dependance for the initial reaction rate an activation energy of 130 kJ/mol was found for the regeneration with methane. This value is higher than that found for regeneration with hydrogen, which is consistent with the higher exothermicity of the methane reaction. Figure 5 shows the effect of temperature on conversion. Temperature affects conversion in two ways. It increases the rate of regeneration reaction thus tends to increase the conversion at
Conversion for Regeneration with CH4 on 4.39% Cerium on Alumina

Figure 4. T=925 K
Conversion for Regeneration with CH4 on 4.39% Cerium on Alumina
any time, but, it also increases the rate of the coking reaction thus decreasing the available surface for regeneration. As seen in Figure 5, the first effect results in increasing conversions with temperature up to 923 K. At higher temperatures the second effect becomes dominant and conversion decreases.

**Effects of SO₂ and CO₂ on regeneration:** Figure 6 shows the effects of CO₂ and SO₂ on the conversion for regeneration with methane. It is clearly seen that the presence of SO₂ in the regeneration gases decreases both the final conversion and the regeneration rate. The removal of SO₂ from the regeneration gases appears to restore the conversion. This observation can be explained by the competitive adsorption of SO₂ and CH₄. Another interesting observation from Figure 8 is the effect of CO₂. It appears that the presence of CO₂ suppresses coking and thus increases the conversion. Figure 7 shows a similar effect of SO₂ on regeneration with hydrogen.

**Effect of heating atmosphere on regeneration:** Figures 8 and 9 show the effect of the atmosphere under which the sorbent is heated to the regeneration temperature. The effect on regeneration with methane is not very significant (Figure 8). If the regeneration gases contain SO₂, the conversion appears to be higher due to the fact that the adsorbed SO₂ is also removed during regeneration. Figure 9 shows that the effect of the presence of SO₂ in the heating atmosphere is quite dramatic when regeneration is done with hydrogen. The regeneration rate is significantly reduced while the conversion appears to be very high due to the removal of adsorbed SO₂ similar to regeneration with methane.

**Cycling behavior of the sorbent with methane regeneration:** A sorbent sample was subjected to 5 sulfation-regeneration cycles with methane as the regeneration gas. Figure 10 shows that there is a significant difference between the sulfur capacities of the fresh and
Conversion for Regeneration with CH4 on 4.39% Cerium on Alumina

Figure 6. Effect of SO2 and CO2
CH4=15%; T=923 K
Conversion for Regeneration with H2
on 4.39% Cerium on Alumina

Figure 7. Effect of SO2

H2=10%; T=873 K
Conversion for Regeneration with CH4 on 4.39% Cerium on Alumina

Figure 8. Effect of heating atmosphere before regeneration
CH4=15%; T=923 K
Figure 9. Effect of heating atmosphere before regeneration
H2=10%
regenerated sorbents. This difference is higher than that observed with hydrogen as the regeneration gas. With methane the final S/Ce ratios obtained with regenerated sorbents were slightly above 1.5 while this number was slightly above 2 when regeneration was done with hydrogen. This may be due to different solid species being formed when regeneration was done with methane. The S/Ce ratios obtained for subsequent cycles indicate that regeneration with methane results in very stable sorbent sulfur capacity which did not change for 4 sulfation-regeneration cycles.
S/ Ce Ratios for SO2 Uptake by 4.39% Ce on ALCOA Alumina Sorbent

Figure 10. Effect of Cycling (with CH4)
T=873 K; SO2=0.3%; CH4=45%; particles
FUTURE WORK

In the next quarter, it is planned:

1) to continue the runs with ammonia to establish its effect on sulfation.
2) to develop a model for methane regeneration which will take all possible solid species into account.
3) to make experimental runs to find the effect of ceria content on sorbent performance.
4) to work with industrial partner Malcolm Pirnie on the economic evaluation of the flue gas cleanup process based on ceria sorbent.

BIBLIOGRAPHY

INVESTIGATION OF COMBINED $\text{SO}_2/\text{NO}_x$ REMOVAL BY CERIA SORBENTS

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Supported by a Grant from U. S. Department of Energy
Department of Energy's Pittsburgh Energy Technology Center (PETC) has been involved with the development of a regenerative fluidized bed process using copper oxide-impregnated alumina spheres for simultaneous removal of $\text{SO}_2$ and $\text{NO}_x$ since late 1960's. This process is expected to operate around 673 K.

A moving bed pilot unit is currently under construction.

Another copper oxide based process is the UOP/Shell Process which uses a cyclic fixed-bed contactor.
\[ CuO + SO_2 + \frac{1}{2} O_2 \rightarrow CuSO_4 \]

\[ 4NO + 4NH_3 + O_2 \rightarrow 4N_2 + 6H_2O \]

\[ 2NO_2 + 4NH_3 + O_2 \rightarrow 3N_2 + 6H_2O \]
Results of Hedges and Yeh

- The fully sulfated sorbent contains predominantly Ce(III).

- The rate of SO$_2$ uptake is independent of humidity (4-18 vol.% H$_2$O).

- The rate of SO$_2$ uptake is independent of CO$_2$ (0-15%), NO (0-500 ppm), and O$_2$ (2.8-12.7%) concentrations.

- Sulfation reaction is first order with respect to SO$_2$ and solid reactant (up to 75% conversion) concentrations.

- For the sulfation reaction:

  activation energy = 12 kJ/mol
Sorbent Preparation

- An aqueous solution of ceric ammonium nitrate \((\text{NH}_4)_2\text{Ce(NO}_3\text{)}\) is impregnated on 1/16" spherical pellets of ALCOA alumina by the incipient wetness technique.

- The resulting solid was dried at 393 K and calcined in air at 923 K for 6 hours.
The sorbents are characterized by the following methods:

1. density measurements by helium pycnometry,
2. surface area measurements by nitrogen adsorption,
3. porosity measurements by mercury intrusion,
4. determination of the cerium loading by atomic absorption measurements (being done by Malcolm Pirnie, Inc.), and
5. measuring the change in mass during calcination of prepared sorbents in air and nitrogen in a thermogravimetric analyzer.
Table 2. PHYSICAL CHARACTERISTICS OF SORBENTS

<table>
<thead>
<tr>
<th>Solid</th>
<th>Cerium Loading, ( \text{I by mass} )</th>
<th>Surface Area, ( \text{m}^2/\text{g} )</th>
<th>Intruded Hg Volume, ( \text{cm}^3/\text{g} )</th>
<th>Mean Pore Radius, ( \mu \text{m} )</th>
<th>True Solid Density, ( \text{g/cm}^3 )</th>
<th>Porosity, ( \times )</th>
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</thead>
<tbody>
<tr>
<td>ALCOA Alumina</td>
<td>none</td>
<td>192 - 219</td>
<td>0.5365</td>
<td>0.00324 &amp; 0.404</td>
<td>2.819</td>
<td>0.602</td>
</tr>
<tr>
<td>ALCOA-CE4-I</td>
<td>0.56</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>ALCOA-CE4-II</td>
<td>0.37</td>
<td></td>
<td>0.7746</td>
<td>0.00424 &amp; 0.5</td>
<td>3.4700</td>
<td>0.7288</td>
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<tr>
<td>ALCOA-CE4-III</td>
<td>0.74</td>
<td>139</td>
<td>0.7467</td>
<td>0.00444 &amp; 0.47</td>
<td>3.1841</td>
<td>0.7039</td>
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<tr>
<td>ALCOA-CE4-IV</td>
<td>1.59</td>
<td>132</td>
<td>0.7145</td>
<td>0.00644 &amp; 0.5</td>
<td>3.2596</td>
<td>0.6996</td>
</tr>
<tr>
<td>ALCOA-CE8-I</td>
<td>4.58</td>
<td>93</td>
<td>0.71</td>
<td>0.00644 &amp; 0.5</td>
<td>3.2382</td>
<td>0.6969</td>
</tr>
<tr>
<td>(ALCOA-CE4-V)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>ALCOA-CE4-VI</td>
<td>4.39</td>
<td>111</td>
<td>0.6307</td>
<td>0.0045 &amp; 0.65</td>
<td>3.2758</td>
<td>0.6738</td>
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<tr>
<td>ALCOA-CE8-II</td>
<td>7.64</td>
<td>97</td>
<td>0.5727</td>
<td>0.0038, 0.49</td>
<td>3.3931</td>
<td>0.6602</td>
</tr>
<tr>
<td>ALCOA-CE8-III</td>
<td>7.04</td>
<td>107</td>
<td>0.6039</td>
<td>0.004, 0.0063, 0.45</td>
<td>3.5669</td>
<td>0.6569</td>
</tr>
<tr>
<td>ALCOA-CE12-I</td>
<td>9.28</td>
<td>81</td>
<td>0.3121</td>
<td>0.0045, 0.0072, 0.45</td>
<td>3.5738</td>
<td>0.5270</td>
</tr>
<tr>
<td>ALCOA-CE12-II</td>
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<td>100</td>
<td>0.4766</td>
<td>0.0035, 0.0055, 0.45</td>
<td>3.7122</td>
<td>0.6389</td>
</tr>
<tr>
<td>ALCOA-CE12-III</td>
<td>14.7</td>
<td>64</td>
<td>0.438</td>
<td>0.0035, 0.008, 0.5</td>
<td>3.8265</td>
<td>0.6260</td>
</tr>
</tbody>
</table>
Figure 1:

Surface Area of Ceria Sorbents

Surface Area (m²/g)

Cerium Loading (mass %)

0 10
0 8
2 6
4 4
10 2
Porosity of Ceria Sorbents

Figure 2.
STANDARD SULFATION-REGENERATION CYCLE

- Sulfation gas composition: 0.3% SO₂, 3% O₂, 14% CO₂, balance N₂ and He.

- Regeneration gas composition: 100% H₂

- Sulfation temperature: 873 K

- Regeneration temperature: 873 K

- Gas flow rate: 200 cm³(NTP)/min
\[ \text{O}_2\text{O}^\varphi_{\text{C} \text{C}} + \text{O}^\varphi_{\frac{2}{1}} + \text{O}^\varphi_{\text{C} \text{C}} \text{C}^\varphi_{\frac{2}{1}} \]

\[ \text{O}_2\text{H} \text{E} + \text{SO}_2 \text{E} + \text{O}_2\text{C} \text{O}^\varphi_{\text{C} \text{C}} + \text{H} \text{E} + \text{OS}_2 \text{C}^\varphi_{\text{C} \text{C}} \]

\[ \text{OS}_2 \text{C}^\varphi_{\text{C} \text{C}} + \text{O}_2 \text{E} \text{C}^\varphi_{\frac{2}{1}} + \text{OS}_2 \text{E} \text{C}^\varphi_{\frac{2}{3}} + \text{O}_2 \text{E} \text{C}^\varphi_{\text{C} \text{C}} \]
S/Se Ratios for SO2 Uptake by 4.39% Ce on ALCOA Alumina Sorbent

Figure 5. Effect of Cycling.
T=873 K; SO2=0.3%
S/Ce > 1.5 (stoichiometric) can be explained by a mechanism similar to that for Cu.

- $\text{SO}_2 \rightarrow \text{SO}_3$ on the surface, catalyzed by copper. This step may control the rate of sulfation.
- Copper species are involved in the formation of sulfate from $\text{SO}_3$.
- Migration of $\text{SO}_3$ to alumina sites forming sulfated alumina species.
- Re-oxidation of copper.
S/Ce Ratios for SO2 Uptake by 4.39% Ce on ALCOA Alumina Sorbent

![Graph showing S/Ce ratios over time for different temperatures.]

Figure 6. Effect of Temperature
SO2=0.3%; no water
III. CONCLUSIONS

1. The sulfur capacity decreases by about 10% after the first cycle but the change 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 the fresh sorbent. This indicates substantial contribution by the support to sulfur retention.

2. Even at 673 K the sorbents can bind over 1.5 sulfur atoms per cerium atom. The highest S/Ce ratios are obtained in the temperature range 773-873 K. The optimum operating temperature will be determined by the process economics.

3. Activation Energy of the sulfation reaction was found to be 19 kJ/mol. This is somewhat higher than the 12 kJ/mol reported by Hedges and Yeh.
S/ Ce Ratios for SO2 Uptake by 4.39% Ce on ALCOA Alumina Sorbent

Figure 8. Effect of Ammonia
T=873 K; SO2=0.3%; no water
TABLE 2. Effect of Temperature and Ammonia Concentration on S/Ce at 50 minutes. \( \text{SO}_2 = 0.3\%\), no water

<table>
<thead>
<tr>
<th>Test #</th>
<th>Cycle #</th>
<th>( T, \text{K} )</th>
<th>( C_{\text{NH}_3}, \text{ppm} )</th>
<th>S/Ce</th>
</tr>
</thead>
<tbody>
<tr>
<td>51</td>
<td>3</td>
<td>673</td>
<td>0</td>
<td>1.498</td>
</tr>
<tr>
<td>54</td>
<td>6</td>
<td>723</td>
<td>0</td>
<td>1.626</td>
</tr>
<tr>
<td>53</td>
<td>5</td>
<td>773</td>
<td>0</td>
<td>1.988</td>
</tr>
<tr>
<td>55</td>
<td>7</td>
<td>823</td>
<td>0</td>
<td>2.045</td>
</tr>
<tr>
<td>52</td>
<td>4</td>
<td>873</td>
<td>0</td>
<td>2.085</td>
</tr>
<tr>
<td>59</td>
<td>11</td>
<td>673</td>
<td>250</td>
<td>1.336</td>
</tr>
<tr>
<td>61</td>
<td>13</td>
<td>773</td>
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<td>1.673</td>
</tr>
<tr>
<td>57</td>
<td>9</td>
<td>873</td>
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<td>1.858</td>
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<tr>
<td>60</td>
<td>12</td>
<td>673</td>
<td>500</td>
<td>1.388</td>
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<tr>
<td>62</td>
<td>14</td>
<td>773</td>
<td>500</td>
<td>1.543</td>
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<tr>
<td>58</td>
<td>10</td>
<td>873</td>
<td>500</td>
<td>1.923</td>
</tr>
</tbody>
</table>
The reduction of sulfation capacity by NH$_3$ becomes more significant in the presence of H$_2$O.

This may be due to the change in the active support sites. The acidity of alumina sites will be reduced by NH$_3$ (a base).
S/ Ce Ratios for SO2 Uptake by 4.39\% Ce on ALCOA Alumina Sorbent

![Graph showing S/ Ce ratios over time for different temperatures and water conditions.](image)

**Figure 7.** Effect of Temperature and H2O
SO2=0.3\%; NH3=500 ppm
4. The sorbent capacity is significantly reduced by the water vapor in the reactants in the presence of ammonia. This may be due to the competitive adsorption of water on active sites.

5. It appears that a small amount of ammonia is sufficient to cause about 10-15% reduction in sorbent capacity but this effect does not seem to depend strongly on ammonia concentration. Preliminary kinetic studies indicated a 12% decrease in the initial rate of sulfation upon the addition of 500 ppm ammonia.
Centi’s explanation of the reduction of S/Cu with NH$_3$:

- NH$_3$ adsorbs as ammonium ions forming ammonium bisulfate.
- Ammonium bisulfate then dissociates resulting in loss of sulfate.
- Due to capillary condensation of ammonium bisulfate in catalyst micropores, rate of loss of bisulfate depends on porosity.
- Time of contact between the sample and the NH$_3$-containing stream should be minimized to reduce ammonium bisulfate formation.
Data Evaluation for Regeneration with $H_2$

$$\text{Ce}_2(\text{SO}_4)_3 + 3H_2 \rightarrow \text{Ce}_2O_3 + 3\text{SO}_2 + 3H_2O$$

$$x = \frac{(m_o - m)(M_{\text{Ce}_2(\text{SO}_4)_3})}{(m_{o,\text{Ce}_2(\text{SO}_4)_3})(M_{\text{Ce}_2(\text{SO}_4)_3} - M_{\text{Ce}_2O_3})}$$

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

$$r = \frac{1}{(M_{\text{Ce}_2(\text{SO}_4)_3} - M_{\text{Ce}_2O_3})}\left(\frac{dm}{dt}\right)$$
\[
\begin{align*}
CeO_2 + 0.17H_2 & \rightarrow CeO_{1.83} + 0.17H_2O \\
CeO_2 + 0.5H_2 & \rightarrow 0.5Ce_2O_3 + 0.5H_2O \\
CeO_2 + 0.5Al_2O_3 + 0.51H_2 & \rightarrow CeAlO_3 + 0.5H_2O \\
CeO_2 + 0.28H_2 & \rightarrow CeO_{1.72} + 0.28H_2O
\end{align*}
\]
Conversion for Regeneration on 4.39% Cerium on Alumina

Figure 3. T=873 K
REDUCTION BY HYDROGEN

4.39% Ce (by mass) on alumina with 111 m²/g gives 1.43 μmol CeO₂/m² Al₂O₃ indicating less than monolayer coverage. Under these conditions, according to literature, small CeO₂ crystallites and CeAlO₃ precursor is expected.

Current results are based on reduction to Ce₂O₃, but CeAlQ₃, CeOₓ, and Ce₂O₃ may all be present.

In the future calculations will be made using a model which will account for all the species present.
Conversion for Regeneration
on 4.39% Cerium on Alumina

Figure 4. H2= 50%
Effect of hydrogen concentration on initial reaction rate

Figure 2. $T = 873 \text{ K}$
CONCLUSIONS

Regeneration reaction is first order with respect to the solid reactant up to 40% conversion.

For regeneration with hydrogen, the activation energy $= 114 \text{ kJ/mol} \ (27 \text{ kcal/mol})$

The reaction order with respect to hydrogen $= 0.56$ at $873 \text{ K.}$
The correlation coefficient for the fit is $0.95844$ and the estimates for $K_1$ and $k_2$ are

$$K_1 = 9.23$$
$$k_2 = 1.17$$
REGENERATION WITH METHANE

\[ \text{Ce}_2(\text{SO}_4)_3 + \text{CH}_4 \rightarrow \text{Ce}_2\text{O}_3 + 3\text{SO}_2 + \frac{1}{2}\text{CO} + 2\text{H}_2\text{O} \]

\[ \text{CH}_4 \rightarrow \text{C} + 2\text{H}_2 \]

\[ 3\text{C} + 2\text{Ce}_2\text{O}_3 \rightarrow 4\text{Ce} + 3\text{CO}_2 \]
Thermogram for Regeneration with 
Methane on 4.39% Cerium on Alumina

Change in Mass, mg x 1000

Figure 1. CH4 = 100%, T = 873 K
Thermogram for Regeneration with Methane on 4.39% Cerium on Alumina

Figure 2. CH4: 100%, T: 923 K
Thermogram for Regeneration with
Methane on 4.39% Cerium on Alumina

Change in Mass, mg x 1000

Time, min

Figure 3. CH4 × 15%, T × 923 K
OBSERVATIONS ON COKING DURING REGENERATION WITH METHANE

- As temperature increases, the time to reach minimum mass during regeneration with 100% CH₄ decreases. This indicates that the activation energy of the coking reaction is greater than the activation energy of the regeneration reaction.
- At 923 K, as partial pressure of CH₄ decreases the time to reach minimum mass increases. This indicates that the order of the regeneration reaction w.r.t. CH₄ is positive and is smaller than the order of the coking reaction w.r.t. CH₄.
Conversion for Regeneration with CH4 on 4.39% Cerium on Alumina

![Figure P1. T=925 K](image-url)
REGENERATION WITH METHANE

\[ r = k^r(p_{CH_4})^a \]

\[ a = 0.762 \quad \text{corr. coeff.} = 0.945 \]

\[ r = k_0 e^{-\frac{E}{RT}} \]

\[ \frac{E}{R} = 16,300 \quad E = 135 \text{ kJ/mol} \]

\[ \text{corr. coeff.} = 0.642 \]

If 650° C data is deleted: \[ \frac{E}{R} = 15,600 \quad \text{corr. coeff.} = 0.871 \]