EXECUTIVE SUMMARY
OF
RESULTS DEVELOPED UNDER A DOE/ERIP GRANT
BY
GAS DESULFURIZATION CORP.

The objective of this work was to demonstrate that solid solutions of cerium oxide (CeO$_2$) and other altervalent oxides (doped CeO$_2$) were capable of removing more H$_2$S from fuel gases than CeO$_2$ without any dopant. The ability of undoped CeO$_2$ to remove H$_2$S from fuel gases had been determined with a previous DOE/SBIR grant. To make the results obtained under the two grants comparable, the procedures for all phases of this work duplicated that used previously as closely as possible.

The sorbents GDC proposed to investigate were: 1. undoped CeO$_2$, 2. CeO$_2$ doped with 5 mole % (5 m/o) magnesium oxide (MgO), and 3. CeO$_2$ doped with 5 m/o lanthanum oxide (La$_2$O$_3$). Three additional sorbents: 1. CeO$_2$ doped with 5 m/o strontium oxide (SrO), 2. CeO$_2$ doped with 10 m/o SrO, and 3. CeO$_2$ doped with 10 m/o La$_2$O$_3$ were also investigated. All of these sorbents were prepared using the Marcilly technique.

GDC has adopted the practice of describing the composition of synthetic fuel gases on the basis of the ratio of the reducing gases to the oxidizing gases: (\%CO + \%H$_2$)/(\%CO$_2$ + \%H$_2$O) or Quality Factor or QF. QF at any temperature is directly related to the partial pressure of oxygen in the gases (pO$_2$), and the extent of desulfurization of a fuel gases with CeO$_2$ is directly related to its pO$_2$. The QF of the gases exiting available gasifiers ranges from less than one to as high as twenty five. The gases chosen for this work had Quality Factors of 1.5, 3.5, 7.5 and 22.5. During the previous work done under the DOE/SBIR grant the QF of the gases desulfurized ranged from 1.49 to 12.99. The relationship between QF and the extent of desulfurization at 1000C from a starting level of 1.0% (10000 ppm) for the work performed under the previous DOE/SBIR program is shown in Figure 1. Also included on this diagram are curves showing the extent of desulfurization with CeO$_2$ without any doping, CeO$_2$ doped with 5 m/o La$_2$O$_3$, and CeO$_2$ doped with 10 m/o La$_2$O$_3$ when exposed to various QF gases containing 1% H$_2$S at 1000C.

Based on work performed in the microreactor designed for the DOE/SBIR program and reconstructed for the DOE/ERIP program it has been determined that:

1. Differences in the BET surface area of the undoped CeO$_2$ used in the two programs can account for the increase in sulfur removal from the gases in the DOE/ERIP program. The undoped CeO$_2$ used in the DOE/SBIR program had a surface BET of 1.1 m$^2$/gm and the CeO$_2$ used in the DOE/ERIP work had a surface BET of 2.4 m$^2$/gm. Since both sorbents were made
with the same technique and the same raw materials, subtle differences in the manufacture of the sorbent must account for the difference in their BET surface area.

2. The addition of 5 m/o La$_2$O$_3$ to the CeO$_2$ increased the ability of CeO$_2$ to remove H$_2$S from fuel gases compared to undoped CeO$_2$. An increase to 10 m/o La$_2$O$_3$ provided an additional increase in the ability to remove H$_2$S. The BET surface area of the CeO$_2$ doped with 5 m/o of La$_2$O$_3$ was 2.4 m$^2$/gm. Although the surface area of the CeO$_2$ doped with 10 m/o La$_2$O$_3$ was not measured, it was made with the same techniques which would indicate it would have a similar surface area. Because of lack of time, only the extent of desulfurization at a QF of 7.5 was determined for the CeO$_2$ doped with 10 m/o La$_2$O$_3$.

3. CeO$_2$ doped with 5 m/o La$_2$O$_3$ can be sulfided and regenerated for ten times without discernable loss in its ability of desulfurize fuel gases.

4. Utilization of the 5 m/o La$_2$O$_3$ sorbent averaged over 118% of that required to convert CeO$_2$ to Ce$_2$O$_2$S.

5. When the sulfided sorbent is regenerated with a gas mixture of 10% air 90% nitrogen, elemental sulfur is produced.

6. MgO was ineffective as a dopant for CeO$_2$.

7. Increasing the weight of sorbent in the microreactor from 2 grams to 4 grams (cutting the space velocity in half) had little or no effect on the extent of desulfurization.

8. Reducing the H$_2$S content of the gases entering the microreactor from 1% to 0.5% reduce the H$_2$S content of the effluent gas by 18 % in one case and 27 % in another.

Based on the work completed to date, additional work should be performed to systematically investigate the effect of surface area on the ability of CeO$_2$ doped with 10 m/o La$_2$O$_3$. During the preparation of the sorbents, it has been determined that after the pyrolysis step at 400°C the surface area is about 20 m$^2$/gram. As the sintering temperature is increased, the surface area decreases to the values shown above after sintering at 1250°C. It is proposed to make additional sorbent through the pyrolysis stage, and then vary the sintering temperature to achieve various BET surface areas. These sorbents with varying BET surface areas would be exposed to a fuel gas of one QF to determine the effect of surface area on the ability of doped CeO$_2$ to desulfurize fuel gases.
QF VS H2S CONC AFTER REACTION
TEMP. 1000°C, 1% H2S AT START

RELATIONSHIP FROM DOE/SBIR PROGRAM

EXTRAPOLATION AFTER QF 12

H2S CONC (PPM) AFTER REACTION

QUALITY FACTOR (QF)

RELATION - 5 M/O LA2O3 - NO DOPANT - 10 M/O LA2O3

DISCLAIMER

This report was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor any agency thereof, nor any of their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof.
END

DATE FILMED

3/6/92