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Sulphur removal using regenerable sorbents of rare earth/transition metal oxides

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SULFUR REMOVAL USING REGENERABLE SORBENTS OF RARE EARTH / TRANSITION METAL OXIDES

A Thesis

Submitted to the Graduate Faculty of the Louisiana State University and Agricultural and Mechanical College in partial fulfillment of the requirements for the degree of Master of Science in Chemical Engineering

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By
Vikram Reddy Kalakota
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ABSTRACT

Hot gas desulfurization of gases from primary gasifier can be accomplished using sorbents composed of Zn, calcium and transition metal oxide sorbents. The problem with metal oxide sorbents alone is that they are easily reduced at high temperature above 873 K to metallic state under reducing atmosphere decreasing their desulfurization capacity.

Sorbents studied for hot gas desulfurization were based on Ce/La/M (M = transition metal) oxides and Ce/La/RE (RE = a rare earth) oxide. Sorbents were prepared using sol-gel method and the rare earth oxides were doped with transition metals using incipient wetness impregnation. Sulfidation experiments were carried out at 873 K using a reacting gas composition of 23.4 mol% H₂, 41.4% N₂, 3.1% water, 32.0% CO₂, and 0.1% H₂S. Reduced Ce/La oxides adsorb H₂S at temperatures of 873 K and above, and were regenerable in O₂ mixtures. The addition of group VII-VIII transition metals to Ce/LaOₓ increases the sulfur removal capacity significantly. Among the transition metals (Mn, Fe, Cu) studied, Ce/LaOₓ mixtures impregnated with Mn had the highest capacity followed by Fe and Cu. The optimum ratio of M/(Ce+La) is around 0.1 and the sulfur capacity was higher in sorbents which are rich in La, and the optimum ratio of Ce/La for high sulfur capacity is around 0.9. Addition of oxides such as ZrO₂ or a third rare earth oxide increases surface area, sintering resistance, oxygen mobility of CeOₓ/La₂O₃ at high temperatures, and sulfur capacity. These ternary REOs maintained their capacity in next successive four runs and these were easily regenerated in air.
CHAPTER 1
INTRODUCTION AND REVIEW OF LITERATURE

1.1 Goals and Project Summary

During a coal gasification process, sulfur present in the gas exiting the primary gasifier is transformed into mostly \( \text{H}_2\text{S} \) (Yasyerli, 2008). The amount of \( \text{H}_2\text{S} \) released from the integrated gasification combined cycle (IGCC) is limited to 150 ppmv (Ben-Slimane and Hepworth, 1994; Liang et al., 1999; Karayilan et al., 2005). This \( \text{H}_2\text{S} \) must be removed as it causes deactivation of reforming and water-gas shift catalysts and poses serious environmental problems (Liang et al., 1999). Initially for the removal of sulfur in IGCC the gas is cooled down. Then after desulfurization the gas is reheated. This process results in the loss of thermal efficiency (Kyotani et al., 1989; Mojtabaei et al., 1994). Therefore in order to increase the thermal efficiency of IGCC, hot gas desulfurization is being developed (Fan et al., 2005).

The important factors a hot gas desulfurization sorbent should possess are (Bakker et al., 2003):

- The sorbent should have good sulfur removal capacity and fast adsorption kinetics.
- The sorbent should be chemically stable, that is, it should not evaporate or sinter during regeneration.
- The sorbent should be physically stable, that is, it should withstand attrition.
- The sorbent should catalyze formation of elemental sulfur upon reductive regeneration, should hydrolyze carbonyl sulfide (COS), and should react other contaminants such as tars.
- The sorbent should be regenerable and it should maintain its sulfur removal capacity for many cycles.
The sorbent replacement cost should be affordable.

Hot gas desulfurization can be accomplished by using metal oxide-based sorbents like zinc, manganese, iron, and copper. Typically, these metal oxides are converted to sulfides during a sulfur-loading stage under reducing hot gas conditions (Van Der Ham et al., 1996).

\[
\text{Me}_x\text{O}_y(s) + x \text{H}_2\text{S}(g) + (y-x) \text{H}_2(g) \rightarrow x \text{MeS}(s) + y \text{H}_2\text{O}(g)
\]

Biomass gasification is a process in which biomass is converted into gaseous compounds, mainly hydrogen, carbon oxides, methane and water. The initial elemental feed composition of biomass for a typical gasification in wt% is: carbon, 49-52%; hydrogen, 5-7%; nitrogen 0.1-2%; oxygen, 40-43%; sulfur, 0.02-0.3%; chlorine < 0.1% (Pengmei et al., 2007; Zhang et al., 2005; Juutilainen et al., 2006). The composition of gas from the exit of a typical primary gasifier during biomass gasification at temperatures between 773-1073 K is 33-35% hydrogen, 18–35% carbon monoxide, 12-25% carbon dioxide, 3–6% methane, 7–12% water, 1.3–3.5% C\textsubscript{2+} fraction, 0.2–0.5% nitrogen, 0–0.05% hydrogen sulfide, 0–0.02% chlorides, 0–0.003% potassium (Kuramochi et al., 2005). The tars are normally taken to be any hydrocarbons >C\textsubscript{2}. For further reforming of methane and for water-gas shift, the sulfur, chlorine and tars, all of which poison reforming or water-gas shift catalysts, must be removed.

The aim of this project is to identify suitable sorbents/catalysts based on mixed rare earth oxides (REO) CeO\textsubscript{2}/M\textsubscript{1}O\textsubscript{x}/M\textsubscript{2}O\textsubscript{y} and CeO\textsubscript{2}/M\textsubscript{1}O\textsubscript{x}/M\textsubscript{2}O\textsubscript{y}Al\textsubscript{2}O\textsubscript{3} (M\textsubscript{1} is a REO and M\textsubscript{2} is either a third REO or a group VIIB–VIIIB transition metal oxide) for hot gas desulfurization and the cracking of tars. We are searching for materials which are stable at 873 K and higher temperatures, especially in the presence of steam.

The tars produced during gasification result in coke formation on reforming and shift catalysts. Tar removal is typically by two methods: 1, primary removal inside the gasifier; 2,
secondary removal from the product gas after the gasifier. Initially, Ni-based catalysts were studied for the removal of tar. These catalysts can completely remove tar at up to 1173K. But a problem is that the activity of the Ni-based catalysts decreases rapidly. Ni-based catalysts promoted by cerium oxide and supported on Al₂O₃ have improved coking resistance (Devi et al., 2003; Jazbec et al., 2005).

Rare earths are also proven secondary reforming catalysts at temperatures of 573–1173 K. Gd-Ce mixtures, La, Ce and Ni mixtures, and cerium oxide have all been observed to catalyze reforming of methane. For the Gd-Ce mixed oxides it was observed that they are completely resistant to coke during reforming of methane which began at 943 K. As temperature increased the production of hydrogen increased up to 1173 K (Ferrandon and Krause, 2006; Cabrera et al., 2004). For catalysts with La and Ni, when Ce is added the stability and the production of hydrogen increased (Qi et al., 2005).

The use of REOs for hot gas desulfurization at temperatures up to 1073 K is possible because of their excellent sulfidation equilibria, allowing removal of sulfur to sub-ppmv levels at high temperatures (Flytzani-Stephanopoulos et al., 2006). REOs may be able to desulfurize and remove tars simultaneously in biomass and coal gasification, while at the same time catalyzing methane reforming. In this manner they could act as three-way catalysts/sorbents.

### 1.2 Rare Earth Oxides for Hot Gas Desulfurization

Cerium oxide, because of its reducibility, is a potential candidate for hot gas desulfurization (Zeng et al., 1999, 2000). The catalytic activity of CeOₓ in reforming or tar cracking reactions is due to the high mobility of oxygen vacancies in the crystal structure (Tschope et al., 2005). Cerium oxide (CeO₂), is reduced at 560-900 K to CeOₓ, 1.7< n <2 (Trovarelli, 1996; Rogemond et al., 1997; Ferrizz et al., 2003; Kay et al., 1993; Wang and
Flytzani-Stephanopoulos, 2005). Thermodynamically, CeO$_2$ alone cannot reduce H$_2$S concentrations below 20 ppm, whereas partly reduced cerium oxide can reduce H$_2$S concentrations further (Zeng et al., 2000; Zheng and Flytzani-Stephanopoulos, 2005).

Cerium oxide under high temperature reducing conditions reacts with H$_2$S to form cerium oxysulfide (Ce$_2$O$_2$S) (Yi et al., 2005; Zeng et al., 2000). According to the phase diagram of sulfided cerium oxide, other sulfides such as CeS, Ce$_3$S$_4$, Ce$_2$S$_3$ can also be formed depending upon the temperature and the partial pressure of sulfur (Ferrizz et al., 2003). From Figure 1, it is seen that Ce$_2$S$_3$ is formed only when the partial pressure of sulfur (P$_{S2}$) is very high and in general the most likely product is Ce$_2$O$_2$S. The inner dots in Figure 1.1 are based on $\Delta$G$_f$ of Ce$_2$O$_2$S.

Thermodynamic calculations based on a typical effluent gas composition (H$_2$ - 29%, CO - 40%, CO$_2$ - 2%, H$_2$O - 5% and H$_2$O - 1%, balance N$_2$, Zeng et al., 2000) showed that the reaction between CeO$_2$ and H$_2$S is endothermic; therefore as the temperature increases the equilibrium concentration of H$_2$S decreases. However, the reaction between Ce$_2$O$_3$ and H$_2$S to Ce$_2$S$_3$ is exothermic (Zeng et al., 2000). The entire sequence of reactions is:

Reduction of cerium oxide

$$\text{CeO}_2(s) + (2-n) \text{H}_2(s) \rightarrow \text{CeO}_n(s) + (2-n) \text{H}_2\text{O}(s)$$

Sulfidation of cerium oxides

$$\text{CeO}_2(s) + \frac{1}{2} \text{H}_2\text{S}(g) + \frac{1}{2} \text{H}_2(g) \rightarrow \frac{1}{2} \text{Ce}_2\text{O}_2\text{S}(s) + \text{H}_2\text{O}(g)$$

$$\text{CeO}_2(s) + \frac{3}{4} \text{H}_2\text{S}(g) + \frac{1}{2} \text{H}_2(g) \rightarrow \frac{1}{2} \text{Ce}_2\text{S}_3(s) + 2 \text{H}_2\text{O}(g)$$

$$\text{Ce}_2\text{O}_3(s) + \text{H}_2\text{S}(g) \rightarrow \text{Ce}_2\text{O}_2\text{S}(s) + \text{H}_2\text{O}(g)$$

$$\text{Ce}_2\text{O}_3(s) + 3\text{H}_2\text{S}(g) \rightarrow \text{Ce}_2\text{S}_3(s) + 3\text{H}_2\text{O}(g)$$
For the last reaction, \( \Delta H \) (298 K) = -56.04 kJ/mol (Hartman and Trnka, 2006).

Figure 1.1: Phase diagram of cerium oxide at 873 K (taken from Ferrizz et al., 2003)

Only a slight difference in performance was observed between sulfidation of the prereduced CeO\(_2\) and simultaneous sulfidation and reduction, for a feed gas composition of 10% H\(_2\), 1% H\(_2\)S, balance N\(_2\) (Zeng et al., 2000). The presence of water in the reacting gas composition reduced the sulfur removal capacity. CeO\(_2\) showed maximum capacity at 923 K, 1.0-1.2 mg of S/g of sorbent for a reacting gas concentration of 0.1% H\(_2\)S, 50% H\(_2\), 10% H\(_2\)O, balance He (Flytzani-Stephanopoulos et al., 2006).

The problem with CeO\(_2\) alone for the removal of H\(_2\)S in hot gas desulfurization is the slow kinetics of the CeO\(_2\)-H\(_2\)S reaction and the relatively slow reduction kinetics of Ce(+4) to Ce(+3). But the redox kinetics of CeO\(_x\) can be increased by adding La, Zr, Gd, or Tb into the
CeO$_2$ lattice, forming solid solutions (Colon et al., 1998; Flytzani-Stephanopoulos et al., 2005). Such additions increase the number of oxygen vacancies and oxygen ion mobility, while stabilizing CeO$_2$ against sintering up to 1073 K (Tschope et al., 2005; Wang and Flytzani-Stephanopoulos, 2005). For CeO$_x$-30 at% LaO$_x$ no phase segregation is observed. Cerium keeps lanthanum in a highly dispersed state for up to 70 at% LaO$_x$ concentrations (Wang and Flytzani-Stephanopoulos, 2005).

Similar to CeO$_2$, La$_2$O$_3$ reacts with H$_2$S to form the oxysulfide.

$$\text{La}_2\text{O}_3 (s) + \text{H}_2\text{S} (g) \rightarrow \text{La}_2\text{O}_2\text{S} (s) + \text{H}_2\text{O} (g)$$

The sulfur removal capacity of pure La$_2$O$_3$ is 0.8–0.9 mg of S/g of sorbent for a reacting gas of 0.1% H$_2$S, 50% H$_2$, 10% H$_2$O and balance He at 1073 K (Flytzani-Stephanopoulos et al., 2006). As the concentration of La$_2$O$_3$ in CeO$_2$/La$_2$O$_3$ increased, the surface area decreased. For 30 and 70 at% La$_2$O$_3$, sorbents, the 70 at% sorbent had the highest initial sulfur removal capacity, with maximum capacity at 923 K. For 30 at% La$_2$O$_3$ the initial sulfur capacity was 3.5–7.0 mg of sulfur/g of sorbent at 923 K and 1.5-3.0 mg/g at 1073 K. For 70 at% La$_2$O$_3$, the initial capacity is 19.1-32.5 mg/g. Space velocity had no effect on sulfur removal capacity, although breakthrough time decreased with increased space velocity as expected (Flytzani-Stephanopoulos et al., 2006). Temperature also had little effect on the sulfur capacity of CeO$_2$-70% La$_2$O$_3$, but the capacity decreased by more than 75% after two sulfidation cycles (Wang and Flytzani-Stephanopoulos, 2005). Oxidative regeneration followed by reduction was carried out on these sorbents. After five sulfidation/regeneration cycles the sulfur capacity of both CeO$_2$/La$_2$O$_3$ sorbents decreased to around 3-4 mg/g and thereafter it stabilized.

Addition of ZrO$_2$ to CeO$_2$ increases sulfidation performance and sintering resistance at temperatures greater than 873 K (Yi et al., 2005; Trovarelli et al., 1997). It was also observed
that the addition of ZrO$_2$ to CeO$_2$ increased the redox kinetics and surface area (Colon et al., 1998; Trovarelli et al., 1997; Yi et al., 2005). ZrO$_2$ intimately mixes with cerium oxide without any phase segregation (Yi et al., 2005; Trovarelli et al., 1997) up to ~50 at% ZrO$_2$.

The addition of ZrO$_2$ to CeO$_2$ also increases the bulk reducibility of CeO$_2$; the temperature at which bulk reduction occurs decreases (Fornasiero et al., 1995; Ranga Rao et al., 1999). The optimum concentration for maximum reducibility is ~20 at% Zr (Yi et al., 2005; Fornasiero et al., 1995). The reactions during sulfidation are presumed to be as follows.

\[
\text{Ce}_{1-x}\text{Zr}_x\text{O}_2 (s) + (2 - n) \text{H}_2 (g) \rightarrow \text{Ce}_{1-x}\text{Zr}_x\text{O}_n (s) + (2 - n) \text{H}_2\text{O} (g)
\]

\[
2 \text{Ce}_{1-x}\text{Zr}_x\text{O}_2 (s) + \text{H}_2\text{S} (g) + \text{H}_2 (g) \rightarrow \text{Ce}_{2(1-x)}\text{Zr}_{2x}\text{O}_2\text{S} (s) + 2 \text{H}_2\text{O} (g)
\]

CeO$_2$-ZrO$_2$ mixtures are able to reduce H$_2$S to sub-ppmv levels for a feed containing 0.25% H$_2$S, 10% H$_2$ and balance N$_2$ from 873-1023 K. For 20 at% Zr, the breakthrough time increased compared to CeO$_2$ and 10 at% ZrO$_2$/CeO$_2$. As the temperature increased the breakthrough time increased; the optimum temperature was 973 K (Yi et al., 2005).

1.3 Transition Metal Oxides for Hot Gas Desulfurization

Based on thermodynamic calculations the metal oxides of Fe, Zn, Mn, Mo, V, Ca, Sr, Ba, Co, Cu and W are feasible for hot gas desulfurization (Westmoreland and Harrison, 1976). In the temperature range 573-1073 K, desulfurization performance (% of sulfur adsorbed from the gas phase) of some metal oxides decreased in the order MnO > CaO = ZnO > V$_2$O$_3$ (Westmoreland and Harrison, 1977).

The kinetics of the ZnO-H$_2$S reaction is rapid and ZnO can reduce the H$_2$S concentration from 5000 to less than 10 ppmv (Lew et al., 1989). The problems with zinc sorbents arise upon operation at high temperatures, and during regeneration. A typical coal gasifier operates at
temperatures from 773–1073 K; zinc sorbents cannot be used at temperatures above 823 K. At temperatures above 823 K and in reducing atmospheres, ZnO is reduced to metallic Zn; the subsequent vaporization of Zn results in rapid decrease in the sulfur capacity (Garcia et al., 2000; Zeng et al., 2000; Ko, et al., 2005).

The ZnS formed by the ZnO-H₂S reaction is stable in O₂ to 993 K; regeneration is at higher temperature (Garcia et al, 2000). Stable ZnSO₄ is made when regeneration is carried at lower temperatures or in high partial pressures of oxygen. Regeneration at higher temperatures leads to excessive thermal sintering (White et al., 1998; Garcia et al., 2000).

A similar problem occurs with CaO. During regeneration of CaS using oxygen, CaSO₄ is formed and is stable to 1473 K. Regeneration at high temperatures leads to thermal sintering. Sulfidation and regeneration must be carried at very different temperatures resulting in a loss in thermal efficiency for the overall process (Uddin and Sasaoka, 2005). The regeneration reaction is:

$$\text{CaS} (s) + 1.5 \text{O}_2 (g) \rightarrow \text{CaO} (s) + \text{SO}_2 (g)$$

Kinetics studies have shown that manganese oxide is stable for hot gas desulfurization up to ~973 K with high sulfur capacity between 873 - 973 K (Ben-Slimane and Hepwaorth, 1994). The stable form of Mn at these conditions is MnO. Higher oxides of manganese are easily reducible to MnO (Ben-Slimane and Hepwaorth, 1994). In reducing atmospheres, Mn₂O₃ is reduced to Mn₃O₄, a highly exothermic reaction. Then Mn₃O₄ is reduced to MnO.

$$3 \text{Mn}_2\text{O}_3 (s) + \text{H}_2 (g) \rightarrow 2 \text{Mn}_3\text{O}_4(s) + \text{H}_2\text{O} (g) \quad (\Delta H = -147.1 \text{ kJ mol}^{-1})$$

$$\text{Mn}_3\text{O}_4(s) + \text{H}_2(g) \rightarrow 3 \text{MnO} (s) + \text{H}_2\text{O} (g)$$
MnO reacts with \( H_2S \) to form MnS.

\[
\text{MnO} \ (s) + H_2S \ (g) \rightarrow \text{MnS} \ (s) + H_2O \ (g)
\]

At high temperatures in reducing atmospheres, MnO does not vaporize (Westmoreland et al., 1977), and kinetics studies have shown that the sulfidation rate of Mn-based sorbents is faster than that of Zn- or Fe-based sorbents (Alonso et al., 2000).

At either 673 or 1073 K, Mn-based sorbents showed increased sulfidation rates with increases in \( H_2S \) feed content (Yoon et al., 2003). But as the Mn content increases, \( \text{MnO}_X \) forms clusters during calcining, resulting in decreased sulfur capacity. At greater than 16\% \( \text{Mn}_2O_3 \) in Mn-Al\(_2\)O\(_3\), large clusters appeared (Liang et al., 1999). Water in the feed also decreases the capacity of Mn-based sorbents. If water is present, then supported MnO-type sorbents are better than MnAl\(_2\)O\(_4\) for hot gas desulfurization, as MnO is less affected by the water (Bakker et al., 2003).

For Cu-based sorbents, the kinetics of the sulfidation reaction are fast for Cu in the +2 or +1 oxidation states (Swisher et al., 2000). However, \( \text{CuO}_X \) is easily reduced to Cu, which has slow kinetics for \( H_2S \) removal (Flytzani-Stephanopoulos et al., 2005). For Cu-based sorbents, the optimum temperature of operation for hot gas desulfurization is \( \sim 873 \) K (Abbasian and Slimane, 1998). The following reactions take place:

\[
\text{CuO} \ (s) + \frac{1}{2} \text{H}_2 \ (g) \rightarrow \frac{1}{2} \text{Cu}_2\text{O} \ (s) + \frac{1}{2} \text{H}_2\text{O} \ (g)
\]

\[
\text{CuO} \ (s) + \text{H}_2 \ (g) \rightarrow \text{Cu} \ (s) + \text{H}_2\text{O} \ (g)
\]

\[
2 \text{Cu} \ (s) + \text{H}_2\text{S} \ (g) \rightarrow \text{Cu}_2\text{S} \ (s) + \text{H}_2 \ (g)
\]

During cyclic sulfidation and regeneration operations at 873-1073 K, the Cu in Cu-based sorbents undergoes crystal growth and thermal sintering, decreasing the sulfur capacity.
Therefore in order to increase the thermal stability and to maintain copper in the +2 or +1 oxidation states, and to keep the copper oxide in a highly dispersed state, copper-based sorbents are mixed with other metal oxides (Alonso et al., 2000; Flytzani-Stephanopoulos et al., 1997; Abbasian and Sliman, 1998).

Manganese-based sorbents, when doped with different concentrations of copper, showed increased reactivity and increased stability of the copper oxide, but excessive thermal sintering (Alonso et al., 1999; Alonso et al., 2000).

Iron oxide-based sorbents can be used for hot gas desulfurization up to ~973 K. At these temperatures, the iron is initially Fe₃O₄. In a reducing atmosphere near 973 K, Fe₃O₄ is reduced to FeO, which slows the kinetics of the Fe-H₂S reaction. For desulfurization with 39% H₂, 27% CO, 12% CO₂ and 2000–3000 ppm of H₂S at 773 K, the sulfur capacity of the iron oxide-based sorbent was 20–24 mg of sulfur/g of sorbent, with no decrease in capacity for five cycles (Fan et al., 2005).

1.4 Mixed REO/Transition Metal Oxides for Hot Gas Desulfurization

Compared to pure REOs, REOs doped with metal oxides show higher sulfur capacity in hot gas desulfurization. A high sulfidation rate with no deactivation was observed for Ce/Mn mixed oxide sorbents (Yasyerli, 2008). For a gas composition of 1% H₂S, 10% H₂, balance He at 873 K, the capacity was 4.5 mg of S/g of sorbent for CeO₂, 6.1 mg of S/g for CeOₓ/MnOₓ with Ce/Mn ratio of 3/1, 8.5 mg/g for a Ce/Mn of 1, and 11.5 mg/g for a Ce/Mn of 1/3. At these conditions, the sulfidation rate of Ce/Mn = 1/3 is higher than for the mixed metal oxides of Zn-Mn, V-Mn, and Fe-Mn (Yasyerli, 2008).

Addition of CuO to CeO₂ increased both reducibility and the sulfur removal capacity of CeO₂ (Kobayshi and Flytzani-Stephanopoulos, 2002). CuO and CeO₂ are immiscible, but CeO₂
keeps the copper in a highly dispersed state. But as the amount of copper increased, CuO
clusters were formed, eventually leading to decreased breakthrough times. During reduction of
mixed CuO-CeO$_2$ sorbents, the CuO is reduced to metallic Cu at temperatures above 873 K. The
sulfidation reaction was optimal at a molar ratio of Ce/Cu of 1:1 (Akyurtlu, 1999). In the fresh
sorbent CuO and CeO$_2$ phases were identified, but after sulfidation the Cu is present as
crystalline Cu$_8$O$_5$ and Cu$_{1.8}$S while the Ce is present as Ce$_2$O$_2$S and Ce$_2$S$_3$ (Li and Flytzani-
Stephanopoulos, 1997).

The capacities of CuO-CeO$_2$ sorbents with Cu/Ce molar ratios of 1:1, 3:1 and 1:3 are
0.64, 1.77, and 0.27 mg of S/g of sorbent for a reacting gas of 2% H$_2$S, 20% H$_2$ and balance inert
gas at 1123 K (Li and Flytzani-Stephanopoulos, 1997). For 10 at% Cu – CuO$_2$ the capacity was
4.1 mg/g for 0.1% H$_2$S, 50% H$_2$, 10% H$_2$O and balance He at 923 K (Wang and Flytzani-
Stephanopoulos, 2005). The activation energies for sulfidation varied between 16–19 kJ/mole
for 5–15 at% Cu/CeO$_2$, increasing to 34 kJ/mole for 40 at% Cu (Harrison et al., 2005).

Addition of transition metals also increased the sulfur removal capacity of La-based
sorbents. Some of these mixed oxide sorbents react to form LaMnO$_3$, LaCoO$_3$, LaFeO$_3$, and
La$_2$CuO$_4$. While formation of these phases increased the sulfur capacity, the regenerability of
most of the sorbents was greatly reduced (Rajagopalan and Amiridis, 1999). Among these
sorbents, LaMnO$_3$ had the highest initial sulfur capacity.

After sulfidation of La$_2$CuO$_4$ the crystalline phases present were LaCuS$_2$ and Cu$_2$S. For
LaCoO$_3$ the phases present were La$_2$O$_2$S, La$_2$O$_2$SO$_4$ and CoO. For LaMnO$_3$ the phases present
were La$_2$O$_2$S and MnS, while for LaFeO$_3$ the phases were LaFeO$_3$, Fe$_2$O$_3$, La$_2$FeS$_4$, FeSO$_4$.
Regeneration with air decreased the capacities of LaMnO$_3$, LaCoO$_3$, and La$_2$CuO$_4$ very much,
because the oxysulfate (La$_2$O$_2$SO$_4$) was produced. In the case of LaFeO$_3$ regeneration at 993 K
restored most of the original structure and thus most of the sulfur capacity was retained (Rajagopalan and Amiridis, 1999).

Sorbents containing copper, cerium and lanthanum oxides have also been prepared. The XRD analysis of a fresh sorbent with 30 at% Cu-Ce-30% LaOx showed crystalline CeO2, La2CuO4, CuO. After deep sulfidation the XRD showed CeO2, La2O2S, Ce2S3, and Cu2S (Wang and Flytzani-Stephanopoulos, 2005).

### 1.5 Regeneration Strategies for Oxide Sorbents

General regeneration reactions for hot gas desulfurization are

\[
\text{MeS (s)} + \text{H}_2\text{O (g)} \rightarrow \text{MeO (s)} + \text{H}_2\text{S (g)}
\]

\[(x) \text{MeS (s)} + (y/2) \text{SO}_2 (g) \rightarrow \text{Me}_x\text{O}_y (s) + (x+y/2) \text{S (g)}
\]

\[(x) \text{MeS (s)} + (x+y/2) \text{O}_2 (g) \rightarrow \text{Me}_x\text{O}_y (s) + x \text{SO}_2 (g)
\]

An unwanted side reaction is the formation of sulfate:

\[
\text{MeS (s)} + 2 \text{O}_2 (g) \rightarrow \text{MeSO}_4 (s)
\]

The formation of sulfates should be avoided because they are difficult to decompose.

Manganese-based sorbents can be oxidatively regenerated at 1073-1273 K, at which conditions sulfates do not form. Unlike ZnO-based sorbents, which require very low concentrations of oxygen to prevent excessive temperature rise during regeneration, manganese-based sorbents can be regenerated with air. The initial product gas during regeneration is rich in SO2 (Ben-Slimane and Hepworth 1994).

\[
3 \text{MnS (s)} + 5 \text{O}_2 (g) \rightarrow \text{Mn}_3\text{O}_4 (s) + 3 \text{SO}_2 (g) \quad \Delta G = -296 \text{ kcal/mol}
\]

\[
\text{MnS (s)} + 2 \text{O}_2 (g) \rightarrow \text{MnSO}_4 (s) \quad \Delta G = -109 \text{ kcal/mol}
\]

\[
3 \text{MnSO}_4 (s) \rightarrow \text{Mn}_3\text{O}_4 (s) + 3 \text{SO}_2 (s) + \text{O}_2 (g)
\]
During regeneration of manganese based sorbents with SO$_2$ the only observed regeneration product is elemental sulfur.

\[ \text{MnS (s)} + \frac{1}{2} \text{SO}_2 (g) \rightarrow \text{MnO (s)} + 0.75 \text{S}_2 (s) \]

Regeneration using SO$_2$ has to be carried out at temperatures greater than 973 K in order to prevent the formation of sulfate (Liand et al., 1999; Bakker et al., 2003). For regeneration using SO$_2$, thermodynamic calculations predict around 10% S$_2$O should be formed, but no S$_2$O was observed (Bakker et al., 2003). Regeneration with SO$_2$ is two times faster than regeneration with steam at 1123 K (Bakker et al., 2003). However, regeneration with either SO$_2$ or H$_2$O requires a lot of regeneration gas.

In order to prevent excessive temperature rise during regeneration with O$_2$, regeneration with a mixture of O$_2$ and SO$_2$ was suggested by Bakker et al.; the SO$_2$ regeneration reaction is endothermic. Using steam also prevents excessive temperature rise but the reaction is slow and the sorbent may not be completely regenerated (Atakul et al., 1995, 1996). Regeneration with H$_2$/N$_2$ mixtures removes only 20-25% of the adsorbed sulfur, but if steam is used also the MnO$_x$ can be completely regenerated (Atakul et al., 1995, 1996).

Cu-based sorbents can be regenerated oxidatively using a very low concentration of O$_2$, or reductively with H$_2$.

\[ 2 \text{Cu}_2\text{S (s)} + 4 \text{O}_2 (g) \rightarrow \text{Cu}_2\text{SO}_4 (s) + 2 \text{CuO (s)} + \text{SO}_2 (g) \]

\[ \text{CuSO}_4 (s) + 2 \text{H}_2 (g) \rightarrow \text{Cu (s)} + \text{SO}_2 (g) + 2 \text{H}_2\text{O (g)} \]

Iron-based sorbents can be completely regenerated with a gas composition of 5% O$_2$, 10% steam (Fan et al., 2005).
Oxidative regeneration of CuO-CeO$_2$ sorbents with molar ratios of 1:1, 3:1 and 1:3 was carried out using 6% O$_2$, balance N$_2$. During regeneration the following phase changes occurred: Cu$_2$S $\rightarrow$ CuSO$_4$/CuO $\rightarrow$ CuO. For some CuO-CeO$_2$ sorbents there exists some sulfate phase even after regeneration at high temperature (Li and Flytzani-Stephanopoulos, 1997).

A sorbent of 10 at% Cu–CeO$_2$ was regenerated by combining oxidation and reduction, first 3% O$_2$, balance He, then 50% H$_2$, 10% H$_2$O, balance He. During oxidative regeneration at 923 K and 16000 h$^{-1}$ space velocity, 24% of the sulfur was eluted as H$_2$S and 26% as SO$_2$. During the reduction, 23% was eluted as H$_2$S and 15% as SO$_2$. The further evolution during reduction suggests sulfate formation during the oxidation. Regeneration at 1073 K gave less sulfates (Wang and Flytzani-Stephanopoulos, 2005).

Regeneration of Ce/La mixed oxide sorbents can be by either oxygen or steam. Oxidative regeneration was carried out with 3% O$_2$, balance He. During regeneration of CeO$_2$ – 70 at% La$_2$O$_3$ at 1073 K, of the total sulfur adsorbed 7% was eluted as SO$_2$, and 56% as H$_2$S. After this, reduction was done using 50% H$_2$, 10% H$_2$O, balance He. During the reduction 2% of the sulfur was eluted as SO$_2$ and 25% as H$_2$S. Again, the evolution of H$_2$S and SO$_2$ during reduction indicates that there was some sulfate formation during oxidative regeneration. The regeneration of the sorbents was actually improved at high sulfidation space velocities (Wang and Flytzani-Stephanopoulos, 2005).

Steam regeneration of Ce and La based sorbents can be done using steam alone or H$_2$-rich steam. In both the cases it was found that the sorbent was completely regenerated. For steam regeneration, 3% H$_2$O and balance He was used; the H$_2$-rich stream was 50% H$_2$, 10% H$_2$O and balance He (Flytzani-Stephanopoulos, Sakbodin and Wang, 2006).
1.6 Formation/Destruction of COS

Since the coal or biomass gasifier product includes CO and CO$_2$, there can be unwanted reactions with H$_2$S to form carbonyl sulfide. The COS must be removed because it is highly toxic and is also a catalyst poison. (Zhang et al., 2004; Wakker et al., 1993).

\[
\text{CO}_2 (g) + \text{H}_2\text{S} (g) \rightarrow \text{COS} (g) + \text{H}_2\text{O} (g) \quad \text{K}_\text{eq} = 0.022 \text{ at } 1000 \text{ K}
\]

\[
\text{CO} (g) + \text{H}_2\text{S} (g) \leftrightarrow \text{H}_2 (g) + \text{COS} (g) \quad \text{K}_\text{eq} = 0.032 \text{ at } 1000 \text{ K}; \text{K}_\text{eq} = 0.054 \text{ at } 875 \text{ K}
\]

At first no COS is produced because most of the CO is utilized in the reduction of the sorbent. But after a certain time COS production is observed, increasing with the number of cycles, for Cu and Fe sorbents at 873 K with a feed gas of 11% CO$_2$, 12.5% CO, 13.8% H$_2$, 1% CH$_4$, 0.2% H$_2$S, 19% H$_2$O, balance N$_2$ (Atimtay et al, 1993, Wakker et al, 1993). The reaction between COS and Mn-based sorbents is thermodynamically favorable between 600–1100 K:

\[
\text{COS} (g) + \text{MnO/γ-Al}_2\text{O}_3 (s) \leftrightarrow \text{MnS/γ-Al}_2\text{O}_3 (s) + \text{CO}_2 (g) \quad \text{K}_\text{eq} = 44 \text{ at } 875 \text{ K}
\]

As temperature was increased from 673 to1173 K, the formation of COS decreased for a La$_2$O$_3$ sorbent (Ma et al, 1997), in agreement with the K$_\text{eq}$ values shown above. But COS may react with water to re-form H$_2$S (Wakker et al, 1993).

\[
\text{COS} (g) + \text{H}_2\text{O} (g) \leftrightarrow \text{H}_2\text{S} (g) + \text{CO}_2 (g) \quad \text{K}_\text{eq} = 8 \times 10^{18} \text{ at } 875 \text{ K}
\]

It was observed that the oxysulfide of REOs formed during sulfidation catalyzes the hydrolysis of COS, leading to the formation of H$_2$S which is then adsorbed (Zhang et al., 2004; Ma et al., 1997; Ma et al., 1999).

The activity of the various rare earth oxysulfides for the hydrolysis of COS is La $\approx$ Pr $\approx$ Nd $\approx$ Sm $>$ Eu $>$ Ce $>$ Gd $\approx$ Ho $>$ Dy $>$ Er. At $>$673 K, the conversion of COS was complete for almost all of the REOs (Zhang et al., 2004), and was not affected by SO$_2$ or H$_2$S.
1.7 Focus of This Work

From the literature it is clear that both the rare earth oxides (Ce and La) and the transition metal oxides such as Mn, Cu, and Fe can desulfurize at high temperatures under reducing atmospheres. The kinetics of reduction and the oxygen storage capacities of Ce/La mixtures can be increased by adding a third REO.

The focus of this project is to identify the REOs impregnated with transition metals (Mn, Fe, Cu) which have the highest capacity, and to find whether the addition of a third REO will increase the sulfidation capacity and stability over several cycles. It is also of interest whether the supported REOs (on Al₂O₃, e.g.) would be more stable than the pure REOs, and how much of the REOs are actually used in a sulfidation cycle. The bulk and surface oxides may behave differently, and this can be determined through testing of supported and unsupported REOs.

In order to understand sulfidation under realistic conditions, the sorbents were tested with feed mixtures containing H₂, H₂S, H₂O, and CO₂. In the literature most of the sorbent sulfidation tests were carried out using feed gas containing H₂ and H₂S only. The use of CO₂ and water in the reacting gas decreases the capacity of the sorbent since these two also compete for active sites on the sorbent along with sulfur.
CHAPTER – 2

EXPERIMENTAL

2.1 Catalyst Preparation

The catalysts/sorbents we used for the sulfidation tests were prepared using:

- Templated sol-gel method.
- Incipient wetness impregnation.

2.1.1 Sol-Gel Method:

- Ceria and lanthanum oxide mixtures were prepared using ceric (IV) ammonium nitrate (FW 558; Ce(NH$_4$)$_2$(NO$_3$)$_6$ Aldrich, 99.99%) as ceria precursor and La nitrate (FW 433; La(NO$_3$)$_3$•6H$_2$O) as precursor for lanthanum oxide.
- The desired amounts of the precursors were dissolved in deionized water in 1 L beakers by magnetic stirring without heating. Both readily dissolve in ~5 min. To this mixture a sufficient amount of 25% TMAOH solution was added as the surfactant template.
- To this mixture NH$_4$OH (Alfa Aeser, 28–30% NH$_3$) was added dropwise until the pH reached 10.5. When the pH was ~10.5 a precipitate was formed and further addition of NH$_4$OH was stopped as no more precipitation occurred.
- The temperature of the mixture was slowly increased to 363 K and left stirring.
- Each day the mixture was cooled down, the pH measured and brought back to 10.5 by adding NH$_4$OH dropwise, and then reheated. This procedure was repeated for four days.
- The precipitate was filtered using a centrifuge and the filter cake washed using deionized water followed by acetone and again deionized water.
- The filter cake was dried overnight at 373 K.
- The dried product was calcined in flowing air at 773 K for 6h, with a 2 K ramp to 773 K.
Table 2.1: Sorbent compositions prepared using sol-gel method

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Composition (molar)</th>
</tr>
</thead>
<tbody>
<tr>
<td>REOM_4</td>
<td>Ce/La = 0.9</td>
</tr>
<tr>
<td>REOM_14</td>
<td>Ce/La = 3.0</td>
</tr>
<tr>
<td>REOM_37</td>
<td>Ce/La = 6.0</td>
</tr>
</tbody>
</table>

2.1.2 Incipient Wetness Impregnation

- The impregnation precursor salt was weighed and slowly added to water, such that the total impregnating solution volume was nearly double the total weight in grams of oxide to be impregnated.
- The oxide to be impregnated was spread in a thin layer in a dish, and the impregnating solution was added dropwise such that the entire solid was covered.

Table 2.2: Impregnation of Ce/La or Al₂O₃ sorbents with Mn, Fe, Cu

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Composition</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mn_Al₂O₃</td>
<td>25 wt% MnO₂ / Al₂O₃</td>
</tr>
<tr>
<td>Fe_Al₂O₃</td>
<td>25 wt% FeO / Al₂O₃</td>
</tr>
<tr>
<td>REOM4_Mn, REOM14_Mn</td>
<td>M/(Ce+La) = 0.1, precursor 50.8% Mn(NO₃)₂</td>
</tr>
<tr>
<td>REOM4_Fe, REOM14_Fe</td>
<td>M/(Ce+La) = 0.1, precursor FeCl₂ *4 H₂O</td>
</tr>
<tr>
<td>REOM4_Cu, REOM14_Cu</td>
<td>M/(Ce+La) = 0.1, precursor Cu(NO₃)₂*2.5 H₂O</td>
</tr>
</tbody>
</table>

Table 2.2 continued
<table>
<thead>
<tr>
<th>Sorbent</th>
<th>Composition (molar)</th>
</tr>
</thead>
<tbody>
<tr>
<td>SRE-1</td>
<td>La/Zr = 0.88</td>
</tr>
<tr>
<td>SRE-2</td>
<td>20 wt % of Ce/La = 3 on Al₂O₃ support</td>
</tr>
<tr>
<td>SRE-3</td>
<td>20 wt % of Ce/La = 0.9 on Al₂O₃ support</td>
</tr>
<tr>
<td>SRE-4</td>
<td>20 wt % of Gd/Ce/La = 0.2/0.9/1 on Al₂O₃</td>
</tr>
<tr>
<td>SRE-5</td>
<td>20 wt % of Tb/Ce/La = 0.2/0.9/1 on Al₂O₃</td>
</tr>
</tbody>
</table>

Table 2.3: Impregnation of Al₂O₃ or ZrO₂ with REOs

2.1.3 Commercial Sorbent

For comparison purposes a commercial sorbent (BASF Selexsorb CDX, 7x14 mesh) was also used. Its composition is Al₂O₃/Zeolite with 15-40% zeolite of unspecified phase.

2.2 Characterization of Sorbents

The surface areas of the sorbents were measured using a Quantachrome AS-1 BET apparatus. First 0.3 g sorbent were weighed and dried under vacuum at 573 K for 1 h. A 3-point BET measurement was typical, and the adsorption data were analyzed using the BET equation with Quantachrome software.

To test the sintering of some sorbents at high temperature hydrothermal conditions, 0.5 g of sorbent was placed in a calcining furnace and contacted with flowing (165 mL/min at NTP) 3% H₂O, 97% air at 323-973 K, 5 K/min, with a hold at 973 K for 12 h. After cooling the surface area of the sorbent was measured using the BET apparatus.
Using thermogravimetric analysis / differential scanning calorimetry (TGA-DSC) the amount of heat liberated or absorbed from the sample as compared to a reference sample was observed as a function of temperature. Using TGA-DSC the phase transitions of a sample can be observed and pure phase changes distinguished from reactions such as drying or reduction. TGA-DSC experiments were done using a TA 2950 SDT instrument. The reference sample was 3.0 micron Buehler α-alumina. About 15-20 mg of sorbent were used with a temperature program of 313-673 K at 10 K/min and 673-1373 K at 5 K/min under flowing N₂.

The crystalline structure of the sorbents was determined using a Rigaku Miniflex 2005C103 X-Ray diffractometer (XRD) using Cu-Kα radiation. Data were collected from 2θ = 5 to 60° at 1°/min with a step of 0.05°.

2.3 Sulfidation Tests

All sulfur adsorptions were carried out at 873 K using a reacting gas composition of 23.4 mol% H₂, 41.4% N₂, 3.1% water, 32.0% CO₂, and 0.1% H₂S. The reacting gas mixture was prepared by mixing gases from high pressure cylinders. First, a 1480 kPa mixture of 2% H₂S/N₂ was made from a pure H₂S cylinder (Matheson, 99.99% pure) and a nitrogen cylinder (Airgas, UHP). To add hydrogen a 40% H₂ / 60% N₂ cylinder (Airgas, grade 5) was used; CO₂ was added from a liquefied cylinder (Airgas, industrial grade). The flow rates of these gases were adjusted using mass flow controllers and the gases then passed through a water bubbler at 298 K. The total reacting gas flow rate was ~100 mL/min at NTP. All sulfidation tests carried out in a ½” U-tube of 316 stainless steel. A separate tube was used for each type of sorbent. The rest of the U-tube was filled with quartz wool. The reactor was heated using a sand-filled tube furnace controlled by a Eurotherm 818-P PID temperature controller. A K-type thermocouple measured the furnace temperature and another read the sand bath temperature.
Figure 2.1: Hot gas desulfurization adsorption / temperature-programmed desorption (TPD) experimental setup.

Before sulfidation the sorbents were heated in air flowing at 60 mL/min to remove volatile materials and kept at 873 K for 40 min. Then the gas was switched to He (60
mL/min) using a Valco 8-port valve controlled by a Red Lion Libra timer. After 5 min the gas was switched to the reaction mixture. The exit gas from the reactor flows through 1/16” heated stainless steel tubing to a Valco 10-port valve where it is sampled to one of two possible detectors. It then exhausts in a fume hood. Samples of the exit gas were taken every 15 s and analyzed by a sulfur-specific detector (PFPD) attached to a Varian 3800 GC. There was no GC column; the sample was carried from the sample loop to the detector by He (15 mL/min) through heated (373 K) 0.32 mm fused silica capillary tubing. Further details on the analysis are given in Appendix A.

The reacting gas was passed through the reactor until the detector measured a total exit sulfur concentration equal to the inlet concentration for at least 1 min.

2.4 Temperature Programmed Desorption and Sorbent Regeneration

After switching from reacting gas to He at 60 mL/min, the temperature was raised from 873-1073 K at 10 K/min. The gas exiting the reactor was sampled every 15 s for total sulfur. The reactor was maintained at 1073 K until no sulfur was observed in the exit gas, then cooled down under flowing He. Final regeneration of the sorbent was with air (industrial grade) at 60 mL/min for 40 min at 873 K.

2.5 Thermogravimetric Analysis of Reduction

To measure the oxidation/reduction behavior of the sorbents a Perkin Elmer TGA7 microbalance was used. For oxidation, 15-20 mg of sorbent was placed in a platinum pan and contacted with air at 50 mL/min. The temperature program was 323-823 K at 2 K/min with a final hold of 120 min. This experiment was used to determine if the calcination of synthesized, calcined samples was complete.
For reduction tests a gas of composition 23% H₂, 32% CO₂, 0.1% H₂S, 5% H₂O and balance N₂ was used. The gas mixture was prepared the same way as described above and then passed through a water bubbler at 308 K. The total reacting gas flow rate was ~95 mL/min. About 15-20 mg of sorbent was placed in an alumina pan. The sample was dried in He (50 mL/min) at 923 K for 180 min or longer until the change in wt% was less than 0.1% for 30 min. Then the gas was switched to the reducing gas, with an initial hold of 30 min followed by a temperature increase from 923-993 K at 10 K/min, then a hold for 30 min, then from 993-1043 K at 10K/min, then a final hold for 30 min.
CHAPTER-3

RESULTS AND DISCUSSION

3.1 Characterization by Surface Area, Pore Size, TGA and Calorimetry

The surface area of the sorbents was calculated by the BET method. The Barrett-Joyner-Halenda (BJH) algorithm was used to calculate the pore size distribution for a few of the sorbents. In the BJH method the values of the pore radii were calculated assuming all the pores are cylindrical. To obtain the pore size a full 20 point adsorption and desorption was performed. The pore sizes were obtained from the desorption curve by the BJH algorithm. The average pore radius calculated for REOM_14 (Ce/La = 3) is 1.92 nm.

Table 3.1: Surface area of the fresh sorbents before and after sintering

<table>
<thead>
<tr>
<th>Catalyst(fresh)</th>
<th>Surface area (m²/g)</th>
<th>Surface area (m²/g) after sintering</th>
</tr>
</thead>
<tbody>
<tr>
<td>REOM_4</td>
<td>110</td>
<td>40</td>
</tr>
<tr>
<td>REOM_14</td>
<td>242</td>
<td>55</td>
</tr>
<tr>
<td>REOM_37</td>
<td>200</td>
<td>25</td>
</tr>
<tr>
<td>SRE-1</td>
<td>65</td>
<td>55</td>
</tr>
<tr>
<td>SRE-2</td>
<td>160</td>
<td>120</td>
</tr>
<tr>
<td>SRE-3</td>
<td>160</td>
<td>110</td>
</tr>
<tr>
<td>SRE-4</td>
<td>160</td>
<td>140</td>
</tr>
<tr>
<td>SRE-5</td>
<td>170</td>
<td>110</td>
</tr>
<tr>
<td>Mn_ Al₂O₃</td>
<td>150</td>
<td>NA</td>
</tr>
<tr>
<td>Fe_ Al₂O₃</td>
<td>170</td>
<td>NA</td>
</tr>
<tr>
<td>REOM4_Mn2</td>
<td>60</td>
<td>NA</td>
</tr>
</tbody>
</table>
In order to understand the sintering effects of water vapor and temperature, the sorbents were sintered for 12 h at 973 K in flowing air/water (3% water). It was observed for unsupported REOs (REOM_4, REOM_14 and REOM_37) that the surface area decreased significantly. Among the unsupported REOs, REOM_37 (Ce/La =6) had the highest percentage decrease in surface area and REOM_4 (Ce/La =0.9) had the lowest (Table 3.1), indicating that the rate of sintering increases with the Ce/La ratio. The thermal stability of CeO$_2$ is increased by the addition of La (Wang and Flytzani-Stephanopoulos, 2005). For the REOs supported on Al$_2$O$_3$ or ZrO$_2$, there is much less sintering.

In order to determine if the entire template had been removed during calcining, thermogravimetric analysis was performed in flowing air. The initial weight loss up to 623 K is associated mainly with the evaporation of water and dehydroxylation of the surface. From 623 K to 823 K, the temperature range associated with template combustion, the weight decrease is less than 1% (Table 3.2). This suggests that almost the entire template was removed during the high temperature calcinations.

Table: 3.2 TGA results of the sorbent

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>%Wt loss in (323 – 623 K) range</th>
<th>%Wt loss in (623 – 823 K) range</th>
</tr>
</thead>
<tbody>
<tr>
<td>REOM_4</td>
<td>2</td>
<td>0.6</td>
</tr>
<tr>
<td>REOM_14</td>
<td>2.5</td>
<td>0.8</td>
</tr>
</tbody>
</table>

From the DSC data of REOs, the heat flow curve consists of three peaks (see Figs. 3.1-3.6). For the binary and ternary REOs SRE-4 and SRE-5 there is an initial endothermic peak below 400 K followed by an exothermic peak in the temperature range of 400 – 1100 K (Figures 3.1 – 3.6). For the ternary REOs and the binary oxides Ce/La = 3 or 6 there is another endothermic peak at above 1100-1130 K (Figs. 3.3-3.6).
The initial endothermic peak is due to the evaporation of water present in the sample, corresponding to the initial decrease in weight observed in the TGA profile. The exothermic -$\Delta H$’s for all the REOs were obtained from the integration of the exotherms for heat flow greater than > 2 mW.

Table: 3.3 $\Delta H$ calculated from the DSC exotherms

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>-$\Delta H$ (W/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>REOM_1</td>
<td>810</td>
</tr>
<tr>
<td>REOM_4</td>
<td>1080</td>
</tr>
<tr>
<td>REOM_14</td>
<td>270</td>
</tr>
<tr>
<td>REOM_37</td>
<td>95</td>
</tr>
<tr>
<td>SRE-4</td>
<td>460</td>
</tr>
<tr>
<td>SRE-5</td>
<td>480</td>
</tr>
</tbody>
</table>

The extent of crystallization can be examined using DSC. The exothermic peaks in the medium temperature range are due to crystallization. Crystallization results in the formation of clusters thereby decreasing the surface area. For the sorbents REOM_4 and the pure CeO$_2$ sorbent (REOM_1) there is a highly exothermic transition (Table 3.3) corresponding to more crystallization. The sorbents REOM_14 (Ce/La = 3) and REOM_37 (Ce/La = 6) show a lower exothermic heat of transition. As the Ce content increased in the sorbents REOM_14 (Ce/La = 3) and REOM_37 (Ce/La = 6) the exothermic heat liberated decreased compared to REOM_4. The sorbents SRE-4 and SRE-5 with a third REO exhibit intermediate crystallization compared to REOM_4 and REOM_14.

For the REO REOM_4 the very small endotherms at 950 K may be due to the decomposition of La carbonates. La carbonates decompose at around 1000 K (Shirsat et al.,
2003; Shu et al., 2006). This is evident from the small decrease in weight from the TGA profile at the same temperature. For the samples containing Gd (SRE-4) and Tb (SRE-5) there is no real evidence of carbonate decomposition in the appropriate temperature range (Figs. 3.5-3.6), although these carbonate decompositions are also endothermic (Sharov and Bezdenzhykh, 1981).

The endothermic peaks observed for the sorbents at very high temperature were due to the reduction of CeO$_2$. From the DSC data for the ternary sorbents SRE-4 and SRE-5 (Figs. 3.5 and 3.5) and for the binary sorbents of Ce/La = 3 or less (Figs. 3.2 and 3.3) the heat flow curve is a single peak in the temperature range of 650 to 1100 K, suggesting homogeneity of the mixed oxides and the formation of solid solutions in this range. The binary oxides rich in CeO$_2$ (REOM_1, REOM_37, Figs. 3.1 and 3.4) show evidence of multiple peaks in this key temperature range.

![DSC-TGA, Ce/La = inf., exo = UP](image)

Figure: 3.1 DSC-TGA data of REOM_1 (pure CeO$_2$)
Figure: 3.2 DSC-TGA data of REOM_4 (Ce/La = 0.9)

Figure: 3.3 DSC-TGA data of REOM_14 (Ce/La = 3)
Figure: 3.4  DSC-TGA data of REOM_37 (Ce/La = 6 )

Figure: 3.5  DSC-TGA data of SRE-4
The presence of crystalline phases and their average particle sizes can be evaluated using XRD. The reflections of the CeO$_2$ fluorite phase were obtained by comparing them with standards (Zou et al., 2004; Ray et al., 1975; Bernal et al., 1998; Colon et al., 2000).

The average particle size ($\beta$) was calculated using the Scherrer equation.

$$\beta = \frac{K \times \lambda}{L_w \times \cos \theta}$$

Where,

$\lambda$ = wavelength of the CuK$\alpha$ radiation, 1.5406 Å

$L_w$ = full width of the reflection at half maximum (FWHM)

$K$= 0.94

$\theta$ = the Bragg angle.
Figure: 3.7 XRD analysis of sorbents. (A) Ce/La = 0.9 (B) Ce/La =0.65 (C) CeO$_2$

The average particle size of pure CeO$_2$ calculated using the 111 reflection is 18 nm. The average particle size of REOM$_4$ (Ce/La =0.9), calculated the same way, is 8.7 nm. The peaks of the sorbents containing La (Fig. 3.7) are shifted to higher 2θ values compared to pure CeO$_2$ (REOM$_1$). For the XRD data of Ce – 40 at% La, as the calcining temperature was increased from 773 to 1223 K, the peaks also shifted to higher 2θ values (Bernal et al., 1998). The shifts indicate formation of a solid solution.

The reduction characteristics of the REOs in the presence of H$_2$ were analyzed using TGA only. Starting at a temperature of 923 K after the samples had been dried in He, it is observed that the sorbents are reduced instantly in the strongly reducing gas of molar composition 0.1 % H$_2$S, 24% H$_2$, 32% CO$_2$, 3.3 % H$_2$O, balance N$_2$. In order to take into account the change in the weight of the sample holder seven blank runs were performed using the sample holder only. The total weight change obtained from the reduction test of the blank sample holder was -0.01 mg and the standard deviation of the runs was 0.088 mg. The actual weight change of the sorbent
was calculated by subtracting the blank run weight changes from the raw data at the respective times.

From the weight decreases at various temperatures the maximum amounts of reduction of CeO$_2$ can be estimated, assuming it is accompanied by the desorption of the product water. These amounts are maxima because this calculation does not take into account any H$_2$O, H$_2$S or CO$_2$ adsorption. For La$_2$O$_3$ the lanthanum is not reduced at these conditions (Huang et al., 1998). A typical calculation is shown below.

Weight of sorbent REOM$_{37}$ = 18.72 mg

Moles of CeO$_2$ present in 18.72 mg (Ce/La = 6) = 8.27 × 10$^{-5}$

Moles of O in 18.2 mg of CeO$_2$ in sorbent (Ce/La = 6) = 2 × 8.27 × 10$^{-5}$ = 16.54 × 10$^{-5}$

Weight loss due to reduction at 923 K: 0.10756 mg

Moles of O corresponding to the weight loss due to reduction at 923 K = 6.7 × 10$^{-6}$

Value of n in CeO$_n$ after reduction at 923 K is obtained

\[ n = \left( \frac{165.4 - 6.7 \times 10^{-6}}{165.4 \times 10^{-6}} \right) \times 2 = 1.92 \]

Table: 3.4 Reduction data of REOs

<table>
<thead>
<tr>
<th>Sorbent</th>
<th>% Weight loss at 923 K</th>
<th>% Weight loss at 993 K</th>
<th>% Weight loss at 1043K</th>
<th>Value of n in CeO$_n$ after reduction at 923 K</th>
<th>Value of n in CeO$_n$ after reduction at 993 K</th>
<th>Value of n in CeO$_n$ after reduction at 1043 K</th>
</tr>
</thead>
<tbody>
<tr>
<td>REOM_4</td>
<td>0.22</td>
<td>0.32</td>
<td>0.34</td>
<td>1.92</td>
<td>1.89</td>
<td>1.88</td>
</tr>
<tr>
<td>REOM_14</td>
<td>1</td>
<td>1.66</td>
<td>1.73</td>
<td>1.82</td>
<td>1.72</td>
<td>1.69</td>
</tr>
<tr>
<td>REOM_37</td>
<td>0.59</td>
<td>0.68</td>
<td>0.89</td>
<td>1.92</td>
<td>1.90</td>
<td>1.87</td>
</tr>
</tbody>
</table>
Table 3.5 Percentage reduction of CeO$_2$ to CeO$_{1.5}$ in REOs

<table>
<thead>
<tr>
<th>Sorbent</th>
<th>% of CeO$<em>2$ to CeO$</em>{1.5}$ at 923 K</th>
<th>% of CeO$<em>2$ to CeO$</em>{1.5}$ at 993 K</th>
<th>% of CeO$<em>2$ to CeO$</em>{1.5}$ at 1043 K</th>
</tr>
</thead>
<tbody>
<tr>
<td>REOM_4</td>
<td>14.7</td>
<td>21.3</td>
<td>22.7</td>
</tr>
<tr>
<td>REOM_14</td>
<td>35</td>
<td>56</td>
<td>60.7</td>
</tr>
<tr>
<td>REOM_37</td>
<td>16.7</td>
<td>19.2</td>
<td>25.2</td>
</tr>
</tbody>
</table>

Among the three REOs, REOM_14 (Ce/La = 3) is reduced more than either REOM_4 or REOM_37 (Table 3.5). The redox kinetics of CeO$_x$ can be increased by adding La (Colon et al., 1998; Flytzani-Stephanopoulos et al., 2005) and these results suggest faster reduction at intermediate Ce/La molar ratio.

The weight loss of REOM_4 (Ce/La = 0.9) from 923 – 1043 K in the reducing atmosphere is 130% less than in an inert atmosphere from 623 – 1043 K (Table 3.4 and Figure 3.2). But the weight loss of REOM_14 from 923 – 1043 K in the reducing atmosphere is 47% higher than in an inert atmosphere from 623 – 1043 K; the weight loss of REOM_37 from 923 – 1043 K in the reducing atmosphere is 37% higher than in an inert atmosphere from 623 – 1043 K. These results suggest more adsorption of H$_2$S, CO$_2$ or H$_2$O at high temperatures with a low Ce/La molar ratio.

### 3.2 Sulfur Capacity Tests - Rare Earth Oxides and Related Materials

To determine the sulfur adsorption capacity of the sorbents, tests were performed with the mixed oxides Ce-La, Ce-La-Mn, Ce-La-Fe, Ce-La-Cu, La-Zr, Ce-La-Al, Gd-Ce-La-Al, Tb-Ce-La-Al.
All the sulfur adsorption/desorption tests were performed with ~1 g of the sorbent packed with quartz wool in a ¼” stainless steel tube reactor at atmospheric pressure. The tests were carried using a gas of molar composition 0.1 % H₂S, 24% H₂, 32% CO₂, 3.3 % H₂O, balance N₂. The stainless steel tube reactor and quartz wool themselves adsorb H₂S. In order to get the actual capacity of the sorbents, the capacity of the reactor and quartz wool has to be taken into account. First, blank desorption tests were performed with the stainless steel reactor and quartz wool packing. In order to eliminate the fluctuations multiple blank runs are performed and their average data is used. The blank data shown in figure 3.8 is the average GC intensity of four blank runs obtained for the desorption of sulfur from 873 K to 1073 K using He after adsorption for five minutes in reacting gas.

\[
A_B = \frac{A_1 + A_2 + A_3 + A_4}{4}
\]

Where \(A_1, A_2, A_3, A_4\) are the GC intensity obtained from the individual blank runs using only stainless steel reactor and quartz wool

The amount of sulfur adsorbed by the blank reactor with quartz wool packing is subtracted at the respective times in order to obtain the actual capacity of the sorbent.

\[
A_S = A_A - A_B
\]

Where,

\(A_B\) = GC intensity corresponding to amount desorbed by blank reactor

\(A_S\) = Corrected GC intensity corresponding to the amount of sulfur

\(A_A\) = Raw GC intensity
Figure: 3.8 Average intensity obtained corresponding to amount of sulfur desorbed after five minutes of adsorption of four sulfidation tests using stainless steel reactor with quartz wool packing

The corrected GC intensity is three-point averaged according to the equation shown below.

\[ A_j = \frac{(A_{j-1} + 2A_j + A_{j+1})}{4} \]

if the value of \( \frac{(A_{j-1} + 2A_j + A_{j+1})}{4} \) is less than zero then the averaged area at time \( t \) min is zero.

Where,

\( A_{j-1} \) GC intensity obtained from GC at time \( t - 0.25 \) min.

\( A_j \) GC intensity obtained from GC at time \( t \) min.

\( A_{j+1} \) GC intensity obtained from GC at time \( t + 0.25 \) min.

The amount of sulfur coming out of the reactor in \( \mu \) moles at any particular time (t) is

\[ \mu_i = \frac{\mu_{j} + \mu_{j+1}}{2} \times \frac{\text{(flow rate of He)}}{\text{(Volume of loop)}} \times \frac{\text{(sampling time)}}{\text{(Weight of sorbent)}} \times \frac{T_S}{T_R} \]
Cumulative amount of sulfur desorbed \( = \sum_{i=0}^{i=n} \mu_i \)

\( n = \text{time to complete desorption of removable sulfur from the sorbent.} \)

Where

\( \mu_j \) is \( \mu \) moles of H\textsubscript{2}S at time \( t \) min.

\( \mu_{j+1} \) is \( \mu \) moles of H\textsubscript{2}S corresponding to GC intensity at time \( t + 0.25 \) min.

\( T_S = \) Temperature of the sampling loop, 373 K.

\( T_R = \) Ambient temperature, 298 K.

Total \( \mu \) moles of H\textsubscript{2}S fed = (\( \mu \) moles of H\textsubscript{2}S/min fed) x (time to complete saturation).

Amount of H\textsubscript{2}S adsorbed = total \( \mu \) moles of H\textsubscript{2}S fed – cumulative amount of sulfur exiting the reactor.

In order to compare the sulfur capacities of the sorbents prepared in this work with a commercial sorbent, sulfur adsorption (873 K) followed by TPD tests were carried out using a BASF Selexsorb CDX 7x14 mesh sorbent, composed of Al\textsubscript{2}O\textsubscript{3}/Zeolite with 15-40% zeolite of unspecified phase. The total sulfur removal capacity was determined from the adsorption experiment, while the amount of easily removed sulfur was determined from the temperature programmed desorption. The TPD was carried out with He from 873 K to 1073 K at 10K/min. While the initial capacity of Selexsorb CDX is relatively high (Table 3.6), in the following run the capacity decreased by 85%. This can be attributed to hydrothermal sintering of its more active zeolite component. The Al\textsubscript{2}O\textsubscript{3} support itself, which should not sinter much under these conditions, clearly has minimal sulfur capacity at these conditions.
Table 3.6: Adsorption / Desorption capacities of BASF CDX sorbent

<table>
<thead>
<tr>
<th>Run</th>
<th>μ moles of H₂S/g of sorbent adsorbed</th>
<th>μ moles of H₂S/g of sorbent desorbed</th>
</tr>
</thead>
<tbody>
<tr>
<td>Run-1</td>
<td>90</td>
<td>15</td>
</tr>
<tr>
<td>Run-2</td>
<td>15</td>
<td>5</td>
</tr>
</tbody>
</table>

Adsorption at 873 K followed by TPD tests were also carried out using three sorbents of varying Ce/La ratio, REOM_4 (Ce/La =0.9), 14 (Ce/La =3), and 37(Ce/La = 6.0). It was found that most of the adsorbed sulfur cannot be removed by inert gas, in agreement with the literature for REOs (Wang and Flytzani-Stfanopoulou, 2005). Results are summarized in Table 3.7 below.

Table: 3.7 Adsorption / Desorption capacities of pure Ce/LaOₓ sorbents

<table>
<thead>
<tr>
<th>Sorbent</th>
<th>Run</th>
<th>μ moles of H₂S/g of sorbent adsorbed</th>
<th>μ moles of H₂S/g of sorbent desorbed</th>
</tr>
</thead>
<tbody>
<tr>
<td>REOM_4</td>
<td>1</td>
<td>NA</td>
<td>10</td>
</tr>
<tr>
<td>REOM_14</td>
<td>1</td>
<td>NA</td>
<td>20</td>
</tr>
<tr>
<td></td>
<td>2</td>
<td>55</td>
<td>20</td>
</tr>
<tr>
<td></td>
<td>3</td>
<td>70</td>
<td>30</td>
</tr>
<tr>
<td>REOM_37</td>
<td>1</td>
<td>65</td>
<td>25</td>
</tr>
</tbody>
</table>

Some typical results for adsorption are shown below for REOM_4 (Fig. 3.9). Note that the breakthrough is not always sharp. This could in part be due to mass transfer effects, but it is more likely the result of irregular velocity profiles due to the use of a very small amount of sorbent and a small diameter tube reactor. The purpose of these experiments is not to determine
breakthrough behavior, but to determine which sorbent has the highest sulfur removal capacity and can maintain its capacity in successive runs, after regeneration with air.

It was observed that the sorbents containing pure CeO₅/LaOₓ mixtures have relatively low sulfur capacities and are not very effective in removing H₂S from a more realistic gasifier effluent containing water and CO₂. For the pure REOs containing different ratios of Ce/La it was observed that there is not much difference in the capacity of the sorbents.

![Figure:3.9 Adsorption profiles of H₂S using the REOM-14 sorbent](image)

Sulfur adsorption/TPD tests for REO-Al₂O₃ and REO-ZrO₂ mixtures were carried out using the series of sorbents denoted SRE. The results for single or binary REOs are shown in Table 3.8. Both supports – Al₂O₃ and ZrO₂ – can be expected to improve thermal and steam stability for the REOs covering their surface (Yi et al., 2005; Trovarelli et al., 1997). The amounts of REOs used here are amounts typically associated with roughly monolayer coverage of Al₂O₃ and ZrO₂ supports. These supports themselves have been used for sulfur adsorption, but at lower temperatures. For the Ce/LaOₓ sorbents SRE-2 (Ce/La = 3 on Al₂O₃) and SRE-3
(Ce/La = 0.9 on Al₂O₃) there is not much increase in the total sulfur capacity compared to pure Ce/LaOₓ sorbents. The total capacities of pure Ce/La sorbents are similar to the supported Ce/La sorbents on Al₂O₃. However, since the adsorption due to Al₂O₃ is negligible, based on the active weight of REOs (20 wt%), the REOs supported on Al₂O₃ have a much higher capacity than unsupported REOs. In the supported REOs, the amounts of the REOs correspond to roughly monolayer coverage, and since the REO-only adsorption capacities of the supported REOs are more than five times higher (compare Tables 3.7 - 3.8), while the surface area of the supported REOs is only 2-2.5 times that of the unsupported REOs after sintering (Table 3.1), it appears likely that almost all the sulfidation is occurring at the surface in the unsupported REOs, and that the presence of the Al₂O₃ enhances (“promotes” in the language of catalysis) the sulfidation of the REOs.

On the other hand, sulfur capacity tests with the sorbent SRE-1 (La/Zr = 0.088) yielded a higher initial sulfur capacity than the Ce/La REOs, and the capacity increased further over the next two runs (Table 3.8). The SRE-1 then stabilized in further runs.

Table: 3.8 Adsorption / Desorption capacities of supported rare earth oxide sorbents

<table>
<thead>
<tr>
<th>Sorbent</th>
<th>μ moles of H₂S/g of sorbent adsorbed based on REO only wt, basis</th>
<th>μ moles of H₂S/g of sorbent desorbed (REO only wt. basis)</th>
</tr>
</thead>
<tbody>
<tr>
<td>SRE-2</td>
<td>200</td>
<td>125</td>
</tr>
<tr>
<td>SRE-3</td>
<td>300</td>
<td>250</td>
</tr>
<tr>
<td>SRE-1-1</td>
<td>NA</td>
<td>25</td>
</tr>
<tr>
<td>SRE-1-2</td>
<td>70</td>
<td>10</td>
</tr>
<tr>
<td>SRE-1-3</td>
<td>130</td>
<td>55</td>
</tr>
<tr>
<td>SRE-1-4</td>
<td>130</td>
<td>30</td>
</tr>
<tr>
<td>SRE-1-5</td>
<td>110</td>
<td>10</td>
</tr>
</tbody>
</table>
The same general behavior as for SRE-1 was observed in sulfur capacity tests of ternary REOs supported on Al₂O₃, as shown in Table 3.9. Addition of a third REO to CeOₓ/LaOₓ mixtures increased the sulfur removal capacity of the sorbents. The increase in capacity may be due to the increased number of oxygen vacancies and increased oxygen mobility provided by these third REOs (Bernal et al., 2002; Huang et al., 2005; Tschope et al., 2005; Colon et al., 1998). The qualitative breakthrough behavior did not change much in successive runs (Fig. 3.10), but the total sulfur capacity did. This indicates further formation of a solid solution of ternary REOs during successive runs, increasing the reducibility of CeO₂. For SRE-4 and SRE-5 using inert gas the total amount of sulfur desorbed is in the range of 10 - 35% of the total sulfur adsorbed except for an anomalous fourth run of SRE-5 where almost 80 % of the adsorbed sulfur was removed (Table 3.9). Comparing the percentage of sulfur desorbed using the ternary REOs and the binary REOs, there is no much difference in the percentage of sulfur desorbed. This indicates that addition of a third REO does not enhance the physical regenerability of the sorbents.

The total sulfur capacities of the REOs SRE-4 and SRE-5 with added Tb or Gd were much higher than for the pure Ce/La REOs, especially when compared on an REO-only basis. They were also higher than for the Ce/La REOs supported on Al₂O₃ (SRE-2, SRE-3).

Table: 3.9 Adsorption / Desorption capacities of ternary REOs on Al₂O₃ support

<table>
<thead>
<tr>
<th>Sorbent</th>
<th>μ moles of H₂S/g of sorbent adsorbed</th>
<th>μ moles of H₂S/g of sorbent desorbed</th>
</tr>
</thead>
<tbody>
<tr>
<td>SRE-4-1</td>
<td>NA</td>
<td>20</td>
</tr>
<tr>
<td>SRE-4-2</td>
<td>80</td>
<td>30</td>
</tr>
<tr>
<td>SRE-4-3</td>
<td>95</td>
<td>10</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>--------</td>
<td>--------</td>
<td>--------</td>
</tr>
<tr>
<td>SRE-4-4</td>
<td>140</td>
<td>45</td>
</tr>
<tr>
<td>SRE-4-5</td>
<td>110</td>
<td>20</td>
</tr>
<tr>
<td>SRE-5-1</td>
<td>NA</td>
<td>15</td>
</tr>
<tr>
<td>SRE-5-2</td>
<td>105</td>
<td>25</td>
</tr>
<tr>
<td>SRE-5-3</td>
<td>210</td>
<td>25</td>
</tr>
<tr>
<td>SRE-5-4</td>
<td>110</td>
<td>90</td>
</tr>
<tr>
<td>SRE-5-5</td>
<td>90</td>
<td>20</td>
</tr>
</tbody>
</table>

Figure: 3.10 Adsorption profiles of H₂S using the SRE-5 sorbent

The breakthrough curve of SRE-5 in figure 3.10 is not perfect. This is due to the mass transfer effects and irregular velocity profiles due to small amount of the sorbent used and small size of the reactor. Multiple sulfidation tests are performed on the sorbent until the capacities are stabilized.
3.3 Sulfur Capacity Tests – Rare Earth Oxides / Transition Metal Oxide Mixtures

While Fe, Mn and Cu are all effective adsorbents for sulfur at high temperatures, this does not mean that they will work effectively at realistic gasifier effluent conditions, with water, CO₂, H₂ and H₂S present. To test this possibility, sulfur adsorption-TPD tests of M-Al₂O₃ mixtures were carried out using simply Mn/Al₂O₃ and Fe/Al₂O₃ at loadings near a monolayer. Both sorbents - Mn_Al₂O₃ and Fe_Al₂O₃ - gave low initial sulfur removal capacity (Table 3.10).

Table: 3.10 Adsorption / Desorption capacities of M-Al₂O₃ sorbents

<table>
<thead>
<tr>
<th>Sorbent</th>
<th>Run</th>
<th>μ moles of H₂S/g of sorbent adsorbed</th>
<th>μ moles of H₂S/g of sorbent desorbed</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fe_Al₂O₃</td>
<td>Run-1</td>
<td>45</td>
<td>20</td>
</tr>
<tr>
<td></td>
<td>Run-2</td>
<td>40</td>
<td>20</td>
</tr>
<tr>
<td>Mn_Al₂O₃</td>
<td>Run-1</td>
<td>30</td>
<td>25</td>
</tr>
</tbody>
</table>

Figure: 3.11 Adsorption profiles of H₂S using the Fe_Al₂O₃ sorbent.
The breakthrough curves of Fe\textsubscript{2}Al\textsubscript{2}O\textsubscript{3} (Fig.3.11) are similar to that of Mn\textsubscript{2}Al\textsubscript{2}O\textsubscript{3}. For Fe\textsubscript{2}Al\textsubscript{2}O\textsubscript{3} the breakthrough curves for the two runs are qualitatively similar and with nearly the same total adsorption capacity.

Sorbents of Ce-La-MnO\textsubscript{x} (or Fe or Cu substituted for Mn) oxide mixtures were prepared by varying the Ce/La ratio in the range 0.9 - 3 and varying the amount of impregnated transition metal. The Ce-La-Mn-O sorbents tested were REOM4\textsubscript{Mn} (Ce/La = 0.9 and Mn/(Ce+La) = 0.1), REOM14\textsubscript{Mn} (Ce/La = 3 and Mn/(Ce+La) = 0.1), and REOM4\textsubscript{Mn2} (Ce/La = 0.9 and Mn/(Ce+La) =0.3).

For REOM4\textsubscript{Mn} the initial sulfur removal capacity of the sorbent is 180 μmoles/g of sorbent. These materials gave relatively high initial sulfur capacities, compared to pure REOs or even REOs on Al\textsubscript{2}O\textsubscript{3} or ZrO\textsubscript{2} (Table 3.7-3.8). These capacities typically decreased only slightly in successive runs; most of the sulfur capacity was retained. The adsorption capacity of REOM4\textsubscript{Mn} is 130 – 260 μ moles of H\textsubscript{2}S/g of sorbent and the adsorption capacity of REOM14\textsubscript{Mn} is around 130 μ moles of H\textsubscript{2}S/g of sorbent (Table 3.11). Comparing the capacity of REOM4\textsubscript{Mn} and REOM14\textsubscript{Mn}, sorbents with more La content appear to be superior. The REO sorbents with increased Mn content showed high initial sulfur removal capacity compared to the REOs with lower Mn content, but after the initial run there was not much difference between the two.

For all REOs impregnated with Mn, the desorption of sulfur was not complete with inert gas. For REOM\textsubscript{Mn} using the inert gas the total amount of sulfur desorbed is in the range of 17 - 40% of the total sulfur adsorbed. For REOM\textsubscript{Mn2} using the inert gas the total amount of sulfur desorbed is the range of 8 - 25% of the total sulfur adsorbed (Table 3.11).
It is apparent that more of the sulfur adsorbed on REOM4_Mn can be easily removed using inert gas compared to REOM4_Mn2. Since the total capacities of REOM4_Mn and REOM4_Mn2 were nearly the same after the second run, it can be concluded that REOM4_Mn is superior to REOM4_Mn2.

Comparing the amount of sulfur desorbed using inert gas from REOM4_Mn and the pure REOs (Table 3.7 and Table 3.11), there is not much difference, indicating that impregnating with Mn did not improve the physical regenerability. The breakthrough curves for the lower Mn content were qualitatively similar to breakthrough curves of REOs without transition metals. For example breakthrough curves, see Figure 3.12.

Table: 3.11 Adsorption / Desorption capacities of Ce-La-MnOₓ sorbents

<table>
<thead>
<tr>
<th>Run</th>
<th>μ moles of H₂S/g of sorbent adsorbed</th>
<th>μ moles of H₂S/g of sorbent desorbed</th>
</tr>
</thead>
<tbody>
<tr>
<td>REOM4_Mn-1</td>
<td>180</td>
<td>55</td>
</tr>
<tr>
<td>REOM4_Mn-2</td>
<td>260</td>
<td>40</td>
</tr>
<tr>
<td>REOM4_Mn-3</td>
<td>150</td>
<td>70</td>
</tr>
<tr>
<td>REOM4_Mn-4</td>
<td>130</td>
<td>25</td>
</tr>
<tr>
<td>REOM4_Mn-5</td>
<td>150</td>
<td>55</td>
</tr>
<tr>
<td>REOM4_Mn2-1</td>
<td>270</td>
<td>30</td>
</tr>
<tr>
<td>REOM4_Mn2-2</td>
<td>180</td>
<td>15</td>
</tr>
<tr>
<td>REOM4_Mn2-3</td>
<td>155</td>
<td>40</td>
</tr>
<tr>
<td>REOM14_Mn-1</td>
<td>130</td>
<td>30</td>
</tr>
<tr>
<td>REOM14_Mn-2</td>
<td>130</td>
<td>20</td>
</tr>
</tbody>
</table>
The same procedures were followed for Ce-La-FeO\textsubscript{x} oxide mixtures, but here only the amount of impregnated Fe was varied. The Ce-La-FeO\textsubscript{x} sorbents tested were REOM\textsubscript{4}_Fe (Ce/La = 0.9 and Fe/(Ce+La) = 0.1) and REOM\textsubscript{4}_Fe2 (Ce/La = 0.9 and Fe/(Ce+La) = 0.3). After the first run the sulfur removal capacities of both sorbents were similar (Table 3.12). For the sorbent REOM\textsubscript{4}_Fe the sulfur removal capacity did not change. For REOM\textsubscript{4}_Fe2 the initial sulfur capacity was higher but then decreased by around 40%. For REOM_\text{Fe} using the inert gas the total amount of sulfur desorbed is in the range of 35 - 70% of the total sulfur adsorbed, while for REOM_\text{Fe}2 it is in the range of 6 - 12% of the total sulfur adsorbed (Table 3.12). Therefore the sulfur adsorbed on REOM\textsubscript{4}_Fe can be more easily removed compared to REOM\textsubscript{4}_Fe2. This is in agreement with the trend for Mn/REOs. Comparing the amount of sulfur desorbed using inert gas from REOM\textsubscript{4}_Fe and pure REOs (Table 3.7 and Table 3.12), more sulfur can be easily removed by impregnating with Fe (Fe / (Ce + La) = 0.1).
Table: 3.12 Adsorption / Desorption capacities of Ce-La-FeOx sorbents

<table>
<thead>
<tr>
<th>Sorbent</th>
<th>Run</th>
<th>μ moles of H₂S/g of sorbent adsorbed</th>
<th>μ moles of H₂S/g of sorbent desorbed</th>
</tr>
</thead>
<tbody>
<tr>
<td>REOM4_Fe</td>
<td>Run-1</td>
<td>NA</td>
<td>10</td>
</tr>
<tr>
<td></td>
<td>Run-2</td>
<td>100</td>
<td>70</td>
</tr>
<tr>
<td></td>
<td>Run-3</td>
<td>105</td>
<td>40</td>
</tr>
<tr>
<td>REOM4_Fe2</td>
<td>Run-1</td>
<td>170</td>
<td>10</td>
</tr>
<tr>
<td></td>
<td>Run-2</td>
<td>100</td>
<td>10</td>
</tr>
</tbody>
</table>

The same procedures were followed for the Ce-La-CuOx oxide mixtures. Sulfidation tests were carried out using two different sorbents, REOM4_Cu (Ce/La = 0.9 and Cu/Ce+La =0.1), and REOM14_Cu (Ce/La = 3 and Cu/Ce+La =0.1). Both had low initial sulfur removal capacity (Table 3.13), and were not examined further.

Table: 3.13 Adsorption / Desorption capacities of Ce-La-CuOx sorbents

<table>
<thead>
<tr>
<th>Sorbent</th>
<th>Run</th>
<th>μ moles of H₂S/g of sorbent adsorbed</th>
<th>μ moles of H₂S/g of sorbent desorbed</th>
</tr>
</thead>
<tbody>
<tr>
<td>REOM4_Cu</td>
<td>Run-1</td>
<td>NA</td>
<td>15</td>
</tr>
<tr>
<td></td>
<td>Run-2</td>
<td>40</td>
<td>10</td>
</tr>
<tr>
<td>REOM14_Cu</td>
<td>Run-1</td>
<td>NA</td>
<td>15</td>
</tr>
</tbody>
</table>

3.4 Comparison of All Sorbent Sulfur Capacities

Among the sorbents tested the pure Ce/LaOx and the sorbents impregnated with Cu gave the lowest sulfur removal capacities, and there was no significant increase in adsorption capacity.
observed in successive runs (Fig. 3.13 and 3.17). Comparing the supported REOs (Ce/LaOₓ / Al₂O₃) with the unsupported Ce/LaOₓ and assuming the active phase in both sorbents is an REO, supported Ce/LaOₓ mixtures have much higher capacities than the unsupported REOs (Figs. 3.13 – 3.14). This is in agreement with observations in the literature that monolayer dispersions of REOs on Al₂O₃ have superior reduction properties, oxygen storage capacity and thermal stability compared to unsupported REOs (Rogemond et al., 1997; Yao et al., 1997; Haneda et al., 1993). From the literature the observed capacity of Ce and La mixed sorbents is in the range of 25 to 254 μmoles of H₂S adsorbed/g of sorbent for a gas composition of 0.1% H₂S, 50% H₂, 10% H₂O, balance He at 923 K (Flytzani-Stephanopoulos et al., 2006; Wang and Flytzani-Stephanopoulos, 2005). For Ce and Cu sorbents with a Ce/Cu ratio varying from 0.66 to 3 the observed capacity is in the range of 8 to 120 μmoles of H₂S/g of sorbent for a gas composition of 1% H₂S and 10% H₂, balance He at 873 K (Li and Flytzani-Stephanopoulos, 1997; Wang and Flytzani-Stephanopoulos, 2005). The lower capacity of Ce/LaOₓ sorbents impregnated with Cu can be attributed to easy reduction of CuO to metallic copper at the present conditions. According to the literature, metallic Cu has low sulfidation capacity (Swisher et al., 2000; Flytzani-Stephanopoulos et al., 2005). The sulfur removal capacities of pure Ce/LaOₓ and Ce/LaOₓ sorbents impregnated with Cu are nearly same (Figure 3.13 and Figure 3.17). This indicates that in REOM4_Cu sorbents the Cu is reduced to metallic state and the adsorption is due only to the REOs. This is in agreement with previous conclusions (Li and Flytzani-Stephanopoulos, 1997).

Among the sorbents impregnated with transition metal, those containing Mn showed the highest capacities (Mn > Fe >> Cu) (Figures 3.16 and 3.17). Among the sorbents with impregnated Mn the one with the higher La content (Ce/La = 0.9) showed the greater sulfur
removal capacity (Figure 3.16). REOs impregnated with Fe and having higher La content also had higher sulfur removal capacities. The sorbent REOM4_Mn retained most of its initial capacity after five runs; the adsorption capacity decreased by only 16% (Table 3.11, Fig 3.16).

From the literature for Ce/Mn oxide sorbents with Ce/Mn ratio varying from 0.66 to 3, the observed capacities for multiple runs is in the range of 610 to 1150 μmole S/g of sorbent at 873 K for a gas composition of 1% H2S and 10% H2, balance He (Yasyerli, 2008). The capacities observed with Mn/(Ce+La) ratio varying from 0.1 to 3 at the same temperature were lower here, probably because the feed gas composition used for sulfidation tests here consists of CO2 and H2O, both of which compete for active sites on the sorbent and decrease capacity.

For pure Mn and Fe sorbents supported on Al2O3 the capacities were low (Figs. 3.16 and 3.17). Comparing the capacities of the pure Ce/LaOx on Al2O3 and Mn and Fe oxide on Al2O3 based on the active weight (that is, excluding Al2O3), the pure Ce/LaOx mixtures had higher capacities compared to the pure Mn and Fe oxide sorbents at 873 K. Comparing sorbents with pure Mn or Fe oxide supported on Al2O3 with Mn or Fe oxide impregnated on Ce/LaOx based on the active weight of the metal, the latter have much higher capacities.

From the literature on the mixed oxide sorbents La-Mn, La-Fe, and La-Cu used for hot coal gas desulfurization at 773 K, the La-Mn oxide has the highest capacity followed by La-Fe and La-Cu with nearly the same capacity. The capacities of these sorbents for multiple runs are in the range of 450 to 1000 μmole S/g of the sorbents at 873 K, for a gas composition of 0.3% H2S and balance N2 (Rajagopalan and Amiridis, 1999).

Increasing the amount of transition metal (Mn, Fe) gave an increase in the initial sulfur capacity of the sorbent. The sorbent REOM4_Mn2 gave the highest initial sulfur capacity among all the sorbents tested. However, for both Mn- and Fe-containing sorbents these high
capacities slowly decreased to the point where the sorbents with higher transition metal content
(M/REO = 0.3) were no better than those with lower content (M/REO = 0.1) (Figs. 3.16 – 3.17).

Introducing certain other rare earths Tb and Gd, or Zr (which is electronically similar to Ce) also improved the thermal stability of the common REO sorbents, because they maintained high sulfur capacity in successive runs (Figs. 3.14 – 3.15). For SRE-1 (La/Zr = 0.088) and SRE-4 (Gd/Ce/La = 0.2/0.9/1) the adsorption capacities increased for the first three adsorption/desorption runs and by the fourth run the adsorption capacity appeared stabilized. For SRE-5 (Tb/Ce/La = 0.2/0.9/1) the first two runs gave a very high adsorption capacity, but in the third run it decreased and stabilized (Fig. 3.15). The increase in capacities during the first three runs might be due to the gradual formation of a solid solution of the LaOₓ with ZrO₂ or the CeOₓ/LaOₓ with the third REO (Gd or Tb). If so, the solid solutions adsorb more H₂S than the individual oxides. The redox capacities, oxygen ion vacancies and oxygen ion mobilities are all increased when Zr (Tschope et al., 2005; Colon et al., 1998) or Gd (Huang et al., 2005) or Tb (Bernal et al., 2002) form solid solutions with CeO₂. The supported ternary REO sorbents SRE-4 and SRE-5 have higher adsorption capacities than either the REO/Al₂O₃ sorbents or the pure REO sorbents (Figs. 3.13 – 3.15).

The adsorption capacities of the sorbents REOM4_Mn, REOM4_Fe, REOM4_Mn2, REOM4_Fe2, REOM14_Mn, SRE-1, SRE-4, and SRE-5 were all greater than for the commercial CDX sorbent, and all of them retained more of their adsorption capacity in successive runs (Figs. 3.13 – 3.17). The data for all adsorption/TPD runs are compared in these figures, and it is evident that both the supported REOs and the REOs containing Mn are better sulfur sorbents by any standard of comparison.
Figure : 3.13  Adsorption/Desorption capacities of pure CeO$_x$/LaO$_x$ mixtures and BASF CDX sorbent

Figure : 3.14  Adsorption / Desorption capacities of SRE-1, SRE-2, SRE-3
Figure 3.15 Adsorption / Desorption capacities of ternary REOs on Al₂O₃ support

Figure: 3.16 Adsorption / Desorption capacities of REOs impregnated with Mn
Figure: 3.17 Adsorption / Desorption capacities of REOs impregnated with Cu and Fe

3.5 Thermodynamic Analysis of the Formation of Rare Earth Sulfides

During the sulfidation of CeO$_2$ and La$_2$O$_3$ the main reactions are shown as equations 3.5-1 to 3.5-5. Based on the phase diagram (Figure 1.1) under reducing conditions the main products formed are oxysulfides and sulfides. Under reducing, sulfiding conditions at temperatures above 873 K the formation of sulfates on REOs is negligible (Kay et al., 2003, Ferrizz et al., 2003). Under reducing, sulfiding conditions below 773 K the sulfidation of CeO$_2$ results in the formation of Ce(SO$_4$)$_2$. As the temperature increases above 773 K cerium sulfate decomposes to
Ce₂O₂S (Luo and Gorte, 2002). Reduction and sulfidation of CeO₂ yields principal products Ce₂O₃, Ce₂O₂S and Ce₂S₃; sulfidation of La₂O₃ yields principal products La₂O₂S and La₂S₃.

\[
\text{CeO}_2 (s) + 0.5 \text{H}_2 (s) \rightarrow 0.5 \text{Ce}_2 \text{O}_3 (s) + 0.5 \text{H}_2 \text{O} (g) \quad (3.5-1)
\]

\[
\text{Ce}_2 \text{O}_3 (s) + \text{H}_2 \text{S} (g) \rightarrow \text{Ce}_2 \text{O}_2 \text{S} (s) + \text{H}_2 \text{O} (g) \quad (3.5-2)
\]

\[
\text{Ce}_2 \text{O}_2 \text{S} (s) + 2 \text{H}_2 \text{S} (g) \rightarrow \text{Ce}_2 \text{S}_3 (s) + 2 \text{H}_2 \text{O} (g) \quad (3.5-3)
\]

\[
\text{La}_2 \text{O}_3 (s) + \text{H}_2 \text{S} (g) \rightarrow \text{La}_2 \text{O}_2 \text{S} (s) + \text{H}_2 \text{O} (g) \quad (3.5-4)
\]

\[
\text{La}_2 \text{O}_2 \text{S} (s) + 2 \text{H}_2 \text{S} (g) \rightarrow \text{La}_2 \text{S}_3 (s) + 2 \text{H}_2 \text{O} (g) \quad (3.5-5)
\]

To calculate equilibrium compositions for a given feed, ΔH_{rxn} and ΔG_{rxn} for 3.5-1 to 3.5-5 are required. The values of ΔH_{rxn}, ΔG_{rxn} and K_e were calculated from C_p, ΔH_f, and ΔG_f of the individual compounds. The ΔH_f^0 (298 K, standard state) and C_p values of H₂O, H₂ and H₂S were obtained from a reference database (NIST, 2001), as were the S_o (298 K) values of H₂O, H₂, H₂S, O₂ and S. The ΔS_f^0 values were calculated from the S_o values, and then ΔG_f^0 (298 K, standard state) was calculated from its definition. The ΔH_f^0, ΔG_f^0 and C_p values of CeO₂, Ce₂O₃, Ce₂O₂S, Ce₂S₃, La₂O₃, and La₂S₃ were obtained from compilations of data (Ihsan, 1993; Binneswies and Mike, 2002). The ΔH_f^0 and ΔG_f^0 values of La₂O₂S were obtained from Suponitsky et. al. (Suponitsky et. al, 1988, 1997).

Table 3.14: S_o values of compounds

<table>
<thead>
<tr>
<th>Compound</th>
<th>S_o ( J / mol/ K ) at 298 K</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ce₂O₂S</td>
<td>130</td>
</tr>
<tr>
<td>Ce</td>
<td>69.4</td>
</tr>
<tr>
<td>H₂O</td>
<td>188.8</td>
</tr>
<tr>
<td>H₂S</td>
<td>205.7</td>
</tr>
</tbody>
</table>

53 Table 3.14 Continued
Table 3.15: Standard thermodynamic data (298 K) for various compounds

<table>
<thead>
<tr>
<th>Compound</th>
<th>$\Delta H_f^0$ (J/ mol)</th>
<th>$\Delta G_f^0$ (J/ mol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>CeO$_2$</td>
<td>-1088677</td>
<td>-1025379</td>
</tr>
<tr>
<td>Ce$_2$O$_3$</td>
<td>-1796191</td>
<td>-1707925</td>
</tr>
<tr>
<td>Ce$_2$O$_2$S</td>
<td>-1188256</td>
<td>-1623255.1</td>
</tr>
<tr>
<td>Ce$_2$S$_3$</td>
<td>-1696600</td>
<td>-1171933</td>
</tr>
<tr>
<td>La$_2$O$_3$</td>
<td>-1793700</td>
<td>-1705400</td>
</tr>
<tr>
<td>La$_2$O$_2$S</td>
<td>-1205000</td>
<td>-1538700</td>
</tr>
<tr>
<td>La$_2$S$_3$</td>
<td>-1670500</td>
<td>-1208312</td>
</tr>
<tr>
<td>H$_2$O</td>
<td>-241830</td>
<td>-228577.23</td>
</tr>
<tr>
<td>H$_2$S</td>
<td>-20500</td>
<td>-33311.5</td>
</tr>
<tr>
<td>H$_2$</td>
<td>0</td>
<td>0</td>
</tr>
</tbody>
</table>

All C$_p$ data were expressed as functions of temperature as in eq. 3.5-6 below. For the solids only constants A, B and E were used.

$$C_p = A + \frac{B \times T}{10^3} + \frac{C \times T^2}{10^6} + \frac{D \times T^3}{10^9} + \frac{E \times T^6}{T^2} \quad (3.5 - 6)$$

The C$_p$'s of La$_2$O$_2$S were obtained from H(T) – H(298) data (Suponitsky et. al, 1988, 1997)
\[
\int_{298.2}^{T} C_p \, dT = A (T - 298.2) + \frac{B (T^2 - 298.2^2)}{10^3} + E \times 10^6 \times (298.2^{-1} - T^{-1})
\]

\[
= H(T) - H(298)
\]

(3.5 – 7)

where \(T\) in Kelvin, \(C_p\) in \((\text{J/mol/K})\)

Table 3.16: \(H(T) - H(298)\) values of \(\text{La}_2\text{O}_2\text{S}\)

<table>
<thead>
<tr>
<th>Temperature(K)</th>
<th>(H(T) - H(298)) (kJ/mol/K)</th>
<th>(C_p) (J/mol/K) at average T</th>
</tr>
</thead>
<tbody>
<tr>
<td>383</td>
<td>10.2</td>
<td>30</td>
</tr>
<tr>
<td>483</td>
<td>22.2</td>
<td>56.8</td>
</tr>
<tr>
<td>573</td>
<td>33.3</td>
<td>76.5</td>
</tr>
<tr>
<td>673</td>
<td>45.3</td>
<td>93.3</td>
</tr>
<tr>
<td>1090</td>
<td>107.5</td>
<td>154.9</td>
</tr>
<tr>
<td>1350</td>
<td>131</td>
<td>159</td>
</tr>
</tbody>
</table>

Using regression analysis for \(\int C_p \, dT\) (eq. 3.5-7), the constants \(A\), \(B\) and \(E\) of eq. 3.5-6 were obtained. All constants for eq. 3.5-6 are given in Table 3.17

Table 3.17: Constants for heat capacity

<table>
<thead>
<tr>
<th>Compound</th>
<th>A</th>
<th>B</th>
<th>C</th>
<th>D</th>
<th>E</th>
<th>F</th>
</tr>
</thead>
<tbody>
<tr>
<td>CeO(_2)</td>
<td>64.8</td>
<td>17.7</td>
<td>0</td>
<td>0</td>
<td>-0.76</td>
<td>-22.5</td>
</tr>
<tr>
<td>Ce(_2)O(_3)</td>
<td>130.8</td>
<td>13.8</td>
<td>0</td>
<td>0</td>
<td>-1.59</td>
<td>-44.0</td>
</tr>
<tr>
<td>Ce(_2)O(_2)S</td>
<td>124.9</td>
<td>23.6</td>
<td>0</td>
<td>0</td>
<td>-2.09</td>
<td>-45.3</td>
</tr>
<tr>
<td>Ce(_2)S(_3)</td>
<td>124.9</td>
<td>12.7</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>-37.8</td>
</tr>
<tr>
<td>La(_2)O(_3)</td>
<td>118</td>
<td>16</td>
<td>0</td>
<td>0</td>
<td>-0.124</td>
<td>-40.0</td>
</tr>
<tr>
<td>La(_2)O(_2)S</td>
<td>257.9</td>
<td>-117.5</td>
<td>0</td>
<td>0</td>
<td>-14.3</td>
<td>-119</td>
</tr>
</tbody>
</table>
The standard heat of formation of compounds at other temperatures was found by

\[ H(T) = H_f^{0\ 298} + \int_{298}^{T} C_p \ dT \quad (3.5 - 8) \]

Substituting \( C_p \) and integrating the above equation, where \( F \) is the constant of integration

\[ H(T) = H_f^{0\ 298} + \left( A \times T + \frac{B \times T^2}{2 \times 10^3} + \frac{C \times T^3}{3 \times 10^6} + \frac{D \times T^4}{4 \times 10^9} - \frac{E \times 10^6}{T} + F \right) \quad (3.5 - 9) \]

Equilibrium constants \( (K_e) \) for 3-2-1 to 3-2-5 were calculated using the Van’t Hoff equation:

\[ \ln \left( \frac{K_e}{K_e^{0}} \right) = \int_{T_0}^{T} \frac{\Delta H_{\text{rxn}}}{RT^2} \ dT \quad (3.5 - 10) \]

### 3.5.1 Cerium Oxide

During reduction and sulfidation the most likely products are Ce\(_2\)O\(_3\), Ce\(_2\)O\(_2\)S, and Ce\(_2\)S\(_3\). All calculations assume a basis of one mole of CeO\(_2\) before the reaction. Let \( G_o \) be the total moles of gas required per mole of solid for stoichiometric conversion to Ce\(_2\)S\(_3\). During reduction 0.5 mole of Ce\(_2\)O\(_3\) is formed from 1 mole of CeO\(_2\). The formation of Ce\(_2\)S\(_3\) from Ce\(_2\)O\(_3\) requires 3 moles of H\(_2\)S, so sulfidation of CeO\(_2\) requires 1.5 moles H\(_2\)S per mole of solid. All calculations were done based on the stoichiometric amount of H\(_2\)S contacting the solids.
\[ G_o = \frac{\text{Total moles of gas}}{\text{Mole of solid}} = \frac{1.5 \times P_t}{P_{H2S}^o} \quad (3.5 - 11) \]

Where

Pt is the total pressure in atm,

\( P_{H2S}^o \) is the initial partial pressure of H\(_2\)S.

\( P_{H2S} \) is the partial pressure of H\(_2\)S.

If an ideal solid solution of CeO\(_2\), Ce\(_2\)O\(_3\), and Ce\(_2\)O\(_2\)S is formed (Case 1) then the atom balance for Ce is:

\[ \text{CeO}_2 + 2 \text{Ce}_2\text{O}_3 + 2 \text{Ce}_2\text{O}_2\text{S} = 1 \quad (3.5-12) \]

From reaction 3.5-1:

\[ K_1 = \frac{(2 \text{Ce}_2\text{O}_3)^{0.5} \times (P_{H2O})^{0.5}}{\text{CeO}_2 \times (P_{H2})^{0.5}} \quad (3.5 - 13) \]

From reaction 3.5-2:

\[ K_2 = \frac{(2 \text{Ce}_2\text{O}_2\text{S}) \times P_{H2O}}{(2 \text{Ce}_2\text{O}_3) \times P_{H2S}} \quad (3.5 - 14) \]

The sulfur atom balance is:

\[ G_o \times \frac{(P_{H2S}^o - P_{H2S})}{P_t} = \text{Ce}_2\text{O}_2\text{S} \quad (3.5 - 15) \]

The concentrations of H\(_2\) and H\(_2\)O were always assumed constant, because they were in excess.

In the above four equations (3.5-12 to 3.5-15) the unknowns were the molar amounts of CeO\(_2\), Ce\(_2\)O\(_3\), Ce\(_2\)O\(_2\)S, and P\(_{H2S}\). Solving these equations simultaneously yields the unknowns. Maple 11 programs to solve these equations simultaneously are given in Appendix C.
If a separate sulfide phase is formed and only the oxides form a solid solution (Case 2), then from reaction 3.5-1:

\[
K_1 = \left( \frac{2 \text{Ce}_2\text{O}_3}{\text{CeO}_2 + 2 \text{Ce}_2\text{O}_3} \right)^{0.5} \times (P_{\text{H}_2\text{O}})^{0.5} \times \frac{\text{CeO}_2}{\text{CeO}_2 + 2 \text{Ce}_2\text{O}_3} \times (P_{\text{H}_2})^{0.5} \quad (3.5 - 16)
\]

From reaction 3.5-2:

\[
K_2 = \frac{(1) \times (P_{\text{H}_2\text{O}})}{2 \text{Ce}_2\text{O}_3} \times \frac{\text{Ce}_2\text{O}_2 + 2 \text{Ce}_2\text{O}_3}{(P_{\text{H}_2\text{S}})^2} \quad (3.5 - 17)
\]

Solving 3.5-12, 3.5-15, 3.5-16 and 3.5-17 simultaneously again yields the molar amounts of the solid compounds and the final partial pressure of H\(_2\)S.

For cases 3 and 4, formation of the sulfide Ce\(_2\)S\(_3\) was also considered. If a single ideal solid solution is formed (Case 3), the cerium atom balance is:

\[
\text{CeO}_2 + 2 \text{Ce}_2\text{O}_3 + 2 \text{Ce}_2\text{O}_2\text{S} + 2 \text{Ce}_2\text{S}_3 = 1 \quad (3.5-18)
\]

From reaction 3.5-3:

\[
K_3 = \frac{(2 \text{Ce}_2\text{S}_3)}{(2 \text{Ce}_2\text{O}_2\text{S})} \times \frac{(P_{\text{H}_2\text{O}})^2}{(P_{\text{H}_2\text{S}})^2} \quad (3.5 - 19)
\]

The sulfur atom balance is:

\[
G_0 \times \frac{(P_{\text{H}_2\text{S}}^0 - P_{\text{H}_2\text{S}})}{P_t} = \text{Ce}_2\text{O}_2\text{S} + 3 \times \text{Ce}_2\text{S}_3 \quad (3.5 - 20)
\]

The equations for \(K_1\) and \(K_2\) (3.5-13 and 3.5-14) are unchanged from Case 1. For the above five equations (3.5-13, 3.5-14, 3.5-18 to 3.5-20) the unknowns are the molar amounts of
CeO₂, Ce₂O₃, Ce₂O₂S, and Ce₂S₃, and P_H₂S. These equations were solved simultaneously (see Appendix C for Maple 11 program).

For the case of two solid solutions, an ideal sulfide and an ideal oxide (Case 4), the atom balances and K₃ (3.5-18 and 3.5-20) are the same as Case 3. From reaction 3.4.1:

\[ K₁ = \frac{\left( \frac{2 \text{Ce}_2\text{O}_3}{\text{CeO}_2 + 2 \text{Ce}_2\text{O}_3} \right)^{0.5} \times (\text{P}_{\text{H}_2\text{O}})^{0.5}}{\left( \frac{\text{CeO}_2}{\text{CeO}_2 + 2 \text{Ce}_2\text{O}_3} \right) \times (\text{P}_{\text{H}_2})^{0.5}} \]  \hspace{2cm} (3.5 - 21)

From reaction 3.5.2:

\[ K₂ = \left( \frac{\left( \frac{2 \text{Ce}_2\text{O}_2\text{S}}{2 \text{Ce}_2\text{O}_2\text{S} + 2 \text{Ce}_2\text{S}_3} \right)}{\left( \frac{\text{Ce}_2\text{O}_3}{2 \text{Ce}_2\text{O}_3 + \text{CeO}_2} \right)} \right) \times \text{P}_{\text{H}_2\text{O}} \]  \hspace{2cm} (3.5 - 22)

In the above five equations (3.5-18 to 3.5-22) the unknowns are the molar amounts of CeO₂, Ce₂O₃, Ce₂O₂S, and Ce₂S₃, and P_H₂S. These equations were solved simultaneously as before.

### 3.5.2 Lanthanum Oxide

For La₂O₃, the most likely products during reduction and sulfidation are La₂O₂S and La₂S₃. All calculations assume a basis of one mole of La₂O₃ before reaction. Let Go be the total moles of gas required for stoichiometric conversion to La₂S₃ per mole of solid. The formation of La₂S₃ from La₂O₃ requires 3 moles of H₂S, so:

\[ G₀ = \frac{\text{Total moles of gas}}{\text{Mole of solid}} = \frac{3 \times \text{P}_t}{\text{P}_{\text{H}_2\text{S}}} \]  \hspace{2cm} (3.5 - 23)

For Case 1 an ideal solid solution of La₂O₃ and La₂O₂S is formed. The La atom balance is:

\[ \text{La}_2\text{O}_3 + \text{La}_2\text{O}_2\text{S} = 1 \]  \hspace{2cm} (3.5-24)

From reaction 3.5.4:

\[ K₁ = \frac{(\text{La}_2\text{O}_2\text{S}) \times \text{P}_{\text{H}_2\text{O}}}{(\text{La}_2\text{O}_3) \times \text{P}_{\text{H}_2\text{S}}} \]  \hspace{2cm} (3.5 - 25)
The sulfur atom balance is:

\[ G_0 \times \frac{(P_{H_2S}^0 - P_{H_2S})}{P_t} = La_2O_2S \quad (3.5 - 26) \]

In the above three equations (3.5-24 to 3.5-26) the unknowns are the molar amounts of La$_2$O$_3$ and La$_2$O$_2$S, and P$_{H_2S}$. These equations were solved simultaneously (Appendix C, Maple 11 program).

For Case 2 an ideal solid solution of La$_2$O$_3$, La$_2$O$_2$S and La$_2$S$_3$ is formed. The La atom balance is:

\[ La_2O_3 + La_2O_2S + La_2S_3 = 1 \quad (3.5-27) \]

The equation for $K_1$ is the same as Case 1. From reaction 3.4-5:

\[ K_2 = \frac{(La_2S_3) \times (P_{H_2O})^2}{(La_2O_2S) \times (P_{H_2S})^2} \quad (3.5 - 28) \]

The sulfur atom balance is

\[ G_0 \times \frac{(P_{H_2S}^0 - P_{H_2S})}{P_t} = La_2O_2S + 3 \times La_2S_3 \quad (3.5 - 29) \]

There are four equations (3.5-25 and 3.5-27 to 3.5-29). The unknowns are the molar amounts La$_2$O$_3$, La$_2$O$_2$S, and La$_2$S$_3$, and P$_{H_2S}$. These equations were solved simultaneously (Appendix C, Maple 11 program).

The solutions of the equilibrium equations can be used to estimate the maximum theoretical capacities of a Ce or La oxide sorbent used in sulfur capacity tests. For these calculations, replace Go by the actual mols of gas mixture used per mol of sorbent and then multiply the final equilibrium results for the number of mols of solid compound/mol sorbent by the mols/g sorbent. The calculations in Table 3.18 were based on 1 g sorbent with 100 mL/min of gas mixture (0.1 mol% H$_2$S) for 20 min of flow.
Table: 3.18 Theoretical capacities of sorbents calculated using thermodynamic data

<table>
<thead>
<tr>
<th>Case</th>
<th>CeO$_2$ ppm H$_2$S out</th>
<th>CeO$_2$ μ mol H$_2$S/g</th>
<th>La$_2$O$_3$ ppm H$_2$S out</th>
<th>La$_2$O$_3$ μ mol H$_2$S/g</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>7.9</td>
<td>81</td>
<td>500</td>
<td>0</td>
</tr>
<tr>
<td>2</td>
<td>270</td>
<td>60</td>
<td>500</td>
<td>0</td>
</tr>
<tr>
<td>3</td>
<td>7.9</td>
<td>81</td>
<td>19</td>
<td>118</td>
</tr>
<tr>
<td>4</td>
<td>260</td>
<td>60</td>
<td>19</td>
<td>118</td>
</tr>
</tbody>
</table>

From the Table 3.13 for CeO$_2$ it is evident that the μ mol H$_2$S/g adsorbed is same for the cases 1 and 3, and for cases 2 and 4. The difference between case 1 and 3 is that case 3 assumes the formation of Ce$_2$S$_3$ but case 1 did not. Since cases 1 and 3 give similar results this indicates that based on thermodynamic calculations the only product formed during sulfidation is Ce$_2$O$_2$S. For La$_2$O$_3$ the major product formed based on thermodynamic calculations is La$_2$S$_3$ and there is little or no La$_2$O$_2$S formed.

These thermodynamic calculations were done assuming pure CeO$_2$ and La$_2$O$_3$. Therefore the maximum experimental sulfur capacities of pure Ce/LaO$_x$ oxide sorbents should be between those of the thermodynamic calculations in Table 3.18. For pure Ce/ LaO$_x$ sorbent with Ce/La = 3 the maximum capacity of the sorbent was estimated from Table 3.18 assuming that the Ce oxide and La oxide are separate phases. For Ce/La = 3 this theoretical capacity is 90 μmole of H$_2$S/g of sorbent. The experimental capacity of the sorbent Ce/La = 3 was 55 – 70 μmole of H$_2$S/g of sorbent, so this estimation procedure is valid. The experimental capacities would be expected to be somewhat lower than the theoretical capacities due to less than equilibrium conversion, and the loss of active surface area in the actual sorbents at high temperatures.
CHAPTER 4

CONCLUSIONS

In this study the sorbents Ce/La/M (M = transition metal) oxides and Ce/La/REO (RE = a third rare earth) oxide were studied for the desulfurization of synthetic gasifier effluents typical of a biomass or coal gasifier. The REO sorbents were prepared by sol-gel and impregnation (of Al₂O₃ or ZrO₂) methods. Successive sulfidation and regeneration runs were carried out in order to evaluate the sorbent capacity and sorbent deactivation.

For the pure Ce/LaOₓ sorbents the capacity of the sorbents was relatively low, in agreement with thermodynamic calculations of sulfide and oxysulfide formation from the bulk oxides. Monolayer addition of pure Ce/LaOₓ to Al₂O₃ sorbents improved the capacity of the sorbents compared pure REOs, based on an active (REO) weight basis. Addition of a third rare earth oxide, either TbOₓ or GdOₓ, to Ce/LaOₓ mixtures increased the sulfur removal capacity and the capacity retention of the sorbents. The sulfur adsorption capacity of SRE-5 (CeOₓ/LaOₓ/GdOₓ) for five runs was in the range of 90 - 210 μmol of H₂S adsorbed/g of sorbent. The sulfur adsorption capacity of SRE-4 (CeOₓ/LaOₓ/GdOₓ) for five runs was in the range of 80 - 140 μmol of H₂S adsorbed/g of sorbent. Addition of monolayer coverage of an REO (La₂O₃) to ZrO₂ (SRE-1) also increased the capacity and retention ability of the sorbent. The sulfur adsorption capacity of SRE-1 for five runs was in the range of 70 - 130 μmol of H₂S adsorbed/g of sorbent.

Among all sorbents tested, the supported Ce/La REOs impregnated with Mn showed the highest sulfur capacities. For REOs impregnated with Mn, a Ce/La ratio of approximately 0.9 was observed to be optimal. The sulfur adsorption capacity of REOM4_Mn for five runs was in the range of 130 - 260 μmol of H₂S adsorbed/g of sorbent. The sulfur removal capacities of REOs impregnated with transition metals were in the order Mn > Fe >> Cu.
Desorption of sulfur from the sorbents was carried out using an inert gas (He), where the sorbents were heated from 873 to 1073 K. By comparing the adsorption and desorption capacities it was found that with an inert gas alone most of the adsorbed sulfur cannot be removed. However, in most cases almost complete regeneration with air was observed.

4.1 Recommendations

- Regeneration studies should be carried out with other gas mixtures and at other temperatures since regeneration using air is a highly exothermic process which can lead to thermal sintering.

- Structural analysis of the sorbents after sulfidation and after regeneration must be carried out in order to understand the changes in their surface structure.

- A reacting gas with a heavier carbon fraction (tar) should be tested in order to evaluate the performance of some of the REO materials for the simultaneous removal of tar and sulfur.

- The reforming ability of the transition metal/REOs should be tested.
REFERENCES


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APPENDIX A - SULFUR DETECTOR / GAS CHROMATOGRAPHY DETAILS

Table A.1: General GC Settings for product analysis

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Setting</th>
</tr>
</thead>
<tbody>
<tr>
<td>Column Oven temperature</td>
<td>373 K</td>
</tr>
<tr>
<td>Sampling valve temperature</td>
<td>373 K</td>
</tr>
<tr>
<td>TCD Detector temperature</td>
<td>473 K</td>
</tr>
<tr>
<td>PFPD Detector temperature</td>
<td>473 K</td>
</tr>
</tbody>
</table>

The Varian 3800 GC is equipped with two detectors – a pulsed flame photometric detector (PFPD) and a thermal conductivity detector (TCD). The PFPD is a sulfur- specific detector which can measure concentration as low as 1 ppmv sulfur. The TCD can only measure higher sulfur concentrations, above ~500 ppmv. The TCD settings and retention times are shown in Tables A-2 and A-3. The PFPD settings are in Table A-4.

The PFPD was calibrated for the absolute amount of total sulfur using a 1% H\textsubscript{2}S/N\textsubscript{2} mixture, diluted with CO\textsubscript{2}. For each mixture three samples were analyzed and averaged.

The micromoles of H\textsubscript{2}S in the 2 mL sample loop was calculated using the ideal gas law.

The response factor (RF) is:

\[ RF_{H2S} = \frac{X_{H2S}^0}{A_{H2S}} \]

Where \( X_{H2S}^0 \) is μmoles of H\textsubscript{2}S and \( A_{H2S} \) is the area of H\textsubscript{2}S measured by the PFPD. The calibration is shown in Figure A-1; the response factor is 0.339 x 10\textsuperscript{-6} μ mol/area with an \( R^2 \) of 0.997
The TCD was calibrated using mixtures of CO$_2$ and N$_2$ passing through a water bubbler. For each mixture three samples were analyzed. The response factor for N$_2$ is:

$$RF_{N_2} = \frac{x_{N_2}^0}{A_{N_2}}$$

The calibration is shown in Figure A-2; the response factor is $12.8 \times 10^{-6}$ micromol/area with an $R^2$ of 0.992.

Table A.2: TCD settings

<table>
<thead>
<tr>
<th>Column</th>
<th>Hayesep A silicosteel</th>
</tr>
</thead>
<tbody>
<tr>
<td>Carrier and reference gas</td>
<td>He, 30 mL/min</td>
</tr>
<tr>
<td>Range</td>
<td>0.5</td>
</tr>
<tr>
<td>Filament Temperature</td>
<td>523 K</td>
</tr>
<tr>
<td>Sample Loop Size</td>
<td>2 mL</td>
</tr>
</tbody>
</table>

Table A.3: TCD retention Times

<table>
<thead>
<tr>
<th>Compound</th>
<th>Retention time (min)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Nitrogen</td>
<td>0.6</td>
</tr>
<tr>
<td>Carbon dioxide</td>
<td>1.15</td>
</tr>
<tr>
<td>Hydrogen sulfide</td>
<td>3.25</td>
</tr>
<tr>
<td>Water</td>
<td>7.75</td>
</tr>
</tbody>
</table>

Table A.4: PFPD settings

<table>
<thead>
<tr>
<th>Column</th>
<th>None, 0.53 mm capillary tube</th>
</tr>
</thead>
<tbody>
<tr>
<td>Carrier Gas</td>
<td>He, 15 mL/min</td>
</tr>
<tr>
<td>Air 1, Air 2</td>
<td>34 mL/min, 10 mL/min</td>
</tr>
</tbody>
</table>

72 Table A.4 continued
### Calibration of PFPD

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Hydrogen</td>
<td>20 mL/min</td>
</tr>
<tr>
<td>Range</td>
<td>9.0</td>
</tr>
<tr>
<td>Gate width</td>
<td>20 ms</td>
</tr>
<tr>
<td>Gate Delay</td>
<td>6.0 ms</td>
</tr>
<tr>
<td>Trigger level</td>
<td>220 mv</td>
</tr>
<tr>
<td>Photomultiplier Voltage</td>
<td>630 V</td>
</tr>
<tr>
<td>Sample Loop Size</td>
<td>2 mL</td>
</tr>
</tbody>
</table>

**Figure A.1:** Calibration of PFPD for sulfur

\[ R^2 = 0.999 \]
Figure A.2: Calibration of TCD for N$_2$.

All other TCD calibrations were made relative to N$_2$. For CO$_2$:

\[
\frac{x_{CO2}^0}{x_{N2}^0} = 0.7887 \frac{A\%_{CO2}}{A\%_{N2}}
\]

Where $x_{CO2}^0$ and $x_{N2}^0$ are in \(\mu\)moles, and $A\%_{CO2}$ and $A\%_{N2}$ are area percentages.

Since the mole fraction of H$_2$O was very small in the mixture the calibration for H$_2$O was calculated in this manner.

\[
\frac{x_{H2O}^0}{x_{N2}^0} = 1.8324 \frac{A\%_{H2O}}{A\%_{N2}} \times N_{tot}
\]

Where $x_{N2}$ is the mole fraction of N$_2$ and $N_{tot}$ is the total moles of mixture in the 2 mL sample loop. The calibrations for CO$_2$ ($R^2 = 0.9985$) and water ($R^2 = 0.9931$) are graphed below.

\[ \text{Nitrogen Calibration} \]

\[
\begin{array}{c|c}
\text{Area X } 10^{-6} & \mu \text{ moles of N}_2 \\
0 & 0 \\
0.5 & 5 \\
1 & 10 \\
1.5 & 15 \\
2 & 20 \\
2.5 & 25 \\
3 & 30 \\
\end{array}
\]

$R^2 = 0.992$
Figure A.3: Calibration of TCD for CO₂

Figure A.4: Calibration of TCD for water
APPENDIX B – MAPLE 11 PROGRAM FOR THERMODYNAMIC CALCULATION OF CERIUM COMPOUNDS

```maple
restart;
Vectors V1 to V7 correspond to the coefficients for calculating the enthalpies
V1 corresponds to Coeff of H2S
V2 corresponds to Coeffs of H2O
V3 corresponds to Coeff of H2
V4 Corresponds to Coeff of CeO2
V5 Corresponds to Coeff of Ce2O3
V6 Corresponds to Coeff of Ce2O2S
V7 Corresponds to Coeff of Ce2S3

> V1 := vector(6, [26.88412, 18.67809, 3.434203, -3.378702, 0.135882, -8.41]);
> V2 := vector(6, [30.09, 6.83, 6.793, -2.534, 0.08214, -9.05]);
> V3 := vector(6, [33.07, 11.36, 11.43, -2.773, -0.1586, -9.98]);
> V4 := vector(6, [64.78, 17.69, 0, 0, -0.76, -22.6495]);
> V5 := vector(6, [130.8, 13.77, 0, 0, -1.59, -44.9429]);
> V6 := vector(6, [124.89, 23.64, 0, 0, -2.09, -45.2996]);
> V7 := vector(6, [124.93, 12.72, 0, 0, 0, -37.8132]);

> RR := 8.314;
> Tf := 873.15; Pt := 2;

For calculating all Cp's the equation used is
Cp = A + Bt + Ct^2 + Dt^3 + E/t + F

For calculating all enthalpies:
H - H0 = 1000*(A t + B t^2/2 + C t^3/3 + D t^4/4 - E/t + F)

For calculating the Cp at 873 K is
int (Cp) dT from 298.15 K to 873K

= 298.15..873;  \text{CpH2S := 22289.16394} \tag{1.1}

> CpH2O := int(V2[1] + V2[2]*T/10^3 + V2[3]*T^2/10^6 + V2[4]*T^3/10^9 + V2[5]*10^6*T^-2, T)
= 298.15..873;  \text{CpH2O := 20861.32446} \tag{1.2}

= 298.15..873;  \text{CpH2 := 16872.80866} \tag{1.3}
```

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% > CpCeO2 := int\( \left[ \frac{V4[1]}{10^3} + \frac{V4[2] \cdot T}{10^6} + \frac{V4[3] \cdot T^2}{10^9} + \frac{V4[4] \cdot T^3}{10^9} + V4[5] \cdot 10^6 \cdot T^{-2}, T \right] \);

\( \text{CpCeO2} := 41515.06048 \) (1.4)

% > CpCeO3 := int\( \left[ \frac{V5[1]}{10^3} + \frac{V5[2] \cdot T}{10^6} + \frac{V5[3] \cdot T^2}{10^9} + \frac{V5[4] \cdot T^3}{10^9} + V5[5] \cdot 10^6 \cdot T^{-2}, T \right] \);

\( \text{CpCeO3} := 76314.02666 \) (1.5)

% > CpCeO2S := int\( \left[ \frac{V6[1]}{10^3} + \frac{V6[2] \cdot T}{10^6} + \frac{V6[3] \cdot T^2}{10^9} + \frac{V6[4] \cdot T^3}{10^9} + V6[5] \cdot 10^6 \cdot T^{-2}, T \right] \);

\( \text{CpCeO2S} := 75134.81021 \) (1.6)

% > CpCeO3S := int\( \left[ \frac{V7[1]}{10^3} + \frac{V7[2] \cdot T}{10^6} + \frac{V7[3] \cdot T^2}{10^9} + \frac{V7[4] \cdot T^3}{10^9} + V7[5] \cdot 10^6 \cdot T^{-2}, T \right] \);

\( \text{CpCeO3S} := 76097.78877 \) (1.7)

Heat of reaction at that temperature is calculated using
\( \text{del Hf} = \text{del Ho} + (\int \text{Cp} \, dT \text{ from 298 to 873}) \)
Heat of reaction del Ho is obtained from the spreadsheet
Heat of reaction at 873 for each species is labeled as Hf(species)

% > HfH2S := proc(T)
-20500 + 1000 \( \times \left( \frac{V1[1] \cdot T}{1000} + \frac{V1[2] \cdot T^2}{2 \cdot 1000^2} + \frac{V1[3] \cdot T^3}{3 \cdot 1000^3} + \frac{V1[4] \cdot T^4}{4 \cdot 1000^4} - \frac{V1[5] \cdot 1000}{T} \right) + V1[6] \)
end proc;

\( \text{HfH2S} := \text{proc}(T) \)

\( \begin{align*}
& -20500 + \frac{V1[1] \cdot T}{1000} + \frac{V1[2] \cdot T^2}{2 \cdot 1000^2} + \frac{V1[3] \cdot T^3}{3 \cdot 1000^3} + \frac{V1[4] \cdot T^4}{4 \cdot 1000^4} - \frac{V1[5] \cdot 1000}{T} \\
& + V1[6]
\end{align*} \) (1.8)

% end proc

% > HfH2O := proc(T)
-241830 + 1000 \( \times \left( \frac{V2[1] \cdot T}{1000} + \frac{V2[2] \cdot T^2}{2 \cdot 1000^2} + \frac{V2[3] \cdot T^3}{3 \cdot 1000^3} + \frac{V2[4] \cdot T^4}{4 \cdot 1000^4} - \frac{V2[5] \cdot 1000}{T} \right) + V2[6] \)
end proc;

\( \text{HfH2O} := \text{proc}(T) \)

% end proc
\[
0 + 1000 \cdot \left( \frac{V3[1] \cdot T}{1000} + \frac{V3[2] \cdot T^2}{2 \cdot 1000^2} + \frac{V3[3] \cdot T^3}{3 \cdot 1000^3} + \frac{V3[4] \cdot T^4}{4 \cdot 1000^4} - \frac{V3[5] \cdot 1000}{T} \right) + V3[6]
\]

end proc;

> HfCe2O2 := proc(T)
-1088677 + 1000 \cdot \left( \frac{V4[1] \cdot T}{1000} + \frac{V4[2] \cdot T^2}{2 \cdot 1000^2} + \frac{V4[3] \cdot T^3}{3 \cdot 1000^3} + \frac{V4[4] \cdot T^4}{4 \cdot 1000^4} - \frac{V4[5] \cdot 1000}{T} \right) + V4[6]
end proc;

> HfCe2O3 := proc(T)
-1796191 + 1000 \cdot \left( \frac{V5[1] \cdot T}{1000} + \frac{V5[2] \cdot T^2}{2 \cdot 1000^2} + \frac{V5[3] \cdot T^3}{3 \cdot 1000^3} + \frac{V5[4] \cdot T^4}{4 \cdot 1000^4} - \frac{V5[5] \cdot 1000}{T} \right) + V5[6]
end proc;

> HfCe2O2S := proc(T)
-1696600 + 1000 \cdot \left( \frac{V6[1] \cdot T}{1000} + \frac{V6[2] \cdot T^2}{2 \cdot 1000^2} + \frac{V6[3] \cdot T^3}{3 \cdot 1000^3} + \frac{V6[4] \cdot T^4}{4 \cdot 1000^4} - \frac{V6[5] \cdot 1000}{T} \right) + V6[6]
end proc;

> HfCe2S3 := proc(T)
-1188256 + 1000 \cdot \left( \frac{V7[1] \cdot T}{1000} + \frac{V7[2] \cdot T^2}{2 \cdot 1000^2} + \frac{V7[3] \cdot T^3}{3 \cdot 1000^3} + \frac{V7[4] \cdot T^4}{4 \cdot 1000^4} - \frac{V7[5] \cdot 1000}{T} \right) + V7[6]
end proc;

> int1 := HfH2S(873) + 20500;
\text{int1 := 22292.75843} \quad (1.9)

> int2 := HfH2O(873) + 241830;
\text{int2 := 20865.7371} \quad (1.10)

> int3 := HfH2(873) + 0;
\text{int3 := 16875.16205} \quad (1.11)

> int4 := HfCeO2(873) + 1088677;
\text{int4 := 41515.032} \quad (1.12)

> int5 := HfCe2O3(873) + 1796191;
\text{int5 := 76314.064} \quad (1.13)

> int6 := HfCe2O2S(873) + 1696600;
\text{int6 := 75131.779} \quad (1.14)

> int7 := HfCe2S3(873) + 1188256;
\text{int7 := 76097.830} \quad (1.15)
\[ G_{f1} := -33311.5 \]
\[ G_{f2} := -228577 \]
\[ G_{f3} := 0 \]
\[ G_{f4} := -1025379 \]
\[ G_{f5} := -1707925 \]
\[ G_{f6} := -1623255 \]
\[ G_{f7} := -1171933 \]

\[ c1 := \text{int}\left( \frac{HfH2S(TT)}{RR \cdot TT^2}, TT = 298.15 \ . T \right) \]
\[ c2 := \text{int}\left( \frac{HfH2O(TT)}{RR \cdot TT^2}, TT = 298.15 \ . T \right) \]
\[ c3 := \text{int}\left( \frac{HfH2(TT)}{RR \cdot TT^2}, TT = 298.15 \ . T \right) \]
\[ c4 := \text{int}\left( \frac{HfCeO2(TT)}{RR \cdot TT^2}, TT = 298.15 \ . T \right) \]
\[ c5 := \text{int}\left( \frac{HfCeO3(TT)}{RR \cdot TT^2}, TT = 298.15 \ . T \right) \]
\[ c6 := \text{int}\left( \frac{HfCeO2S(TT)}{RR \cdot TT^2}, TT = 298.15 \ . T \right) \]
\[ c7 := \text{int}\left( \frac{HfCe2S3(TT)}{RR \cdot TT^2}, TT = 298.15 \ . T \right) \]

\[ \text{zz} := c1; \quad \text{zz} := -3.616435748 \] (1.16)

Reaction 1 (R1)
\[ \text{CeO2} + 0.5 \text{H}_2 \rightarrow 0.5 \text{CeO3} + 0.5 \text{H}_2\text{O} \]

Reaction 2 (R2)
\[ \text{CeO2S} + \text{H}_2\text{S} \rightarrow \text{CeO2S} + \text{H}_2\text{O} \]

Reaction 3 (R3)
\[ \text{CeO2S} + 2 \text{H}_2\text{S} \rightarrow \text{CeS3} + 2 \text{H}_2\text{O} \]

K10 is the equilibrium constant at 298K of reaction 1 calculated using
\[ K = \exp\left(-\frac{\Delta G \text{ rxn}}{RT}\right) \]
similarly K20 is the equilibrium constant at 298K of reaction 2
and K30 is the equilibrium constant at 298K of reaction 3

K1 corresponds to equilibrium constant of reaction 1 at T of interest using Vant Hoff equation:
\[ \ln \left( \frac{K1}{K10} \right) = \text{int}\left( \frac{\Delta \text{rxn}}{RT^2} \right) dT \text{ from } 298K \text{ to } 873K \text{ etc. for reactions 2,3} \]
\[
> K10 := \exp \left( -\frac{0.5 \cdot Gf2 + 0.5 \cdot Gf5 - 0.5 \cdot Gf2 - Gf4}{8.314 \cdot 298.15} \right); \\
K10 := 9.796038046 \times 10^{11} \tag{1.17}
\]

\[
> K20 := \exp \left( -\frac{(Gf2 + Gf5 - Gf5 - Gf0)}{8.314 \cdot 298.15} \right); \\
K20 := 2.379969573 \times 10^{19} \tag{1.18}
\]

\[
> K30 := \exp \left( -\frac{2 \cdot Gf2 + Gf7 - Gf0 - 2 \cdot Gf1}{8.314 \cdot 298.15} \right); \\
K30 := 2.235038297 \times 10^{11} \tag{1.19}
\]

\[
> K1 := K10 \cdot \exp(0.5 \cdot c5 + 0.5 \cdot c2 - c4 - 0.5 \cdot c3); \\
> K2 := K20 \cdot \exp(c6 + c2 - c5 - c1); \\
> K3 := K30 \cdot \exp(c7 + 2 \cdot c2 - c6 - 2 \cdot c1); \\
K1 := 0.009844816457 \\
K2 := 1.584917182 \times 10^{5} \\
K3 := 0.001036442234 \tag{1.20}
\]

PP vector corresponds to partial pressure
In PP the order is partial pressure H2So, H2O, H2 and final one is total pressure all in atm

\[
> pp := vector([0.001 \cdot Pt, 0.0313 \cdot Pt, 0.24 \cdot Pt]);
\]

Go corresponds to total mol of gas required (or used) per mol of solid = Go = 1 \times 10^{-6} \times 1.5/ (ppH2So/Pt)
Here partial pressure of H2 and H2O are assumed constant. The "Ce" and "La2" are the mols of Ce and mols
of La2 in a g of sorbent.

\[
> Go := \frac{(1 \cdot 1.5)}{pp[1];} \\
Go := 1500.000000 \tag{1.21}
\]

\[
> Ce := 5.81 \times 10^{-3}; \\
> La2 := 3.07 \times 10^{-3}; \\
Ce := 0.005810000000 \\
La2 := 0.003070000000 \tag{1.22}
\]

\[
> Go := \frac{0.0818}{Ce} \\
Go := 14.07917384 \tag{1.23}
\]

m1 corresponds to partial pressure of H2S
m4 corresponds to moles of CeO2
m5 corresponds to moles of CeO3
m6 corresponds to moles of CeO2S
m7 corresponds to moles of Ce2S3
MM1 is the ppm H2S at equilibrium
MM4 is the umol CeO2/g total sorbent
MM5 is the umol CeO3/g total sorbent etc.

**Ideal Solid Solution**
Cerium atom balance is
\[ m_4 + 2 \cdot m_5 + 2 \cdot m_6 = 1 \]
from the reaction 1 the equilibrium constant is
\[ K_1 = \frac{(2 \cdot m_5)^{0.5} \cdot (pH2O)^{0.5}}{(m_4 \cdot (pH2^0.5))} \]
from the reaction 2 the equilibrium constant is
\[ K_2 = \frac{(2 \cdot m_6 \cdot (pH2O))}{(2 \cdot m_5 \cdot m_1)} \]
Balance on the sulfur atom is
\[ Go \cdot ((pH2So - m_1)/Pt) = m_6 \]
Solving these four equations the final composition and the PH2S concentration can be found.

\[
\text{Ideal Solid Solution}
\]
\[
> \text{polynomials1 := \{ m_4 + 2 \cdot m_5 + 2 \cdot m_6 = 1, (2 \cdot m_5)^{0.5} \cdot pp[2]^{0.5} = m_4 \cdot pp[3]^{0.5} \cdot K_1, (2 \cdot m_6) \cdot pp[2] = 2 \cdot m_3 \cdot m_1 \cdot K_2, Go \cdot (pp[1] - m_1) = (m_6) \cdot Pt \}}:
\text{fsolve(\{polynomials1\});}
\]
\[
\{m_6 = 0.01396839747, m_1 = 0.00001573620365, m_4 = 0.9713620011, m_5 = 0.0003506019898\}
\]
\[
> \text{MM1 := 15.7}:
\text{MM4 := 0.9714 \cdot Ce \cdot 1e + 6}:
\text{MM5 := 0.000351 \cdot Ce \cdot 1e + 6}:
\text{MM6 := 0.013968 \cdot Ce \cdot 1e + 6}:
\]
\[
\text{MM1 := 7.850000000}\]
\[
\text{MM4 := 5.643834000}\]
\[
\text{MM5 := 2.039310000}\]
\[
\text{MM6 := 8.154080000}\]

\[
\text{No Solid Solution with the sulfide and only oxides form the solid solution}
\]
Then cerium atom balance is
\[ m_4 + 2 \cdot m_5 + 2 \cdot m_6 = 1 \]
From the reaction 1 the equilibrium constant is
\[ K_1 = \frac{(2 \cdot m_5 \cdot (m_4 + 2 \cdot m_5)^{0.5} \cdot (pH2O)^{0.5})}{(((m_4 + 2 \cdot m_5) \cdot m_1) \cdot (pH2^0.5))} \]
K2 = (1 \cdot pH2O) / ((2 \cdot m_5 / (2 \cdot m_5 + m_4)) \cdot m_1)
Go \cdot ((pH2So - m_1)/Pt) = m_6

\[
\text{No Solid Solution with the sulfide and only oxides form the solid solution}
\]
\[
> \text{polynomials2 := \{ m_4 + 2 \cdot m_5 + 2 \cdot m_6 = 1, \left( \frac{2 \cdot m_5}{m_4 + 2 \cdot m_5} \right)^{0.5} \cdot pp[2]^{0.5} = K_1, (2 \cdot m_6) \cdot \left( \frac{m_4}{m_4 + 2 \cdot m_5} \right) \cdot pp[3]^{0.5}, 1 \cdot pp[2] = K_2 \cdot \left( \frac{2 \cdot m_5}{2 \cdot m_5 + m_4} \right) \cdot m_1, Go \cdot (pp[1] - m_1) \}}:
\text{solve(\{polynomials2\});}
\]
\[
\{m_5 = 0.0003633614855, m_6 = 0.01033222671, m_1 = 0.0005322680400, m_4 = 0.9786088236\}
\]
$$> \text{MM1} := \frac{532}{2};$$

$$\text{MM4} := 0.9786 \cdot \text{Ce} \cdot 1e+6;$$

$$\text{MM5} := 0.000363 \cdot \text{Ce} \cdot 1e+6;$$

$$\text{MM6} := 0.010332 \cdot \text{Ce} \cdot 1e+6;$$

$$\text{MM1} := 266$$

$$\text{MM4} := 5685.666000$$

$$\text{MM5} := 2.109030000$$

$$\text{MM6} := 60.02892000$$

\hspace{2cm} (1.27)$$

### Ideal Solid Solution

If a sulfide is form by reaction 3

\begin{align*}
\text{cerium atom balance is} & \\
\text{m4+ 2*m5 + 2*m6 + 2*m7} = & 1 \\
\text{K1 = ((2*m5) \cdot 0.5*(pH2O)\cdot 0.5) / ((m4)\cdot (pH2\cdot 0.5))} & \\
\text{K2 = ((2*m6) (pH2O)) / ((2*m5)(m1))} & \\
\text{K3 = ((2*m7)(pH2O)2)/((2*m6)(m1*2))} & \\
\text{sulfur balance is} & \\
\text{Go} (\text{pH2So - m1})/\text{Pt} = m6+m7
\end{align*}

\begin{align*}
> \text{polynomials3} := \{ m4 + 2 \cdot m5 + 2 \cdot m6 + 2 \cdot m7 = 1, (2 \cdot m5)^{0.5} \cdot pp[2]^{0.5} = m4 \cdot pp[3]^{0.5} \cdot K1, 2 \cdot m6 \cdot pp[2] = 2 \cdot m5 \cdot m1 \cdot K2, (2 \cdot m7) \cdot pp[2]^{2} = K3 \cdot (2 \cdot m6) \cdot m1^{2}, Go \cdot (pp[1] - m1) = Pt \\
\} \cdot (m6 + m7) \};

> \text{fsolve}(\text{polynomials3});

\{m4 = 0.9713620011, m5 = 0.0003506019898, m6 = 0.01396839747, m1 = 0.00001573620365, m7 = 9.148353845 \cdot 10^{-13}\}

\hspace{2cm} (1)

$$> \text{MM1} := \frac{15.7}{2};$$

$$\text{MM4} := 0.9714 \cdot \text{Ce} \cdot 1e+6;$$

$$\text{MM5} := 0.000351 \cdot \text{Ce} \cdot 1e+6;$$

$$\text{MM6} := 0.013968 \cdot \text{Ce} \cdot 1e+6;$$

$$\text{MM7} := 9.15e-13 \cdot \text{Ce} \cdot 1e+6;$$

$$\text{totalS} := \text{MM6} + 3 \cdot \text{MM7};$$

\begin{align*}
\text{MM1} := & 7.850000000 \\
\text{MM4} := & 5643.834000 \\
\text{MM5} := & 2.039310000 \\
\text{MM6} := & 81.15408000 \\
\text{MM7} := & 5.316150000 \cdot 10^{-9} \\
\text{totalS} := & 81.15408002
\end{align*}

\hspace{2cm} (2)

### Ideal Sulfide Solution + an ideal oxide solution.

\begin{align*}
\text{cerium atom balance is} & \\
\text{m4+ 2*m5 + 2*m6 + 2*m7} = & 1 \\
\text{K1 = ((2*m5)/(m4 + 2*m5) \cdot 0.5 \cdot (pH2O)\cdot 0.5) / ((m4 / (m4 + 2*m5)) \cdot (pH2\cdot 0.5))} & \\
\text{K2 = ((2*m6) (pH2O) (2*m5 + m4)) / ((2*m6 + 2*m7) \cdot (m1))(2*m5))}
\end{align*}
K3 = (2 \cdot m7)(pH2O^2)/(2 \cdot m6)(m1^2))
sulfur balance is
G0( pH2So - m1)/Pt = m6+m7

\[
polynomials4 := \left\{ m4 + 2 \cdot m5 + 2 \cdot m6 + 2 \cdot m7 = 1, \left( \frac{2 \cdot m5}{m4 + 2 \cdot m5} \right)^{0.5} \cdot pp[2]^{0.5} = K1 \cdot \left( \frac{m4}{m4 + 2 \cdot m5} \right)^{0.5} \cdot pp[3]^{0.5}, (2 \cdot m6) \cdot pp[2] \cdot (2 \cdot m5 + m4) = (2 \cdot m5) \cdot m1 \cdot K2 \cdot (2 \cdot m6 + 2 \cdot m7), (2 \cdot m7) \cdot pp[2]^2 = K3 \cdot (2 \cdot m6) \cdot m1^2, G0 \cdot (pp[1] - m1) = Pt \cdot (m6 + m7) \right\};
\]

\[> \text{solve}(\text{polynomials4}); \]
\[
\{ m5 = 0.0003633614853, m4 = 0.9786088231, m6 = 0.01033222621, m7 = 7.741962366 \times 10^{-10}, m1 = 0.0005322680001 \}, \{ m4 = 0.9673763238 + 27.35625069 I, m5 = 0.0003591908121 + 0.01015748852 I, m6 = 50005.79150 + 65.12207758 I, m7 = -50005.77554 - 78.81036042 I, m1 = -0.0002661340001 + 1.944472451 I \}, \{ m4 = 0.9673763238 - 27.35625069 I, m5 = 0.0003591908121 - 0.01015748852 I, m6 = -50005.77554 - 78.81036042 I, m7 = 50005.79150 - 65.12207758 I, m1 = 0.0002661340001 + 1.944472451 I \}, \{ m7 = 0., m6 = 0., m5 = 0.0003710285885, m4 = 0.9992579428, m1 = 0.00200000000 \} \]

\[> \text{MM1} := \frac{532}{2} ; \]
\[\text{MM4} := 0.9786 \cdot Ce \cdot 1e+6; \]
\[\text{MM5} := 0.000363 \cdot Ce \cdot 1e+6; \]
\[\text{MM6} := 0.010332 \cdot Ce \cdot 1e+6; \]
\[\text{MM7} := 7.74e-10 \cdot Ce \cdot 1e+6; \]
\[\text{totalS} := \text{MM6} + 3 \cdot \text{MM7}, \]
\[\text{MM1} := 266 \]
\[\text{MM4} := 5685.666000 \]
\[\text{MM5} := 2.109030000 \]
\[\text{MM6} := 60.02892000 \]
\[\text{MM7} := 0.000004496940000 \]
\[\text{totalS} := 60.02893349 \]
APPENDIX C - MAPLE 11 PROGRAM FOR THERMODYNAMIC CALCULATION OF LANTHANUM COMPOUNDS

\[ \text{restart; } \]

Vectors V1 to V10 correspond to the coefficients for calculating the enthalpies

V1 corresponds to Coeffs of H2S
V2 corresponds to Coeffs of H2O
V3 corresponds to Coeff of H2
V8 Corresponds to Coeff of La2O3
V9 Corresponds to Coeff of La2O2S
V10 Corresponds to Coeff of La2S3

\[ \text{> V1 := vector}(6, [26.88412, 18.67809, 3.434203, -3.378702, 0.135882, -8.41]) : \]
\[ \text{> V2 := vector}(6, [30.09, 6.83, 6.793, -2.534, 0.08214, -9.05]) : \]
\[ \text{> V3 := vector}(6, [33.07, -11.36, 11.43, -2.773, -0.1586, -9.98]) : \]
\[ \text{> V8 := vector}(6, [118, 16, 0, 0, 1.24, -40.0518]) : \]
\[ \text{> V9 := vector}(6, [148.381, 49.39, 0, 0, -17.3874, -104.753]) : \]
\[ \text{> V10 := vector}(6, [116.52, 14.64, 0, 0, 35.3911]) : \]

\[ \text{> RR := 8.314; } \]
\[ \text{Tf := 873.15; } \]
\[ P_{t} := 2; \]

For calculating all Cp's the equation used is

\[ C_{p} = A + Bt + Ct^2 + Dt^3 + E/t^2 \] where \( t = T(K)/1000 \)

For calculating all enthalpies:

\[ H - H_{0} = 1000^0(A t + B t^2/2 + C t^3/3 + D t^4/4 - E/t + F) \]

For calculating the Cp at 873 K is \( \int \text{(Cp)} \; dT \) from 298.15 K to 873 K

\[ \text{> CpH2S := int} \left( \frac{V1[1]}{10^3} + \frac{V1[2] \cdot T}{10^3} + \frac{V1[3] \cdot T^2}{10^3} + \frac{V1[4] \cdot T^3}{10^9} + V1[5] \cdot 10^6 \cdot T^{-2}, T \right) \]
\[ = 298.15 \ldots 873 \];

\[ C_{pH2S} := 22289.16394 \] (1.1)

\[ \text{> CpH2O := int} \left( \frac{V2[1]}{10^3} + \frac{V2[2] \cdot T}{10^3} + \frac{V2[3] \cdot T^2}{10^6} + \frac{V2[4] \cdot T^3}{10^9} + V2[5] \cdot 10^6 \cdot T^{-2}, T \right) \]
\[ = 298.15 \ldots 873 \];

\[ C_{pH2O} := 20861.32446 \] (1.2)

\[ \text{> CpH2 := int} \left( \frac{V3[1]}{10^3} + \frac{V3[2] \cdot T}{10^3} + \frac{V3[3] \cdot T^2}{10^6} + \frac{V3[4] \cdot T^3}{10^9} + V3[5] \cdot 10^6 \cdot T^{-2}, T \right) \]
\[ = 298.15 \ldots 873 \];

\[ C_{pH2} := 16872.80866 \] (1.3)
\[
CpLa2O3 := \int \left( \frac{V8[1]}{10^3} + \frac{V8[2] \cdot T}{10^6} + \frac{V8[3] \cdot T^2}{10^9} + \frac{V8[4] \cdot T^3}{10^9} + V8[5] \cdot 10^6 \cdot T^{-2}, T \right) \\
= 298.15 \cdot 873
\]

\[
CpLa2O3 := 70479.59370 \quad (1.4)
\]

\[
CpCe2O2S := \int \left( \frac{V9[1]}{10^3} + \frac{V9[2] \cdot T}{10^6} + \frac{V9[3] \cdot T^2}{10^9} + \frac{V9[4] \cdot T^3}{10^9} + V9[5] \cdot 10^6 \cdot T^{-2}, T \right) \\
= 298.15 \cdot 873
\]

\[
CpCe2O2S := 63521.58357 \quad (1.5)
\]

\[
CpLa2S3 := \int \left( \frac{V10[1]}{10^3} + \frac{V10[2] \cdot T}{10^6} + \frac{V10[3] \cdot T^2}{10^9} + \frac{V10[4] \cdot T^3}{10^9} + V10[5] \cdot 10^6 \cdot T^{-2}, T \right) \\
= 298.15 \cdot 873
\]

\[
CpLa2S3 := 71909.60643 \quad (1.6)
\]

Heat of reaction at that temperature is calculated using
\[ \text{del Hf} = \text{del Ho} + (\int \text{Cp dT from 298 to 873}) \]
Heat of reaction del Ho is obtained from the spread sheet
Heat of reaction at 873 for each species is labeled as Hf(species)

\[
HfH2S := \text{proc}(T) \\
-20500 + 1000 \cdot \left( \frac{V1[1] \cdot T}{1000} + \frac{V1[2] \cdot T^2}{2 \cdot 1000^2} + \frac{V1[3] \cdot T^3}{3 \cdot 1000^3} + \frac{V1[4] \cdot T^4}{4 \cdot 1000^4} - \frac{V1[5] \cdot 1000}{T} \right) + V1[6]
\]

end proc:

\[
HfH2O := \text{proc}(T) \\
-241830 + 1000 \cdot \left( \frac{V2[1] \cdot T}{1000} + \frac{V2[2] \cdot T^2}{2 \cdot 1000^2} + \frac{V2[3] \cdot T^3}{3 \cdot 1000^3} + \frac{V2[4] \cdot T^4}{4 \cdot 1000^4} - \frac{V2[5] \cdot 1000}{T} \right) + V2[6]
\]

end proc:

\[
HfH2 := \text{proc}(T) \\
0 + 1000 \cdot \left( \frac{V3[1] \cdot T}{1000} + \frac{V3[2] \cdot T^2}{2 \cdot 1000^2} + \frac{V3[3] \cdot T^3}{3 \cdot 1000^3} + \frac{V3[4] \cdot T^4}{4 \cdot 1000^4} - \frac{V3[5] \cdot 1000}{T} \right) + V3[6]
\]

end proc:

\[
H8 := \text{proc}(T) \\
-1793700 + 1000 \cdot \left( \frac{V8[1] \cdot T}{1000} + \frac{V8[2] \cdot T^2}{2 \cdot 1000^2} + \frac{V8[3] \cdot T^3}{3 \cdot 1000^3} + \frac{V8[4] \cdot T^4}{4 \cdot 1000^4} - \frac{V8[5] \cdot 1000}{T} \right)
\]
\[ + V8[6] \]

end proc:

\[ H9 := \text{proc}(T) \]
\[ -1670500 + 1000 \left( \frac{V9[1] \cdot T}{1000} + \frac{V9[2] \cdot T^2}{2 \cdot 1000^2} + \frac{V9[3] \cdot T^3}{3 \cdot 1000^3} + \frac{V9[4] \cdot T^4}{4 \cdot 1000^4} \right) - \frac{V9[5] \cdot 1000}{T} + V9[6] \]

end proc:

\[ H10 := \text{proc}(T) \]
\[ -1205000 + 1000 \left( \frac{V10[1] \cdot T}{1000} + \frac{V10[2] \cdot T^2}{2 \cdot 1000^2} + \frac{V10[3] \cdot T^3}{3 \cdot 1000^3} + \frac{V10[4] \cdot T^4}{4 \cdot 1000^4} \right) - \frac{V10[5] \cdot 1000}{T} + V10[6] \]

end proc:

\[ int1 := HfH2S(873) + 20500; \]
\[ int1 := 22292.75843 \] (1.7)

\[ int2 := HfH2O(873) + 241830; \]
\[ int2 := 20865.7371 \] (1.8)

\[ int3 := HfH2(873) + 0; \]
\[ int3 := 16875.16205 \] (1.9)

\[ int8 := H8(873) + 1793700; \]
\[ int8 := 70479.621 \] (1.10)

\[ int9 := H9(873) + 1670500; \]
\[ int9 := 63521.227 \] (1.11)

\[ int10 := H10(873) + 1205000; \]
\[ int10 := 71909.644 \] (1.12)

\[ Gf1 := -33305.06; \]
\[ Gf2 := -228583.9; \]
\[ Gf3 := 0; \]
\[ Gf8 := -1705400; \]
\[ Gf9 := -1538700; \]
\[ Gf10 := -1208312; \]

\[ c1 := \text{int} \left( \frac{HfH2S(TT)}{RR \cdot TT^2}, TT = 298.15 .. T_f \right); \]
\[ c2 := \text{int} \left( \frac{HfH2O(TT)}{RR \cdot TT^2}, TT = 298.15 .. T_f \right); \]
\[ c3 := \text{int} \left( \frac{HfH2(TT)}{RR \cdot TT^2}, TT = 298.15 .. T_f \right); \]
\[ c8 := \text{int} \left( \frac{H8(TT)}{RR \cdot TT^2}, TT = 298.15 .. T_f \right); \]
\[c9 := \text{int} \left( \frac{H9(TT)}{RR \cdot TT^2}, TT = 298.15 \cdot Tf \right);\]
\[c10 := \text{int} \left( \frac{H10(TT)}{RR \cdot TT^2}, TT = 298.15 \cdot Tf \right);\]
\[c1 := -3.616435748\]
\[c2 := -62.49856940\]
\[c3 := 1.461178416\]
\[c8 := -470.6186350\]
\[c9 := -440.3459184\]
\[c10 := -313.9629283\]

\[zz := c9 + c2 - c1 - c8;\]
\[zz := -28.6094171\]

(1.13)

\[\text{Reaction 1 (R1)}\]
\[\text{La}_2\text{O}_3 + \text{H}_2\text{S} \rightarrow \text{La}_2\text{O}_2\text{S} + \text{H}_2\text{O}\]

\[\text{Reaction 2 (R2)}\]
\[\text{La}_2\text{O}_2\text{S} + 2\text{H}_2\text{S} \rightarrow \text{La}_2\text{S}_3 + 2 \text{H}_2\text{O}\]

\[H_{r1} := H9(600) + HfH2O(600) - HfH2S(600) - H8(600);\]
\[H_{r2} := H10(600) + 2HfH2O(600) - H9(600) - 2HfH2S(600);\]
\[H_{r1} := -1.12170424 \times 10^5\]
\[H_{r2} := 36870.58726\]

(1.14)

(1.15)

K10 is the equilibrium constant at 298K of reaction 1 calculated using
\[K = \exp \left( \frac{-dG_{rxn}}{RT} \right)\]
similarly K20 is the equilibrium constant at 298K of reaction 2
and K30 is the equilibrium constant at 298K of reaction 3

K1 corresponds to equilibrium constant of reaction 1 at T of interest using Vant Hoff equation:
\[\ln \left( \frac{K1}{K10} \right) = \int \left( \frac{\text{d}H_{rxn}}{RT^2} \right) \text{dT} \text{ from 298K to 873K etc. for reactions 2,3}\]

\[K10 := \exp \left( -\frac{(Gf9 + Gf2 - Gf1 - Gf8)}{8.314 \cdot 298.15} \right);\]
\[K10 := 1.016423543 \times 10^5\]

(1.16)

\[K20 := \exp \left( -\frac{(2 \cdot Gf2 + Gf10 - Gf9 - 2 \cdot Gf1)}{8.314 \cdot 298.15} \right);\]
\[K20 := 3.482237789 \times 10^{10}\]

(1.17)

\[K1 := K10 \cdot \exp(c9 + c2 - c8 - c1);\]
\[K2 := K20 \cdot \exp(c10 + 2 \cdot c2 - c9 - 2 \cdot c1);\]
\[ K_1 := 3.820874390 \times 10^{8} \]
\[ K_2 := 1.927179573 \times 10^{14} \] (1.18)

PP vector corresponds to partial pressure
In PP the order is partial pressure H2So, H2O, H2 and final one is total pressure all in atm

\[ \text{Go corresponds to Total moles of gas required for mol of solid = Go = 1 * 0.5/ (pH2So/Pt)} \]
Here partial pressure of H2 and H2O are assumed constant;

\[ \text{La2} := 3.07 \times 10^{-3} ; \]
\[ \text{Go :=} \frac{0.0818}{\text{La2}} ; \]

\[ \text{Go := 26.64495114} \] (1.19)

Cerium atom balance is
m8 + m9 = 1
from the reaction 1 the equilibrium constant is
K1 = ((m95) (pH2O)) / (m8)(m1)
Balance on the sulfur atom is
Go *((pH2So - m1)/Pt) = m9
Solving these four equations the final composition and the PH2S concentration can be found
m1 corresponds to partial pressure of H2S
m8 corresponds to moles of La2O3
m9 corresponds to moles of La2O2S
m10 corresponds to moles of La2S3

\[ \text{polynomials}1 := \{ \text{m8 + m9 = 1}, \text{m9} \cdot \text{pp}[2] = \text{m8} \cdot \text{m1} \cdot \text{K1}, \text{Go} \cdot (\text{pp}[1] - \text{m1}) = \text{m9} \cdot \text{Pt} \} \ ; \]
fsolve (polynomials1):
\[ \{ \text{m9 = 1.220726529 \times 10^{-5}}, \text{m1 = 0.0009999999084}, \text{m8 = 0.9999999988} \} \] (1.20)

\[ \text{MM1 :=} \frac{999.99}{2} ; \]

\[ \text{MM1 := 499.9950000} \] (1.21)

\[ \text{MM8 := 0.9999\cdot La2\cdot 1e+6}; \]
\[ \text{MM9 := 1.22\cdot 10^{-9}\cdot La2\cdot 1e+6}; \]

\[ \text{MM8 := 3069.693000} \]
\[ \text{MM9 := 0.000003745400000} \] (1.22)

If a sulfide is formed by reaction 3
cerium atom balance is
m8+ m9 + m10 = 1
K1 = ((m9) (pH2O))/ (m8) (pH2S)
K2 = ((m10)(pH2O^2))/((m9)(pH2S3^2))
sulfur balance is
Go((pH2So - m1)/Pt) = m9 + m10

\[ \text{polynomials}0 := \{ \text{m08 + m09 + m10} = 1, \text{m09} \cdot \text{pp}[2] = \text{m08} \cdot \text{m1} \cdot \text{K1}, \quad (\text{m10}) \cdot \text{pp}[2] = \text{K2} \cdot \text{m09} \cdot \text{m1}^2, \quad \text{Go} \cdot (\text{pp}[1] - \text{m1}) = \text{Pt} \cdot (\text{m09} + 3 \cdot \text{m10}) \} ; \]
\[
\text{solve}(\text{polynomials0});
\]

\[
\begin{aligned}
\{m10 &= 0.004324257653, m1 = 0.00002624906898, m09 = 3.190437592 \times 10^{-11}, m08 \\
&= 0.9956757423 \}, \{m09 &= -1.595223853 \times 10^{-11} + 2.811777790 \times 10^{-11} L m08 \\
&= 0.9955008912 + 0.001027566520 L m10 = 0.004499108774 - 0.0001027566801 L m1 \\
&= -0.00001312449288 + 0.00002313909383 I, \{m08 &= -3.696050294 \times 10^{-10}, m09 \\
&= 1.011485582 \times 10^{-16}, m1 = -.2241833742, m10 = 1.000000000 \}, \{m09 = \\
&-1.595223853 \times 10^{-11} - 2.811777790 \times 10^{-11} L m10 = 0.004499108774 + 0.0001027566801 L \\
m08 = 0.9955008912 - 0.0001027566520 L m1 = -0.00001312449288 \\
&- 0.00002313909383 I}\}
\end{aligned}
\]

\[\text{MM1} := \frac{37.8}{2};\]

\[\text{MM8} := 0.9871 \cdot \text{La2} \cdot 1 e + 6;\]

\[\text{MM9} := 4.555 \cdot 10^{-11} \cdot \text{La2} \cdot 1 e + 6;\]

\[\text{MM10} := 0.01281 \cdot \text{La2} \cdot 1 e + 6;\]

\[\text{MM1} := 18.90000000\]

\[\text{MM8} := 3030.397000\]

\[\text{MM9} := 1.398385000 \times 10^{-7}\]

\[\text{MM10} := 39.32670000\]

\[\text{Total } S = \text{MM9} + 3 \cdot \text{MM10};\]

\[\text{Total } S = 117.9801001\]

\[\text{corr1} := \left( \begin{array}{c} -\text{Hr1} \\ 8.314 \end{array} \right) \cdot \left( \begin{array}{c} 1 \\ 873 \end{array} - \frac{1}{298.2} \right);\]

\[\text{corr2} := \left( \begin{array}{c} -\text{Hr2} \\ 8.314 \end{array} \right) \cdot \left( \begin{array}{c} 1 \\ 873 \end{array} - \frac{1}{298.2} \right);\]

\[\text{corr1} := -29.78950029\]

\[\text{corr2} := 9.791853597\]

\[\text{K1calc := K10} \cdot \exp(\text{corr1});\]

\[\text{K2calc := K20} \cdot \exp(\text{corr2});\]

\[\text{K1calc} := 1.173975737 \times 10^{8}\]

\[\text{K2calc} := 6.228829009 \times 10^{14}\]
VITA

Vikram Reddy Kalakota was born in 1985, to Malleswari and Sudarsan R Kalakota, in Vijayawada, Andhra Pradesh, India. He completed his high school education in Vijayawada in 2002. He was accepted by Andhra University into the Department of Chemical Engineering and earned a Bachelor of Technology in 2006. Upon graduation, he continued his education in the graduate program of Louisiana State University, Department of Chemical Engineering. This thesis completes his requirements to receive the degree of Master of Science in Chemical Engineering.