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Regenerable sulfur sorbents in coal combustion. Thermodynamics and testing by TG [☆]

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Abstract

Fluidized bed coal combustion (FBC) at low temperatures (1100–1300 K) can be combined with sulfur removal by regenerable sorbents.

Thermodynamic calculations prove that CaO-containing sorbents, chemically bound to a second compound like Al_2O_3, will be the best. These compounds can be tested by thermogravimetry (TG) in an SRO (sulfation, regeneration, and oxidation) cycle by which essential properties such as sulfation rate and capacity, and regeneration behavior can be determined.

Keywords: Coal; Fluidized bed combustion; Low-temperature combustion; Sorbent regeneration; Sulfur removal; TG

1. Introduction

Coal is a very important source of energy, but combustion causes many environmental problems as a result of the production of nitrogen- and sulfur-oxides and the large amount of solid residue [1].

Low temperature combustion (1100–1300 K) in fluidized beds decreases NO_x production, and sulfur oxides can be removed by reaction with appropriate sorbent materials. However, this results in an increase of the amount of solid waste. For that reason, regeneration of the sulfated sorbent will be attractive. Of course, robust sorbent pellets are needed for a long lifetime in FBC conditions. Further, easy separation

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should be possible between the heavy sorbent pellets and the light and bulky ash particles [1, 2]. Important reactions are, for instance with CaO:

$$\text{Sulfation:}\quad CaO + SO_2 + \tfrac{1}{2}O_2 \rightarrow CaSO_4 \qquad (1)$$

$$\text{Reduction:}\quad CaSO_4 + H_2 \rightarrow CaO + SO_2 + H_2O \qquad (2)$$

$$CaSO_4 + 4H_2 \rightarrow CaS + 4H_2O \qquad (3)$$

$$3CaSO_4 + CaS \rightarrow 4SO_2 + 4CaO \qquad (4)$$

$$\text{Oxidation:}\quad CaS + 2O_2 \rightarrow CaSO_4 \qquad (5)$$

Reaction (4) is a combination of the reactions (2) and (3).

These reactions can be measured by TG. It is possible to make a complete sulfation/regeneration/oxidation cycle in one experimental run, the SRO test [2]. From these measurements it is found, that pure CaO has bad regeneration behavior, giving too much CaS according to reaction (3), namely more than 40% of CaS (at 1123 K) [2].

A possible solution is to make reaction (2) the real regeneration reaction; this is more attractive than reaction (3). This can be achieved by addition of a second compound which stabilizes CaO by chemical reaction. In that case, of course, the sulfation reaction (1) also will be influenced.

With Al_2O_3 as a second compound, we get the following reaction schemes:

$$\text{Stabilization:}\quad CaO + xAl_2O_3 \rightarrow CaO \cdot xAl_2O_3 \qquad (6)$$

$$\text{Sulfation:}\quad CaO \cdot xAl_2O_3 + SO_2 + \tfrac{1}{2}O_2 \rightarrow CaSO_4 + xAl_2O_3 \qquad (7)$$

$$\text{Reduction:}\quad CaSO_2 + H_2 + xAl_2O_3 \rightarrow CaO \cdot xAl_2O_3 + H_2O + SO_2 \qquad (8)$$

$$CaSO_4 + 4H_2 \rightarrow CaS + 4H_2O \qquad (9)$$

$$3CaSO_4 + CaS + 4xAl_2O_3 \rightarrow 4CaO \cdot xAl_2O_3 + 4SO_2 \qquad (10)$$

$$\text{Oxidation:}\quad CaS + 2O_2 \rightarrow CaSO_4 \qquad (11)$$

Now regeneration reaction (8) is promoted, compared to reaction (2), while CaS formation (9) is unchanged, compared to (3). In the best case, using sol–gel pellets, less than 2% CaS is formed during regeneration [1, 2].

2. Thermodynamics

Since in the FBC process the ash phase (highly voluminous and with a low specific weight) is completely separated from the sorbent materials (compact pellets with high specific weight), the absorption/regeneration process in the sorbent pellets will not be influenced by the ash phase. So thermodynamic calculations may be done for the sorbent pellets alone.

First of all, the composition of the exhaust gas and the regeneration gas mixture must be defined. A reasonable assumption will be:

combustion and regeneration temperature 1123 K; pressure 1×10^5 Pa; exhaust gas concentration, $pO_2 = 3400$ Pa, $pSO_2 < 10$ Pa.

SO_2 concentration after regeneration: $PSO_2 > 10^4$ Pa.

2.1. *Sulfation reaction (1)*

$$CaO + SO_2 + \tfrac{1}{2}O_2 \rightleftharpoons CaSO_4 \qquad (1)$$

Equilibrium condition: $RT \ln [K_p(1)] = -\Delta_r G^\circ(1) = -\Delta_r H^\circ(1) + T\Delta_r S^\circ(1)$

$K_p(1) = (P^\circ)^{3/2}/(pSO_2 pO_2{}^{1/2})$, P° being 1×10^5 Pa.

From Refs. [3–6] the values of $\Delta_r H^\circ$ and $\Delta_r S^\circ$ can be calculated at 1123 K. The result is:

$\Delta_r G^\circ(1) = -188.8\,\mathrm{kJ\,mol^{-1}}$

$K_p(1) = 6.03 \times 10^8$; $(pSO_2)\mathrm{eq.} = 9 \times 10^{-4}$ Pa.

For a higher SO_2 pressure $p^*SO_2 = 10$ Pa, can be calculated:

$K_p^*(1) = (0.034)^{-1/2}(1 \times 10^{-4})^{-1} = 5.42 \times 10^4$

$\Delta_r G^*(1) = -RT \ln [K_p^*(1)] = -101.8\,\mathrm{kJ\,mol^{-1}}$

This means that stabilization of CaO (according to Eq. (6)) will be possible with a maximum value of the Gibbs energy

$\Delta_r G^\circ(\mathrm{stab}) = (-188.8 + 101.8) = -87.0\,\mathrm{kJ\,mol^{-1}}$

This is shown in Fig. 1.

2.2. *Reduction with hydrogen at 1123 K*

The SO_2 pressure produced after reduction must be high enough for further application, at least: $p^*SO_2 = 1 \times 10^4$ Pa.

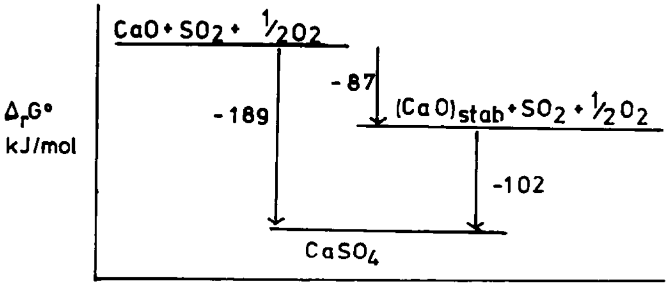

Fig. 1. The Gibbs energy $\Delta_r G^\circ$, in kJ $\mathrm{mol^{-1}}$, according to Eqs. (1) and (7), for the sulfation of CaO or CaO-containing compounds at an oxygen pressure of 3400 Pa, and at 1123 K. The situation at the right corresponds to an equilibrium SO_2 pressure of 10 Pa.

The equilibrium value of $p\mathrm{SO_2}$ follows from Eq. (4):

$$\Delta_r G^\circ(4) = +202.1\ \mathrm{kJ\ mol^{-1}} = -RT\ln(K_p)_4$$

Since $K_p(4) = \{(p\mathrm{SO_2})\ \mathrm{eq}/\mathrm{P}^\circ\}^4$, we can calculate:

$$(p\mathrm{SO_2})\ \mathrm{eq} = 447\ \mathrm{Pa}.$$

This value is much lower than 1×10^4 Pa. For $p^*\mathrm{SO_2} = 1 \times 10^4$ Pa we get:

$$K_p^*(4) = 1 \times 10^{-4};\ \Delta_r G^*(4) = +86.0\ \mathrm{kJ\ mol^{-1}}$$

The difference $(86 - 202.1) = -116.1$ kJ mol^{-1} corresponds to 4 moles of CaO, so the Gibbs energy of stabilization of CaO should be at least $-116.1/4 = -29.0$ kJ mol CaO (see Fig. 2).

Consequently the stabilization region at 1123 K is:

$$29.0 < -\Delta_r G^\circ(6) < 87.0\ \mathrm{kJ\ mol\ CaO}$$

In the same way these figures can be calculated for different temperatures and also for BaO and SrO. The values are summarized in Table 1.

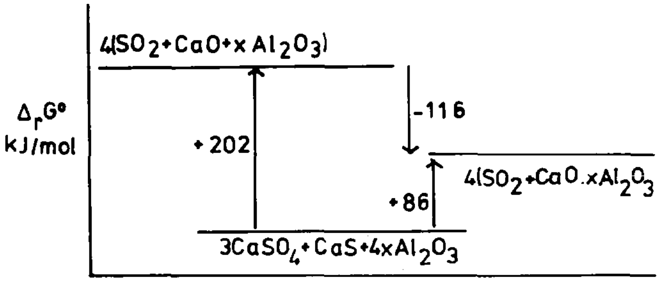

Fig. 2. The Gibbs energy $\Delta_r G^\circ$, in kJ mol^{-1}, for the regeneration step according to Eqs. (4) and (10) at 1123 K. The situation at the right corresponds to an equilibrium $\mathrm{SO_2}$ pressure of 1×10^4 Pa.

Table 1
Minimum and maximum values of the Gibbs energy $\Delta_r G^\circ(6)$, for the stabilization of CaO, SrO, and BaO at 1123 and 1273 K

Compound	Temp/K	$-\Delta_r G^\circ(6)/(\mathrm{kJ\ mol^{-1}})$	
		Min	Max
CaO	1123	29	87
	1273	1	36
SrO	1123	63	159
	1273	28	106
BaO	1123	126	191
	1273	85	136

It can be seen that SrO and BaO demand higher values of stabilization, compared to CaO.

For a number of CaO-containing compounds, the real value of the Gibbs energy of stabilization is calculated and is summarized in Table 2 and Fig. 3 (see Refs. [3–6]). From these figures, it can be concluded that at 1123 K all compounds are within the required range, except CaO and $Ca_3Al_2O_6$, but that at 1273 K only $Ca_3Al_2O_6$ can be used.

Fig. 3 gives a survey of these compounds for the whole temperature region between 1123 and 1273 K. This figure shows the thermodynamic possibility of using compounds as sorbent material, but gives no information about the real behavior in sulfation/regeneration cycles, since then other properties, like kinetics, strength, and porosity also play an important role [1, 2, 9]. This information can be partly obtained by TG experiments.

3. TG Measurements (Refs. [1, 2, 9])

The experimental set up for the testing of sorbents is given in Refs. [1] and [2].

In Fig. 4 the SRO test is shown. A more complete evaluation of such an SRO test is given in Ref. [2].

A certain amount of sorbent is heated in air to 1123 K (calcination), flow rate: 200 ml min^{-1} (measured at 273 K and 10^5 Pa). During this calcination, volatiles are evaporated, e.g. H_2O and CO_2, originating from the preparation or atmospheric storage [10].

When temperature and weight are constant, the gas flow is changed into a gas mixture of 0.5% SO_2 in air. Now the sulfation reaction starts (Eqs. (1) and (7); the duration is 3–60 h, depending on the type of crucible [9] and the structure of the sorbent.

When the sulfation step is completed, the gas is changed (via pure N_2 during 30 min) into 5% H_2–N_2. Then the reduction starts, according to Eqs. (2)–(4) and (8)–(10). This step proceeds very fast (some minutes). As mentioned in Refs. [1, 2], use of 100% H_2 is

Table 2
Gibbs energy $\Delta_r G°(6)$, for the stabilization of calcium-containing compounds, according to reaction (6).

Compound	$-\Delta_r G°(6)/(kJ\ mol^{-1})$ CaO at	
	1123 K	1273 K
CaO	0	0
$CaAl_2O_4$	39	42
$CaAl_4O_7$	41	47
$1/3(Ca_3Al_2O_6)$	15	16
$CaTiO_3$	87	88
β-$CaSiO_3$	67	64
Min/max value	29–87	1–36

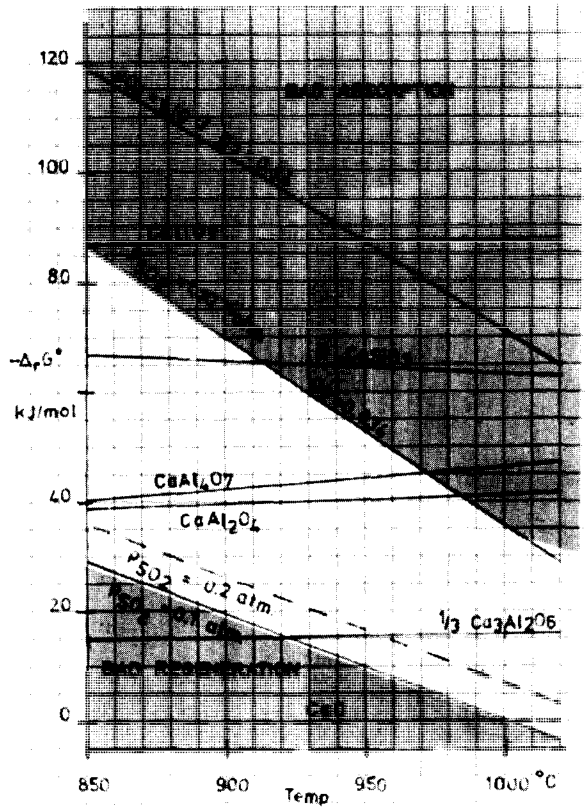

Fig. 3. The Gibbs energy of stabilization ($\Delta_r G°$) in kJ mol^{-1} CaO, according to Eq. (6) is given for several CaO-containing compounds in the temperature region 1123–1273 K. This diagram shows the possible application of CaO-containing compounds for use as regenerable sorbents, depending on the required conditions. Lower region: bad regeneration, giving a too low SO_2 pressure. Top region: bad absorption of SO_2, leading to an SO_2 pressure that is too high. Middle region: good sorption–regeneration behavior. The regions are calculated for regeneration up to SO_2 pressures of 1×10^4 and 2×10^4 Pa, respectively (0.1 and 0.2 Atm), and for sulfation at a total pressure of 1×10^5 Pa, with $pSO_2 = 10$ Pa (1×10^{-4} Atm.) and $pO_2 = 3400$ Pa (0.034 Atm) and at a total pressure of 1×10^6 Pa, with $pSO_2 = 100$ Pa (1×10^{-3} Atm.) and $pO_2 = 34000$ Pa (0.34 Atm).

not suitable, since the TG baseline will shift when going from N_2 to pure H_2. Further, the regeneration efficiency is lower in pure H_2. The regeneration efficiency indicates, which fraction of the $CaSO_4$, formed in the sulfation step, is regenerated into the wanted compounds CaO and $CaO \cdot xAl_2O_3$.

When the weight is constant, the gas is changed, via pure N_2 during 30 min, into air. Then the oxidation proceeds according to Eqs. (5) and (11). From this step the exact

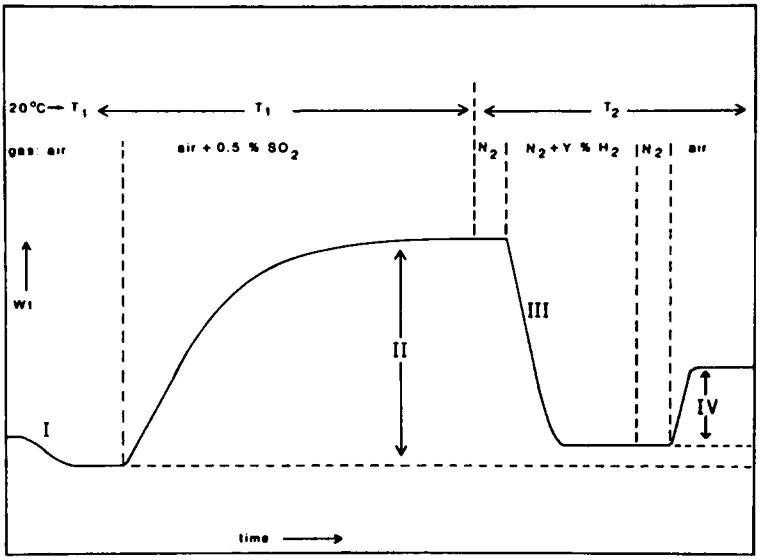

Fig. 4. The SRO test: I, calcination; II, sulfation; III, regeneration; IV, oxidation [2]. T_1 and T_2 are between 1073 and 1273 K (in most cases 1123 K), being the temperature limits of coal combustion in FBC reactors.

amount of CaS, formed during the reduction step, can be determined. From this SRO test a number of properties can be determined.

The sulfation step gives information about the sorbent capacity, from the maximum weight increase, and the sulfation rate, from the rate of the weight increase. The capacity depends on the CaO content, but it is possible that not all CaO can react because of the formation of a tight $CaSO_4$ shell on the outside of the sorbent particles. An important factor for influencing the sulfation rate consists in the porous structure of the sorbent pellets. A fast rate demands a porous structure with large pore diameters. Ref. [9] shows how rate figures, measured by TG, can be applied in totally different conditions, for instance in FBC measurements.

In the ideal situation the regeneration step produces only CaO or $CaO \cdot xAl_2O_3$, according to Eqs. (2) and (8). As discussed in the thermodynamic section, pure CaO produces a lot of CaS. Only when the solid $CaSO_4$, formed during the sulfation step, is in the direct vicinity of Al_2O_3, nearly no CaS is formed. In practice, this can be obtained by using sorbent pellets, consisting of θ-Al_2O_3 with a monolayer of CaO. This kind of sorbent can be prepared with a sol–gel process [10].

From the oxidation step the exact amount of CaS, and the regeneration efficiency (= the proportion of the amount of CaO, formed during the regeneration step, and the total amount of CaO, reacted in the sulfation step) can be determined. Reiteration of the SRO test gives information about the cyclic behavior of the tested sorbent: change of sulfation rate, capacity, and regeneration efficiency.

Other compounds (titanates, silicates) were also tested, and not only containing CaO, but also SrO and BaO [1, 2]. Comparison of all these experiments proved that only $CaO-Al_2O_3$ mixtures will satisfy, for reasons of strength, porosity, sulfation rate, and regeneration behavior.

4. Conclusions

The search for regenerable sulfur sorbents during coal combustion proceeds in several steps. Firstly, thermodynamic calculations indicate which samples could be used, both for sulfation and regeneration. Secondly, testing by TG in variable gas atmospheres is required in order to determine behavior during sulfation and regeneration.

The SRO test (sulfation, regeneration, oxidation) gives reliable and fast information for comparison of different sorbents. For a fast sulfation reaction, highly porous sorbents are required. For a good regeneration behavior, good contact is necessary between the active component (CaO, SrO, BaO) and the carrier material (SiO_2, TiO_2, Al_2O_3). The sorbent must further more be strong enough to survive many sulfation/regeneration cycles.

The best sorbent so far consists of spherical pellets of θ-Al_2O_3, covered with a monolayer of CaO and prepared by a sol–gel process [10].

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