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KINETIC INVESTIGATION OF SORBENTS FOR DESULFURIZATION OF COMBUSTION GASES, MEASURED WITH A TUBULAR REACTOR/TG COMBINATION

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ABSTRACT

A tubular reactor/thermobalance combination is applied for study of gas-solid interaction at high pressures and flow rates. The kinetics of sulfation and regeneration of CaO/Al_2O_3 sorbents are investigated.

INTRODUCTION

In our department in situ sulfur capture during fluidized bed combustion of coal is investigated, using pellets of regenerative sorbent materials [1]. The temperature and pressure conditions in such a process are 850–1000°C and 1–10 bar respectively.

For the screening of sorbents a combined thermobalance/flow-through tubular reactor is developed [2], to study reactions between sorbent and gas phase at more realistic pressures and gas velocities, than obtainable in conventional thermobalances.

In experiments with this set-up it was seen that the SO_2 breakthrough for a tubular reactor filled with sorbent not only depends on the column length, but also in a complicated way on factors such as the gas velocity and the pressure in the fixed bed of sorbent.

EXPERIMENTAL

Apparatus Fig. 1 shows a diagram of the apparatus, which is described more extensively in [2]. A tubular reactor (e), made of quartz glass (internal diameter 5 mm) rests on an electronic balance (j). The construction of the capillaries for gas in- and outlet (g) is essential for obtaining undisturbed weight signal, with a sensitivity of 0.1 mg. These capillaries must be long

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(about 70 cm) and thin. The inlet is a stainless steel capillary (0.5 x 0.3 mm) and the outlet a glass capillary (0.8 x 0.5 mm). Both are flexible enough for the desired sensitivity to be reached. The complete reactor weight, including the gas phase inside, is measured. Therefore a correction is necessary for weight change, caused by change of temperature, pressure or gas composition $\Delta W(x)$.

Sorbents [3]. Three different sorbents were used in the experiments: cylindrical pellets of -Al_2O_3, impregnated with 8.4 wt & CaO (I); cylindrical pellets of γ-Al_2O_3, impregnated with 7 wt % Ca O (II) and spheres, made by a sol-gel process (III), consisting of γ-Al_2O_3 with 9 wt % CaO. Some characteristics of I, II and III are given in Table 1.

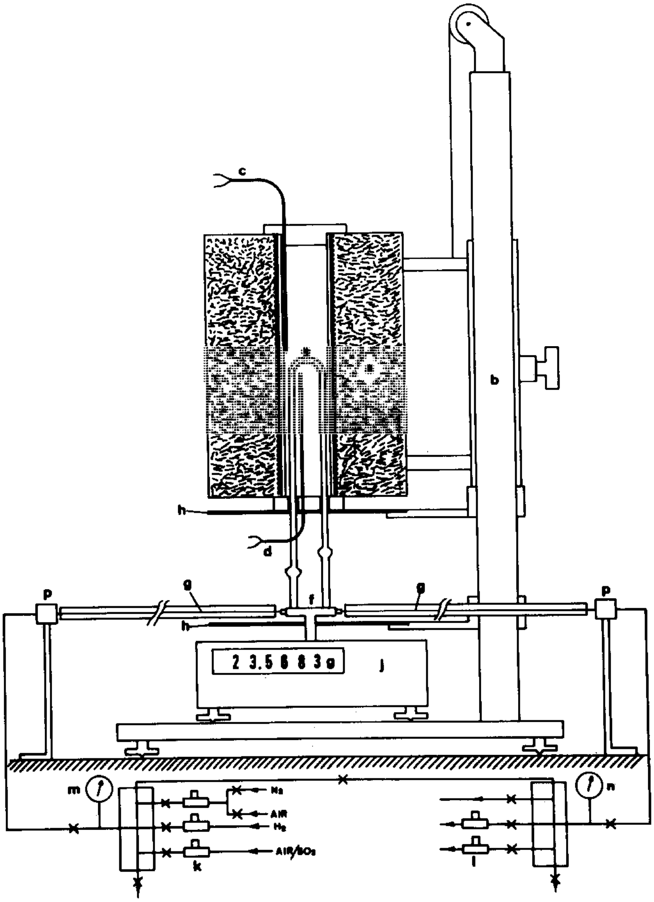
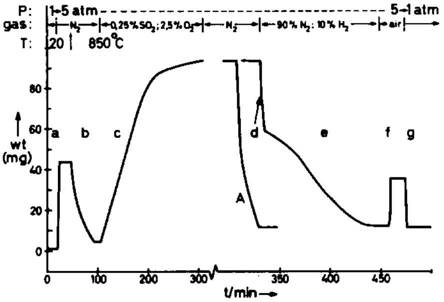


Fig. 1 Diagram of the tubular reactor/thermobalance combination.

TABLE 1. Characteristics of sorbents

			I	II	III
heigt	(mm)	h	2.69	2.82	-
diameter	(mm)	d	2.57	2.49	2.58
weight	(mg/pellet)	W	17.7	16.6	15.5
surface area	m^2/g)	S(BET)	22	137	120
void fraction between the pellets		θ	0.66	0.62	0.57
bed length of 1g sample (mm)		L	112	110	74
pore radius	(nm)	r	43	8.2	5.8



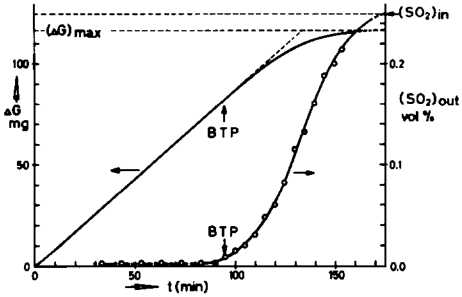


Fig. 2 (left) SRO curve of 759.3 mg of sorbent I, at 850 °C and 5 atm; c sulfation, d and e reduction, f oxidation; A: reduction at 1 atm.

Fig. 3 (right) Sulfation of 968 mg (dry weight) of sorbent I, at 850 °C and 5 atm. Also the calculated SO_2-outlet concentration is shown. Gas flow 100 ml/min (STP), containing 0.25% SO_2 and 2.5% O_2.

RESULTS AND DISCUSSION

The experiments are SRO tests (Sulfation, Regeneration, Oxidation, see [1,3]), performed at several reaction conditions. Fig. 2 shows an example. The most important reactions are:

1 Sulfation $SO_2 + 1/2\ O_2 + CaO.x\ AlO \rightarrow CaSO_4 + x\ Al_2O_3$

2 Reduction $CaSO_4 + H_2 + x\ Al_2O_3 \rightarrow CaO.x\ Al_2O_3 + SO_2 + H_2O$

3 Reduction $CaSO_4 + 4H_2 \rightarrow CaS + 4H_2O$

4 Oxidation $CaS + 2\ O_2 \rightarrow CaSO_4$

5 Oxidation $CaS + x\ Al_2O_3 + 1.5\ O_2 \rightarrow CaO.x\ Al_2O_3 + SO_2$

In the particular experiment of Fig. 2 we used 759.3 mg of sorbent I at 5 atm and 100 ml/min (STP, measured at 1 atm and 0 °C). A number of consecutive weight changes ΔW can be observed, which are the result of changes of temperature, pressure or gas composition:

a	Increase of pressure 1 → 5 atm, 20 °C	$\Delta W(a) = + 42.5$ mg
b	Heating 20 °C → 850 °C	$\Delta W(b) = - 39.1$ mg
c	Sulfation	$\Delta W(c) = + 88.8$ mg
d	and e Reduction	$\Delta W(r) = - 81.8$ mg
f	Oxidation	$\Delta W(f) = + 23.6$ mg
g	Decrease of pressure 5 → 1 atm, 850 °C	$\Delta W(g) = - 24.3$ mg

The SRO-test can be interpreted as follows: the measured weight loss $\Delta W(b)$ is the sum of two effects, evolution of gases from the sorbent $-\Delta W(calc)$- and change of the baseline $\Delta W(x)$, caused by heating from 20 → 850 °C. From the results in a and g the value of $\Delta W(x)$ can be calculated: $\Delta W(x) = -1.25 (\Delta W(a) - \Delta W(x)) = -22.8$ mg. So $\Delta W(calc) = \Delta W(b) - \Delta W(x) = -16.3$ mg, and the dry sample weight is 743 mg, corresponding to a maximum possible weight increase during sulfation of 89.2 mg (calculated from the weight percentage of CaO).

The regeneration capacity is an important aspect of the quality of different sorbents [1,3]. In order to obtain the product distribution after reduction it is necessary to make an assumption about the amount of unreacted $CaSO_4$ or about the ratio of the oxidation reactions 4 and 5. If we assume that in sorbent I, having big pores, no $CaSO_4$ is left after reduction, the product composition can be calculated:

CaO 60.6%; CaS 39.4%; $CaSO_4$ 0%.

Consequently the oxidation of CaS gives 84% $CaSO_4$ and 16% CaO.x Al_2O_3, according to reaction 5. The occurence of this last reaction is confirmed in other reactor experiments by detection of SO_2 in the outlet gas during oxidation.

For sorbents II and III, with smaller pores, the presence of $CaSO_4$ after reduction may not be excluded. Here we assume that the oxidation of CaS gives the same product distribution as with sorbent I. In that case mean values of the product composition after reduction are:

Sorbent I	CaO.x Al_2O_3 61%;	CaS 39%;	$CaSO_4$ 0%
II	76	5	19
III	90	9	1

For the art of desiging an optimum sorbent for regenerative SO_2-absorption in coal combustion it is necessary to relate these differences to the texture and the composition of the different sorbents. A good sorbent gives a high amount of CaO (or CaO.x Al_2O_3) and only little CaS and $CaSO_4$ at reduction.

Thermodynamically the most stable compound at reduction is CaO.x Al_2O_3, followed by CaS and then pure CaO (at the applied conditions). The formation of CaO.x Al_2O_3 is promoted by an intimate contact between $CaSO_4$ and Al_2O_3. This is possible when the calcium compound is spread out in a thin layer over a large surface area of alumina. This is particularly the case for sorbents II and III, having a large surface area compared to sorbent I. Also, the γ-Al_2O_3 of sorbents II and III is more reactive towards formation of CaO.x Al_2O_3, than the α-Al_2O_3 in sorbent I.

For these reasons the reduction products of sorbents II and III contain more CaO.x Al_2O_3 and less CaS than in the case of sorbent I. The differences in the amounts of unreacted $CaSO_4$ after reduction can not be explained at this moment. It may be concluded that sorbent III has the best regeneration behaviour at the applied experimental conditions.

The reduction of sorbent I at 5 atm shows two steps: a fast step (d) and a slow accelerating step (e). This behaviour can also be distinguished at 1 atm. (see Fig. 2 line A), but there the second step proceeds much faster than at higher pressure. Further investigation is necessary for finding an explanation.

Sorbents II and III have only been investigated at 1 atm. Also here we see a first fast weight decrease, followed by a slow one, but now the second part does not accelerate any more.

An important aspect of a sorbent is its rate of sulfation. The sulfation step is shown separately in Fig. 3. In this figure also the SO_2 concentration at the reactor outlet is given, calculated from the rate of weight increase and the inlet conditions. Initially almost 100% of the incoming SO_2 is absorbed, resulting in a very low SO_2-outlet concentration. This concentration increases after the break through point (BTP). The exact value of the BTP can depend on several factors, such as residence time, gascomposition, pore diffusion, chemical surface reactivity and rate of SO_3 formation in the gas phase.

Generally a reactive sorbent has a high BTP and shows a sharp increase of SO_2 concentration after break through.

Results of sulfation experiments are given in Table 2 and Fig. 4. In Table 2 the residence time τ is calculated for every experiment. The value of τ depends on the gas velocity v, inversely proportional to the porosity θ, and the bedlength, proportional to the sample mass. For 1g of sorbent I at 100 ml/min (STP), 1 atm and 850 °C the values are:

$v = 0.529$ m/s and $\tau = L/v = 0.21$ s

Exp	Sorbent	Dry wt.	gasflow	p	SO_2	O_2	BTP		ε	τ
No		mg	ml/min	atm	%	%	mg	%	%	s
a1	I(α-Al_2O_3)	767	100	1	0.25	2.5	31	34	96	0.16
a2	I(α-Al_2O_3)	971	100	1	0.25	2.5	40	35	97	0.21
a3	I(α-Al_2O_3)	1569	100	1	0.25	2.5	91	48	99	0.33
d1	I(α-Al_2O_3)	743	100	5	0.25	2.5	55	62	98	0.79
d2	I(α-Al_2O_3)	968	100	5	0.25	2.5	83	71	99	1.02
d3	I(α-Al_2O_3)	1483	100	5	0.25	2.5	139	78	100	1.57
c	I(α-Al_2O_3)	981	50	1	0.25	2.5	68	58	100	0.42
b	I+Pt metal	980	100	1	0.25	2.5	54	46	99	0.21
e	I+Pt impregn.	980	100	1	0.25	2.5	84	71	100	0.21
f	I (α-Al_2O_3)	1000	100	1	0.5	20	66	55	95	0.21
g	II(γ-Al_2O)	1000	100	1	0.5	20	29	29	95	0.20
h1	III(sol-gel)	1000	100	1	0.5	20	0	0	-	0.12
h2	III(sol-gel)	1500	100	1	0.5	20	27	13	95	0.18

TABLE 2. Sulfation at 850 °C and pressure p, using a gas consisting of SO_2, O_2 and N_2. The break through point (BTP) is given in mg and as percentage of the maximum possible SO_3 load. Further the residence time τ and the efficiency for sulfur capture ε is given, being the relative amount of sulfur that is absorbed before the BTP, compared to the amount of sulfur, fed to the reactor.

From Table 2 and Fig. 4 it follows that for constant experimental conditions of gas flow the BTP increases linearly with the mass of the samples and the residence time, but that the relation between BTP and τ becomes complicated when these conditions are varied. The curves in Fig. 4 represent sorbent I in different conditions. The intersections of the extrapolated straight part of these curves with the horizontal axis give the minimum amount of sorbent for complete removal of all the SO_2 from the gas under a given condition and at the beginning of the experiment. With a lower sample mass the SO_2 concentration at the outlet can never become zero. It is interesting to note the effects of changing the experimental conditions with constant sample weight. Halving the gas flow rate will double the residence time. Such lowering the gas flow rate gives an increase in BTP, but from curves a and c it follows that the incrase is not proportional with the residence time τ. This effect is more pronounced at higher pressures. Increasing the gas pressure from 1 to 5 atm. not only raises the residence time, but also the partial pressures of the reactants. These two conditions combine into a more effective sulfur removal (curve a and d). Here the chemistry in the gas atmosphere enters into the performance of the sorbent. At equilibrium only about 8% of the sulfur is present as SO_3, the remainder as SO_2 (at 1 atm.).

The sulfation of the sorbent is by way of the reaction of SO_3 molecules with Ca-compounds, and this depletes the atmosphere from SO_3. The conversion rate of SO_2 with O_2 into SO_3 can then become rate limiting for the overall process.

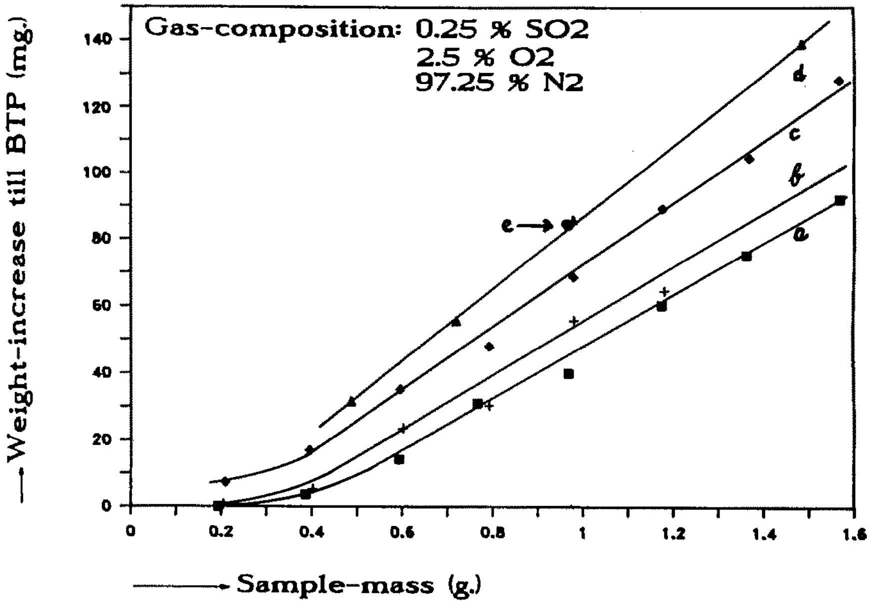


Fig.4 Break through points for the sulfation reaction at 850 °C on sorbent I, at different experimental conditions. a: 100 ml/min (STP) and 1 atm; b: 100 ml/min, 1 atm + Pt gauze between the pellets; c: 50 ml/min, 1 atm; d: 100 ml/min, 5 atm; e: 100 ml/min, 1 atm + Pt impregnated.

That this is indeed the case is shown by the curves a and b and point e of fig. 4, where the reaction conditions were kept equal. In experiment b particles of Pt metal were added to the sample to catalyze the regeneration of SO_3 in the gas atmosphere, giving a slight increase in BTP. This would indeed be expected to be small since the depletion and subsequent regeneration of SO_3 in the pore volume of the sorbent is not affected. But when, as in experiment e, the sorbent was impregnated with 1 $^0/_{00}$ wt of Pt this resulted in a large increase of the BTP, and therefore in the apparent reactivity of the sorbent I. This experiment demonstrates that the depletion of SO_3 inside the pores of the sorbent, rather than the transport of SO_2 and O_2 through the pores, is a rate limiting factor in sulfur absorption from gas atmospheres of this type. With this observation in mind, it is interesting to compare sulfation results with different sorbents (experiments f, g.

h). Sorbent I -without Pt- has a much higher BTP than II and III, which have indeed smaller pore sizes, but also the largest internal surface area. Here the reactivity is smaller than in sorbent I, where we know it is determined by the rate of SO_3 formation. Since this rate is the same under equal experimental conditions we must conclude that in the sorbents with small pores and high surface area it is indeed a limitation of gas transport through the pores which limits the sorption rate, and therefore the apparent sulfation reactivity.

CONCLUSIONS

- The tubular reactor/TG combination is well suitable for study of gas-solid reactions.
- Experimental conditions like gas pressure, velocity and composition can be chosen in better accordance with real technical processes, than should be possible with conventional thermobalances.
- The sulfation reaction of CaO/Al_2O_3 sorbents is rather complicated. Important rate limiting steps are gas phase SO_3 formation and pore diffusion.
- The product composition after reduction is, within the applied conditions, mainly dependent on the properties of the sorbent material.

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