

Thermogravimetric study of regenerable sulphur sorbents for H₂S retention at high temperature

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Abstract

The behaviour of a series of mixed oxides including zinc titanate (ZT), zinc ferrite (ZF) and zinc ferrite doped with copper (ZFC) or titanium (ZFT) oxides as hot-gas desulphurizing sorbents was investigated by thermogravimetric techniques. The stability of sorbents against reduction was strongly affected by the temperature that limits the use of the prepared sorbents > 600°C. Intrinsic rate constants for the reaction between H₂S and the sorbents at 550°C were obtained in a thermal balance. The incorporation of titanium and copper oxides to zinc ferrite improved the sorbent reactivity. Five sulphidation–regeneration cycles were also carried out in order to provide information concerning the durability of sorbents. A loss of sorbent activity with the cycle number due to sintering in regeneration was found for zinc ferrite sorbents but not for titanium-containing sorbents. © 1997 Elsevier Science B.V.

Keywords: Gas desulphurization; H₂S sorbents; Kinetics; Thermal stability

1. Introduction

Coal-gas desulphurization to sufficiently low levels at temperatures > 500°C is now recognized as crucial to efficient and economical coal utilization in the integrated gasification with combined cycle (IGCC) process. The implementation of hot coal-gas desulphurization relies on the development of regenerable sorbent materials that have high sulphur capacity and can efficiently remove H₂S (from several thousands levels to a few ppm) over many cycles of sulphidation–regeneration.

The sorbents are solid mixtures of metal oxides such as zinc ferrite (ZnFe₂O₄), CuO–Fe₂O₃, MnO–

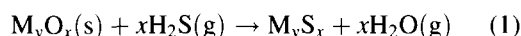
CuO and Fe₂O₃–MoO₃ [1] or mixtures of an inert oxide with a solid reactant like zinc titanates [2], FeO–Al₂O₃ and MnO–Al₂O₃ [3,4]. A mixture of two reactive metal oxides acts as follows: the one metal oxide (e.g. Fe₂O₃, MnO) has large desulphurization capacity expressed as kilogram of sulphur absorbed per kilogram of metal oxide and the other has high affinity for desulphurization (e.g. ZnO, CuO). The combination of these two chemical compounds is expected to lead to enhanced sorbent performance during sulphidation [5].

When sorbents containing iron, copper and zinc oxides are used, reduction to lower oxidation states proceeds simultaneously with sulphidation, thus complicating the kinetics and the equilibria of the reaction. Since sulphidation becomes less favourable with

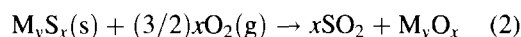
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decreasing oxidation state, the outlet H₂S level increases once the higher oxide is reduced to a lower oxide or the element. Zinc-based sorbents are potentially attractive for high-temperature applications because of their favourable thermochemical properties and despite the reduction to zinc element and subsequent vaporization at temperatures > 600°C [6]. The addition of an inert solid in a metal oxide sorbent is expected to stabilize the metal oxide against its reduction to the metal form [7]. The inert solid can also be used as a porous solid carrier where another metal oxide is impregnated [8].

The basic reaction occurring during desulphurization of the hot coal gas is the noncatalytic gas–solid reaction between H₂S and the reactive metal oxide:



where M_yO_x and M_yS_x are the metal oxide and metal sulphide, respectively. The sorbent is generally regenerated through reaction with oxygen:



In this paper, four different sorbents were prepared and studied by means of the thermogravimetric technique. Reduction and sulphidation tests of the sorbents were carried out in order to determine their stability against the reductor coal gas and their reactivity in the sulphidation process. In addition, a series of multi-cycle runs, consisting of five sulphidation–regeneration cycles, were also conducted to gather information on long-term performance of the sorbents.

2. Experimental

2.1. Sorbent preparation

Four zinc-based mixed oxides, whose stoichiometric molar ratios showed the best behaviour in

previous studies [9,10], were selected for this study. All samples were prepared from commercial oxides (Merck, reagent grade) as powders of particle size < 1 μm by calcination at 650°C for 16 h and then ground to a particle size of 50 μm. The N₂ isotherms were measured at 77 K using Micromeritics ASAP-2000 equipment. Pore-volume distributions were obtained by Hg intrusion with a Micromeritics pore sizer 9310 instrument up to a final pressure of 2.1 × 10⁷ Pa, which allowed filling of pores down to 3 nm diameter. Table 1 shows the textural properties of the four sorbents used.

2.2. TG measurements

The study of sorbent reactivity via thermogravimetric analysis (TGA) has been carried out by other investigators [11]. This TGA testing is divided into three sections: the first is the study of the sorbent reduction (TPR), the second a comparative study for the sulphidation, and the third focuses on regeneration and repeated cyclic sulphidation and regeneration.

The TG apparatus used in this study was a Setaram TA92 thermogravimetric analyser (TGA) interfaced through an analogue-to-digital converter to a computer which measured the sample weight continuously.

2.2.1. Temperature-programmed reduction (TPR)

The stability of sorbents against reduction by the gas stream coming from coal gasification is a useful property because sorbent layers placed at the top of a fixed bed reactor are initially subjected to the strong reducing action of gases previously cleaned by layers placed at the bottom. In order to evaluate the sorbent behaviour in a reductive atmosphere as a function of temperature, temperature-programmed reduction (TPR) tests were carried out. Tests were conducted in a thermal balance CAHN 2000 with a gaseous

Table 1
Sorbent formulations and textural characterization

Sample	Initial oxides	Stoichiometry	V _p ml g ⁻¹	D _p nm	e _p %	α m ² g ⁻¹
ZF	ZnO, Fe ₂ O ₃	1 : 1	0.60	99	0.62	11.0
ZFT	ZnO, Fe ₂ O ₃ , TiO ₂	1 : 0.5 : 0.5	0.30	204	0.47	5.90
ZFC	ZnO, Fe ₂ O ₃ , CuO	0.86 : 1 : 0.14	0.36	55	0.56	25.9
ZT	ZnO, TiO ₂	0.8 : 1	0.42	179	0.48	9.40

mixture consisting of 25% H₂ in He, a flow rate of 50 cm³ min⁻¹ and a heating rate of 5°C/min.

2.2.2. Consecutive reduction–sulphidation

In any application of these sorbents for the removal of H₂S from a fuel gas, reduction and sulphidation occur simultaneously as in the experiments described by other authors [12]. For the purpose of estimating the reactivity of different phases and measuring reaction rates, however, it is useful to separate the two reactions [13].

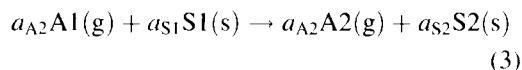
In order to obtain correct results, the thermobalance must behave like a differential reactor, therefore, gas conversion must be low (< 5%). In addition, gas diffusion into the sample must be avoided in order to obtain effective differential boundary conditions. In this sense, some preliminary experiments were carried out using different sample weights and sizes, and gas flow rates in order to determine the conditions that minimized the effect of gas diffusion into the sample.

To reduce a possible mass-transfer resistance around the sorbent sample, 10 mg of sorbent and a flow rate of 200 ml/min were used. On the other hand, to reduce the internal diffusion, a particle size of less than 50 μm was used.

The sample was brought from room temperature to the selected reaction temperature using a constant heating rate of 20°C min⁻¹. In order to protect the weighing unit from corrosion, pure N₂ was fed through this part at a flow rate of 100 ml min⁻¹.

When the selected temperature was reached, a gaseous mixture consisting of 10% H₂ in N₂ was fed continuously for ca. 6000 s with a total flow rate of 200 ml min⁻¹, under isothermal conditions. Then the H₂-pretreated sorbent was exposed to a gaseous mixture containing 0.5% H₂S in N₂ at the same temperature and flow rate. Gas flows were set by mass flow controllers (Brooks).

The chemical reaction studied may be represented by the general stoichiometric equation:



where a_A and a_S are the stoichiometric coefficients for gaseous and solid species.

In the absence of both diffusional and mass-transfer resistances, which is our case, the initial molar reac-

tion rate is only due to the kinetic reaction and can be expressed in the form:

$$R_0 = a_{A1}k_S C_{S10} C_{A10}^N \quad (4)$$

Experimentally [15], conversion of metal oxide to metal sulphide produces an increase in mass which is directly proportional to the fractional conversion of the oxide. Consequently, the variation of weight with time is directly proportional to the initial molar reaction rate, R_0 . This may be calculated from the measured slope of the thermobalance response curve by the following equation:

$$R_0 = \frac{(a_{A1}/a_{S1})(dW/dt)_0}{m_0 \alpha_0 (M_{S1} + (a_{S2}/a_{S1})M_{S2})} \quad (5)$$

N is the order of reaction with respect to A1. In a previous work [14], it was found that the reaction is of the first order with respect to H₂S in these reaction conditions and, thus, N is one in Eq. (5).

2.2.3. Multicycle tests

Commercial interest in any sorbents is determined not only on the basis of its behaviour during sulphidation but also upon its regeneration characteristics and durability through a number of sulphidation–regeneration cycles. Thus, in order to complete this thermogravimetric study, five cycles were carried out to provide initial information concerning the durability of the sorbents.

Regeneration was carried out with an oxygen/nitrogen mixture. Because regeneration is a highly exothermic reaction, only low oxygen concentrations need be used to prevent overheating and consequent sintering and deterioration of sorbent reactivity. The lower temperature limit of regeneration is related to the avoidance of sulphate formation. Therefore, it is necessary that sorbent material be able to withstand temperatures > 700°C without closure of pores.

The operation conditions were set equal to those used by other authors [16]. The sample was heated to 600°C using a constant heating rate of 20°C min⁻¹. When this temperature was reached, a gaseous mixture composed of 0.5% H₂S, 10% H₂ balanced with N₂ was fed continuously for 8000 s with a flow rate of 200 ml min⁻¹. Beyond this time, the sulphidation was over and the temperature was brought to the regeneration temperature (760°C). When the thermobalance

furnace was heated to this temperature, the sulphidation gas was changed to 200 ml min⁻¹ of a gas containing 3% O₂ in N₂ that was fed for 4000 s. Thereafter, the temperature was allowed to decrease and another cycle started.

3. Results and discussion

3.1. Temperature-programmed reduction

The stability of the prepared sorbents was studied through TPR curves. With the objective of understanding the behaviour against reduction of the mixed oxides in a TPR test, TPR curves of the initial oxides were obtained previously (Fig. 1). CuO suffers a 10% weight loss at 170°C due to the reduction to Cu₂O. The reduction to Cu is not observed in the temperature range of study. ZnO undergoes a 100% weight loss at 680°C, produced by the reduction to Zn and the subsequent evaporation. Finally, Fe₂O₃ experiences a 30% weight loss at 450°C due to reduction to Fe.

Fig. 2 illustrates the TPR curves for the mixed oxides. The TPR curves of the sorbents can differ from the simple oxides depending on whether the crystalline phase has been formed after calcination or not. For zinc ferrite (ZF) sorbent, the curve shows two steps corresponding to the reduction of Fe₂O₃ and ZnO, respectively. This behaviour is similar to the reduction of simple oxides showing that, in a reducing atmosphere, zinc ferrite breaks down into its components and these are reduced independently. These results are consistent with those observed by other authors [6]. For the titanium-containing zinc ferrite sorbent (ZFT) the TPR curves also show the behaviour

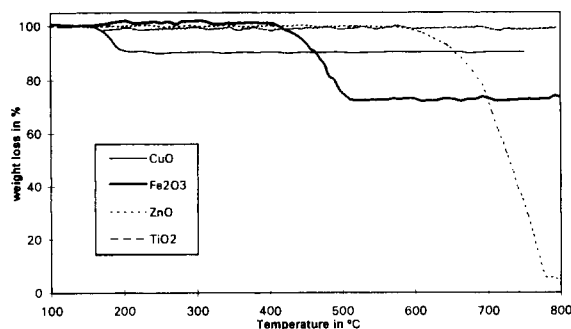


Fig. 1. TPR curves of the starting oxides.

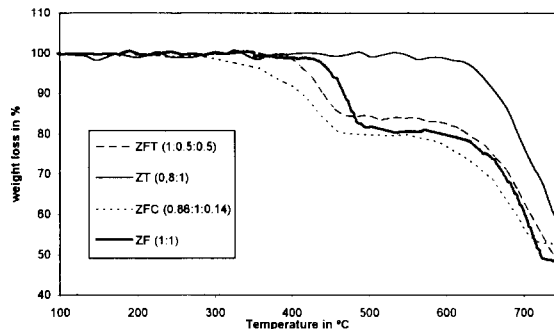


Fig. 2. TPR curves for mixed oxides: ZF (1:1); ZFT (1:0.5:0.5); ZT (0.8:1); and ZFC (0.86:1:0.14).

expected for a mechanical mixture of the single oxides with reduction temperature of 420°C for Fe₂O₃ and 650°C for ZnO. However, for the zinc titanate (ZT) sorbent, the incorporation of titanium produces a slight stabilization of the ZnO increasing the reduction temperature from 670° to 700°C. For copper-containing zinc ferrite (ZFC) sorbent, three reduction steps at 160°C (very small, reduction of CuO to Cu), 410°C (reduction of Fe₂O₃ to Fe) and 650°C (reduction of ZnO to Zn and, subsequent, volatilization) can be observed. Consequently, the presence of Cu does not seem to alter the stability of zinc ferrite.

3.2. Consecutive reduction–sulphidation

Fig. 3 shows the curves at three different temperatures for the ZFT (1:0.5:0.5) sorbent. It can be observed in the reduction step that the curves have two zones of different slope associated with two processes. The first slope, which is associated with

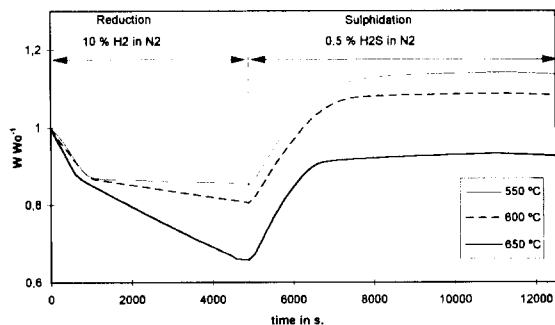


Fig. 3. Reduction and subsequent sulphidation at different temperatures for the ZFT (1:0.5:0.5) sorbent.

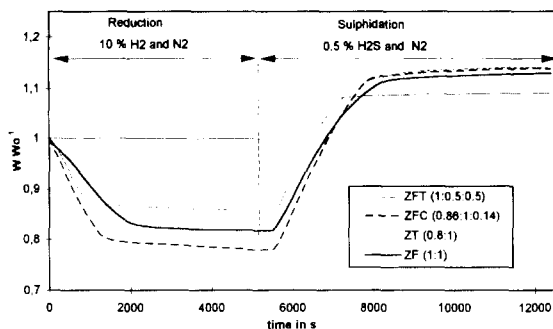


Fig. 4. Reduction and subsequent sulphidation for the sorbents.

the reduction of Fe_2O_3 , is more slanting than the second one, which is associated with the reduction and volatilization of zinc. The weight-loss drop is steeper and the overall extent of the sulphidation reaction is lower for the run at 650°C , since the volatilization of zinc is higher at this temperature in accordance with the TPR experiments. Thus, a temperature of 550°C was chosen for comparing the reactivity of the sorbents because the reduction and volatilization of zinc is negligible at this temperature. The comparative experimental results in the form of W/W_0 vs. time have been plotted in Fig. 4.

In the reduction phase, all the sorbents show a weight loss except the ZT sorbent which does not undergo any reduction at this temperature. The percentage of weight loss in each sorbent corresponds to the reduction of Fe_2O_3 to FeO . This reduction is higher for the ZF (1 : 1) and ZFC (0.86 : 1 : 0.14) sorbents with 18.3 and 22% weight loss, respectively, than for the ZFT (1 : 0.5 : 0.5) sorbent with 14.6%. This fact can be explained easily because ZFT sorbent has a lower percentage of Fe_2O_3 in the starting sorbent. ZFC and ZF have the same Fe_2O_3 percentage but the loss weight is higher for ZFC sorbent since CuO is also reduced.

Sulphidation behaviour of all sorbents is quite similar. All the sorbents containing Fe_2O_3 have a final weight gain of around 13%. However, for the ZT sorbent the extent of reaction is lower due to the inert. As shown in Fig. 4, the sulphidation curves were characterized by an initial linear increase in mass as a function of time (neglecting the transient period where reactive gases were initially introduced). As time and fractional weight increase, the slope of the response curve decreases and asymptotically approaches zero. The decreasing slope may be attributed to a combination of decreasing reactant surface area and an increasing diffusional resistance through a product layer of increasing thickness. Thus, a measure of the reactivity of the sorbents is the initial rate of change in weight $(dW/dt)_0$ since, in the first stages of reaction, the product layer diffusion is considered unimportant [15].

The $(dW/dt)_0$ values, which are summarized in Table 2, show the velocity of H_2S retention on the basis of the weight gain due to the change of the metal oxide to metal sulphide. These values have been calculated from the slope of the curves in Fig. 4 multiplied by the initial weight. In order to calculate the slope, the initial linear increase in mass which corresponds to the first 600 s was considered, without taking into account the first 150 s of non-linearity produced by the introduction of reactive gas. The initial weight-change rate values of the ZFC sorbent are the fastest followed very closely by the ZFT sorbent. In sulphidation, the sorbent ZT has a $(dW/dt)_0$ value of an order of magnitude less than the other sorbents.

The sorbent with a higher value of R_0 and k_s is the ZFT sorbent. The initial intrinsic rate constants (calculated) follow the trend: ZFT > ZFC > ZF > ZT. Both R_0 and k_s are independent of the surface area of the sorbent. Thus, increase in surface area will imply the same increase in the initial weight-

Table 2
Initial rate of change of weight in the sulfuration of mixed oxides

Sample	Stoichiometry	$(dW/dt)_{t=0}$ $\text{mg s}^{-1} \times 10^{-4}$	R_0 $\text{mg mol s}^{-1} \text{cm}^{-2} \times 10^{-8}$	k_s $\text{cm}^4 \text{s}^{-1} \text{mg mol}^{-1} \times 10^{-5}$
ZF	1 : 1	15.07	9.93	8.37
ZFT	1 : 0.5 : 0.5	21.78	18.20	44.30
ZFC	0.86 : 1 : 0.14	22.90	4.98	10.50
ZT	0.8 : 1	3.47	1.97	2.98

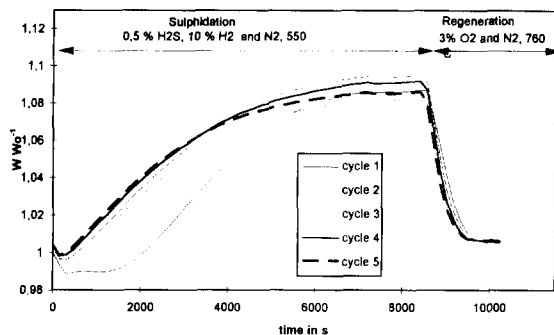


Fig. 5. Five cycles of sulphidation–regeneration for ZFT (1 : 0.5 : 0.5) sorbent.

change rate to hold R_0 constant in Eq. (5). This suggests that the kinetic behaviour of sorbents can be improved by preparing sorbents with higher surface area.

3.3. Multicycle tests

Figs. 5–8 show the curves for five cycles of sulphidation–regeneration of the sorbents. The regeneration of all the samples is complete on reaching their starting weight in a short time. Therefore, in the experimental conditions, there is neither loss of zinc by volatilization nor zinc sulfate formation (this fact was corroborated by IR spectroscopy and elemental sulphur analysis). The behaviour of the sorbents in every cycle is quite similar, which points to the feasibility of the utilization of these materials in multicycle runs.

In general, all iron-containing sorbents show a greater reduction in the first cycle than in the following

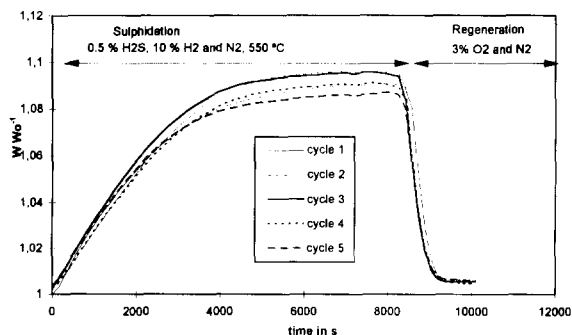


Fig. 6. Five cycles of sulphidation–regeneration for ZT (0.8 : 1) sorbent.

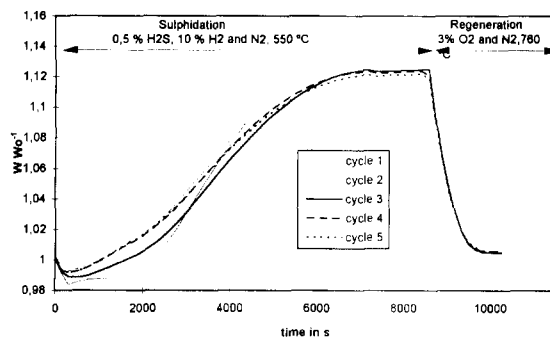


Fig. 7. Five cycles of sulphidation–regeneration for ZF (1 : 1) sorbent.

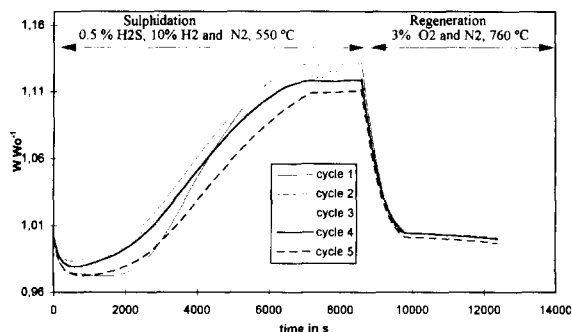


Fig. 8. Five cycles of sulphidation–regeneration for ZFC (0.86 : 1 : 0.14) sorbent.

ones. This fact could, probably, be due to the sintering and formation, in the regeneration step, of a mixed oxide less reducible than the fresh sorbent since the regeneration temperature (760°C) is higher than the calcination temperature of the fresh sorbent (650°C). This effect is more pronounced for the ZFT sorbent, thus suggesting the formation of zinc titanate in the regeneration step. A recent characterization of this sorbent by XRD, FT-Raman and XPS techniques [18] has proved the formation of a spinel structure phase of $ZnFeTiO_4$ at temperatures $> 950^\circ\text{C}$.

From Figs. 5–8, it is possible to obtain the sulphur loading (g of S/100 g of sorbent) which is represented as a function of the cycle number in the Fig. 9. In sorbents without titanium dioxide (ZF, ZFC), a slight trend towards decrease in the sulphur loading with the number of cycles can be observed. In ZT sorbent, the first cycle shows a lower sulphur loading value than the second cycle. However, in the following cycles, the same decreasing trend as in the other sorbents is

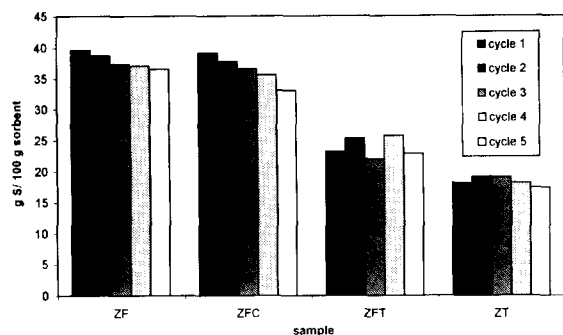


Fig. 9. Sulphur loading (g S/100 g sorbent) as function of the cycle number for the sorbents.

observed. ZFT sorbent has oscillations of the sulphur loading with the cycle number. The anomalous behaviour of ZT and ZFT sorbents can be explained on the ground that the mixed oxide (zinc titanate) is not formed in the fresh sorbent due to the low temperature of calcination (650°C) [18].

The trend shown by ZF and ZFC sorbents may be attributed to the sintering of the sorbent in the regeneration that produces a reduction in surface area and, therefore, a reduction in the activity of the sorbent. Experimentally, it was found [17] that the sintering velocity of a metal oxide that is exposed to high temperatures can be described by the following equation:

$$\alpha(t) = \alpha_0 e^{-kt} \quad (6)$$

where $\alpha(t)$ is the specific surface area of the sintered solid as a function of time, k a temperature-dependent constant which is determined experimentally, and α_0 a constant that is related to the initial surface area. Since the surface area is directly proportional to the sulphur loading of the sorbent and the time is proportional to the cycle number, Eq. (6) can acquire the form:

$$L(c) = L_0 e^{-k'c} \quad (7)$$

where c is the cycle number, $L(c)$ the sulphur loading reached in the cycle c and, L_0 and k' constants determined experimentally. The values of $L(c)$ obtained for sorbents without titanium dioxide (ZF and ZFC) adequately fit to Eq. (7). The values of the constants, calculated for linear regression, are summarized in Table 3.

The ZFC sorbent suffers the greatest loss of activity in the five cycles (15%). Assuming that the Eq. (7) is

Table 3
Parameters of the Eq. (7)

Sample	k'	L_0	R
ZF	0.0205	40,23	0.97
ZFC	0.0394	40,89	0.98

valid for a higher value of the cycle number (that has to be verified), we may expect that ZFC sorbent would have reduced its activity to 50% in cycle 18. Thus, ZFC sorbent would be unsuitable for commercial use.

4. Conclusions

The results presented here show that thermogravimetric analysis is a useful technique for determining the feasibility of mixed oxides as H_2S regenerable sorbents at high temperatures. In the reducing atmosphere of a gas from coal gasification, operational temperatures must be selected to avoid reduction of ZnO and subsequent volatilization of zinc. Intrinsic rate constants for the reaction between H_2S and the prepared sorbents were obtained. All the sorbents showed favourable properties from the viewpoint of kinetics, and the relative magnitude of the intrinsic rate constants followed the order: ZFT > ZFC > ZF > ZT.

The sulphur loading can also be used as a measure of the sorbent reactivity in sulphidation. In the cyclic sulphidation/regeneration tests, ZF and ZFC sorbents showed a decreasing sulphur loading as function of the cycle number. The loss of activity in these sorbents without titanium may be attributed to sintering in the regeneration process. These sorbents would be unsuitable for commercial use, since their activity is reduced to low levels in a short number of cycles. Titanium-containing sorbents showed a better behaviour, but additional work on long-term testing of these sorbents is needed in order to prove their commercial feasibility for hot-gas desulphurization.

5. List of symbols

C_{S10} initial molar concentration of solid species S1 ($mg \text{ mol cm}^{-3}$)

C_{A10}	bulk fluid concentration of gas species A1 (mg mol cm^{-3})
D_p	pore diameter (nm)
e_p	particle porosity (%)
k_s	intrinsic rate constant ($\text{cm}^4 \text{s}^{-1} \text{mg mol}^{-1}$)
L	sulphur loading $\text{gS}/100 \text{g sorbent}$
M	molecular weights of solid
m_0	initial mass of solid reactant (g)
R	regression coefficient
R_0	initial molar rate of reaction of gas species A1 per unit surface area of solid species S1 ($\text{mg mol s}^{-1} \text{cm}^{-2}$)
t	time
V_p	pore volume (ml g^{-1})
$(dW/dt)_0$	initial rate of change in weight (mg s^{-1})
α_0	initial specific surface area of solid reactant ($\text{m}^2 \text{g}^{-1}$)

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