THE REDUCTIVE DECOMPOSITION OF CALCIUM SULPHATE—I. KINETICS OF THE APPARENT SOLID–SOLID REACTION

B. KAMPHUIS, A. W. POTMA, W. PRINS[†] and W. P. M. VAN SWAAIJ

Faculty of Chemical Engineering, University of Twente, PO Box 217, 7500 AE Enschede, The Netherlands

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Abstract—The reductive decomposition of calcium sulphate by hydrogen is used for the regeneration of calcium-based atmospheric fluidized bed combustion (AFBC) SO₂ sorbents. The apparent solid–solid reaction between CaS and CaSO₄, one of the steps involved in the reaction mechanism of the reductive decomposition of CaSO₄, has been investigated in a thermobalance construction provided with a coupled system for the analysis of product gases. By creating suitable reaction conditions in the experimental set-up, it is possible to study this step separately. The apparent solid–solid reaction between CaS and CaSO₄ takes place when a mixture of these compounds is heated in an inert atmosphere to temperatures above 1100 K:

The fractional production rate of CaO (or SO₂) appears to depend on the ratio in which CaSO₄ and CaS are present initially. A simple model is formulated to calculate the fractional production rate as a function of the fractional degree of production and the initial composition of the reactants. One of the principal assumptions of the model is the presence of a liquid phase formed by mixtures of CaS and CaSO₄. Fractional production rates calculated after determining the required model parameters (kinetic constants and volume plus composition of the liquid phase) show close agreement with experimentally obtained values.

1. INTRODUCTION

For the past five years regenerative flue gas desulphurization processes have attracted renewed interest in Europe. Introduction of SO₂ control in the case of atmospheric fluidized-bed combustion (AFBC) by *in situ* desulphurization with limestone has increased the quantity of waste material to be managed. Uncertainty over the actual waste composition exists, especially with respect to the presence of unhydrated calcium oxide and heavy metals. This makes AFBC waste streams quite unpopular.

Regeneration of spent sulphated sorbent and sales of sulphur by-products reduces considerably the amount of waste and related costs. The decomposition of CaSO₄ in a reductive atmosphere is used for the regeneration of spent sorbent:

This reaction takes place at relatively high temperatures, above 1300 K. However, at somewhat lower temperatures (1150 K), the main product formed is CaS rather than CaO, viz. according to reaction (2):

The production of CaS decreases the efficiency of the regenerative process and increases the consumption of reducing agent.

Another possible reaction, which is known to take place simultaneously under the conditions mentioned

above, is the apparent solid–solid reaction between CaSO₄ and CaS:

Thermodynamic calculations do not exclude any of these reactions. Knowledge of the mechanism and kinetics of reactions (1)–(3a) will contribute to the assessment of optimal regeneration conditions (Kamphuis *et al.*, 1989) and is also relevant for control of *in situ* SO₂ removal in AFBC. Recently, the reductive decomposition of calcium sulphate was related to insufficient SO₂ capture occurring in fluidized-bed boilers (Lyngfelt and Leckner, 1989). The observed re-emission of SO₂ has been explained by the reaction of CaSO₄ with combustion intermediates (CO and H₂) in the dense phase of the bed.

In this paper, the apparent solid–solid reaction between CaS and CaSO₄ [reaction (3)] is considered to be one of the rate-determining steps taking place during the regenerative decomposition of CaSO₄. It has been studied separately by heating mixtures of calcium sulphate and calcium sulphide to temperatures above approximately 1100 K. A proper description of the kinetics of this step is necessary for understanding the overall reductive decomposition reaction of CaSO₄ and for selecting the optimal process conditions for sorbent regeneration.

Determination of the kinetics of the apparent solid–solid reaction is complicated by the influence of composition changes in the solid phase during reaction. Therefore, in this study a kinetic model for reaction (3) is proposed and used to interpret the experimental data. The model is based on the assumption

[†]Author to whom correspondence should be addressed.

tion that the apparent solid–solid reaction between CaS and CaSO₄ proceeds in a liquid phase. The kinetic constants of this reaction will be evaluated using the model. In addition, this kinetic model can be used in the evaluation of other reaction steps involved with the reductive decomposition of CaSO₄, as well as in the development of a single-particle model for sorbent regeneration, which accounts for simultaneous reactions and transport phenomena. These are the subjects of separate studies to be published soon.

2. PREVIOUS WORK

The reactions involved in the reductive decomposition of calcium sulphate have been studied from the beginning of the 20th century. During the last two decades in particular, some disagreement has arisen concerning the precise mechanism of the reaction. Examining the various interpretations of the observed phenomena, two “schools” can now be distinguished. The first type of interpretation is based on the involvement of a gaseous intermediate component (i.e. sulphur trioxide); the second suggests the presence of a liquid phase. The arguments used by both schools will be discussed in this section.

For the temperature range of 1223–1473 K, Chen and Yang (1979), Yang and Shen (1979), Ruth (1975) and Kikuchi *et al.* (1983) have proposed a two-step reaction scheme with respect to the reductive decomposition of CaSO₄, involving a gaseous intermediate in the second step:

The second step would be the apparent solid–solid reaction between CaSO₄ and CaS, the reaction presently being studied:

The presence of a gaseous intermediate, viz. sulphur trioxide, was supposed to be essential for reaction (3a):

The rate-controlling step in this proposed reaction scheme for the apparent solid–solid reaction, particularly at relatively low temperatures, would be the decomposition of CaSO₄ according to reaction (3b). In the other intermediate step [reaction (3c)] the CaS is “oxidized” by the SO₃ to form CaO and SO₂. Chen and Yang (1979) and Kikuchi *et al.* (1983) concluded the presence of this reaction mechanism on the basis of thermobalance experiments for mixtures of pure CaSO₄ and pure CaS in different weight ratios at 1273 K. Variation of the CaSO₄/CaS weight ratio implies a variation of the mole fraction CaSO₄ initially present. In the experiments of Chen and Yang, this initial CaSO₄ mole fraction has been varied in this way from 0.43 to 0.75, and in Kikuchi *et al.*'s experiments from 0.42 to 0.92. The weight change per unit time was used directly as a measure of the reac-

tion rate. Neither Chen and Yang nor Kikuchi *et al.* observed any influence on this reaction rate resulting from changes in the amount of CaS in the solids mixture. But increases in the amount of CaSO₄ caused the reaction rate to increase proportionally. Some critical remarks on the evaluation of these experiments can be made. With the definition used by Chen and Yang and Kikuchi *et al.*, the reaction rate expression will have an extensive form. In fact it depends on the total amount of reactants present; deviations from the stoichiometric optimal proportions of the reactants will influence the value of the reaction rate. It is, therefore, inappropriate to compare these reaction rate values for different CaSO₄/CaS weight ratios, if the maximum amount that can be converted is not kept constant. For example, increasing the amount of CaS, while CaSO₄ is present in excess, would increase the amount of SO₂ released per unit time by definition. Later in this study, reinterpretations of these authors' results, in which the reaction rate is correctly based on the total amount of reactants that can be converted according to the stoichiometry of reaction (3c), will be included in the discussion.

The assumed role of SO₃ seemed to be supported by Yang and Shen's (1979) experiments in a thermobalance using a cylindrical pellet of CaS (1.3 cm in diameter) placed separately above a similar pellet of CaSO₄. An upward flow of inert gas was maintained. A small decrease in weight (< 4% in 120 min) was indeed observed during these experiments, which has been explained by assuming SO₃ release from the CaSO₄ pellet [reaction (3b)] and the subsequent reaction of SO₃ with the CaS [reaction (3c)]. However, the weight loss was so small that an alternative explanation may be provided. First, it should be noticed that the larger part of the weight decrease was observed just after the beginning of the reaction. A second observation from Yang and Shen's study is that the resulting reaction rate for the apparent solid–solid reaction in the set-up of two pellets is very much (orders of magnitude) lower than measured for powder mixtures of CaSO₄ and CaS under the same experimental conditions [see Chen and Yang (1979) or Kamphuis *et al.* (1991)]. With these two considerations in mind, the possibility cannot be excluded that the observed small weight decrease is only the result of thermal decomposition of a small amount of CaSO₄ initially present in the CaS pellet.

Considering Yang and Shen's (1979) results, it should also be noted that the occurrence of SO₃ as a decomposition product of CaSO₄ is not very likely at temperatures above 1140 K. Lou *et al.* (1977) carried out effusion studies for the thermal decomposition of MgSO₄ and CaSO₄. They found that, in the case of CaSO₄, SO₂ and O₂ are the only gaseous products liberated. Only with MgSO₄ could the formation of SO₃ be demonstrated clearly.

An alternative mechanism for the apparent solid–solid reaction (3) to be presented here is based

on the work by Kostylkov and Nosov (1982). They suggested that, below 1173 K, CaSO_4 is reduced to CaS [reaction (2)] through an intermediate liquid phase. In the case of the apparent solid–solid reaction (3), both CaS and CaSO_4 are present as well and, therefore, the liquid phase may also be involved here. The occurrence of a CaSO_4/CaS eutectic has been reported by Zinzen (1944) at temperatures above 1103 K. Its formation appears to be strongly dependent on the presence of impurities, such as metal oxides. Additionally, the formation of a transient liquid phase was observed by Curren *et al.* (1969), viz. in a bench-scale set-up of the calcium sulphate regeneration process during the course of the reaction between CaS and CaSO_4 .

In an earlier paper by Kamphuis *et al.* (1989) it has already been concluded from experimental evidence that a CaS/CaSO_4 liquid phase could be involved in the reaction between CaS and CaSO_4 . This conclusion was derived from results of an experimental study of the thermal decomposition of CaSO_4 [reaction (3b)], which would be the rate-controlling step in the proposed (Chen and Yang, 1979; Yang and Shen, 1979; Ruth, 1975; Kikuchi *et al.*, 1982) reaction mechanism with a gaseous intermediate. The decomposition experiments were carried out in a TGA set-up fed by nitrogen gas, at a range of temperatures, and including the temperature regime of the present investigation. The mere fact that the rate of the thermal decomposition of CaSO_4 appeared to be so much lower than the measured reaction rate of the apparent solid–solid reaction at the same temperature (Kamphuis *et al.*, 1989), is sufficient to reject the possibility of SO_3 being a gaseous intermediate in the apparent solid–solid reaction (3). On the other hand, a direct solid–solid reaction is unlikely as well. The reaction rate of a true solid–solid reaction would be governed by solids diffusion. Various authors [see e.g. Budnikov and Ginstling (1968)] argue that the reaction rate of a true solid–solid reaction between CaS and CaSO_4 is much lower than the actually measured reaction rate values, considering the estimated values of the diffusion fluxes of the reactants.

Because neither a gaseous intermediate nor a true solid–solid reaction can explain all the observations, and because of the possible occurrence of an eutectic, the liquid-phase reaction seems likely. Reaction (3a) may only be an *apparent* solid–solid reaction. It is known that many melts are often completely ionized (Charlot and Trémillon, 1969). Therefore, the liquid phase, formed by CaS and CaSO_4 , will probably be made up of ions rather than molecules. The oxidation–reduction reaction will then occur between the SO_3^{2-} and S^{2-} anions; during this reaction the oxidation state of sulphur is changed from -2 (in the S^{2-} anion) and $+6$ (in the SO_4^{2-} anion) to $+4$ (in the SO_2 molecule). This reaction has already been studied in aqueous solutions and it was observed that concentrated sulphuric acid, when warmed, decomposes to sulphide, while liberating gaseous sulphur dioxide

(Mellor, 1930). A reaction mechanism in aqueous solutions, in which intermediate thiosulphate is involved, has been proposed by Hiroshi and Lasaga (1982).

3. EXPERIMENTAL CONDITIONS AND METHOD OF DATA EVALUATION

The apparent solid–solid reaction between CaS and CaSO_4 was studied by thermogravimetric analysis (thermobalance: Seteram, TG 85) while simultaneously measuring the SO_2 concentration in the outlet gas (continuous infrared SO_2 gas analyser: Maihak Defor). During the time the reaction was in progress, a computer sampled weight and gas composition data every 10 s.

To eliminate the cross-sensitivity of the SO_2 analyser with respect to H_2O , the outlet gases passed through a drying column filled with P_2O_5 pellets. Separate tests have shown that the reaction of SO_2 with these pellets can be excluded. A special problem arises at temperatures above 1223 K if hydrogen is also present in the outlet gas. A certain amount of SO_2 is then converted to H_2S , which is not detected by the analysis system. The correction factor for this effect was established by a series of tests with different, but known SO_2 concentrations in a H_2/N_2 gas mixture passing through the thermobalance without a sample present. At the highest temperatures and hydrogen concentrations applied in the experiments, the value of this correction factor could rise to 1.32. Usually, however, the required correction was much less.

The experimental procedure was simply to heat the thermobalance sample to the desired temperature while passing an inert gas flow through it. Three types of starting material were used. For two sample types, the CaSO_4 in the sample had been partially reduced to CaS by reaction (2) in a preceding step:

- Partially reduced sulphated sorbent, *DUWA pearl 95*: The mole fraction CaO converted to CaSO_4 was 0.67 (determined by X-ray fluorescence). A sieve fraction of particle diameters ranging from 0.60 to 0.85 mm was used. In a preceding sample treatment, reduction was carried out with 5 (vol) % H_2 at 1123 K. At this relatively low temperature only CaS is formed; SO_2 could hardly be detected in the off-gas. Different CaSO_4 mole fractions were obtained by varying the reduction time from 8 to 15 min. The fraction CaS formed can be calculated from weight losses. The values obtained for the initial CaSO_4 mole fractions [$\text{CaSO}_4/(\text{CaSO}_4 + \text{CaS})$] vary between 0.19 and 0.93. Obviously, there was always a certain amount of CaO still present in the sample.
- Partially reduced CaSO_4 powder: Reduction in the preceding treatment of the sample was carried out with 5 (vol) % H_2 in N_2 at 1123 K, to

achieve an initial CaSO_4 mole fraction of about 0.75. Again, hardly any SO_2 was liberated during reduction, indicating that only CaS and no CaO was formed. The original material was anhydrous calcium sulfate powder: "Janssen" cat. no. 21.752.24, particle size $< 75 \mu\text{m}$.

- Mixtures of CaSO_4 and CaS powder of high purity; CaSO_4 : Janssen, particle size $< 75 \mu\text{m}$; CaS : "CERAC Pure", particle size $< 45 \mu\text{m}$. Different CaSO_4 mole fractions were obtained simply by varying the weight ratio of the solids mixture.

For the study of the apparent solid-solid reaction, only nitrogen or a nitrogen-sulphur dioxide mixture was passed along the solid sample. The initial weight of the sample was always about 15 mg, the superficial gas velocity approximately 0.17 m/s and the applied pressure 1 bar. Experiments were carried out at different temperatures between 1100 and 1400 K. (The lowest temperature at which a weight change due to reaction could be observed was 1098 K.) In a series of separate experiments, the rate of mass transfer from the sample basket to the gas phase was determined by the naphthalene evaporation method. Because the measured transfer rate exceeded the reaction rates measured in this study, effects of mass transfer limitation can be neglected.

In this paper the concept of fractional production rate (R_f) is used to evaluate the experimental data. This fractional production rate is similar to a fractional conversion rate, but it is based on the amounts of product formed per unit time

$$R_f = \frac{d}{dt} \left(\frac{N}{N_{\max}} \right) = \frac{d}{dt} \chi \quad (4)$$

where N is the number of moles CaO or SO_2 produced (kmol), $N_{\max}$ is the maximum number of moles that can be produced, according to the stoichiometry of the reaction and the initial number of moles present (kmol), and χ is the fractional production degree ($N/N_{\max}$) (dimensionless).

While reading the following part of the paper, it is important to keep the above definitions in mind constantly. The dimension of the fractional production rate is (s^{-1}). It can be derived easily from the slope of the observed fractional conversion vs time function. The conversion of the reactants and the product yield are calculated as a function of time using the observed weight changes.

The change of the fractional production rate with the fractional production degree is a proper illustration of the phenomena taking place during the reaction. The fractional production degree (χ) has been derived from the experimental results as the ratio of the number of moles of product actually obtained over the maximum possible number of moles of the product. The product may then either be SO_2 or CaO :

$$\chi = \frac{N_{\text{CaO}}}{(N_{\text{CaO}})_{\max}} = \frac{N_{\text{SO}_2}}{(N_{\text{SO}_2})_{\max}} \quad (5)$$

However, the maximum possible number of moles of product is not related directly to the initial number of moles, because for non-optimal stoichiometric proportions one of the reactants is present in excess and cannot be converted completely. Excluding this "inert" amount from the initial-rate expression for reaction (3) leads to simpler model equations (Section 5) which clearly demonstrate the influence of the initial reactant proportions.

Another useful parameter for the interpretation of experimental results of the apparent solid-solid reaction is the molar fraction (m_f) of sulphur present as sulphate, at the beginning of the reaction. This initial molar CaSO_4 fraction is expressed as the number of moles of CaSO_4 initially present divided by the total number of moles of CaSO_4 and CaS initially present:

$$m_f = \left(\frac{N_{\text{CaSO}_4}}{N_{\text{CaSO}_4} + N_{\text{CaS}}} \right)_{t=0} \quad (6)$$

The initial CaSO_4 mole fraction (m_f) is calculated directly from the applied weight ratio of the powder mixture, or (if required) from the weight changes of the preceding partial reduction step.

4. RESULTS OF MEASUREMENTS

The apparent solid-solid reaction between CaS and CaSO_4 was studied in an atmosphere of nitrogen or a nitrogen-sulphur dioxide gas mixture: the two (solid) reactants being present from the beginning of the reaction.

The parameters that were varied, besides the type of sample (see Section 3), were:

- the temperature ($1223 < T < 1373 \text{ K}$; Section 4.1).
- the initial composition [$0.1 < m_f < 0.9$ (dimensionless); Section 4.2].

Results of the measurements are presented in Figs 1–3. The presentation of data for "powder" in Fig. 1 is omitted; they were very similar to those obtained for the two other materials. Variation of temperature (Fig. 2) was only carried out for "mixtures" and "powder", and variation of the initial composition (Fig. 3) only for "DUWA pearl 95" and mixtures.

4.1. Influence of temperature

The thermogravimetric measurements were carried out for two different temperature intervals, viz. (i) 1223–1298 K and (ii) 1319–1373 K. The applied atmosphere was pure nitrogen for the low-temperature interval, or 5 (vol) % SO_2 in nitrogen for the high-temperature range. Each experiment was started by heating (100 K/min) to the desired temperature. Unfortunately, a certain degree of conversion, during the period of heating, could not be prevented, which implies that values of the initial fractional production rate (R_f) _{$t=0$} can only be estimated from Fig. 1 by extrapolation to $\chi = 0$.

Fig. 1. Fractional production rate of the apparent solid-solid reaction between CaS and CaSO_4 as a function of the fractional production degree, for different initial CaSO_4 mole fractions m_f . Sample types: partially regenerated 'DUWA pearl 95' and mixtures; temperature = 1273 K.

This Fig. 1 shows some typical results obtained for the low-temperature interval ($T = 1273$ K) in diagrams of the fractional production rate R_3 vs. the fractional degree of production. Obviously, data ob-

tained during the heating are left out: low conversion results are missing, especially in the right-hand side diagrams referring to DUWA pearl 95 samples. On the other hand, Fig. 1 illustrates that the final

Fig. 2. Pseudo-Arrhenius diagram of the apparent solid-solid reaction of CaS and CaSO₄. Sample types: partially reduced powder ($m_f = 0.75$) and mixtures ($m_f = 0.33$, 0.75 and 0.90).

Fig. 3. Initial fractional production rate of the apparent solid-solid reaction as a function of the initial CaSO₄ mole fraction (temperature = 1273 K): (upper diagram) present experimental data and model calculations compared; (lower diagram) comparison of data from different sources. A minimum occurs at the initial CaSO₄ mole fraction value predicted by theory ($m_f = 0.75$).

amounts of CaO and SO₂ produced were almost maximal, the fractional production degree reaching a value fairly close to one [see eq. (5)]. It should be noted, however, that for non-stoichiometric conditions ($m_f \neq 0.75$), a fraction of the excess reactant will always remain.

Measurements in the high-temperature interval were only carried out for a series of powder samples which had all been partially reduced to approximately the same initial mole fraction of $m_f = 0.75$, a value which allows complete conversion of both reactants.

For these measurements, SO₂ was added to the gas phase to create realistic conditions with respect to the feasibility of the apparent solid-solid reaction as a possible regeneration route for sulphated sorbent from AFBC. Here, an additional advantage of such conditions was the suppression of the apparent solid-solid reaction during part of the sample heating. At 1319 K the equilibrium SO₂ concentration in the gas phase has been experimentally determined to be approximately 10 (vol) % SO₂ (Kamphuis *et al.*, 1989). Because the applied SO₂ concentration was considerably smaller (a factor of 2) than the corresponding equilibrium concentration, its influence on the reaction kinetics can be discounted.

Initial fractional production rate values $(R_3)_{t=0}$, estimated from diagrams like those presented in Fig. 1 by extrapolation to $\chi = 0$, are used to construct the pseudo-Arrhenius diagram of Fig. 2. This figure shows that for both temperature intervals and for all types of sample used, irrespective of their m_f value, a straight line is obtained with approximately the same slope. Consequently, a single value for the activation energy can be derived: $E \approx 358$ kJ/mol. Other values of E reported in literature are 343 kJ/mol (Chen and Yang, 1979) and 242 kJ/mol (Kikuchi *et al.*, 1983), the latter value being derived for partially sulphated dolomite (CaCO₃ · MgCO₃). Finally, it can be observed that the Arrhenius-plot is not affected by the fractional production degree. Using fractional production rates at any other fixed value of χ than $\chi = 0$, would yield the same result.

4.2. Influence of initial composition

At 1273 K the apparent solid-solid reaction between CaS and CaSO₄ according to eq. (3a) was studied for various values of the molar CaSO₄ fraction present at the beginning of the reaction (m_f). Experimental results are presented in diagrams of the fractional production rate R_3 vs the fractional production degree χ (Fig. 1), and in a diagram of the initial fractional production rate $(R_3)_{t=0}$ vs the initial CaSO₄ mole fraction m_f (Fig. 3).

The applied atmosphere for this study was pure nitrogen. As usual the samples were heated at a rate of 100 K/min. For DUWA pearl 95, a certain degree of conversion, occurring before the desired temperature was reached, could not be prevented. As indicated earlier in Section 4.1, data obtained during the heating are left out in Fig. 1. Consequently, the DUWA pearl 95 R_3 vs χ curves reported in Fig. 2 start beyond $\chi = 0.5$. Especially important in calculating the fractional production rate and the fractional production degree is the maximum number of moles that can be produced [see eq. (4)]. Basically, this number is determined by the initial composition of the solids mixture and the stoichiometry of the reaction. However, the theoretically expected value of $N_{\max}$ is not always reached. In case of excess CaSO₄, a certain fraction of CaS (viz. between 6 and 10%) appears to remain [see also Kamphuis *et al.* (1991)]. This phenomenon of incomplete conversion of both reactants is prob-

ably related to imperfect mixing of the solid reactants. Hereafter, the maximum number of moles that can be produced is taken to be the number of moles experimentally observed to be produced. In fact, $N_{\max}$ is calculated as the actual number of moles that was produced, instead of the number of moles that theoretically can be produced according to the stoichiometry of the reaction and the initial composition of the sample. In Fig. 1 results for three different initial CaSO_4 mole fractions are shown: $m_f = 0.36, 0.74$ and 0.84 in the case of partially reduced sulphated DUWA pearl 95; and $m_f = 0.33, 0.74$ and 0.85 for mixture. The fractional production rate is continuously decreasing with the fractional production degree, because of diminishing reactant quantities. Initial fractional production rate values can be obtained by extrapolating such data linearly to zero production. A plot showing these initial fractional production rates for different sample types as a function of the initial CaSO_4 fraction (m_f), is shown in Fig. 3. The lowest initial fractional production rate is found at an initial CaSO_4 mole fraction near 0.75. Increasing or decreasing from this specific value results in a higher fractional production rate. The optimal value of m_f , viz. according to the reaction stoichiometry, corresponds to the minimum in the fractional production rate. This phenomenon can partly be explained by the way in which the fractional production rate has been defined [eq. (4)]. A deviation from the optimal stoichiometric proportions leads to a lower $N_{\max}$ -value in the denominator of eq. (4). The mathematical result is a higher fractional production rate. According to Fig. 3 the highest initial fractional production rate is achieved for the partially regenerated DUWA pearl 95: $(R_3)_{t=0} = 25 \times 10^3 \text{ s}^{-1}$ for DUWA pearl 95 and $2.2 \times 10^3 \text{ s}^{-1}$ for the powder mixtures. The differences in initial fractional production rate between the two samples in the present study could be attributed to the differences in contact between CaS and CaSO_4 . In the case of partially regenerated sorbent, the contact is obviously better than in the case of powder mixtures.

Figure 3 also shows a comparison between the results of the present experiments and recalculated data from Kikuchi *et al.* (1983) with m_f values in the range of 0.42–0.92. With respect to the data of Kikuchi *et al.*, calculations of the maximum number of moles that can be produced are based on initial conditions, because the experimentally observed maximal production is unfortunately not reported in their paper. The applied temperature was 1223 K in their experiments, that is 50 K lower than in our case. Consequently, relatively low values for the fractional production rate have been observed. The data of Chen and Yang (1979), consisting of a few experiments with m_f between 0.43 and 0.75, are also plotted in this figure.

Measurements for relatively small or large values of m_f are less accurate because the total change in sample weight is then quite small. Yet, the experimental results for DUWA pearl 95 presented in Fig.

3 seem to indicate that the initial fractional production rate becomes constant when approximately $m_f < 0.4$ and $m_f > 0.85$.

5. INTERPRETATION MODEL

The phenomena observed with the apparent solid–solid reaction between CaS and CaSO_4 can largely be explained by the following simple model. This model is meant as a basic interpretation tool and improves the understanding of the overall reductive decomposition of CaSO_4 [see Kamphuis *et al.* (1991)].

Two reaction steps are supposed to be involved in the reaction mechanism of the apparent solid–solid reaction. The presence of a liquid phase, in which the CaS and the CaSO_4 molecules are completely ionized, is assumed to be essential. The rate-determining reaction between S^{2-} and SO_4^{2-} anions takes place according to eq. (3e). The CaO formed is not ionized. In the expression for the liquid phase formation [reaction (3d)], x and y obviously are the (mole) fractions of solid reactant transformed to the liquid phase:

Other assumptions are:

- CaSO_4 and CaS form an eutectic liquid phase at temperatures above 1100 K. The formation of the liquid phase [reaction (3d)] is instantaneous. The CaSO_4 and the CaS molecules in the liquid phase are completely ionized. The rate-limiting step is the redox reaction between the SO_4^{2-} and S^{2-} anions. The CaO formed is not ionized.
- The reaction rate does not depend on the SO_2 concentration in the gas phase, as long as the gas-phase equilibrium concentration of SO_2 has not been reached.
- No intraparticle mass transport limitations for SO_2 occur for the low fractional production rates measured. For increased reaction rates, at higher temperatures, the validity of this assumption will be less certain.
- Liquid-phase locations are probably highly dispersed; in this model the liquid phase is treated as a single volume (V_l).
- The CaO, present in a number of samples, is considered to be inert.

Unfortunately, the formation of a liquid phase during reaction cannot be observed with an experimental set-up such as we used. It was noticed, however, that after an experiment the sample powder displayed clearly increased coherence, apparently caused by some kind of sintering between particles. This may be a small indication of the presence of a liquid phase during reaction.

The composition of the liquid phase is the basic parameter in deriving an expression for the fractional production rate of reaction (3e). Three intervals, based

on the limiting availability of the two compounds forming the liquid phase, can be distinguished. In Fig. 4 the outline of a possible composition vs temperature diagram for the system CaS–CaSO₄ is presented. Liquid-phase composition coefficients will be defined, in which the number of moles of each component is related to the total number of moles present in the liquid phase.

Interval I. When only a small amount of CaS has been formed, CaSO₄ is present in excess. Consequently all CaS will form a liquid phase with only part of the CaSO₄. At a certain temperature, the number of moles of CaSO₄ in the liquid phase is derived from the transition line I/II in Fig. 4 by the liquid phase composition coefficient m_2 :

$$m_2 = \frac{N_{\text{SO}_4^{2-}}}{N_{\text{SO}_4^{2-}} + N_{\text{S}^{2-}}} \quad (7)$$

The fraction of CaS transformed to the liquid state, x in eq. (3d), equals unity; the fraction of CaSO₄ transformed to the liquid state (y) in this interval can be expressed as

$$y = \left(\frac{m_2}{1 - m_2} \right) \left(\frac{1 - m_f}{m_f} \right) \quad (8)$$

Interval II. In this intermediate situation all CaS as well as all CaSO₄ is present in the liquid phase. The values of both x and y are one. The total number of moles in the liquid phase is constant in this interval. In the case of a pure CaSO₄ sample, this should lead to a single liquid phase.

Interval III. In this situation CaSO₄ is the limiting compound for the formation of the liquid phase: all CaSO₄ is in the liquid phase. The amount of CaS present in the liquid phase is determined by the liquid phase composition coefficient m_1 (see Fig. 4, transition line II/III):

$$m_1 = \frac{N_{\text{S}^{2-}}}{N_{\text{SO}_4^{2-}} + N_{\text{S}^{2-}}} \quad (9)$$

Fig. 4. Schematic TX-diagram, probably valid for the CaS–CaSO₄ system. The figure illustrates the formation of an eutectic liquid phase between CaS and CaSO₄.

The fraction of CaSO₄ in the liquid phase, y , in eq. (3d) equals unity, while the fraction of CaS in the liquid phase (x) in this interval can be expressed as

$$x = \left(\frac{m_1}{1 - m_1} \right) \left(\frac{m_f}{1 - m_f} \right) \quad (10)$$

The values of the liquid phase composition coefficients m_1 and m_2 depend on the form of the composition vs temperature diagram for the system CaSO₄/CaS (Fig. 4) and are a function of temperature. Both liquid-phase composition coefficients are dimensionless.

In the absence of independent data, it is speculated that the fractional production rate can be expressed as a product of the concentrations of the S²⁻ and SO₄²⁻ anions, to the power of their stoichiometric coefficients, the volume of the liquid phase and an Arrhenius-like rate constant (k_3):

$$R_3 = \frac{k_3^0 \times e^{(-E_3/RT)} V_l \left(\frac{N_{\text{SO}_4^{2-}}}{V_l} \right)^{3/4} \left(\frac{N_{\text{S}^{2-}}}{V_l} \right)^{1/4}}{N_{\text{max}}} \quad (11)$$

where k_3^0 is the pre-exponential factor of the rate constant of reaction (3e) (s⁻¹) and E_3 is the activation energy of reaction (3e) (kJ/kmol).

The model requires three equations, one for each interval. When the unknown concentrations in the liquid phase are eliminated by using the definition of the liquid-phase composition coefficients, the expressions for the fractional production rate in Table 1 are obtained. The transition between the intervals I and II, or II and III, takes place when the initial CaSO₄ mole fraction m_f equals $(1 - m_1)$ or m_2 . When m_f is smaller than $(1 - m_1)$ (interval III) or larger than m_2 (interval I) the composition in the liquid phase is constant and independent of the initial CaSO₄ mole fraction (m_f). In interval II the initial composition of the liquid phase is directly determined by m_f . At the end of the reaction a transition from interval II to either I or III takes place, depending on which of the two reactants is running out.

The total number of moles CaO or SO₂ that can be produced, that is the total number of moles CaSO₄ and CaS that can be converted (N_{max}), is a function of the initial CaSO₄ mole fraction. If there is excess CaSO₄, i.e. when $m_f > 0.75$, not all the CaSO₄ can be consumed by reaction. The total number of moles that can be converted is then determined by the initial amount of CaS, according to the stoichiometry of reaction (3e):

$$N_{\text{max}} = 4(N_{\text{CaS}})_{t=0} \quad (12)$$

Similarly, if there is excess CaS, i.e. when $m_f < 0.75$, the total number of moles that can be converted is determined by the initial amount of CaSO₄:

$$N_{\text{max}} = \frac{4}{3}(N_{\text{CaSO}_4})_{t=0} \quad (13)$$

For intervals I and III, the expression for the initial fractional production rate (at zero degree of fractional

Table 1. Fractional production rate expressions of the apparent solid-solid reaction of CaSO_4 and CaS for the three intervals distinguished

Intervals	Number of moles reactant	Fractional production rate (s^{-1})
I (excess CaSO_4)	$(N_{\text{CaS}})_t = N_{\text{CaS}}$	$R_3 = \frac{k_3 \left(\frac{m_2}{1 - m_2} \right)^{3/4} N_{\text{CaS}}}{N_{\text{max}}}$
	$(N_{\text{CaSO}_4})_t = \frac{m_2}{(1 - m_2)} N_{\text{CaS}}$	
II (intermediate)	$(N_{\text{CaS}})_t = N_{\text{CaS}}$	$R_3 = \frac{k_3 N_{\text{CaSO}_4}^{3/4} N_{\text{CaS}}^{1/4}}{N_{\text{max}}}$
	$(N_{\text{CaSO}_4})_t = N_{\text{CaSO}_4}$	
III (excess CaS)	$(N_{\text{CaS}})_t = \frac{m_1}{(1 - m_1)} N_{\text{CaSO}_4}$	$R_3 = \frac{k_3 \left(\frac{m_1}{1 - m_1} \right)^{1/4} N_{\text{CaSO}_4}}{N_{\text{max}}}$
	$(N_{\text{CaSO}_4})_t = N_{\text{CaSO}_4}$	

Table 2. Initial fractional production rate expressions of the apparent solid-solid reaction of CaSO_4 and CaS as a function of the initial CaSO_4 mole fraction (m_f)

Intervals	Initial CaSO_4 mole fraction	Initial fractional production rate (s^{-1})
I (excess CaSO_4)	$m_f > m_2$	$(R_3)_{t=0} = 1/4 k_3 \left(\frac{m_2}{1 - m_2} \right)^{3/4}$
		$(m_f > 0.75):$ $(R_3)_{t=0} = 1/4 k_3 \left(\frac{m_f}{1 - m_f} \right)^{3/4}$
II (intermediate)	$1 - m_1 \leq m_f \leq m_2$	$(m_f < 0.75):$ $(R_3)_{t=0} = 3/4 k_3 \left(\frac{1 - m_f}{m_f} \right)^{1/4}$
		$(R_3)_{t=0} = 3/4 k_3 \left(\frac{m_1}{1 - m_1} \right)^{3/4}$
III (excess CaS)	$m_f < 1 - m_1$	

production) can be found by eliminating N_{max} from eq. (11), using eq. (12) or eq. (13). The resulting expressions for the initial fractional production rate (Table 2) are independent of the initial composition, i.e. the initial CaSO_4 mole fraction (m_f). Only the liquid-phase composition coefficients m_1 and m_2 and the rate constant k_3 determine the constant value of the initial fractional production rate in interval I or III. For interval II, two equations for the initial fractional production rate are presented in Table 2. The first one should be used when $m_f < 0.75$, and the other one when $m_f > 0.75$. The volume in which the reaction takes place is a function of the fractional production degree. The diminishing volume of the liquid phase

will cause the fractional production rate to decrease with the degree of fractional production.

Unknown parameters in the model for the apparent solid-solid reaction of CaS and CaSO_4 are:

- the liquid phase composition coefficients m_1 and m_2 ,
- the activation energy of reaction (3e) E_3 ,
- the pre-exponential factor of reaction (3e) k_3^0 .

As stated before, in intervals I and III, the initial fractional production rate is not dependent on the initial CaSO_4 mole fraction m_f . Therefore, liquid phase composition coefficients m_1 and m_2 can be

derived from experiments in which m_f is varied. Results obtained for intervals I and III are characterized by a single value for the initial fractional production rate: when $(R_3)_{t=0}$ is plotted as a function of m_f , a horizontal line is obtained for the intervals I ($m_f < m_1$) and III ($m_f > 1 - m_2$). The value of the rate constant k_3^0 should be calculated from the value of the initial fractional production rate in these intervals, while using the expressions from Table 1. The activation energy of the apparent solid–solid reaction E_3 has already been evaluated simply by plotting the values of the initial fractional production rate vs $1/T$ in a pseudo-Arrhenius diagram (last part of Section 4.1; see also Fig. 2). Obviously, this plot should be based on experiments with a single m_f value.

The optimum value of m_f , viz. according to the reaction stoichiometry, corresponds to the minimum in the fractional production rate. This phenomenon can be explained by the way in which the fractional production rate has been defined [eqs (4) and (11)]. A deviation from the optimal stoichiometric proportions leads to (i) a higher concentration of one of the reactants in the liquid phase and (ii) a lower total number of moles that can be produced ($N_{\max}$). According to eq. (11), both effects result in a higher fractional production rate.

6. DISCUSSION

The most important feature of the proposed model for the apparent solid–solid reaction is that it enables an analysis of the effect of the initial mole fraction on the fractional production rate to be made. It predicts a fractional production rate which is independent of the initial mole fraction (m_f) in the intervals I and III. Model calculations based on the rate equations presented in Table 2 are represented in Fig. 3 by the solid line in the upper diagram.

Apparently, transition from interval II to interval III occurs around m_1 ($= 1 - 0.4$) = 0.6, and transition from interval I to II when $m_2 = 0.85$ (see also Table 2). Using these values for m_1 and m_2 , the rate constant k_3 can now be determined by fitting the level of the initial production rate as calculated from the model expressions (Table 1, interval I or III) to the experimentally observed one (open circles in Fig. 3). In this way k_3^0 was found to be $14.9 \times 10^{12} \text{ s}^{-1}$. Parameters established for the mixtures sample are uncertain. Unfortunately, the accuracy of the measurements was insufficient due to the considerably lower fractional production rate. From Fig. 3 it was deduced that $m_1 = 0.75$ and $m_2 = 0.85$; the value for k_3^0 was found to be $1.3 \times 10^{12} \text{ s}^{-1}$.

All the parameters required for model calculations are now available. After fitting the findings of the model to the experimental results by selecting the best values of m_1 , m_2 and k_3^0 , the model should predict the correct relationship between fractional production rate and the degree of fractional production. Figure 1 shows that for DUWA pearl 95 and three different values of the CaSO_4 mole fraction m_f , the agreement

between model calculations (solid lines) and experimental results is quite satisfactory. The predicted fractional production rate of the mixtures samples shows much less agreement with the experimentally obtained values. As indicated before, this is due to the inevitable inaccuracy of the measurements (small weight changes as a consequence of the low fractional production rates) and non-perfect mixing of the solid particles. The model also predicts the correct relationship between the initial fractional production rate and the initial CaSO_4 mole fraction for interval II conditions (solid line in Fig. 3). The location of the observed minimum in the $(R_3)_{t=0}$ vs m_f curve is quite close to the one calculated from the model (solid line). This phenomenon can be explained by the way in which the fractional production rate has been defined [eq. (11)]. A deviation from the optimal stoichiometric proportions leads to (i) a higher concentration of one of the reactants in the liquid phase and (ii) a lower total number of moles that can be converted ($N_{\max}$). Both effects result in a higher fractional production rate according to eq. (11).

Also, the recalculated data of both Chen and Yang and Kikuchi *et al.* fit completely in the pattern of the present experimental results. Consequently, they do not lead specifically (as suggested by these authors) to the assumption of a gaseous intermediate.

7. CONCLUSIONS

The reaction mechanism of the reductive decomposition of CaSO_4 is supposed to consist of two reaction steps. In the first step CaSO_4 is reduced by H_2 producing CaS . The second step, the apparent solid–solid reaction between CaS and CaSO_4 , has been studied separately by creating appropriate reaction conditions for measurements in a thermobalance construction.

The reaction between CaS and CaSO_4 takes place when a mixture of these compounds is heated in an inert atmosphere to a temperature higher than 1100 K. Depending on the amounts initially present, an almost complete conversion can be achieved. The fractional production rate of this apparent solid–solid reaction between CaSO_4 and CaS also depends on the ratio in which CaSO_4 and CaS are present initially. A minimum of the initial fractional production rate occurs when the reactants are present in stoichiometrically ideal proportions (initial CaSO_4 mole fraction $m_f = 0.75$); complete conversion is then achieved. The fractional production rates measured for the apparent solid–solid reaction, are of the same order of magnitude as the rates measured for the reductive decomposition of CaSO_4 according to reaction (1). This indicates that CaO production does indeed proceed according to the proposed two-step mechanism.

For the apparent solid–solid reaction a simple model has been formulated to calculate the fractional production rate as a function of the fractional production degree. Expressions and parameter values for the rate constant and for the concentration-dependent

terms have been established. Model calculations show close agreement with the experimental results. Apparently, the measurements can be interpreted with a model which assumes complete transformation to, and ideal mixing of reactants in a single liquid phase, preceding to the reaction. It should be noticed, however, that the real picture of physical events during the solid–solid reaction remains unclear for the moment.

One of the main practical consequences of the reaction mechanism proposed for the reductive decomposition of CaSO_4 concerns the maximal SO_2 partial pressure in the gas phase. Basically SO_2 can be produced whether by direct reduction or by a two-step reduction via CaS . The latter method is applicable above approximately $T = 1100 \text{ K}$ and has the following advantage. Even when both reaction steps proceed simultaneously, SO_2 is produced mainly by the apparent solid–solid reaction (3a). Consequently, SO_2 formation is practically independent of the H_2 partial pressure in the gas phase. A higher SO_2 concentration in the gas phase can be achieved by affecting the equilibrium of reaction (3a) through an increase in temperature. The experimentally determined kinetics of the apparent solid–solid reaction indicate the practical feasibility of an alternative regeneration route for CaSO_4 . Using this route, reaction (2) could be carried out at a high H_2 partial pressure and a relatively low temperature in order to create the optimal CaSO_4/CaS ratio for a second step according to the apparent solid–solid reaction (3a). The SO_2 release during the first step should be minimized by careful control of the reaction conditions. In the second step, carried out separately, liberation of SO_2 from the sorbent reaction mixture should be realized by creating proper conditions for the apparent solid–solid reaction. A high SO_2 partial pressure in the regenerator product gas is only achieved if the temperature of this second process step is maintained above 1273 K . The important advantage of the proposed regeneration route will be the production of a SO_2 -rich gas. No other gaseous reaction components will be released in the second step. This regeneration route has already been suggested by Hubble *et al.* (1975).

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NOTATION

E_i activation energy of reaction i , kJ/kmol
 k_i rate constant of reaction (i) = $k_i^0 \exp(-E_i/RT)$, s^{-1}

k_i^0 pre-exponential factor in the rate constant of reaction i , s^{-1}
 m_f initial CaSO_4 mole fraction
 $m_{1,2}$ liquid-phase composition coefficients
 N number of moles CaO or SO_2 , kmol
 R_i fractional production rate reaction i , s^{-1}
 R gas-law constant, kJ/kmol K
 T temperature, K
 t time, s
 V_l volume of liquid phase, m^3
 x mole fraction CaS in liquid phase
 y mole fraction CaSO_4 in liquid phase

Greek letter

χ fractional production degree

Subscripts

$t = 0$ initial
 s solid
 l liquid
 max maximal

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