THE SULPHIDATION OF CALCINED LIMESTONE WITH HYDROGEN SULPHIDE AND CARBONYL SULPHIDE

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Abstract—The sulphidation of calcined limestone with H₂S, COS and mixtures of H₂S and COS was studied in a thermogravimetric analyzer at temperatures between 500 and 700°C. The applied H₂S- and COS-pressures corresponded with those in coal gas produced by modern coal gasifiers, i.e. 50–12,000 Pa for H₂S and 50–1000 Pa for COS. The reaction orders in H₂S and COS as well as the activation energies of the involved reactions were determined. The mechanism of sulphidation was examined by simulating measured conversion vs time behaviour with the grain size distribution model of Heesink *et al.* (1993, *Chem. Engng J.* 53, 25–37).

1. INTRODUCTION

Thermodynamic calculations have shown that the oxides of the metals Ca, Sr, Ba, V, Mo, W, Mn, Fe, Co, Cu and Zn can be used as sulphur sorbents to be applied for high-temperature coal gas desulphurization (Westmoreland and Harrison, 1976). On basis of these metals, many sorbents have been developed [see e.g. Venkataraman *et al.* (1991) and Clift and Seville (1993)]. One can roughly discriminate between synthetic sorbents, which are relatively expensive but have a long lifetime, and natural sorbents which are cheap but possibly are less stable. Sorbents that belong to the category of natural sorbents are iron ore and limestone, either in raw or calcined form. Borgwardt and Roache (1984), and more recently Illerup *et al.* (1993), examined the reaction between limestone and H₂S. Borgwardt and Roache concluded that limestone conversion extents of more than 25% can only be obtained with very small limestone particles (< 10 µm). In agreement with that, Illerup *et al.* found that bigger limestone particles (360–1500 µm) only show satisfactory sulphidation rates at CO₂-pressures low enough to allow calcination of the limestone. Therefore, in this work we concentrated on calcined limestone. The application of calcined limestone (which mainly consists of CaO) in coal gas clean-up processes may offer the following advantages.

- Thermodynamic calculations [based on data from Barin (1989)] show that the concentrations of both H₂S and COS can be reduced to sufficiently low values according to the reactions

- Calcined limestone is also able to absorb halogens like HCl (van der Ham *et al.*, 1995) and HF:

- Limestone has a low price of typically some 40 US \$ or 30 ECU per ton, including transport. Because of its low price, limestone may be applied for non-regenerative desulphurization.
- In most cases regenerative desulphurization is to be preferred. Sulphided limestone can be regenerated by partial oxidation with SO₂ and subsequent reaction between remaining CaS and CaSO₄, according to (van der Ham *et al.*, 1995)

This regeneration route offers the advantage that elemental sulphur is obtained. A drawback, however, is the high temperature (about 950°C) which is needed for reaction (R6) to proceed.

- Spent sulphided limestone could be (partly) used as a fluxing agent in entrained flow coal gasifiers or as a building material after oxidation towards gypsum.

A disadvantage of calcined limestone is its ability to absorb CO₂. At partial CO₂-pressures higher than the equilibrium pressure, the absorption of CO₂ may interfere with the absorption of H₂S and COS. A future paper will deal with that matter.

To enable the design of an absorber in which coal gas is desulphurized with calcined limestone, sulphidation kinetics must be known. These can be revealed by measuring the sulphidation rate of calcined limestone in the presence of (simulated) coal gas. In general, the conversion rate of a reacting solid can be

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formulated as

$$\frac{dX}{dt} = k_A \exp\left[-\frac{E_{act}}{RT}\right] C^n f(X). \quad (1)$$

The values of the Arrhenius constant k_A , the activation energy E_{act} , the reaction order n and the function $f(X)$ will thus determine the rate of sulphidation at given values of temperature T and concentration C . It is to be expected that the value of k_A will depend on the chemical and physical properties of the calcined limestone (e.g. specific surface area) which in their turn are related to the origin of the limestone and/or the calcination history. It is likely that the values of E_{act} , n and $f(X)$ are less dependent on limestone type. The function $f(X)$ expresses the dependency of the sulphidation rate on the extent of conversion, X . This dependency is determined by the sulphidation mechanism.

The sulphidation kinetics of calcined limestone and fully calcined dolomite (i.e. $\text{CaO} \cdot \text{MgO}$ with CaO being reactive only) have been studied in the past (Squires *et al.*, 1969; Pell, 1971; Westmoreland *et al.*, 1977; Yang and Chen, 1979; Attar and Dupuis, 1979; Kamath and Petrie, 1981; Proy, 1982; Borgwardt *et al.*, 1984; Yumura and Furimsky, 1985) and more recently by Abbasian *et al.* (1991, 1993), Sotirchos (1991), and Nguyen and Watkinson (1993). Nevertheless, there is no consensus yet about the magnitude of typical kinetic data like reaction orders and activation energies. Westmoreland *et al.* (1977), for example, examined the reaction between calcined limestone and H_2S and reported first-order behaviour in H_2S and an activation energy of 22 kJ mol^{-1} . Yang and Chen (1979) examined the reaction between calcined limestone and COS and found first-order behaviour in COS and an activation energy of 18 kJ mol^{-1} . Others measured much higher activation energies of about 130 kJ mol^{-1} for both reactions (Squires *et al.*, 1969; Borgwardt *et al.*, 1984). The sulphidation mechanism has been examined by Borgwardt *et al.* (1984) and by Nguyen and Watkinson (1993). Borgwardt *et al.* (1984) concluded that diffusion of the H_2S through the sulphided layer towards the unreacted CaO -surface is rate determining. However, Nguyen and Watkinson (1993) reported that the reaction at the surface is rate determining during the initial stage of sulphidation and that diffusion through the product layer becomes rate determining thereafter.

To get a better insight we examined the sulphidation of calcined limestone in an atmospheric thermogravimetric analyzer. Sulphidation was performed with either H_2S , COS or mixtures of H_2S and COS at temperatures between 500 and 700°C . The applied H_2S - and COS -pressures corresponded with those in coal gas, i.e. 50–12,000 Pa for H_2S and 50–1000 Pa for COS . For reactions (R1) and (R2) the respective orders in H_2S and COS as well as the activation energies were established. It was also examined how sulphidation is affected by the presence of H_2 and CO , which are the main constituents of coal gas. Finally, the sulphidation mechanism was examined by means

of the grain size distribution model of Heesink *et al.* (1993).

2. EXPERIMENTAL DETAILS

A simplified flow scheme of the applied experimental set-up is shown in Fig. 1. The applied Thermo-Gravimetric Analyser (TGA) was of the Setaram TG85 type. The samples were kept in a small cup ($\varnothing = 9.5 \text{ mm}$) made out of quartz, which hung on a platinum wire inside a quartz tube ($\varnothing = 15 \text{ mm}$). The tube was placed in an oven which can be operated at temperatures between 20 and 1000°C . The sample temperature was indirectly measured by a thermocouple placed at sample height in between the quartz tube and the inner wall of the oven. Previous tests had shown that the difference between the temperature at this location and the temperature of the sample (measured inside the quartz tube just below the sample cup) was not more than 2°C . The TGA was connected to a computer for data acquisition and control purposes. The gas mixture, which could contain H_2S , COS , H_2 , CO and He , was composed with the help of electronic mass flow controllers that received their set-points from the computer. All gases were taken from bottles. The stream through the TGA, which was directed downwards to optimize mass transfer between the gas bulk and the particles inside the sample cup, was adjusted to 400 ml min^{-1} (STP). The upper section of the TGA, containing the delicate electronic parts of the balance, was continuously purged with He (at a flow rate of 40 ml min^{-1} STP) to prevent the corrosive sulphidation gas from entering.

It was found that quite some sulphur adsorbed at the inner surface of the stainless steel supply line. In some cases it took about 1 h before the gas entering the TGA had the composition that was selected by means of the mass flow controllers. Therefore, before starting an experiment, the supply line was purged for at least 90 min with the selected gas mixture. During purging the gas mixture was bypassed to the scrubber. In the meantime, the TGA (already containing the sample) was purged with He that was supplied through a separate line. After purging, the sulphidation gas was switched to the TGA, whereas the He purge stream was simultaneously switched to the scrubber by means of two three-way valves. Before entering the TGA and coming into contact with the sample, each gas stream was sent through separate packed-bed reactors containing copper-based catalyst pellets (type BASF R3-11). This was done to remove any O_2 possibly present in the gas streams in order to avoid the unwanted oxidation of the sulphided limestone sample. In the catalyst beds O_2 is either converted towards H_2O (if H_2 is present) or absorbed under the formation of CuO . To avoid the absorption of sulphur by the catalyst, H_2S and COS were added to the sulphidation gas behind the catalyst bed. H_2 was used for periodic regeneration of the catalyst.

Sulphidation experiments were performed with limestone from the quarry at Wülfrath (Germany). All

Fig. 1. A simplified flowsheet of the applied experimental set-up.

samples were taken from a single batch of 1 g limestone which was previously calcined in the TGA at 850°C for 30 min while purging with He. This batch was stored in an airtight chamber which was purged with N₂. Table 1 gives the composition of the applied limestone before and after calcination. Figure 2 shows a mercury porosigram of the calcined material indicating a specific surface area of 16.8 m² g⁻¹. The diameter of the applied particles ranged from 150 to 210 µm.

Table 1. Chemical composition of the applied Wülfrath limestone before and after calcination (in wt %)

Component	Before calcination	After calcination [†]
CaCO ₃	97.20	—
MgCO ₃	0.90	—
CaO	—	95.90
MgO	—	0.76
Si	0.54	0.95
Fe	0.09	0.16
Al	0.06	0.11
S	0.02	0.04
K	0.02	0.04
Sr	0.02	0.04

[†] Calculated from the composition before calcination assuming complete calcination.

Experiments were carried out with relatively small samples of 3 mg to ensure differential operation and to minimize the influence of mass and heat transport resistances located around the sample cup and between the particles inside the cup. Before starting a sulphidation experiment, the samples were heated at 850°C for 10 min while purging with He to remove impurities possibly absorbed by the calcined material during storage. Then the temperature was adjusted. When the desired sulphidation temperature was reached, the He purge gas was replaced by sulphidation gas. Unless stated otherwise, 4 vol.% of H₂ was supplied to the sulphidation gas when sulphidation was carried out with H₂S. This was done to suppress the dissociation of H₂S to elemental sulphur. For similar reasons 8 vol.% CO was supplied when sulphidation was carried out with COS. When sulphidation was carried out with a mixture containing both H₂S and COS H₂ (4 vol.%) as well as CO (8 vol.%) were supplied. To optimize mass transfer all experiments were performed using helium as carrier gas.

Conversion vs time curves were derived from the corresponding weight vs time curves obtained during sulphidation. Before doing so, the weight vs time curves were smoothed by means of curve fitting to get rid of any noise (typically 50 µg). When the sample weight registered at the end of a sulphidation experiment was at least 95% of the weight expected on basis

Fig. 2. Mercury porosigram of the applied calcined limestone particles (Wülfrath limestone).

of complete sulphidation (assuming an initial CaO-content of 95.9 wt%), complete conversion was assumed to be reached. In other cases conversion was calculated by assuming an initial CaO-content of 95.9 wt%.

3. RESULTS

3.1. The influence of O₂-removal

The first sulphidation experiments were performed without employing the catalyst beds for O₂-removal. In many cases ultimate conversion extents of more than 100% were calculated; values up to 130% were obtained. The formation of CaSO₄, which has a much higher molecular weight than CaS (136 vs 72 g mol⁻¹), was thought to be responsible for this. According to thermodynamics, the presence of very little O₂ may lead to the formation of CaSO₄ at the conditions applied. Although CaSO₄ is likely to be reduced towards CaS by the H₂ present in the sulphidation gas, a net production of CaSO₄ exists when the rate of reduction is slower than the rate of oxidation. Chemical analysis showed that the sulphided samples indeed contained some 5 wt% CaSO₄. After installation of the catalyst beds, conversions above 100% were seldom observed, whereas the sulphate content of the sulphided samples had dropped to values of 1–2 wt%. The sulphate still detected was probably produced while the samples were contacted with air in the period between experiments and chemical analysis.

A remarkable phenomenon is shown in Fig. 3 which compares the sulphidation rates obtained with H₂S before and after installation of the catalyst beds. The presence of small amounts of O₂ apparently enhances sulphidation. This "enhancement" may merely be due to the higher molecular weight of CaSO₄ or to some catalytic effect exercised by CaSO₄. To avoid any difficulties in interpretation, all further experiments were performed with the catalyst beds in operation.

Fig. 3. Order plots for the sulphidation of calcined limestone with H₂S at 500°C, measured before and after the installation of O₂-removing catalyst beds (conversion rates calculated at a conversion extent of 30%).

3.2. Sulphidation with H₂S

The influence of H₂S-pressure on sulphidation behaviour is illustrated in Fig. 4. The sulphidation rate clearly increases when raising the H₂S-pressure. The reaction order in H₂S can be obtained by plotting the sulphidation rate at constant conversion extent (here 30%) against H₂S-pressure in a double-logarithmic way. Figure 5 shows the results obtained at temperatures of 500, 600, 650 and 700°C. At temperatures of 500 and 600°C the reaction order appears to be 0.5 over the whole range of applied H₂S-pressures. At 650 and 700°C the reaction order seems to be unity at H₂S-pressures below some 1000 Pa and 0.5 at H₂S-pressures above 1000 Pa. However, by varying the sample weight it was found that mass transfer from the gaseous bulk to the sample cup limited the sulphidation rate when H₂S-pressures below 1000 Pa were applied at temperatures of 650 or 700°C. It is therefore concluded that the reaction order in H₂S is 0.5 at all applied temperatures and H₂S-pressures. It was checked whether the reaction order in H₂S remains constant while sulphidation proceeds. This appeared to be roughly true: only during the first stage

Fig. 4. Conversion vs time curves obtained for the sulphidation of calcined limestone with H_2S at 600°C and different H_2S -pressures.

Fig. 6. Conversion vs time curves obtained for the sulphidation of calcined limestone with H_2S at a H_2S -pressure of 2000 Pa and different temperatures.

Fig. 5. Order plots for the sulphidation of calcined limestone with H_2S at 500, 600, 650 and 700°C (conversion rates calculated at a conversion extent of 30%).

Fig. 7. Arrhenius plot for the sulphidation of calcined limestone with H_2S derived at a H_2S -pressure of 2000 Pa (conversion rates calculated at a conversion extent of 30%).

of sulphidation ($X \approx 0$), where the reaction rate is so high that mass transfer may limit the rate of reaction, an order of unity was sometimes found. This was especially observed when low H_2S -pressures and/or high temperatures were applied.

Figure 6 shows the influence of temperature on sulphidation behaviour at a fixed H_2S -pressure of 2000 Pa. As to be expected, the sulphidation rate increases with temperature. The activation energy can be derived from the Arrhenius plot given in Fig. 7. A value of 160 kJ mol^{-1} is found for temperatures ranging from 500 to 700°C . The low activation energy found at temperatures above 700°C is the consequence of mass transfer limitation which was clearly demonstrated by varying the sample weight, higher weights showing lower sulphidation rates.

Borgwardt *et al.* (1984) found that the presence of H_2 may significantly suppress the rate of sulphidation. We therefore investigated the influence of H_2 -pressure on sulphidation behaviour. Figure 8 shows the results obtained at 500°C . The sulphidation rate indeed decreases at increasing H_2 -pressures. A similar trend was observed at 600°C .

Since the main constituent of coal gas is CO , it was also examined whether the presence of CO affects sulphidation behaviour. Experiments were performed at a temperature of 600°C . The maximum applied CO -pressure was 8000 Pa to ensure that no more

Fig. 8. Conversion vs time curves obtained for the sulphidation of calcined limestone with H_2S at temperature of 500°C , a H_2S -pressure of 2000 Pa and different H_2 -pressures.

than 5% of the H_2S was being converted towards COS , according to the reaction

with $K_{\text{eq}} = 0.032$ at 600°C .

(R7)

Figure 9 shows that sulphidation is slightly inhibited by the presence of CO .

3.3. Sulphidation with COS

The influence of COS -pressure on the rate of sulphidation is not very pronounced (see Fig. 10). The

Fig. 9. Conversion vs time curves obtained for the sulphidation of calcined limestone with H_2S at a temperature of 600°C, a H_2S -pressure of 1000 Pa and different CO-pressures.

Fig. 11. Conversion vs time curves obtained for the sulphidation of calcined limestone with COS at 700°C and high COS-pressures.

Fig. 10. Order plots for the sulphidation of calcined limestone with COS at 600, 650 and 700°C (conversion rates calculated at a conversion extent of 30%).

Fig. 12. Conversion vs time curves obtained for the sulphidation of calcined limestone with COS at a COS-pressure of 700 Pa and different temperatures.

reaction orders in COS at 600 and 650°C amount to 0.18 and 0.32, respectively. The reaction order at 700°C appears to be about unity. However, some tests performed at 700°C showed lower sulphidation rates at increasing sample weight, indicating that measurements were affected by mass transfer limitation.

A remarkable phenomenon was observed at relatively high COS-pressures (see Fig. 11). During a certain period the weight of the limestone samples was considerably higher than the value obtained after complete sulphidation. A possible explanation for this strange behaviour will be given later on.

The pronounced influence of temperature on sulphidation behaviour is demonstrated in Fig. 12. Since the reaction order is temperature dependent, the apparent activation energy (not corrected for this dependency) varies with COS-pressure. However, from the known reaction orders at 600 and 650°C the activation energy as defined by eq. (1) could be determined at 200 kJ mol⁻¹.

3.4. Sulphidation with mixtures of H_2S and COS

Kamath and Petrie (1981) performed sulphidation experiments with calcined limestone and mixtures of H_2S and COS. They concluded that a so-called synergistic effect occurs: the sulphidation rate observed with a gas containing both COS and H_2S (in

a ratio of 1 : 20) appeared to be some 30% higher than the rate obtained with a gas containing solely H_2S (and an equal amount of sulphur). We also performed some experiments with mixtures of H_2S and COS. All experiments were carried out at a temperature of 600°C. To avoid misinterpretation of the experimental results, the composition of the applied gas mixtures was chosen such that conversion of H_2S into COS or *vice versa* according to reaction (R7) could not occur. Since the concentrations of CO and H_2 were fixed at 8 and 4 vol.%, respectively, H_2S and COS were added in a ratio of 15.6 : 1. As shown in Fig. 13, sulphidation behaviour becomes worse when COS is added to a gas mixture already containing H_2S . This rather surprising result is in conflict with the observations of Kamath and Petrie (1981), but has been reproduced many times (see Fig. 14).

4. DISCUSSION

In this section we will interpret our results and compare them with those obtained by other investigators. We will further try to determine the mechanism of sulphidation. For this purpose the grain size distribution (GSD) model of Heesink *et al.* (1993) will be applied. According to this model, which is based on

Fig. 13. Conversion vs time curves obtained for the sulphidation of calcined limestone with H_2S (2670 Pa), COS (170 Pa) and a mixture of H_2S and COS (2670 + 170 Pa) at a temperature of 600°C .

Fig. 14. Order plots for the sulphidation of calcined limestone with H_2S (1...6), COS (a...f) and mixtures of H_2S and COS (1a...6f) at 600°C (conversion rates calculated at a conversion extent of 30%).

the grain model developed by Szekely and Evans (1970), a porous solid consists of small non-porous spheres (or grains) with various sizes which are converted according to a somewhat modified version of the classical shrinking core model developed by Yagi and Kunii (1955). SEM-pictures confirm the grainy structure of calcined limestone particles (Heesink *et al.*, 1993; Nguyen and Watkinson, 1993) and thereby the applicability of the GSD model. Before explaining the GSD model in somewhat more detail, we will first examine the possible mechanisms by which a single grain of calcined limestone may be sulphided.

4.1. Reaction mechanism of a single grain

Figure 15 illustrates the different steps that may play a role during the sulphidation of a single grain. Distinction is made between two situations, i.e. the formation of a non-porous and the formation of a porous layer of sulphided limestone. When a non-porous product layer is formed (left-hand side of Fig. 15), the following steps can be distinguished (Heesink *et al.*, 1993).

— Adsorption of the H_2S (or COS) at the surface of the product layer as well as desorption of the produced H_2O (or CO_2):

— Reaction of adsorbed H_2S (or COS) with O^{2-} ions (delivered by the CaO -core) towards S^{2-} ions and H_2O (or CO_2) according to a so-called grain reaction:

— Counterdiffusion of the S^{2-} and O^{2-} ions through the product layer.

— Reaction of the S^{2-} ions with CaO towards CaS and O^{2-} at the core surface (core reaction):

In principle, each step may influence the overall sulphidation rate. However, as sulphidation is performed at relatively high temperatures it is reasonable to assume that the various adsorption and desorption steps proceed relatively fast as compared to the other steps and therefore are not rate determining. Thus, when a non-porous product layer is formed three extremes can be distinguished (Heesink *et al.*, 1993).

1. *Grain reaction limitation.* The conversion rate of a grain is then given by

$$\frac{dX}{dt} = \frac{3k_g C^n}{N_0 R_0} (1 + KX)^{2/3} \quad (2)$$

where K represents the expansion factor defined as

$$K = N_0 (V_{\text{sol, prod}} - V_{\text{sol, reac}}) \quad (3)$$

with $V_{\text{sol, prod}}$ and $V_{\text{sol, reac}}$ representing the molar volumes of the solid product (i.e. $2.76 \times 10^{-5} \text{ m}^3 \text{ mol}^{-1}$ for CaS) and the solid reactant (i.e. $1.67 \times 10^{-5} \text{ m}^3 \text{ mol}^{-1}$ for CaO), respectively.

2. *Solid state product layer diffusion limitation,* with

$$\frac{dX}{dt} = \frac{3D_s C^n}{N_0 R_0^2 [1/(1-X)^{1/3} - 1/(1+KX)^{1/3}]} \quad (4)$$

3. *Core reaction limitation,* with

$$\frac{dX}{dt} = \frac{3k_c C^n}{N_0 R_0} (1-X)^{2/3} \quad (5)$$

Both core and grain reaction may well be first order in the *adsorbed* reactants (either H_2S or COS). Furthermore, the rate of product layer diffusion by definition is proportional to the concentration of the *adsorbed* reactants at the grain surface. Note, however, that the dimensions of the reaction rate constants k_g and k_c as well as the product layer diffusivity D_s depend on the value of the reaction order n which is defined on the basis of the concentration of the reactants in *gaseous* form.

Fig. 15. Schematic representation of a grain and the shrinking core mechanism by which it is converted. Left-hand side: in case a non-porous product layer is formed. Right-hand side: in case a porous product layer is formed.

When a porous product layer is formed (right-hand side of Fig. 15), two parallel reaction routes can be distinguished. The first route is the one already described for a non-porous product layer. The second route comprises of the following steps.

- Gaseous counterdiffusion of H_2S (or COS), on the one hand, and H_2O (or CO_2) on the other hand through the pores in the product layer.
- Adsorption of H_2S (or COS) at the surface of the CaO -core as well as desorption of the produced H_2O (or CO_2):

- Core reaction of the adsorbed H_2S (or COS) with CaO towards CaS and H_2O (or CO_2):

Most of the H_2S or COS presumably passes the product layer in gaseous form according to the second route. The permeability of the pores through the product layer is much higher than that of the solid CaS -lattice; the respective diffusivities typically range from 10^{-7} to $10^{-5} \text{ m}^2 \text{ s}^{-1}$ for the pores and from 10^{-10} to $10^{-15} \text{ m}^2 \text{ s}^{-1}$ for the solid lattice. Even when no more than 1% of the product layer were porous, the transport through the pores would outweigh the transport through the solid matrix. It is therefore concluded that the route through the pores is the only route of interest. Once again assuming that the adsorption and desorption steps are not limiting, only two extremes can be distinguished when a porous product layer is formed, i.e. product layer diffusion limitation and core reaction limitation.

4.2. The grain size distribution model

According to the GSD model a porous particle consists of spherical grains with various sizes. The size distribution of the grains is derived from the pore size distribution which is measured by mercury porosimetry. It is assumed that the radius of a pore is proportional to the radius of the grains that surround this pore. A pore-to-sphere factor F is defined as the ratio of the respective radii of grains and pores. The mercury porosigram is divided into a number of pore size classes. The relative contribution of pores from a certain pore size class to the porosity of a solid is assumed to be equal to the weight fraction of grains from the corresponding grain size class (having a radius of F times the relevant pore radius). F is determined from the mercury porosigram under consideration and typically adapts values between 1 and 2. A single value is used for all size classes. Once the grain size distribution has been determined, the conversion behaviour is calculated for each grain size class by one of the equations (2), (4) or (5). Finally, the overall conversion extent of a solid is obtained by weighed averaging of the conversion extents calculated for the various grain size classes. For more detailed information about the GSD model, refer to Heesink *et al.* (1993).

The GSD model was applied to simulate measured conversion behaviour in order to determine the sulphidation mechanism. Calculations were based on the mercury porosigram of Fig. 2. This porosigram was divided into 38 size fractions, the smallest pores having a radius of 8 nm and the largest having a radius of 102 nm. Pores with radii larger than 102 nm were regarded as macropores surrounding clusters of grains rather than grains. Anyhow, the surface area (and thus reactivity) ascribable to these large pores is negligible; see Fig. 2. The pore-to-sphere factor was calculated to be 1.56.

Although the phenomenon of pore plugging is included in the GSD model, none of the simulations indicated that pore plugging would occur. This corresponds to the experimental results showing that complete sulphidation can be obtained.

4.3. Sulphidation with H_2S

The reaction order in H_2S was found to be 0.5 at all applied temperatures and H_2S -pressures. This value differs from the value of unity that was reported by Westmoreland *et al.* (1977), who performed TGA measurements at temperatures between 300 and 800°C. However, it is very likely that the measurements of Westmoreland *et al.* were affected by mass transfer limitation. These investigators measured the extremely low activation energy of 22 kJ mol⁻¹ indicating that external mass transfer might have been rate determining during their experiments. Though they varied the gas velocity through the TGA and observed no significant influence on conversion behaviour, the possibility of external mass transport limitation may not be excluded (Wigmans *et al.*, 1983). Better agreement exists with the results of Pell (1971) who examined the sulphidation of fully calcined dolomite powder in a TGA. By elaborating the data that Pell obtained at different H_2S -pressures, reaction orders of 0.9 and 0.5 were found for temperatures of 700 and 625°C, respectively. The data obtained by Pell at 700°C may have been affected by mass transfer limitation as rather large samples (50–150 mg) were applied.

The activation energy of the reaction between H_2S and calcined limestone was determined at 160 kJ mol⁻¹. This value is much higher than the value of 22 kJ mol⁻¹ reported by Westmoreland *et al.* (1977). However, as stated before, the measurements of Westmoreland *et al.* were probably affected by mass transfer limitation. Borgwardt *et al.* (1984) measured an activation energy of 130 kJ mol⁻¹. However, before sulphidation was performed, Borgwardt *et al.* first sintered the calcined limestone samples for 30 min at 950°C. Such treatment may have affected the intrinsic reactivity of the limestone and therefore could explain the difference in activation energy. Our result compares better with the value of 155 kJ mol⁻¹ reported by Attar and Dupuis (1979), and the values that can be derived from the results obtained by Abbasian *et al.* (1991), i.e. 168 kJ mol⁻¹ for calcined limestone and 177 kJ mol⁻¹ for fully calcined dolomite.

In order to establish the mechanism of sulphidation, it was tried to simulate measured conversion vs time behaviour with the GSD model. While doing so, only the extreme cases of core reaction limitation, product layer diffusion limitation and grain reaction limitation were considered. Figure 16 shows the agreement between measured and simulated behaviour for the experiments performed at a H_2S -pressure of 2000 Pa and temperatures of 500, 600 and 700°C, respectively. The conversion extent that was calculated on assuming core reaction limitation had to

Fig. 16. GSD-model predictions together with experimental data obtained during sulphidation with H_2S (2000 Pa): (a) $T = 500^\circ\text{C}$, $k_c = 2.3 \times 10^{-7} \text{ mol}^{0.5} \text{ m}^{-0.5} \text{ s}^{-1}$, $D_s = 1.7 \times 10^{-15} \text{ mol}^{0.5} \text{ m}^{0.5} \text{ s}^{-1}$, $k_g = 4.2 \times 10^{-7} \text{ mol}^{0.5} \text{ m}^{-0.5} \text{ s}^{-1}$; (b) $T = 600^\circ\text{C}$, $k_c = 4.0 \times 10^{-6} \text{ mol}^{0.5} \text{ m}^{-0.5} \text{ s}^{-1}$, $D_s = 3.2 \times 10^{-14} \text{ mol}^{0.5} \text{ m}^{0.5} \text{ s}^{-1}$, $k_g = 1.3 \times 10^{-5} \text{ mol}^{0.5} \text{ m}^{-0.5} \text{ s}^{-1}$; (c) $T = 700^\circ\text{C}$, $k_c = 3.0 \times 10^{-5} \text{ mol}^{0.5} \text{ m}^{-0.5} \text{ s}^{-1}$, $D_s = 4.0 \times 10^{-13} \text{ mol}^{0.5} \text{ m}^{0.5} \text{ s}^{-1}$, $k_g = 7.5 \times 10^{-5} \text{ mol}^{0.5} \text{ m}^{-0.5} \text{ s}^{-1}$.

be increased by 0.1 to obtain good fits for the experiments performed at 500 and 600°C [Figs 16(a) and (b)]. This was also necessary when assuming grain reaction limitation at 500°C [Fig. 16(a)]. A plausible explanation for this necessity can only be given in case of core reaction limitation; see later on. All together 20 conversion vs time curves, which were obtained at various H_2S -pressures and temperatures, were simulated with the GSD model. Overall, the best fits were obtained on assuming core reaction limitation. The best-fit values of the core reaction rate constant k_c (at the applied H_2S -pressure of 4000 Pa) obey the

following equation (within 10%):

$$k_c = 5946 \exp\left(-\frac{154,000}{RT}\right) \text{ mol}^{0.5} \text{ m}^{-0.5} \text{ s}^{-1}. \quad (6)$$

The activation energy resulting from the simulations amounts to 154 kJ mol^{-1} and agrees reasonably well with the value of 160 kJ mol^{-1} which was derived from Fig. 7.

Our conclusion that some reaction at the core surface most probably determines the rate of sulphidation differs from the conclusion of Borgwardt *et al.* (1984) stating that product layer diffusion is rate determining. Borgwardt *et al.* came to their conclusion by examining the influence of surface area, A , on the rate of sulphidation. They prepared calcined limestone samples with different specific surface areas by means of controlled sintering. From the relationship

$$A = \frac{3}{\rho_{\text{sol, reac}} R_0} \quad (7)$$

it follows that the initial radius of the grains, R_0 , within a certain sample can be derived from A , higher values of A corresponding to lower values of R_0 . The samples thus obtained were sulphided under equal conditions. According to the grain model, the time needed to reach a certain conversion extent X , here denoted as $t(X)$, is a function of R_0 . In case of core reaction limitation, $t(X)$ is proportional to R_0 [see eq. (5)]. However, when product layer diffusion is limiting, $t(X)$ is proportional to R_0^2 [see eq. (4)]. Borgwardt *et al.* measured the time needed to obtain a conversion extent of 70% and found that this time was proportional to $R_0^{2.4}$. Based on this result they concluded that product layer diffusion is the limiting step in the sulphidation mechanism. In deriving this conclusion they implicitly assumed that sintering did not affect the reactivity at the core surface. However, it is quite well possible that this reactivity drops during sintering as the number of dislocations in the CaO-lattice most probably diminishes during heat treatment. From material sciences it is known that the presence of dislocations increases reactivity. In fact, Borgwardt *et al.* (1984) arrived at a similar conclusion as they found that their best-fit values of D_s were smallest for those samples that were sintered longest: a more ideal CaO-lattice was supposed to result in the formation of a more ideal (and therefore less permeable) CaS-lattice during sulphidation. When the value of the core reaction rate constant k_c indeed decreases during sintering, $t(X)$ will be proportional to R_0^x , with x being greater than unity even in the case of core reaction limitation. Therefore, x being 2.4 is no guarantee that product layer diffusion is the limiting step in the sulphidation mechanism.

The bare fact that some core reaction seems to determine the rate of sulphidation does not yield information to the question whether the product layer is porous or not. When a non-porous layer is formed

reaction (R9) might be the limiting step in the sulphidation mechanism. However, reaction (R10) might be rate determining if a porous layer is formed. By examining the adsorption of H_2S on sulphided limestone, Heesink and van Swaaij (1995) conclude that the layer of sulphided limestone remains porous during conversion. Porosity may be maintained by a continuous process of crack formation.

Based upon our results the following sulphidation mechanism is now proposed. During the initial stage of sulphidation a certain amount of H_2S is rapidly converted at the fresh (and uncovered) CaO-surface resulting in the registration of a relatively large weight increase by the TGA. With the reaction order in H_2S being 0.5, one might suggest that dissociative adsorption precedes reaction, possible fragments being H and HS (Anderson, 1971). In fact, Pell (1971) also suggested the existence of an adsorbed H_2S -layer. However, Pell regarded this layer to be a barrier for further sulphidation which can only be passed at higher temperature. Here it is suggested that this layer is some kind of lock chamber that the H_2S -molecules have to pass before they can react. As conversion proceeds the CaO-surface becomes covered by a porous product layer. As a consequence H_2S can only react at those places where the CaO is not covered by sulphided material. This implies that the sulphidation rate per m^2 of core surface drops once a product layer has been formed. Since this drop is most clearly observed at lower temperatures it is assumed that the porosity of the product layer (and thus the fraction of core surface available for reaction) increases with temperature. This agrees with the conclusions of Duo *et al.* (1994), who examined product layer formation on the basis of crystal growth thermodynamics. It should be noted that the value of k_c as delivered by eq. (6) refers to the sulphidation rate once a product layer has been formed. Since a single value of k_c can be used to calculate the rate of sulphidation over a wide range of conversion, it is concluded that the porosity of the product layer remains practically constant after the first stage of sulphidation. The above theory also explains the necessity to adjust the initial conversion extent in order to obtain good GSD-fits when assuming core reaction limitation: the initial reaction rate per m^2 of core surface is higher than the constant rate which remains when the core surface is partly covered with a product layer. This explanation is not valid in case of grain reaction limitation, making it more likely that the rate of sulphidation is governed by some core reaction and not by a grain reaction.

Our finding that H_2 inhibits the rate of sulphidation agrees with the observations of Borgwardt *et al.* (1984). Whereas Borgwardt *et al.* assumed that the permeability of the solid product layer is reduced by the penetration of H_2 -molecules into this layer, we believe that co-adsorption of H_2 on the CaO surface may cause the inhibiting effect. We presume that the inhibiting effect of CO on sulphidation also is the consequence of competitive co-adsorption at the CaO-surface. Like H_2S , H_2 and CO are assumed to

penetrate through the porous product layer by gaseous diffusion and to be adsorbed by the CaO-surface.

4.4. Sulphidation with COS

The reaction order in COS was determined at 0.18 for a sulphidation temperature of 600°C and at 0.32 for a temperature of 650°C. The observed dependency of the reaction order on temperature is probably caused by adsorption phenomena. Yang and Chen (1979) also examined the reaction between COS and calcined limestone and measured a reaction order of unity in COS at a temperature of 800°C. However, these investigators reported the extremely low activation energy of 18 kJ mol⁻¹ indicating that their TGA-measurements were probably affected by mass transfer limitation. This is quite well possible considering the large samples of about 50 mg that were applied.

The fact that the reaction order in COS depends on temperature implies that the activation energy varies with COS-pressure. Borgwardt *et al.* (1984) measured an activation energy of 130 kJ mol⁻¹ at a COS-pressure of 430 Pa and temperatures ranging from 600 to 900°C. From our results (see Fig. 10) an activation energy of about 125 kJ mol⁻¹ can be derived for the same COS-pressure. When correction is made for the temperature dependency of the reaction order a value of 200 kJ mol⁻¹ is obtained for the activation energy as defined by eq. (1).

The mechanism of the reaction between calcined limestone and COS was investigated by means of the GSD model. Figure 17 shows the results. When assuming that some core or grain reaction is rate determining the calculated conversion extent had to be increased by 0.13, respectively, 0.1 to obtain good fits of the runs performed at 600 and 650°C. Again some reaction at the core surface seems to limit the rate of sulphidation. The best-fit values of k_c , as obtained by simulating five runs at each temperature, obey the following equation:

$$k_c = 6.35 \times 10^4 \exp\left(-\frac{200,000}{RT}\right) \text{ mol}^{1-n} \text{ m}^{3n-2} \text{ s}^{-1} \quad (8)$$

with n being 0.18 and 0.32 at 600 and 650°C, respectively. The activation energy that follows from the simulations amounts to 200 kJ mol⁻¹ and corresponds to the value directly obtained from measurements. The mechanism as described above for the sulphidation with H₂S may also be valid when sulphidation is carried out with COS. Initially, a certain amount of COS is rapidly adsorbed and converted at the fresh CaO-surface. Once a porous product layer has been formed part of the CaO-surface becomes covered and the rate of sulphidation drops. The value of k_c as delivered by eq. (8) refers to this lower rate of reaction.

The conversion vs time curves obtained at 700°C and COS-pressures above about 2000 Pa show a certain overshoot in conversion (see Fig. 11). This overshoot vanishes in time resulting in a conversion extent

Fig. 17. GSD-model predictions together with experimental data obtained during sulphidation with COS (700 Pa): (a) $T = 600^\circ\text{C}$, $k_c = 6.5 \times 10^{-7} \text{ mol}^{0.82} \text{ m}^{-1.46} \text{ s}^{-1}$, $D_s = 6.0 \times 10^{-15} \text{ mol}^{0.82} \text{ m}^{-0.46} \text{ s}^{-1}$, $k_g = 2.1 \times 10^{-6} \text{ mol}^{0.82} \text{ m}^{-1.46} \text{ s}^{-1}$; (b) $T = 650^\circ\text{C}$, $k_c = 2.9 \times 10^{-6} \text{ mol}^{0.68} \text{ m}^{-1.04} \text{ s}^{-1}$, $D_s = 5.0 \times 10^{-14} \text{ mol}^{0.68} \text{ m}^{-0.04} \text{ s}^{-1}$, $k_g = 6.5 \times 10^{-6} \text{ mol}^{0.68} \text{ m}^{-1.04} \text{ s}^{-1}$.

of 100% at the end of each experiment. The described phenomenon suggests that some intermediate product is formed which has a higher molecular weight than CaS and which is able to react with COS towards CaS. We believe that CaCO₃ is that intermediate. It may be formed according to the following side reaction:

The produced CaCO₃ may either be calcined towards CaO, which then reacts towards CaS, or directly react with COS towards CaS. To get a better insight the following test was performed (see Fig. 18). First a calcined limestone sample was sulphided with COS at a temperature of 750°C and a COS-pressure of 2280 Pa in the usual way. At the time that the maximum extent of conversion (i.e. 120%) was reached, the COS supply was stopped (while keeping all other conditions constant) to see whether possibly formed CaCO₃ would calcine. This was hardly the case (see curve B in Fig. 18). Then the supply of COS was restarted yielding curve A (shifted to the left in Fig. 18) which is similar to the curves depicted in Fig. 11. Another sample was then sulphided at equal conditions. Again the COS-supply was stopped at the time that the maximum conversion extent was reached.

Fig. 18. Conversion vs time behaviour during sulphidation with COS at 750°C and a COS-pressure of 2280 Pa: (a) normal run; (b) after stopping the COS-supply; (c) after stopping the COS-supply and subsequent heat treatment at 850°C; (d) like C after re-starting the COS-supply.

Then the temperature was raised to 850°C. This time a decrease in weight was observed. The real extent of sulphidation (corresponding to the weight remaining after calcination) is given by C. After the weight signal had stabilized, the COS-supply was restarted. This resulted in curve D which, like the curves depicted by Fig. 11, shows an overshoot in conversion. Apparently, the product formed during the heat treatment at 850°C shows the same sulphidation behaviour than calcined limestone (i.e. CaO). The obtained results support the theory that CaCO₃ is formed when calcined limestone is sulphided with COS. This CaCO₃ can obviously be calcined towards CaO at temperatures of 850°C (or above) but not at temperatures of 750°C or below. The gradual vanishing of the overshoot in conversion extent observed during sulphidation at temperatures of 750°C or below is therefore thought to be caused by the reaction between CaCO₃ and COS:

$$\text{with } K_{\text{eq}} = 3072 \text{ at } 700^\circ\text{C}. \quad (\text{R12})$$

Though reaction (R11) may also proceed at lower temperatures and/or lower COS-pressures, it only causes an overshoot at temperatures of 700°C or higher and at COS-pressures above about 2000 Pa. This indicates that the rate of CaCO₃-formation [according to reaction (R11)] is more dependent on temperature and/or COS-pressure than the rate by which CaCO₃ is converted towards CaS [according to reaction (R12)]. As far as the dependency on COS-pressure concerns, this agrees with the fact that two COS-molecules are involved in reaction (R11), whereas only one COS-molecule is involved in reaction (R12).

4.5. Sulphidation with mixtures of H₂S and COS

The addition of a small amount of COS to a H₂S-containing gas mixture was found to have a strong inhibiting effect on the sulphidation rate attainable with that gas mixture. To get a better understanding

of this remarkable phenomenon, conversion vs time behaviour observed with H₂S alone and with mixtures of H₂S and COS was simulated with the GSD model. Figure 19 shows a typical result. As to be expected on the basis of the above findings, the sulphidation behaviour obtained when solely H₂S is applied can be best described assuming core reaction limitation. The k_c value that was used to obtain the core reaction limitation fit in Fig. 19(a) is about 60% higher than the value predicted by eq. (6) which was derived from earlier sulphidation experiments. A possible explanation for this discrepancy may be that the calcined limestone samples that were applied to investigate sulphidation behaviour with mixtures of H₂S and COS were much older than those applied for former experiments. Some process might have affected the reactivity of these samples during storage (about 3 months from calcination). Apart from this, the result of Fig. 19(b) is quite remarkable. Not only the sulphidation rate drops when COS is added, but apparently also the sulphidation mechanism changes: whereas some core reaction was found to be rate determining when sulphidation is carried out with either H₂S or COS, product layer diffusion appears to be rate determining when a mixture of H₂S and COS is applied. The formation of CaCO₃, which is induced by the presence of COS according to reaction (R11), is

Fig. 19. GSD-model predictions together with experimental data obtained during sulphidation at 600°C: (a) with H₂S only (2670 Pa), $k_c = 6.5 \times 10^{-6} \text{ mol}^{0.5} \text{ m}^{-0.5} \text{ s}^{-1}$, $D_s = 9.8 \times 10^{-14} \text{ mol}^{0.5} \text{ m}^{0.5} \text{ s}^{-1}$; (b) with H₂S (2670 Pa) and COS (170 Pa), $k_c = 3.5 \times 10^{-6} \text{ mol}^{0.5} \text{ m}^{-0.5} \text{ s}^{-1}$, $D_s = 5.0 \times 10^{-14} \text{ mol}^{0.5} \text{ m}^{0.5} \text{ s}^{-1}$.

thought to play a role in this. CaCO_3 not only has a larger molecular volume than CaS (3.69×10^{-5} vs $2.76 \times 10^{-5} \text{ m}^3 \text{ mol}^{-1}$ for CaS) but also is more susceptible to sintering because of its relatively low melting temperature (1340°C vs 2450°C for CaS). Although no CaCO_3 remains after complete conversion because it reacts with COS or H_2S towards CaS , its temporary presence may reduce the permeability of the product layer by contributing to the formation of bridges between pieces of material that are separated by small gaps or pores. In this way, product layer diffusion may become the rate determining step in the sulphidation mechanism. The fact that some core reaction and not product layer diffusion was found to be rate determining when sulphidation is performed with COS only (though CaCO_3 is also formed then) might indicate that the sintering of CaCO_3 is enhanced by the presence of H_2S as was suggested by Illerup *et al.* (1993). Another explanation for this apparent discrepancy is obtained when the reaction rates of H_2S and COS are compared. For a temperature of 600°C eqs (6) and (8) deliver k_c -values of $3.6 \times 10^{-6} \text{ mol}^{0.5} \text{ m}^{-0.5} \text{ s}^{-1}$ and $6.9 \times 10^{-7} \text{ mol}^{0.82} \text{ m}^{-1.46} \text{ s}^{-1}$ for H_2S and COS , respectively. H_2S thus reacts faster than COS . Therefore, at equal product layer permeability, core reaction limitation can be observed when sulphidation is carried out with COS , whereas product layer diffusion limitation is observed when sulphidation is carried out with H_2S (or a mixture of H_2S and COS).

5. CONCLUSIONS

The sulphidation of calcined limestone with H_2S , COS and mixtures of H_2S and COS has been studied at temperatures between 500 and 700°C . The reaction order in H_2S was found to be 0.5 at all applied temperatures, whereas the order in COS appeared to be dependent on temperature: 0.18 at 600°C and 0.32 at 650°C . The activation energy of sulphidation was determined at 160 and 200 kJ mol^{-1} for H_2S and COS , respectively. It was found that sulphidation with H_2S is inhibited by the presence of COS , H_2 and CO . Indications were obtained for the side reaction $\text{CaO} + 2 \text{COS} \rightarrow \text{CaCO}_3 + \text{CS}_2$ to proceed when sulphidation is carried out with COS .

The mechanism of sulphidation was investigated by means of the GSD model. From model simulations it appeared that some reaction at the surface of the unreacted CaO -core most probably determines the rate of sulphidation when either H_2S or COS are applied. During the initial stage of sulphidation reaction takes place at the entire CaO -surface. However, as conversion proceeds the CaO -core becomes partly covered by a product layer which is assumed to remain porous. Reaction then only takes place at the uncovered parts of the CaO -surface. The porosity of the product layer and consequently the fraction of CaO -surface available for reaction are assumed to be higher at increasing temperature. Competitive co-adsorption of H_2 or CO at the CaO -surface is believed

to cause the inhibiting effect of these compounds on sulphidation.

When sulphidation is carried out with a mixture of H_2S and COS , product layer diffusion was found to be rate determining. This change in mechanism is thought to be caused by the formation of CaCO_3 (induced by the presence of COS) and the subsequent sintering of this CaCO_3 which reduces the permeability of the product layer.

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NOTATION

A	specific surface area, $\text{m}^2 \text{ kg}^{-1}$
C	concentration of H_2S and/or COS in the gas bulk, mol m^{-3}
D_s	product layer diffusivity, $\text{mol}^{1-n} \text{ m}^{3n-1} \text{ s}^{-1}$
E_{act}	activation energy, J mol^{-1}
F	pore-to-sphere factor, dimensionless
k_c	reaction rate constant of the core reaction, $\text{mol}^{1-n} \text{ m}^{3n-2} \text{ s}^{-1}$
k_g	reaction rate constant of the grain reaction, $\text{mol}^{1-n} \text{ m}^{3n-2} \text{ s}^{-1}$
k_A	Arrhenius constant, $\text{m}^{3n} \text{ mol}^{-n} \text{ s}^{-1}$
K	expansion factor, dimensionless
K_{eq}	equilibrium constant, dimensionless
n	reaction order in gaseous reactant, dimensionless
N_0	initial concentration of solid reactant in grains, mol m^{-3}
P	(partial) pressure, Pa
R	gas constant, $\text{J mol}^{-1} \text{ K}^{-1}$
R_0	initial radius of grain, m
t	time, s
T	temperature, K
X	conversion, dimensionless
$V_{\text{sol, reac}}$	molecular volume of solid reactant, $\text{m}^3 \text{ mol}^{-1}$
$V_{\text{sol, prod}}$	molecular volume of solid product, $\text{m}^3 \text{ mol}^{-1}$

Greek letters

$\rho_{\text{sol, reac}}$	density of solid reactant, kg m^{-3}
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