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Thermogravimetric combined with mass spectrometric studies on the oxidation of calcium sulfide

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Abstract

The oxidation of CaS particles has been investigated by means of a thermogravimetric analyzer combined with a mass spectrometer, especially under fluidized bed combustion conditions. The products are $CaSO_4$ or both $CaSO_4$ and CaO, depending on the temperature and O_2 concentration. The oxidation reaction results in the evolution of SO_2 when CaO is formed in the products. The conditions under which the undesirable SO_2 will be released, or not, have been obtained. There is always an overall sample weight gain, even when SO_2 is evolved during the reaction. The investigation of the kinetics of the CaS oxidation in the no SO_2 releasing conditions shows that the oxidation reaction is of first order with respect to O_2, and a higher conversion can be achieved at higher temperature and by reducing the particle size. The maximum conversion of CaS to $CaSO_4$ is 48.67% in 60 min at 865°C and 4 vol% O_2 in N_2 for 17 μm CaS particles. The rate constant and the effective product layer diffusivity are 4.1×10^{-4}–2.88×10^{-3} m s^{-1} and 3.15×10^{-11}–4.39×10^{-10} m^2 s^{-1} at 500–865°C in the light of the shrinking unreacted core model for gas–solid reaction, the former yielding an activation energy of 39.5 kJ mol^{-1} for the CaS oxidation reaction. © 1997 Elsevier Science B.V.

Keywords: Calcium sulfide; Kinetics; Mass spectrometer; Oxidation; TG

1. Introduction

There is a growing interest in the disposal of calcium sulfide [1–5]. It is formed when limestone or dolomite is used to remove H_2S released from coal gasification. High efficiency advanced electric power generation systems, such as integrated coal gasification combined cycle (IGCC) and the second generation pressurized fluidized bed combustion (2G PFBC), involve a coal gasification or partial gasification step. Recently, calcium sulfide was found in bed ashes from stationary and circulating fluidized bed boilers when SO_2 was captured in situ by limestone [6–8].

Calcium sulfide is not stable. It can react with acid leachate or water releasing H_2S to the atmosphere. Therefore it is imperative to oxidize calcium sulfide to stable calcium sulfate which is environmentally more acceptable compound for disposal.

The oxidation of CaS can occur through the following reaction

$$CaS(s) + 2O_2(g) \rightarrow CaSO_4(s) \qquad (1)$$

Besides reaction (1), there is a possibility that SO_2 evolves according to the reaction

$$CaS(s) + \tfrac{3}{2}O_2(g) \rightarrow CaO(s) + SO_2(g) \qquad (2)$$

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or according to the apparent solid–solid reaction

$$CaS(s) + 3CaSO_4(s) \rightarrow 4CaO(s) + 4SO_2(g) \quad (3)$$

Torres-Ordonez et al. [9] studied the oxidation of CaS crystals using a laminar flow oxidation furnace and suggested that the reaction was of first order in bulk O_2 partial pressure 0–0.2 atm at 1127°C and 0–0.1 atm at 1227–1477°C and the oxidation of CaS resulted in the formation of CaO and $CaSO_4$. Davies et al. [1] investigated the oxidation of pure (99.99%) CaS of mean particle size 45 µm with an atmosphere thermobalance and found that below 850°C no SO_2 was released significantly, but in the temperature range 850–1050°C although $CaSO_4$ was formed, CaO was also produced with the evolution of SO_2. The conversions of CaS to $CaSO_4$ at 850°C and 950°C after 30 min of oxidation with 4.2 vol% O_2 were about 8 and 32%, respectively. They attributed the SO_2 evolution to the apparent solid–solid reaction (3). Ninomiya et al. [4] observed the evolution of SO_2 above 1063°C as sulfided limestone particles were oxidized in 21 vol% O_2 applying thermal analysis. They found that the oxidation reaction of CaS began from about 600°C. Below 1063°C, the outside shell of the sample got covered with a $CaSO_4$ product layer and the oxidation reaction ceased due to increasing intraparticle diffusional resistance to the reactant gas. As a result of the large diffusional resistance, 10 to 50% of unreacted CaS remained inside the shell. Abbasian et al. [2] explored the sulfation of partially sulfided calcium-based sorbents with an atmosphere thermobalance with a gas mixture containing 5.25 vol% O_2. They reported that the conversion of CaS to $CaSO_4$ increased in the temperature range of 820 to 900°C and the maximum conversion to $CaSO_4$ was different for partially sulfided limestone particles with different sulfidation levels. In a later research, Abbasian et al. pointed out that at 980°C the conversion to $CaSO_4$ decreased to below 12% for sulfided limestone, dolomite and dolomitic limestone because of a significant SO_2 production [3].

The objective of this study was to characterize experimentally the reaction process between calcium sulfide and oxygen, and determine the kinetics of the oxidation of calcium sulfide especially under fluidized bed combustion conditions by means of a thermogravimetric analyzer coupled with a mass spectrometer. A theoretical model was employed to obtain the kinetic parameters.

2. Experimental

2.1. Chemicals

CaS particles used in the present work contained 98% CaS (Alfa). The CaS particles were selected and ground into three particle sizes: 17, 30 and 42 µm. The particle sizes were measured by the laser beam diffraction method (2600 particle sizes, Malvern Instrument).

2.2. Instrumentation

An ambient-pressure thermogravimetric analyzer (Mettler TA1 apparatus with a middle range quartz furnace and controlled atmosphere accessary) with a computer-aided data evaluation system was used to study the oxidation of CaS particles while the SO_2 concentration in the outlet gas was monitored simultaneously employing a quadrupole mass spectrometer (Balzers QM311).

The desired inlet gas mixtures of O_2 and N_2 were obtained from the appropriate flow rates through precalibrated rotameters. The gas-flow rate was predetermined so that the effect of the gas-film diffusion was minimized. A platinum–platinum 10% rhodium standard thermocouple was used to measure the temperature near the reaction site, below a platinum crucible sample holder (diameter 12 mm, depth 3 mm). About 30 mg of the CaS sample was placed centrally in the sample holder for each run. A small portion of the outlet gas flow was introduced into the quadrupole mass spectrometer through a capillary sampling tube (diameter 0.5 mm, length 75 mm). There are two modes of operation of the mass spectrometer. It can either be operated at mass scan (1–100 mass/charge/(m/e) scale) predetermined (m/e) limits and sweep rates (1 amu s^{-1}, atomic mass unit), or a continual measurement of a single gas with predetermined (m/e) ratio. For the purpose of this study the latter was chosen. In order to verify that $CaSO_4$ and CaO (if reaction (2) or (3) occurred) were the only products formed, the solid products from the experiments were analyzed by means of X-ray powder diffraction. X-ray diffraction was performed using a modern powder diffractometer (D5000, Siemens, Karlsruhe, Germany). The diffractometer is equipped with a position sensitive detector (PSD).

2.3. Procedure

The oxidation experiments were conducted based upon two experimental procedures. In the first procedure attention was focused on the determination of the conditions under which reaction (2) or (3) would take place or not. In other words, the temperature and the O_2 concentration which resulted in the evolution of SO_2 were determined. In this procedure the sample was heated at 10°C min^{-1} up to a maximum temperature (1000°C). The sample was exposed to the reactant gas with 1–40 vol% O_2 concentration. The experimental procedure two was adopted to perform time-resolved oxidation experiments. This consists of heating the sample at 30°C min^{-1} to a predetermined temperature, establishing isothermal condition with a gas stream of nitrogen, and then changing the gas to the gas mixture containing the desired O_2 concentration. The isothermal reaction temperature of the time-resolved experiments was varied from 500 to 865°C. The gas-flow rate in all tests was 600 cm^3 min^{-1}. In the experimental procedures, the mass spectrometer was operated in a single ion mode, permitting the simultaneous monitoring of SO_2 as it evolved during the reaction. At the end of the oxidation reaction, the solid products were allowed to cool to ambient temperature under nitrogen. Subsequently, the products were immediately analyzed by X-ray diffraction.

3. Results

3.1. The evolution conditions of SO_2

A series of tests was conducted with CaS particles of 42 μm to determine the conditions under which SO_2 evolved as the CaS was oxidized according to the experimental procedure one. The results are presented in Fig. 1. It was found that at lower temperature and higher O_2 concentration the product tended to be $CaSO_4$ and no SO_2 was detected by mass spectrometer, whereas when the temperature increased above 865°C with 1 vol% O_2 concentration or above 873°C with 4 vol% O_2 concentration the oxidation reaction resulted in SO_2 evolution. Fig. 1 shows that SO_2 was always released above 920°C. The release of SO_2 indicated that reaction (2) or (3) took place and CaO was formed. It should be noted that the sample weight continued to increase after significant SO_2 evolution appeared and an overall weight gain always occurred within the range of the experimental temperature. This means that the $CaSO_4$ was still formed as reaction (2) or (3) occurred. The kinetics of the oxidation reaction of CaS particles could, therefore, be explored in the TG under the conditions under which SO_2 did not evolve, and only $CaSO_4$ was formed according to reaction (1).

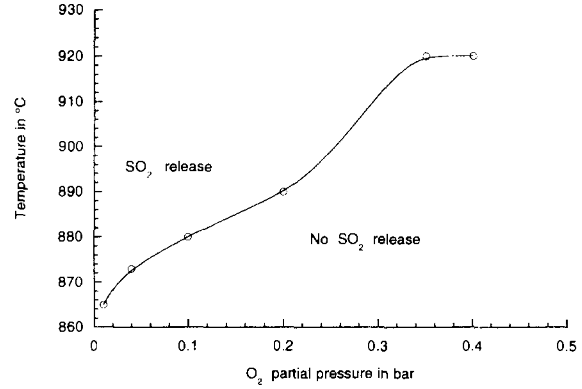

Fig. 1. The effect of O_2 concentration and temperature on SO_2 release as the oxidation of the CaS proceeds.

3.2. Kinetics of $CaSO_4$ formation during the CaS oxidation

The usual way to perform time-resolved experiments, assessing the rate of reaction by the isothermal method, is to measure the weight changes (corrected for buoyancy effect) as a function of time. All TG curves were calculated to $CaSO_4$ conversions vs. the reaction time. The conversions of CaS to $CaSO_4$ were investigated with essentially pure CaS as functions of the reaction time, temperature, particle size and oxygen concentration, and presented in Figs. 2–4, respectively.

Fig. 2 shows that the overall rate of the oxidation reaction is strongly influenced by the temperature in the range of 500–865°C with 4 vol% O_2 concentra-

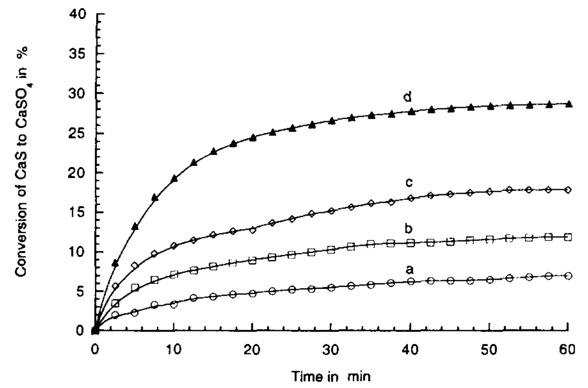

Fig. 2. The effect of temperature on the conversion of CaS to $CaSO_4$ for the oxidation of the CaS. Gas composition: 4 vol% O_2 in N_2. Temperature: a – 500°C; b – 750°C; c – 800°C; and d – 865°C.

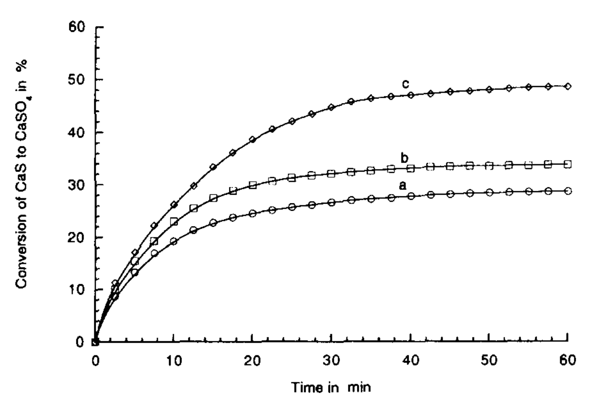

Fig. 3. The effect of particle size on the conversion of CaS to $CaSO_4$ during the CaS oxidation. Gas composition: 4 vol% O_4 in N_2. Temperature: 865°C. Particle size: a – 42 μm; b – 30 μm; and c – 17 μm.

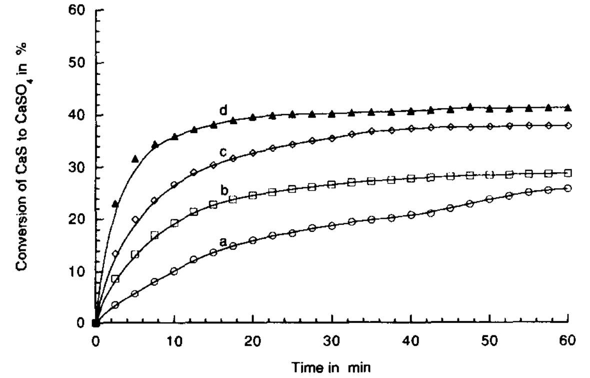

Fig. 4. The effect of O_2 partial pressure on the conversion of CaS to $CaSO_4$ for the CaS oxidation. Temperature: 865°C. Gas composition: a – 1 vol% O_2 in N_2; b – 4 vol% O_2 in N_2; c – 20 vol% O_2 in N_2; and d – 40 vol% O_2 in N_2.

tion. The lower reaction rates at lower temperatures are expected because of the lower reaction rate constant at lower temperatures. The sulfation rate is reasonably slow at 500°C. The result that the extent of the reaction increased clearly with temperature indicated that CaS particles should be oxidized at higher temperature in the no SO_2 release region, as shown in Fig. 1. The rate was high in the initial stages of the oxidation, and then decreased gradually as the sulfation reaction proceeded. The initial rapid rate resulted from the larger area of CaS particles, acting in combination with a fairly fast intrinsic kinetics. The decrease of reaction rate with time was due to the build-up of a continuously growing $CaSO_4$ product layer, which increased the intraparticle diffusional resistance to oxygen. The effect of CaS particle size on the oxidation was investigated at 865°C in the oxidizing atmosphere of 4 vol% O_2. The particle size was varied between 17–42 μm. In Fig. 3, the results from different particle size tests are shown and it can be seen that CaS particle size has an influence on both the oxidation rate and the maximum conversion. The decrease in CaS particle size produced an increase in the initial reaction rate and the final conversion. A 48.67% maximum conversion was obtained for 17 μm CaS particles in 60 min. The explanation is that the smaller particles have larger surface area over which the reaction can take place, smaller diffusional resistances of O_2 through the product layer and gas film.

Some experiments were conducted with different oxygen concentrations at 865°C. The experiments also lasted 60 min. The oxygen concentration was varied between 1–40 vol%. Fig. 4 shows that the oxidation rate increases as oxygen concentration increases. Reaction (1) proved to be of approximately first order with respect to O_2, as analysed later. When O_2 concentration was higher than 15 vol%, in addition to the rapid initial rate, a rise in particle temperature was found from DTA curve, due to the exothermicity of the reaction. Because of the small size of the sample particles and the cooling effect of the gas flow, no large temperature rise was observed during the oxidation experiments. Although there was some rise in particle temperature, no SO_2 evolution was detected. The reason is probably that the oxygen concentration was higher accordingly.

3.3. *X-ray diffraction*

The products of the reaction between the CaS particles and O_2 in TG were usually analysed using X-ray diffraction. The results obtained by X-ray diffraction showed excellent agreement with the above results from thermogravimetric combined with mass spectrometric analyses, that is, $CaSO_4$ was the only product formed when SO_2 was not evolved during the oxidation reaction while both $CaSO_4$ and CaO were formed when the evolution of SO_2 was detected during the reaction. Besides $CaSO_4$ or $CaSO_4$ and CaO, there was also a considerable amount of unreacted CaS in the samples, as expected.

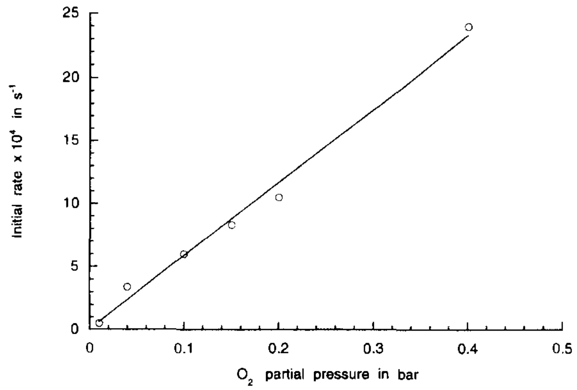

Fig. 5. The initial rate of reaction (1) as a function of O_2 concentration. Temperature: 865°C.

4. Discussion

Fig. 1 indicates that at lower temperature and higher O_2 concentration the product of the CaS particle oxidation is $CaSO_4$ and no SO_2 is released, as mentioned earlier, and when the temperature is beyond the limit the reaction leads to the undesirable evolution of SO_2 and the products are both $CaSO_4$ and CaO. The above results are in agreement with the thermodynamic stability diagram for the system $CaSO_4$-CaO-CaS [5]. According to the $CaSO_4$-CaO-CaS stability diagram, the variation of the SO_2 concentration will also have an effect on the products of the oxidation reaction. When the SO_2 concentration in the atmosphere increases the product tends to be $CaSO_4$, otherwise CaO will be formed during the oxidation. Lynch and Elliott [10] demonstrated the influence of O_2 and SO_2 on the processes involved in the oxidation of CaS at around 1300°C and they explained that the oxidation of a CaS pellet might initially involve the formation of CaO and SO_2, followed by the formation of the sulfate because of an increase in SO_2 concentration near the reaction front. Lynch and Elliott observed the sample's weight loss with the formation of CaO and SO_2 at relatively high temperature. In the present investigation the experiments were conducted below 1000°C, which is suitable for fluidized bed combustion conditions. The weight loss was not found even when significant release of SO_2 was detected. There was always an overall weight gain, which suggested that the formation of $CaSO_4$ was kept on to some extent in spite of the SO_2 liberation. An explanation may be that while the reaction front moves toward the centre of the particle SO_2 produced through reaction (2) or (3) is taken up in part by the layer of CaO in the outer region of the particle in the presence of counter-diffusing O_2 at 850–1000°C according to reaction [1]:

$$CaO(s) + SO_2(g) + \tfrac{1}{2}O_2(g) \rightarrow CaSO_4(s) \qquad (4)$$

Another observation worthy to be pointed out is that the apparent solid–solid reaction (3) plays an important role in the SO_2 release during the CaS oxidation. This is the subject of separate studies to be published soon.

The order of the oxidation reaction was examined with respect to O_2 at 865°C, O_2 concentration ranging from 1 to 40 vol% in N_2. The initial rate of reaction (1) was obtained from the initial slope of the mass plots against time. The slope was divided by the initial sample's weight to a normalised rate, which was then plotted against the corresponding O_2 concentration, as shown in Fig. 5. It can be seen in Fig. 5 that a satisfactory linear fit can be made, which indicates that reaction (1) is of first order with respect to O_2. The same conclusion was reached by Davies et al. [1]. Davies et al. also reported that during the initial period, each mass plot was slight sigmoidal. They explained that the phenomenon was probably due to the exothermicity of the reaction and the subsequent rise in particle temperature, which resulted in the increase in the rate of reaction with time. In this work no clear sigmoidal picture was observed, perhaps because of the good cooling effect of the gas flow.

To describe the kinetics of the oxidation reaction of the CaS particles the shrinking unreacted core model [11] has been used here. The basic assumptions of the model are as follows: The reaction occurs at the sharp interface between the outer product layer and the unreacted core of the solid. The reaction is irreversible and of first order. The influence of external mass transfer is neglected [1]. The relationship between conversion x and time t can be expressed as

$$\frac{t}{\tau} = g(x) + \sigma^2 p(x) \tag{5}$$

where τ is the reaction time for complete conversion ($x = 1$) in the absence of diffusional resistance, σ the ratio of diffusional to chemical reaction resistance, $g(x)$ the conversion function under complete chemical control and $p(x)$ the conversion function under complete diffusion control. τ and σ are given by

$$\tau = \frac{2\rho_{\mathrm{ms}} R_{\mathrm{p}}}{k_{\mathrm{s}} C} \tag{6}$$

and

$$\sigma = \sqrt{\frac{k_{\mathrm{s}} R_{\mathrm{p}}}{6 D_{\mathrm{e}}}} \tag{7}$$

where ρ_{ms} is the CaS solid molar density (kmol m^{-3}), R_{p} the initial particle radius (m), C the O_2 concentration (kmol m^{-3}), k_{s} the rate constant for surface reaction (m s^{-1}) and D_{e} the effective product layer diffusivity (m^2 s^{-1}). For spherical particles, the conversion functions $g(x)$ and $p(x)$ are

$$g(x) = 1 - (1 - x)^{1/3} \tag{8}$$

and

$$p(x) = 3\left[\frac{Z - (1 + Zx - x)^{2/3}}{Z - 1} - (1 - x)^{2/3}\right] \tag{9}$$

Table 1

Values of the rate constant for surface reaction k_{s} and the effective product layer diffusivity D_{e}

Temperature (°C)	$k_{\mathrm{s}} \times 10^{-3}$ (m s^{-1})	$D_{\mathrm{e}} \times 10^{-10}$ (m^2 s^{-1})
500	0.41	0.315
750	1.84	2.27
800	2.46	1.94
865	2.88	4.39

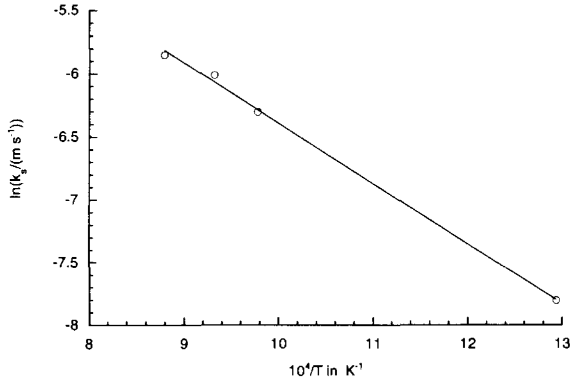

Fig. 6. Arrhenius plot for the rate constant k_{s} of reaction (1).

with Z being the ratio of the molar volume of product solid to that of reactant solid, for $CaSO_4$ and CaS, $Z = 1.8$. This means that the particle size will become larger as the oxidation reaction proceeds. The kinetic parameters k_{s} and D_{e} were obtained by fitting the calculations of the above model to the experimental conversions versus time with a least-squares method for different reaction conditions [11]. The resulting values of k_{s} and D_{e} are listed in Table 1. The rate constant, k_{s} is also presented in the usual Arrhenius coordinates in Fig. 6, yielding an activation energy of 39.5 kJ mol^{-1}. The activation energy is relatively low and can lead to reaction (1) being fast if only chemical kinetics is taken into consideration. Moreover, for oxidation reaction (1), ΔH^0 is -951.7 kJ mol^{-1} at 25°C, ΔG^0 is -844.6 kJ mol^{-1} at 25°C and -547.92 kJ mol^{-1} at 850°C. Therefore, there is no thermodynamic constraint to the exothermic reaction. The activation energy of reaction (1) was given by Davies et al. [1] as 47 ± 12 kJ mol^{-1} according to the initial rate of the reaction, and the rate constant calculated was $2.2 \pm 1.0 \times 10^{-6}$ m s^{-1} at 800°C. It can be seen in Table 1 that no clear activated mechanism for the product layer diffusion was found, whereas it was proposed that the diffusion through the $CaSO_4$ product layer occurred via an activated mechanism for the reaction between CaO or $CaCO_3$ and SO_2 in the presence of O_2 [12,13]. The lack of an activation energy suggests that the process of the product layer diffusion could involve reactant gas being transported through the solid product rather than the diffusion of ions [14,15], which would perhaps have an associated activation energy. Nevertheless, the product layer diffusion significantly controlled the oxidation of CaS particle after a $CaSO_4$ product layer outside the sample particle was formed. Without any SO_2 formation, a complete conversion of CaS to $CaSO_4$ is difficult to achieve, particularly for large CaS particles. If a fluidized bed is used to oxidize CaS particles, collision and friction between the particles as a consequence of fluidization may make the $CaSO_4$ product layer break away to some extent, lowering the product layer resistance. In that case a higher extent of the reaction can be expected.

5. Conclusions

The oxidation of CaS particles was studied using a thermogravimetric analyzer combined with a mass spectrometer at 500–1000°C with 1–40 vol% O_2 concentration in N_2, in particular at the operation temperature of fluidized bed combustor. The products of the reaction were found to be $CaSO_4$ or both $CaSO_4$ and CaO, depending on the temperature and O_2 concentration. When both $CaSO_4$ and CaO were formed, evolution of SO_2 occurred, but there was an overall sample weight gain. The conditions under which SO_2 would release or not during the oxidation reaction were determined over a relatively wide range. At lower temperature and higher O_2 concentration the product is inclined to be the sulfate. If temperature is beyond some limit with a fixed O_2 concentration the undesirable liberation of SO_2 and the formation of CaO is inevitable. For instance, the limits are 865°C with 1 vol% O_2 concentration and 873°C with 4 vol% O_2 concentration. As O_2 concentration increases, so does the temperature at which SO_2 is evolved, but the evolution of SO_2 will always take place above 920°C at any O_2 concentration within 40 vol%. The kinetics was investigated when only $CaSO_4$ was formed. The oxidation reaction was found to be of approximately first order with respect to O_2. A higher conversion of CaS to $CaSO_4$ can be achieved by the reduction of CaS particle size and at higher temperature in the range of no SO_2 release. A 48.67% conversion of CaS to $CaSO_4$ has been achieved for 17 μm CaS particle at 865°C with 4 vol% O_2 concentration in 60 min. The kinetic parameters k_s and D_e are obtained using the shrinking unreacted core model for gas–solid reaction. The effect of temperature on the CaS oxidation is correlated by the activation energy of 39.5 kJ mol^{-1} for the reaction forming only $CaSO_4$, which is fairly low and would lead to a fast reaction process from the point of view of chemical kinetics. Reaction (1) appears to be controlled significantly by the product layer diffusion when a certain $CaSO_4$ product layer is yielded, since the value of D_e is quite limited.

Acknowledgements

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