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The influence of carbon monoxide on the reaction between sulphur dioxide and calcium oxide

S. Ghardashkhani and O. Lindqvist

Department of Inorganic Chemistry, Chalmers University of Technology and University of Göteborg, S-412 96 Gothenburg (Sweden)

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Abstract

The influence of carbon monoxide on the reaction between SO_2 and CaO prepared from reagent grade $CaCO_3$ and two different naturally occurring limestones was investigated using thermogravimetric analysis, mass spectrometry, X-ray diffraction and infrared spectroscopy. The experiments covered the temperature range 600-950 °C with SO_2-CO-N_2 mixtures varying from 0.1% to 0.9% SO_2 and from 1% to 9% CO, with N_2 providing the balance.

The reaction between SO_2 and CaO in the presence of CO led initially to the formation of a mixture of $CaSO_4$, $CaSO_3$ and CaS. The formation of $CaSO_3$ and $CaSO_4$ increased with increasing SO_2 concentration at a given CO concentration and temperature. The product composition changed from a mixture of $CaSO_3$ and $CaSO_4$ to CaS as sole product, by increasing temperature and/or increasing CO concentration. The rate at which a complete conversion of CaO to CaS occurred was relatively fast. The results also suggested that the extent of the overall conversion of CaO to the product compounds, particularly CaS, differed between reagent grade $CaCO_3$ and natural limestones. The formation of $CaSO_3$ as an intermediate, followed by direct reduction to CaS, is discussed and is assumed in a proposed reaction pathway.

INTRODUCTION

The combustion of fossil fuels, particularly coal, for the production of steam power is known to be a major source of sulphur dioxide. Atmospheric fluidized bed coal combustion (AFBC) represents, however, a method for burning coal without significant sulphur oxide emissions. This is achieved through the addition of calcium-based sorbents such as limestone or dolomite which undergo a rapid calcination in the combustion environment, resulting in porous oxides, prior to the desulphurization process.

The reaction between calcium oxide (CaO) and sulphur dioxide has been the subject of numerous investigations. For the most part previous investigations have focused on this reaction under oxygen-rich conditions [1]. Although reducing atmospheres are also inherent in AFBC [2-4], the influence of reducing environments on the desulphurization reaction has

TABLE 1
The physical and chemical properties of the calcareous materials

Major chemical constituent (wt.%)	$CaCO_3$ Reagent grade	Ignaberga limestone	Messinghauser limestone
Ca		38.87	32.36
Mg		0.39	0.97
Fe		0.00	0.97
K		0.05	1.00
Na		0.02	0.10
Si		0.32	5.18
Al		0.45	2.20
$CaCO_3$ content (wt.%) [a]	98.70	96.80	78.30
Particle size (μm)	10–20	4–5	10–20
BET surface area (m^2g^{-1}) [b]	10.5	14.85	9.64

[a] $CaCO_3$ content represents an average weight loss of calcination of 15 samples.
[b] BET surface area represents an average of 5 calcined samples.

not yet been fully examined. In this study, carbon monoxide was used to simulate reducing conditions in AFBC and the resulting effect on the CaO/SO_2 reaction was investigated. The reaction between SO_2 and CaO in the presence of CO can be described by the overall reaction

$$CaO(s) + 3CO(g) + SO_2(g) \rightleftharpoons CaS(s) + 3CO_2(g) \quad (1)$$

Thermodynamic calculations show that this reaction from left to right is exothermic [5].

EXPERIMENTAL

Reagent grade $CaCO_3$ (Merck, 99%) and two different natural limestones, Ignaberga and Messinghauser limestone, were used to prepare samples of CaO. The limestones were ground and sieved through a < 63 μm sieve and the actual particle sizes were determined by laser spectroscopy (Mellvan instrument, 2600 particle sizes). Table 1 gives the characteristics and the major chemical constituents of the materials as determined by atomic absorption spectroscopy (AAS). High purity grade sulphur dioxide (2% SO_2 in N_2), nitrogen and carbon monoxide (20% CO in N_2 and 100% CO) were used to blend the desired gas mixtures by adjusting the appropriate flow rates using precalibrated rotameters. The reaction progress was followed by thermogravimetric analysis, TGA (Mettler TA1 apparatus with a middle-range quartz furnace located vertically and equipped with a controlled atmosphere accessory). The feed gas entered from the top of the quartz furnace and passed downwards in contact with the sample. The balance housing was protected by an N_2 purge during all experiments. A platinum–platinum,10% rhodium standard thermocouple was used to measure the temperature near the reaction site, below a platinum semi-spherical crucible sample holder (diameter 15 mm, depth 10 mm). Approximately 40 mg samples of reagent grade $CaCO_3$, 43 mg of Ignaberga and 52 mg of Messinghauser limestone (i.e. equal amounts of $CaCO_3$) were placed in the sample holder for each run. The solid products of the reactions were analysed by X-ray powder diffraction (XRD, Huber vertical Guinier Camera 620) and Fourier transform infrared spectroscopy (IR) (FTIR, Mattson Polaris FTIR system) using the KBr pellet technique. In addition, the gas composition from several TGA experiments was analysed simultaneously employing a quadrupole mass spectrometer (Balzers QMS 311) equipped with a by-pass gas system.

Procedure

Calcium oxide (CaO) was prepared by calcining a preweighed sample of calcareous material under nitrogen (flow rate of 200 ml min^{-1} at 25 ° C) in the TG apparatus. Heating of the furnace was carried out at a rate of 25 ° C min^{-1} up to 850 ° C, at which temperature virtually complete calcination was achieved, and the amount of CaO present in each sample was determined from the total weight loss measured. At this point the N_2 flow rate was readjusted to the total flow rate of the reacting gas mixture. This was done in order to minimize the buoyancy effect experienced by the balance when the exchange between the N_2 and the reacting gas mixture was made. The sample was kept under this N_2 flow rate at the same temperature (850 ° C) for about 10 minutes. The temperature of the furnace was then reset to the desired reaction temperature (heating or cooling rate of 25 ° C min^{-1}) and when temperature equilibration was observed the N_2 flow was instantaneously changed to the reacting gas mixture using four port valves. The total reaction time was set to 120 min for all experiments unless otherwise stated.

During some TGA experiments, simultaneous gas analyses were carried out for the first 20 minutes of reaction time by a mass spectrometer at a scan speed of 1 a.u. s^{-1} from m/z 38 to 68 which covers the responses of Ar (40, atomic weight), CO_2 (44), SO (48), COS (60) and S_2 (64) or SO_2 (64). The interference of S_2 (64) with SO_2 (64) was avoided by choosing the SO (48) responses resulting from the ionization of SO_2 to SO and O [6] as the measure of SO_2 concentration. The reacting gas mixture was always analysed through a by-pass gas system before the start of the reaction and after the reaction was terminated.

The quantity of $CaSO_4/CaSO_3$ formed after the reaction was terminated was determined through weight changes (corrected for buoyancy effects) by reducing the solid products to CaS using 100% CO at a flow rate of 200 ml min^{-1} and a temperature of 850 ° C (any temperature adjustment was effected by heating or cooling at a rate of 10 ° C min^{-1}) for all experiments. Although the presence of $CaSO_3$ could be detected by IR spectroscopy in some samples reacted over temperatures of 600–950 °C, a quantitative determination was not possible for those samples reacted at > 700 °C due to the low $CaSO_3$ levels.

In other similar experiments, the samples were allowed to cool to ambient temperature at the end of the reaction time under N_2 at an average cooling rate of 100 °C min^{-1}. The samples were then removed from the TG apparatus and analysed by FTIR and XRD.

RESULTS

From the XRD and FTIR analyses of the solid reaction products, it was evident that some experiments showed formation of virtually pure CaS whereas in other cases a mixture of $CaSO_4$, $CaSO_3$ and CaS could be detected. Thus a molecular conversion on the basis of eqn. (1) for all experiments could not be simply made due to the existence of different molecular weights. Therefore, the TGA results plotted in the figures (1–4, 7 and 9) are in terms of percent weight gain against time, which refers to the weight gain per initial amount of CaO present in each sample. Although this treatment gives an overall measure of the reactions taking place, it should be noted that the rates discussed below refer to a weight gain and not a molecular conversion.

Reagent grade $CaCO_3$

The effect of flow rate on the rate of weight increase for the experiments with reagent grade $CaCO_3$ at 850 °C with 1% CO and 0.3% SO_2 in N_2 is shown in Fig. 1. It was found that the weight gain of the sample increases sharply in the initial stage, but passes through a maximum and begins to slowly decline without stabilizing after 120 minutes. On increasing the flow rate from 400 to 500 and 600 ml min^{-1}, the initial and overall rates of weight gain were slightly affected. This effect was presumably caused by the external mass transfer of the bulk SO_2 gas to the surface of the CaO sample matrices [7] and/or the effect of SO_2 diffusion through the non-dispersed CaO sample. Hence gas mixtures at flow rates of 600 ml min^{-1} were used throughout this work. In addition, during the course of the experiments, some elemental sulphur (S(s)) deposition on the cooler parts of the quartz furnace always occurred; this was assumed to be the product of a side reaction between SO_2 and CO.

The influence of CO concentration on the rate of weight gain was examined at a fixed SO_2 concentration of 0.3%, in balance N_2, and at a temperature of 850 °C. The results are presented in Fig. 2. The results suggested that the CO concentration between 1% and 3% had a slight effect on the rate of weight gain, whereas increasing the CO concentration

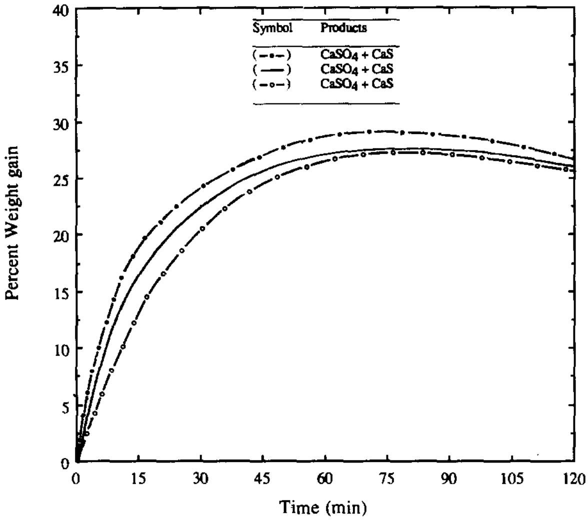

Fig. 1. The effect of flow rate on the rate of weight gain at 850 °C with 1% CO and 0.3% SO_2 in balance N_2 using CaO (derived from reagent grade $CaCO_3$): (o), 400 ml min^{-1}; (————), 500 ml min^{-1}; and (•), 600 ml min^{-1}.

from 3% to 9% did not significantly affect the initial or overall rates and the rates were approximately constant up to a stable equilibrium level. The IR and XRD analyses revealed the presence of $CaSO_4$ and CaS at 1%, while CaS was the sole product from the reactions with 3–9% CO concentrations.

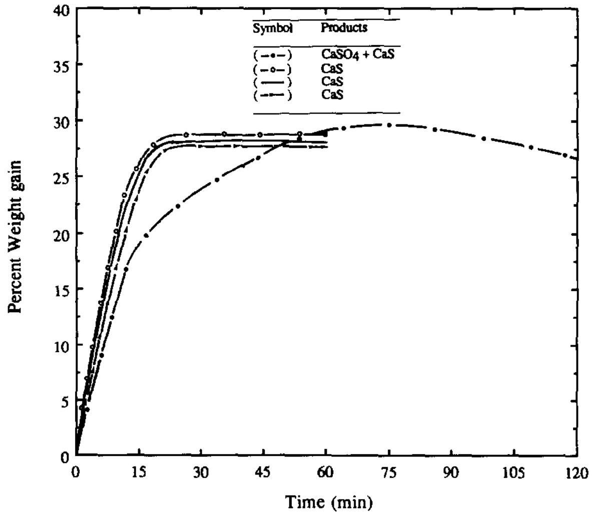

Fig. 2. The effect of CO concentration on the rate of weight gain at 850 °C with 0.3% SO_2 in balance N_2 using CaO (derived from reagent grade $CaCO_3$): (•), 1% CO; (►), 3% CO; (————), 6% CO; and (o), 9% CO.

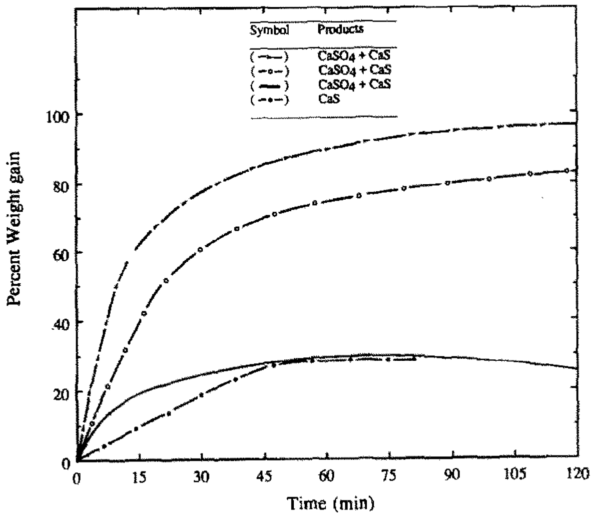

Fig. 3. The effect of SO_2 concentration on the rate of weight gain at 850 °C with 1% CO in balance N_2 using CaO (derived from reagent grade $CaCO_3$): (•), 0.1% SO_2; (———), 0.3% SO_2; (o), 0.6% SO_2; and (▸), 0.9% SO_2 concentration.

Figure 3 shows the effect of SO_2 concentration (0.1–0.9%) on the rate of weight gain at 850 °C with 1% CO in balance N_2. The rates of weight gain increased successively with increasing SO_2 concentration. The solid phase analyses of the reaction products as determined by IR spectroscopy showed the presence of a mixture of $CaSO_4$ and CaS at SO_2 concentrations of 0.3–0.9% whereas CaS was the sole product at an SO_2 concentration of 0.1%

The effect of temperature on the rate of weight gain with 1% CO and 0.3% SO_2 in balance N_2 is illustrated in Fig. 4. The rates of weight gain generally decreased by increasing the temperature from 600 to 850 °C, while increasing the temperature from 900 to 950 °C did not affect the initial or the overall rates. Although the presence of $CaSO_4$, $CaSO_3$ and CaS was detected in the temperature range of 600–800 °C and $CaSO_4$ and CaS were detected at 850 °C, CaS was the only reaction product at 900–950 °C.

The results of the simultaneous mass spectrometer analyses during the TGA experiments at 600–900 °C are presented as percent SO_2 and CO_2 against time in Fig. 5. In general, the SO_2 concentrations (trace (I) at the initial stage of the reaction rapidly decreased and after a short time, increased successively to the initial values. In contrast, the corresponding CO_2 concentrations increased rapidly to a maximum level at the initial stage of the reaction and subsequently dropped back to the lower concentration levels. At 600 °C, the SO_2 concentration initially reached its lowest value; after 2 to 3 minutes it increased substantially, while the correspond-

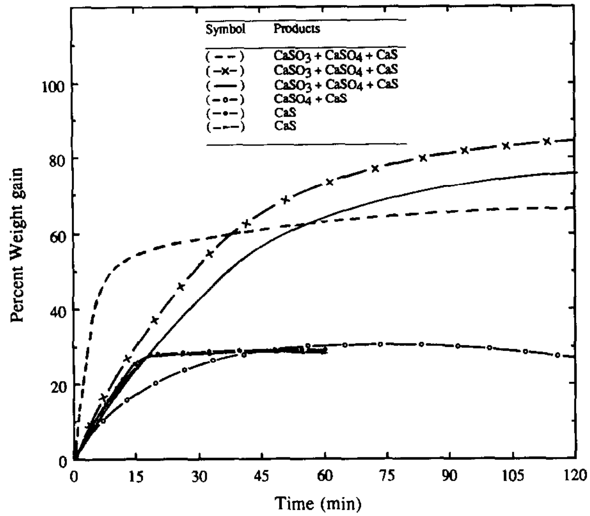

Fig. 4. The effect of temperature on the rate of weight gain with 1% CO and 0.3% SO_2 in balance N_2 using CaO (derived from reagent grade $CaCO_3$): (— —), 600 °C; (×), 700 °C; (———), 800 °C; (o), 850 °C; (•), 900 °C and (▸), 950 °C.

ing CO_2 concentration reached its lowest value. Increasing the temperature from 600 to 900 °C increased the early CO_2 concentration. The rapid decline in SO_2 concentration at the initial stage of the reaction was presumably due to the formation of sulphated products ($CaSO_4$ and $CaSO_3$) on the outer surface of the CaO particles followed by a rapid surface reduction reaction. Subsequent slow increase/decrease in SO_2/CO_2 could be due to the slow diffusion of SO_2 and CO through the layer of newly formed products. In addition, a further decrease in SO_2 concentration and increase in the corresponding CO_2 concentration was observed after around 15 minutes reaction time at 900 °C (trace (I) and trace (II)). This was assumed to be due to the formation of COS(g)

$$3CO(g) + SO_2(g) \rightleftharpoons COS(g) + 2CO_2(g) \qquad (2)$$

The m/z signal corresponding to COS(60) was not observed at 600–800 °C or even initially at 900 °C. It appeared, however, after about 15 min of reaction time at 900 °C. The intensity of the COS peak increased successively, indicating an increase in COS formation, as the conversion front of CaO moved towards a CaS completion as determined by TGA. It seems probable that the formation of COS is catalytically promoted by the presence of a sole CaS product at higher temperature.

In Fig. 6, traces (II)–(VI) show infrared spectra obtained from similar products after experiments with 0.3% SO_2 and 1% CO in balance N_2. Trace (I) shows the spectrum of the calcined reagent grade $CaCO_3$ prior to sulphation where the 3400 cm^{-1} band is assigned to $Ca(OH)_2$ and the

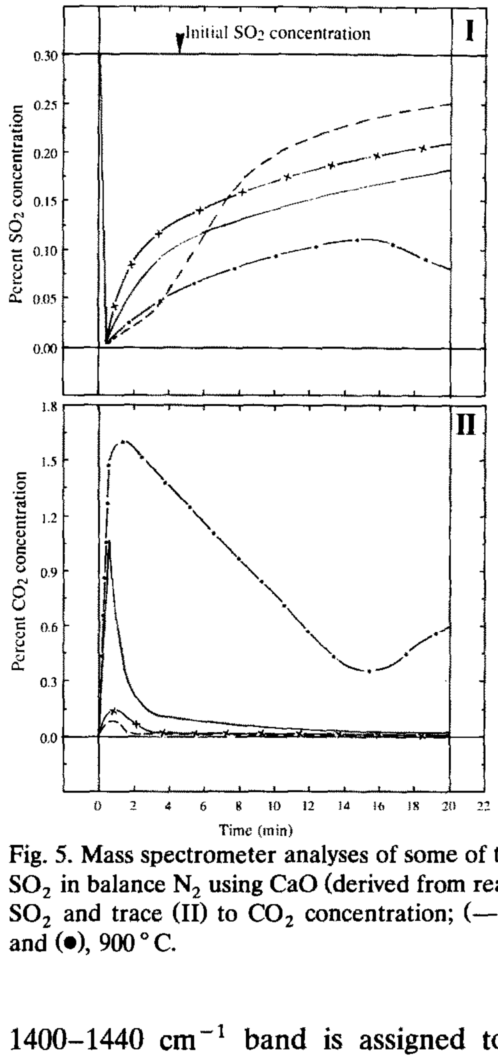

Fig. 5. Mass spectrometer analyses of some of the TGA experiments with 1% CO and 0.3% SO_2 in balance N_2 using CaO (derived from reagent grade $CaCO_3$): trace (I) corresponds to SO_2 and trace (II) to CO_2 concentration; (— —), 600 °C; (×), 700 °C; (———), 800 °C; and (●), 900 °C.

1400–1440 cm^{-1} band is assigned to $CaCO_3$ [8]. Trace (II) shows the spectrum of the product obtained at 600 °C. The strong bands between 980 and 990 cm^{-1}, and at 657 cm^{-1} and 495 cm^{-1} are characteristic for SO_3^{2-} ($CaSO_3$), while the additional band observed at 1090–1140 cm^{-1} corresponds to SO_4^{2-} ($CaSO_4$) frequencies [7]. Trace (III) shows the IR spectrum of the product obtained at 700 °C. In comparison to trace (II), a decrease in intensity of the 980 cm^{-1} sulphite band and several changes in the 600–700 cm^{-1} region of the spectrum are observed together with more intense sulphate bands at 1140, 595, 612 and 676 cm^{-1}. This tendency of weakened sulphite and strengthened sulphate band frequencies with increased reaction temperature is also reflected in trace (IV). In trace (V) (900 °C), the sulphite and sulphate bands are completely absent indicating that at this temperature virtually complete conversion of CaO to CaS is achieved. This was further confirmed by XRD.

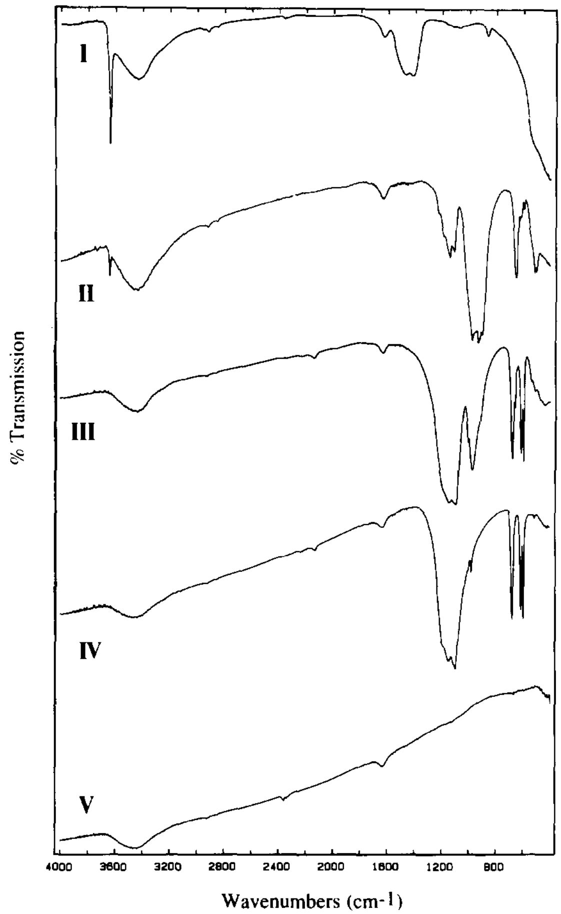

Fig. 6. The IR analyses of the TGA experiments with 1% CO and 0.3% SO_2 in balance N_2 using CaO (derived from reagent grade $CaCO_3$): trace (I) the spectrum of the calcined $CaCO_3$ and reaction products at: (II), 600 ° C; (III), 700 ° C; (IV), 800 ° C; and (V), 900 ° C.

Limestones

The effect of temperature on the rate of weight gain with 1% CO and 0.3% SO_2 in balance N_2 using Ignaberga limestone is illustrated in Fig. 7. The rates of weight gain are analogous with the results in Fig. 4, i.e. the rates generally decrease with increasing temperature. The rates of weight gain between 850 and 950 ° C were unchanged, in contrast to the corresponding observation with CaO derived from reagent grade $CaCO_3$.

The delayed weight loss observed in Fig. 4 at 850 ° C also occurred for the calcined limestone, but at 800 ° C and the rate of weight loss was more pronounced. In similar experiments at 800 ° C, samples were taken for the IR analysis when the weight gain reached the maximum level, as indicated by point (A), and after 120 minutes as indicated by point (B) in Fig. 7, and

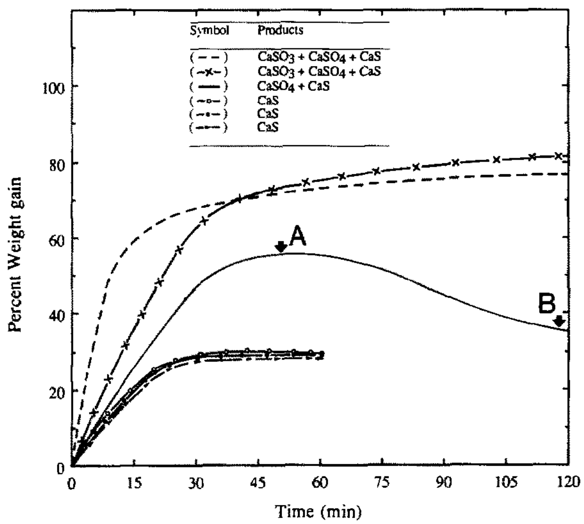

Fig. 7. The effect of temperature on the rate of weight gain with 1% CO and 0.3% SO_2 in balance N_2 using calcined Ignaberga limestone ((A) and (B) refer to where the reaction products were obtained for IR analysis): (— —), 600 °C; (×), 700 °C; (———), 800 °C; (o), 850 °C; (•), 900 °C; and (►), 950 °C.

when the weight of sample was stable (i.e. after about 265 minutes). The results of the IR analyses, together with those for calcined Ignaberga lime prior to reaction are presented in Fig. 8. Trace (I) shows the calcined Ignaberga lime. Traces (II), (III) and (IV) represent the spectra of the reaction products from points A and B, and after 265 minutes, respectively. It can be seen that the intensity of the $CaSO_4$ bands in trace (II) (compare with the IR results in Fig. 6) are markedly reduced in trace (III) and disappear in trace (IV). The results clearly indicate that the weight loss at longer reaction times was due to the reductive decomposition of $CaSO_4$ to CaS.

Figure 9 shows the effect of temperature on the rate of weight gain with 0.3% SO_2 and 1% CO in balance N_2 using Messinghauser limestone. In comparison to the results obtained with reagent grade $CaCO_3$ (Fig. 4) and Ignaberga lime (Fig. 7), Messinghauser lime showed different reaction characteristics. In contrast to the other samples, the IR analyses of the reaction products from the calcined Messinghauser lime revealed the presence of $CaSO_4$ at all temperatures (600–950 °C).

DISCUSSION

Although some elemental S(s) deposition always occurred in the cooler parts of the furnace, any reaction between S_2 and CaO is unlikely to lead to the formation of $CaSO_3$ or $CaSO_4$. Hence, the results obtained by TGA,

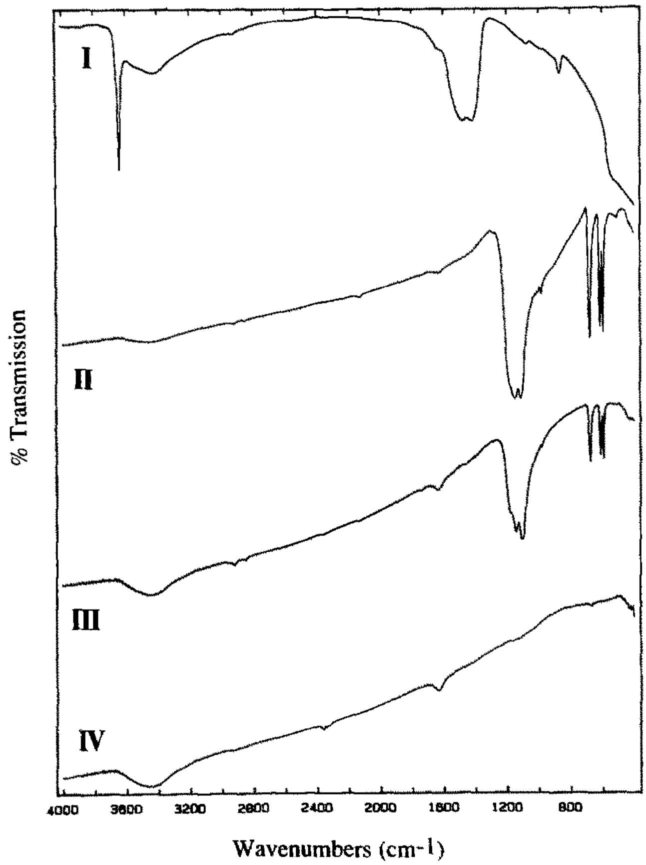

Fig. 8. The IR spectra for calcined Ignaberga lime and the products obtained at 800 °C with 1% CO and 0.3% SO_2: trace (I) represents the calcined lime; trace (II) the product obtained at point (A); trace (III) the product at point (B); and trace (IV) the product after 265 minutes.

IR, XRD and the mass spectrometry indicate that reaction (1) could initially occur through

$$CaO(s) + SO_2(g) \rightleftharpoons CaSO_3(s) \qquad (3)$$

Reaction (3) under a N_2 atmosphere is known to be followed by a subsequent disproportionation reaction at higher temperature through [8]

$$4CaSO_3(s) \rightarrow 3CaSO_4(s) + CaS(s) \qquad (4)$$

Under the given circumstances of this study, the same reactions presumably account for the presence of $CaSO_3$, $CaSO_4$ and CaS in the reaction products (Fig. 6).

In addition, other possible routes can exist by which CaS can form: either via a simultaneous reduction of $CaSO_3$ formed in reaction (3) by CO

$$CaSO_3(s) + 3CO(g) \rightleftharpoons CaS(s) + 3CO_2(g) \qquad (5)$$

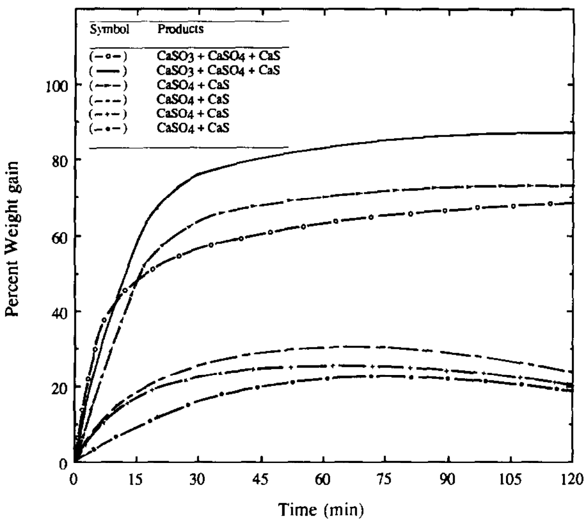

Fig. 9. The effect of temperature on the rate of weight gain with 1% CO and 0.3% SO_2 in balance N_2 using calcined Messinghauser limestone: (o), 600 °C; (———), 700 °C; (▸), 800 °C; (- - -), 850 °C; (×), 900 °C; and (•), 950 °C.

or via a simultaneous reduction of $CaSO_4$ in reaction (4) by CO

$$CaSO_4(s) + 4CO(g) \rightleftharpoons CaS(s) + 4CO_2(g) \qquad (6)$$

From the thermodynamic point of view, both reactions (5) and (6) are involved in transforming the products of reaction (3) and (4) to a unified CaS product. Consequently the equilibrium constraints of reactions (3) and (4) are further altered, and the reactions proceed from left to right.

The reductive decomposition temperature of $CaSO_4$ under a 100% CO atmosphere (reaction (6)) is approximately 790 °C [9], while the approximate decomposition temperature of bulk $CaSO_3$ (reaction (4)) is 400–410 °C [10]. Although the rates of both reactions (5) and (6) increase with increasing temperature, the rate of reaction (5) should increase faster than the rate of reaction (6) due to its lower decomposition temperature. It seems reasonable to propose that the rate and the progress of CaS formation (reaction (1)) is governed by the separate influences of temperature and gaseous concentrations on the rates of reactions (3), (4) and (5). Increasing the SO_2 concentration at a given temperature and CO concentration, increases the rate of reaction (3). Because the rate of reaction (4) is dependent on the rate of reaction (3), the production of $CaSO_4$ increases, causing $CaSO_4$ to appear in the final products (Fig. 3) (in good agreement with the results obtained under N_2 atmosphere [8]). Similarly increasing the CO concentration at a given temperature and SO_2 concentration increases the rate of reaction (5) although this cannot exceed the rate of formation of $CaSO_3$ (reaction (3)). Thus the rate of reaction (5) approaches a certain point where it becomes independent of higher CO concentrations. This would explain the observed result in Fig. 2 where increasing the CO concentration from 3% to 9% did not affect the rate of reaction. Because the rates of reactions (4) and (5) increase with increasing temperature, $CaSO_3$ and $CaSO_4$ were only detected at lower temperatures, 600–800 °C (Fig. 6). In addition, this reasoning would account for the insensitivity of the rate of reaction (1) to temperatures above 850 °C (Fig. 4).

The evidence in support of the proposed reaction pathways can be seen more specifically from the results of the mass spectrometric and IR analyses. From the mass spectrometer analysis, it was evident that the SO_2 concentrations decreased rapidly, while the CO_2 concentrations increased rapidly at the initial stage of reaction. The results reflect the initial surface reaction of SO_2 with CaO to give $CaSO_3$ (reaction (3)) which is presumably followed by the rapid surface reduction reaction to CaS resulting in a substantial increase of the CO_2 concentration (reaction (5)) (Fig. 5). The IR spectra of the reaction products (Fig. 6) are in good agreement with the results of the mass spectrometer analyses: increasing temperature decreased the overall fraction of $CaSO_3$, while the $CaSO_4$ fraction first increased with increasing temperature up to 800 °C and then decreased. Apparently the complete conversion of CaO to CaS occurred in some experiments because the formation of CaS can be considered to be less limited by transport resistance caused by product accumulation in the pores or on the surface of CaO particles in comparison to $CaSO_4$, due to its smaller molar volume (CaS, 27.722 $cm^3\ mol^{-1}$, $CaSO_4$, 45.94 $cm^3\ mol^{-1}$ [11]).

The overall degree of conversion of CaO, Ignaberga lime and Messinghauser lime to CaS (trace(I)), $CaSO_4$ (trace (II)) and $CaSO_3$ (trace (III)), i.e. after reaction was terminated, was determined using 100% CO at 850 °C. The results are presented in Fig. 10 in terms of percent conversion of CaO samples to the corresponding compound against reaction temperature. In general, it is evident that the formation of $CaSO_3$ was greatest at 600 °C but decreased as the temperature increased. The corresponding $CaSO_4$ formation was at a minimum at 600 °C and markedly increased to a maximum at 700 °C. At higher temperatures, 800–950 °C, the amount of $CaSO_4$ in the product decreased. The formation of CaS increased, however, with increasing temperature. The results indicate that Ignaberga lime had a greater CaS formation capacity than reagent CaO and Messinghauser lime under the same conditions. In contrast to the other calcines, Messinghauser lime showed an increase in CaS formation from 600 to 900 °C but a decrease from 900 to 950 °C and, interestingly, $CaSO_4$ was present at all temperatures (600–950 °C). The nature of the differing degrees of conversion of calcines to CaS in relation to particle size and the surface area variations between the sorbents (Table 1) is not well understood. Although no general correlation has been found between the chemi-

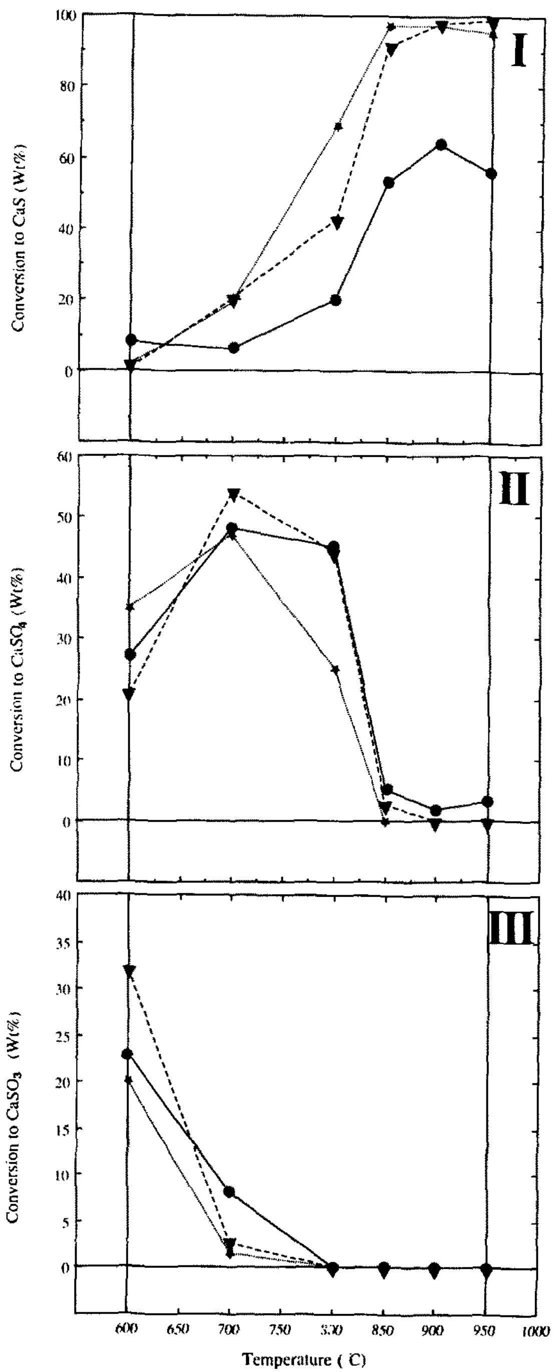

Fig. 10. Quantitative determination of overall distribution of the reaction products with 1% CO and 0.3% SO_2 in N_2 after the reaction was terminated against reaction temperature (in balance unreacted CaO): (▼), reagent grade CaO (derived from reagent $CaCO_3$); (★), Ignaberga lime; and (●), Messinghauser lime.

cal impurities and the limestone reactivity with respect to SO_2 under oxidizing conditions [12], it is conceivable that the mineral impurities present in the limestone influence the course of the reaction under reducing conditions.

It is believed that reaction (6) corresponds to the weight loss occurring at longer reaction times, as illustrated in Fig. 7 for the reaction of Ignaberga lime at 800 ° C. The rate of reductive decomposition of $CaSO_4$ using CO as a reducing agent has previously been shown to be catalytically promoted by the presence of CaS [13]. Thus, it is more likely that the presence of greater quantities of CaS generally accounts for the observed weight loss, particularly for Ignaberga lime (Fig. 10) at 800 ° C as compared to reagent grade CaO (Figs. 1, 2 and 4).

The results obtained indicate that SO_2 absorption by CaO under reducing conditions generally leads to the formation of CaS. The degree of CaS formation is governed by temperature and CO and SO_2 concentrations. Increasing the temperature at a given SO_2/CO concentration increased the CaS formation, and complete conversion of CaO to CaS at a relatively fast rate occurred above 850 ° C, although different calcareous materials showed different capacities of CaS formation.

The presence of CaS in the solid wastes from fluidized bed combustion (AFBC) (sub-scale pilot and large scale plants) has been previously reported [14,15]. Although CaS is a stable compound under a reducing or an inert atmosphere, it rapidly reacts with O_2 in an oxidizing atmosphere to give a mixture of solid products of CaO and $CaSO_4$ with release of SO_2 [16]. Considering now that the CaO particles in the fluidized bed combustion application are cyclically exposed to a SO_2/CO atmosphere in the fuel-rich part of the bed, CaS formation would appear to be likely. In the oxidizing part of the bed, however, the CaS formed would be exposed to O_2 resulting in the regeneration of CaO with the release of SO_2. Alternatively, the reaction between any water vapour present and CaS could lead to H_2S formation with the regeneration of CaO [17]. Under the conditions prevailing in an AFBC, these processes could to some extent lower the desulphurization efficiency and possibly contribute to the appearance of the optimum temperature ranges for sulphation [4].

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