Thermochimica Acta, 190 (1991) 307-318
Elsevier Science Publishers B V , Amsterdam

Some aspects of calcium sulphite reduction with carbon monoxide

S. Ghardashkhani and O. Lindqvist

Department of Inorganic Chemistry, Chalmers University of Technology and University of Göteborg, S-41296 Göteborg (Sweden)

(Received 13 March 1991)

Abstract

The non-isothermal reductive decomposition reaction of crystalline $CaSO_3 \cdot 0\,5H_2O$ and anhydrous $CaSO_3$ under CO, CO_2 and CO–CO_2 gas mixtures at the two heating rates of 25°C min^{-1} and 6°C min^{-1} up to 900°C, respectively, was investigated employing thermogravimetric analysis, X-ray powder diffraction, IR spectroscopy and continuous SO_2 measurement by on-line fluorescence spectroscopy. During the heating process the reaction involved a multistage weight loss, in both cases, with a corresponding multistage SO_2 release The multistage weight loss and the corresponding SO_2 release were presumed to be the consequence of different sequential reactions taking place along with the direct reduction of $CaSO_3$ to CaS, including the formation and decomposition of $CaCO_3$ and $CaSO_4$, respectively The corresponding SO_2 evolution was found to be considerably lower at slow heating rates. In the presence of additional CO_2, the SO_2 release was increased and the highest SO_2 concentration was found for a feed-gas mixture of 70% CO_2 and 30% CO, and also in pure CO_2 The $CaCO_3$ product also increased with increasing CO_2 concentration The possible reaction pathway is discussed.

INTRODUCTION

The reaction of CaO (calcium oxide) with sulphur dioxide is of considerable interest for the control of sulphur dioxide pollution in combustion processes, particularly coal combustion. The chemistry of the absorption of SO_2 by CaO at high temperatures is rather complex because several solid phases are involved. Calcium sulphite ($CaSO_3$) is presumably the first solid formed in the reaction [1–5]. The reaction of $CaSO_3$ with O_2 and SO_2 [6,7] and the chemical behaviour under vacuum [8] and N_2 [3,9,10] have been previously investigated. This work forms part of on-going research dealing with the fundamental mechanisms behind the chemistry of the absorption of SO_2 by calcined limestone, CaO, particularly with $CaSO_3$ as an intermediate. It is aimed specifically at the study of some aspects of calcium sulphite

0040-6031/91/$03.50

TABLE 1

Thermodynamic data calculated for reactions (1) and (5)

T (K)	Reaction (1)			Reaction (5)			
	ΔH (kcal mol^{-1})	ΔG (kcal mol^{-1})	ln K	ΔH (kcal mol^{-1})	ΔG (kcal mol^{-1})	ln K	$P(SO_2)$ (%)
700	−37 421	−36.792	26.45	15 057	11.065	−7.95	0 035
800	−37.596	−36.692	23 08	15 151	10.489	−6.60	0.136
900	−37 669	−36.576	20 45	15 206	9.902	−5.54	0.392
1000	−37 832	−36.452	18.34	15 217	9.312	−4.70	0.910

reduction using CO as the reducing agent. The reaction between $CaSO_3(s)$ and CO(g) can be described by the overall reaction

$$CaSO_3(s) + 3CO(g) \rightarrow CaS(s) + 3CO_2(g) \qquad (1)$$

Reaction (1) is, in principle, exothermic; its thermodynamic properties are presented in Table 1 [11]. Further motivation to study reaction (1) is due to its apparent similarity with the well-known reductive decomposition of $CaSO_4$ [12]

$$CaSO_4(s) + 4CO(g) \rightleftharpoons CaS(s) + 4CO_2(g) \qquad (2)$$

EXPERIMENTAL

Materials

The solid materials used in this study were $CaSO_3 \cdot 0.5H_2O$ (calcium sulphite hemihydrate) and $CaSO_3$ (anhydrous calcium sulphite). An approximately 50 mg sample of calcium sulphite material was used in each run for all experiments. High purity N_2, CO_2 and CO were used and the desired gas mixtures were obtained 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, controlled atmosphere accessory and a vacuum system). The off-gas SO_2 concentration was diluted and measured continuously by a fluorescence spectroscopic SO_2-analyser (Monitor Labs Inc. model 8859). A platinum–platinum, 10% rhodium standard thermocouple was used to measure the temperature near the reaction site, below a platinum semispherical crucible sample holder (diameter 15 mm, depth 10 mm). The solid phase analysis was carried out employing X-ray powder diffraction (XRD, Huber vertical Guinier camera 620) and Fourier transform IR spectroscopy (FTIR, Mattson polaris FTIR system) using the KBr pellet technique.

Preparation

Calcium sulphite hemihydrate ($CaSO_3 \cdot 0.5H_2O$) was prepared by very slow addition of aqueous $CaBr_2$ to a solution of Na_2SO_3 (de-aired by continuously bubbling a helium stream through the solution at ambient temperature). The precipitate, a fine powder, was filtered under a helium atmosphere and was then dried in a current of helium at 150 °C for 160 min [3]. Despite this drying procedure, thermogravimetric analysis (heating rate 6 °C min^{-1} to 400 °C in N_2) of the precipitate revealed the presence of excess H_2O over that required for the complete dehydration of $CaSO_3 \cdot 0.5H_2O$. Consequently, a sample of the precipitate was placed in the TG apparatus and evacuated (0.1 mbar). Heating of the sample was performed at a heating rate of 10 °C min^{-1} up to 250 °C. When weight stabilization was reached (heating period of 160 min), cooling of the sample was initiated at a cooling rate of 10 °C min^{-1} down to ambient temperature. The vacuum chamber was then filled with N_2 and the sample was removed to a desiccator and stored under N_2. Thermogravimetric analysis of this sample then revealed the presence of an amount of H_2O consistent with stoichiometrically formed $CaSO_3 \cdot 0.5H_2O$.

The X-ray diffraction and IR analysis of the sample were also in good agreement with $CaSO_3 \cdot 0.5H_2O$ spectra reported in the literature [13–15]. These results suggested that all excess H_2O could be removed successfully from the sample by the above pre-treatment. Although rigorous chemical analysis was not conducted on the sample, the presence of $CaSO_4$ was not detected by IR or by XRD.

Anhydrous $CaSO_3$ was prepared by slow heating (6 °C min^{-1} up to 350 °C) of a sample of $CaSO_3 \cdot 0.5H_2O$ under vacuum (0.1 mbar). After about 270 min reaction time at the temperature stated, a weight equilibrium was established as determined by TGA. The cooling of the sample was then carried out at a rate of 6 °C min^{-1} to ambient temperature. The vacuum chamber was filled with N_2 and the sample was then removed to a desiccator and stored under N_2. The X-ray diffraction pattern and IR analysis of the sample were consistent with the spectra of anhydrous $CaSO_3$ previously reported [14–16].

Procedure

A pre-weighed sample of calcium sulphite material was placed in the TG apparatus and a gas mixture with a flow rate of 200 ml min^{-1} was introduced. The SO_2 analyser was calibrated against a standard 190 ± 10 ppm pre-mixed SO_2/N_2 gas sample for all experiments. Two heating modes were employed: in one case the sample was heated at a rate of 6 °C min^{-1} and in the other at a rate of 25 °C min^{-1} up to 900 °C.

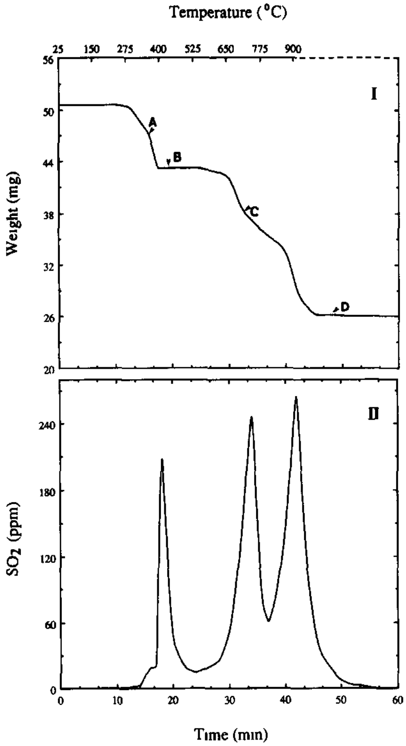

Fig. 1 Trace I, TGA results for the reaction between CO and $CaSO_3 \cdot 0.5H_2O$ at a heating rate of $25 \pm 1°C\ min^{-1}$ up to 900 °C. Trace II, the results of the corresponding SO_2 concentration measurement.

In similar experiments after the temperature reached the set point, the reaction was terminated and a number of samples were allowed to cool to ambient temperature under $N_2(g)$ at an average cooling rate of $100°C\ min^{-1}$. The samples were then removed from the TG apparatus and were analyzed by IR (KBr pellets pressed at 5 kbar) and XRD.

RESULTS

Figure 1 illustrates a typical non-isothermal experiment carried out at a heating rate of $25 \pm 1°C\ min^{-1}$ up to 900 °C using a sample of $CaSO_3 \cdot 0.5H_2O$ in an atmosphere of 100% CO. The TGA result is presented as weight vs. temperature in trace I and as the corresponding SO_2 concentration measurement against time in trace II. The TGA results presented in Figs. 3–6 are in terms of weight per cent.

As can be seen from trace I in Fig. 1, a multistage weight loss took place during the heating from 25 °C up to 900 °C, where each weight-loss step was successively followed by an increase in SO_2 concentration (trace II). Such multistage weight loss is known to characterize sequential decomposition

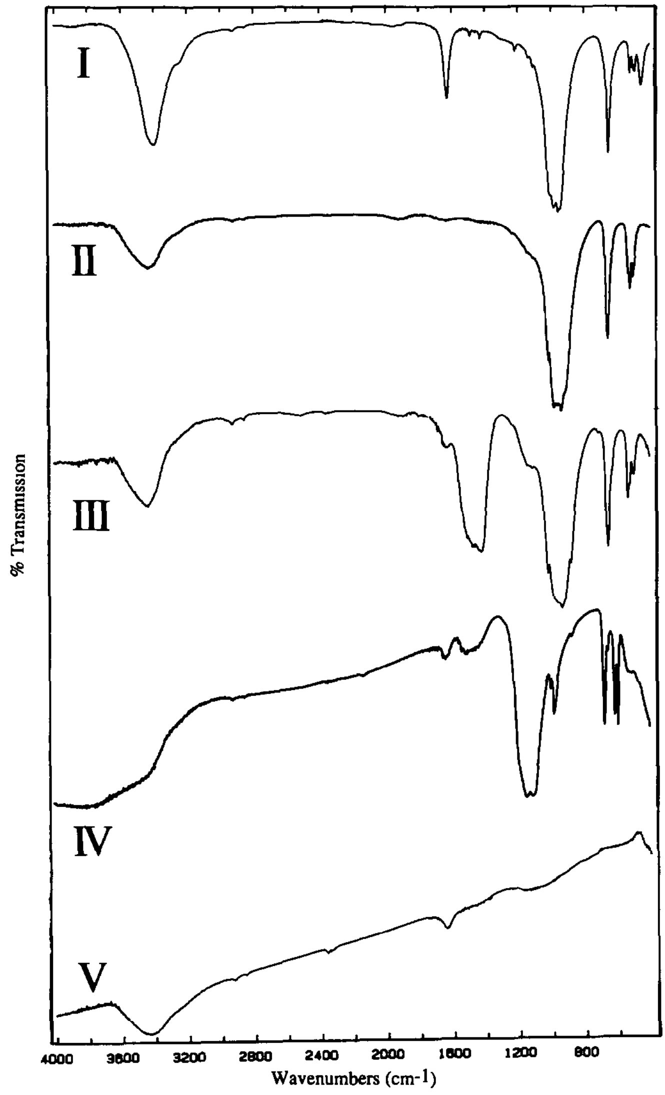

Fig. 2. IR spectra of $CaSO_3 \cdot 0.5H_2O$ (trace I) and of the products from experiments: trace II, at 390 °C, trace III, at 450 °C; trace IV, at 700 °C; trace V, at 900 °C.

reactions [17]. In similar experiments, samples were taken at 390 °C (point A), 450 °C (point B), 700 °C (point C) and 900 °C (point D), as indicated on Fig. 1, trace I, for IR and X-ray diffraction analyses.

The results of the IR analysis are presented in Fig. 2. Trace I of Fig. 2 shows the IR spectrum of the original sample of $CaSO_3 \cdot 0.5H_2O$ while trace II represents the corresponding spectrum obtained at 390 °C (point A). At the higher temperature, the 450 and 1625 cm^{-1} (H_2O) bands of $CaSO_3 \cdot 0.5H_2O$ have vanished and a significant decrease in the intensity of the 3400 cm^{-1} (OH) streching band has also taken place, indicating virtually com-

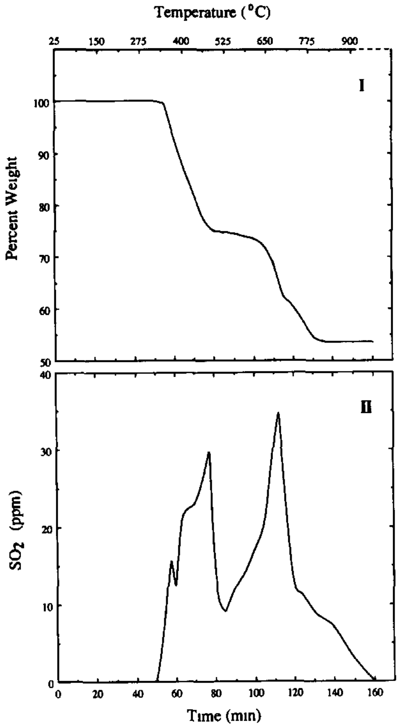

Fig 3. Trace I, TGA results for the reaction between CO and $CaSO_3 \cdot 0.5H_2O$ at a heating rate of 6 °C min^{-1} up to 900 °C Trace II, the corresponding SO_2 measurement.

plete dehydration of the sample to anhydrous $CaSO_3$. Trace III represents the spectrum of the sample obtained at 450 °C (point B). In comparison with trace II, a new strong broad band at 1400–1470 cm^{-1} corresponding to a CO_3^{2-} ($CaCO_3$) frequency [18] has appeared. Trace IV represents the spectrum of the sample obtained at 700 °C (point C). In this case several changes can be noted: a new broad band at 1100–1150 cm^{-1} and shoulders at 675, 615 and 595 cm^{-1} were assigned to SO_4^{2-} ($CaSO_4$) frequencies [18] while a marked intensity decrease in the 980 cm^{-1} ($CaSO_3$) band and the 1400–1700 cm^{-1} ($CaCO_3$) band was observed. Trace V represents the spectrum of the sample obtained at 900 °C (point D) where the bands of $CaCO_3$, $CaSO_3$ and $CaSO_4$ have all disappeared.

The corresponding X-ray analysis of the sample from point A indicated anhydrous $CaSO_3$ only, while the sample from point B implied the presence of $CaCO_3$, $CaSO_3$ and CaS. The sample from point C was consistent with CaS, CaO and $CaSO_4$, while the diffraction pattern for sample D showed the presence of CaO and CaS. It should be noted that the sensitivity of IR analysis for $CaSO_3$ and $CaCO_3$ is higher than XRD, so that the appearance of these phases in sample C could not be inferred conclusively from XRD.

Figure 3 represents the results obtained from the experiment carried out with a sample of $CaSO_3 \cdot 0.5H_2O$ under a 100% CO atmosphere at a heating

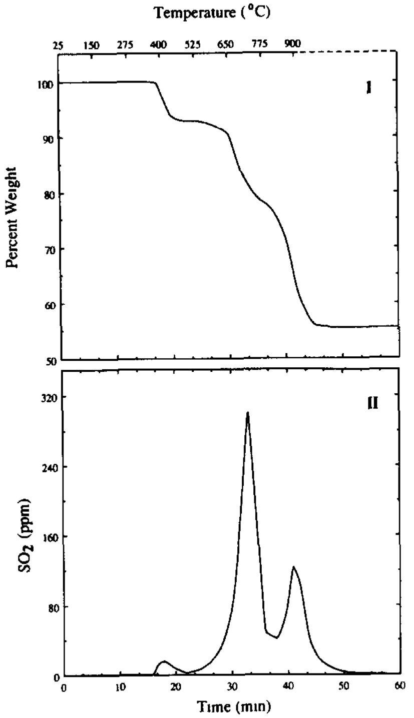

Fig. 4 Trace I, TGA results for the reaction between CO and anhydrous $CaSO_3$ at a heating rate of 25 ± 1 °C min^{-1} up to 900 °C. Trace II, the corresponding SO_2 measurement.

rate of 6 °C min^{-1} up to 900 °C. In comparison with the results shown in Fig. 1, a significant overall decrease in the corresponding SO_2 release was observed while the same thermogram profile was obtained.

Figures 4 and 5 (trace I and II) represent the results obtained from the experiments carried out with samples of anhydrous $CaSO_3$ under a 100% CO atmosphere at heating rates of 25 ± 1 and 6 °C min^{-1}, respectively. By comparing with the results previously presented in Figs. 1 and 3, similar weight-loss steps, though without the first step, can be observed over almost the same temperature ranges. The SO_2 profile also resembled the results from trace II in Figs. 1 and 3.

Figure 6 (trace I and II) shows the results obtained from the experiment conducted with samples of $CaSO_3 \cdot 0.5H_2O$ in different CO–CO_2 gas mixtures and also in the complete absence of CO (100% CO_2) at a heating rate of 25 ± 1 °C min^{-1} up to 900 °C. As a result of adding as little as 10% CO_2 to the feed gas stream (90% CO), the efficiency of the second SO_2 release step was increased while the overall weight loss was only slightly affected. Increasing the CO_2 concentration to 50% further increased the second SO_2 release stage but delayed it to a higher temperature. In the presence of 70% CO_2 in 30% CO, and also for pure CO_2, the SO_2 release exceeded the

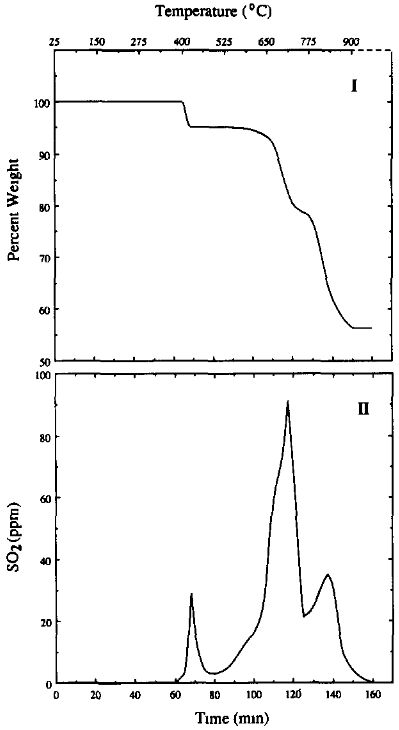

Fig 5 Trace I, TGA results for the reaction between CO and anhydrous $CaSO_3$ at a heating rate of 6 °C min^{-1} up to 900 °C Trace II, the corresponding SO_2 measurement.

maximum capacity of the SO_2 analyser. The overall weight loss was highest at 70% CO_2 and lowest at 100% CO_2.

DISCUSSION

The non-isothermal investigation of the reductive decomposition of $CaSO_4$ under a 100% CO atmosphere (reaction (2)) has been reported to occur in a single weight-loss step throughout the heating processes from 25 to 1000 °C at heating rates of 10 and 25 °C min^{-1}, respectively, as determined by TGA, DTA and DTG [12]. Conversely, the non-isothermal reductive decomposition of anhydrous $CaSO_3$ after the dehydration step, under a 100% CO atmosphere, as studied here, proceeds through a multi-stage weight loss as determined by TGA. Under the circumstances given and on the basis of the results obtained from the solid phase analysis (IR and XRD), the first low temperature weight-loss step (Fig. 1) can be assigned to the removal of water of crystallization:

$$CaSO_3 \cdot 0.5H_2O(s) \rightleftharpoons CaSO_3(s) + 0.5H_2O(g) \tag{3}$$

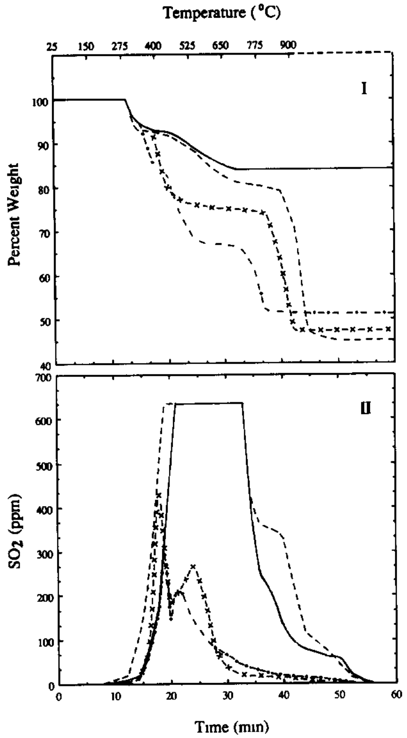

Fig. 6. Trace I, TGA results for the reaction between $CaSO_3 \cdot 0.5H_2O$ and CO-CO_2 gas mixtures, and 100% CO_2 at a heating rate of 25 ± 1 °C min^{-1} up to 900 °C Trace II, the corresponding SO_2 measurement· ●, 10% CO_2, ×, 50% CO_2; — — —, 90% CO_2, ——, 100% CO_2

The weight loss due to this dehydration (reaction (3)) was initially observed when the temperature approached about 350 °C [3,19]. The rate of the weight loss then accelerated as the temperature increased to 390 °C where virtually complete H_2O removal was achieved. During the course of the dehydration reaction (3), a small amount of SO_2 was also released (Figs. 1 and 2, trace II). This SO_2 release apparently accompanies the rapid collapse of the hydrated $CaSO_3$ crystal lattice. In addition, reaction (3) could be considered as a typical heterogenous solid phase decomposition reaction yielding solid and gaseous products similar to the well-known decomposition of $CaCO_3$. Such reactions usually leave solid products of high porosity, in this case porous anhydrous $CaSO_3$.

A short period after the dehydration step, however, over a temperature range of 390–400 °C, a rapid weight loss occurs. This second step was accompanied by a substantial SO_2 release. Although the nature of this behaviour is not fully understood, it is presumably allied with the parallel formation of $CaCO_3$ as determined by IR analysis (Fig. 2, trace III) and indicated by the overall reductive reaction

$$4CaSO_3(s) + 3CO(g) \rightarrow CaS(s) + 3CaCO_3(s) + 3SO_2(g) \qquad (4)$$

The in situ formation of $CaCO_3$ is apparently initiated by the interaction of the CO_2 formed with a small CaO surface area, previously formed at the dehydration step. The formation of $CaCO_3$ continues by absorption of CO_2 with emission of SO_2 in a CO_2–SO_2 substitution-type reaction.

In the complete absence of CO (see Fig. 6) the formation of $CaCO_3$ by direct interaction of CO_2 (bulk CO_2) and $CaSO_3$ could be described as a full substitution reaction, i.e.

$$CaSO_3(s) + CO_2(g) \rightarrow CaCO_3(s) + SO_2(g) \qquad (5)$$

The thermodynamic data calculated for reaction (5) (Table 1) reveal that the equilibrium constant for reaction (5), assuming unit activity of the solids and 100% CO_2 concentration, equals the partial pressure of SO_2. The predicted SO_2 concentration shown in Table 1 is in good agreement with the experiment. The reaction mechanism by which CO_2 chemically replaces SO_2 in both reaction (4) and reaction (5) is rather complicated. However, the formation of $CaCO_3$ with absorption of CO_2 and emission of SO_2 by some such substitution mechanism can only continue until the decomposition temperature of $CaCO_3$ is reached as in eqn. (6):

$$CaO(s) + CO_2(g) \Leftrightarrow CaCO_3(s) \qquad (6)$$

The decomposition of the $CaCO_3$ formed was found to occur in the temperature range 660–670 °C, indicated by the third weight-loss step, followed by an increase in SO_2 concentration (Fig. 1, trace I and II). The decomposition temperature was respectively shifted to a higher temperature in the presence of 10, 50 and 70% additional CO_2, while at 100% CO_2 the calcination was suppressed entirely by the thermodynamic equilibrium constraint (Fig. 6, trace I). The latter experiment was examined subsequently by instantaneously exchanging the 100% CO_2 flow for pure N_2 at 900 °C. The resulting calcination weight loss indicated an overall conversion of about 90% of the initial $CaSO_3 \cdot 0.5H_2O$ to $CaCO_3$ in the presence of 100% CO_2. The remaining 10% could be attributed to $CaSO_4$ formation, as determined by IR spectroscopy.

After the third weight loss step (see Fig 1), the presence of $CaSO_4$ in the product from point C (700 °C) (see IR results, Fig. 2, trace IV) is assigned to the parallel homogeneous disproportionation reaction of $CaSO_3$ [3,5,14,19] according to

$$4CaSO_3(s) \rightleftharpoons 3CaSO_4(s) + CaS(s) \qquad (7)$$

It seems likely that the non-isothermal reduction of $CaSO_3$ to CaS (reaction (1)) proceeds relatively slowly in comparison to the disproportionation reaction (7). It has been shown previously that the isothermal reductive decomposition of $CaSO_4$ with a thermodynamic CO/CO_2 ratio over the temperature range 1000–1300 °C results successfully in the regeneration of CaO and SO_2 [20,21]. Assuming the development of a local thermodynamic equilibrium between bulk gas CO and produced CO_2 (i.e. a gas ratio of CO/CO_2) in the pores or on the surface of the $CaSO_4$ formed via reaction (7), the same type of regeneration process could also occur, although at lower temperatures. The last weight-loss step (790–900 °C) and the corresponding SO_2 release were presumably the consequence of the reductive decomposition of $CaSO_4$ coupled with the $CO-CO_2$ equilibrium.

The non-isothermal thermogravimetric investigation of the reductive decomposition of $CaSO_3 \cdot 0.5H_2O$ and anhydrous $CaSO_3$ using CO as the reducing agent was shown to be a rather complex reaction involving multistage SO_2 release, together with formation and decomposition of $CaCO_3$ and $CaSO_4$, respectively. The CO_2 produced as the product of reduction of $CaSO_3$ to CaS is absorbed in situ. The absorption of the CO_2 produced leads to the formation of $CaCO_3$ with evolution of SO_2. In comparison with the faster heating rate (25 ± 1 °C min^{-1}), the SO_2 release was considerably lower when the samples were heated at a rate of 6 °C min^{-1} up to 900 °C. In the presence of additional CO_2, the SO_2 release was increased and the highest SO_2 release occurred at 70% CO_2 and in the total absence of CO (100% CO_2), while the formation of $CaCO_3$ was increased with increasing CO_2 content. It seems likely that over the temperature range 390–700 °C, the chemical stability of $CaSO_3$ is sharply decreased and, thus, in the presence of such reactive gases as O_2, CO_2 and CO, is transformed to other thermodynamically stable products such as $CaSO_4$, $CaCO_3$ and CaS. The results also indicated that the reductive decomposition of the bulk $CaSO_3$ using CO as reducing agent occurred at lower temperatures (i.e. at 400–420 °C) than predicted previously [5].

The practical aspect of these findings is related to the important commercially accepted approaches to flue gas desulphurization by aqueous scrubbing with production of $CaSO_3$–$CaSO_4$ solids, generally known as "throwaway" scrubbing [22]. The most significant problem associated with "throwaway" scrubbing is the disposal of a large amount of solid waste. In the light of the results presented here, it seems possible to regenerate CaO and SO_2 from $CaSO_3$–$CaSO_4$ mixtures using an appropriate CO/CO_2 ratio or pure CO_2 at the optimal temperature, which could offer a potentially attractive recovery process. In order to meet this demand, more fundamental and applied research is required.

ACKNOWLEDGEMENTS

We express our gratitude to the Swedish National Energy Administration for financial support and to Robert Penfold, Dr. Dan Strömberg and Dr. Lars-Gunnar Johansson for helpful discussions.

REFERENCES

1 R.W. Coutant, R.E. Barret and E.H. Lougher, J. Eng. Power, 92(2) (1970) 113.

2 E.P. O'Neill, D.L. Keairns and W.F. Kittle, Thermochim Acta, 14 (1976) 209.

3 T.R. Ingraham and P. Marier, J Air Pollut. Control Assoc., 21(16) (1971) 347.

4 J S. Dennis and A.N Hayhurst, Chem. Eng. Sci., 45(5) (1990) 1175.

5 S Ghardashkhani and D A. Cooper, Thermochim. Acta, 161 (1990) 327.

6 G. Van Houte and B. Delmon, Bull Soc. Chim. Belg., 87(4) (1978) 241.

7 G. Van Houte, L Rodrique, M. Genet and B. Delmon, Environ Sci. Technol., 15(6) (1981) 327

8 D Cubicciotti, A Sanjurjo and D.L. Hildenbrand, J. Electrochem. Soc., 124(6) (1977) 933

9 R Matsuzaki, H. Masumizu, N. Murakami and Y. Saeki, Bull Chem. Soc. Jpn., 51(1) (1978) 121

10 F. Foerster and K. Kuble, Z Anorg. Chem., 139 (1924) 261.

11 I Barin, O. Knacke and O. Kubaschewski, Thermochemical Properties of Inorganic Substances, Supplement, Springer, Berlin, 1977.

12 R. Kuusik, P Saikonen and L. Niinistö, J Therm. Anal., 30 (1985) 187

13 ASTM Cards 39-725, JCPDS-ICDD (1989)

14 N. Tsuyuki and J. Kasai, Nippon Kagaku Kaishi, 1 (1979) 59 (in Japanese with English abstract)

15 H.D. Lutz and S Elsuradi, Z. Anorg. Allg. Chem, 425 (1976) 134.

16 ASTM Cards 36-529, JCPDS-ICDD (1989)

17 C Duval, Inorganic Thermogravimetric Analysis, 2nd edn, Elsevier, Amsterdam, 1963

18 K Nakamoto, Infrared and Raman Spectra of Inorganic and Coordination Compounds, 4th edn., Wiley, New York, 1986.

19 D.R. Glasson and P O'Neill, Proc. 1st Eur Symp. Therm. Anal., Heyden, London, 1976, p 283.

20 T D. Wheelock and D.R. Boylan, Ind. Eng Chem., 52(3) (1960) 215.

21 T.D. Wheelock and D.R. Boylan, Ind. Chem., 36 (1960) 590.

22 T F. Edgar, Coal Processing and Pollution Control, 1st edn., Gulf Publishing, Houston, TX, 1983.