

The reaction between limestone and SO₂ under periodically changing oxidizing and reducing conditions – effect of temperature and limestone type

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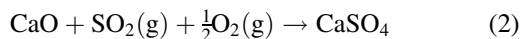
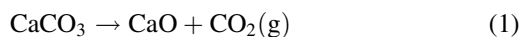
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Abstract

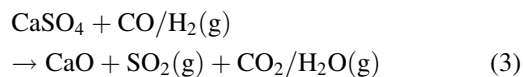
The reaction between limestone and SO₂ was investigated under both oxidizing and periodically changing oxidizing and reducing conditions at atmospheric pressure in a fixed-bed quartz reactor. Three limestones of different reactivities were sulfated at temperatures between 800° and 875°C with a gas mixture of 1500 ppm SO₂, 10% CO₂ and alternating O₂ and CO (0% or 4%). The experimental data found that periodically changing oxidizing and reducing conditions could have either a positive or a negative effect on the degree of conversion of CaO to CaSO₄ compared to limestone samples sulfated under constant oxidizing conditions. In the temperature range 825–875°C the conversion was relatively constant for all three limestones under oxidizing conditions. However, when the limestone samples were sulfated with periodically changing oxidizing and reducing gas mixtures a wide range of conversions were found. The highest degree of conversion was found at 825°C for all three limestones and the lowest degree of conversion was found at 875°C. The rapid decrease in conversion at high temperatures was due to the rapid release of SO₂ due to both the decomposition of CaSO₄ as well as a high rate of CaS oxidation. A comparison of the sulfation rates of several experiments performed with Köping limestone under alternating conditions showed a wide range of rates, indicating the difficulties in using laboratory rate data in sulfur capture modelling for fluidized-bed boilers. © 1999 Elsevier Science B.V. All rights reserved.

1. Introduction

During combustion of coal in fluidized-bed boilers (FBB), sulfur is released predominantly as SO₂. To capture SO₂, limestone or dolomite is added to the combustion chamber and the sulfur is captured as calcium sulfate according to the consecutive reactions:



Several investigators have observed that the sulfur capture efficiency in fluidized-bed combustors and boilers is highly temperature dependent, with a rapid decrease in the sulfur capture efficiency at temperatures above ca. 850°C [1–5]. There have been several proposed theories to explain this temperature dependence, and these have been reviewed extensively in earlier literature (e.g. [6]). The most accepted theory, first proposed by Jonke et al. [7], suggests that the CaSO₄ formed through reaction (2) is reductively decomposed in reducing regions of the combustor:



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It was suggested that sulfur capture in fluidized-bed combustion (FBC) is a competition between reaction (2) and (3), and that reaction (3) becomes faster than reaction (2) at high temperatures. Reaction (3) has been shown to be important in full-scale boiler investigations [3,4] in addition to pilot plant combustors [1,2]. Although a decrease in the degree of sulfur capture has been seen in boiler investigations at high temperatures, in an investigation of the sulfur capture in a 40 MW circulating fluidized-bed boiler (CFBB) a much higher conversion was found for Köping limestone when compared to laboratory tests under oxidizing conditions [8]. The low conversion in the laboratory tests had the effect that laboratory reactivity data could not be used for modelling purposes. In this respect, the Köping limestone differed from the reactive Ignaberga limestone where good modelling results were accomplished [9]. This large difference in conversion between laboratory and boiler investigations prompted an extensive laboratory investigation of the effects of periodically changing oxidizing and reducing conditions using Köping limestone [10]. It was found that, depending upon the fraction of time under reducing conditions and the cycle time, large differences in conversion could be obtained when compared to experiments conducted under oxidizing conditions. The present paper is a continuation of the previous study but with the effects of temperature investigated. In addition to Köping limestone, two other Swedish limestones of varying reactivity were evaluated.

2. Experimental

The details of the experimental set-up and procedure have been discussed in detail elsewhere [10] and only a brief description will be given here. All experiments were conducted in a fixed-bed quartz reactor shown in Fig. 1. The limestone was heated in a CO₂ atmosphere from room temperature to the reaction temperature before the limestone sample was exposed to a reactant gas mixture alternating every 60 s between an oxidizing (1500 ppm SO₂, 10% CO₂, 4% O₂) and reducing (1500 ppm SO₂, 10% CO₂, 4% CO) gas for a total reaction time of 2 h. The experiments performed with constant oxidizing conditions used the same reactant gas composition as was

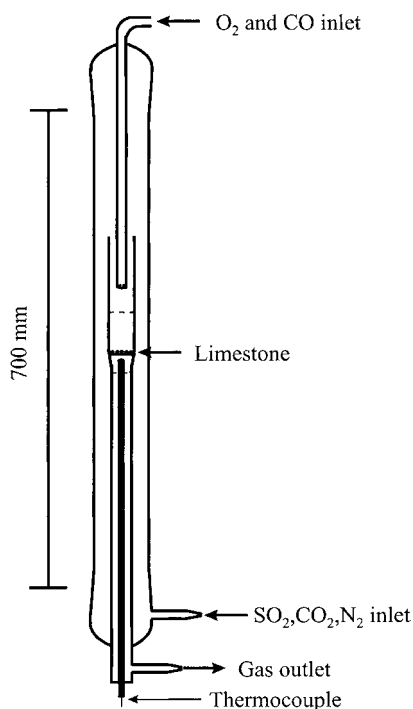


Fig. 1. Fixed-bed quartz reactor.

used during the oxidizing periods of the alternating experiments. The SO₂ concentration was measured continuously during the experiment and logged to a data file with 1 s intervals. Table 1 shows the experimental conditions used in the present work. The conversion of CaO was calculated by two methods: (i) integration of the absorbed SO₂; and (ii) gravimetrically. The conversion as determined from a mass balance of absorbed SO₂ can be calculated by,

Table 1
Reaction conditions

Mass of limestone sample (mg)	600
Temperature (°C)	800–875
Inlet SO ₂ (ppm)	1500
CO ₂ (%)	10
N ₂ (%)	balance
O ₂ (%)	0 or 4
CO (%)	4 or 0
Flow (mol/min)	4.5×10^{-2}
Oxidizing time/Reducing time (s)	60/60
Sulfation time (h)	2 (4)

$$X = \frac{M_{\text{CaCO}_3} \dot{n}}{mf} \int_0^t \frac{(p_i - p_o)}{p_{\text{tot}}} dt \quad (4)$$

where X is the degree of conversion, M_{CaCO_3} the molecular weight of CaCO_3 , \dot{n} the total molar flow rate, m the initial mass of limestone, f the fraction of CaCO_3 in the limestone sample, p_{tot} the total pressure, and p_i and p_o the inlet and outlet partial pressures of SO_2 . The final conversion could also be calculated by weighing the limestone sample before and after sulfation. Assuming that the only solid components in the sulfated limestone sample were CaO and CaSO_4 the conversion could be calculated by,

$$X = \frac{M_{\text{CaCO}_3} (W_f - W_i(1-f)) - M_{\text{CaO}} W_i f}{W_i f (M_{\text{CaSO}_4} - M_{\text{CaO}})} \quad (5)$$

where W_i is the initial weight of sample and W_f the weight of the sample after sulfation. It was assumed that there was no CaS formed in the samples. This was confirmed by wet chemical sulfide analysis on several of the samples, which showed small amounts of CaS , not affecting the conversion as calculated by Eq. (5). It is believed that the conversion as calculated gravimetrically is more accurate and, unless otherwise indicated, this is the method used in this paper.

Three limestones of widely varying geological age were studied in this work. The chemical composition together with physical data is presented in Table 2. Ignaberga is a reactive, geologically young limestone. The limestone has been used extensively in both boiler, e.g. [3,4,8,9], and laboratory investigations, e.g. [11–13], of the reaction between limestone and SO_2 . Storugns limestone is of intermediate age and reactivity and has been evaluated earlier in a TGA apparatus [13]. Köping is an old and unreactive limestone which has also been studied extensively in the literature [8,10,13]. Though the limestones have a similar chemical composition, calcined Ignaberga has the highest porosity followed by Storugns and Köping limestone.

3. Results

3.1. Effect of limestone type

The outlet SO_2 concentration is shown as a function of time for an experiment conducted with the three limestones at 850°C in Fig. 2(a)–(c). The three figures are qualitatively similar, with a series of SO_2 peaks that can be more easily explained using Fig. 3, which is an enlargement of Fig. 2(a) with only a few of the peaks shown:

Table 2
Limestone characteristics

	Ignaberga	Storugns	Köping
Size (mm)	0.5–0.7	0.5–0.7	0.5–0.7
Chemical composition (%):			
Ca	37.4	34.0	36.6
Si	0.904	0.706	1.73
Mg	0.365	0.576	0.683
Fe	0.276	0.511	0.523
Al	0.000	0.268	0.246
Mn	0.040	0.028	0.138
Zn	0.010	0.012	0.016
Cu	0.002	0.005	0.013
Na	0.035	0.033	0.070
K	0.068	0.211	0.167
Structural parameters:			
Porosity ^{a,b}	0.59	0.53	0.46
BET area ^{a,c} ($\text{m}^2 \text{g}^{-1}$)	14.6	12.9	15.5
Average pore radii (μm)	60.3	52.7	33.5

^a Samples were calcined in an atmosphere of 4% O_2 and 10% CO_2 at 850°C . Calcination time: Köping 30 min, Ignaberga, Storugns: 15 min.

^b As determined from Hg porosimetry data (Micromeritics Pore Sizer 9305). Only pores $<10 \mu\text{m}$ have been used in the calculation.

^c Micromeritics Flowsorb II 2300.

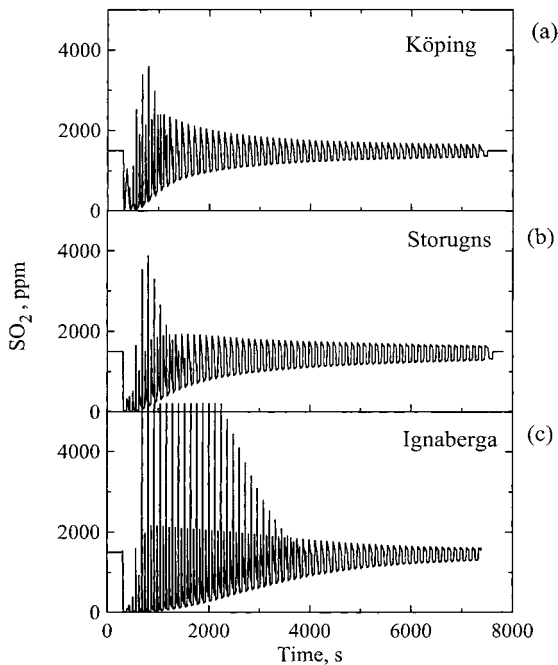


Fig. 2. The outlet SO_2 concentration as a function of time for three different limestones at 850°C : (a) Köping; (b) Storugns; (c) Ignaberga.

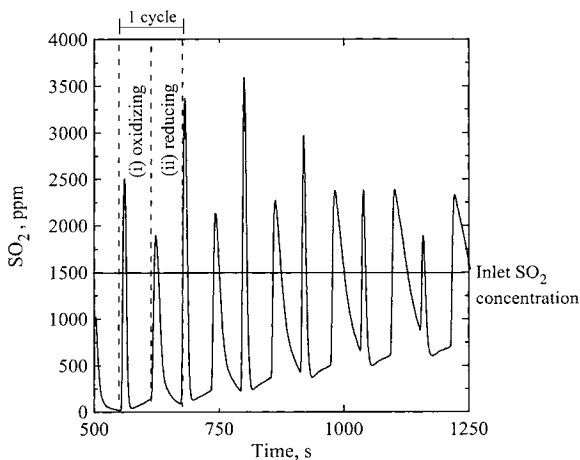
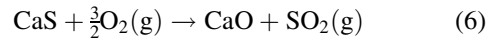


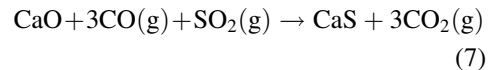
Fig. 3. An enlargement of part of Fig. 2(a).

- i) The oxidizing period is initiated by a SO_2 peak which exceeds the inlet concentration to the reactor (1500 ppm). This peak is due to the oxidation of CaS formed in the prior reducing period:



This peak is followed by a much lower but increasing SO_2 concentration due to the formation of CaSO_4 which progressively plugs the pores of the CaO, and results in a higher degree of intraparticle diffusion resistance and subsequently a lower rate of reaction.

- ii) After the O_2 has been replaced by CO there is an immediate SO_2 peak attributed to the reductive decomposition of CaSO_4 , reaction (3), followed by a rapid decrease in the SO_2 concentration due to the formation of CaS,



From Fig. 2 it is evident that the peaks due to oxidation of CaS are much more pronounced for Ignaberga limestone compared to Köping and Storugns. In general, however, the rate of both reductive decomposition of CaSO_4 and oxidation of CaS decreases with time.

Fig. 4 shows the final conversion after 2 h of reaction for the three limestones at 850°C . The reactivity is very similar for oxidizing and alternating conditions for the three limestones, with the final conversion increasing with increasing initial porosity (see Table 2). Köping limestone, however, displays a somewhat higher degree of conversion under alternat-

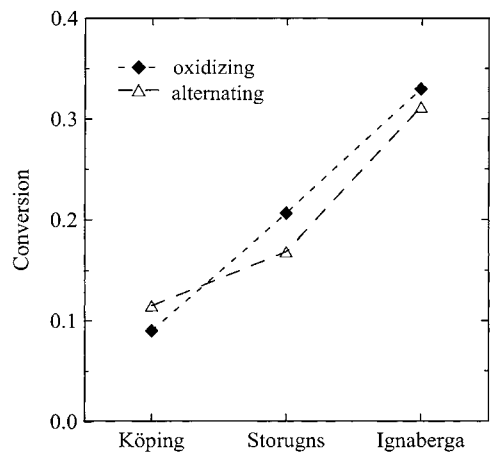


Fig. 4. Conversion after 2 h as a function of limestone for oxidizing and alternating conditions.

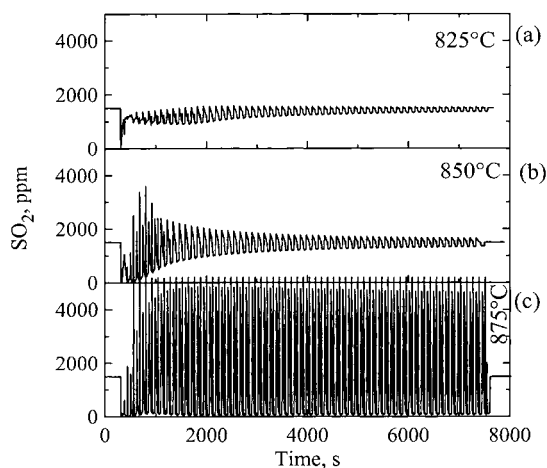


Fig. 5. The outlet SO_2 concentration as a function of time for Köping limestone sulfated at temperatures in the range 825°C – 875°C : (a) 825°C , (b) 850°C , (c) 875°C .

ing conditions, whereas Storugns and Ignaberga have somewhat less sulfur capacity under alternating conditions. The small difference in conversion between alternating and oxidizing conditions is in agreement with earlier findings where limestone has been investigated under alternating conditions using similar cycle times and fraction of time under reducing conditions [11,14].

3.2. Effect of temperature

Fig. 5(a)–(c) shows the SO_2 concentration as a function of time for three trials with Köping limestone sulfated at temperatures between 825° and 875°C . Fig. 5(a) shows Köping limestone sulfated at 825°C . Peaks due to the decomposition of CaSO_4 are seen throughout the experiment, and several peaks due to the oxidation of CaS were also detected in the initial stages of the reaction. No CaCO_3 was detected in the final sample, but from analysis of the exit CO_2 gas concentration it was found that the calcination reaction was very slow and continued in principal throughout the experiment. As the temperature is increased the rate of reductive decomposition, reaction (3), increases in addition to the rate of CaS oxidation, reaction (6). At 875°C , the rate of decomposition and oxidation are very high throughout the experiment, indicating that no product layer is accu-

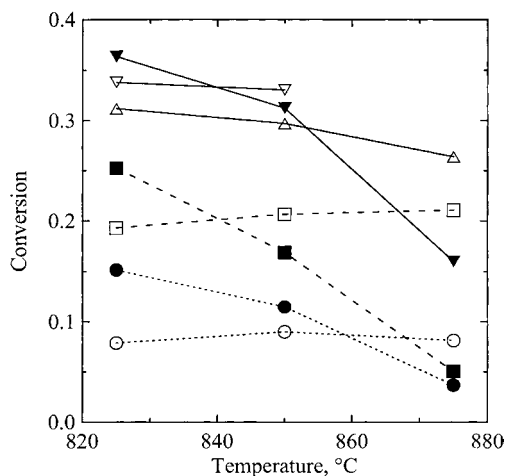


Fig. 6. The conversion as a function of temperature after 2 h experiment: Köping alternating (●), oxidizing (○); Storugns alternating (■), oxidizing (□); Ignaberga alternating (▼), oxidizing (▽), oxidizing from test series with somewhat different conditions (△).

mulating in the particle, but rather the reactions are taking place near the surface of the particle. The very low conversion, ca. 4%, confirms this low sulfur capture. Fig. 6 shows the degree of conversion as a function of temperature for the three limestones investigated in this paper, both for oxidating and alternating conditions. The following can be said about Fig. 6:

1. The porous and reactive limestone Ignaberga showed the greatest sulfur capacity at all temperatures for both alternating and oxidizing conditions, followed by Storugns and finally Köping limestone.
2. The conversion was relatively constant in the temperature range 825 – 875°C for samples sulfated under oxidizing conditions.
3. For samples sulfated under alternating conditions a maximum in the degree of conversion was seen at 825°C , with the conversion exceeding the conversion found under oxidizing conditions for all three limestones.
4. A drastic decrease in the conversion was seen for alternating conditions as the temperature was increased from 850° to 875°C . This rapid decrease may be due to the rapid release of SO_2 through both reaction (3) and reaction (6) (see Fig. 5(c)).

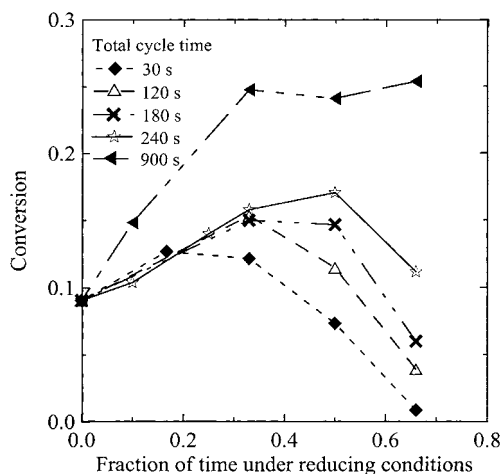


Fig. 7. The conversion as a function of the fraction of time under reducing conditions after 2 h sulfation of Köping limestone (0.5–0.7 mm) using a reactant gas of 1500 ppm SO₂, 10% CO₂, 0–4% O₂, and 0–4% CO. Data are taken from [10].

Several experiments were conducted at 800°C but at this temperature the conversion was considerably lower compared to experiments performed at 825°C. At the low temperature the reaction is limited by the slow calcination of CaCO₃ which was confirmed by the presence of CaCO₃ in the sulfated samples.

3.3. Comparing the reactivity of limestone under oxidizing and alternating conditions

In this study, it was found that in some cases alternating oxidizing and reducing conditions result in an increased degree of sulfur capture, i.e. Fig. 6 at 825°C, compared to constant oxidizing conditions. This is consistent with previous results, [10], depicted in Fig. 7, which shows the degree of conversion after 2 h of sulfation with Köping limestone as a function of the fraction of time under reducing conditions at 850°C and with varying cycle time. From this figure it is evident that the 9% conversion obtained under oxidizing conditions can be both considerably increased and decreased. This raises the question whether reaction rate data based on laboratory investigations under oxidizing conditions for Köping limestone are suitable for use in modelling of sulfur capture in FBC.

A previous work on sulfur capture modelling for CFBB was based on the use of an effective first-order reaction constant, k_{eff} , derived from laboratory experiments, [9], and defined as,

$$\frac{dX}{dt} = k_{\text{eff}} p_m \quad (8)$$

where p_m is the SO₂ partial pressure and k_{eff} a function of the conversion. In the case of alternating conditions the behavior is much more complex, with SO₂ capture during the oxidizing and reducing periods and release during the shifts. Therefore, a similar reaction rate constant cannot be derived for alternating conditions. However, for comparison purposes it is possible to calculate a reactivity parameter versus conversion. This reactivity parameter, k_{reac} , is defined just like the previously used rate constant k_{eff} , with the exception that data are averaged for a complete cycle, i.e. one period of oxidizing and one of reducing conditions (see Fig. 3). The basis for the comparison of k_{reac} as obtained under alternating conditions with the rate constant k_{eff} is that the SO₂ concentration was the same in the tests. However, it should be noted that the comparison in reactivity cannot be extended to other SO₂ concentrations since the reactivity parameter cannot be expected to be independent on the SO₂ concentrations. The Appendix A shows how k_{reac} is derived.

Fig. 8 shows a comparison of k_{eff} obtained under oxidizing conditions with k_{reac} from sulfation experiments with Köping limestone under alternating conditions at 850°C. From Fig. 7, it is obvious that there is a large spread in reactivity under alternating conditions, and the trials shown in Fig. 8 are those with a reactivity considerably higher than that obtained under oxidizing conditions. Fig. 8 clearly illustrates the large spread in reactivity, and indicates that a reaction constant, k_{eff} , derived under oxidizing conditions cannot be expected to give relevant information for the behavior under alternating conditions. It must be concluded that a way to express the reactivity of Köping limestone under alternating conditions, which can be used for modelling purposes, is lacking at present.

The reactivity of Ignaberga limestone under oxidizing conditions at 850°C has been used in a sulfur capture model for CFBBs [9]. Naturally, the question arises whether the conclusion above for Köping

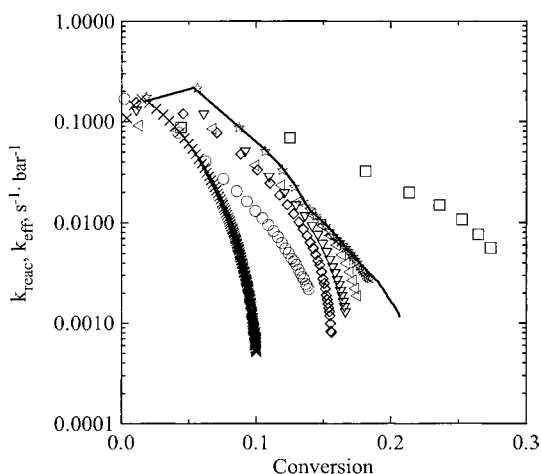


Fig. 8. The rate parameters, k_{eff} and k_{reac} as a function of conversion for several of the experiments shown in Fig. 7: oxidizing (X), 20 s ox/10 s red (O), 80 s ox/40 s red (\diamond), 120 s ox/60 s red (∇), 160 s ox/80 s red (\square), 120 s ox/120 s red (*), 600 s ox/300 s red (\square), 120 s ox/120 s red –4 h (—).

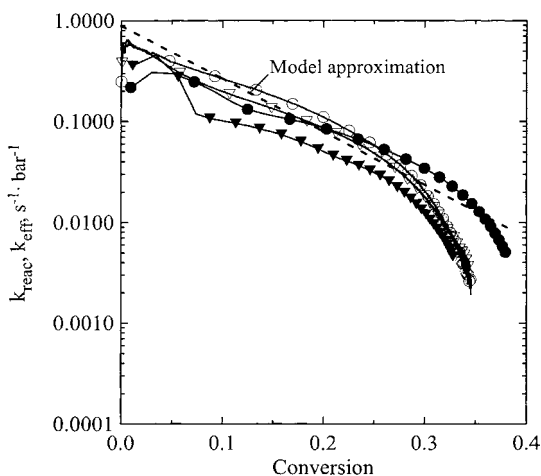


Fig. 9. The rate parameters k_{eff} and k_{reac} as a function of conversion for Ignaberga limestone: 850°C alternating (\blacktriangledown), oxidizing (∇); 825°C alternating (\bullet), oxidizing (O); approximation used in a sulfur capture model for CFBBs at 850°C [9] (—).

limestone also applies to Ignaberga. Fig. 9 shows k_{eff} and k_{reac} as a function of conversion for Ignaberga under oxidizing and alternating conditions (60/60 s) at 825° and 850°C. Also included in the figure is the approximation of the reaction constant from laboratory experiments used in the model for CFBBs. A comparison of Köping and Ignaberga limestones

clearly shows that the large spread seen in Fig. 8 is not present in Fig. 9. The spread in the data seen in Fig. 9 is of the same order as the spread in the data obtained under oxidizing conditions [15]. However, on the basis of the presently available limited data for Ignaberga it is not possible to make any safe conclusions on the possibility to use laboratory data from oxidizing conditions in modelling. Nevertheless the modelling results obtained were reasonably good and it is not unlikely that the underprediction of the conversion [9] can be explained by the positive effect of alternating conditions.

4. Discussion

At the conditions investigated in this paper it is clear that alternating oxidizing and reducing conditions have an effect on the sulfur capture process, especially at high temperatures, where the sulfur capture drops considerably for the three limestones tested. The rapid decrease seen at 875°C for alternating conditions compared to oxidizing is consistent with the ‘reduction’ theory originally proposed by Jonke et al. [7] and confirmed in both boiler investigations by Lyngfelt and Leckner [3,4] and in laboratory investigations by Hansen [11,14].

In addition to the negative effect of reduction, Jonke et al. [16] also suggested the possibility that the alternating reducing and oxidizing zones in the bottom bed of a fluidized-bed combustor and the continual uptake and release of sulfur from the sorbent particles enables greater penetration of the sulfur into the sorbent particle and hence a greater degree of conversion compared to when the limestone was sulfated in an oxidizing environment. In support of this theory, Mattisson and Lyngfelt [10] found that, depending upon the cycle time and fraction of time under reducing conditions, higher degrees of sulfur capture could be obtained under alternating conditions (Fig. 7). In this work, a higher degree of conversion was found at 825°C under alternating conditions compared to oxidizing for all three limestones (Fig. 6). This indicates that the observation that Köping limestone can obtain a higher conversion in some cases of alternating conditions, is probably more or less valid also for other limestones. The relative impact can be speculated to be larger for more unreactive limestones, as in Fig. 6, where the most unreactive limestone, Köping,

showed the greatest relative increase at 825°C, 92%, whereas the most reactive limestone, Ignaberga, shows the smallest relative increase, ca. 8%. This is also in agreement with previous results for the very reactive limestone Stevns Chalk, ca. 70% conversion, where no significant difference between the conversion under oxidizing and alternating conditions was found in the temperature range 800–900°C [11,14].

5. Conclusions

The reaction between limestone and SO₂ was investigated under alternating oxidizing and reducing conditions in the temperature range 800–875°C. Three limestones of widely varying geological age and porosity were investigated. The main conclusions of the present work were:

- At oxidizing conditions no great difference in conversion was found in the temperature range 825–875°C. At 800°C, the reaction was limited by the calcination of CaCO₃ resulting in a low conversion to CaSO₄.
- For alternating conditions an optimum temperature of 825°C was found for all three limestones. The conversion was higher for alternating conditions compared to oxidizing at this temperature for the three limestones investigated.
- At higher temperatures the conversion for alternating conditions decreased due to the rapid release of SO₂ through reductive decomposition of CaSO₄ and oxidation of CaS.
- A rate parameter was used for comparing the reactivity of experiments conducted under alternating with experiments performed under oxidizing conditions. This comparison shows that the reactivity data obtained for Köping limestone under oxidizing conditions are not suitable for modelling purposes and with the present state of knowledge there is no available way to express the reactivity of this limestone which can be used for modelling under alternating conditions.

Acknowledgements

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Appendix A

It will be assumed that the rate of reaction under alternating conditions can be expressed as,

$$\frac{\Delta X}{\Delta t} = k_{\text{reac}} p_m \quad (\text{A1})$$

where p_m is an average SO₂ partial pressure and k_{reac} the rate parameter that is dependent on the degree of conversion, X . Similarly, from Eq. (4) follows that the rate can be expressed as:

$$\frac{\Delta X}{\Delta t} = \frac{M_{\text{CaCO}_3} \dot{n} (p_i - p_o)}{mf p_{\text{tot}}} \quad (\text{A2})$$

The rate, $\Delta X/\Delta t$, was evaluated for a complete cycle (one oxidizing period + one reducing period), using Eq. (A2). In order to evaluate the average concentration of SO₂ in the limestone layer, a log-mean partial pressure was used:

$$p_m = \frac{p_i - p_o}{\ln(p_i/p_o)} \quad (\text{A3})$$

A mean value of p_i and p_o was calculated for each cycle and a value of p_m determined using this equation for each cycle. Thus using Eq. (A1)–Eq. (A3) it is possible to calculate the reactivity parameter, k_{reac} , as a function of conversion for each cycle.

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