

CaS Oxidation by Reaction with CO₂

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Abstract

Calcium sulphide is an undesirable product from both FBC and topping cycle gasifiers. Unfortunately, its direct oxidation in a FBC environment is made difficult due to the fact that unreacted CaS is protected from further reaction with O₂ by formation of a CaSO₄ shell. In previous work it was often implied that oxidation of CaS occurred solely by reaction with O₂. However, this study shows that CO₂ can be an effective oxidant for CaS at temperatures above 600°C. Furthermore, it appears that the principal gas phase products are SO₂ and CO, and direct attempts to measure COS using mass spectrometry suggest that its formation is negligible. Somewhat surprisingly SO₂/CO molar ratios are in the range of 0.4 to 0.5, which is problematic, if the dominant reaction is $\text{CaS} + 3\text{CO}_2 = \text{CaO} + 3\text{CO} + \text{SO}_2$, unless CO₂ is reacting to form elemental carbon, which appears unlikely, or side reactions occur, leading to a variety of gaseous products. These results also suggest that CO itself has no significant part in the oxidation process at least up to 850°C or more. Reaction with H₂O also begins above 600°C, but it is a much less effective oxidant, and experiments with CO₂/H₂O further support the idea that CO₂ is the more important oxidant in that system and might be used to destroy CaS from the topping cycle gasifier.

Keywords: CaS, Oxidation, FBC, Gasification, Topping Cycles

Introduction

Topping cycle gasifiers burning high-sulphur fuels must employ some method of sulphur removal, typically by means of limestone or dolomite addition [1]. The CaS so produced is then transferred together with unburnt char to another reactor, either a pressurized fluidized bed (PFBC) or circulating fluidized bed combustor (CFBC), where it is hoped that both char burnout and oxidation of CaS to CaSO₄ will occur. Unfortunately, it has proven to be much more difficult to oxidize the CaS in a FBC environment than hitherto supposed and this has been discussed elsewhere [2]. One solution is to use dolomites that have been shown to give good conversion of CaS [1]. However, the use of dolomitic limestones in FBC has a number of problems not the least of which is their lack of general availability, and the fact that the Mg component is unable to participate in the sulphur capture reaction at typical FBC conditions. Calcitic limestones are, therefore, due to these considerations, the preferred type of sorbent, although effective elimination of CaS may then not occur in a PFBC or CFBC environment [2].

Oxidation by O₂ is often assumed to be the sole effective route for CaS oxidation although Illerup and his co-workers [3,4] did carry out limited regeneration tests of sulphided limestone at 850°, 900° and 950°C with a CO₂/N₂ mixture. Regeneration of sulphided dolomite has also been studied using various mixtures of O₂/CO₂ and H₂O [5, 6]. More recently, Qiu et al. [2] have shown that CO₂ can convert CaS, under both pressurized and atmospheric conditions over a wide range of temperatures, to CaO, CaSO₄ and CaCO₃. However, the exact mechanism by which these transformations occur is far from clear, although it is possible to write a series of balanced equations in which CaS is converted to these products such as:



The choice between CaO and CaCO₃ formation is determined by whether the CO₂ partial pressure exceeds that for CaCO₃ formation (for these experiments the limiting temperature for CaCO₃ formation occurs at 898°C). It has also been suggested in the work of Qiu et al. [2] that CaSO₄ formation might occur due to secondary reaction between SO₂ and CaO. An implication of the overall reactions is that on a molar basis, more CO than SO₂ should be produced. If reactions (3) or (4) + (5) dominate, the SO₂/CO molar ratio should be 1/3. With CaSO₄ formation as in reactions (2) or (4) even less SO₂ would be formed. It should be noted that reaction (5) does not occur below about 850-900°C [7-9].

It was decided to examine the reaction of CaS in a CO₂ gas stream using CO and SO₂ analyzers to determine which if any of these gas products were formed over a nominal temperature range of 400°-1000°C. As earlier work had failed to find any carbon in the solid residues produced, it was initially assumed that CO itself ought not to be involved in any direct reaction with CaS [2]. However, since elemental carbon might also be subsequently removed by direct reaction with CO₂, at higher temperatures, it was decided to carry out an experiment with a CO gas stream. Finally, because conventional gas analyzers cannot detect COS, experiments were carried out in which the resulting gas streams were subjected to analysis using mass spectrometry. Subsequently, because of evidence of impurities in the first sample of CaS a new sample of fresh CaS was obtained and further experiments were carried out on it.

Experimental

A tube furnace was used to carry out the tests. Typically, a small sample of CaS was placed in a ceramic boat, and the system flushed with CO₂ or CO for 20 minutes prior to heating the sample at a programmed rate. The particle size was fine (less than 325 mesh), and the CO₂ used was of Coleman grade with total impurities < 100 ppm and should therefore contain negligible amounts of O₂. For initial tests a CO₂ flow rate of 0.6 dm³/min was maintained for all experiments. For the first series of tests a sample of CaS from Fisher Scientific was used, and subsequently because of concerns about possible

contamination during storage of this sample a second series of tests was carried out with a new sample of “pure” CaS from Aldridge Chemicals. During the second series of tests the effect of water addition was also studied. Water vapor was generated with de-ionized water in a customer made evaporator. Water feed rate was controlled with a syringe pump. In these tests, the CO₂ or N₂ flow rate was increased to 1 dm³/min. The water vapor flow rate was kept at 0.1 dm³/min.

The tube furnace is capable of reaching 850°C from room temperature in about 20 minutes. The gas stream was then fed to CO and SO₂ NDIR analyzers. The CO analyzer had a range of 0-10000 ppm, so that the lowest readings to be expected is about 10 ppm (0.1% of the range). Following the first two tests, two additional tests were carried out, one with CO₂ and one with CO as the reactant. Gas samples were taken at about 850°C with a syringe for GC-MS analysis. In addition, a bag gas sample was taken at about 700°C for GC analysis. Subsequently, because of problems with the SO₂/CO ratios, which were too high to be explainable on the basis of obvious chemical reactions, the new sample of CaS (obtained from Aldridge Chemicals) was used. A number of tests were repeated. The experimental setup is shown in Fig. 1 and a list of runs and run conditions are given in Table 1.

Results and Discussion

Two initial runs were carried out with CaS sample weights of 0.52g and 0.232 g (Figs. 2a and 2b). Quite surprisingly, there appeared to be indications of initial activity at temperatures as low as 400°C, with some evidence for at least two different regimes between 400°-600°C. However, it is clear that at 600°C and above, SO₂ production accelerates and the rate starts to fall again only at 700°C. Various explanations can be offered involving pore blocking, etc. However, what is surprising is the extremely large difference in production of SO₂ which is of the order of 10-20 times that of the CO production, something that is certainly not compatible with a reaction like (3) or reactions (4) and (5) combined for example. The very high production rate of SO₂ relative to CO might suggest for instance that CO₂ is reacting to form elemental carbon. Unfortunately, this seems a most unlikely reaction at temperatures much below 900°C, and in any case no elemental carbon was previously found in sample residues, although again this might be due to reaction with CO₂ at the later stages of reaction.

A thermodynamic analysis of this system using the FACT program (Fig. 3) was then carried out to see if that would give useful insights. Assuming a CO₂/CaS molar ratio of 10 over the temperature range of 800-1100 K, SO₂/CO ratios of 12% to 33% resulted, which are not in good agreement with the experimental results (Figs. 2a and 2b). Moreover, this analysis indicates none of the evidence of distinct regimes for SO₂ production, although in line with these results it does suggest the formation of COS is negligible.

As initial experimental work was not designed to give any information about the involvement of CO in this process or the formation of COS, it was decided to do two more experiments with mass spectrographic sampling of the off gases. In one test CO₂

was employed (Fig. 4) and in the other CO was supplied at the same flow rate as the CO₂ used in the previous three experiments (Fig. 5).

Tests with CO₂ showed the same SO₂ and CO profiles as before (Fig. 4). However, the GC analysis failed to find any evidence of COS, which means that COS had to be present in concentrations below 100 ppm (the detection limit of the instrument). The GC-MS did show a very small peak at a m/e of 60 which could be COS, and did detect strong peaks at 64 and 28, which should be SO₂ and CO respectively. However, it should be noted that since some air entered the sample owing to the fact that the syringe needle was thick the later peak might also be due to N₂. In these tests the CaS sample lost 5.3% of its mass over the duration of the run.

Tests with CO produced very low SO₂ and CO₂ readings (Fig. 5), and it is difficult to conclude whether the results are simply due to drift of the analyzer at least at the lower levels. Here, the GC-MS results showed no evidence of CO₂ or COS formation at 850°C. A very small peak at m/e of 44 might be CO₂ but if so it was of the level that could have easily resulted by contamination from the air (it is inevitable for some air to get into the GC-MS sample during sample injection). From these results it can be concluded that CaS does not react with CO at an appreciable rate at temperatures up to 850°C. It should also be noted that the CO₂ readings from the CO₂ analyzer were very much more than those indicated by the GC-MS at 850°C, which suggests that the results from this analyzer should not be treated with much confidence given that it was operating near its lower limits.

The problem of the initially high SO₂/CO readings left a few possible alternatives. One was that some other product was being formed such as CaC₂ for instance. However, this seems most unlikely because this is normally formed at high temperatures (2200-2250°C) by reaction between CaO and C [10], nor did the formation of elemental carbon seem much more probable given the inability of CO to react with this sample. The sample of “nominally” pure CaS was submitted for analysis by quantitative X-ray diffraction (QXRD), and the following results obtained (Table 2).

The QXRD analysis showed the presence of a considerable amount of impurities. These impurities explain why the SO₂/CO ratio was elevated as CaSO₃ is known to decompose at or near 700°C [11] which explains the first SO₂ peak, and the presence of any water from the decomposition of hannebachite would also lower CO concentrations. The presence of CaSO₄ in the original sample is evidently caused by reaction with moist air. Similarly, this must be the cause of the formation of CaSO₃, although it should be noted that in work on the decomposition of CaS at ambient temperature, the presence of CaSO₃ was reported but it was not the preferred form [12, 13].

A new CaS sample was obtained from Aldrich Chemicals. The test apparatus was first flushed with CO₂ for 20 min before switching on the furnace. The results of the test are given in Fig. 6. With the new sample of CaS the SO₂/CO ratio is very much lower and takes values ranging from 0.4 to 0.5 in the temperature window of 800-850°C. This is still larger than one would expect on the basis of reaction (3) or (4) + (5), suggesting that

those simple relationships do not adequately describe the oxidation of CaS by CO₂. Nonetheless, these results are in much better agreement with the thermodynamic analysis and clearly indicate the importance of sample purity in such experiments.

Another test was carried out with the new sample (Fig. 7). In this test as in all previous tests with CaS and CO₂, a small SO₂ peak was observed in the 400-550EC temperature window. To verify if this peak was caused by reaction of CaS and CO₂ or by impurities in the CaS sample the furnace temperature was raised first from room temperature to about 550EC and then cooled down to near room temperature. When the furnace was cool, a second pass was initiated with the furnace heated from near room temperature to 900EC. In the first pass, there was a small SO₂ peak in the temperature window of 400-550EC, but on the second pass this peak was no longer present. In both heating passes, the CO concentration virtually overlapped. This supports the hypothesis that the first small SO₂ peak was caused by impurities in the CaS sample. Hence, when the impurities were “burned off” during the first heating pass, the remaining “pure” CaS reacted with CO₂ giving the same CO and SO₂ profile as previously, less the peak at 400-550EC.

Finally, tests were done to study the effect of water vapor. In the first test only water vapor was supplied, and the results are shown in Fig. 8. Fig. 8 showed that reaction started at about 610EC and several peaks of SO₂ were observed from 610E-900EC. Interestingly, the lower peak seen with the CO₂ runs was absent which implies that the impurity does not react with water vapor at this temperature. The production of SO₂ also seems to be about half that of tests with CO₂.

Oscillatory behaviour, in terms of both weight change and SO₂ peaks, has been previously described with TGA and differential reactors for direct oxidation of CaS with O₂. This has been explained by blocking of pores due to CaSO₄ formation followed by opening of pore channels via CaO and SO₂ formation due to reaction between CaS and CaSO₄ (reaction 5) [14,15]. It is therefore possible that the multiple peaks seen with H₂O are a reflection of a similar process since it seems most unlikely that there are indeed multiple reaction regimes over such a narrow temperature range. It is also interesting that no such similar behaviour is seen on oxidation with CO₂. This suggests either the smaller molar volume of CaCO₃ is not sufficient to cause noticeable perturbations in the CaS oxidation rate, or the fact that relatively little CaSO₄ forms, reducing the potential for such behaviour [2]. Another point is that previous work on CaS oxidation showed that reaction with O₂ also started around 600°C and that until temperatures over 1050°C were achieved complete oxidation of CaS was blocked by the formation of a CaSO₄ shell [16].

The water vapor was condensed in an ice bath. The condensate was washed out of the condenser giving a total volume of 28.62 mL. The condensate was analyzed for sulphur ions by ion chromatography. It was found that SO₄ ion concentration was 15.21 Φg/mL. The total amount of SO₄ ions was 435.3 Φg. Interestingly enough there was no evidence for the formation of SO₃ ions.

Finally, a test was carried out with CaS in mixtures of CO₂ and water vapor and the results are shown in Fig. 9. The CO and SO₂ profiles are very similar to that of CaS in

CO₂ alone except the ratio of CO/SO₂ was slightly lower due presumably to the influence of the water gas shift reaction. The water vapor was again condensed in an ice bath and washed out with de-ionized water. The total amount of condensate was 17.9 mL. Ion chromatography was once more used to examine the content of the condensate, which was shown to contain 20.67 Φg/mL of SO₃ and 4.13 Φg/mL SO₄ ions. The total amount of SO₃ ions was 370.0 Φg and the total amount of SO₄ ions was 73.9 Φg. The absolute values of sulphite and sulphate ion in the condensate are not significant. However, the fact that no sulphite was found in the condensate for the tests with water, whereas 85% of the SO_x²⁻ production in the condensate is sulphite for the CO₂/H₂O trial, suggests some change in either the oxidation mechanism or solution chemistry.

Conclusions

CO₂ is capable of oxidizing CaS over a wide range of temperatures starting from about 600°C. In this range it is clear that the SO₂/CO molar ratio adopts relatively high values based on the expected reaction with 0.4 being the lowest seen in this work. There is no evidence that COS formation occurs to any significant extent and the main gas phase products of this reaction appear to be SO₂ and CO at least up to about 900°C. Further, attempts to carry out direct reaction of CO and CaS suggested that oxidation by this reagent is not significant at least up to a temperature of 850°C.

A peak in the 400-550°C range was shown to be due to an impurity, as was a major peak in the 600-800°C range from the earlier tests. A limited series of tests with water vapor showed that rapid reaction begins with this component at about 600°C but that it was characterized by a series of peaks in the 600-900°C range. Oxidation with CO₂ and water vapor gave very similar profiles to those seen with CO₂ alone with a “pure” sample of CaS. Interestingly enough, the oxidation product detected in the condensate with water was different from that observed with CO₂ and H₂O vapor. In the first case the product was entirely SO₄ ion, while in the case of CO₂ and H₂O vapor the predominant form was SO₃ ion. This suggests some differences in the oxidation process. These results also support the view that CaS reacts much more readily with CO₂ than it does with H₂O over the same temperature range. This work shows that CO₂ oxidation can be used to destroy CaS. There are two obvious strategies to achieve CaS destruction with these reagents. The first is to operate at a temperature above the stability of CaCO₃ (above 900°C with pure CO₂) to ensure that the pores remain open, since earlier work has suggested that CaSO₄ formation is negligible with CO₂ oxidation. The second is to operate at lower temperatures with mixtures of CO₂/N₂.

Future Work

Future experiments will include two long runs at a temperature above 850°C, for both H₂O and CO₂ oxidation, together with QXRD to confirm the identity of the major solid products. Long runs will also allow us to determine whether SO₂ production decreases due to the formation of a sulphate shell and whether the multiple peaks seen with H₂O oxidation are similar to the oscillatory peaks seen with O₂ oxidation. The off gases will

also be passed through a series of “bubblers” to attempt to quantitatively trap the SO_x produced and confirm whether there is a difference in the species being produced.

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Table 1 – Run conditions for oxidation experiments

Run No.	Sample Source	Sample Size (g)	Gas Composition and Flow Rate
Run 1	Fischer Scientific	0.54	0.6 dm ³ /min of CO ₂
Run 2	Fischer Scientific	0.23	0.6 dm ³ /min of CO ₂
Run 3	Fischer Scientific	0.26	0.6 dm ³ /min of CO ₂
Run 4	Fischer Scientific	0.259	0.6 dm ³ /min of CO
Run 5	Aldrich Chemicals	0.2815	1 dm ³ /min of CO ₂
Run 6	Aldrich Chemicals	0.3462	1 dm ³ /min of CO ₂
Run 7	Aldrich Chemicals	0.309	0.1 dm ³ /min H ₂ O + 1 dm ³ /min N ₂
Run 8	Aldrich Chemicals	0.3235	0.1 dm ³ /min H ₂ O + 1 dm ³ /min CO ₂

Table 2 -QXRD analysis of CaS sample

Phase ID (3 Overlays)	Chemical Formula	Wt%
Oldhamite, syn	CaS	83.6
Hannebachite, syn	CaSO ₃ .0.5H ₂ O	13.4
Anhydrite	CaSO ₄	3.4

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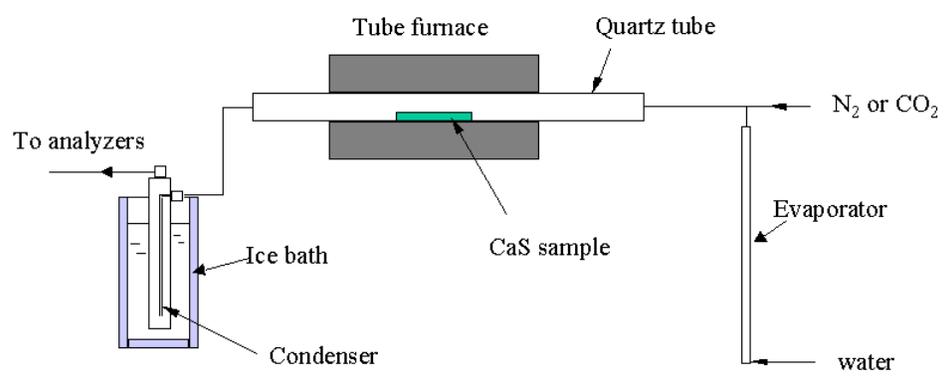
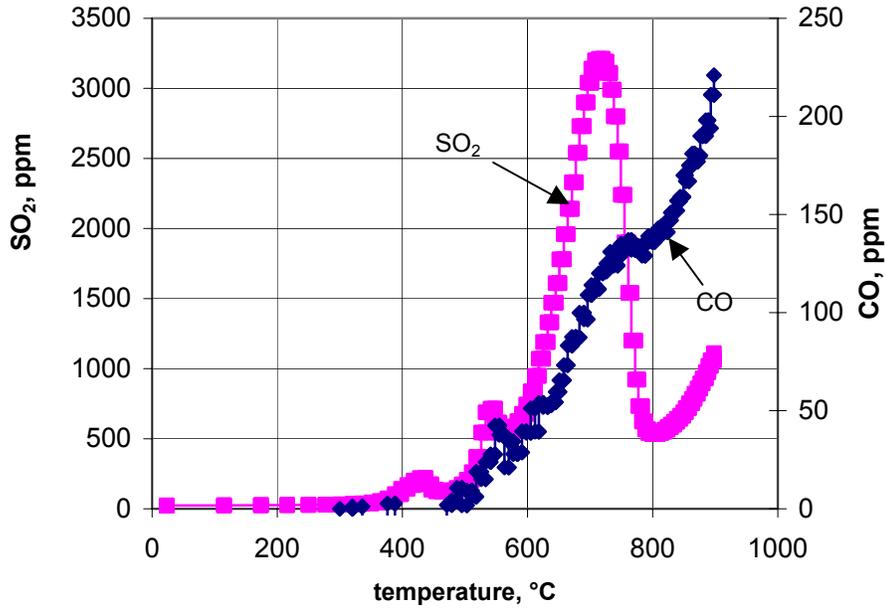
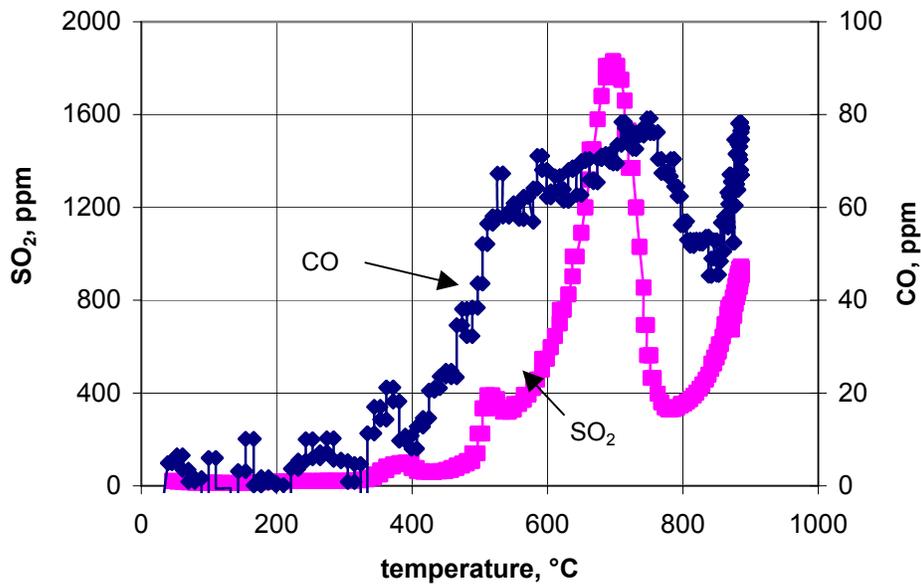


Figure 1. Tube furnace set-up for oxidation experiments.



(a)



(b)

Figure 2. CaS oxidation with 0.53 g (a) and 0.23 g (b) of CaS in a CO₂ atmosphere.

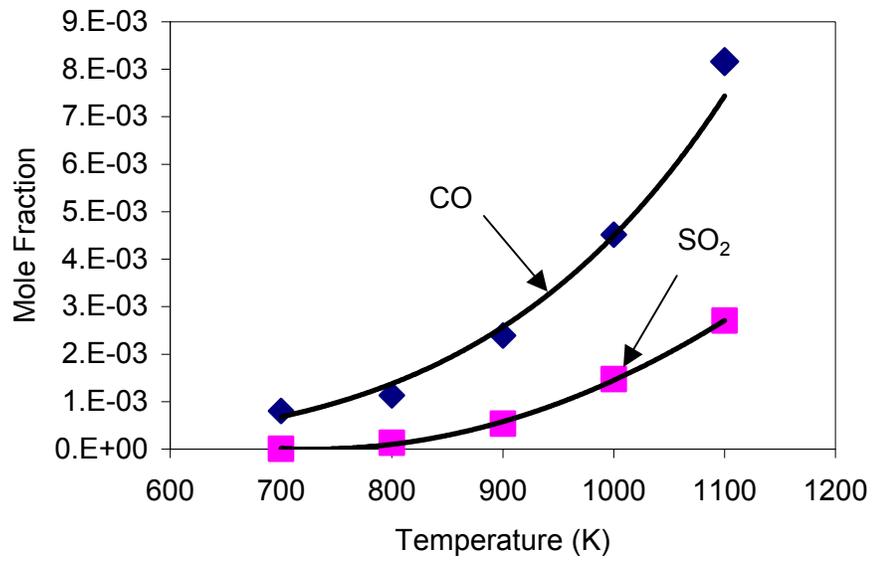


Figure 3. Thermodynamic predictions of CO and SO₂ concentrations from CaS oxidized by an excess of CO₂.

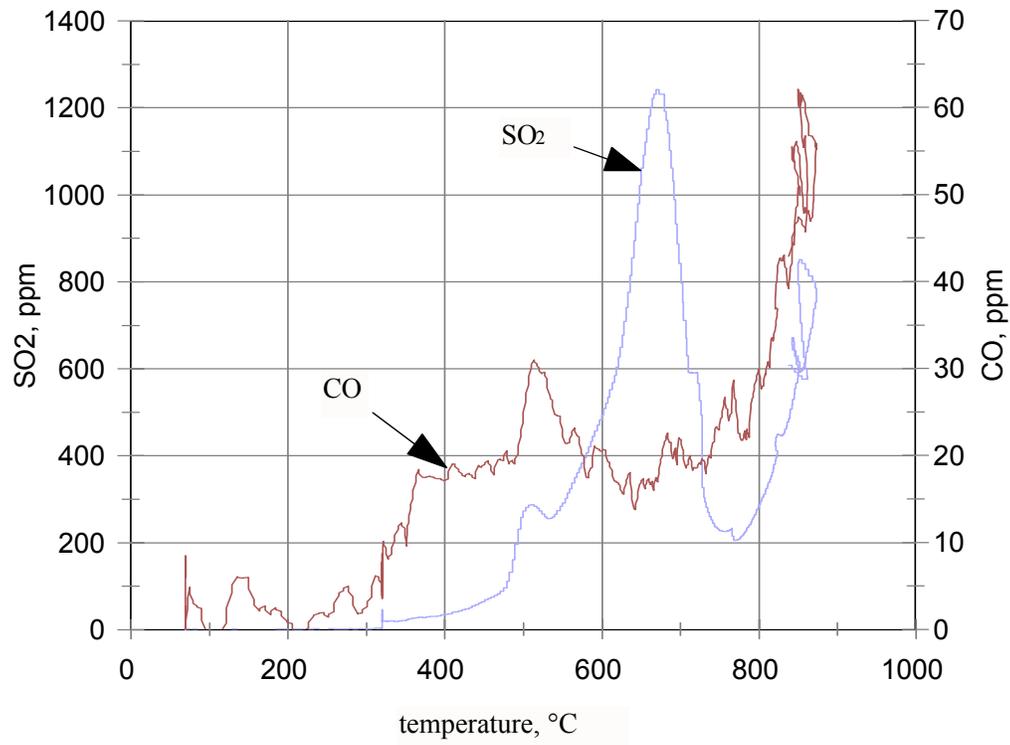


Figure 4. CaS oxidation by CO₂ (run 3).

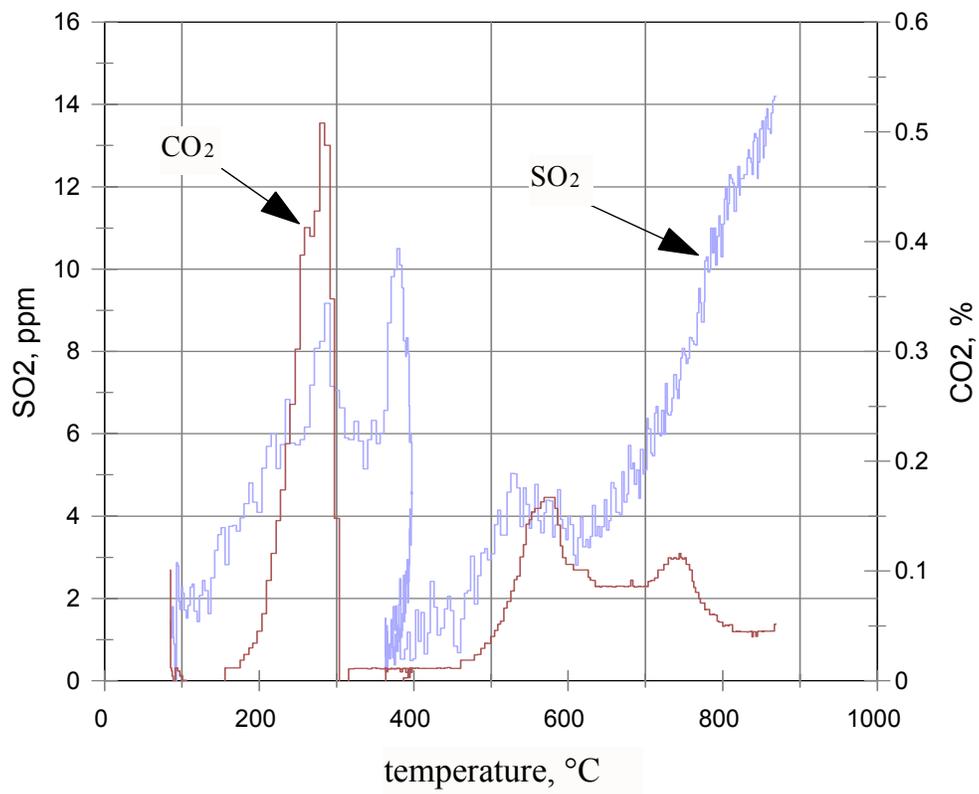


Figure 5. CaS oxidation by CO (run 4).

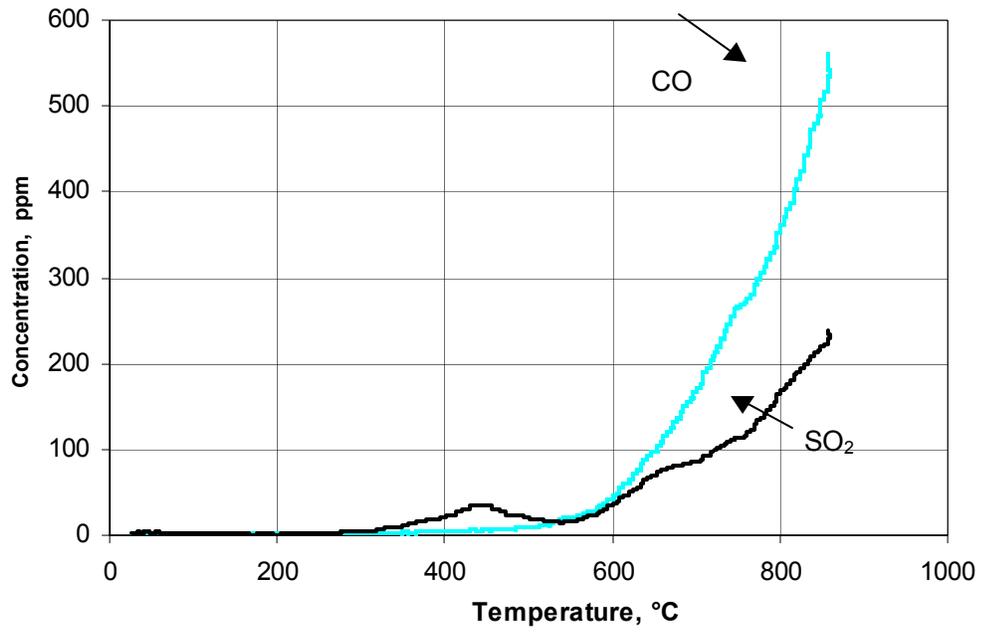


Figure 6. CaS oxidation in a CO₂ atmosphere (run 5).

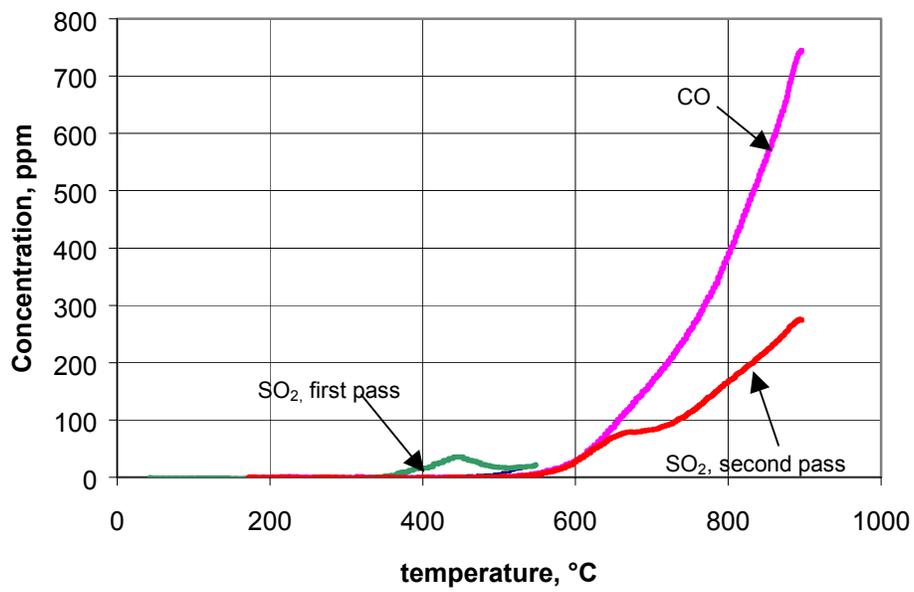


Figure 7. CaS oxidation in CO₂ (run 6).

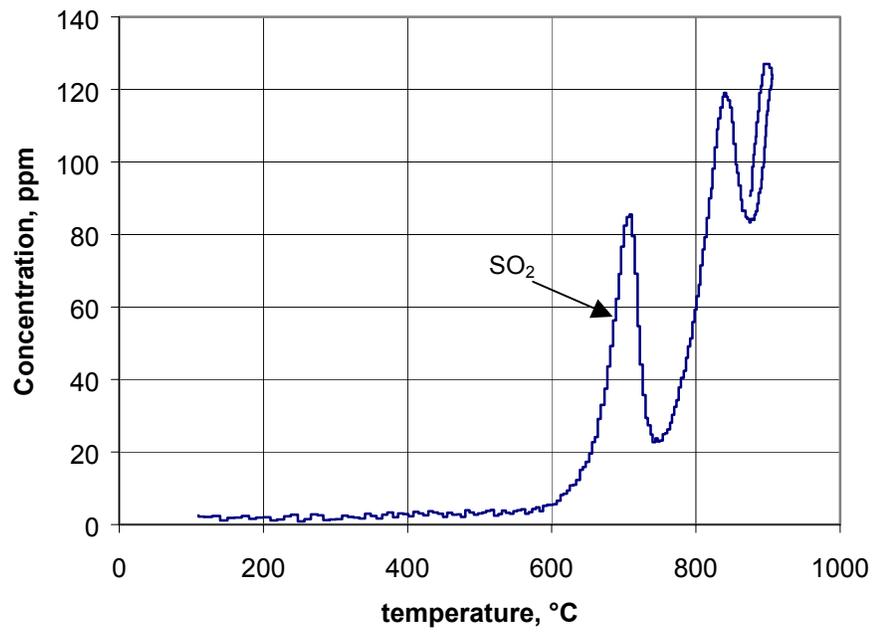


Figure 8. CaS reactions in water vapor and nitrogen (run 7).

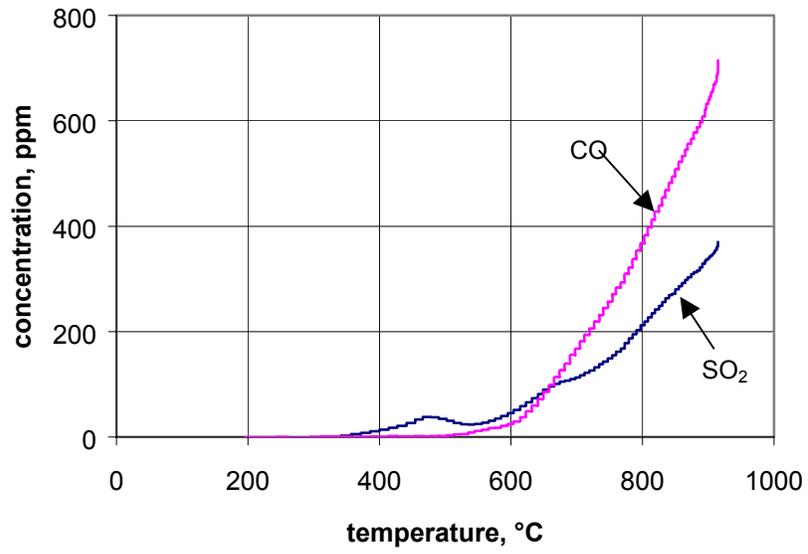


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