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THE CATALYTIC CONVERSION OF SO_2 TO SO_3 BY FLY ASH AND THE CAPTURE OF SO_2 AND SO_3 BY CaO AND MgO*, **

P. MARIER AND H. P. DIBBS†
Control Technology Section, Technology Development Branch, Air Pollution Control Directorate, Ottawa (Canada)

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ABSTRACT

The formation of SO_3 from SO_2 and O_2 is catalyzed by iron oxide in the fly ash from a coal-fired boiler. The amount of SO_3 produced is dependent on the iron oxide content of the fly ash and on the oxygen concentration of the gas stream. Carbon in the fly ash significantly reduces the formation of SO_3. The removal of SO_2 from a gas stream by CaO and MgO is enhanced by the catalytic conversion of the SO_2 to SO_3, as SO_3 is more easily captured than SO_2 by these oxides. The formation of SO_3 and its removal from the gas stream depend on the reaction temperature, the oxygen concentration of the gas stream, and the flow rate of the gas.

INTRODUCTION

Large amounts of sulphur dioxide and particulate matter are emitted annually into the atmosphere from coal-fired sources. The harmful effects of these emissions on health, plant growth, and constructional materials have been reported[1,2] and various methods for SO_2-emission control are now under intensive investigation. These methods include sulphur removal from coal before combustion[3,4], flue-gas desulphurization[5–7] and novel combustion techniques[8,9]. However, a recent survey[3] has concluded that no commercial process is yet available that can economically remove sulphur from coal before combustion. Similarly, although various methods are being investigated for the removal of sulphur oxides from combustion gases[5–7], none have yet been commercially proven for large-scale use[10]. The desulphurization of combustion gases by the injection of CaO or calcined dolomite into coal-fired boilers has undergone large-scale trials[11], but the low utilization of the scavengers is a major disadvantage of this technique. The present study is concerned with methods to improve the utilization of CaO and MgO as scavengers for SO_2 and is based on the

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[†] Research Scientist and Head, respectively, of the Control Technology Section, Engineering Division, Technology Development Branch, Air Pollution Control Directorate, Ottawa, Canada.

greater reactivity of SO_3 than SO_2 with these oxides[12]. The study involved the use of various catalysts, including fly ash from a coal-fired boiler, to increase the SO_3 concentration of the gas stream. Fly ash was chosen because it contains significant quantities of Fe_2O_3, which is known to catalyze the formation of SO_3 in an oxidizing atmosphere[13,14].

EXPERIMENTAL

A sample of fly ash from Ontario Hydro's R. L. Hearn coal-fired power station in Toronto was supplied by Mr. D. Harrison, Managing Engineer, Chemical Research Department, Ontario Hydro. The carbon content of the fly ash, as determined by Ontario Hydro, was 7.1%. X-ray analysis at the Mines Branch (Ottawa) showed that the main constituents of the fly ash were synthetic mullite ($3Al_2O_3 \cdot 2SiO_2$) and iron oxides (Fe_2O_3 and Fe_3O_4 in approximately equal amounts).

Fluidization of a bed of fly ash to expose a large surface area to sulphur dioxide-containing gases was attempted, but this approach was not satisfactory due to channeling in the bed. It was therefore decided to support the fly ash as a dispersed phase on a substrate of Fiberfrax. Fiberfrax is the trade name of a fibrous alumina-silica heat-resisting material manufactured by the Carborundum Company, Niagara Falls, New York. Fiberfrax was stable under all the reaction conditions tested and served as an excellent mechanical support for the solid reactants. The fly ash was deposited on the fibres of the Fiberfrax from a slurry consisting of 25 ml distilled water, 1.5 g Fiberfrax in 0.25 in to 0.50 in pieces, and 5.0 g fly ash. The slurry was thoroughly mixed so that all the particles of fly ash were entrained by the fibres. The pieces of Fiberfrax were then dried and loosely packed in a reaction tube to a standard volume. This method of mounting the fly ash was used in most of the experiments and had the advantage over a fluidized bed of providing a very low pressure-drop across the reaction zone.

It was apparent from initial experiments that carbon in the fly ash had an adverse effect on the formation of SO_3 from SO_2 and O_2. The oxygen in the gas stream was found to react with the carbon, and the resultant exothermic heat of combustion prevented studies under isothermal conditions. Therefore to study the effect of the SO_2/O_2 ratio and temperature on the formation of SO_3, it was necessary to remove the carbon from the ash. This was accomplished by heating the fly ash in nitrogen to the required reaction temperature and then admitting oxygen. The oxidation of the carbon was monitored by differential thermal analysis and completion of the reaction was indicated when the exothermic peak returned to base line.

A diagram of the apparatus used to study the conversion of sulphur dioxide to sulphur trioxide in the presence of fly ash is shown in Fig. 1. The fly-ash-coated Fiberfrax was placed in a 1-in-diameter silica reaction tube (A) and was heated by a vertical tubular furnace (B). Section C contained the combined SO_2 and O_2 inlet which extended above the water level (E). The conversion of sulphur dioxide to sulphur trioxide in the presence of oxygen was determined by the amount of sulphuric acid

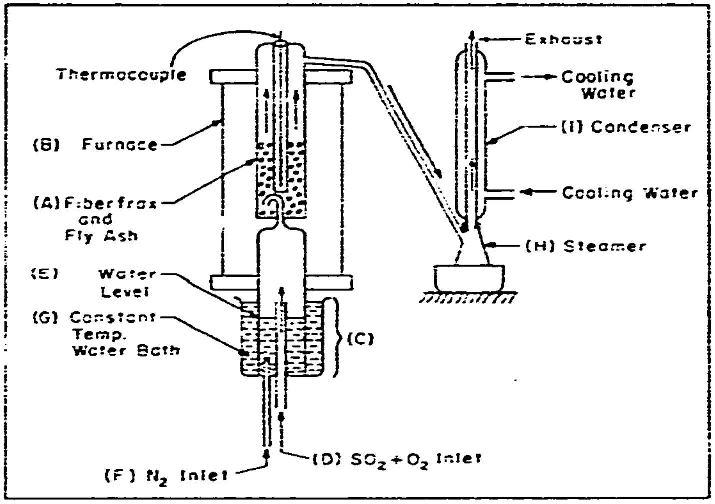

Fig. 1. Apparatus to measure the conversion of SO_2 to SO_3 in the presence of fly ash.

formed during the experimental runs, each of which was for 60 min. The conversion of SO_3 to sulphuric acid was accomplished by maintaining an excess partial pressure of water in the reaction zone. This was done with a water saturator, consisting of a nitrogen inlet tube (F) that had a fritted-disc outlet immersed in water maintained at 80°C by a constant-temperature bath (G). The acid condensate was collected in the steamer (H) which was placed below the condenser (I). This steamer-condenser arrangement prevented the escape of SO_3. The determination of the conversion of SO_2 to SO_3 was done by titrating the sulphuric acid collected in the steamer with a standard NaOH solution. The amount of sulphuric acid formed was found to be equivalent,

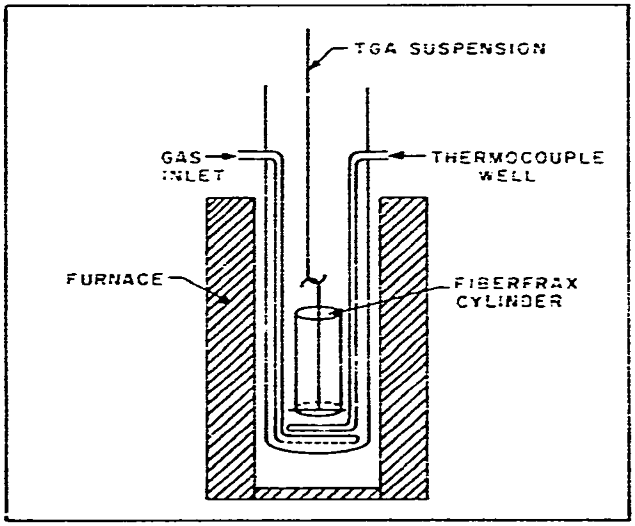

Fig. 2. Reaction zone of the thermogravimetric balance.

within experimental error (±1.5%), to the difference in the SO_2 content of the inlet and outlet gas streams.

Blank runs indicated that approximately 1% of the sulphur dioxide was converted to sulphur trioxide by the heated silica reaction tube and the Fiberfrax, and this value was subtracted from the experimental results.

A thermogravimetric balance (Thermograv) manufactured by the American Instrument Company was used for some of the experiments on the capture of sulphur dioxide and sulphur trioxide by calcium oxide and magnesium oxide. A diagram of the lower section of the balance is shown in Fig. 2. The suspension system included a weight-sensitive transducer whose output was automatically plotted on an X–Y recorder. The bottom of the suspension was attached to a crucible containing the solid reactants or, as illustrated in Fig. 2, to a Fiberfrax cylinder that was used as a mechanical support for the solid reactants.

RESULTS

The formation of SO_3 in the presence of fly ash

A study was made of the effect of temperature, from 500 to 900 °C, on the conversion of SO_2 to SO_3 in the presence of fly ash mounted on a Fiberfrax support. The ferric oxide content of the fly ash, after ignition to remove carbon, was 18.7%. The composition (volume %) of the gas was: H_2O, 18.9; SO_2, 8.1; O_2, 32.4; N_2, 40.6. A flow rate of 185 ml min^{-1} was maintained throughout each experiment, which represented a renewal of the gas through the charge every 1.8 sec. The results of these tests are shown in Fig. 3. It is evident that very little SO_3 is formed at 500 °C and that the maximum conversion (approximately 27%) of SO_2 to SO_3 occurs at about 700 °C. With further increase in temperature the conversion falls to approximately 16% between 800 and 900 °C. Thermodynamic equilibrium data[15] show that maximum

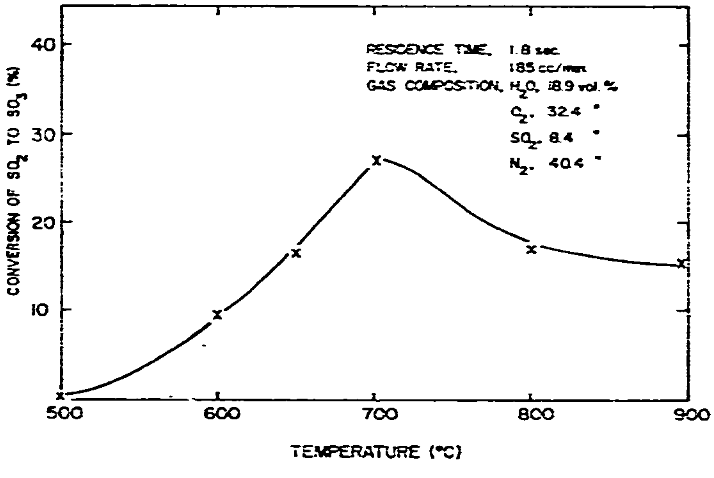

Fig. 3. Conversion of SO_2 to SO_3 in the presence of fly ash as a function of temperature.

conversion of SO_2 to SO_3 (approaching 100%) is favoured at temperatures below 425°C and that the equilibrium concentration of SO_3 decreases with increase in temperature to approximately 10% at 900°C. Moss[16] has reported that although the formation of SO_3 is favoured at low temperatures, its rate of formation at these temperatures is slow. He found that the rate increased as the temperature increased, to a maximum at 850°C. For the present study, in which the experimental conditions were very different from the fluidized-bed system used by Moss, the maximum conversion of SO_2 to SO_3 in the presence of fly ash occurred at approximately 700°C (Fig. 3). A significant observation from this work, and that of Moss, is that the maximum rate of formation of SO_3 occurs at temperatures well in excess of 425°C.

The influence of the Fe_2O_3 content of the fly ash on the formation of SO_3 was also investigated. Samples of fly ash containing different amounts of Fe_2O_3 were prepared by adding ferric oxide to the ash before it was deposited on the Fiberfrax support. The inlet gas contained a 1/4 mixture of SO_2/O_2, the flow rate was 185 ml min^{-1}, and the reaction temperature was 700°C. The results (Fig. 4) show that the conversion of SO_2 to SO_3 is linearly related to the iron oxide content of the fly ash in the range between 7 and 25%.

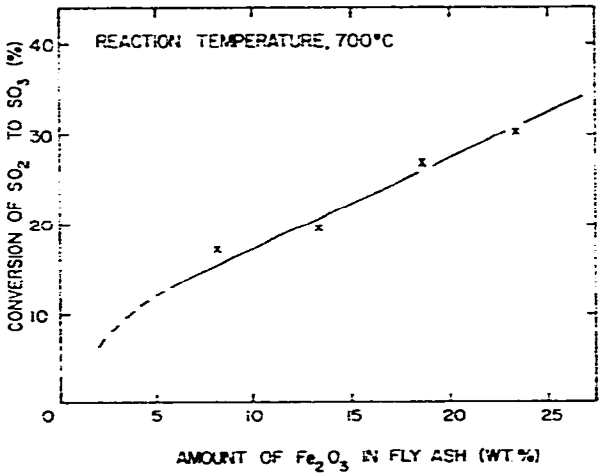

Fig. 4. Conversion of SO_2 to SO_3 at 700°C as a function of the Fe_2O_3 content of fly ash.

The effect of varying the partial pressure of oxygen and the gas flow rate on the formation of SO_3 in the presence of fly ash was studied at 700°C, using the apparatus shown in Fig. 1. The results are given in Table 1.

It is evident from these results that increasing the oxygen content of the gas favours the production of SO_3 (run Nos. 1 and 2). This observation is in accordance with the following equation

$$2SO_2+O_2 \rightleftharpoons 2SO_3$$

where increasing the oxygen concentration will cause the reaction to go to the right.

As shown in Table 1 (run Nos. 2 and 3), increasing the flow rate reduces the formation of SO_3 because of a reduction in the gas–solid reaction time.

TABLE 1

THE EFFECT OF THE SO_2/O_2 RATIO AND THE FLOW RATE ON THE FORMATION OF SO_3

Run No.	*Gas composition (vol. %)*			*Flow rate (ml/min)*	*Contact time (sec)*	*Conversion (%) $SO_2 \rightarrow SO_3$*
	SO_2	*O_2*	*N_2*			
1	8	16	76	185	1.8	16
2	8	32	60	185	1.8	27
3	4	16	80	370	0.9	8

Carbon is a common constituent in fly ash[17], and in a series of experiments its presence in fly ash was found to reduce the formation of SO_3 by preferential reaction with the oxygen in the gas stream. By varying the oxygen flow rate in an oxygen–sulphur dioxide mixture it was found qualitatively that SO_3 was not formed until all the carbon had been oxidized.

The capture of SO_2 and SO_3 by CaO

A study was made of the effect of temperature on the sulphation of CaO in an equilibrium mixture of SO_3–SO_2–O_2. This mixture was obtained by passing a 2–1 volume ratio of SO_2/O_2 over a platinized asbestos catalyst maintained at the reaction temperature. The experiments were done by thermogravimetric analysis, using a crucible to hold the CaO which had been freshly prepared from $CaCO_3$ calcined at 760 °C. It is evident from the results (Fig. 5) that the sulphation of CaO is temperature

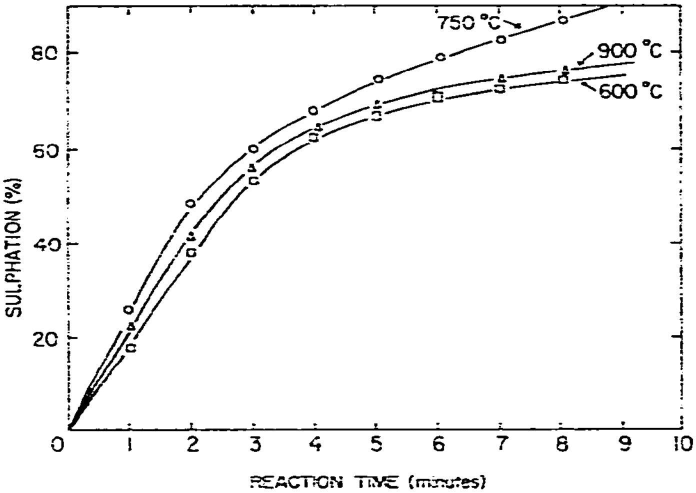

Fig. 5. Sulphation of CaO in an equilibrium mixture of SO_3–SO_2–O_2 at different temperatures.

dependent between 600 and 900 °C. Maximum sulphation occurs at about 750 °C: this temperature is in general agreement with the temperature of maximum formation of SO_3 from SO_2 and O_2 in the presence of fly ash (Fig. 3). Based on this agreement it is reasonable to assume that the sulphation of CaO in an equilibrated mixture of SO_3–SO_2–O_2 is dependent on the SO_3 content of the gas stream.

Isothermal experiments at 900 °C were done to determine the effect of a catalyst on the capture of SO_2 by CaO and the effect of the distance between the catalyst and the scavenger on the amount of sulphation of CaO (Fig. 6). Sulphation experiments were done in a 2–1 mixture of SO_2/O_2. The results shown in curve A represent the sulphation of a homogeneous mixture of 5% Fe_2O_3 in CaO. Curve B was obtained from the sulphation of CaO in an equilibrated mixture of SO_3–SO_2–O_2, catalyzed at 900 °C over platinized asbestos placed approximately 2.5 cm ahead of the CaO.' For curve C the charge consisted of CaO with no catalyst added to the charge or in the gas stream ahead of the charge. The highest percentage sulphation was obtained when the catalyst was intimately mixed with the CaO (curve A). When no catalyst was used (curve C), the sulphation behaviour was quite different. Although the initial rate of sulphation was similar for curves A and C, there is a sharp break in curve C after 2 minutes, following which sulphation occurs very slowly. It is evident from these results that efficient utilization of CaO as a scavenger for the removal of SO_2 from a gas stream is highly dependent on the catalytic oxidation of SO_2 to SO_3, and on the close physical association of the catalyst with the scavenger.

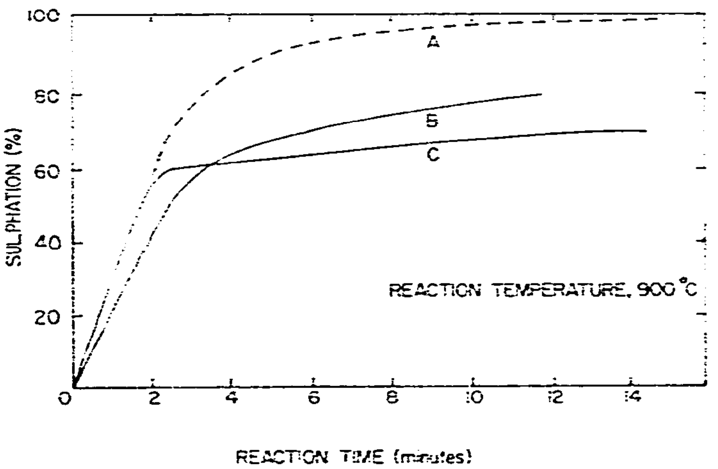

Fig. 6. Sulphation of CaO in the presence and absence of catalysts.

The capture of SO_2 and SO_3 by MgO

The influence of iron oxide on the rate of sulphation of MgO was studied. Magnesium carbonate was placed in a small crucible in the Thermograv balance and was decomposed in nitrogen to give magnesium oxide, which was then sulphated in a

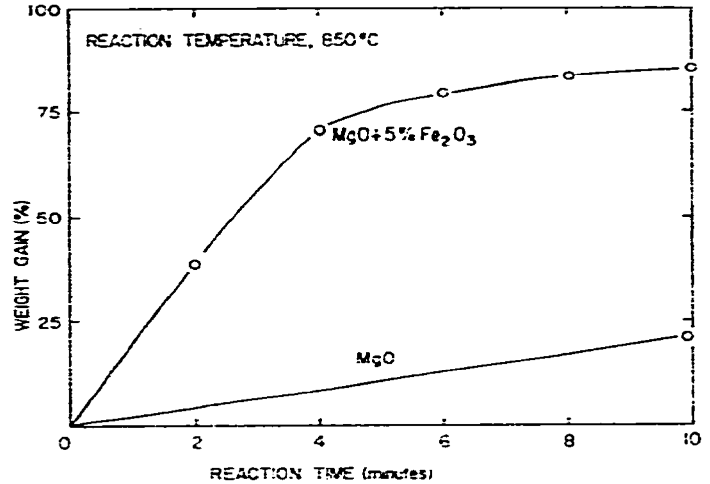

Fig. 7. Sulphation of MgO at 850 °C in the presence and absence of Fe_2O_3.

2/1 mixture of SO_2/O_2. The lower curve in Fig. 7 represents sulphation in the absence of a catalyst. The inefficient utilization of MgO agrees with the work of others[18,19] on the unreactive nature of MgO with pure SO_2. The sulphation of MgO, containing 5% Fe_2O_3 which had been homogeneously mixed with the $MgCO_3$ before its thermal decomposition, is shown in the upper curve in Fig. 7. The rate of sulphation, and the utilization of MgO, are significantly improved by the presence of the catalyst.

Experiments were also done to determine whether the removal of SO_2 from a gas stream by MgO was a function of the catalyst concentration. Mixtures of ferric oxide and magnesium oxide were prepared by evaporating aqueous solutions of ferrous sulphate and magnesium sulphate on a Fiberfrax cylinder which was then hung in the Thermograv balance (Fig. 2) so that the gas mixture had full access to the

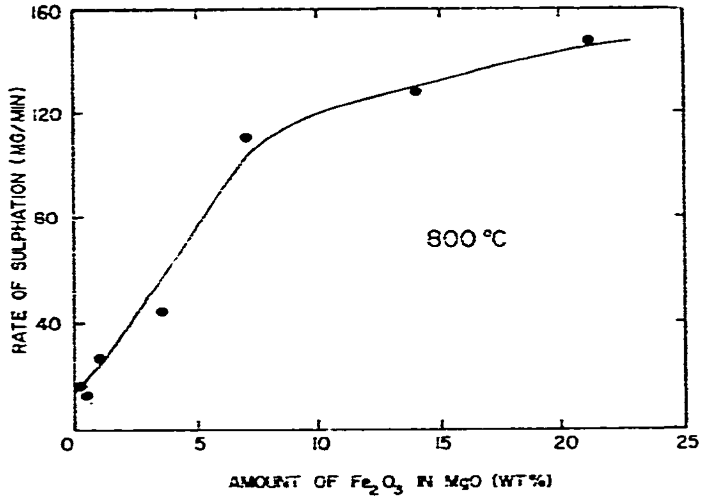

Fig. 8. Sulphation of MgO, containing different percentages of Fe_2O_3, at 800 °C.

dispersed sulphate mixture. The sulphates were converted to the oxides by decomposition at 800 °C in carbon monoxide, followed by oxidation. The experimental results obtained with the MgO–Fe_2O_3 mixtures are shown in Fig. 8, where the initial linear reaction rates (for approximately 4 minutes) for the sulphation of MgO are plotted as a function of the Fe_2O_3 content of the MgO–Fe_2O_3 mixture. The influence of Fe_2O_3 on the rate of sulphation of MgO is most significant for Fe_2O_3 concentrations up to about 7%. This behaviour is similar to that found for the conversion of SO_2 to SO_3 in the presence of Fe_2O_3-containing fly ash (Fig. 4) and indicates that the sulphation of MgO is related to the presence of SO_3 and to the concentration of the catalyst.

The capture of SO_2 by MgO at 825 °C was studied in a further series of experiments[20] in which a mixture of MgO and Fe_2O_3, containing 5% Fe_2O_3, was prepared from their sulphates and supported on Fiberfrax. The percentage of SO_2 removed from the gas stream and the percentage of residual MgO were calculated from periodic weighings of the Fiberfrax. After each weighing the Fiberfrax was preheated to the reaction temperature in nitrogen and then exposed to the SO_2-containing gas for selected times. The flow rate of the gas mixture was chosen to give complete renewal of the gas surrounding the charge in 3, 6, 9, and 12 sec for each series of tests. An experiment was also done to study the effect of varying the oxygen concentration in the gas stream on the removal of SO_2 for a 9 sec contact time.

The results of the experiments on the influence of the flow rate and of the oxygen concentration on the removal of SO_2 by MgO are shown in Fig. 9. For a contact time of 12 sec, 100% removal of SO_2 from the gas stream was obtained for up to 20% conversion of MgO to $MgSO_4$. The percentage of SO_2 removed decreased as the

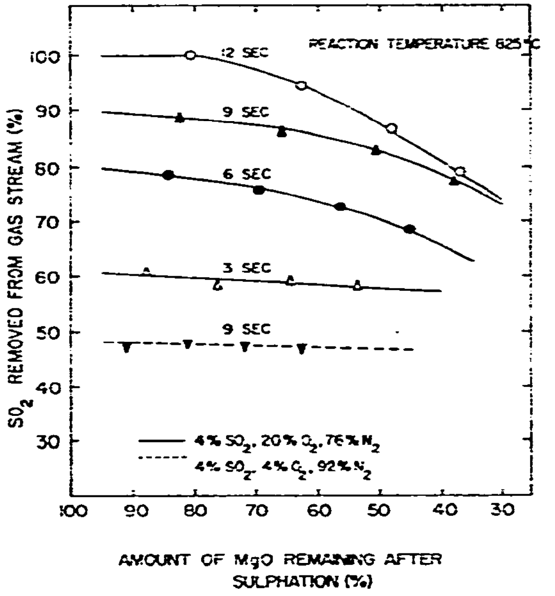

Fig. 9. Effect of contact time and oxygen concentration on the removal of SO_2 from a gas stream by MgO.

contact time was decreased. For a 9 sec contact time the percentage of SO_2 removed from the gas stream was reduced from approximately 90% for a ratio of SO_2/O_2 of 1/5 to 48% for a ratio of SO_2/O_2 of 1/1. The initial effects of the flow rate and of the SO_2/O_2 ratio on the capture of SO_2 from a gas stream by MgO are similar to the effects of these variables on the conversion of SO_2 to SO_3, as shown in Table 1. These results further support the hypothesis that the utilization of MgO as a desulphurizing compound is related to the presence of SO_3 in the gas stream.

CONCLUSIONS

The catalytic conversion of sulphur dioxide to sulphur trioxide in the presence of carbon-free fly ash is dependent on the iron oxide content of the fly ash and is essentially linear from 7 to 25% iron oxide. The oxidation of sulphur dioxide is significantly reduced by the presence of carbon in the fly ash. The optimum temperature for the production of sulphur trioxide, formed under dynamic conditions in the presence of carbon-free fly ash, or iron oxide, is between 700 and 750°C. Increasing the gas–solid contact time and decreasing the ratio of SO_2/O_2 favours the production of SO_3 and the best utilization of CaO and MgO. The homogeneous mixing of the oxidation catalyst (Fe_2O_3) with the scavengers (CaO and MgO) and the availability of large surface areas optimize the desulphurization of the flowing gas and the utilization of the scavengers. The efficient capture of SO_2 from a hot gas stream by CaO and MgO is directly related to the catalytic conversion of SO_2 to SO_3 in an oxidizing atmosphere. These conclusions on the factors which enhance the formation of SO_3 and the scavenging action of CaO and MgO are in general agreement with industrial experience[21] on the causes of SO_3 formation and on the inhibition of corrosion by CaO and MgO in coal-fired burners.

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