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THE REACTION OF SO_2 WITH METAL OXIDES

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THE REACTION OF SO_2 WITH METAL OXIDES

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ABSTRACT

Data is presented on SO_2 absorption by CaO, $Ca(OH)_2$ and $CaCO_3$ in gas-solid and gas-aqueous solution reactions. The results indicate that $CaSO_3$ is formed in both systems via intermediate hydroxides by ionic acid-base type reactions. Analysis of the reaction mechanism explains experimental evidence that limestone injection as commonly practiced is intrinsically inefficient, and that optimum yields are obtained when limestone is preheated.

INTRODUCTION

SO_2 reacts with alkali and alkaline earth oxides to yield metal sulfite (MSO_3). If oxygen is present, part of the sulfite is converted to MSO_4. This reaction is used for the removal of SO_2 from coal combustion gases in coal fired power plants. Flue gases from power plants constitute an attractive system for basic research, because the physical properties and chemical composition of the system are carefully controlled to optimize energy conversion. SO_2 removal constitutes a special challenge, because SO_2 concentrations are small and gas volumes very large. In a large power plant, changing the yield by one percent can amount to metal oxide savings of many carloads a day.

The use of oxides to reduce SO_2 is not new. Limestone, which calcines in the combustion chamber, has been used for over one hundred years to reduce boiler corrosion. Since the thirties metal oxides have been used in England, Germany and other countries to reduce SO_2 emission. However, up to now, the application on full industrial scale is far from satisfactory and yields are far below "theoretical", at least partly, because the basic chemistry is not fully known. There are two reasons for this: The first is that the reaction is very complex, and the second is that, in the last twenty years, most research has focused on select, practical systems, and only very littel research has been done on the basic chemistry (1).

In the last few years an effort has been made to remedy this situation. A large number of government contract reports, government studies and papers in the engineering literature have appeared (2,3). It is impossible to give here a complete list of references because the number of reports is too large, and many are difficult to obtain.

In this paper, we will report some of our recent research results and correlate them with the present knowledge of this field. Most of our discussion will be based on calcium compounds, because limestone is the cheapest source of oxide.

REACTION SYSTEM

We proceed here in two steps. First, we discuss an ideal system, where only the reaction between pure metal oxide and pure SO_2 is considered, and then we tackle the real system where processes between all components of the flue gas are studied.

The net reaction of the ideal system, sulfur oxide with metal oxide, can be written

$$MO_{(s)} + SO_{2(g)} + 1/2\ O_{2(g)} \rightarrow MSO_{4(s)}$$

This gas-solid reaction does not occur in one simple step. SO_2 first absorbs on the oxide surface, forming a sulfite which is later partly oxidized. The reaction speed depends on temperature, SO_2 concentration, and the metal oxide particle size and surface properties. If

the metal is calcium, the reaction is further complicated by the fact that both CaO and $CaSO_4$ can exist in polymorphic forms. Each form has a different reactivity. The chemically best known case is the reverse of reaction I, the burning of gypsum. Three forms of gypsum exist: α or (I) gypsum, the high temperature form, β or (II) gypsum, insoluble anhydrite, and γ or (III gypsum, soluble anhydrite. During the burning of gypsum, up to four phases, including a melt, can be present.

A qualitative measure for the relative reactivity of calcium oxide is shown in Figure 1. Figure 1 represents break through curves for SO_2 passed through a fixed bed of various forms of calcium oxide, and precursors of oxide. In this, and all following curves, experimental conditions are indicated in the caption. In the ideal system, a gas mixture of 95% N_2 and 5% SO_2 is used. Calcium oxide, and all other metal oxides, always absorb less SO_2 than hydroxide. Based on our data on many metal oxides studied under various conditions, we will later postulate that at low temperature SO_2 does not measurably react with dry metal oxides and that the reaction indicated in Figure 1 is due to the presence of traces of hydroxide.

In the real system, involving flue gases and commercial oxides, the presence of all other flue gas constituents must be considered. In proxi, the "metal oxide" is normally not an oxide, but an "oxide equivalent", a material which during the course of the reaction is partly converted to an oxide, or a hydroxide. The most common source of oxide in industry

is limestone or dolomite. These carbonates are "calcined" during the reaction, forming oxides. The pure carbonates are poor SO_2 absorbers (Figure 1).

We will discuss reactions in the real chemical system in three steps: preliminary reactions which are necessary to transform the precursor into the reagent, the main reaction which consists of the absorption and the combination of SO_2 with the metal oxide, and competing reactions which consume oxide and thus reduce the yield of sulfite.

The preliminary reactions involve equilibria with CO_2 and H_2O

$$Ca(OH)_2 \rightleftarrows CaO + H_2O \qquad \text{II}$$

$$CaCO_3 \rightleftarrows CaO + CO_2 \qquad \text{III}$$

The first of these is most important, because flue gas contains 8% H_2O, and as shown in Figure 1, hydroxides react much better with SO_2 than oxides. Figure 2 shows the thermodynamic equilibria of the reaction. The equilibrium constants are computed for standard conditions, and not for a flue gas. The accuracy of literature data is so poor that correction to flue gas conditions seems premature. Figure 2 shows that in reaction I, above 900°F, the formation of oxide is favored. However, even at 2000°F, traces of hydroxide (about 10 ppm) remain. In reality, heated hydroxide converts to a much smaller extent than indicated, because the dehydration is very slow. Reaction III, the "calcination" of limestone is also crucial, because the carbonate must be decomposed before SO_2

absorption can occur. The equilibrium curves in Figure 2 show that calcination sets in at about 1700°F. Increasing temperature favor equilibrium and kinetics. Therefore, limestone should be injected at the highest possible temperature. However, a comparison of equilibrium III with that of the abatement reactions shows that the SO_2 absorption is reduced with temperature. This, and "dead burning" of limestone, establish an upper temperature limit for this reaction.

The main reaction and competing reactions include

$Ca(OH)_2 + SO_2 \rightleftarrows CaSO_3 + H_2O$		IV
$CaO + SO_2 \rightleftarrows CaSO_3$		V
$CaSO_3 + 1/2\ O_2 \rightleftarrows CaSO_4$		VI
$CaSO_3 + CO_2 \rightleftarrows CaCO_3 + SO_2$		VII
$SO_2 + 1/2\ O_2 \rightleftarrows SO_3$		VIII
$H_2O + SO_2 \rightleftarrows H_2SO_3$		IX
$H_2O + SO_3 \rightleftarrows H_2SO_4$		X

It is not practical to discuss here all of these reactions. Each of them is complicated and worth a detailed, separate discussion. From now on we restrict discussion to systems which correspond to industrial abatement conditions as encountered in coal fired power plants.

REACTION CONDITIONS

The reaction system consists of two parts, the flue gas and the solid metal compound. Flue gas contains approximately 75% N_2, 8% H_2O, 14% CO_2,

3% O_2 and 0.1 to 1% SO_2. In addition, it contains slag. Whilte the flue gas components and properties are given quantities, the metal oxide additive is a free parameter. In present practice, powdered solid metal compounds are injected in the hot gas stream. However, preparations are under way for large scale tests of the reaction of limestone slurried in water with flue gases withdrawn from the air preheater.

Solid-Gas Reactions

Figure 3 shows the temperature vs. time profile of the flue gas stream, and the location of limestone injection points. For technical reasons, four points are preferred: (a) injection, together with coal, into the flame, (b) injection in the main combustion chamber, above the water cooled wall, (c) injection in the superheater, or (d) injection before the air preheater. Injection into the flame, although convenient, is unsuitable, because at the flame temperature 3000 to 4000°F, the equilibrium of reaction I and V are shifted in the wrong direction. In addition, calcination of limestone at this temperature leads to an eutectic mixture of CaO with residual carbonate, and the material melts and is burnt dead.

The preferred process is injection in the main chamber, above the water wall. At this point the temperature fluctuates between 1800 to 2400°F. Figure 2 shows that at this temperature carbonates are calicined and that sulfites can be formed. If it would be feasible to control the reaction, injection at this temperature would be theoretically ideal.

However, we will see that the sequence of reactions is complex, and so slow that conversion is intrinsically imcomplete. Injection at the superheater would yield best sulfite formation in reaction VII, but at this point calcination is too slow. Therefore, the material must be preheated to be effective. In the air preheater, at a temperature of 700°F to 350°F, the equilibria would be better, but the kinetics are slower.

Gas Liquid

If SO_2 containing flue gas is bubbled through an aqueous slurry or solution of lime or limestone, almost 100% yield is obtained. We now discuss this reaction, because it helps in understanding the chemical steps of the gas-solid system.

In water about 0.01 g of limestone will dissolve in 1 liter of water (Table I). The solubility depends on temperature pH and CO_2 partial pressure. A saturated solution has a pH = 8.6 and the following equilibria occur:

Preliminary reactions:

$$H_2O + CaCO_3 \rightarrow Ca^{+2} + HCO_3^- + OH^- \qquad \text{XI}$$

$$Ca^{+2} + H_2O \rightarrow Ca(OH)_2 \quad CaO_2H^- + H_3O^+ \qquad \text{XII}$$

$$SO_2 + H_2O \rightarrow HSO_3^- + H_3O^+ \qquad \text{XIII}$$

Main reaction:

$$CaO_2H^- + HSO_3^- \rightarrow CaSO_3 \qquad \text{XIV}$$

Reactions XI to XIV are much more complex than written and involve ions, dissociation and autodissociation of acids and bases, and precipitation of insoluble $CaSO_3$ (Table I). The equilibria are very pH sensitive (4). The reactions are quick, and diffusion limited. Thus, the reaction speed changes with concentration. In the pressure of oxygen, sulfite may oxidize to the much more soluble sulfate. Figure 4 shows a breakthrough curve for SO_2 in solution containing dissolved limestone. The chart shows that the calcium salt absorbs SO_2 at a ratio of 1:1. The same figure also shows the pH change. A saturated limestone solution has about pH 12. Since flue gas contains 14% CO_2, the solution quickly saturates with carbonate which acts as a buffer. Acid-base constants for some of the components are shown in Table II. As SO_2 absorption proceeds the pH drops and the solubility of SO_2 reduces, and the reaction slows down. If O_2 is present, sulfite is partly oxidized to sulfate. This reaction is quickest at pH 6.8. It does not markedly change the SO_2 capacity of the solution. However, sulfate reduces the solubility of sulfite by up to 20%. the situation is further complicated by the fact that during oxidation various thionates are formed. Their yields and stabilities depend on pH and temperature.

In aqueous solution the role of the metal oxide is twofold. Its base character established the pH which induces absorption of SO_2 by conversion into HSO_3^- and SO_3^{-2} ions, and the solubility of the metal oxides in the presence of SO_2 determines the concentration of ions.

Reaction mechanism

The solvation of SO_2 is ionic, as shown in Figure 5. The metal ion does not participate in the solvation. Thus, the mechanism is the same for all dissolved metal ions.

In the gas phase the reaction mechanism has not been explained. Figure 6 shows a proposed reaction mechanism for the oxide and the hydroxide. After reaction, the nascent water molecule may hydrolize a neighboring calcium containing molecule and act as a catalyst. In the hydroxide the electron transfer is enhanced because of the polarization offered by the OH group. This suggests that the ionic reaction is catalyzed by moisture. This is indeed observed. Flue gases contain 8% water, and absorb better than a dry SO_2 mixture, as shown in Figure 7. Addition of more steam enhances absorption further. The hydroxide is such an efficient absorber that it seems likely that in a mixed oxide-hydroxide all absorption occurs via hydroxide.

Competing reactions

If we take another look at the equilibria in Figure 2, we see that if metal oxide, or hydroxide and SO_2 react alone, the best thermodynamic condition is established at low temperature. However, reaction is then very slow. In addition, competing reactions set in, such as carbonate formation from CO_2 in the flue gas. Absorption of CO_2 competes up to 1600°F. However, at that temperature the equilibrium of reaction V shows that the yield of sulfite is small. In a real gas, CO_2 absorption is

greater than shown in Figure 2, because the CO_2 concentration is ten to one hundred times larger than that of SO_2. Figure 8 shows experimental data of the effect of CO_2 on the absorption of SO_2 on Ca(OH) at 800°F.

Direct conversion of carbonate into sulfite

The most convenient way to treat flue gases with metal oxide is injection as a dust, which is then swept with the gas through the heat exchanger into the electrostatic precipitator. The transit time for a particle is less than a second; thus, kinetics are of crucial importance. A good study of kinetics has been reported by Borgwardt (6). It indicates that the exchange reaction of limestone with SO_2

$$CaCO_3 + SO_2 \rightleftarrows CaSO_3 + CO_2 \qquad \text{XV}$$

is critically slow. It can be anticipated that reaction speed increases with temperature. However, we mentioned earlier that the net reaction I, and the exchange reaction XV, are not simple one step processes.

The reaction of limestone is limited by chemical collision probabilities and diffusion. It depends on the surface, particle size and crystal structure. If cold limestone is injected, reaction XV does not occur. Instead, a whole sequence of events occurs. First, the particle is heated by thermal radiation from the gas. The absorbed heat is partly used for dissociation of the carbonate and vaporization of residual moisture. After initial overheating, the particle bursts explosively and leaves a porous structure. The effect of the decomposition and expansion is so large that limestone injected into a hot heater disintegrates into a fine dust. The

particle size is virtually independent of the original particle. Although the resultant material is very reactive, it may not absorb SO_2 to the full extent thermodynamically predicted, because the SO_2 must diffuse against the stream of cooler gas emanating from the particle. At the same time, the particle is cooled because bursting is almost adiabatic . By the time all these processes are over, the particle has been transferred to a cooler zone and absorbs CO_2, H_2O and SO_2 indiscriminately.

If limestone is injected at a hoter place, it may over-heat in the presence of CO_2, until a $CaCO_3$-CaO eutectic mixture forms and melts. The resulting annealing of the surface has been observed with electron microscopy. (7) A "burnt" particle does not absorb SO_2. Thus, direct conversion of carbonate into sulfite is intrinsically inefficient.

CONCLUSION

Our experiments have shown that dry solid CaO is a poor absorber of SO_2 gas. SO_2 absorption is, however, enhanced by partial hydrolysis of the surface. After inducing the reaction of SO_2 and CaO, water can vaporize or act as a catalyst by hydrolizing neighboring calcium containing molecules. In laboratory simulation of the real system, the best yield of reaction I or V is obtained if freshly calcined limestone is injected in the temperature range between 700°F to 1000°F. In this temperature range, steam from the flue gas activates the oxide surface. This catalizes the absorption of SO_2 and favors the exchange between SO_2

and CO_2 (Curve V in Figure 2). The proposed reaction mechanism is shown in Figure 6. The absorption corresponds to an acid-base neutralization.

Analysis of our data shows that the commonly used method of limestone injection at 2000°F is intrinsically inefficient, because calcination and absorption of SO_2 from flue gas in one operation cannot be achieved in the available short transit time. Physical processes occuring during heating of the particles dealy reaction until the gas temperature is so low that CO_2 and H_2O compete with SO_2 absorption. If limestone is injected at a higher temperature, the particles burn "dead". The most efficient SO_2 absorption can only be obtained by preheating or precalcination of lime, or by using a fixed bed process.

References

1) A detailed summary of work before 1960 is given in "Gmelin's Handbuch der Anorganischen Chemie", Calcium, Volume IIB and Sulfur, Volume IIB.

2) For references on U.S. Government reports, see "A Status Report, Process Control Engineering R & D for Air Pollution Control", U. S. Department of H. E. W., November 1969; available through the Government Clearing House, Arlington, Virginia.

3) Literature review in K. Goldschmidt, "Experiments in the Use of Lime Hydrate to Desulfurize Flue Gases", Fortschrittsberichte, 6 (21) VDI- Düsseldorf, August 1968.

4) Landolt-Bornstein, Tables of thermodynamic properties.

5) K. Pitzer, L. Brewer, G. N. Lewis and M. Randall, "Thermodynamics", McGraw-Hill, N. Y. (1961).

6) R. H. Borgwardt, Environmental Science and Technology 4, 58 (1970).

7) Personal Communication, M. Hooper, NAPCA, Cincinnatti, April, 1970.

TABLE I

Solubility of Ca Compounds in Water[a]

Compound	Solubility in mg/l at 30°C	at 100°C
$CaCO_3$	14	17
$CaSO_3$	46.3	7.9
$CaSO_4$	6000	2000

(a) The solubilities are given in weight of the anhydrous compound. Each compound can occur in several hydrated forms, each of which behaves somewhat differently.

TABLE II

Acid Constants at 25°C

Substance	K_1	K_2
H_2CO_3	4×10^{-7}	4×10^{-11}
H_2SO_3	10^{-2}	10^{-7}
H_2SO_4	10^{3}	10^{-2}
CaOH	10^{-12}	$<10^{14}$

Figure Captions

Figure 1: Break-through curves for artificial flue gas (8% H_2O, 75% N_2, 14% CO_2, 3% SO_2) passing through a fixed bed containing 20 g of a) Fredonia limestone (Paducah, Kentucky), b) analytical grade $CaCO_3$, c) analytical grade $Ca(OH)_2$, and d) Fredonia limestone, calcined at 1500°F under vacuum.

Figure 2: Temperature dependence of equilibrium constants for nine SO_2 abatement reactions. Data from references 4 and 5.

Figure 3: Profile of temperature versus transit time for flue gas from a large coal dust fired power plant.

Figure 4: Break-through curve and pH vs. time curve for 200 ml H_2O containing 1 g of a) analytical grade $CaCO_3$, b) Fredonia limestone, and c) pure water. Curve 1 results when CO_2 is present; curve 2 results if CO_2 is absent from the gas.

Figure 5: Mechanism of hydration of SO_2.

Figure 6: Proposed mechanism for SO_2 absorption on metal oxides.

Figure 7: Effect of hydration on SO_2 absorption of dry calcium oxide. a) Dry CaO; b) CaO treated with 90% N_2, 10% H_2O at 900°F for twenty minutes.

Figure 8: Effect of CO_2 on SO_2 capacity of $Ca(OH)_2$. a) Synthetic flue gas, b) same without CO_2.

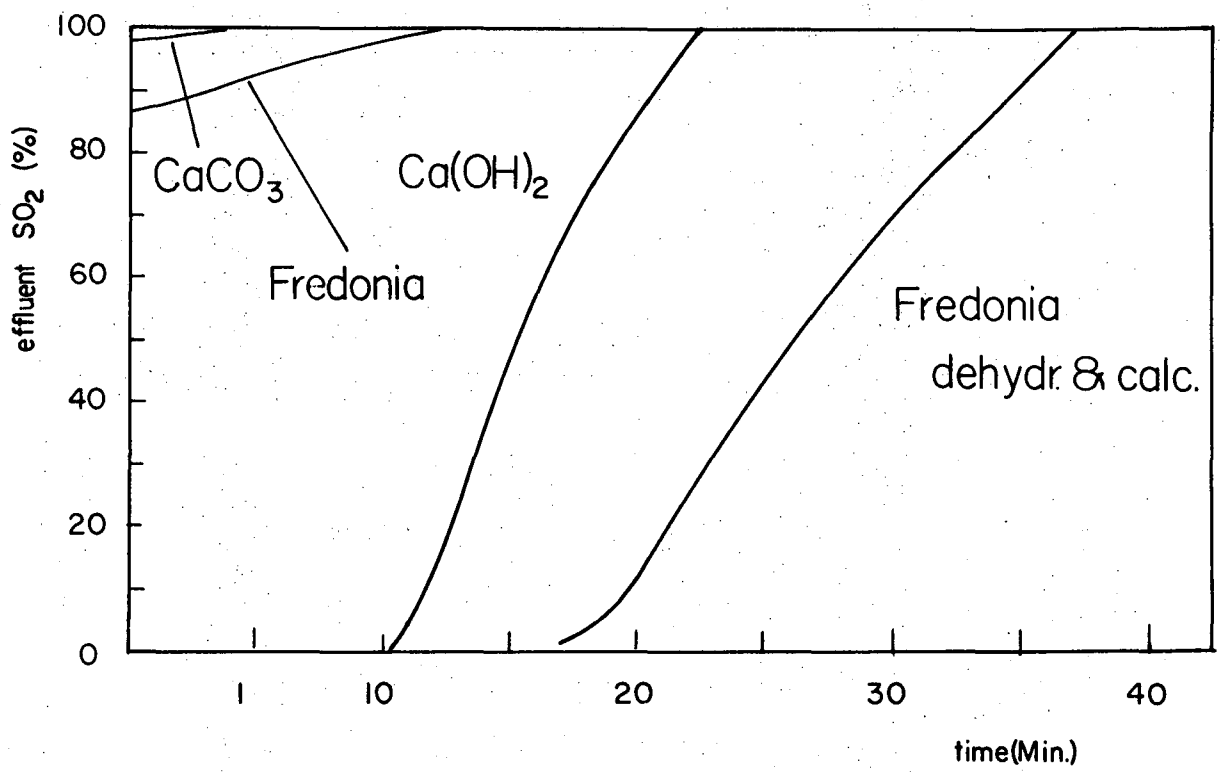

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Fig. 1

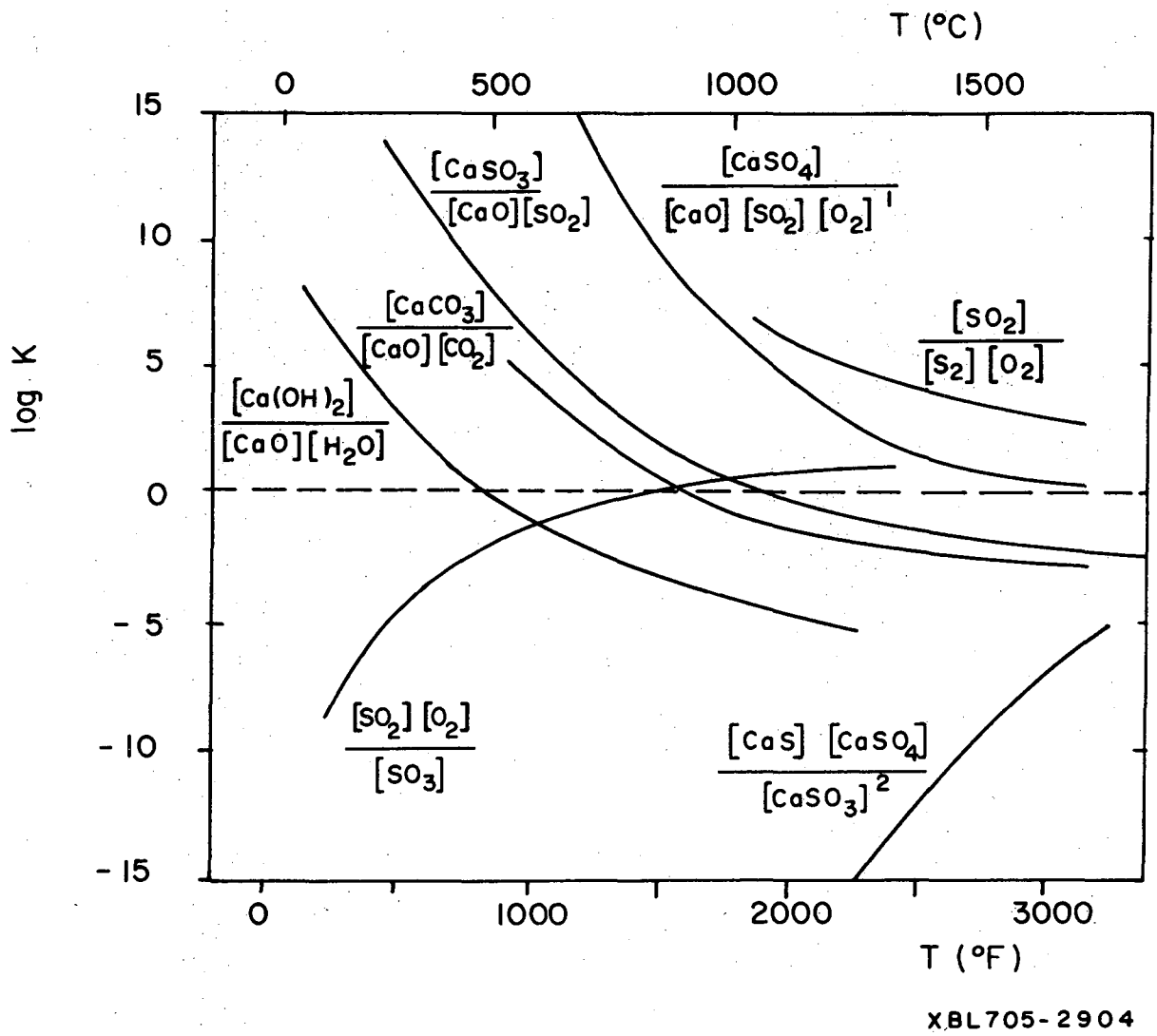
T (°C)
0
500
1000
1500
15
10
5
0
- 5
- 10
- 15
log K
[CaSO3] / [CaO][SO2]
[CaSO4] / [CaO] [SO2] [O2]
[CaCO3] / [CaO] [CO2]
[SO2] / [S2] [O2]
[Ca(OH)2] / [CaO] [H2O]
[SO2] [O2] / [SO3]
[CaS] [CaSO4] / [CaSO3]2
0
1000
2000
3000
T (°F)
XBL705-2904

Fig. 2

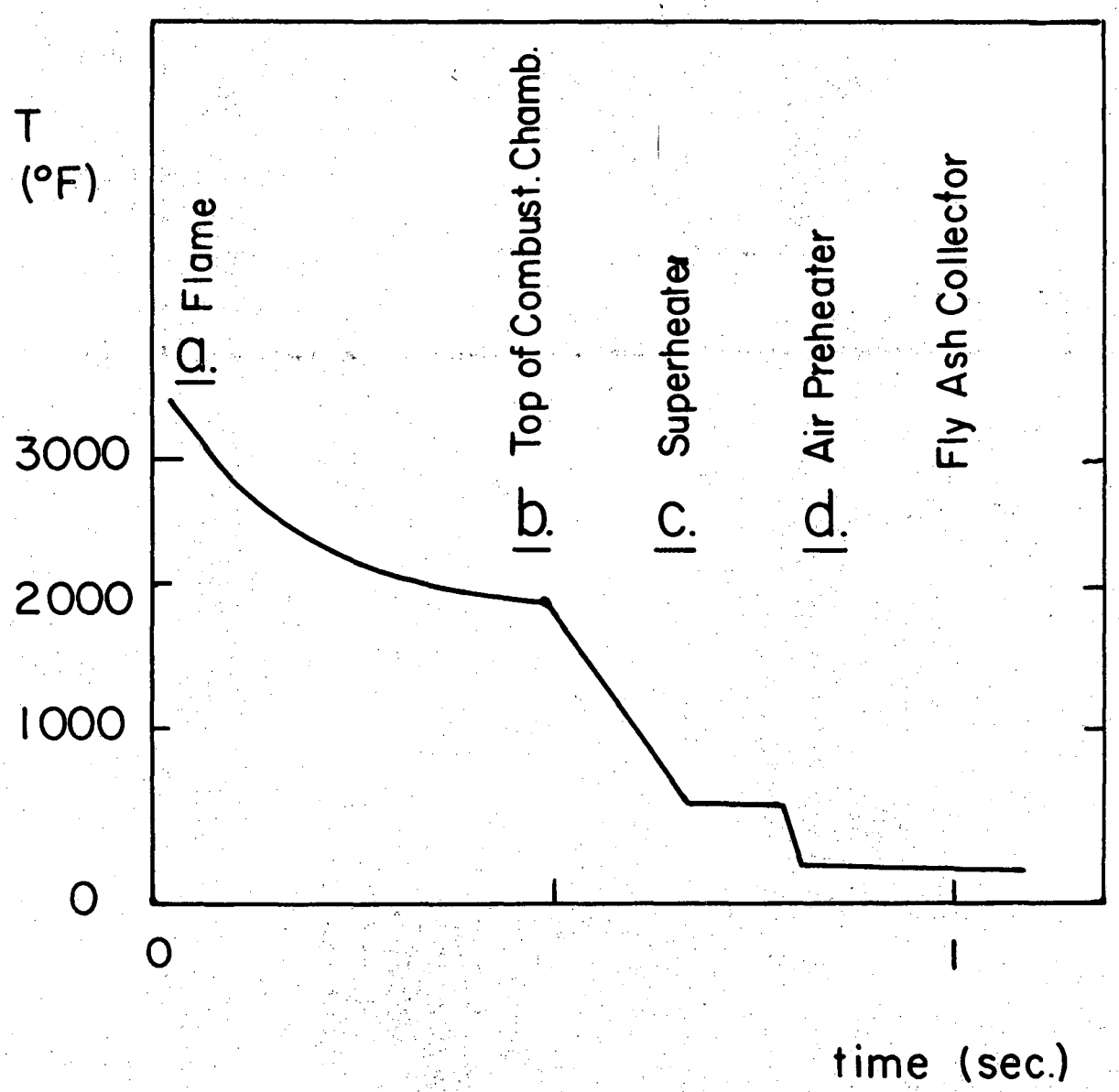

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Fig. 3

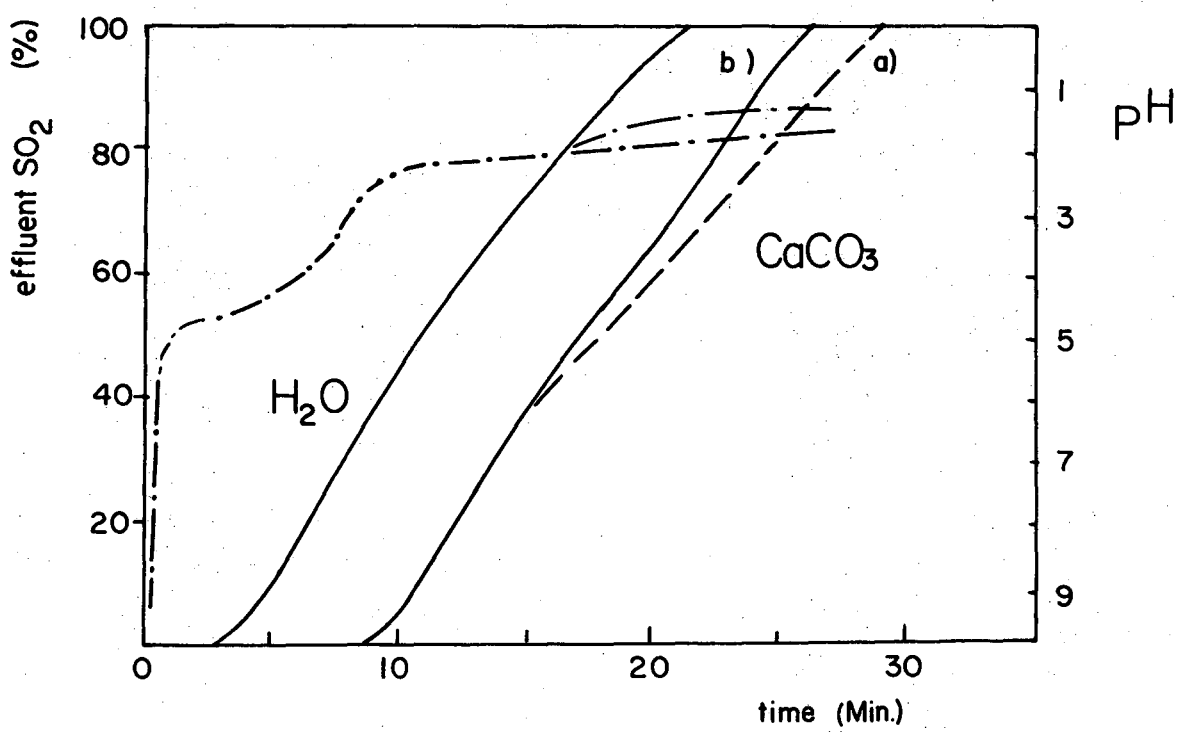

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Fig. 4

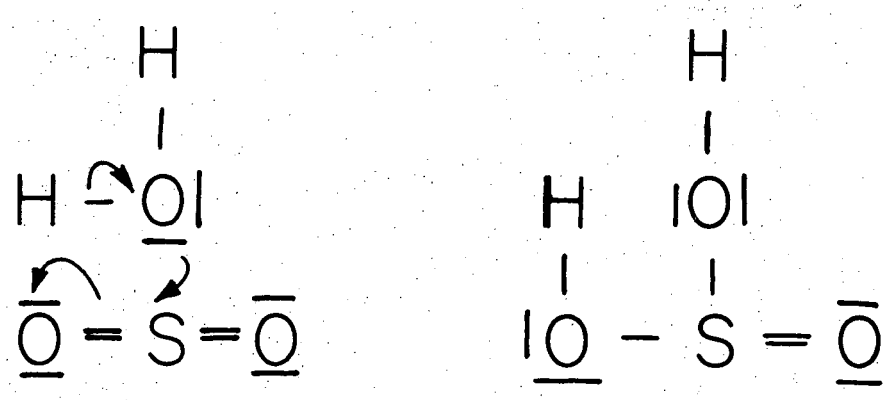

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Fig. 5

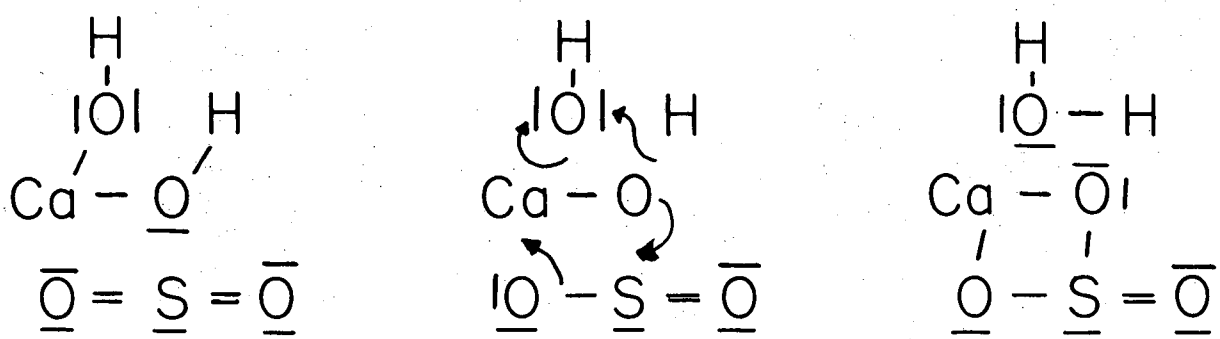

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Fig. 6

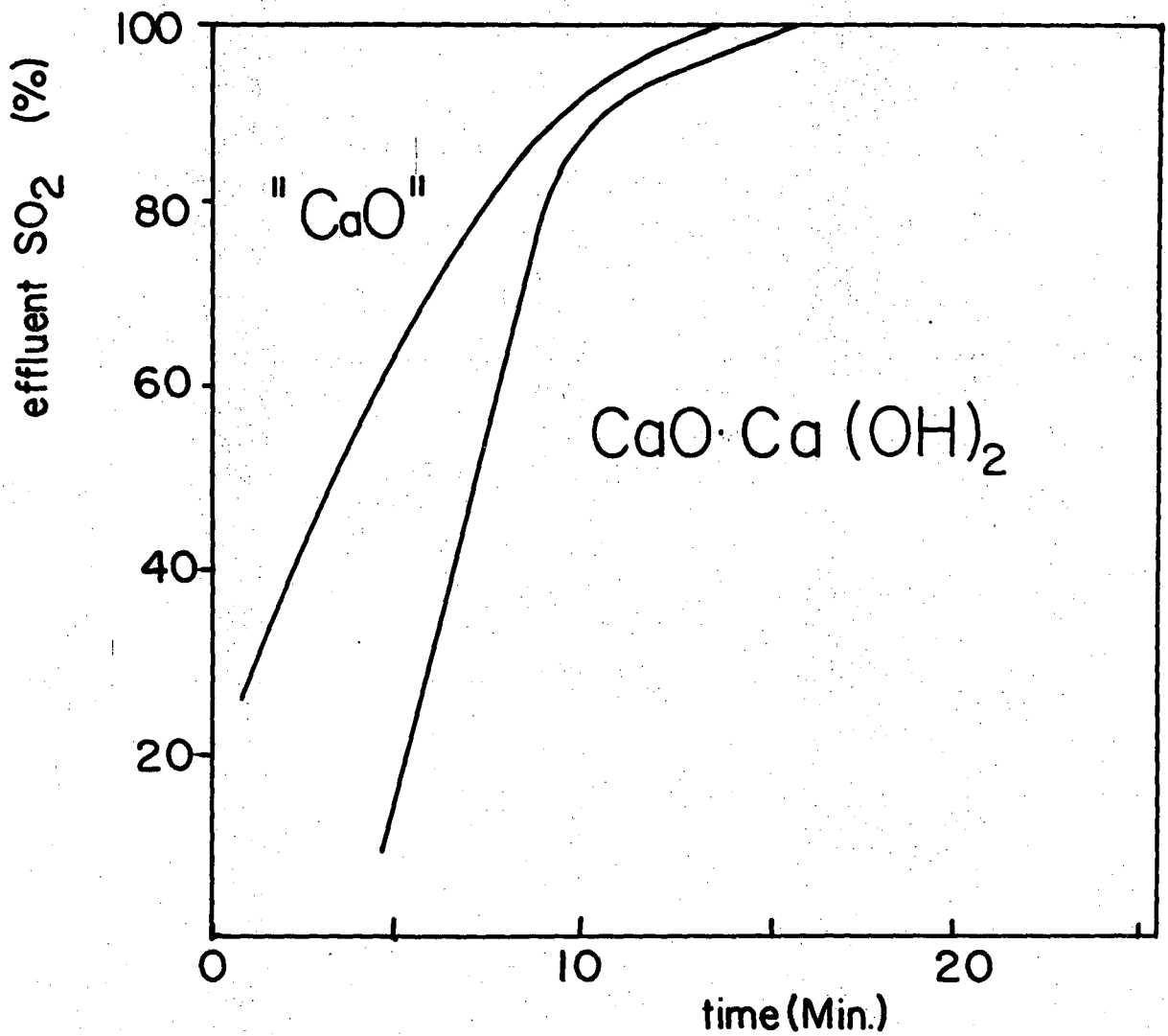

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Fig. 7

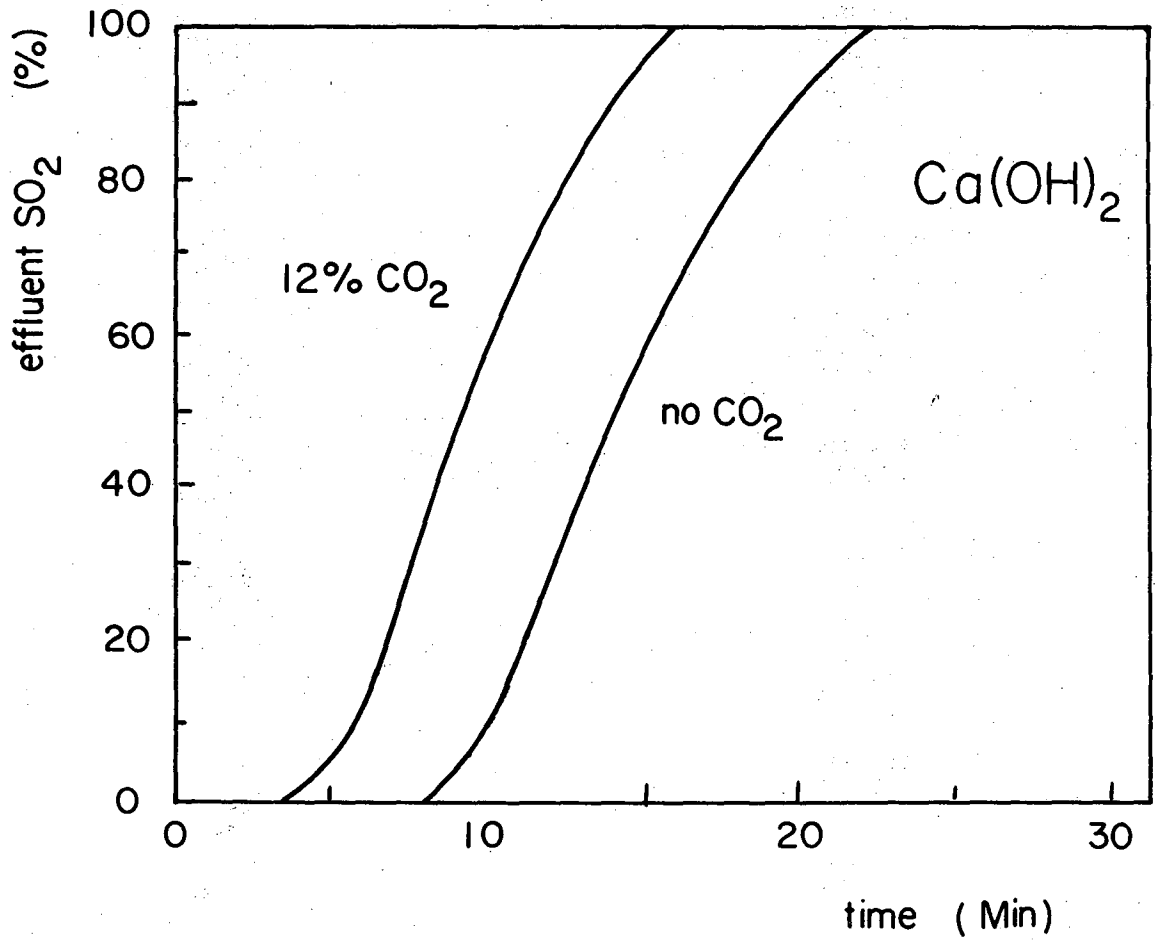

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Fig. 8

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