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IR 70-114

March 4, 1970

EVALUATION FOR ONTARIO HYDRO OF THE  
SO<sub>2</sub> - FIXING CAPABILITY OF SOME  
ONTARIO LIMESTONES AND DOLOMITES

by

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EXTRACTION METALLURGY DIVISION

Mines Branch Research Program  
on Environmental Improvement

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Mines Branch Investigation Report IR 70-14

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SUMMARY

A simple technique involving continuous gas analysis was developed to assess the relative reactivities of a series of commercial samples of limestone and dolomite submitted by Ontario Hydro's Research Division in Toronto. The technique permits assessing the sulphur dioxide absorption of the calcined stones at various temperatures, particle sizes, gas compositions, and after various degrees of conversion to calcium sulphate. The experiments simulate the conditions of limestone injection into steam boilers. The most reactive samples were those limestones that had a high CaO content and a high degree of microcrystallinity.

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## INTRODUCTION

The economic removal of sulphur dioxide from the stack gases produced by fossil-fuel burning plants and by sulphide ore-treating operations is an important current problem. It is being approached at the present time on the basis of near term, intermediate term and long term solutions.

The most promising of the near term solutions for use in steam plants involves limestone injection into the hot boiler gases<sup>(1,2,3)</sup>. The limestone is rapidly calcined to  $\text{CaO}$  in the hot gases and then, as the gases cool, the  $\text{CaO}$  begins to combine with  $\text{SO}_2$  to form  $\text{CaSO}_4$ . The calcium sulphate is collected with the fly ash and is discarded. The process does not yield a saleable product, but it is relatively simple and requires one of the smallest capital investments for older plants<sup>(1,3)</sup>.

The contact time between the limestone and the hot boiler gases is short, generally in the range from 0.5 to 3 seconds. A very high level of reactivity in the limestone is necessary if  $\text{SO}_2$  removal is to be effective in this short time of contact. Most reports on the use of limestone give about 30% as the usual maximum utilization of the limestone<sup>(3)</sup>.

Because of the possibility of overburdening the dust-collection equipment, or of plugging and fouling the boiler tubes, it is not possible to increase the  $\text{SO}_2$  removal substantially by increasing the proportion of lime to  $\text{SO}_2$  in the gas stream. The most acceptable solution would be one in which the conditions for lime utilization were maximized, and only the stones of highest reactivity were used.

On January 28th, 1970, Mr. Douglas Harrison and Dr. K.S. Murthi of Ontario Hydro's Research Division in Toronto visited the Mines Branch. They brought six samples of Ontario limestones and dolomites with them and requested that a method be developed for evaluating their individual capabilities for capturing the  $\text{SO}_2$  from a gas stream and converting it to calcium sulphate. The visit followed earlier discussions of the Ontario Hydro problem by Dr. T.R. Ingraham with Mr. Harrison and Dr. Murthi in Toronto on December 11, 1969, and with Dr. Murthi in Toronto on November 18, 1969, and February 26, 1969.

This report will describe the experimental work done at the Mines Branch on developing a method for testing the stones, and it will discuss their relative merits as sulphur dioxide absorbents.

# MATERIALS FOR TESTING

The identification and chemical composition of the Ontario Hydro samples are shown in Table I. For comparison, a pure single crystal sample of calcite was included in the test work. A fresh sample of MgO was prepared from magnesite and it was also tested.

TABLE I

Identification and Chemical Composition  
of Ontario Hydro Limestone and Dolomite Samples

| <u>Identification</u> | <u>Analysis</u> |       |                               |                  |                 |
|-----------------------|-----------------|-------|-------------------------------|------------------|-----------------|
|                       | CaO             | MgO   | R <sub>2</sub> O <sub>3</sub> | SiO <sub>2</sub> | CO <sub>2</sub> |
| Calcite               | 56.0            | -     | -                             | -                | 43.97           |
| CODE 1217*            | 55.1            | 0.49  | 0.09                          | -                | 44.22           |
| CODE 1211*            | 54.7            | 0.63  | 0.17                          | 0.09             | 43.45           |
| CODE 1214*            | 50.9            | 1.27  | 1.69                          | 3.78             | 41.14           |
| CODE 1216*            | 30.5            | 17.50 | 0.15                          | -                | 47.43           |
| CODE 1212*            | 30.2            | 21.00 | 0.43                          | 0.52             | 46.54           |
| CODE 1220             | 25.6            | 32.4  | -                             | -                | -               |
| Magnesite             | -               | 45.65 | -                             | -                | 54.35           |

\* Analytical data supplied by Ontario Hydro

### Development of Experimental Technique

When finely ground limestone is injected in a steam boiler for sulphur dioxide absorption, the injection is normally made in the region just beyond the flame<sup>(2)</sup>. There the temperature is about 2000°F (1093°C). Because of the heat requirement for calcining, the temperature of the powder particles decreases rapidly as they drift downstream at rates of 30 to 60 ft/sec. They are captured in ash-collection equipment after several seconds and their primary reaction period is then over. The chemistry of the reactions involved in the conversion of limestone to sulphate will be discussed in a subsequent paper from these laboratories<sup>(4)</sup>.

Any credible test of the reactivity of limestones for SO<sub>2</sub> absorption requires a reasonable simulation of the situation existing in a boiler tube during limestone injection. At the Battelle Memorial Institute in Columbus, Ohio, their simulation<sup>(5)</sup> consists of a vertical tower about 12-in. in diameter and 15-ft. in height. The tower is lagged and internally heated by a gas flame. Sulphur dioxide is generated in the gas by sulphide additions to the fuel. Limestone is injected by spoon at the base of the tower and about three percent of the one gram test sample is caught by aspiration at the top of the tower. The design does not permit examination of the course of the reaction as the sulphate layer increases in thickness on the calcium oxide core, and it does not permit an assessment of the efficiency of sulphur dioxide removal from the gas stream.

We have attempted to make a number of different boiler tube simulations. Some have involved externally heated tubes into which limestone was injected in a high velocity flue-gas mixture, and others have involved dust collection by hot cyclones following limestone injection into burned fuel gases. These simulations have not fulfilled the requirements.

## APPARATUS AND PROCEDURE

The apparatus design selected for testing the Ontario Hydro samples is shown in Figure 1. In this apparatus, a 50-mg sample of closely sized limestone or dolomite was supported on a silica frit within the furnace. A dry simulated flue-gas stream containing 86% He, 12% CO<sub>2</sub> and 2% O<sub>2</sub> was passed through the sample at a rate of 50-cc/min. The sample was calcined by heating to 900°C for an hour, then it was cooled to the temperature of the experiment. When a steady state had been reached, a 2.0-cc sample of sulphur dioxide was injected into the gas stream. The contact time of the SO<sub>2</sub> with the calcined sample was 2.4 sec. For most of the samples, about 12-cc of SO<sub>2</sub> were required for complete conversion of the limestone to calcium sulphate or for the conversion of the dolomites to calcium and magnesium sulphates. Normally, seven 2-cc injections of SO<sub>2</sub> were made on each sample. The amount of sulphur dioxide remaining after the passage of each 2-cc gas plug through the sample was determined with a thermal conductivity cell. The amount of residual SO<sub>2</sub> was compared with a blank in which no limestone was used. From their ratio, the percentage of SO<sub>2</sub> that was absorbed during the 2.4-second period was then calculated. The percentage decreased as the CaO or MgO was progressively converted to CaSO<sub>4</sub> or MgSO<sub>4</sub>.

## RESULTS

The temperatures selected for the experiments were chosen with reference to Figure 2, which contains previously unpublished data<sup>(6)</sup> from this laboratory on the temperature to which a pure calcite sample must be heated to initiate decomposition in the presence of various percentages of  $\text{CO}_2$  in the surrounding gas. It is evident from Figure 2 that in the presence of 12%  $\text{CO}_2$ , the minimum decomposition temperature is about  $765^\circ\text{C}$ . Any  $\text{CaO}$  present in the gas at lower temperatures would tend to be converted to  $\text{CaCO}_3$ . This reaction is preferred to sulphation because  $\text{SO}_2$  will not displace  $\text{CO}_2$  from  $\text{CaCO}_3$ .

Some of the typical results are shown in Figure 3 for 50 mg samples of -250 +270 mesh limestone that had been calcined at  $900^\circ\text{C}$  for an hour before being cooled to  $805^\circ\text{C}$  for the series of  $\text{SO}_2$  injections.

The curve in Figure 3 having the greatest area underneath it is the blank. The area corresponds to an injection of 2.00-cc of  $\text{SO}_2$ . The series of curves corresponding to the first, second, etc. injections are identified by the numbers 1, 2, etc. It is apparent that most of the  $\text{SO}_2$  in the 1st 2-cc sample was removed when the sample passed through the bed of calcined lime. A little less was absorbed from the second sample and successively smaller amounts from additional samples.

The theoretical volume of  $\text{SO}_2$  at room conditions that would be required for conversion of the stone to sulphates at room conditions was calculated from the equation:



$$\text{cc of SO}_2 = 0.2412 [(0.8916 \times \% \text{ CaO}) + (1.240 \times \% \text{ MgO})],$$

where % CaO and % MgO are the percentages of each oxide in the original stone.

The results of the calculations and the corresponding absorptions and conversions for each of the samples tested are shown in the following tabulations:

PURE CALCITE

| Injection No.                     | 1    | 2    | 3    | 4    | 5     | 6     | 7     |
|-----------------------------------|------|------|------|------|-------|-------|-------|
| SO <sub>2</sub> supplied (cc)     | 2.00 | 4.00 | 6.00 | 8.00 | 12.00 | 12.00 | 14.00 |
| SO <sub>2</sub> absorbed (cc)     | 1.86 | 3.70 | 5.41 | 6.93 | 7.68  | 7.74  | 7.80  |
| % absorption                      | 92.9 | 91.9 | 85.5 | 76.0 | 37.6  | 3.2   | 3.1   |
| % conversion to CaSO <sub>4</sub> | 15.4 | 30.7 | 44.9 | 57.4 | 63.7  | 64.3  | 64.7  |

CODE 1217

| Injection No.                     | 1    | 2    | 3    | 4    | 5     | 6     | 7     |
|-----------------------------------|------|------|------|------|-------|-------|-------|
| SO <sub>2</sub> supplied (cc)     | 2.00 | 4.00 | 6.00 | 8.00 | 10.00 | 12.00 | 14.00 |
| SO <sub>2</sub> absorbed          | 1.83 | 3.64 | 5.39 | 6.99 | 8.29  | 8.92  | 9.05  |
| % absorption                      | 91.7 | 90.5 | 87.2 | 79.9 | 65.0  | 31.9  | 6.3   |
| % conversion to CaSO <sub>4</sub> | 15.2 | 30.4 | 44.9 | 58.2 | 69.0  | 74.4  | 75.4  |

CODE 1211

| Injection No.                     | 1    | 2    | 3    | 4    | 5     | 6     | 7     |
|-----------------------------------|------|------|------|------|-------|-------|-------|
| SO <sub>2</sub> supplied (cc)     | 2.00 | 4.00 | 6.00 | 8.00 | 10.00 | 12.00 | 14.00 |
| SO <sub>2</sub> absorbed          | 1.81 | 3.62 | 5.42 | 7.07 | 8.32  | 8.72  | 9.01  |
| % absorption                      | 90.5 | 90.4 | 90.3 | 82.5 | 62.3  | 19.9  | 14.6  |
| % conversion to CaSO <sub>4</sub> | 15.2 | 30.3 | 45.4 | 59.2 | 69.6  | 73.0  | 75.3  |

CODE 1214

| Injection No.                        | 1    | 2    | 3    | 4    | 5     | 6     | 7     |
|--------------------------------------|------|------|------|------|-------|-------|-------|
| SO <sub>2</sub> supplied             | 2.00 | 4.00 | 6.00 | 8.00 | 10.00 | 12.00 | 14.00 |
| SO <sub>2</sub> absorbed             | 1.91 | 3.80 | 5.65 | 7.34 | 8.52  | 9.15  | 9.33  |
| % absorption                         | 95.7 | 94.5 | 92.4 | 84.2 | 59.2  | 31.3  | 9.2   |
| % conversion<br>to CaSO <sub>4</sub> | 16.9 | 33.6 | 49.9 | 64.8 | 75.2  | 80.7  | 82.3  |

CODE 1216

| Injection No.                        | 1    | 2    | 3    | 4    | 5     | 6     | 7     |
|--------------------------------------|------|------|------|------|-------|-------|-------|
| SO <sub>2</sub> supplied             | 2.00 | 4.00 | 6.00 | 8.00 | 10.00 | 12.00 | 14.00 |
| SO <sub>2</sub> absorbed             | 1.86 | 3.70 | 5.38 | 6.80 | 7.25  | 7.28  | 7.30  |
| % absorption                         | 93.0 | 91.8 | 84.1 | 71.0 | 22.8  | 1.3   | 1.0   |
| % conversion<br>to CaSO <sub>4</sub> | 15.8 | 31.4 | 45.6 | 57.7 | 61.5  | 61.7  | 61.9  |

CODE 1212

| Injection No.                        | 1    | 2    | 3    | 4    | 5     | 6     | 7     |
|--------------------------------------|------|------|------|------|-------|-------|-------|
| SO <sub>2</sub> supplied             | 2.00 | 4.00 | 6.00 | 8.00 | 10.00 | 12.00 | 14.00 |
| SO <sub>2</sub> absorbed             | 1.88 | 3.74 | 5.45 | 6.79 | 7.05  | 7.16  | 7.27  |
| % absorption                         | 94.0 | 92.9 | 85.8 | 66.7 | 13.2  | 5.6   | 5.2   |
| % conversion<br>to CaSO <sub>4</sub> | 14.7 | 29.2 | 42.7 | 53.1 | 55.1  | 56.1  | 56.9  |

CODE 1220

| Injection No.                     | 1    | 2    | 3    | 4    | 5     | 6     | 7     |
|-----------------------------------|------|------|------|------|-------|-------|-------|
| SO <sub>2</sub> supplied          | 2.00 | 4.00 | 6.00 | 8.00 | 10.00 | 12.00 | 14.00 |
| SO <sub>2</sub> absorbed          | 1.89 | 3.67 | 5.37 | 6.60 | 6.86  | 6.95  | 6.98  |
| % absorption                      | 94.6 | 89.0 | 85.2 | 61.3 | 13.2  | 4.4   | 1.7   |
| % conversion to CaSO <sub>4</sub> | 15.4 | 29.8 | 43.7 | 53.7 | 55.8  | 56.5  | 56.8  |

MAGNESITE

| Injection No.                     | 1     | 2     | 3     | 4     | 5     | 6     | 7     |
|-----------------------------------|-------|-------|-------|-------|-------|-------|-------|
| SO <sub>2</sub> supplied          | 2.00  | 4.00  | 6.00  | 8.00  | 10.00 | 12.00 | 14.00 |
| SO <sub>2</sub> absorbed          | 0.322 | 0.464 | 0.602 | 0.678 | -     | -     | -     |
| % absorption                      | 16.1  | 7.1   | 6.9   | 3.8   | -     | -     | -     |
| % conversion to CaSO <sub>4</sub> | 2.3   | 3.4   | 4.4   | 5.0   | -     | -     | -     |

To permit comparisons of some of the results in the tabulation, the data for magnesite, one of the dolomites (Code 1212), calcite, and the most reactive of the limestones (Code 1214) were plotted in Figure 4. The percentage of reaction to form CaSO<sub>4</sub>\* was plotted against the cumulative volume of SO<sub>2</sub> passed through the sample. It is evident that magnesite has a very low SO<sub>2</sub> absorbency. Dolomite is somewhat better, but sticking problems occurred with all of the dolomite samples. Calcite is a still better absorbent but it is not as good as limestone. All of the limestones were better absorbents

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\* Trace amounts of elemental sulphur were reported, along with CaSO<sub>4</sub> and residual CaO, in most samples.

than calcite. The best absorption was associated with about 1.7%  $R_2O_3$ , 3.8%  $SiO_2$  and a high degree of microcrystallinity<sup>(7)</sup> in the limestone. Attempts to increase the reactivity of calcite with 2% additions of  $Fe_2O_3$  were unsuccessful. At the temperatures of the experiments, silica is inert. On this basis it seems unlikely that the enhanced reactivity is associated with a catalytic action of the  $R_2O_3$  to form  $SO_3$ . It is more probable that the  $CaSO_4$  layer formed on the microcrystalline  $CaO$  is less protective than when it is formed on coarsely grained singly crystalline calcite.

To assess the effect of changing particle size, three specimens of sample No. 1214 were prepared in the size ranges (-200 +250), (-250 +270) and (-270 +325) mesh. If one assumes regular particles, the surface area of the same weight of sample will vary by a factor of 3 from the coarsest to the finest of the above mesh ranges. The samples were given identical sulphation treatments at 805°C, and it was found that the relative utilizations were 79.2, 80.4 and 82.3% respectively. It is evident from the data that neither the rate nor the degree of sulphation is significantly altered by changes in the particle size within the 200 to 325 mesh region.

Additional comparisons of the efficiency of  $SO_2$  removal are shown in Figure 5. The lines for limestone and magnesite at 805°C show clearly the very low level of  $MgO$  activity. The effects of the temperature of reaction between  $CaO$  and  $SO_2$  are also shown on the figure. At 778°C, calcite retains a high degree of reactivity through the first three additions of  $SO_2$ . The reactivity then decreases rapidly in a way that indicates a low rate of transport of the reactants through the  $CaSO_4$  layer. Alternatively, when the reaction temperature is between 886 and 934°C, the reactivity patterns of calcite are almost identical. There is a sharp decrease in reactivity

initially, but then a moderately high degree of reactivity (60-80%) is retained throughout the period of most of the  $\text{SO}_2$  additions.

The areas beneath each of the curves in Figure 5 are proportional to the amount of the oxide that is converted to sulphate. The area under the limestone curve is greater than the areas under the calcite curves at 778, 886 and 934, thus signifying its greater utilization. From area comparisons it is also evident that the greatest utilization of calcite occurs when the reaction temperature is high. Although the lower limit is not known, the evidence suggests that there is no advantage in making the  $\text{SO}_2$  pick-up at temperatures above 886°C.

#### COMMENTS ON METHOD

This method of study had the advantage of having the  $\text{SO}_2$  in contact with the lime for a period of time very close to that in an actual boiler operation. Another advantage is that the actual residual gas analysis following the injection shows how effective the lime is in removing  $\text{SO}_2$  from the gas stream. In addition, the use of small samples of  $\text{SO}_2$  permits the activity of the sulphate-coated lime to be assessed at various periods during its conversion. The time of contact may be changed by varying either the volume of the  $\text{SO}_2$  sample or the total flow-rate of the gases. The effects of particle size may be studied also. The area in which the simulation is farthest removed from actual operating conditions is in the concentration of  $\text{SO}_2$  in the sample. In an actual flue, the  $\text{SO}_2$  concentration is a few tenths of a percent, whereas our injections were at one hundred percent. We recognize that this concentration difference would probably cause a substantial increase in rate, but we believe that the rate change would be unlikely to alter the

order of reactivity of the stones or any of the principal conclusions drawn from the data. The simulation was done in the absence of fly ash. At high temperatures there may be some slagging reactions between the CaO and the ash. This is not likely to be a problem in the range of temperature to be recommended from this work for lime injections. The simulation was done in the absence of water. Because  $\text{Ca}(\text{OH})_2$  and  $\text{Mg}(\text{OH})_2$  are both unstable at the temperatures used in the study, it was assumed that the water would not be involved in the reactions. This assumption may not be entirely valid, because water sometimes has a slight catalytic effect on sintering or deactivating oxides.

#### CONCLUSIONS

1. The activity of limestones and dolomites in absorbing  $\text{SO}_2$  may be estimated by a simple experimental technique involving continuous gas analysis.
2. The decreasing order of reactivity for  $\text{SO}_2$  absorption by the Ontario Hydro samples is No. 1214, No. 1211, No. 1217, No. 1216, No. 1212 and No. 1220.
3. Because  $\text{MgO}$  is deactivated readily by heat, the magnesium carbonate content of limestones and dolomites behaves essentially as an inert diluent.  $\text{MgO}$  does not participate to an appreciable extent in removing  $\text{SO}_2$  from flue gases.
4. The greatest utilization of  $\text{CaO}$  for  $\text{SO}_2$  absorption probably occurs at temperatures in the range 850-950°C. There is no apparent rate advantage in sulphating at higher temperatures. The injection point for limestone additions to a boiler should be selected on the basis of the rate of gas flow and the time required to calcine the lime so that it will arrive

fully calcined at the 900°C zone of the boiler.

5. A high calcium oxide content and a high degree of microcrystallinity are the essential characteristics in determining the reactivity of a limestone.
6. Dolomite samples may cause sticking problems.
7. Changes in the particle size from (-200 +250) to (-270 +325) mesh do not significantly alter the rate or amount of SO<sub>2</sub> absorption.

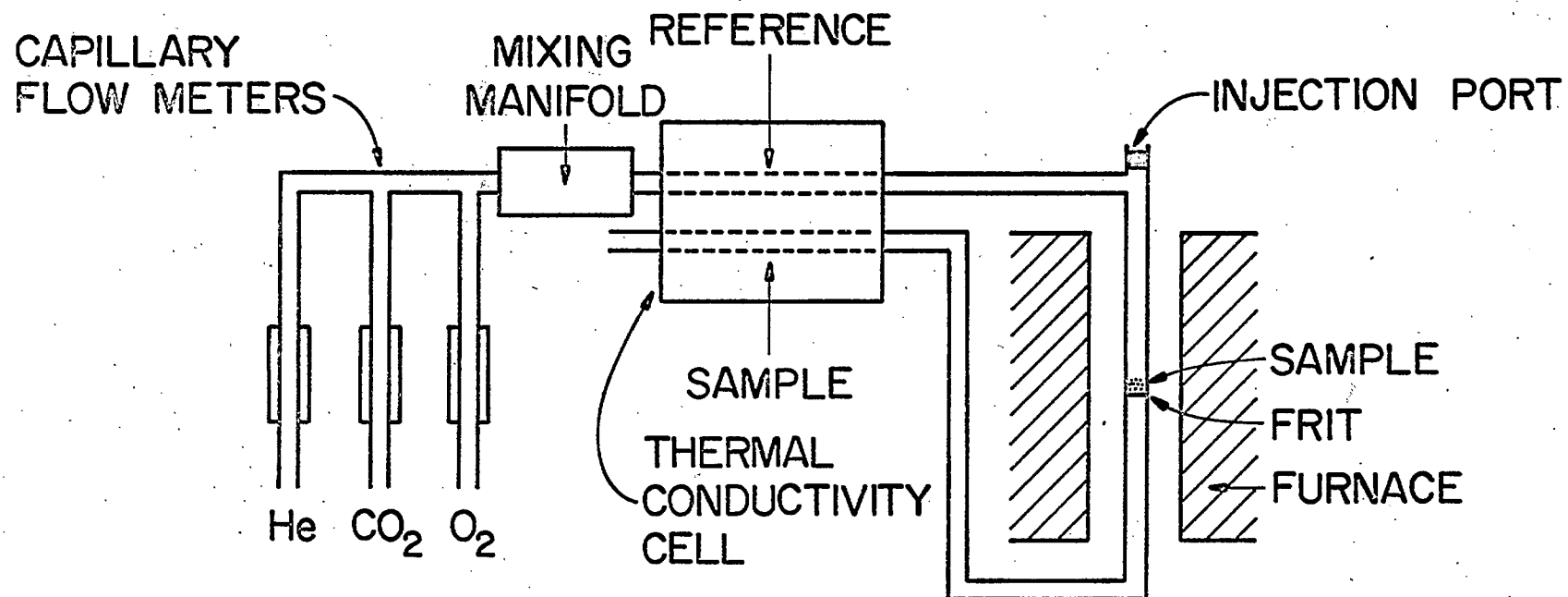
#### ACKNOWLEDGEMENT

Dr. D. MacKinnon made the CaO and MgO analysis shown for Sample No. 1220 and Mr. P. Belanger made the x-ray diffraction analyses to confirm the products.

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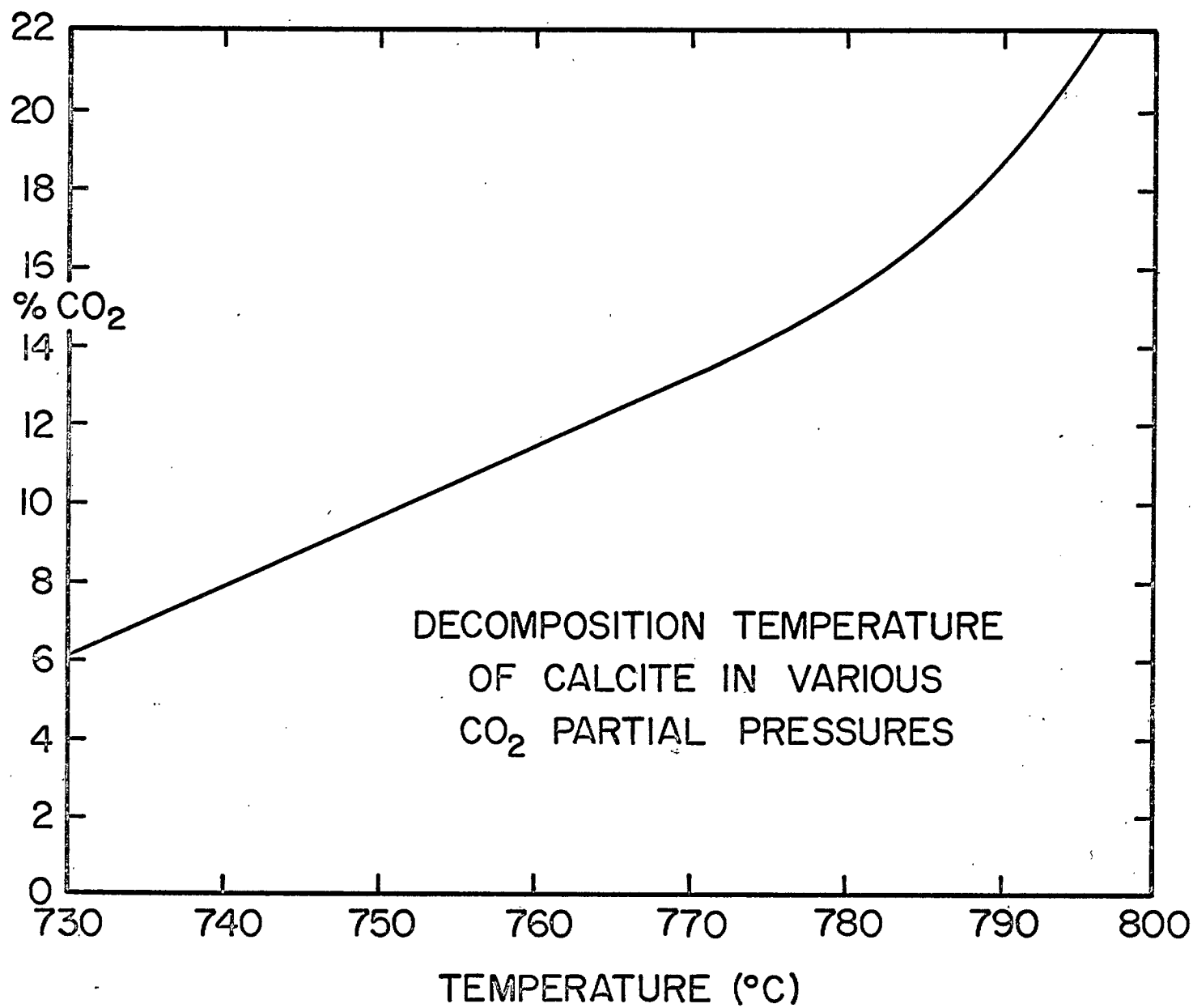
FIGURE 1



APPARATUS FOR MEASURING  
 $\text{SO}_2$  ABSORPTION



FIGURE 2



SO<sub>2</sub> ANALYSIS OF  
RESIDUAL GAS

PARTIAL PRESSURE  
OF SO<sub>2</sub>

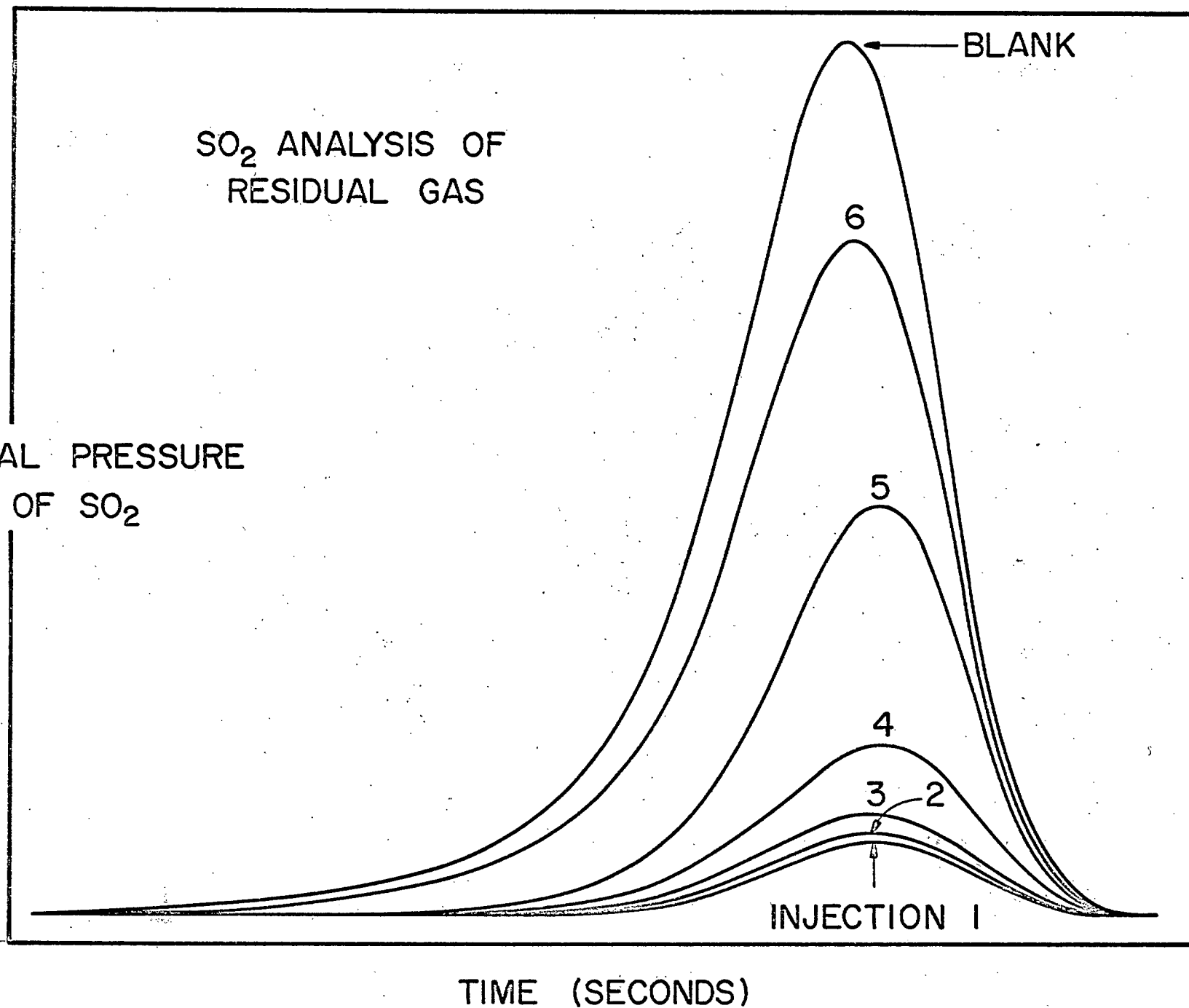


FIGURE 3

FIGURE 4

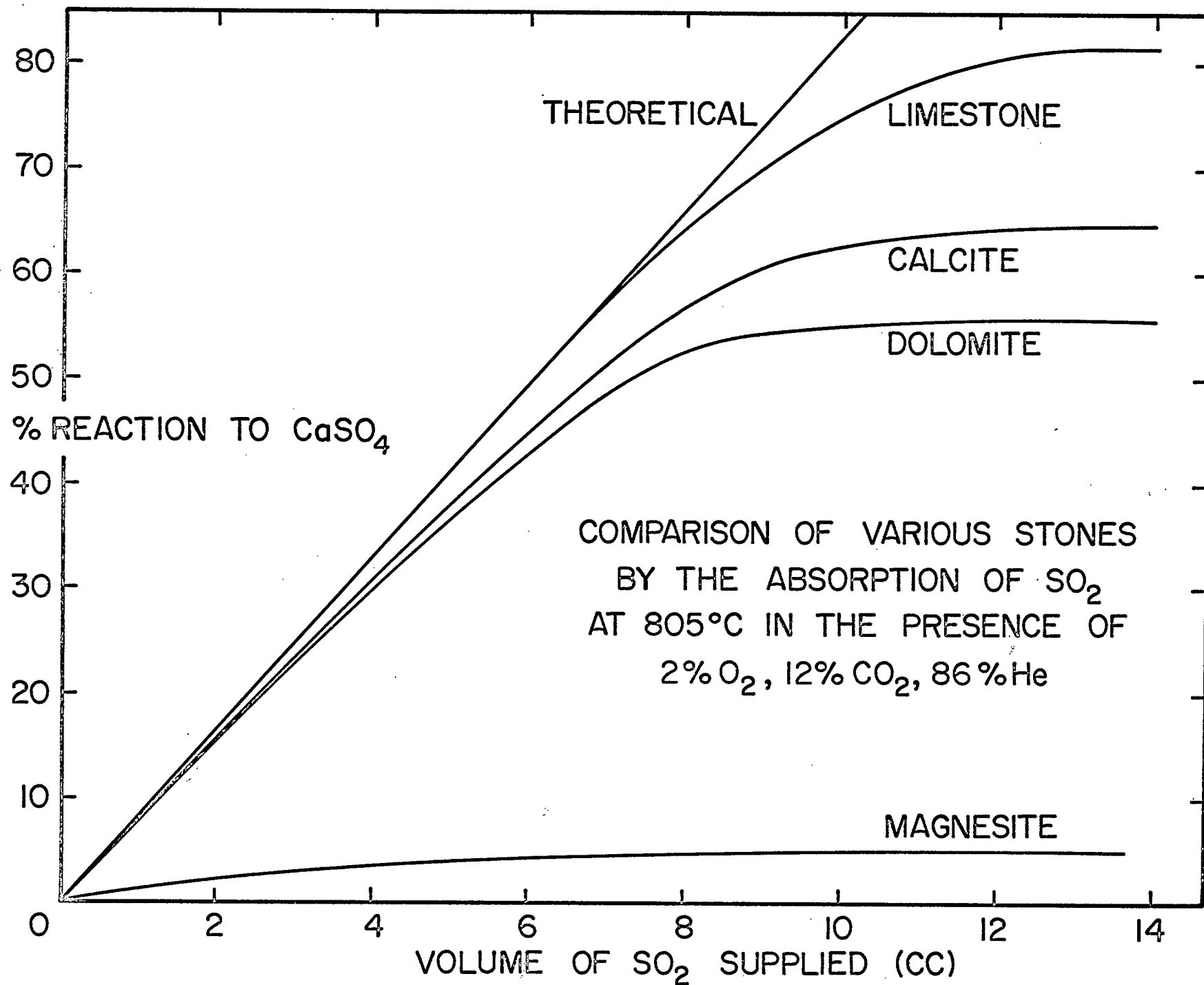


FIGURE 5

