

INFORMATION TO USERS

This dissertation was produced from a microfilm copy of the original document. While the most advanced technological means to photograph and reproduce this document have been used, the quality is heavily dependent upon the quality of the original submitted.

The following explanation of techniques is provided to help you understand markings or patterns which may appear on this reproduction.

1. The sign or "target" for pages apparently lacking from the document photographed is "Missing Page(s)". If it was possible to obtain the missing page(s) or section, they are spliced into the film along with adjacent pages. This may have necessitated cutting thru an image and duplicating adjacent pages to insure you complete continuity.
2. When an image on the film is obliterated with a large round black mark, it is an indication that the photographer suspected that the copy may have moved during exposure and thus cause a blurred image. You will find a good image of the page in the adjacent frame.
3. When a map, drawing or chart, etc., was part of the material being photographed the photographer followed a definite method in "sectioning" the material. It is customary to begin photoing at the upper left hand corner of a large sheet and to continue photoing from left to right in equal sections with a small overlap. If necessary, sectioning is continued again — beginning below the first row and continuing on until complete.
4. The majority of users indicate that the textual content is of greatest value, however, a somewhat higher quality reproduction could be made from "photographs" if essential to the understanding of the dissertation. Silver prints of "photographs" may be ordered at additional charge by writing the Order Department, giving the catalog number, title, author and specific pages you wish reproduced.

University Microfilms

300 North Zeeb Road
Ann Arbor, Michigan 48106

A Xerox Education Company

73-14,382

RUTH, Lawrence A., 1945-
REACTION OF HYDROGEN SULFIDE WITH HALF-
CALCINED DOLOMITE.

The City University of New York, Ph.D., 1973
Engineering, chemical

University Microfilms, A XEROX Company, Ann Arbor, Michigan

REACTION OF HYDROGEN SULFIDE
WITH HALF-CALCINED DOLOMITE

by

LAWRENCE A. RUTH

A dissertation submitted to the Graduate
Faculty in Engineering in partial fulfillment
for the degree of Doctor of Philosophy,
The City University of New York

1972

This manuscript has been read and accepted for the Graduate Faculty in Engineering in satisfaction of the dissertation requirement for the degree of Doctor of Philosophy.

12/22/72

Date

Robert A. Graff

Chairman of Examining
Committee

1/29/73

Date

Jacques E. Benveniste

Executive Officer

Prof. Robert A. Graff (Chairman)

Prof. Arthur M. Squires

Prof. Reuel Shinnar

Prof. Amos Turk

Supervisory Committee

The City University of New York

PLEASE NOTE:

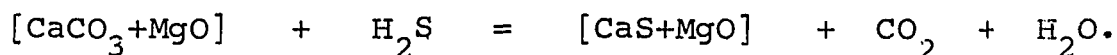
Some pages may have
indistinct print.

Filmed as received.

University Microfilms, A Xerox Education Company

Abstract

Electricity may soon be generated in systems combining gas and steam turbines, not only without polluting the atmosphere, but at higher efficiency and reduced capital cost. In such systems, a clean fuel gas would be provided by gasifying coal or residual oil with air and steam at high pressure and removing sulfur from the gas with half-calcined dolomite via the reaction:



Differential kinetic data are given between 450° and 800°C, for one atmosphere total pressure, and H₂S partial pressures of 0.005-0.20 atmospheres and over a wide range of CO₂ partial pressures. Data were obtained gravimetrically using finely powdered dolomite spread in a thin layer, so as to minimize diffusion effects within each particle and within the bed of powder.

The reaction of H₂S with half-calcined dolomite is extremely fast, faster than the reaction of H₂S with fully calcined dolomite. For example, at 800°C and 0.05 atmosphere H₂S, half-calcined dolomite achieves 50% conversion in only 14 seconds, while the fully calcined

solid requires 280 seconds.

CO_2 has an important effect on the reaction of H_2S with half-calcined dolomite. At low levels of CO_2 , i.e., just above the equilibrium decomposition pressure of CaCO_3 at the run temperature, the reaction displays an order of reaction, with respect to H_2S , of $1/2$, and an activation energy of 20.5 kcal/gm-mole. However, at higher levels of CO_2 , typically 0.60 atm., the reaction is first order in H_2S and has an activation energy of 37.7 kcal/gm-mole.

Even more striking is the spectacular effect of CO_2 on the progress of the reaction at temperatures below 700°C . Runs made below this temperature, with low levels of CO_2 , do not achieve complete conversion, but break very sharply at low conversions of CaCO_3 . However, runs made with high levels of CO_2 achieve complete conversion at good rates. Steam has an effect similar to CO_2 , except that it is more effective than CO_2 in promoting the reaction at 550°C ; however, the reverse is true at 600°C . Below 700°C , both steam and CO_2 have the additional effect of decreasing the initial rate of reaction.

Pulses of a gas containing 0.3% oxygen, and lasting about 10 seconds each, have the ability to revive a solid which has "died" at low conversions, and permit another

increment of conversion.

We suggest an "interfacial blockage" model to explain the main features of our data. We believe that temperature and gas composition affect the way in which CaS grows within the solid microstructure. The CaS may form an impervious layer upon a crystallite of CaCO_3 , in which case the reaction "drops dead;" alternatively, CaS may form a porous layer, so that the interior of the crystallite remains open to the action of H_2S , and the reaction continues. We hypothesize that high temperature, the presence of CO_2 , H_2O , or an oxygen pulse, favors the latter condition.*

*See addendum p. 173.

Acknowledgements

For their guidance and interest in this research, appreciation and thanks are due Professors Robert A. Graff and Arthur M. Squires of the Chemical Engineering Department.

I also thank John Bodnaruk and George DiIorio of the Chemical Engineering Shop for their assistance in setting up the experimental apparatus.

Special thanks are due my wife, Ann, for her encouragement and continued patience.

Grant number AP00945 from the Office of Air Programs of the Environmental Protection Agency supported a major part of this work.

Presentations

Portions of this research appear in papers presented at meetings of the American Chemical Society and American Institute of Chemical Engineers:

L. A. Ruth, A. M. Squires, and R. A. Graff,

"Desulfurization of Fuels With Calcined Dolomite:

III. First Results for Reaction of CaCO_3 with H_2S ,"

presented at meeting of American Chemical Society,

Los Angeles, California, March 31, 1971.

L. A. Ruth, R. A. Graff, and A. M. Squires,

"Desulfurization of Fuels With Calcined Dolomite:

IV. Reaction of CaCO_3 With H_2S ," presented at

meeting of American Institute of Chemical Engineers,

Dallas, Texas, February 22, 1972.

V. L.A. Ruth, A.M. Squires, and R.A. Graff,

"Desulfurization of Fuels with Half-Calcined Dolomite:

First Kinetic Data," Environmental Science &

Technology, Vol. 6, p. 1009, November 1972.

Table of Contents

	<u>Page</u>
Abstract	i
Acknowledgments	iv
Presentations	v
Table of Contents	vi
List of Figures	x
List of Tables	xiv
1.0 Introduction	1
2.0 Object of the Research	4
3.0 Significance of the Research	5
4.0 Technical Background	7
4.01 Dolomite	7
4.02 Calcined Dolomite	7
4.03 Solid-Gas Reactions	11
4.04 Use of Calcined Dolomite in Industrial Processes	12
4.05 Review of Previous Related Work at The City College	15
4.06 Cyclic Use of Calcined Dolomite to Desulfurize Fossil Fuels. A Process Example.	23
5.0 Thermodynamics and Reaction Conditions	28
5.01 Thermodynamic Equilibria	28
5.02 Reaction Conditions	30

	<u>Page</u>
6.0 Experimental Techniques	33
6.01 Equipment	33
6.02 Procedures	40
6.03 Dolomite Supply	42
6.04 Capacity of Samples	43
7.07 Experimental Results	46
7.01 Effect of Temperature and H_2S Concentration on Runs Made at Low CO_2 Concentrations	47
7.02 Effect of Temperature and H_2S Concentration on Runs Made at High CO_2 Concentrations	57
7.03 Effect of CO_2 Concentration	67
7.04 Effect of H_2O	73
7.05 Effect of Oxygen	82
7.06 Effect of Hydrogen	85
7.07 Sulfur Formation in Furnace Tube	85
7.08 Reaction of H_2S with Fully Calcined Dolomite	87
7.09 Physical Measurements: Effective Diffusivity, Surface Area. Electron Micrographs	90
8.0 Discussion of Results	94
8.01 Influence of Diffusion on Reaction Rate	94
8.02 Initial Rate Behavior	98

	<u>Page</u>
8.03 Effect of CO ₂ , H ₂ O, and O ₂ on the Progress of the Reaction	102
8.04 Proposed Reaction Theory: Interfacial Blockage Model	105
8.05 Consideration of Alternative Reaction Models	116
8.06 Variability of Results	120
8.07 Reaction of H ₂ S With Limestone and Calcite	125
8.08 Comparison of the Rate of Reaction of H ₂ S with Half-Calcined and Fully Calcined Dolomite	126
8.09 Data Correlation	128
8.10 Process Implications	130
8.11 Suggestions for Further Work	134
9.0 Conclusions and Recommendations	138
10.0 Appendix	142
10.01 Determination of Capacities of Samples from Calcination Data	142
10.02 Calculation of Effectiveness Factor for Powder. Application of Weisz Criterion for Diffusion	143
10.03 Consideration of Desulfurization Equilibrium. Runs at Shift Equilibrium	146
10.04 Analysis of Greenfield Dolomite Sample	149
10.05 Data Correlation	149
10.06 Design of Panel Bed Filter	154

	<u>Page</u>
10.07 Nomenclature	165
11.0 References	167
12.0 Vita	172
13.0 Addendum, Results of Examination of Reaction Solids under Electron Microscope	173

List of Figures

	<u>Page</u>
1. Log (1-x) plot for run made by Pell on fully calcined Greenfield powder at 700°C and 5% H ₂ S.	17
2. Log (1-x) plots for runs made by Pell on fully calcined Greenfield powder at 550°C with 0.3% H ₂ S and 20% H ₂ S.	18
3. "Final" rates versus concentration of H ₂ S for runs made by Pell with fully calcined dolomite (curves were generated from Pell's adsorption model).	19
4. Runs made by Pell on fully calcined Greenfield powder, at 550°C, 0.3% H ₂ S, with and without water added.	21
5. Runs made by Pell on fully calcined Greenfield powder at 550°C, 10% H ₂ S, with and without water added.	22
6. Concept for power generation by combined-cycle system incorporating a fluidized-bed gasifier for coal and a panel bed filter for simultaneous removal of dust and sulfur.	24
7. The duPont 950 Thermogravimetric Analyzer	35a
8. Our modification of duPont TGA, developed for this research.	35b
9. System to supply reaction gas mixture	39
10. Hydrogen burner for production of water	41
11. Log (1-x) plots at 800°C, 25% CO ₂ , and three H ₂ S levels.	49
12. Log (1-x) plots at 750°C, 15% CO ₂ , and three H ₂ S levels.	50
13. Log (1-x) plots at 700°C, 7% CO ₂ , and three H ₂ S levels.	51

	<u>Page</u>
14. Log (1-x) plots at 650°C, 5% CO ₂ , and three H ₂ S levels.	52
15. Log (1-x) plots at 600°C, 3% CO ₂ , and three H ₂ S levels.	53b
16. Initial reaction rate versus partial pressure of H ₂ S for runs made at low CO ₂ levels.	56
17. Arrhenius plot of initial rate data for runs made at low CO ₂ levels.	58
18. Comparison of data for run at 800°C, 5% H ₂ S, with curve generated from equation 4.	59
19. Comparison of data for run at 700°C, 1% H ₂ S, with curve generated from equation 4.	60
20. Comparison of data for run at 600°C, 20% H ₂ S, with curve generated from equation 4.	61
21. Initial reaction rate versus partial pressure of H ₂ S for runs made at high CO ₂ levels.	63
22. Arrhenius plot of initial rate data for runs made at high CO ₂ levels.	65
23. Log (1-x) plots at 0.5% H ₂ S, 60% CO ₂ , and five temperature levels.	66
24. Initial rate versus concentration of CO ₂ for runs made at 600°C, 5% H ₂ S.	70
25. Log (1-x) plots at 600°C, 5% H ₂ S, and four CO ₂ levels.	72
26. Log (1-x) plots at 550°C, 5% H ₂ S, and two CO ₂ levels.	74
27. Log (1-x) plots at 650°C, 5% H ₂ S, and two CO ₂ levels.	75
28. Log (1-x) plots at 700°C, 5% H ₂ S, and two CO ₂ levels.	76

29. Log (1-x) plots at 550°C, high CO₂ level, and four H₂S levels. 77
30. Log (1-x) plots for runs at 500°C, 5% H₂S, with and without water added. 79
31. Log (1-x) plots for runs at 550°C, 5% H₂S, with and without water added. 80
32. Effect of a pulse of gas containing 0.3% O₂ on the reaction of half-calcined dolomite at 600°C with 5% H₂S, 3% CO₂, 10% H₂, and balance N₂. 83
33. Initial rate versus concentration of O₂ for runs made with 5% H₂S and low CO₂ level at 550°C and 600°C. 84
34. Comparison of data on the reaction of H₂S with fully calcined dolomite at 550°C and 10% H₂S for runs made with the dolomite used in this research and the dolomite used in Pell's research. 88
35. Comparison of the data of Ruth and Pell on the reaction of H₂S with fully calcined dolomite at 800°C and 10% H₂S. 89
36. A run with 0.745 cm sphere of Greenfield stone, at 800°C, 5% H₂S, and 25% CO₂. Conversion data is plotted in the form of the diffusion statistic versus time. 92
37. Electron micrograph of half-calcined, -250+270 mesh Greenfield powder, the dolomite used in this research. 93
38. Initial rate versus sample size for runs made at 800°C, 1% H₂S. 97
39. Arrhenius plots for runs made at 5% H₂S with both large and small sample sizes. 99
40. Schematic illustration showing that the product layer which forms on the surface of a crystallite of reactant solid can have different structures, depending on the relative magnitudes of the interfacial reaction rate and the annealing rate of

41.	Log (1-x) plots for duplicate runs at 800°C, 1% H ₂ S, 25% CO ₂ and at 700°C, 20% H ₂ S, 7% CO ₂ .	121
42.	Log (1-x) plots for six runs made at 650°C, 0.5% H ₂ S, and 60% CO ₂ .	122
43.	Comparison of log (1-x) plots for runs made with half-calcined dolomite, calcite, and limestone, at 800°C, 5% H ₂ S, 25% CO ₂ .	127
44.	Comparison of curves generated by the empirical correlation of equations 17-25 with data for runs at 800°C, 25% CO ₂ , and three H ₂ S levels.	155
45.	Comparison of curves generated by the empirical correlation of equations 17-25 with data for runs at 700°C, 7% CO ₂ , and three H ₂ S levels.	156
46.	Comparison of curves generated by the empirical correlation of equations 17-25 with data for runs at 0.5% H ₂ S, 60% CO ₂ , and five temperature levels.	157
47.	Comparison of curves generated by the empirical correlation of equations 17-25 with data for runs at 600°C, 5% H ₂ S, and four CO ₂ levels.	158
48.	Comparison of curves generated by the empirical correlation of equations 17-25 with data for runs at 550°C, high CO ₂ level, and three H ₂ S levels.	159
49.	Cross-flow filter.	162
50.	Computer program to determine width of cross-current flow filter.	163

List of Tables:

1. Illustrative Energy Balances	27
2. Equilibrium Constant for the Reaction: $\text{MgO(s)} + \text{H}_2\text{S(g)} = \text{H}_2\text{O(g)} + \text{MgS(s)}$	29
3. Initial Rates for Runs Made at Low CO_2 Concentrations	55
4. Initial Rates for Runs Made at High CO_2 Concentrations	62
5. Effect of CO_2 Concentration on Initial Rate	68
6. Effect of H_2O on Initial Rate	81

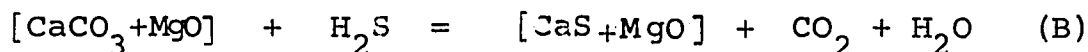
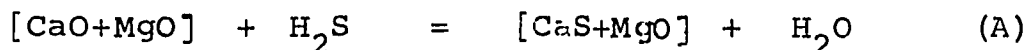
1.0 Introduction

The United States power industry, facing the severe problem of having to suppress emissions of sulfur oxides, had hoped until recently to meet this problem by relying heavily upon low sulfur fuels and upon stack-gas cleaning processes. Unfortunately, supplies of low-sulfur fuels are not adequate and technologies developed to date for removing sulfur dioxide from stack gases are proving expensive or of dubious utility. As a result, power engineers are turning their attention to opportunities for capturing pollutants at an earlier stage in the combustion process.

A research team at The City College is working toward development of fuel-treating processes which are satellite to power generation itself. In such "clean power" systems, a fuel gas would be produced by the partial combustion, or gasification, of coal or oil at high pressure, and the fume and sulfur would be removed from the fuel gas. The clean gas thus produced would make an excellent fuel for a gas turbine, and with the subsequent recovery of waste heat from the turbine for the raising of steam for steam turbines, system efficiencies of 50% appear possible at turbine inlet temperatures achievable within a decade. This is a significant advance in efficiency over even the most modern

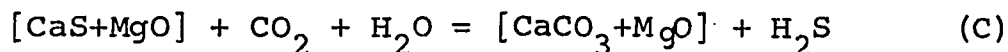
power generating stations of today. Because pressurized equipment would be smaller than the large atmospheric pressure furnaces in current use, and because gas turbines are cheaper than steam turbines, there is good reason to believe that these advances may be realized with no increase in capital expenditure over current practice.

In the gasification step, sulfur would be released in the form of H_2S , which would be captured by either fully calcined or half-calcined dolomite:



Removal of sulfur at a high temperature level by acceptor reactions (A) or (B) is preferable to removal by a wet system at low temperatures because the latter inevitably leads to loss of heat at a temperature too low for practical use. An acceptor process, too, could probably be cheaper than a wet process.

Reaction (B) can be conducted in reverse to regenerate half-calcined dolomite and to obtain H_2S at a concentration sufficient for conversion to elemental sulfur in a Claus system:



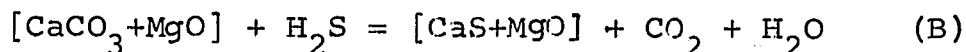
Equilibrium for reaction (B) or (C) is a strong function of temperature, the regeneration being favored at low

temperature. In a cyclic sulfur removal process, reactions (B) and (C) would be used. Alternatively, reactions (A) and (C) can be used, except that reaction (C) would be followed by a calcination step, in order to produce fully calcined dolomite.

As part of its research effort to develop clean power systems, The City College team has undertaken the study of the kinetics of reactions (A), (B), and (C). This thesis is a report of work on reaction (B), the reaction of H_2S with half-calcined dolomite. Reaction (A) has been reported on earlier by Pell (1) and work on reaction (C) at elevated pressures is currently getting underway.

2.0 Object of the Research

The object of this research is to acquire detailed knowledge of the kinetics of the reaction,



conducted at atmospheric pressure, and over a wide range of temperatures and H_2S partial pressures. This knowledge will be used for two purposes: (1) to design fuel desulfurization processes of the aforementioned type; and (2) to gain some understanding of the reaction mechanism involved in this particular reaction, with the hope of providing new insights into the study of non-catalytic solid-gas reactions, in general.

Differential reaction rates will be measured using the thermogravimetric technique. The change in weight of a powdered sample of the solid will be observed continuously while it is exposed to gas streaming at a rate such that changes in gas composition are small.

3.0 Significance of the Research

This research will contribute toward the development of systems to generate clean electric power from fossil fuels at not only higher efficiency but also reduced capital cost. Raw fuel would be gasified, the fuel gas would be cleaned of dust and sulfur, and the clean fuel would be committed to an advanced power cycle specifically engineered to take advantage of the superior qualities of the clean fuel.

Squires (2,3), in 1967, proposed half-calcined dolomite as an agent to capture sulfur from a fuel gas at high pressure and at temperatures greater than about 750°C. At that time, no data were available for reaction (B), but Squires reasoned that tiny crystallites of CaCO_3 embedded in a porous matrix along with tiny crystallites of MgO might display good reactivity toward H_2S . The present work has confirmed this. Furthermore, reaction of H_2S with half-calcined dolomite (reaction B) has been shown to be livelier than the reaction of H_2S with fully-calcined dolomite (reaction A) reported on earlier by Squires, Graff, and Pell (4, 5).

The kinetic data reported here is of a pioneering nature in respect to the behavior of a solid comprising an intimate intermingling of tiny crystallites of magnesium

oxide and a second, reactive constituent. The results of this research may lead one to consider the advantages of MgO as a support for a number of reactive solids which are candidates for use in cyclic processes, e.g., BaO in the Brin process for oxygen and FeO or a higher oxide of iron in the steam-iron process for hydrogen.

Data for reaction (B) show kinetic curiosities, particularly the effect of carbon dioxide, steam, and oxygen on the reaction rate, which, to our knowledge, are unlike any effects previously reported for non-catalytic gas-solid reactions. We believe that these results emphasize the important influence on conversion rate of changes in microstructure which occur in solids undergoing chemical reaction.

4.0 Technical Background

4.01 Dolomite

Dolomite is a true chemical compound, $\text{CaCO}_3 \cdot \text{MgCO}_3$. It is a member of a true class of rhombohedral carbonates, which includes calcite (CaCO_3) and magnesite (MgCO_3). These carbonates are built of alternating layers of carbonate ions and cations. In dolomite, ideally, cation planes populated entirely by Mg^{++} alternate with planes populated entirely by Ca^{++} (6). Natural dolomite often diverges from the ideal of one atom of magnesium for each atom of calcium, the latter being present in excess. True dolomites richer in magnesium are seldom, if ever, encountered (7).

Natural dolomite is a common rock of wide distribution throughout the world, and often occurs in a state of high purity. In the U.S. and Canada, important dolomitic deposits exist in Ohio, California, Wisconsin, Pennsylvania, Nevada, Utah, Illinois, Connecticut, Massachusetts, Ontario, and Quebec.

4.02 Calcined Dolomite

Dolomite decomposes in two steps when heated gently under moderate CO_2 pressures. The first stage of dolomite

decomposition, which is believed to be a diffusion controlled process (8,9), produces an intermingling of microscopic crystallites of CaCO_3 and MgO , written as $[\text{CaCO}_3+\text{MgO}]$ and called half-calcined dolomite. At a higher temperature, which corresponds to the equilibrium decomposition temperature of CaCO_3 at the prevailing partial pressure of CO_2 , the second stage of decomposition occurs, forming fully calcined dolomite, $[\text{CaO}+\text{MgO}]$.

The decomposition of CaCO_3 to CaO and CO_2 is readily reversible but the decomposition of MgCO_3 is not. MgO shows no tendency to react with CO_2 at the experimental conditions used in this research. It should be pointed out, however, that MgO takes up CO_2 readily at room temperature in the presence of water vapor.

There is no volume change, nor indeed any change of particle shape, when dolomite is calcined gently to produce $[\text{CaCO}_3+\text{MgO}]$. The same may be said if dolomite is calcined to produce $[\text{CaO}+\text{MgO}]$ at a temperature below about 1000°C .

Haul (10) gave surface area and porosity data for $[\text{CaCO}_3+\text{MgO}]$ and $[\text{CaO}+\text{MgO}]$ derived from a "dolomite" of unspecified analysis. The table below gives a comparison of Haul's porosity data at 800°C with "ideal" porosities calculated from molar volumes of the relevant chemical species. The calculation assumes that no shrinkage

occurs as CO_2 is expelled from dolomite and that all internal porosity is accessible. Practically no shrinkage should occur when a true dolomite is calcined at 800°C , and Haul's data suggest that at least some of the pores in the calcined materials may not be accessible.

"Ideal" Porosities of Some Solids Derived From Dolomite

	<u>"Ideal" Porosity</u>	<u>Haul's Value at 800°C</u>
[CaO+MgO]	36.2 $\text{cm}^3/\text{gm}-\text{"mole"}$	23.2 $\text{cm}^3/\text{gm}-\text{"mole"}$
[CaCO ₃ +MgO]	16.2	10.8
[CaS+MgO]	27.4	---

Basis of "ideal" porosities: $\text{CaCO}_3 \cdot \text{MgCO}_3 = 64.2 \text{ cm}^3/\text{gm}-\text{"mole"}$; no shrinkage as the various solids are produced; $\text{MgO} = 11.05 \text{ cm}^3/\text{gm}-\text{"mole"}$, $\text{CaO} = 16.9$, $\text{CaCO}_3 = 36.9$, $\text{CaS} = 25.8$.

Haul reported surface areas of [CaO+MgO] and [CaCO₃+MgO] at 800°C to be 56.2 and 6.7 m^2/gm respectively. He did not report surface areas for the latter solid at any other temperature. Surface areas of [CaO+MgO] were reported to decline over the temperature interval 800° to 1000°C , the area at 1000°C being about 5 m^2/gm . Borgwardt and Harvey (11) reported surface areas of about 4 m^2/gm for [CaO+MgO] prepared by fully calcining dolomite at 980°C for two hours.

The internal structure of calcined dolomite is not fully understood. Haul and Wilsdorf (12) showed with X-ray diffraction techniques that half-calcined dolomite prepared at moderate temperatures and CO_2 pressures contains unoriented magnesium oxide crystallites and calcite crystallites oriented in precisely the same way as in the original dolomite. They reported that the magnesite crystals are smaller than the calcite crystals at 700°C , the sizes being 150 Å and 400 Å respectively, but that near 900°C both types of crystals are about 400 Å.

Scanning electron microscope pictures of calcines show clearly the spongy, porous nature of the material. Recent studies indicate that fully calcined dolomite consists of a granular structure in which small, roughly spherical calcium oxide grains are distributed around larger grains of periclase (magnesium oxide). The calcium oxide grains occur in clusters which retain much of the granular character of the original stone, and many of which are partly fused to the underlying grains of periclase. The grains have diameters of approximately 0.1-0.5 micron, while the clusters are generally 1-15 microns (13,14). It is likely that half-calcined dolomite would have a similar structure.

4.03 Solid-Gas Reactions

The reaction of H_2S with half-calcined dolomite is an example of a non-catalytic solid-gas reaction. Both catalytic and non-catalytic reactions are generally complex because physical transport processes interact with the chemical reaction step. It often becomes a formidable task to distinguish between the effects of chemical and physical rate processes on the observed overall reaction rate.

There are several differences between our, non-catalytic, reaction system and the commonly encountered catalytic systems. In non-catalytic systems, the solid reacts with a gas; in catalyst systems, a gas reacts with itself or with another gas, and the solid only provides a surface on which reaction can occur. As a result, our solid steadily loses active surface as the reaction proceeds, whereas catalysts have a constant surface area. In both catalytic and many non-catalytic systems, the overwhelming majority of reaction surface lies within the pores of each particle of solid and, depending on the structure of the solid, pore size distributions of a wide variety can exist. However, in non-catalytic systems, because of the replacement of the solid reactant with a product of usually different structure, the internal pore structure of the solid does not remain

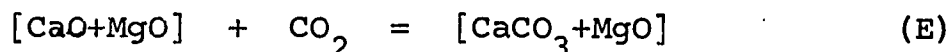
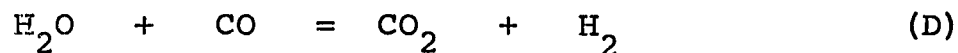
constant, but changes with time. For example, as the solid product forms, pores may be plugged, thereby sealing off reaction surface and stopping the reaction.

The conclusion to be drawn is that the overall rate of non-catalytic solid-gas reactions depends on physical as well as chemical rate processes and that some physical rate processes are intimately related to the solid microstructure encountered during the course of the reaction. If by judicious choice of experimental conditions some physical processes are eliminated or controlled, still others can remain to complicate the true chemical kinetics. This is what makes the study of such reactions difficult.

4.04 Use of Calcined Dolomite in Industrial Processes

The high internal porosity of $[\text{CaCO}_3 + \text{MgO}]$ and $[\text{CaS} + \text{MgO}]$ leads one to hope that the reactivity of half-calcined dolomite toward H_2S might be maintained in a process in which it is converted from CaCO_3 to CaS and back to CaCO_3 by means of reactions (B) and (C). Fortunately, there are further reasons for the hope that calcined dolomite might be suitable for use as an acceptor in a cyclic process to remove H_2S from a fuel gas.

During the 1920's, Gesellschaft für Kohlentechnik (now Bergbau-Forschung) developed a process to promote the shift reaction (15). The reactions involved were:



It was found that MgO in calcined dolomite was catalytic for reaction (D). The process was conducted in a fixed bed until reaction (E) caused the dolomite to be used up, whereupon breakthrough of CO occurred. The dolomite was then calcined at 950°C, and the bed was put back into production.

In a large pilot unit, after more than a score of calcinations at 950°C, each followed by a recarbonation at 500°C, both the catalytic activity of MgO and the activity of CaO toward CO₂ were essentially unimpaired.

More recently, in the Consolidation Coal Company (Consol) acceptor process (16), the exothermic absorption of CO₂ by fully calcined dolomite is used to drive the endothermic gasification of devolatized coal char with steam:



In addition, shift reaction (D) and desulfurization (A) occur. The process is carried out in a fluidized-bed reactor run at about 870°C (1600°F) and 20 atmospheres. Solids consisting

mostly of $[\text{CaCO}_3 + \text{MgO}]$ and $[\text{CaS} + \text{MgO}]$ are withdrawn for regeneration in a second fluidized bed. The regeneration bed operates at about 1060°C (1940°F).

At the high temperature of Consol's regeneration bed, the acceptor suffers drastic loss of capacity for absorbing CO_2 and presumably also suffers loss of reactivity. After 20 cycles between regeneration at 1060°C and recarbonation at 870°C , one of the better dolomites tested absorbed only 40% as much carbon dioxide as the stoichiometric amount corresponding to its CaO content. It is likely that its chemical reactivity, both toward CO_2 and H_2S , had also declined.

The greater loss of reactivity in Consol's work by comparison with the negligible loss experienced by Gesellschaft für Kohlentechnik is plausibly due to the higher temperature employed by Consol in regeneration, 1060°C versus 950°C . Nevertheless, Consol's work appears to establish that the reactivity of CaO in calcined dolomite is sufficient for commercial usefulness, in spite of the high temperature used for regeneration.

4.05 Review of Previous Related Work at The City College

A study of the reaction of hydrogen sulfide with fully calcined dolomite was undertaken at The City College by Melvyn Pell prior to the current study of the reaction of hydrogen sulfide with half-calcined dolomite. Pell obtained differential kinetic data for reaction (A) between 475° and 900°C at H_2S partial pressures between 0.003 and 0.2 atmospheres. Data were obtained gravimetrically for both spherical and powder samples of stone (1).

For an 8 mm. diameter sphere of fully calcined dolomite reacted with a gas containing 5% H_2S at 950°C , the rate of reaction was governed by the diffusion of gaseous species through an "ash" layer of product occupying the outer region of a particle of the solid. Sphere data at temperatures of 750°C and below disclosed that the reaction generally occurred homogeneously throughout the solid and that the rate was proportional to the quantity of unreacted CaO remaining in the sample. Although a gradient in concentration of CaS was observed near the surface of a 6 mm. sphere reacted partially at 625°C , Pell concluded that a negligible gradient in CaS concentration would be expected in a particle of powder size.

All of Pell's powder runs were made with samples taken from a single supply of powdered Greenfield dolomite, -80+325 mesh. Results at temperatures above 700°C followed a simple model in which the rate is first order in H_2S and proportional to the quantity of CaO remaining in the sample. For this model, plots of $\log (1-x)$ versus time, where x is the fractional conversion of CaO to CaS would be linear, with the slopes of these plots proportional to H_2S concentration. Figure 1 shows a typical $\log (1-x)$ plot for data consistent with this model.

At 550°C, however, Pell found that plots of $\log (1-x)$ versus time are not linear. Many runs exhibited a high initial reaction rate, falling away to much slower rates at high conversions of CaO to CaS. The tendency for the reaction to flag at high conversions is more pronounced at higher concentrations of H_2S . Figure 2 illustrates these facts, giving $\log (1-x)$ plots for runs at 550°C with 0.3% and 20% H_2S .

Pell found further that the rate is not first order with respect to H_2S at low temperatures. Figure 3 is a plot of Pell's "final" rates, estimated for each run from the "linear" portion of the $\log (1-x)$ plot, like the range indicated for each run in Figure 2 by a straight line.

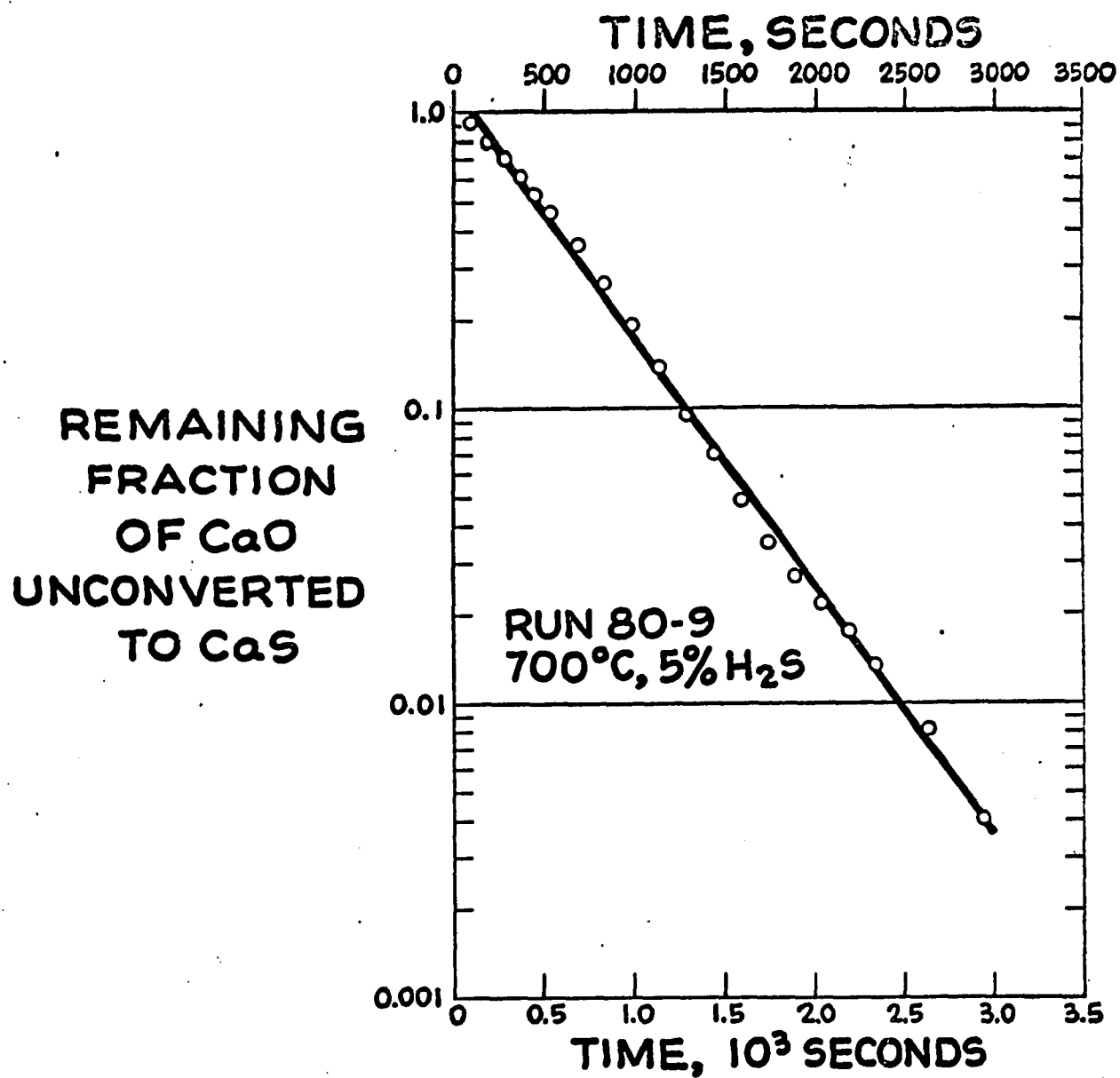


Figure 1. Log(1-x) plot for run made by Pell on fully calcined Greenfield powder at 700°C and 5% H₂S.

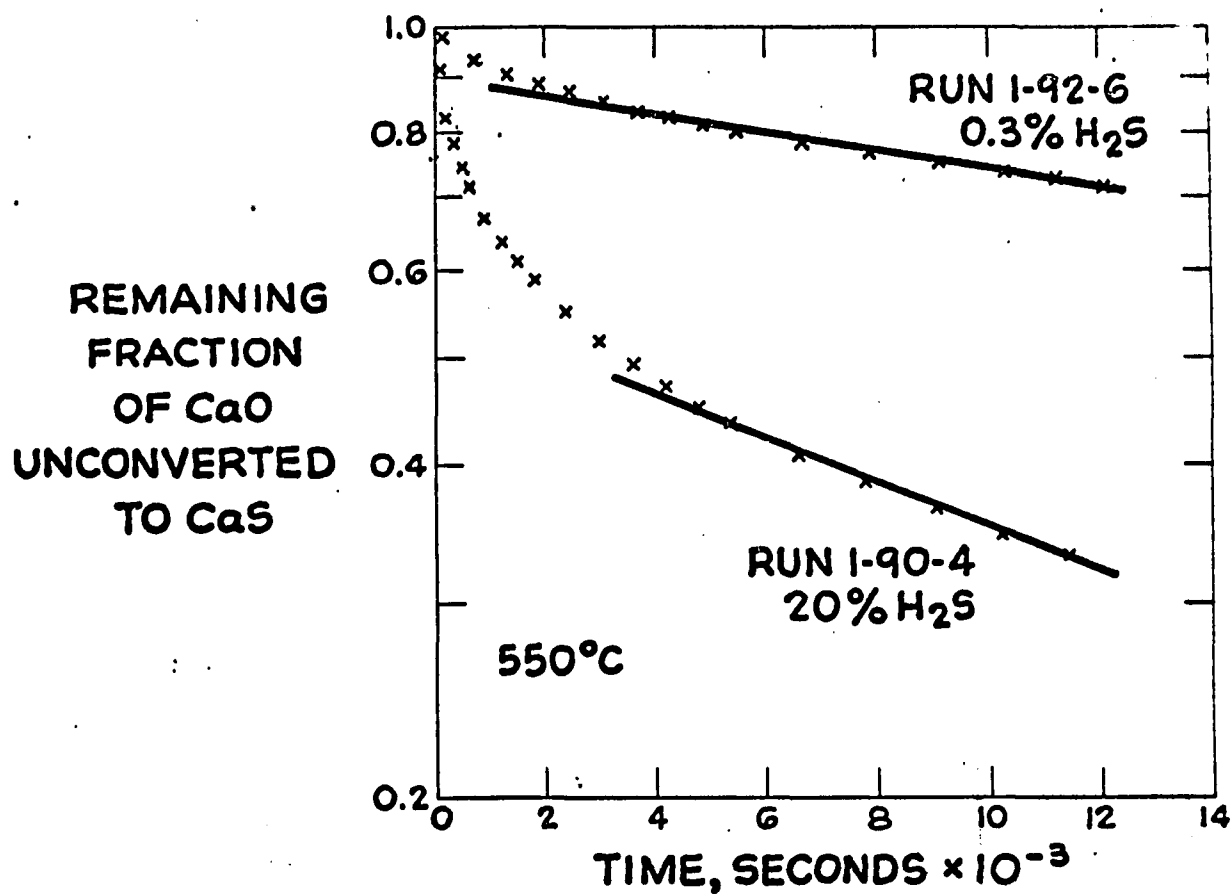


Figure 2. Log(1-x) plots for runs made by Pell on fully calcined Greenfield powder at 550°C with 0.3% H₂S and 20% H₂S.

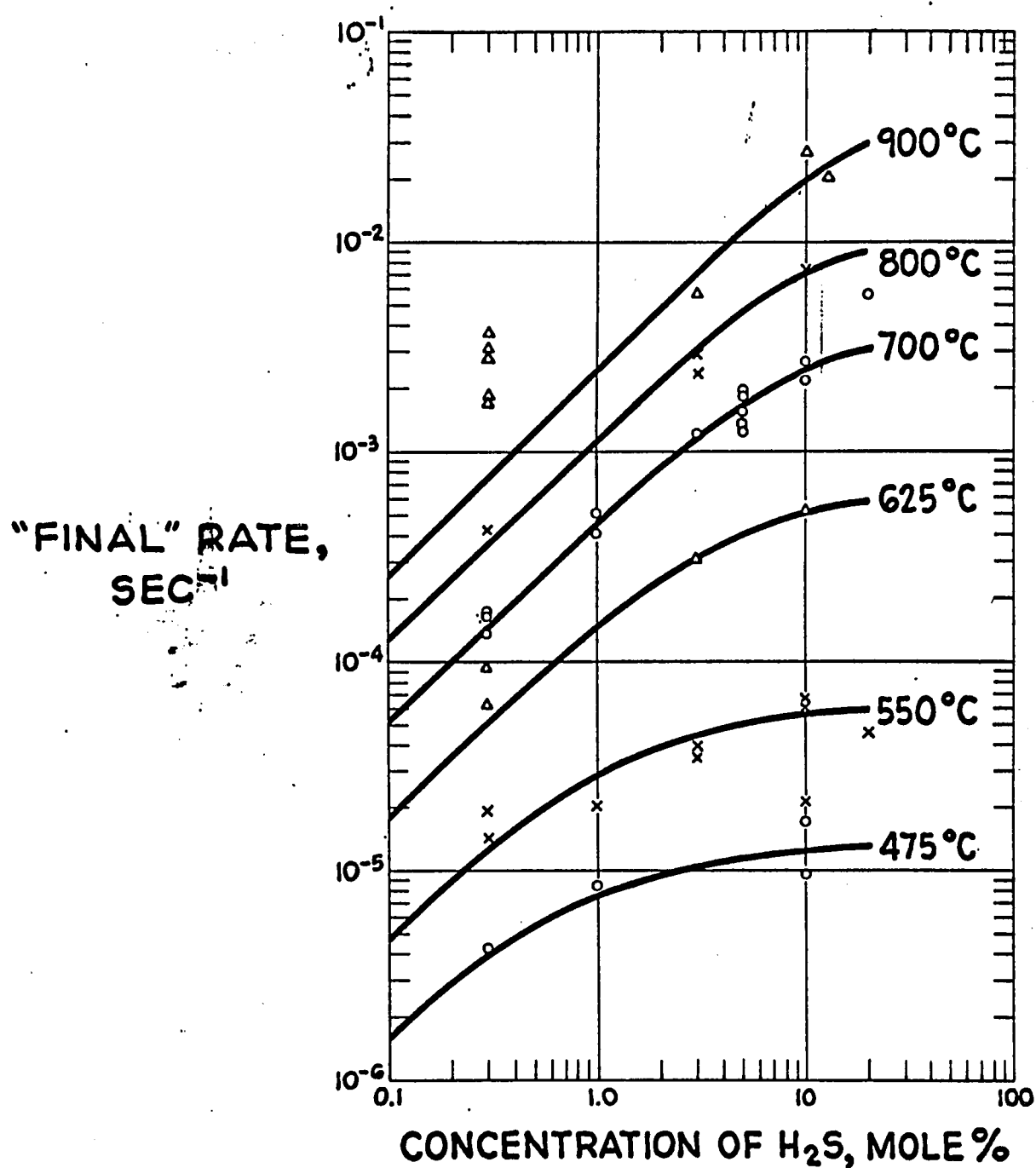


Figure 3. "Final" rates versus concentration of H₂S for runs made by Pell with fully calcined dolomite (curves were generated from Pell's adsorption model).

Clearly, a more complex concentration dependence is involved.

Pell explained his data by hypothesizing that activated adsorption of H_2S by unreacted CaO hinders the reaction rate, the adsorption being in general not at equilibrium. He correlated his data with an expression involving three constants.

Pell also explored the effect of hydrogen concentration and steam on the reaction rate. He reported that large increases in H_2 concentration in the reaction gas mixture caused moderate reduction in the rates of runs made with Greenfield powder at 700°C and Pfizer spheres at 625°C .

The steam effect was more pronounced. Runs were made with Greenfield powder at 550° and 700°C with an addition of 25% H_2O to the reaction gas mixture. Runs at 700°C were indistinguishable from runs made without water; however, at 550°C , water considerably increased the reaction rate for runs at 0.3% and 10% H_2S . Figures 4 and 5 give $\log (1-x)$ plots showing the effect of steam on rate.

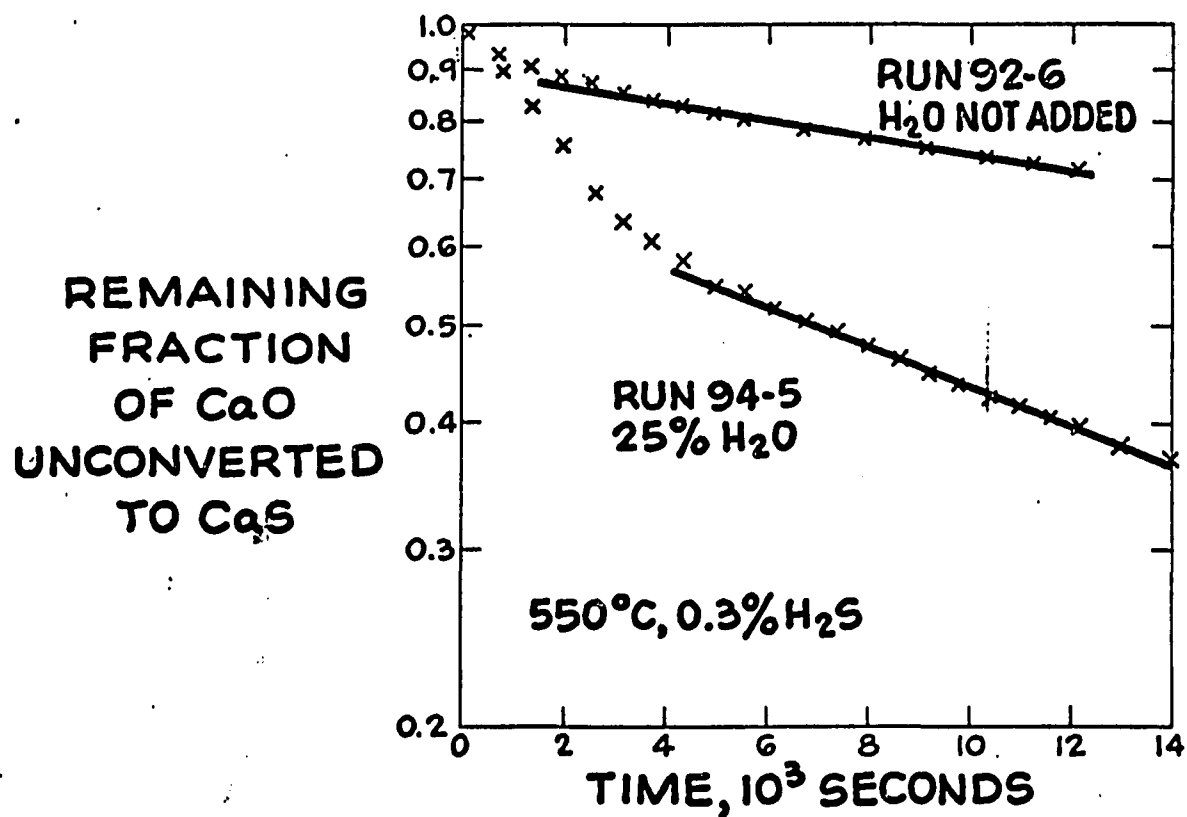


Figure 4. Run made by Pell on fully calcined Greenfield powder, at 550°C, 0.3% H_2S , with and without water added.

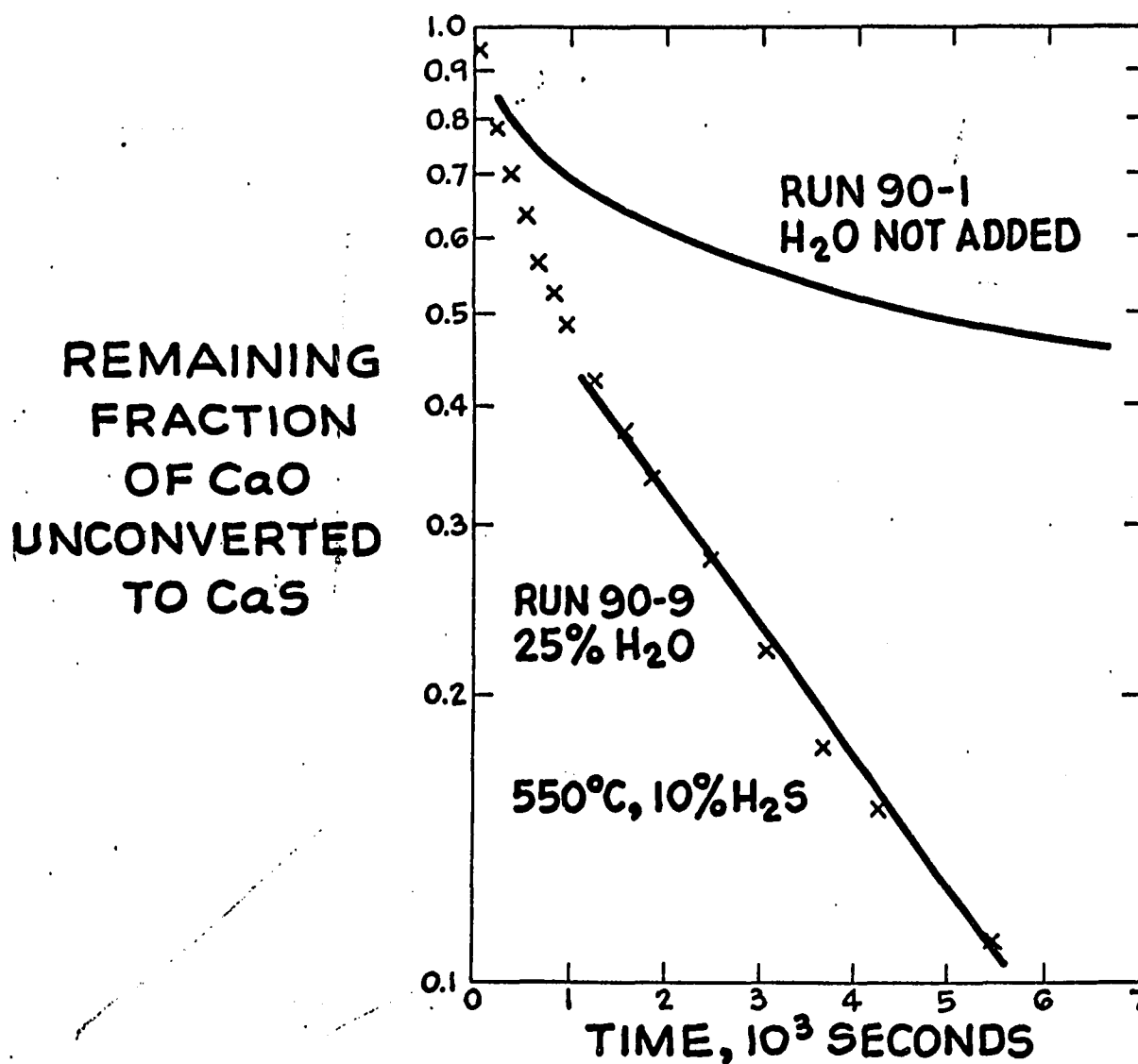


Figure 5. Runs made by Pell on fully calcined Greenfield powder at 550°C, 10% H_2S , with and without water added.

4.06 Cyclic Use of Half-Calcined Dolomite to Desulfurize Fossil Fuels. A Process Example.

We at The City College have been rethinking conventional power generating techniques in the hope that processes can be developed to provide clean power from fossil fuels at attractive costs. Figure 6 presents one such process. It shows a simplified flowsheet for power generation by a combined-cycle system incorporating a fluidized-bed gasifier for coal and gas cleaning at high temperature by means of a panel-bed filter containing half-calcined dolomite.

Coal would be gasified with air, supplied from the compressor of a gas turbine, and steam in a fluidized bed operated at about 1100°C and 21 atm. (A booster compressor, not shown in Figure 6, would raise the pressure of that portion of air which passes to the gasifier.) Fuel gas, after cooling, would be contacted with a bed of granular half-calcined dolomite disposed in a tall narrow "panel," the solid being held in place by louvers resembling venetian blinds. The filter would operate at a temperature just below the equilibrium decomposition temperature of CaCO_3 at the partial pressure of CO_2 prevailing in the fuel gas. Hydrogen sulfide is removed from the raw fuel gas according to reaction (B). When dolomite at the gas entry surfaces of the bed has absorbed sulfur to the limit

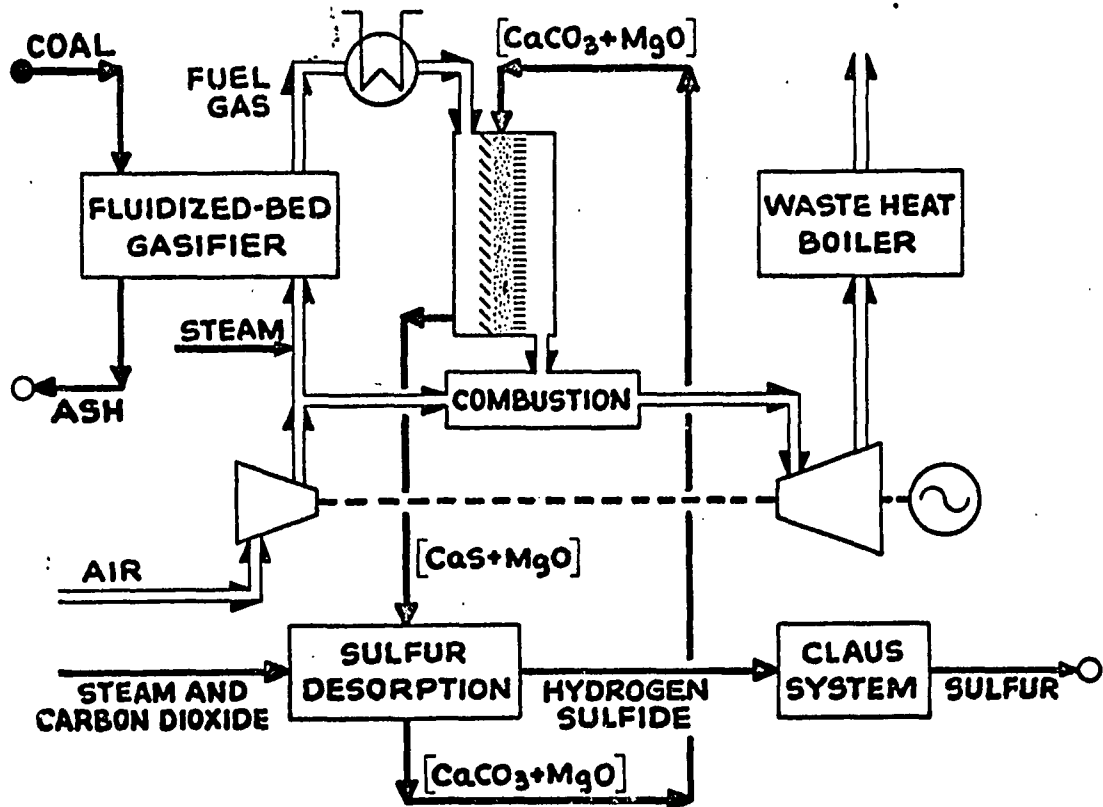


Figure 6. Concept for power generation by combined-cycle system incorporating a fluidized-bed gasifier for coal and a panel-bed filter for simultaneous removal of dust and sulfur.

of its capability, it will be dislodged along with a cake of dust which will have formed at these surfaces. This is done by a "puffback" technique (17) in which a controlled amount of filter solid is removed from each gas-entry surface by applying a surge backflow of gas from the clean side of the panel.

The cleaned fuel gas would be burned with air ahead of a gas turbine, and a waste heat boiler would recover heat from the exhaust of the turbine. Reaction (C) would regenerate $[\text{CaCO}_3 + \text{MgO}]$ for reuse and liberate H_2S for conversion to elemental sulfur in a Claus system.

Table 1 gives illustrative energy balances (18) for conventional steam power equipment and for the City College concept outlined above. The increase in efficiency from 39.5 to 51.2% shows the incentive to provide better power generating machinery and better coal conversion procedures. Because of the smaller size of pressurized equipment and because gas turbines cost less than steam turbines, there is a good possibility that, along with an increase in efficiency, will come a reduction in capital cost.

The energy balance for The City College concept supposes that the fluidized-bed gasifier can provide a

fuel gas at substantially the steam-carbon equilibrium if the gasifier operates at 1050°C or above, and that the power generating system uses a gas turbine with an inlet temperature of 1538°C followed by a steam boiler and conventional steam power equipment. As for the former supposition, data of Dent (19) and a discovery of Godel (20) leads one to hope that the fluid-bed gasification of coal at 1100°C can be successful. As for the latter, United Aircraft has projected turbine inlet temperatures of 1300°C within ten years and temperatures as high as 1700°C by about 1990 (21).

Table 1. Illustrative Energy Balances

Basis:

Coal Input = 100

Conventional Steam Power
Equipment, Without Recovery
of Sulfur

Ash-Agglomerating Fluidized-Bed
Gasifier and Gas Cleaning at
High Temperature, With Recovery
of Sulfur. (A Gas Turbine at 1538° C
is followed by a Steam Boiler and
Conventional Steam Power Equipment)

Net Shaft Work	39.5	50.5
Heating Value of Sulfur	---	1.3
Loss of sensible heat to the atmosphere in stack gases	5.0	4.7
Loss of latent heat to the atmosphere (water vapor in stack gases)	3.8	4.5
Rejection of heat to environment at steam condenser and other heat exchangers	47.7	35.0
Estimate of loss of unburned fuel and leakage of heat from equipment	2.0	2.0
Estimate of mechanical losses and power taken by auxiliary equipment	<u>2.0</u> 100.0	<u>2.0</u> 100.0
Efficiency of conversion of fuel energy to electricity allowing credit for heating value of sulfur	39.5	51.2

5.0 Thermodynamics and Reaction Conditions

5.01 Thermodynamic Equilibria

The equilibrium constant for reaction (B) is given by:

$$\log_{10}[\text{H}_2\text{O}][\text{CO}_2]P/[\text{H}_2\text{S}] = 7.253 - 5280.5/T \quad (1)$$

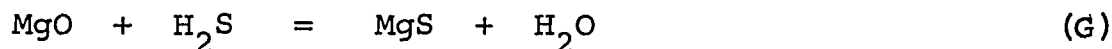
where [...] signifies mole fraction, P is the pressure in atm., and T is the temperature in °K. This expression is based on a least squares fit of data for reaction (A) from Uno (22), Rosenqvist (23), and Curran, Fink and Gorin (16), and data on the decomposition pressure of CaCO_3 given by Hill and Winter (24).

For the decomposition pressure of CaCO_3 , Hill and Winter gave the expression:

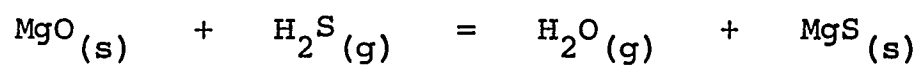
$$\log_{10} P_{\text{CO}_2} = -8799.7/T + 7.521 \quad (2)$$

where P is the pressure in atm., and T is the temperature in °K.

The equilibrium constant for the reaction



as calculated from data taken from the JANAF Tables (25), is given for several temperatures in Table 2. Conversion of MgO to MgS is thermodynamically possible in the absence of H_2O ; however, in our "clean power" process this reaction will not occur because sufficient H_2O is present. In our research, this reaction was suppressed at lower temperatures

Table 2. Equilibrium Constant for the Reaction

$T^{\circ}\text{K}$	K_p
700	.0047
800	.0092
900	.0154
1000	.0230
1100	.0317
1200	.0412
1300	.0511

by very small concentrations of H_2O that are present in the reaction mixture, which arise from the H_2O used in the manometers of the capillary flowmeters. At the highest temperatures and H_2S concentrations, 800°C and 10% for example, some MgS did form but its rate of formation was much slower than the rate of formation of CaS from CaCO_3 .

Hydrogen sulfide can dissociate to a significant extent at our reaction temperatures. The JANAF Tables list values for K_p of formation of H_2S from H_2 and S_2 gas. These may be used to calculate the concentration of H_2 needed to keep H_2S dissociation at a reasonable level.

5.02 Reaction Conditions

The equilibrium ratio for reaction (B), $[\text{H}_2\text{O}][\text{CO}_2]P/[\text{H}_2\text{S}]$, is 16 at 600°C and increases with temperature. Since only traces of water were present in our gas mixture, this reaction can be considered to be irreversible.

Our reaction gas contained H_2S , CO_2 , H_2 , and usually N_2 . In order to preserve CaCO_3 , we had to maintain CO_2 in the reaction gas above the equilibrium decomposition pressure of CaCO_3 at the run temperature. This pressure is less than 0.01 atm. at 600°C , but rises to one atmosphere at about 896°C .

We did not work under conditions conducive to the recarbonation of MgO , a slow reaction in any event. The reaction gas must contain H_2 to prevent dissociation of H_2S , the amount required increasing with temperature. Generally, sufficient H_2 was added to keep the equilibrium concentration of S_2 from H_2S dissociation below 0.05%. Nitrogen was inert and acted as a diluent.

All work was done at one atmosphere total pressure. Reaction (B) was studied over H_2S concentrations of 0.5-20.0%, i.e. 0.005-0.20 atm. H_2S , and temperatures of 450-850°C. An H_2S concentration of 0.5% represents the minimum that our equipment could accurately provide. The H_2S concentration was limited to 20% by the reaction's great speed.

Our maximum reaction temperature was set by the equilibrium decomposition temperature of CaCO_3 at about 0.8 atm. CO_2 , approximately 880°C. Our apparatus did not yield reproducible kinetic data at 850°C, again because of the reaction's great speed; consequently, 800°C is the highest temperature for which kinetic data are reported.

In a clean power process in which reaction (B) is used to remove H_2S from a fuel gas at high pressure, the equilibrium is generally favorable for absorption of sulfur only at high temperatures, above about 750°C. Hence, data

between 700 and 800°C would be of interest to the designer of a fuel desulfurization process utilizing reaction (B). Kinetic data for reaction (B) at lower temperatures should provide information useful for the later study of reaction (C), to which reaction (B) is the back reaction.

The range of H_2S partial pressures studied corresponds well with those occurring in a commercial desulfurization process. A fuel gas produced by the gasification at 20 atm. of a coal containing 3.8 weight percent sulfur would contain about 0.7 mole percent H_2S . This corresponds to the same partial pressure of H_2S as a concentration of 14% at one atmosphere. Our lowest concentration of H_2S studied, 0.5%, would correspond to 0.025% at 20 atm., or 96% sulfur removal from this fuel gas.

6.0 Experimental Techniques

Since the reaction under study produces a weight change, the thermogravimetric method can provide differential kinetics for the reaction of a sample of solid spread as a fine powder in a thin layer on a balance pan, the gaseous reactants flowing past the solid at a rate sufficient to preclude any substantial change in known gas composition. There are numerous instruments by various manufacturers on the market capable of measuring the weight of a solid sample at either constant or programmed temperature; we chose to use the duPont 950 Thermogravimetric Analyzer (TGA) because its compact size made it most suitable for eventual placement in a pressure vessel where the regeneration reaction, reaction (C), could be studied at elevated pressure.

6.01 Equipment

The duPont TGA consists of an electronic balance and a furnace capable of operation at temperatures over 1000°C. The TGA is used with the duPont 900 Thermal Analyzer, which contains a temperature programmer-controller and an X-Y recorder. The balance has a maximum sensitivity of 0.2 mg/inch and a maximum sample size of 200 mg. Thus, for

a typical sample size of 20 mg, weight changes corresponding to as little as 0.5% conversion of $[\text{CaCO}_3 + \text{MgO}]$ to $[\text{CaS} + \text{MgO}]$ can be recorded. The instrument can be used in the isothermal mode, in which case the recorder produces a graph of sample weight versus time, or the temperature can be increased at rates of up to $30^\circ\text{C}/\text{min}$. In this latter mode of operation, a graph of sample weight versus sample temperature is produced.

Figure 7 is a diagram of the TGA, essentially as supplied by duPont. Gases flow through the balance and past the platinum sample pan, which is suspended by a horizontal quartz beam at the center of the furnace. The sample temperature is determined by a chromel-alumel thermocouple located about one millimeter above the center of the sample pan. In the form seen in Figure 7, the duPont TGA cannot handle corrosive H_2S , which would ruin the balance.

Figure 8 depicts the modification of the unit developed for this research. A nitrogen purge flows through the balance housing, and a new quartz furnace tube and baffle provide a separation between balance and reaction zone. The modification has two purposes: to keep corrosive H_2S from the balance, and to keep purge nitrogen away from the solid sample, so that the composition of gas in the reaction zone is not affected.

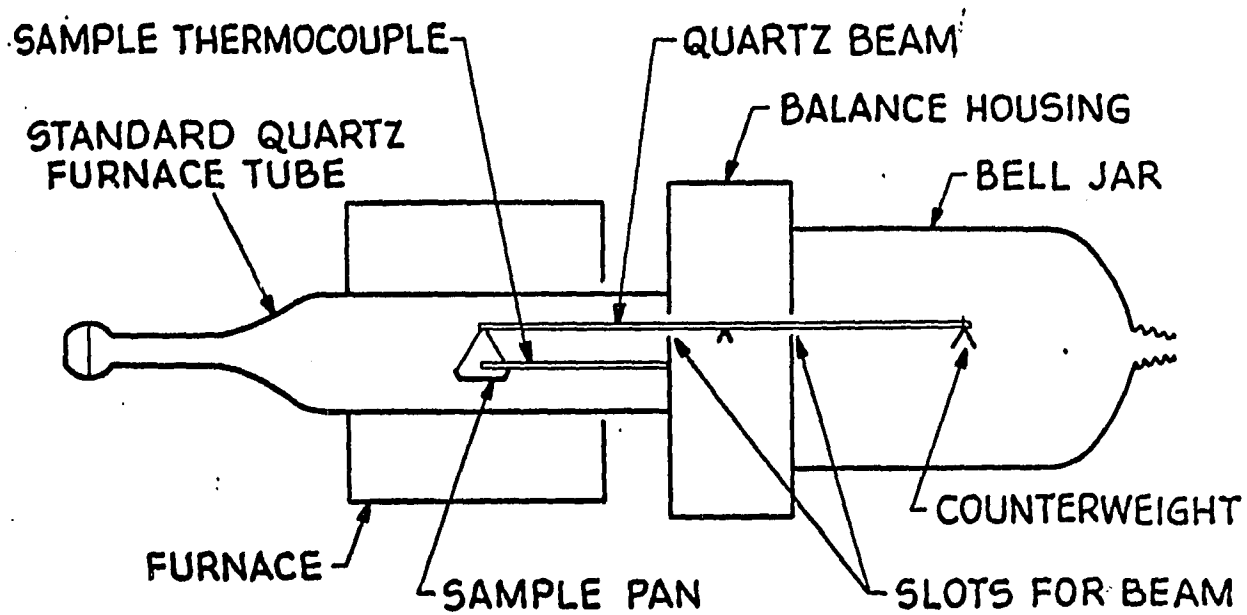


Figure 7. The duPont 950 Thermogravimetric Analyzer.

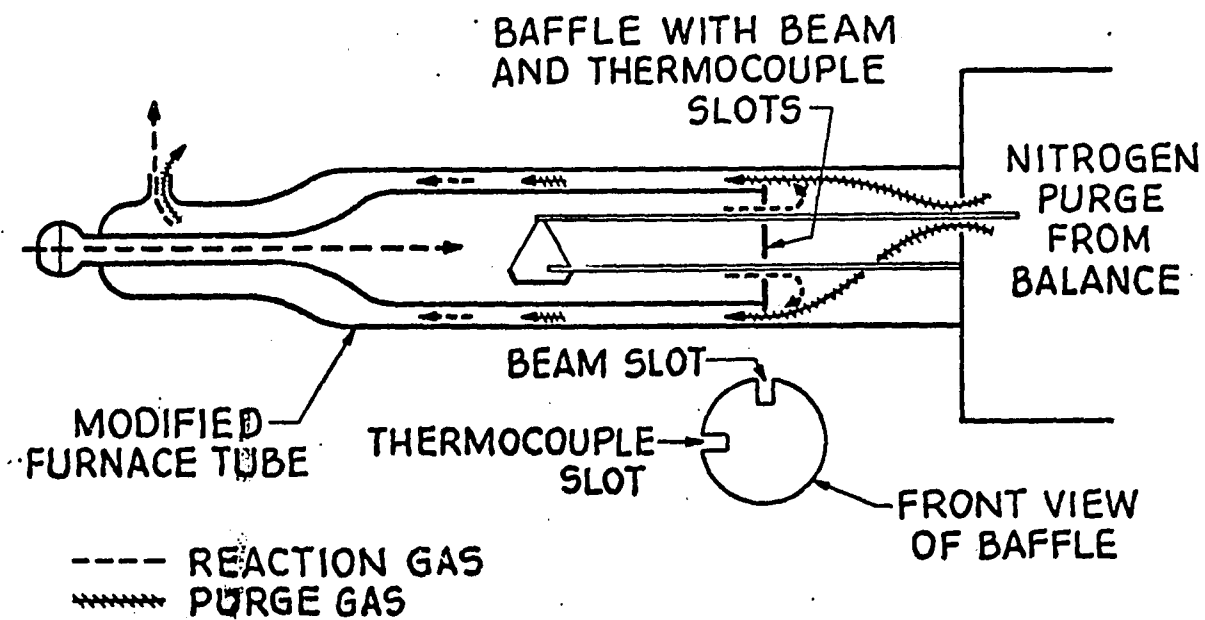


Figure 8. Our modification of duPont TGA, developed for this research.

In the modification, purge gas enters the end of the balance bell jar and flows through a slot in the balance housing for the beam. Reaction gas enters the inner tube of the concentric furnace tube as seen in Figure 8, and passes over the solid sample. The reaction gas leaves the inner tube through slots in the circular platinum baffle held in place at the end of the inner tube by means of a sidearm (not shown in Figure 8) attached to the balance housing. The slots in the baffle provide for passage of balance beam and thermocouple. Reaction gas and nitrogen purge pass together through the annular space between inner and outer tubes and are discharged together through an opening near the end of the outer tube.

Consideration of flow and diffusion in the vicinity of the slot in the balance housing for the beam showed that a purge nitrogen flow of 750 to 800 ml (0°C and 1 atm) /min. would be adequate. After many experiments using flows in this range, there is no change in the appearance of shiny copper wire placed inside the balance housing to detect H_2S .

Greater concern was felt as to the possibility that purge gas might penetrate to the vicinity of the sample. Data were obtained on the weight gain versus time for finely powdered copper exposed at 600°C to mixtures of

oxygen and nitrogen of known composition. These data permitted determination of the penetration in runs in which oxygen was used as the "purge gas," nitrogen as the "reaction gas," and copper powder as the sample.

The penetration was found to depend upon both rate of flow of reaction gas and the ratio of purge gas to reaction gas. For example, at a reaction gas flow of 42.5 ml/min and a purge-to-reaction-gas ratio of 4:1, there resulted a penetration of purge gas amounting to one percent of the reaction gas flow. At a reaction gas flow of 100 ml/min, however, there was negligible penetration at purge gas flows as high as 1000 ml/min. With the baffle provided, the flow of reaction gas needed to be at least 75 ml/min to prevent purge gas penetration at the purge flow rates believed to be necessary. In kinetic work, flows of reaction gas and purge gas have been 100 to 300 ml/min and 750 to 800 ml/min respectively.

The chromel-alumel sample thermocouple supplied with the duPont TGA would be quickly destroyed by exposure to H_2S , so that it was necessary to replace the bare thermocouple with a chromel-alumel thermocouple in a 1/25 inch diameter sheath fabricated of 304 stainless

steel.

The sheath was gradually attacked by H_2S and it was necessary to periodically replace the old sheathed thermocouple with a new one.

Figure 9 shows the system for preparing the gas mixture to be reacted. Mixtures of gaseous reactants were made up to known composition by metering individual components through capillary flowmeters having 600 mm scales. Low-pressure "pancake" regulators maintained constant pressure to the flowmeters. Polyethylene tubing of 1/4" O.D. and polypropylene tube fittings were used throughout the gas flow system. Most of the valves were of stainless steel. During the early part of our experimental work we relied on the mixing that occurred at tees, where streams of two gases come together in the flow system, to be sufficient to produce a homogeneous gas mixture. We later added gas-mixing tubes, shown in Figure 9, to the flow system to ensure thorough mixing of all components in the reaction gas. Comparison of data from runs made before and after the addition of the mixing tube showed that the mixing tube produced no discernable effect.

Reaction steam was provided by burning hydrogen with

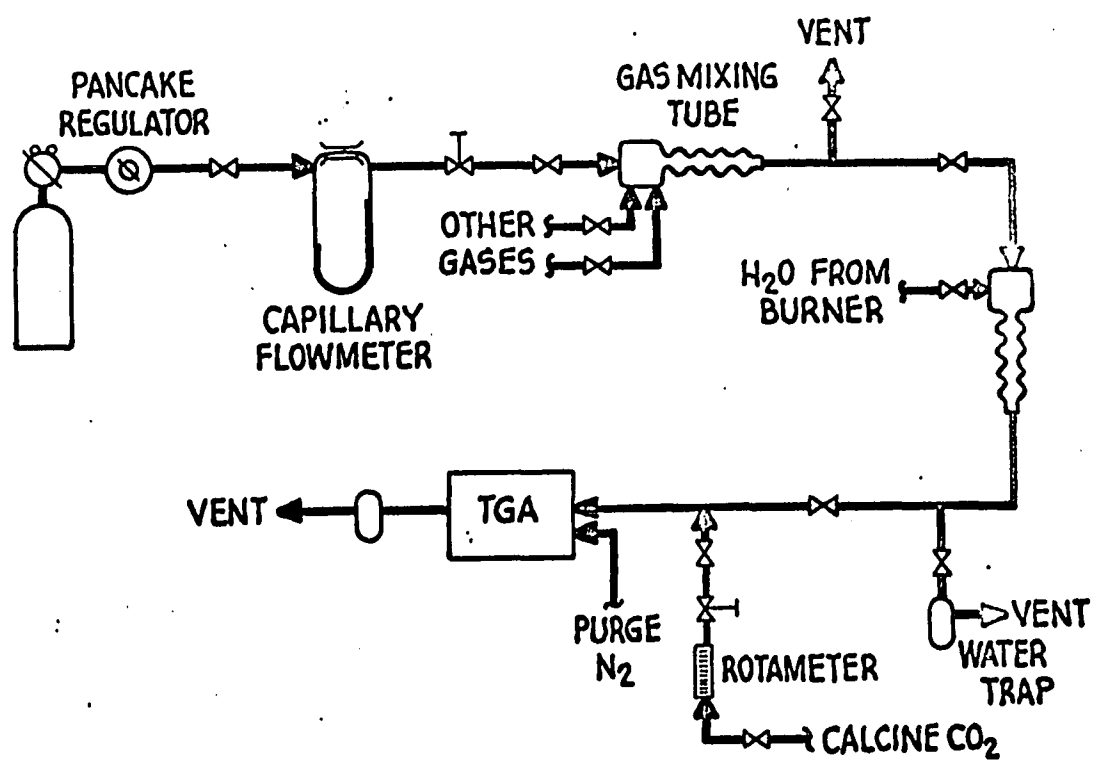


Figure 9. System to supply reaction gas mixture.

oxygen in an apparatus shown in Figure 10, resembling that used by Pell (1), and McKewan (26). This technique made it possible to supply steam, in amounts as small as 60 ml (0°C and 1 atm)/min, at steady and accurate rates. The steam was mixed with other reaction gases in a second, heated, mixing tube.

An Aminco Sor-Bet (Cat. No. 5-7300) was used to measure the surface areas of several samples of dolomite. Porosity and pore size distributions were made with an Aminco Motor-Driven 15,000 psi Digital Readout Porosimeter (Cat. No. 5-7121B). A Phillips EM 300 electron microscope and a Norelco X-ray diffraction unit were available to study solid reaction products.

6.02 Procedures

From 3 to 25 mg of powdered dolomite, -250+270 mesh in size, was spread flat in a platinum sample pan about one centimeter in diameter; smaller samples were used at higher temperatures to avoid diffusional resistance across the samples (see Section 8.01). The mass of the pan is about six times that of the sample; this helped minimize temperature gradients in the sample during calcination and subsequent reaction with H_2S . The dolomite was calcined to yield $[\text{CaCO}_3 + \text{MgO}]$ by heating under CO_2 at $20^{\circ}\text{C}/\text{min}$ until 825°C was reached; the sample was held at 825°C for five minutes

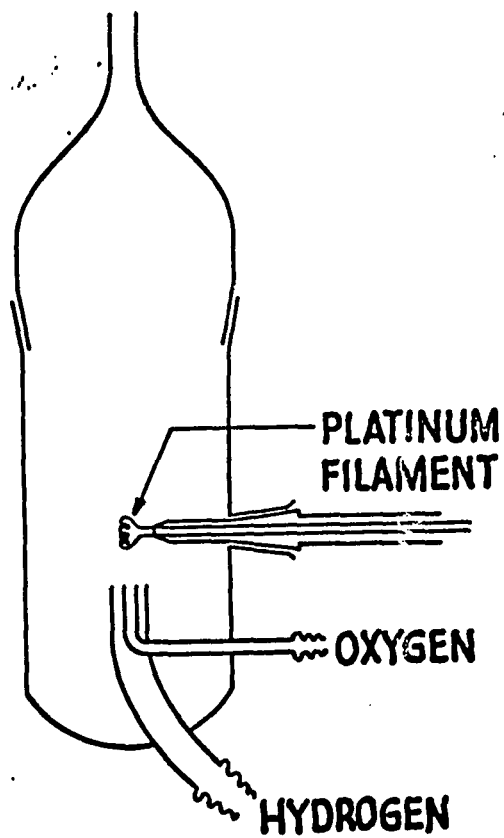


Figure 10. Hydrogen burner for production of water.

to be sure calcination was complete, and then was cooled under CO_2 to the desired reaction temperature. Weight loss was first detected during heating of the dolomite at about 475°C ; however, 80% of the total weight loss observed during the half-calcination occurred at temperatures of from 700° to just below 825°C .

Reaction gas was turned on and vented, rather than being allowed to pass to the sample, at about the time the calcination was begun. This allowed more than sufficient time for the reaction gas to purge the flow system of any gas that had remained from the previous run. When the sample temperature reached the desired reaction temperature, the CO_2 was turned off, the reaction gas mixture was made to flow past the sample, and reaction (B) proceeded isothermally with conversion of $[\text{CaCO}_3 + \text{MgO}]$ to $[\text{CaS} + \text{MgO}]$ while the TGA produced a record of the sample weight versus time.

6.03 Dolomite Supply

All runs were made with dolomite from the Greenfield formation in Ohio supplied by Davon Incorporated from their Plum Run quarry. Pell used the same stone for all of his work with powders. X-ray diffraction study confirmed the

presence of pure dolomite rather than a possible mixture of CaCO_3 and MgCO_3 .

The sample powder was prepared by grinding small chunks of rock with a mortar and pestle and sieving to prepare a -250+270 cut. The small chunks were taken from many rocks, rather than just a few, in order to get a sample more representative of Greenfield stone. Chemical analysis of a sample of our powder showed that the calcium to magnesium ratio was 1.01, and that the major impurities were silicon, aluminum, and iron. A complete analysis is given in Appendix 10.04.

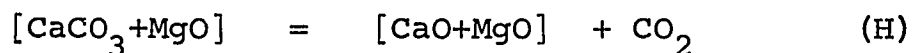
In order to study diffusion effects, several runs were made with Pell's equipment (1) using spheres of dolomite, about 0.7 cm in diameter, rather than powder. Each sphere was suspended from an automatic recording balance into a Vycor reaction tube positioned in a furnace. For making spheres, the stone was first cut roughly into the form of a cube, and was then shaped into a sphere using a lapidary bead mill.

6.04 Capacity of Samples

In order to determine the fractional conversion of $[\text{CaCO}_3 + \text{MgO}]$ to $[\text{CaS} + \text{MgO}]$ from the change in weight, it is necessary to know the capacity of the sample of half-calcined

dolomite to absorb H_2S , i.e., the maximum weight change corresponding to complete conversion. Since complete conversion was not obtained at the temperature and gas concentrations used for many runs, a means was needed for determining the capacity of the samples. Raising the temperature at the end of the run in order to achieve complete conversion was inconvenient because the CO_2 concentration in the reaction gas would have to be increased in order to keep the CO_2 partial pressure above the equilibrium decomposition pressure of CaCO_3 , which increases with temperature. Also, higher temperatures would greatly shorten the life of the sample thermocouple, which was time-consuming to replace.

We determined the capacities from the results of experiments in which we decomposed samples of half-calcined dolomite, according to the calcination reaction,



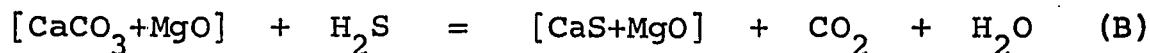
In these experiments we measured total weight loss, which is indicative of the amount of CaCO_3 in each sample, and found that the weight loss per unit initial weight of sample was nearly constant throughout. From this information we calculated the weight loss corresponding to complete conversion of CaCO_3 to CaS . This latter figure is 0.187 mg wt loss/mg half-calcined dolomite, and was used to

calculate capacities for all runs. Details of this calculation are given in Appendix 10.01.

Assuming equimolar amounts of calcium and magnesium in dolomite, purely stoichiometric considerations lead to a value of 0.199 mg wt loss/mg half-calcined dolomite. Comparison of the capacity derived from data on decomposition of half-calcined dolomite to fully calcined dolomite with the capacity derived from stoichiometry alone, raises the possibility that our sample may have contained impurities, such as silica.

7.0 Experimental Results

This section presents kinetic results for reaction (B):



These results are of two-fold interest. Data above about 700°C will be of interest to the designer of a clean-power process in which reaction (B) is used to remove sulfur from a fuel gas at high pressure. It is primarily the high temperature data for reaction (B) which is of practical importance because equilibrium for this reaction is generally favorable for absorption of sulfur only at high temperature. (This is not the case for our measurements of reaction rates because there is far less H₂O present in our reaction gas than in a raw fuel gas.) Data below 700°C are of strong academic interest because reaction (B) displays complex and unusual kinetic behavior at lower temperatures. Fortunately for the designer, most of these kinetic complexities disappear at high temperatures. Data taken below 700°C will be of practical use also in the sense that it may provide information useful for the later study of reaction (C), to which reaction (B) is the back reaction. It will be remembered that reaction (C) would be used in a practical process to regenerate half-calcined dolomite and to provide H₂S at a concentration sufficient

for conversion to elemental sulfur.

All work has been done at one atmosphere total pressure. The ranges of temperature and H_2S partial pressure that have been explored are $450\text{--}850^\circ\text{C}$ and $0.005\text{--}0.20$ atm, respectively. Unless otherwise noted, all runs were made with a single supply of powdered Greenfield dolomite, $-250\text{+}270$ mesh. The powder was spread in a thin layer on the balance pan of the TGA. The use of a fine powder spread in a thin layer helped to minimize diffusion effects, both within each particle and within the bed of powder.

7.01 Effect of Temperature and H_2S Concentration on Runs

Made at Low CO_2 Concentrations

To determine the effect of temperature and H_2S concentration, runs were made at 50°C increments over the temperature range $450\text{--}800^\circ\text{C}$ and at three levels of H_2S concentration, 1, 5, and 20%, at most temperatures. For these runs, the reaction gas contained CO_2 in a concentration corresponding to the equilibrium decomposition pressure of CaCO_3 , plus a little extra for safety. We call this a "low" CO_2 concentration, as distinguished from runs in which the CO_2 concentration

was far in excess of the pressure needed to prevent CaCO_3 decomposition. The reaction gas contained also H_2 and N_2 .

Data are presented on plots of $\log (1-x)$ vs. time, where x is the fractional conversion of CaCO_3 to CaS . A straight line on this type of plot indicates that the reaction rate is proportional to the amount of unreacted CaCO_3 remaining in the sample. That is:

$$dx/dt = k (1-x) \quad (3)$$

where k is a constant which depends on temperature and gas composition.

Data were plotted according to equation (3) because of its simplicity. Even though little data fit this model exactly, the deviation of the data from a straight line on a $\log (1-x)$ vs. t plot indicates the extent to which the reaction rate is not proportional to unreacted CaCO_3 . More complicated models were tried, but none fit the majority of the data any better than did equation (3).

Figures 11, 12, 13 and 14 present data at 800°C , 750°C , 700°C , and 650°C , respectively, for H_2S concentrations of 1, 5, and 20%. It is clearly evident that these data do not fall on a straight line and, in nearly every case, the rate drops off faster than it should if it were proportional to unreacted CaCO_3 . The data taken at 650°C are especially interesting because

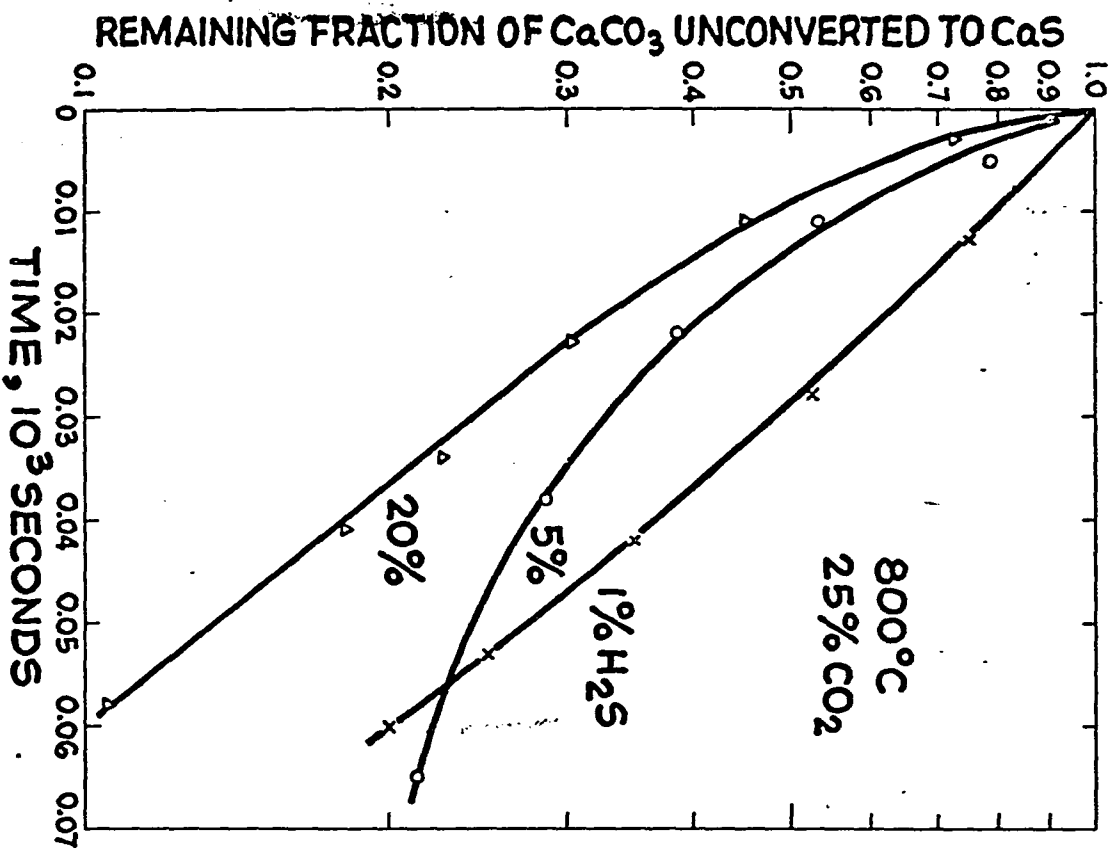


Figure 11. $\log(1-x)$ plots at 800°C , 25% CO_2 and three H_2S levels.

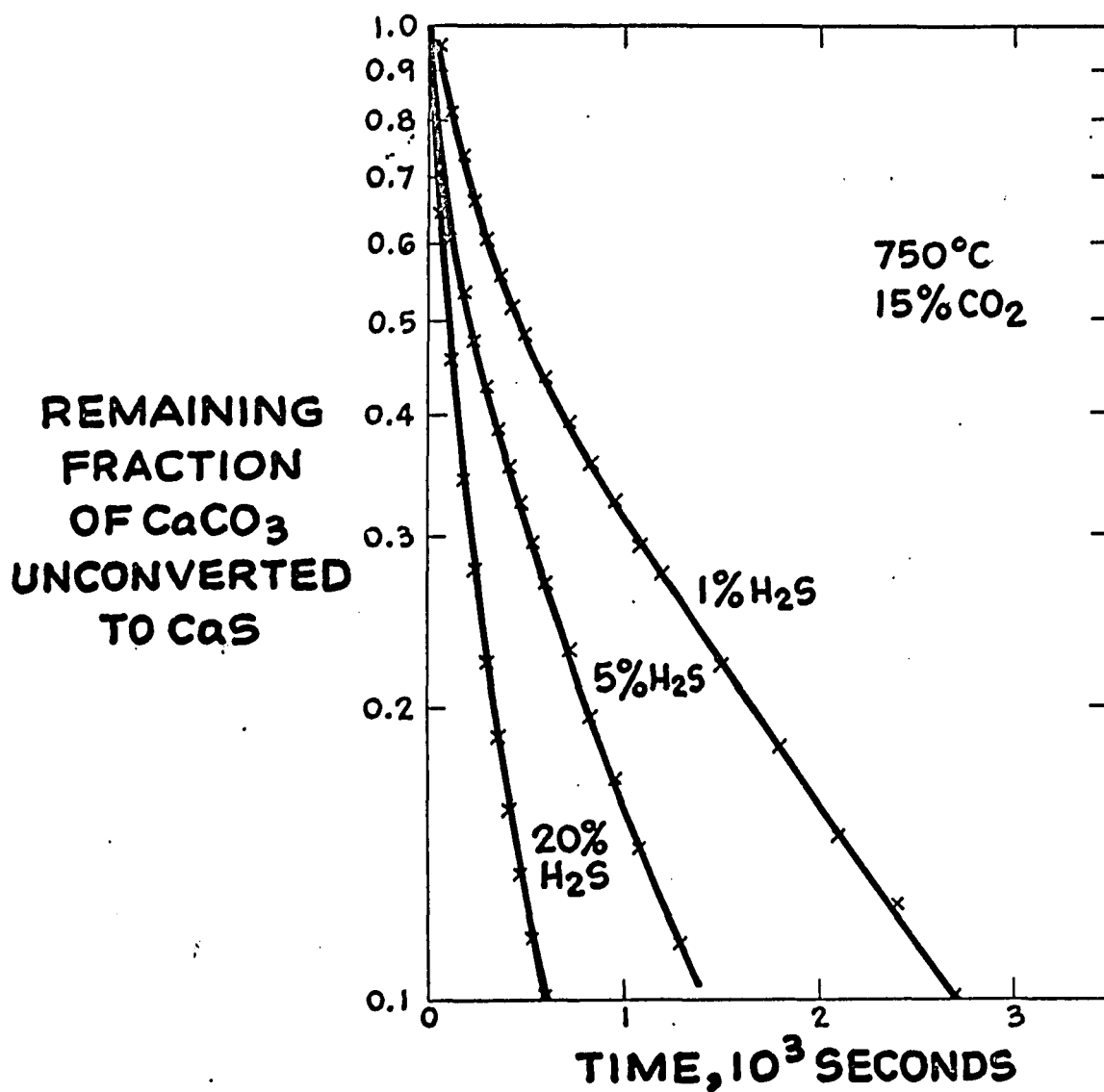


Figure 12. Log(1-x) plots at 750°C, 15% CO_2 , and three H_2S levels.

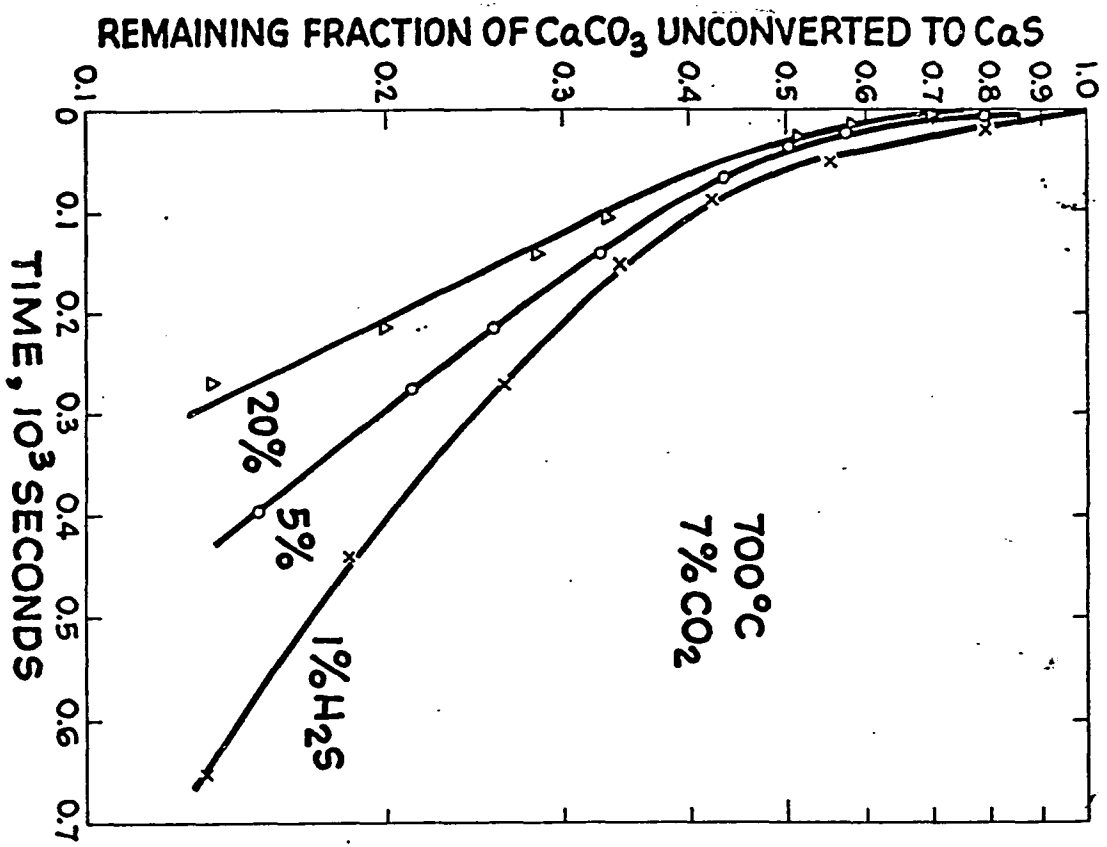


Figure 13. Log(I-X) plots at 700°C , 7% CO_2 , and three H_2S levels.

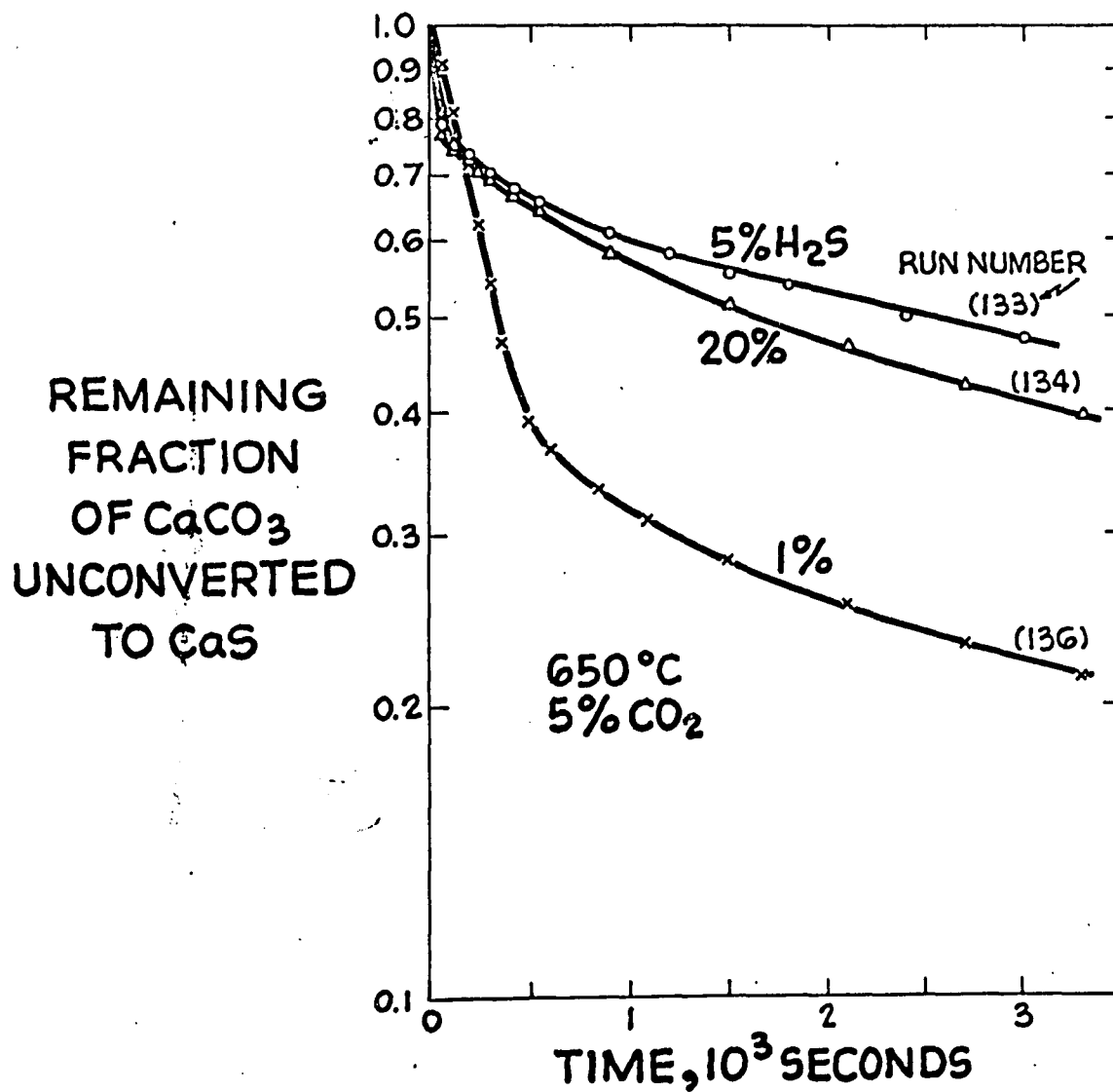


Figure 14. $\text{Log}(1-x)$ plots at 650° C, 5% CO_2 , and three H_2S levels.

the curves for 5 and 20% H_2S cross over the curve for 1% H_2S . The initial rates of these runs, however, do increase with increasing H_2S concentration. Attention is also called to the reaction's great speed. At 800°C and 5% H_2S , for example, 50% of the solid is converted after only about 14 seconds.

Figure 15 presents data for runs made at 600°C . The striking feature is that runs at 1, 5, and 20% H_2S begin rapidly and break sharply when the conversion reaches about 15 to 20%. The decrease in reaction rate is much more acute than for the runs at 650°C . The final rates can be approximated by a straight line on the $\log(1-x)$ plots and are very slow indeed; complete conversions could not be practicably achieved at the conditions of Figure 15. The break in rate for the run at 20% H_2S is the sharpest and occurs at the lowest conversion; that for the run at 1% H_2S is the least sharp and occurs at the highest conversion. The initial rates, however, were highest for the 20% run and lowest for the 1% run, although this comparison cannot be seen at the scale of the plots in Figure 15.

Runs made at temperatures lower than 600°C show the same characteristically high initial rate followed by a very sharp decrease in rate at conversions of only about 15%.

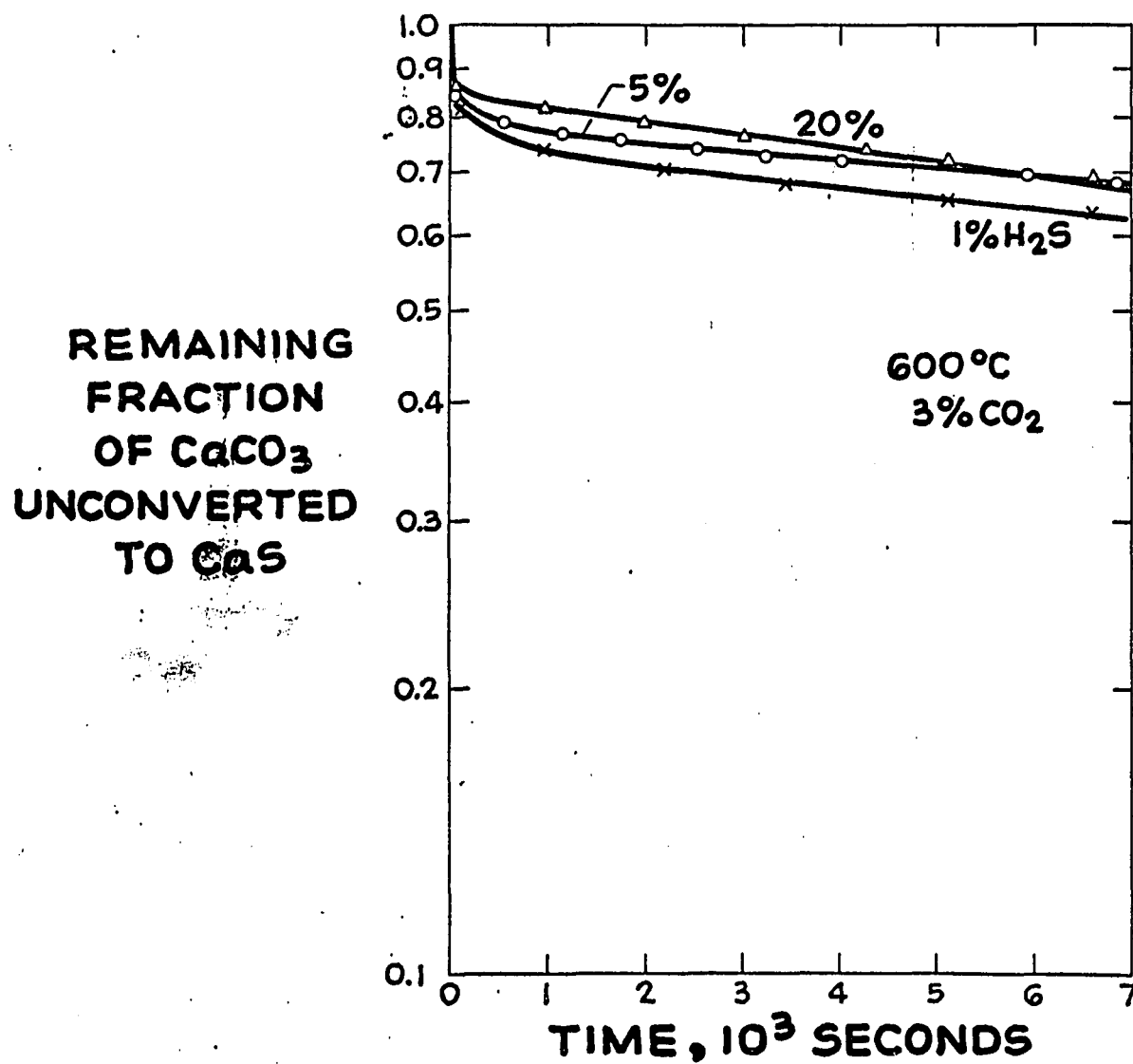


Figure 15. Log(1-x) plots at 600°C, 3% CO_2 , and three H_2S levels.

To summarize the rate data for this study, we estimated an "initial" rate for each run because only data for relatively low conversions of CaCO_3 to CaS appeared amenable to simple kinetic analysis. These initial rates were determined by drawing a straight line tangent to the initial portion of the weight versus time curve produced by the X-Y plotter of the TGA. Table 3 gives initial rates for runs made at low CO_2 concentrations plus the range of conversion for which the straight-line tangent closely approximates the original data.

Figure 16 plots the initial rates versus concentration of H_2S for temperatures of $550^\circ\text{--}800^\circ\text{C}$. The data can well be approximated by straight lines. The average slope of these lines is equal to 0.49, which indicates that the rate is $1/2$ order with respect to H_2S .

It appears that a simple rate expression is applicable, i.e.,

$$\text{rate} = k(p_{\text{H}_2\text{S}})^{1/2} \quad (4)$$

where k is a kinetic constant. Using equation (4), the rate data for each temperature were normalized to 100% or 1 atm H_2S . Table 3 gives these normalized rates, which are really values of k . To test if k depended on temperature according to the "Arrhenius" expression, $k = Ae^{-E/RT}$, a plot was made of $\log(k)$ versus $1/T$. This plot is presented in

Table 3. Initial Rates for Runs Made at Low CO₂ Concentrations

Run #	Temp. °C	Reaction Gas, mole %				Initial Rate, Fractional Conversion/sec x 10 ³	Initial Rate, Normalized to 1 atm H ₂ S, sec ⁻¹ atm ^{-1/2} x 10 ³	Range of Conversion for which Initial Tangent Approximates Data
		H ₂ S	CO ₂	H ₂	N ₂			
152	800	1	25	10	64	21.1	211.	0-0.56
154	800	1	25	10	64	19.7	197.	0-0.43
163	800	5	25	10	60	50.4	225.	0-0.49
155	800	20	25	10	45	84.9	190.	0-0.36
159	750	1	15	10	74	11.8	118.	0-0.42
161	750	5	15	10	70	33.2	148.	0-0.32
162	750	20	15	10	55	47.7	107.	0-0.29
158	700	1	7	10	82	7.40	74.0	0-0.50
160	700	5	7	10	78	19.9	88.9	0-0.39
156	700	20	7	10	63	38.4	85.9	0-0.33
157	700	20	7	10	63	38.0	85.0	0-0.26
135	650	1	5	10	84	3.92	39.2	0-0.39
136	650	1	5	10	84	3.30	33.0	0-0.56
65	650	5	5	10	80	8.65	38.7	0-0.22
133	650	5	5	10	80	8.02	35.9	0-0.19
134	650	20	5	10	65	16.5	36.9	0-0.18
68	600	1	3	10	86	2.32	23.2	0-0.17
4	600	5	3	10	82	4.88	21.8	0-0.16
84	600	5	3	10	82	5.45	24.4	0-0.13
75	600	5	3	38	54	6.13	27.4	0-0.14
70	600	20	3	10	67	9.80	21.9	0-0.14
104	550	5	3	10	82	2.85	12.7	0-0.084
64	550	20	2	10	68	5.53	12.4	0-0.092
98	500	5	2	10	83	0.954	4.27	0-0.091
61	450	20	2	10	68	1.01	2.26	0-0.099

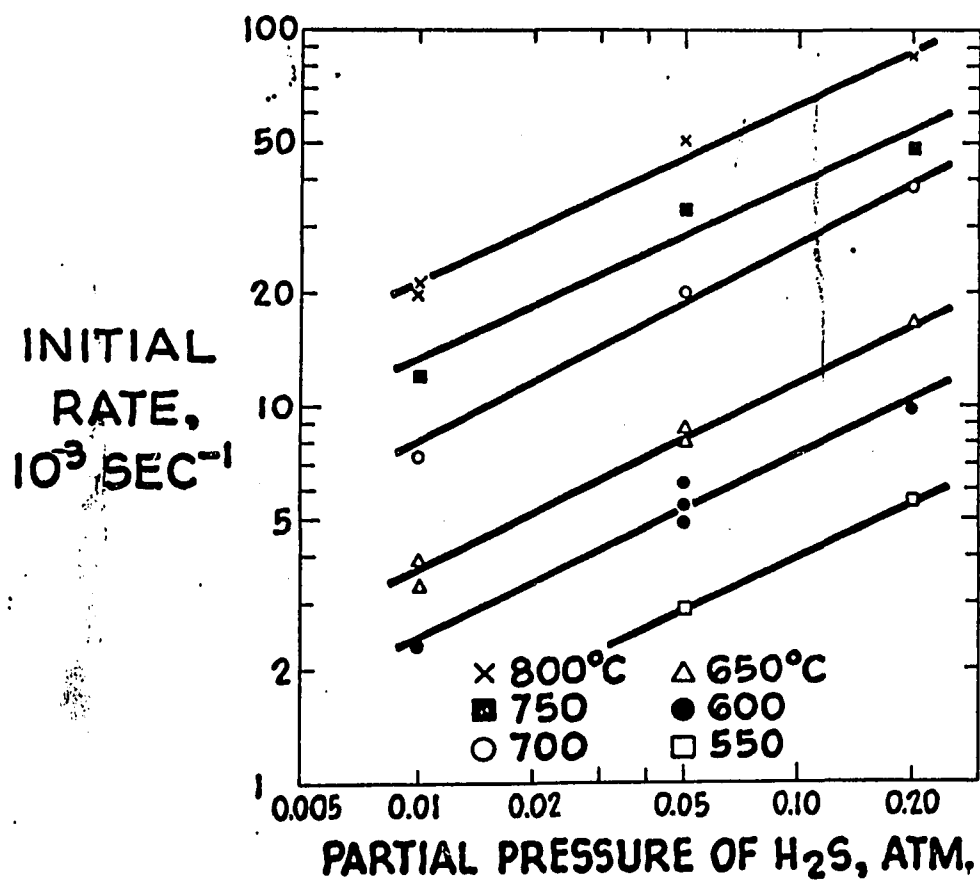


Figure 16. Initial reaction rate versus partial pressure of H_2S for runs made at low CO_2 levels.

Figure 17. As can be seen, the fit to the Arrhenius expression is good.

The activation energy, E , for the reaction rate constant, k , is about 20,500 cal/gm-mole. The pre-exponential factor, A , is about $3040 \text{ sec}^{-1} \text{ atm}^{-1/2}$.

Figures 18, 19, and 20 give plots of $(1-x)$ calculated from equation (4) for the conditions of some actual runs. The run data are plotted for comparison. Equation (4) fits the initial rates well.

7.02 Effect of Temperature and H_2S Concentration on Runs

Made at High CO_2 Concentrations

Some runs were made in which high CO_2 concentrations were used, i.e., CO_2 concentrations considerably in excess of the equilibrium decomposition pressure of CaCO_3 at the temperature of the run. The reaction gas contained H_2S along with CO_2 and H_2 in a 3:2 ratio, and no nitrogen.

The initial rates for runs made at high CO_2 concentrations are given in Table 4. Figure 21 is a plot of initial rate versus H_2S concentration for runs made at temperatures of 550° , 600° , and 650°C . The average slope of straight lines drawn through the data for each temperature is 0.98, indicating that the reaction rate is probably first order with respect to H_2S . This is

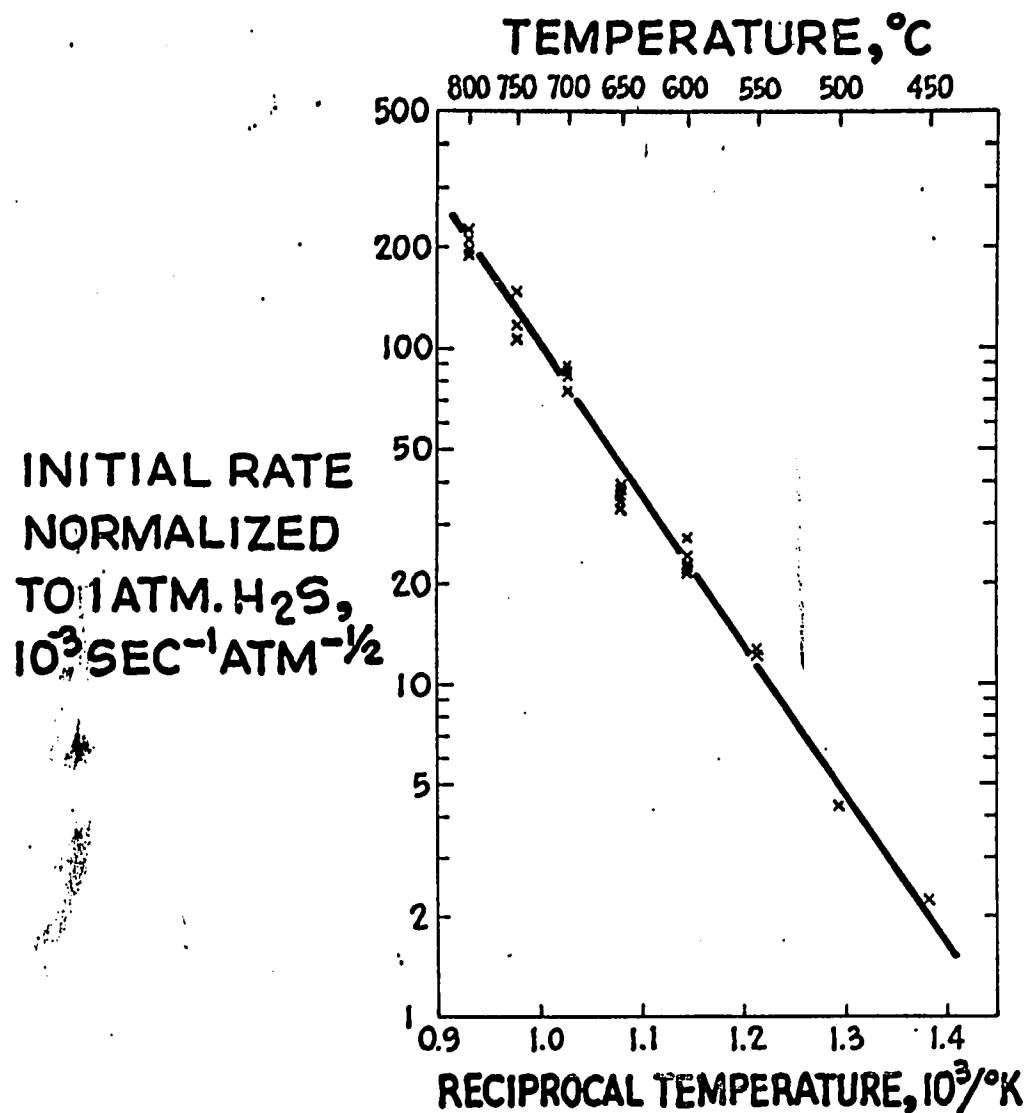


Figure 17. Arrhenius plot of initial rate data for runs made at low CO_2 levels.

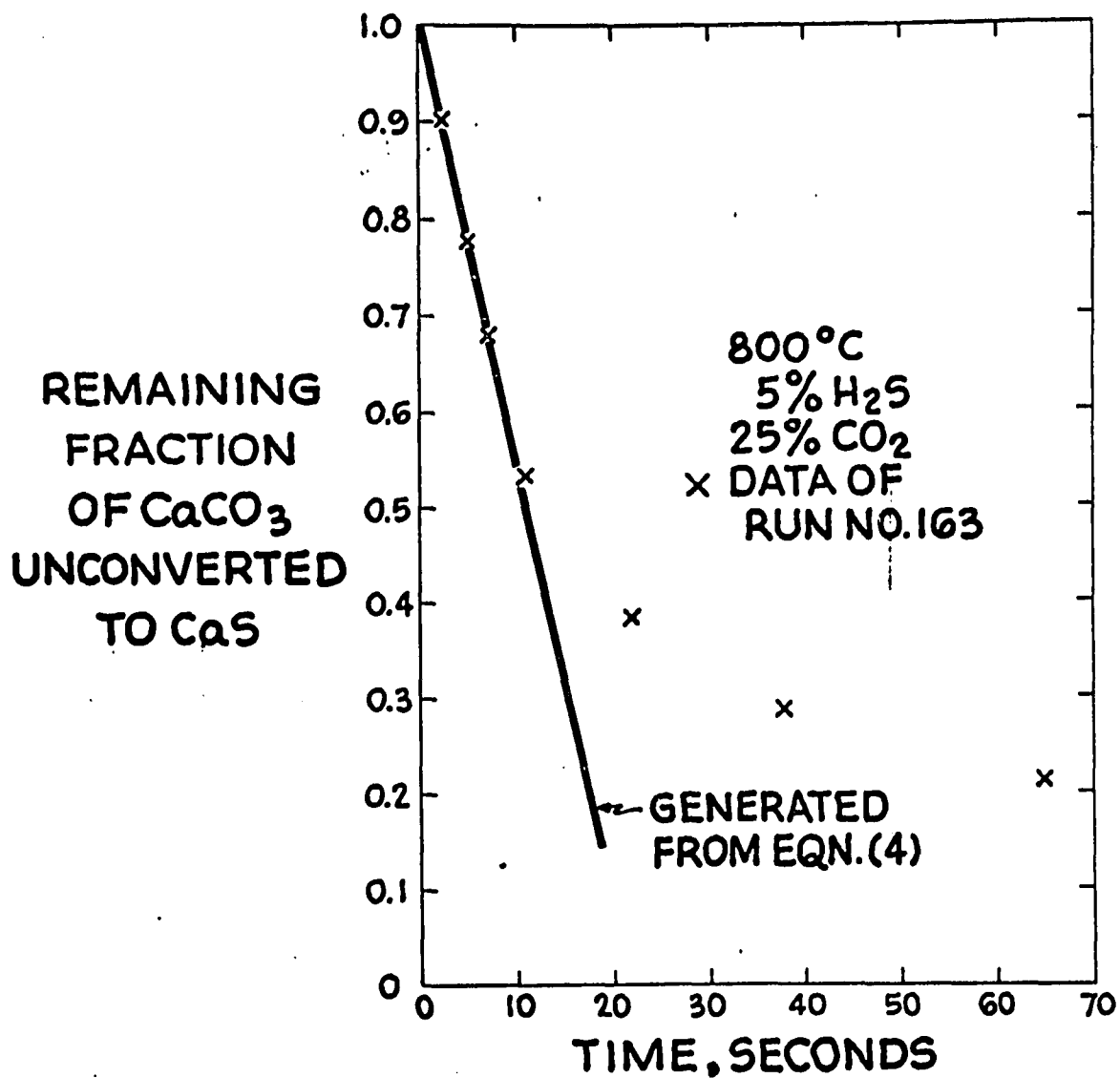


Figure 18. Comparison of data for run at 800° C, 5% H_2S , with curve generated from equation (4).

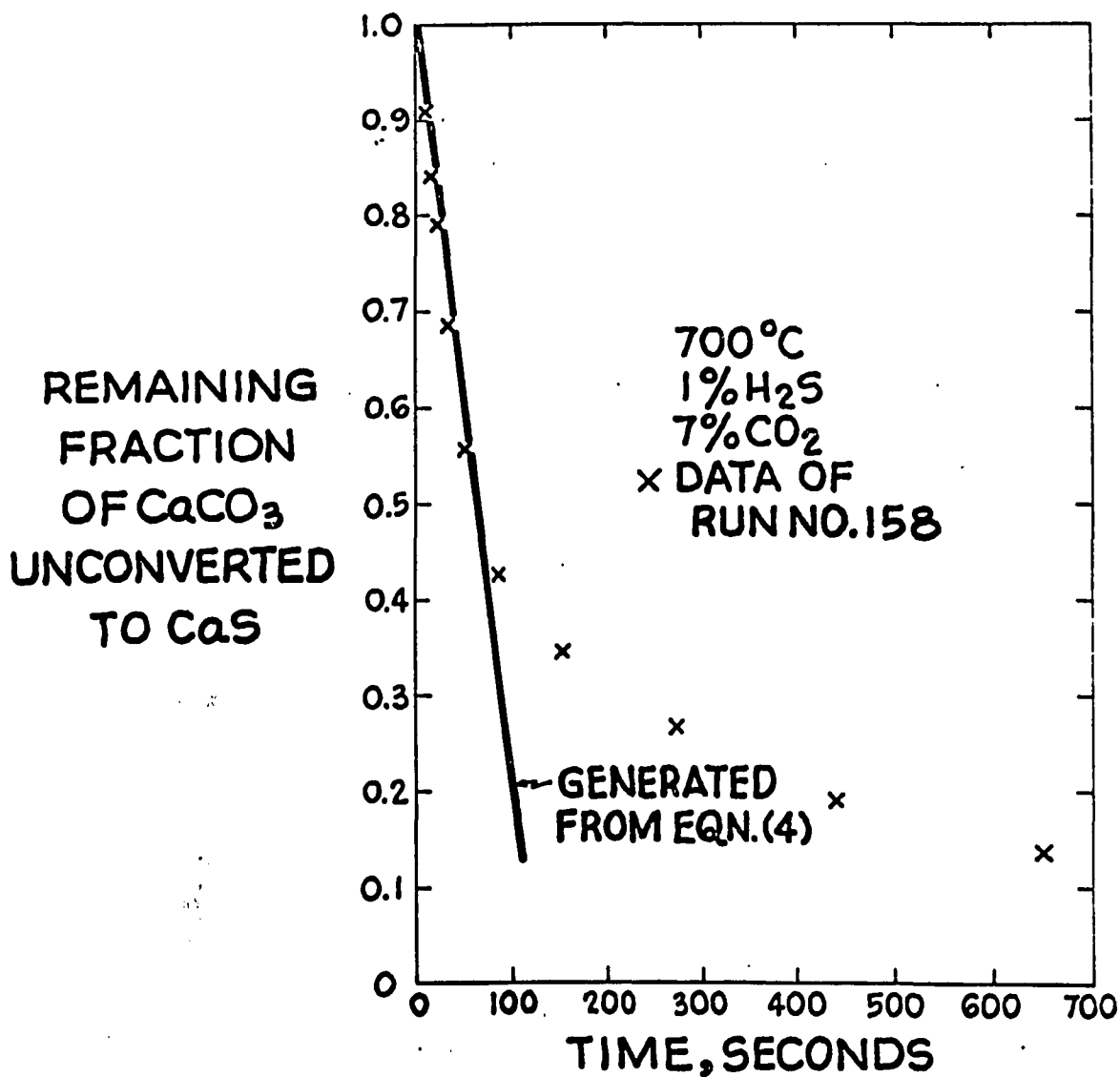


Figure 19. Comparison of data for run at 700°C, 1% H_2S , with curve generated from equation (4).

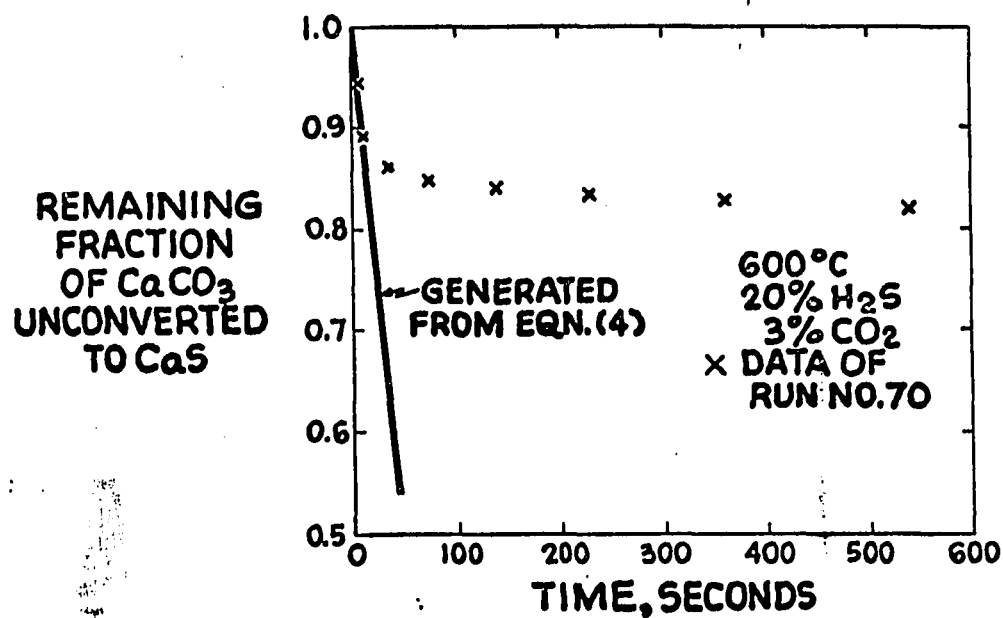


Figure 20. Comparison of data for run at 600° C, 20% H_2S , with curve generated from equation (4).

Table 4. Initial Rates for Runs Made at High CO₂ Concentrations

Run #	Temp. °C	Reaction Gas, mole %			Initial Rate, Fractional Conversion/sec x 10 ³	Initial Rate Normalized to 1 atm H ₂ S, sec ⁻¹ atm ⁻¹ x 10 ³	Range of Conversion for which Initial Tangent Approximates Data
		H ₂ S	CO ₂	H ₂			
30	750	0.5	60	39.5	5.53	1106.	0-0.39
164	700	5	60	35	35.3	706.	0-0.48
25	650	0.5	60	39.5	1.25	250.	0-0.32
28	650	0.5	60	39.5	1.43	286.	0-0.15
35	650	0.5	60	39.5	1.16	232.	0-0.17
36	650	0.5	60	39.5	0.891	178.	0-0.12
50	650	0.5	60	39.5	0.802	160.	0-0.093
52	650	0.5	60	39.5	0.802	160.	0-0.11
54	650	0.5	60	39.5	0.891	178.	0-0.17
55	650	0.5	60	39.5	1.16	232.	0-0.16
31	650	5	57	38	11.7	234.	0-0.71
47	600	0.5	60	39.5	0.490	98.0	0-0.10
48	600	0.5	60	39.5	0.312	62.4	0-0.092
51	600	0.5	60	39.5	0.463	92.6	0-0.12
42	600	1	60	39	0.784	78.4	0-0.091
32	600	5	57	38	3.03	60.6	0-0.37
39	600	5	57	38*	3.57	71.4	0-0.28
77	600	5	60	10*	3.57	71.4	0-0.22
81	600	5	60	10*	3.03	60.6	0-0.22
49	550	0.5	60	39.5	0.0562	11.2	0-0.097
43	550	1	60	39	0.169	16.9	0-0.088
33	550	5	57	38	0.980	19.6	0-0.13
79	550	5	57	38	0.784	15.7	0-0.088
63	550	20	48	32	3.92	19.6	0-0.14
82	550	20	60	20	2.41	12.1	0-0.15

* Balance N₂

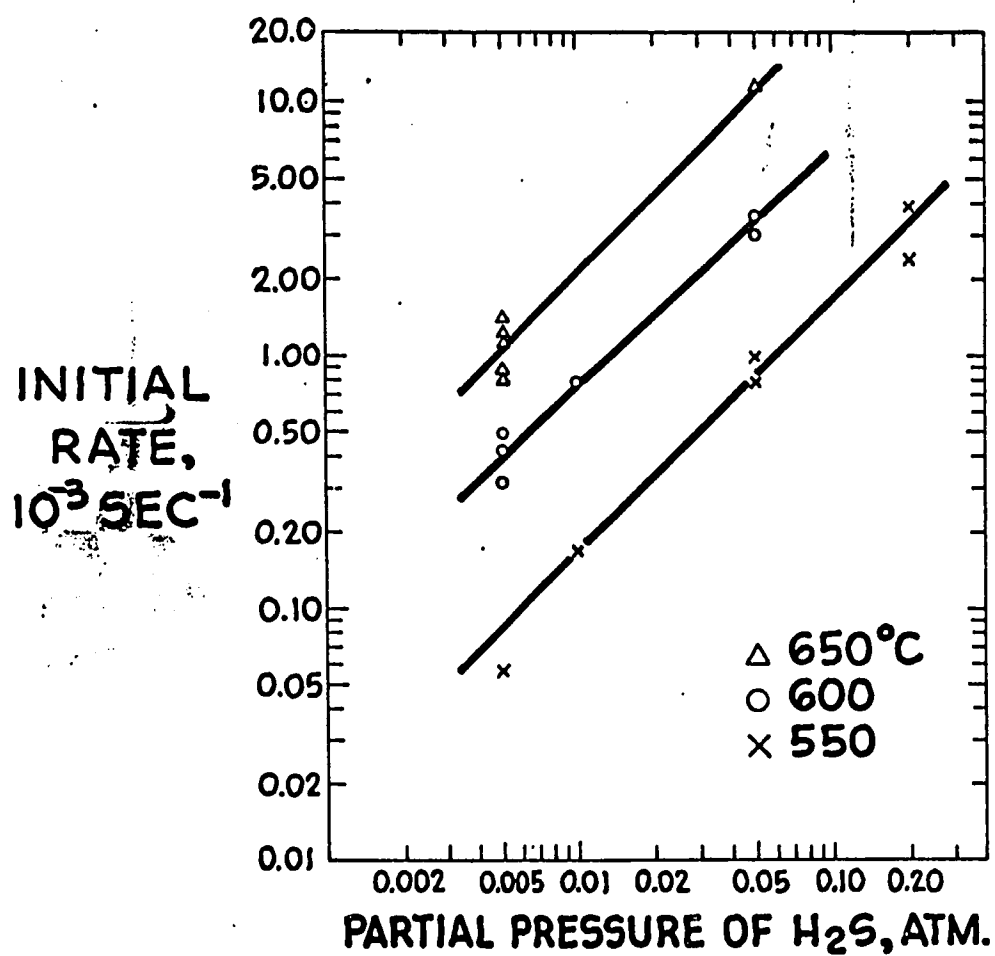


Figure 21. Initial reaction rate versus partial pressure of H_2S for runs made at high CO_2 levels.

most interesting because for runs made at low CO₂ concentrations, the order of reaction is 1/2.

The rate data for runs at each temperature were normalized to one atmosphere H₂S, assuming first order kinetics. Table 4 gives these normalized rates, the logarithms of which are plotted versus 1/T in Figure 22. The initial rates follow the equation:

$$\text{rate} = k(p_{\text{H}_2\text{S}}) \quad (5)$$

where k displays an Arrhenius temperature dependence, as Figure 22 shows. The activation energy is about 37,700 cal/gm-mole. The pre-exponential factor is about $1.82(10)^8 \text{ sec}^{-1} \text{ atm}^{-1}$. These values should be compared to 20,500 cal/gm-mole and $3040 \text{ sec}^{-1} \text{ atm}^{-1/2}$, respectively, for low CO₂ runs.

Figure 23 gives log(1-x) plots for five runs made at a gas composition of 0.5% H₂S, 60% CO₂, and 39.5% H₂, and temperatures ranging from 550° to 750°C. The run at 550°C reaches 10% conversion after 2700 seconds, and the log(1-x) plot is linear beyond 15% conversion. The run at 600°C reaches 30% conversion after 3300 seconds, and the log(1-x) plot is linear beyond 20% conversion. The remaining runs at higher temperatures provide substantially linear plots for all conversion levels. The "final" rates

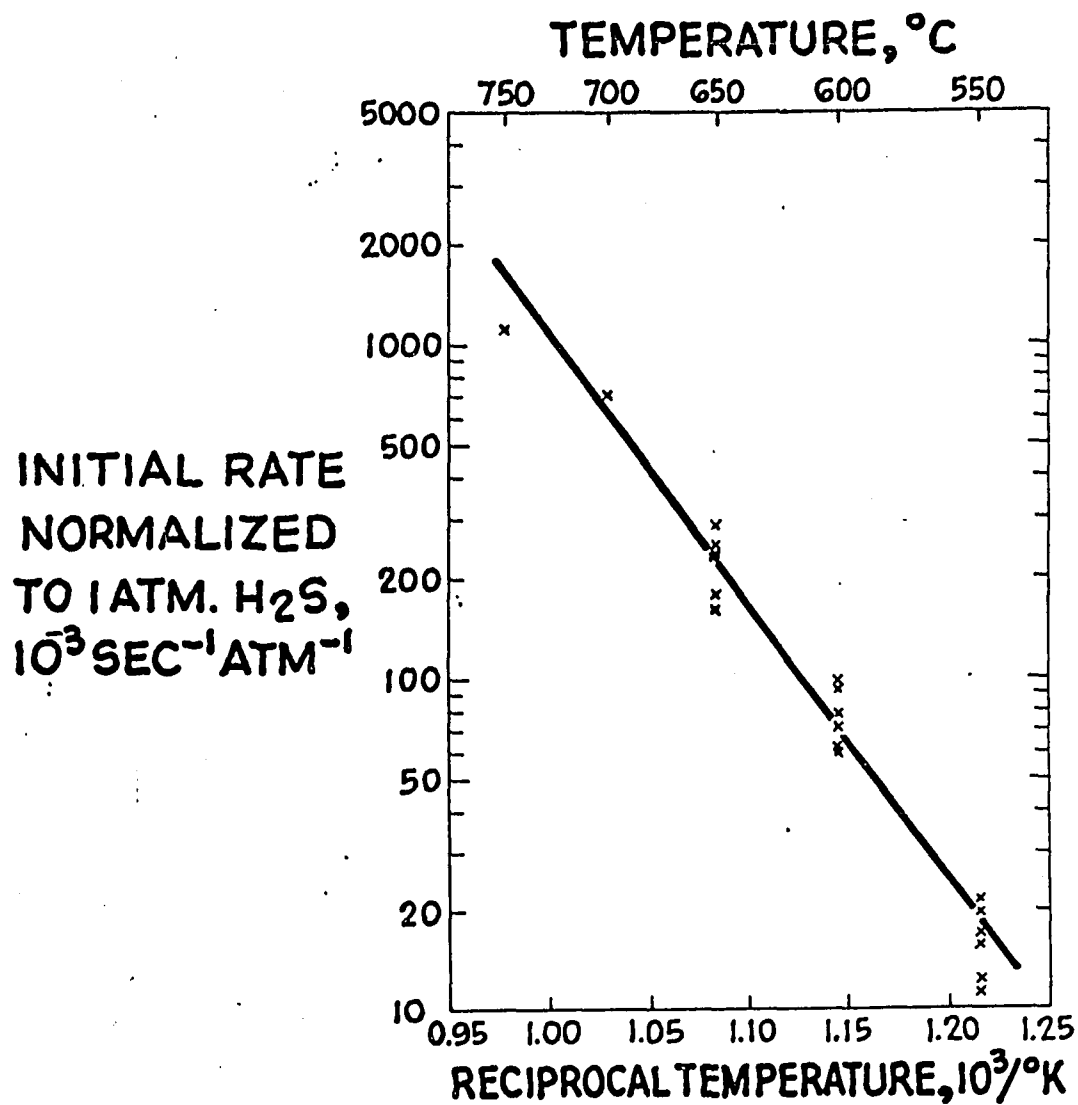


Figure 22. Arrhenius plot of initial rate data for runs made at high CO_2 levels.

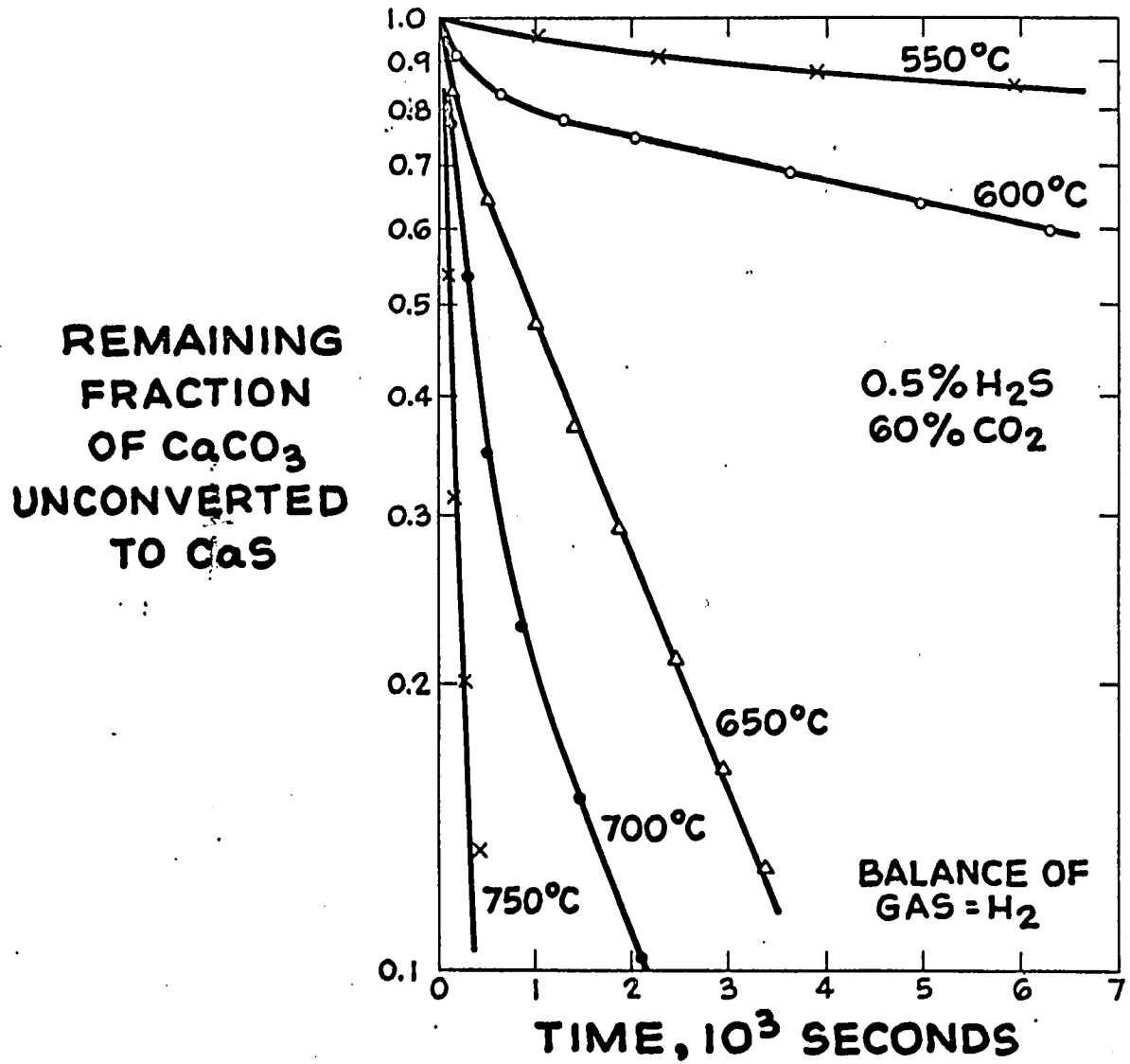


Figure 23. $\text{Log}(1-x)$ plots at 0.5% H_2S , 60% CO_2 , and five temperature levels.

for the runs of Figure 23, estimated from the slopes of the linear portion of each curve, show a stronger temperature dependence than do the initial rates. Based on these final rates, the apparent activation energy is about 60 kcal/gm-mole.

7.03 Effect of CO₂ Concentration

Comparison of equations (4) and (5), which give initial rates for runs made at low and high CO₂ concentrations, respectively, shows that CO₂ affects the initial rate of the reaction of H₂S with half-calcined dolomite. The order of reaction with respect to H₂S, the activation energy, and the pre-exponential factor, all depend on CO₂ concentration, as is shown in the table below:

	<u>Low CO₂ runs</u>	<u>High CO₂ runs</u>
order of reaction with respect to H ₂ S, n	0.5	1
activation energy, E	20.5 kcal/gm-mole	37.7 kcal/gm-mole
pre-exponential factor, A	3040 sec ⁻¹ atm ^{-1/2}	1.82(10) ⁸ sec ⁻¹ atm ⁻¹
$\text{Rate} = Ae^{-E/RT} \cdot (p_{\text{H}_2\text{S}})^n$		

The initial rates for runs made at 550°, 600° and 700°, with 5% H₂S and both high and low concentrations of CO₂ are given in Table 5. The initial rates as calculated from equations (4) and (5) are also given for comparison.

Table 5. Effect of CO₂ Concentration on Initial Rates

Run #	Temp °C	H ₂ S mole %	CO ₂ mole %	Actual* Initial Rate, sec ⁻¹ x10 ³	Calculated* Initial Rat sec ⁻¹ x10 ³
104	550	5	3	2.85	2.52
33,79	550	5	57	0.882	0.945
4,75,84	600	5	3	5.49	5.15
74	600	5	13	6.16	--
76	600	5	30	4.40	--
32,39,77,81	600	5	60	3.30	3.50
160	700	5	7	19.9	17.2
164	700	5	60	35.3	32.4

* Where more than one run number is given, actual rate is an average

** Equation (4) is used for low CO₂ concentration runs; Equation (5) is used for high CO₂ concentration runs.

At 550°C , the initial rate for a run made at 3% CO_2 is about 2.7 times faster than the rate for a run at 57% CO_2 . However, as is evident from a comparison of activation energies, the rates of high CO_2 runs increase with temperature faster than the rates of low CO_2 runs and, at a temperature between 600° and 650° , runs made at high CO_2 concentrations become faster than runs made at low CO_2 concentrations. At 600°C , the initial rate for a run made at 3% CO_2 is only about 1.9 times the rate for a run made at 60% CO_2 ; at 700°C the initial rate for a run at 7% CO_2 is about 0.53 times the rate for a run made at 60% CO_2 .

The high CO_2 runs were made at CO_2 concentrations of about 60%, whereas the CO_2 concentrations for the low CO_2 runs varied from 2% to 25%. At 600°C and 5% H_2S , runs were made at intermediate CO_2 concentrations of 13% and 30%. Figure 24 is a plot of initial rate versus mole percent CO_2 for these runs. The increase in rate from 3 to 13% CO_2 can probably be attributed to experimental "error". Beyond 13% CO_2 the initial rate decreases as CO_2 concentration increases.

The values of activation energy, pre-exponential factor, and order of reaction are reported for runs made at extremes of CO_2 concentration. At intermediate CO_2 concentrations

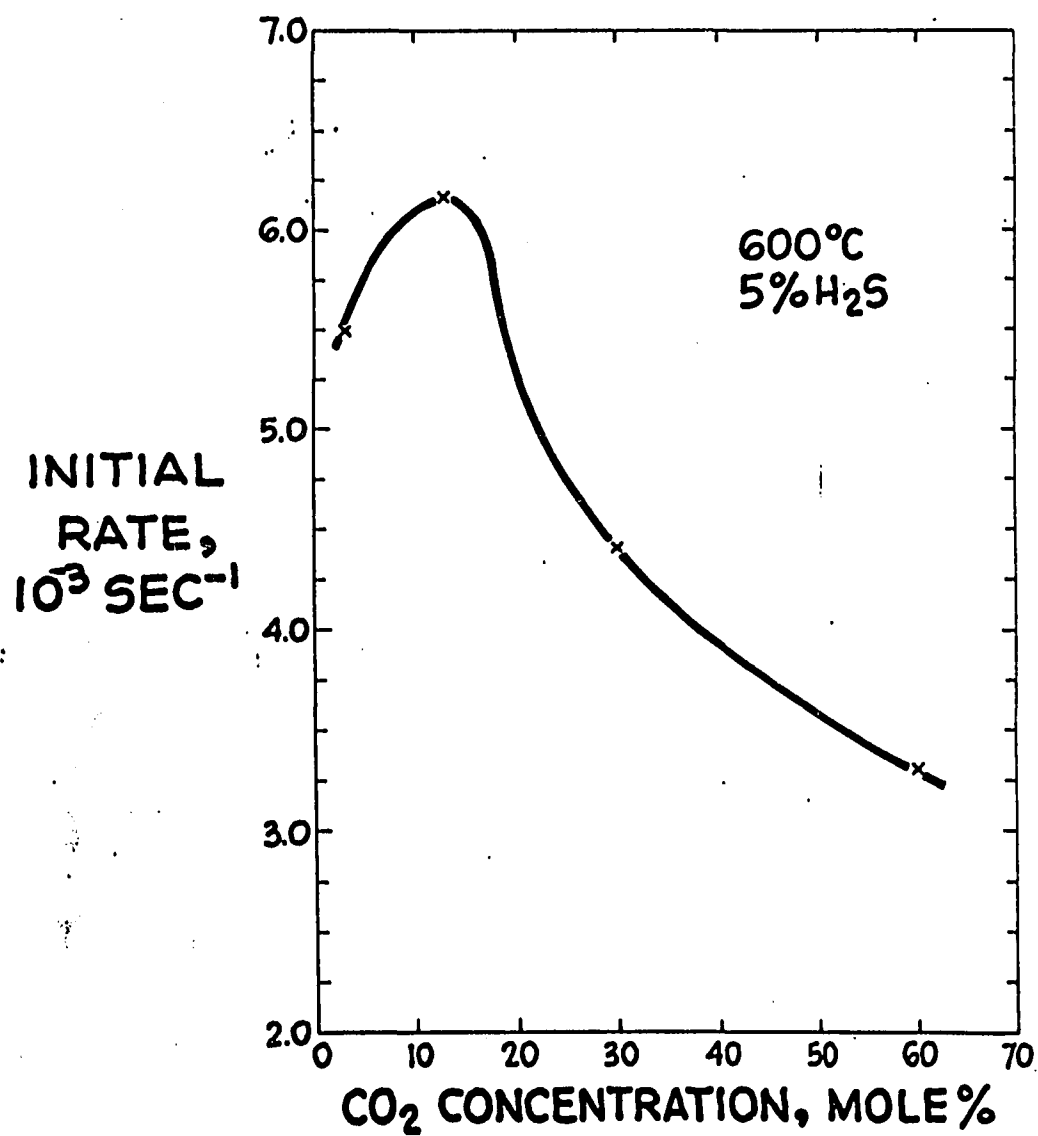


Figure 24. Initial rate versus concentration of CO₂ for runs made at 600° C, 5% H₂S.

the values of these parameters would be expected to be bounded by the values reported.

The effect of CO_2 on the conversion versus time for higher conversions of CaCO_3 is far more interesting than the effect of CO_2 on initial reaction rates. Figure 25 gives data for a run at 600°C made with a reaction gas containing 5% H_2S , 10% H_2 , 60% CO_2 , and 25% N_2 . Compare this with the run at 5% H_2S in Figure 25, made at 3% CO_2 . The difference between the two runs is spectacular. The initial rate of the 3% run is higher, but the run at 3% CO_2 "stops dead" after reaching 20% conversion of CaCO_3 , whereas the run at 60% CO_2 continues at a high rate to reach substantially complete conversion of the solid.

After the discovery of this unanticipated effect of CO_2 upon the rate of reaction (B), runs were made in which only CO_2 was varied. Figure 25 shows the effect of varying CO_2 at 600°C and 5% H_2S . At 3 and 13% CO_2 , the break in rate occurs at about 20% conversion. At 30% CO_2 , a high rate is maintained until the run achieves 30% conversion. At 60% CO_2 , substantially complete conversion is achieved at a good rate, and the $\log(1-x)$ plot is almost linear.

The effect of CO_2 on runs at 550° , 650° , and 700°C , and

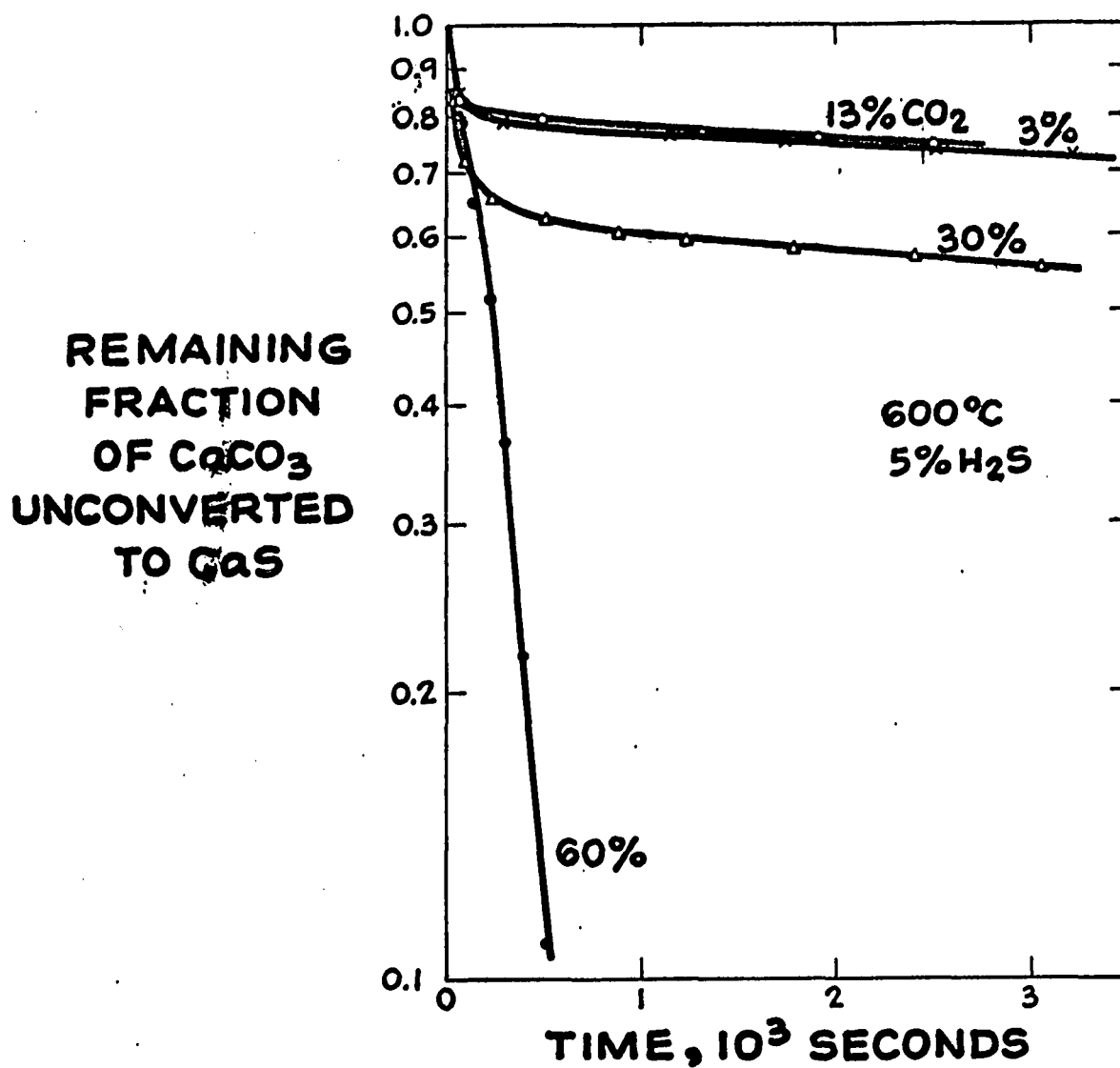


Figure 25. $\text{Log}(1-x)$ plots at 600° C, 5% H_2S , and four CO_2 levels.

5% H_2S , is shown in Figures 26, 27, and 28. In each case the effect of CO_2 on initial rate is overwhelmed by the effect of CO_2 on the behavior of the reaction at higher conversions. At 700°C , the effect of CO_2 is small, presumably because even the run made at low CO_2 continues to complete conversion at a good rate. At temperatures below 550°C , the CO_2 effect diminishes again, presumably because of the decrease in reaction rate, with either high or low CO_2 .

Figure 29 gives data at 550°C and high levels of CO_2 for H_2S levels from 0.5 to 20%. The runs at 20% H_2S provide still another surprise. The rate at 0.5 and 1% H_2S are low; the rate at 5% H_2S is comparatively high and the run achieved complete conversion. The runs at 20% H_2S begin at higher rates but slow sharply well short of complete conversion. At 20% H_2S , 32% H_2 , and 48% CO_2 , the break occurs at about 35% conversion. At 20% H_2S , 20% H_2 , and 60% CO_2 , the break occurs at about 65% conversion.

7.04 Effect of H_2O

Pell (1) had found that water increased considerably the rate of reaction of H_2S with fully calcined dolomite, $[\text{CaO}+\text{MgO}]$, at conditions of 550°C and either 0.3 or 10% H_2S

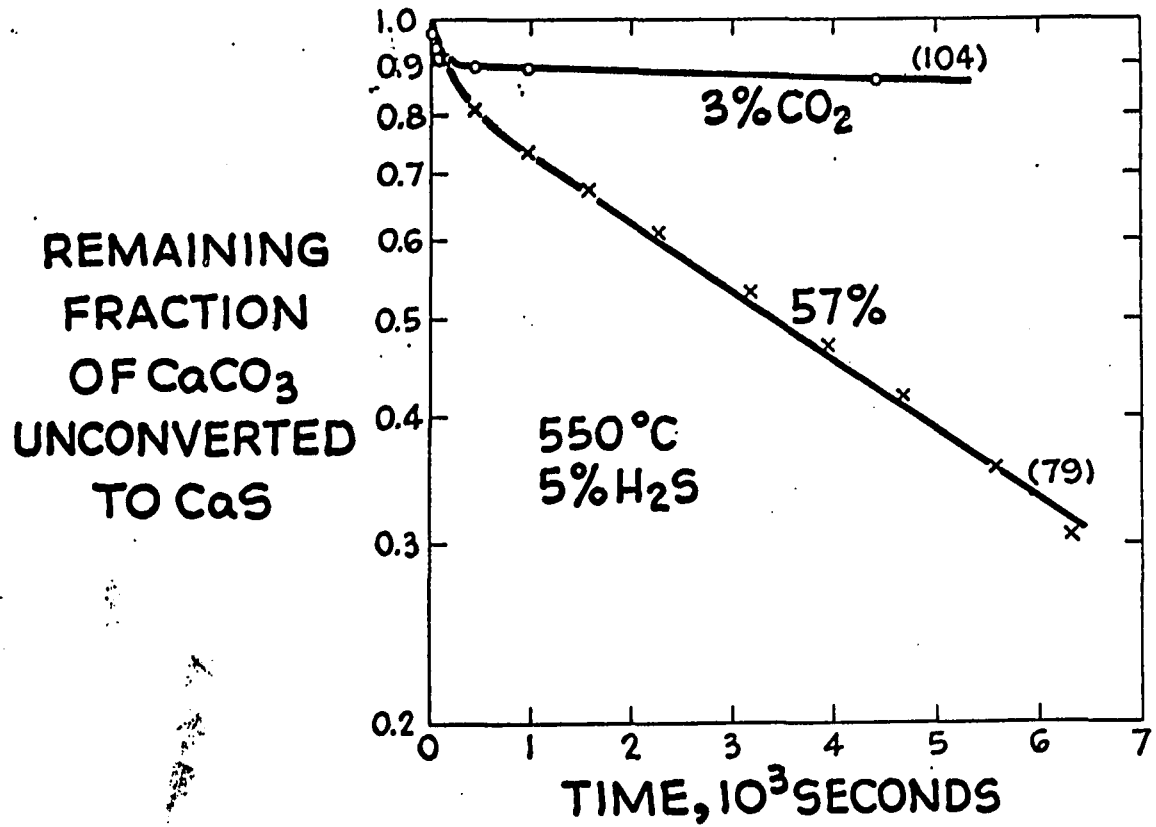


Figure 26. Log(1-x) plots at 550°C, 5% H_2S , and two CO_2 levels.

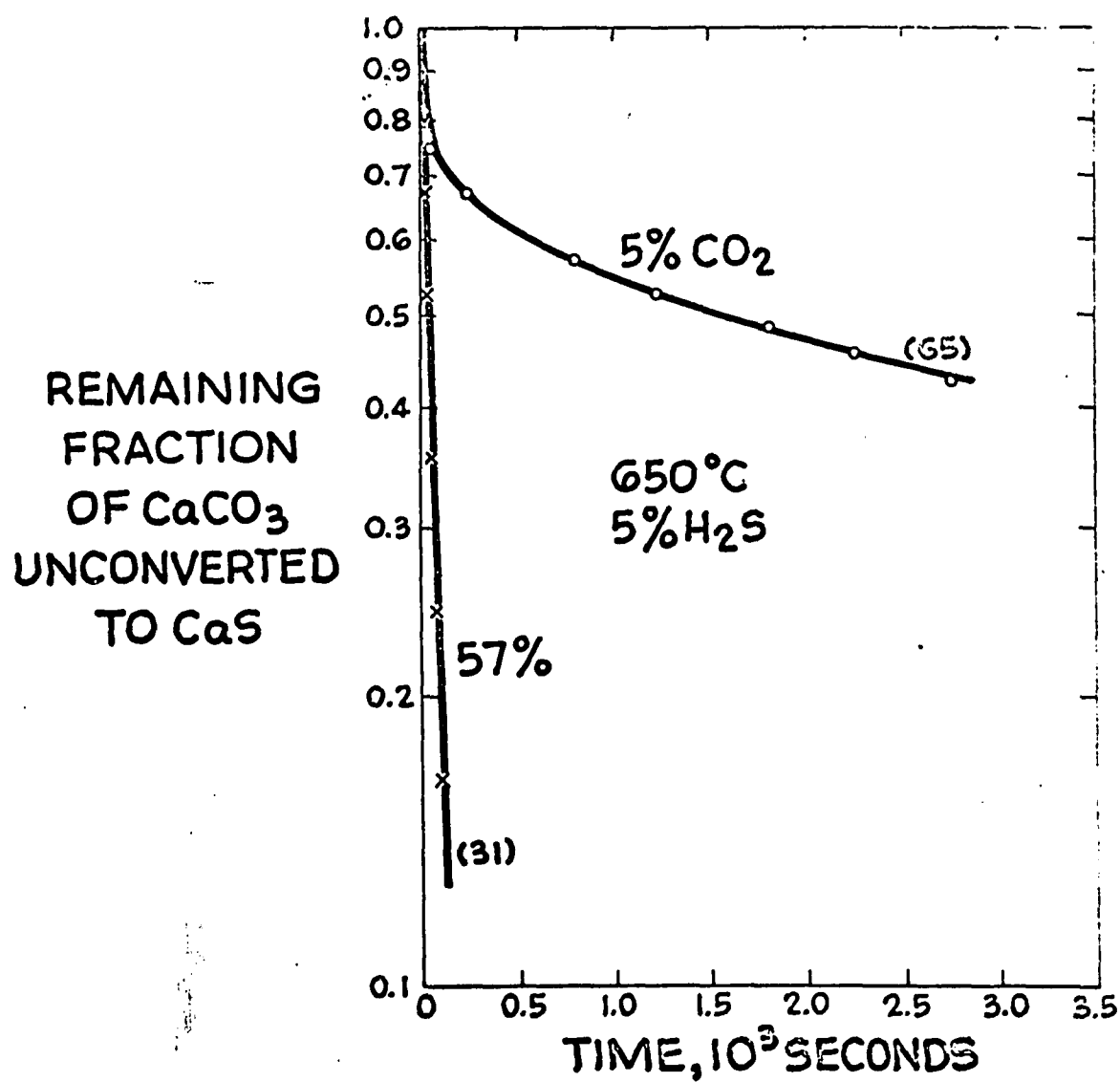


Figure 27. $\text{Log}(1-x)$ plots at 650° C, 5% H_2S , and two CO_2 levels.

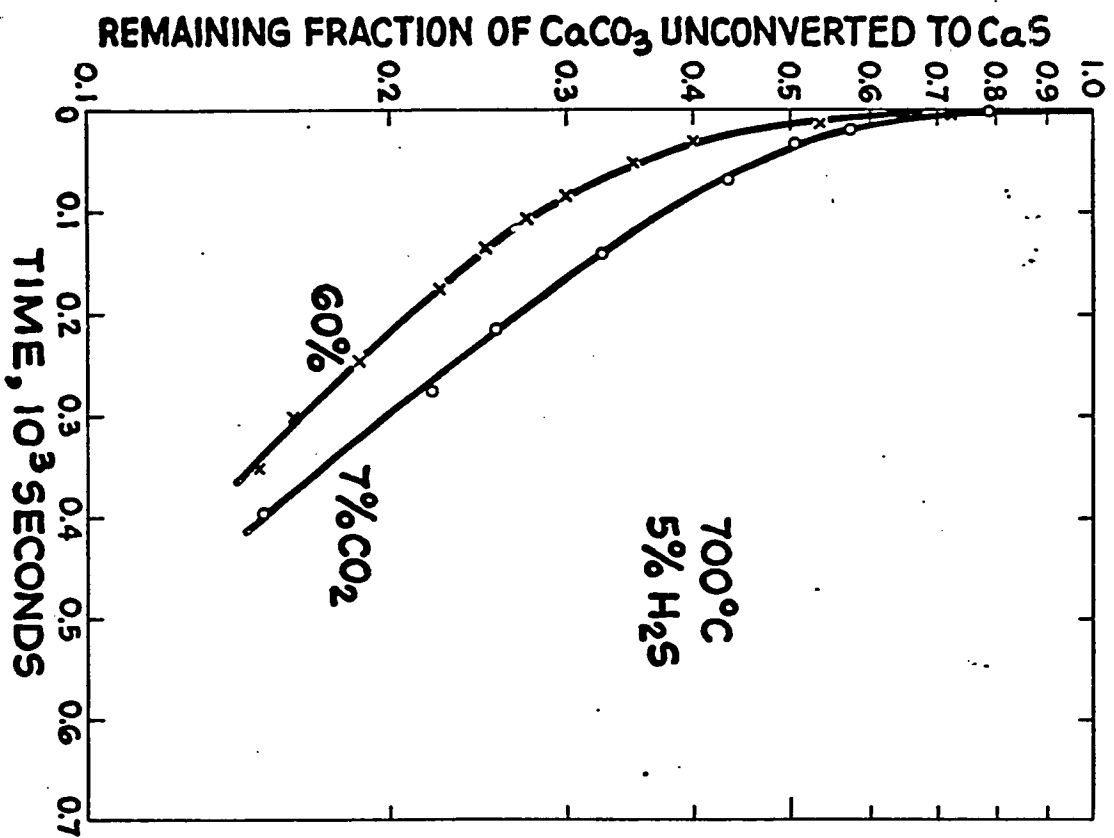


Figure 28. Log(1-x) plots at 700° C, 5% H_2S , and two CO_2 levels.

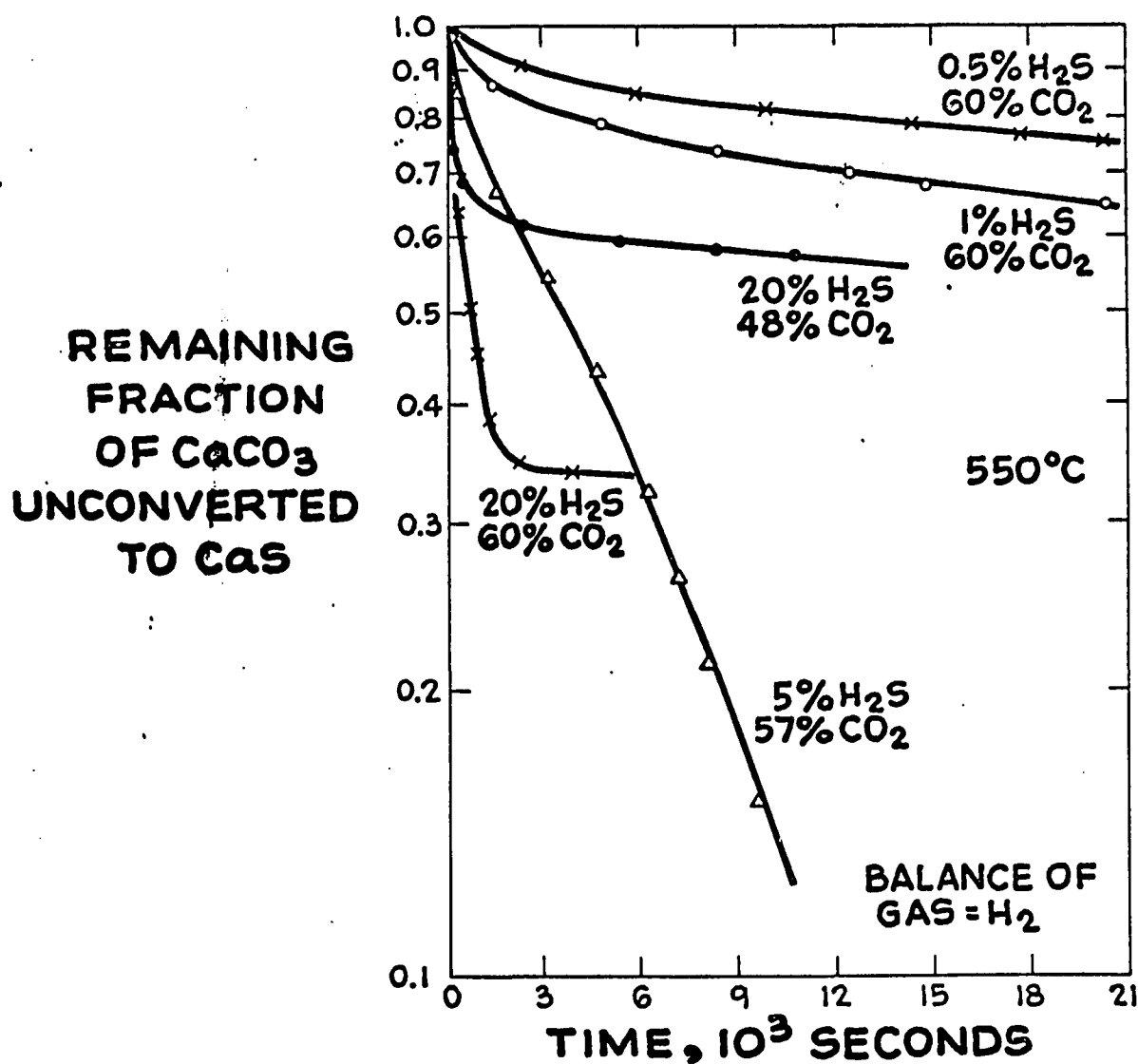


Figure 29. $\text{Log}(1-x)$ plots at 550°C, high CO_2 level, and four H_2S levels.

(see Figures 4 and 5). He found that H_2O had negligible effect on runs made at 700°C . In light of Pell's results, we tested for the effect of H_2O on the reaction of half calcined dolomite with H_2S .

Figure 30 shows the effect of 60% H_2O on runs made at 600°C and 5% H_2S . Figure 31 shows that the effect of 60% H_2O is much more dramatic at 550°C than at 600°C . Comparison of Figures 31 and 26 shows that 60% H_2O is more effective at promoting the reaction than 60% CO_2 at 550°C . Comparison of Figures 30 and 25 shows that the reverse is true at 600°C .

Steam promotes reactivity in a similar manner to CO_2 , having a very strong effect on the reaction rate at higher conversions of CaCO_3 . Steam, like CO_2 , also affects the initial reaction rate, but to a lesser extent. Table 6 shows the initial reaction rates for runs made at 550° and 600°C , both with and without steam. Sixty percent steam slows down the initial rates at both temperatures, but the effect is more marked at 550°C . In comparison to runs made without H_2O , the initial rates of runs with 60% H_2O show a stronger temperature dependence. It will be recalled from the previous section that the initial rates of runs made at high CO_2 concentrations show a stronger temperature dependence than runs made at low CO_2 concentrations.

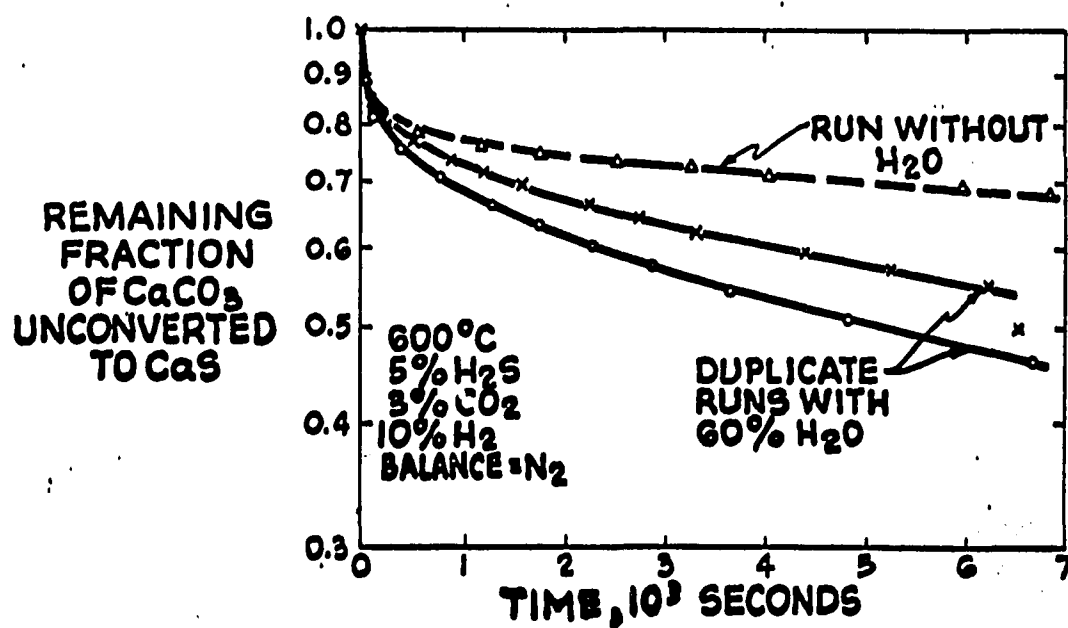


Figure 30. $\text{Log}(1-x)$ plots for runs at 600° C, 5% H_2S , with and without water added.

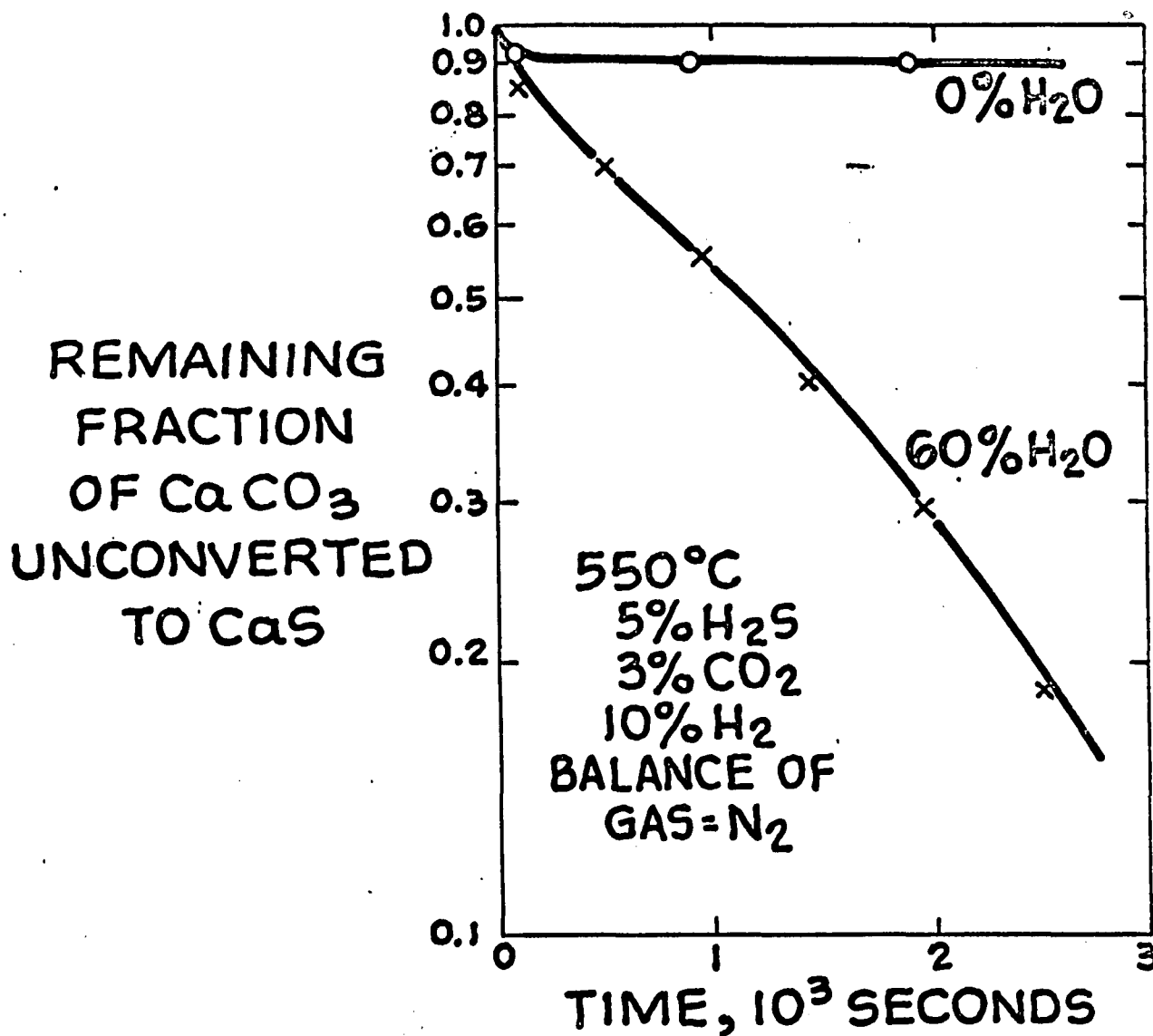


Figure 31. Log(1-x) plots for runs made at 550° C, 5% H_2S , with and without water added.

Table 6. Effect of H₂O on Initial Rates

Run #	Temp °C	Reaction Gas, mole %					Initial Rate, sec ⁻¹ x 10 ³	Range of Conversion for which Initial Tangent Approximates Data	
		H ₂ S	H ₂ O	CO ₂	H ₂	N ₂			
103	550	5	60	3	10	22	0.980	0-0.153	
104	550	5	0	3	10	82	2.85	0-0.084	
99	600	5	60	3	10	22	4.99	} Avg=4.24	0-0.167
101	600	5	60	3	10	22	3.48		0-0.160
4	600	5	0	3	10	82	4.90	} Avg=5.17	0-0.16
84	600	5	0	3	10	82	5.44		0-0.13

7.05 Effect of Oxygen

Bursts of oxygen have a startling effect on the reactivity of $[\text{CaCO}_3 + \text{MgO}]$ toward H_2S . Figure 32 illustrates the effect of two pulses of a gas containing about 0.3% O_2 , each pulse lasting about 10 seconds. The dashed curve in Figure 32 indicates how a run at 600°C , 5% H_2S , 3% CO_2 , and 10% H_2 could have been expected to progress if no pulse of oxygen had been administered. An oxygen pulse apparently revives the solid, permitting another increment of conversion. On the other hand, oxygen supplied steadily from the outset of a run at 600°C , or at 500°C , and at levels up to 0.5% merely alters the conversion, by only a few per cent, at which the reaction "drops dead." Prolonged exposure to oxygen also has the undesirable effect of converting CaS to CaSO_4 .

Oxygen has a moderate effect on the initial rates of runs made at 500°C and 600°C . Figure 33 plots initial rates vs. per cent O_2 in a gas supplied steadily from the outset of runs made at 5% H_2S and low CO_2 . The peaks shown in Figure 33 are probably real because they are observed for both 500° and 600°C runs.

A most interesting effect is observed if the CO_2 is

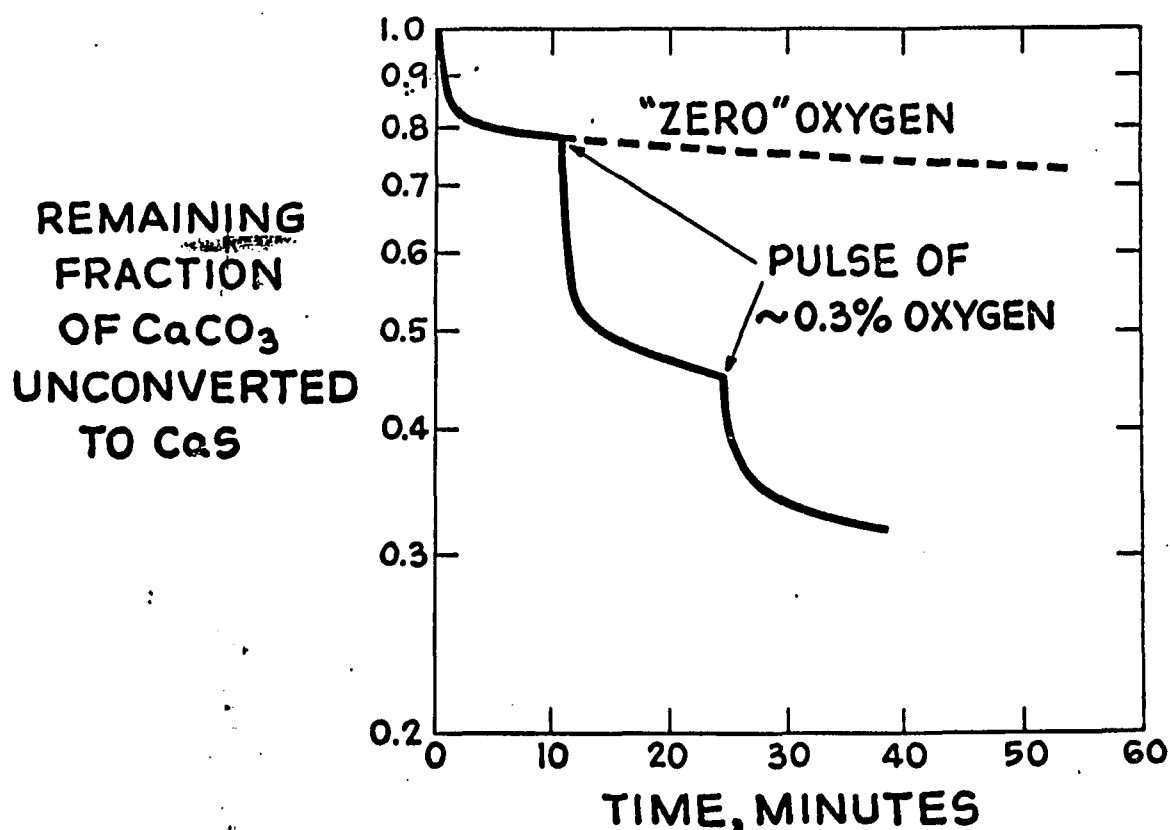


Figure 32. Differential kinetics for reaction of half-calcined dolomite at 600°C with 5% H_2S , 3% CO_2 , 10% H_2 , and balance N_2 . The dashed curve is for gas containing at most a few hundredths per cent O_2 . The solid curve shows effect of two pulses of a gas containing very approximately 0.3% O_2 , each pulse lasting about 10 seconds.

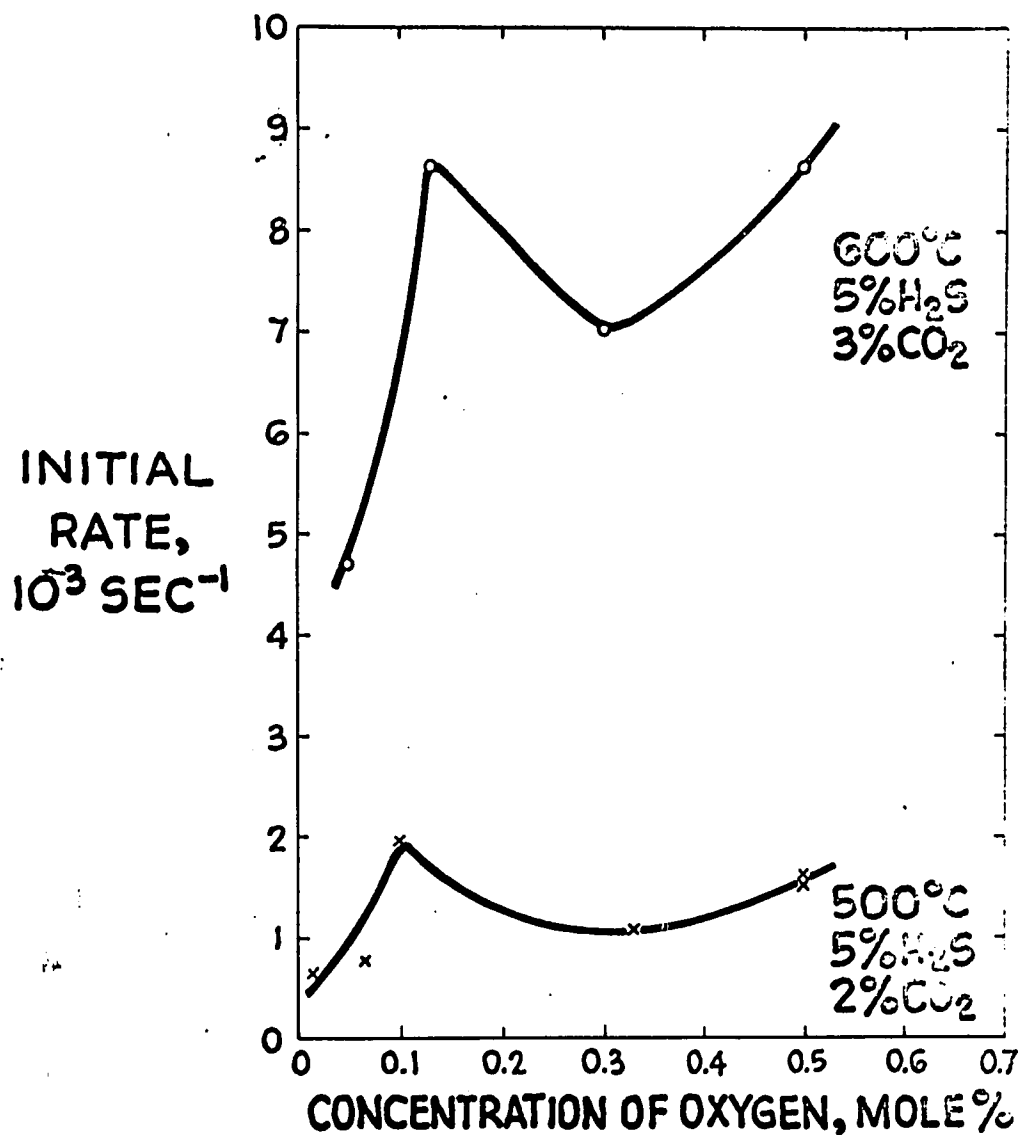


Figure 33. Initial rate versus concentration of O_2 for runs made with 5% H_2S and a low CO_2 level at 550° and 600° c.

increased simultaneously with a pulse of oxygen. Instead of gaining only an increment of conversion, the reaction proceeds to complete conversion at the high rate characteristic of the high CO_2 level, as seen for example in the run at 60% CO_2 in Figure 25. However, if the CO_2 level had been increased from 3 to 60% in the absence of a pulse of oxygen at any time after about 10 minutes into the run illustrated in Figure 32, there would have been no effect upon the rate.

7.06 Effect of Hydrogen

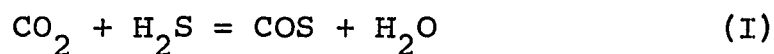
We have observed no effect on the reaction rate due to changes in H_2 concentration. Runs made at 600°C , 5% H_2S , 3% CO_2 with 38% H_2 (run number 75) and 10% H_2 (4, 84) show no significant differences. The same is true for runs made at 600°C , 5% H_2S , 57% CO_2 with 38% H_2 (32, 39) and 10% H_2 (81, 77). The initial rates for these runs are given in Table 3 (75, 4, 84) and Table 4 (32, 39, 81, 77).

7.07 Sulfur Formation in Furnace Tube

During many runs, we observed deposition of sulfur on the cooler ends of the furnace tube and in the

polyethylene tubing through which reaction gas and nitrogen purge are discharged. The amount of sulfur formed increased when the temperature or concentration of CO_2 or H_2S was raised.

Dissociation of H_2S was ruled out as the mechanism by which sulfur is produced since there was always sufficient H_2 in the reaction gas to keep the concentration of S_2 from this source negligible. Instead, we believe sulfur formation occurs via the reactions:



The equilibrium constant for reaction (I) can be calculated from data given by Kubaschewski and Evans (27), and Kelley (28). The equilibrium constant for reaction (J) is given by J.T. Clancey, et. al. (29). Both equilibrium constants increase with temperature.

The above mechanism explains the effect of temperature and concentrations of H_2S and CO_2 on the amount of sulfur formation. It is also consistent with the observation that sulfur formation was negligible for runs in which H_2O was added to the reaction gas.

7.08 Reaction of H_2S With Fully Calcined Dolomite

Several runs were made on the reaction of H_2S with fully calcined dolomite, $[CaO+MgO]$. Figure 34 gives $\log (1-x)$ plots for runs made at $550^\circ C$ and 10% H_2S with the Greenfield dolomite used in this research (-250+270 mesh) and with the Greenfield dolomite used by Pell in his work (-80+325 mesh). Data from a run made by Pell is shown for comparison.

The duplicate runs made with -250+270 powder are in good agreement; however, the run made with -80+325 powder is about twice as fast. Even more striking is the discrepancy between the two runs made with -80+325 powder. The run made by Ruth with Ruth's equipment is much faster than the run made by Pell in his equipment. Moreover, Ruth's run achieves complete conversion whereas Pell's does not achieve complete conversion within a reasonable time.

Figure 35 shows a run made at $800^\circ C$ and 10% H_2S and a run taken from Pell's data. Ruth's run is again faster than Pell's.

The run of Figure 35 made by Ruth was allowed to continue for about 100 minutes after attaining a weight gain of 6.4 mg, which corresponds to complete conversion of CaO to CaS . The sample gained an additional 4.0 mg. X-ray analysis of the sample confirmed that MgS was present,

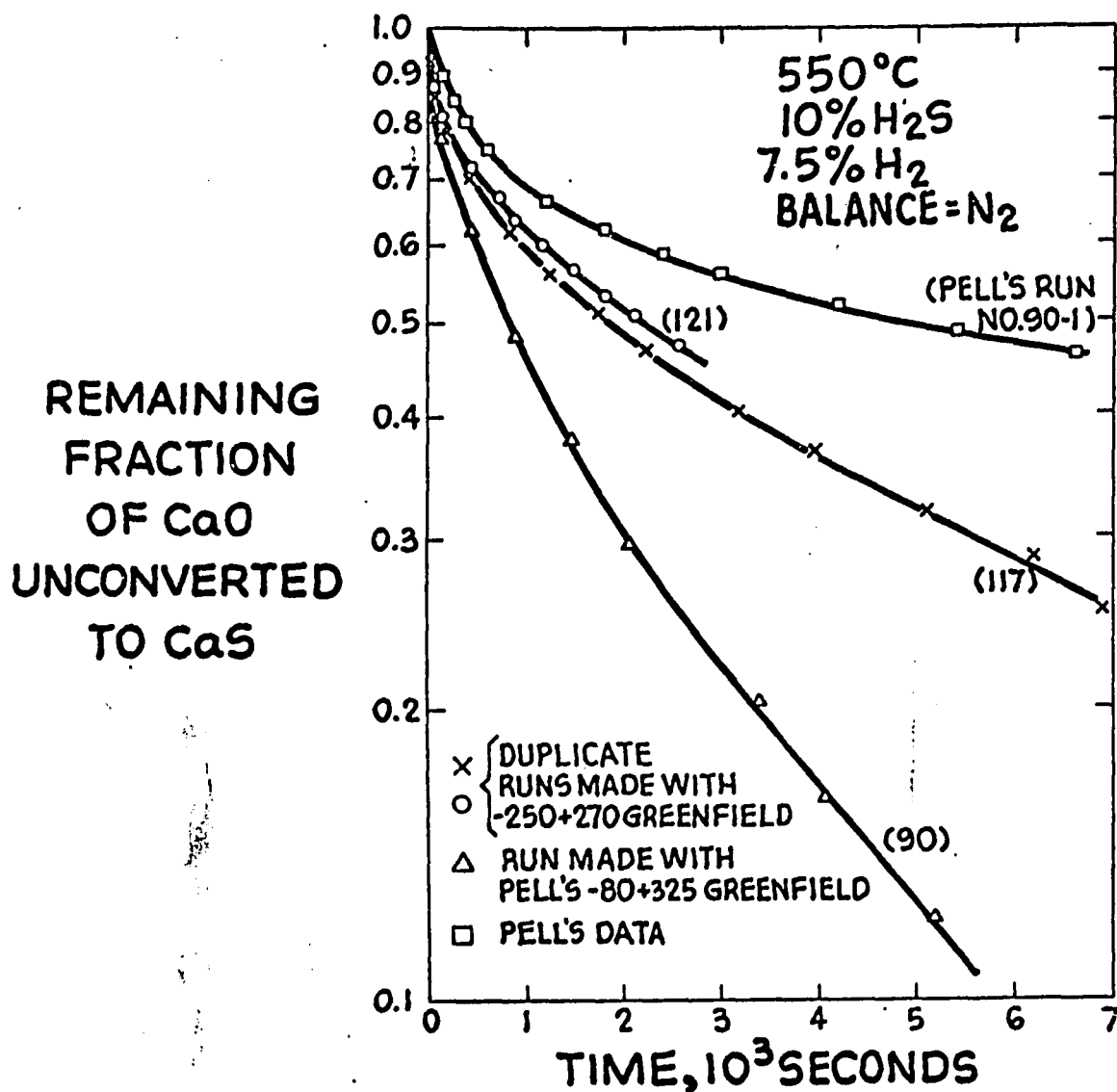


Figure 34. Comparison of data on the reaction of H₂S with fully calcined dolomite at 550°C and 10% H₂S for runs made with the dolomite used in this research and the dolomite used in Pell's research.

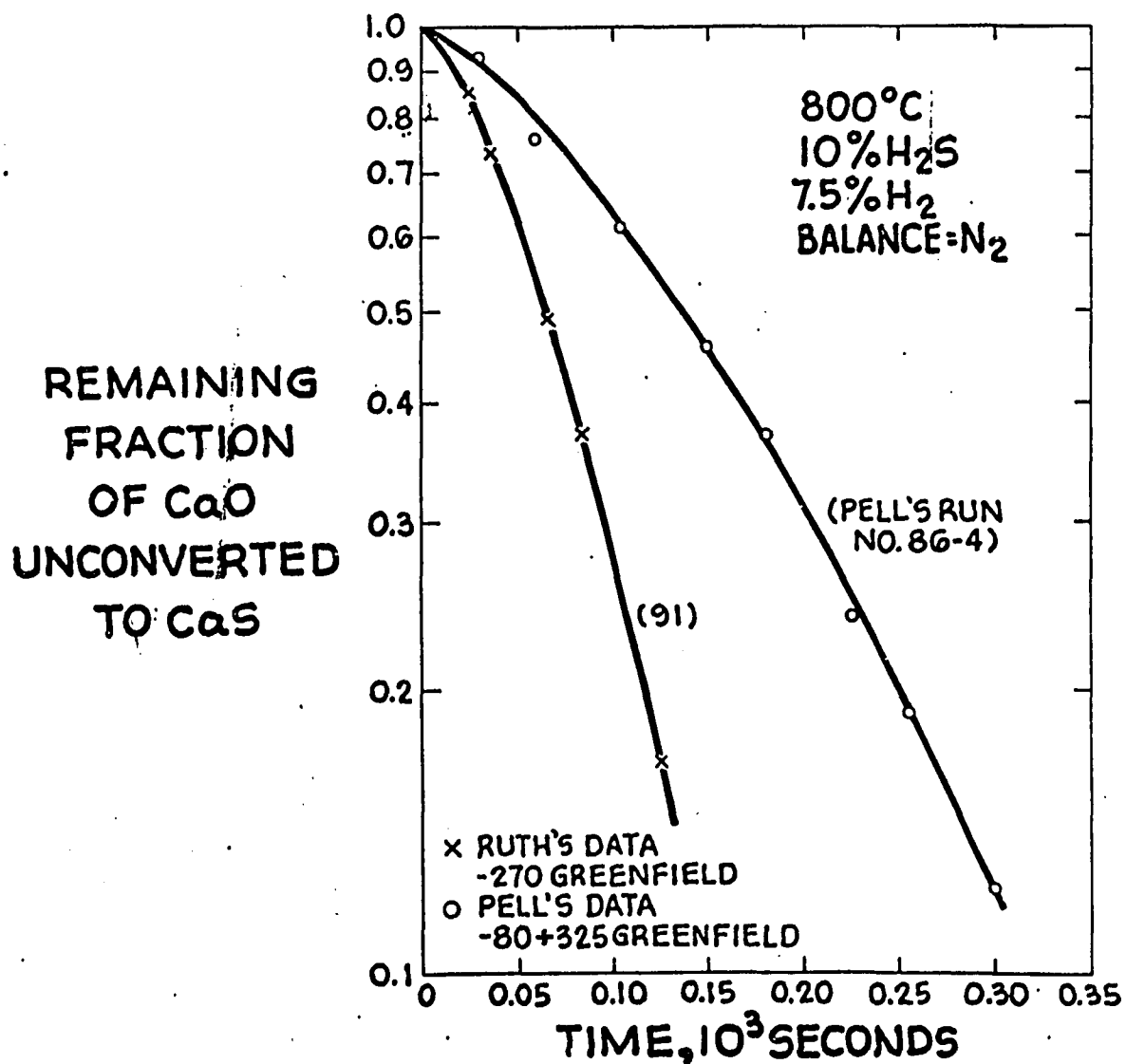


Figure 35. Comparison of the data of Ruth and Pell on the reaction of H₂S with fully calcined dolomite at 800° C and 10% H₂S.

and the 4.0 mg weight gain corresponds to about 60% conversion of MgO to MgS. This result is surprising because formation of MgS had never been reported by Pell even though he had made runs at temperatures as high as 900°C.

The reaction of MgO with H₂S is much slower at 800°C and 10% H₂S than the reaction of CaO with H₂S, which takes only about six minutes to achieve complete conversion. It should be noted that MgS can form only under conditions in which water is absent. Even low concentrations of water prevent formation of MgS because the equilibrium constant for the reaction



is very small (see Table 2)

7.09 Physical Measurements: Effective Diffusivity,

Surface Area, Electron Micrographs

The effective diffusivity was determined for a sphere of half-calcined dolomite, 0.745 cm in diameter, at 800°C with a gas containing 5% H₂S. With a particle of this size, we expected diffusion through a product layer of CaS, rather than chemical reaction, to be the rate controlling resistance. For reactions where product layer diffusion is controlling, a plot of $[1-3(1-x)^{2/3}+2(1-x)]$ versus time is linear, and the effective diffusivity of gaseous reactants in the solid reaction product can be

found from the slope (30). A linear plot, shown in Figure 36, was obtained from the data for the 0.745 cm sphere, and an effective diffusivity of $0.04 \text{ cm}^2/\text{sec}$ was deduced from the plot. The diffusivity ratio, which is the ratio of the effective diffusivity to the diffusivity in open space, was 0.041. This value of the diffusivity ratio was in fair agreement with the value of 0.066 obtained from measurements of the diffusivity made at room temperature according to the method developed by Weisz (31), which we have used to determine the effective diffusivity of helium in nitrogen in a cylindrical plug of $[\text{CaS}+\text{MgO}]$ prepared from half-calcined dolomite.

We measured surface areas, by applying B.E.T. theory to data on adsorption of nitrogen gas, of powdered samples of half-calcined dolomite, fully calcined dolomite, and $[\text{CaS}+\text{MgO}]$ derived from the reaction of H_2S with both half calcined and fully calcined stone. The results were about the same for each sample, $4 \text{ m}^2/\text{gm}$.

Figure 37 shows an electron micrograph of half-calcined dolomite. The sample used in the micrograph was the same -250+270 mesh Greenfield powder that was used in the kinetics runs. The diameter of a single particle from this powder is about one-half million Angstroms. The micrograph is a view of a small section of one particle, and individual crystallites are clearly visible.*

*See Addendum p. 173.

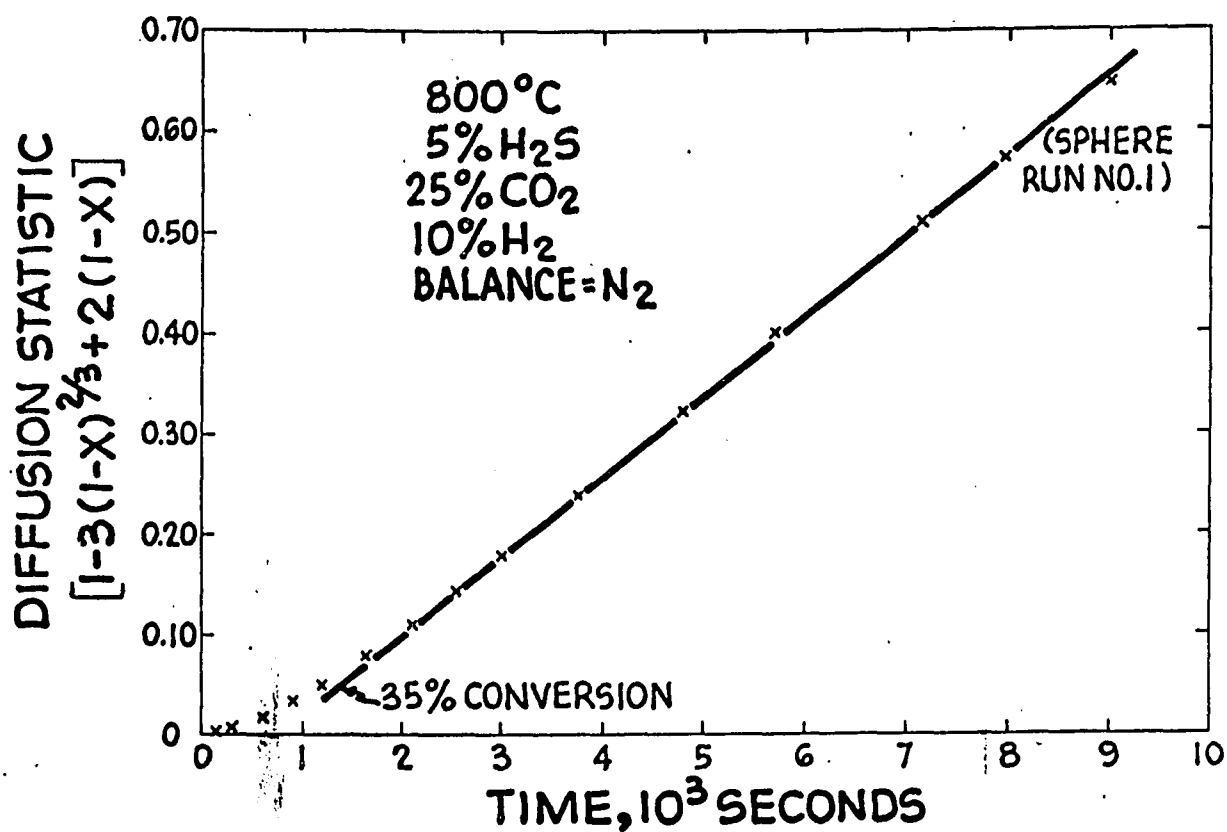


Figure 36. A run with 0.745 cm sphere of Greenfield stone at 800° C, 5% H₂S and 25% CO₂. Conversion data is plotted in the form of the diffusion statistic versus time.

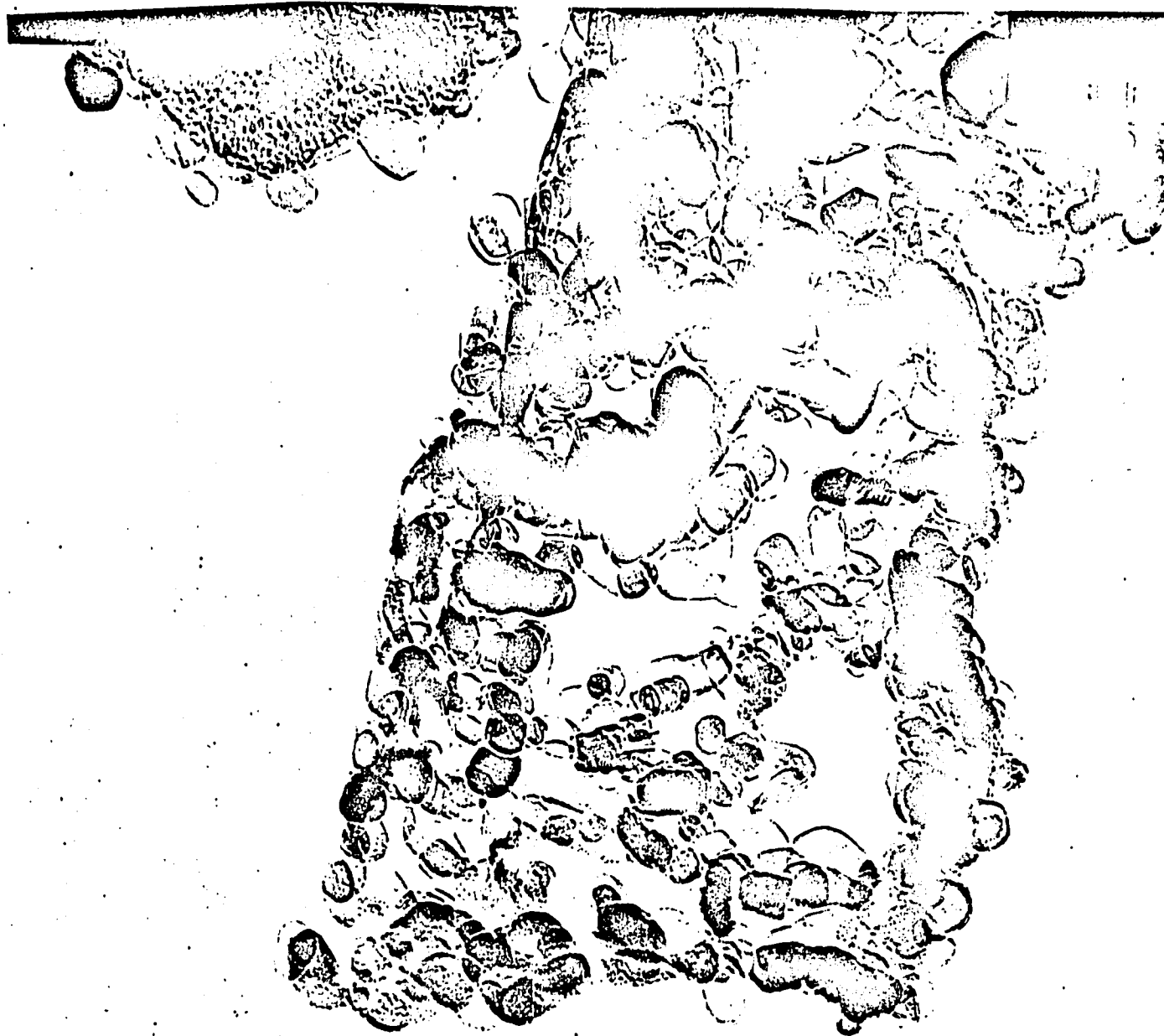


Figure 37. Electron micrograph of half-calcined -250+270

Greenfield powder, the dolomite used in this

research. Magnification = 189,500X.

8.0 Discussion of Results

The data presented in the previous section are now discussed in more detail. Because considerations of diffusion are important in heterogeneous kinetics, we present evidence to support our hypothesis that our data are essentially free of diffusion effects. We discuss the effect of temperature, H_2S , CO_2 , and H_2O on initial reaction rates. We elaborate on several alternative explanations for the spectacular effect of CO_2 , H_2O , and O_2 on the progress of the reaction and present a theory which we believe best accounts for these effects. Some examples of the variability in our experimental results are given, along with some possible explanations. We compare the rate of reaction of H_2S with half-calcined dolomite to that with ordinary CaCO_3 and also with fully calcined dolomite. This section concludes with some process implications of our work and suggestions for future work.

8.01 Influence of Diffusion on Reaction Rates

The rate of reaction of a powder with a gas can be influenced by the effects of diffusion both within particles and within the particle bed. Because diffusion effects must be absent to determine intrinsic reaction kinetics, we used a fine powder spread in a thin layer on the balance pan of

the TGA. We were convinced by both experimental data and numerical calculations that the particles we used were small enough and the particle bed shallow enough to cause diffusion effects to be negligible.

To test the hypothesis that reaction (B) takes place homogeneously, without diffusion effects, in finely powdered samples, we estimated the effectiveness factor for a particle of the size of our experimental powder. The effectiveness factor is the ratio of the observed reaction rate to the rate that would be observed in the absence of diffusion effects, i.e., when the concentration of gaseous reactant which the solid particle sees at its surface is maintained throughout the interior of the particle. This factor for our powder at 800°C and 1% H_2S was 0.97, indicating that intra-particle diffusion effects are probably absent (see Appendix 10.02).

Diffusion will have minimum influence on the overall conversion rate when the ratio of the diffusion rate to chemical reaction rate is highest. Now, the rate at which H_2S can be transported by diffusion is first order with respect to H_2S concentration. On the other hand, the rate of reaction (B) is less than first order in H_2S . Therefore, as we decrease H_2S concentration, the diffusion rate decreases more quickly than the intrinsic reaction velocity, and the

relative importance of diffusion becomes greater. One should appreciate also that, as temperature is increased, chemical reaction rates increase more rapidly than diffusion rates. Hence, a high temperature and low H_2S concentration, e.g. 800°C and 1% H_2S , represents the condition for which diffusion effects are likely to be most severe, and at other conditions the effectiveness factor can be expected to be greater than 0.97.

We made an alternate calculation which shows also that intra-particle diffusion effects are negligible at 800°C and 1% H_2S . Weisz (31) developed a criterion for diffusion which, under these conditions, predicts that the maximum experimental reaction rate which should still permit an effectiveness factor of 0.95, is equal to $0.80 \text{ mmoles/cm}^3\text{-sec}$. We observed a reaction rate of $0.27 \text{ mmoles/cm}^3\text{-sec}$, which indicates that the reaction is safely in the diffusion-free region (see Appendix 10.02).

To test for diffusion effects within the bed of powder, we made runs using different amounts of sample (bed depth). For runs at temperatures below about 650°C , samples of 20 - 30 mg gave the same rates as smaller samples. However, for runs made at higher temperatures, smaller samples gave higher rates. Figure 38 plots initial reaction rate versus sample size for runs made at 800°C and 1% H_2S . A sample size of about 3 mg is needed to prevent large

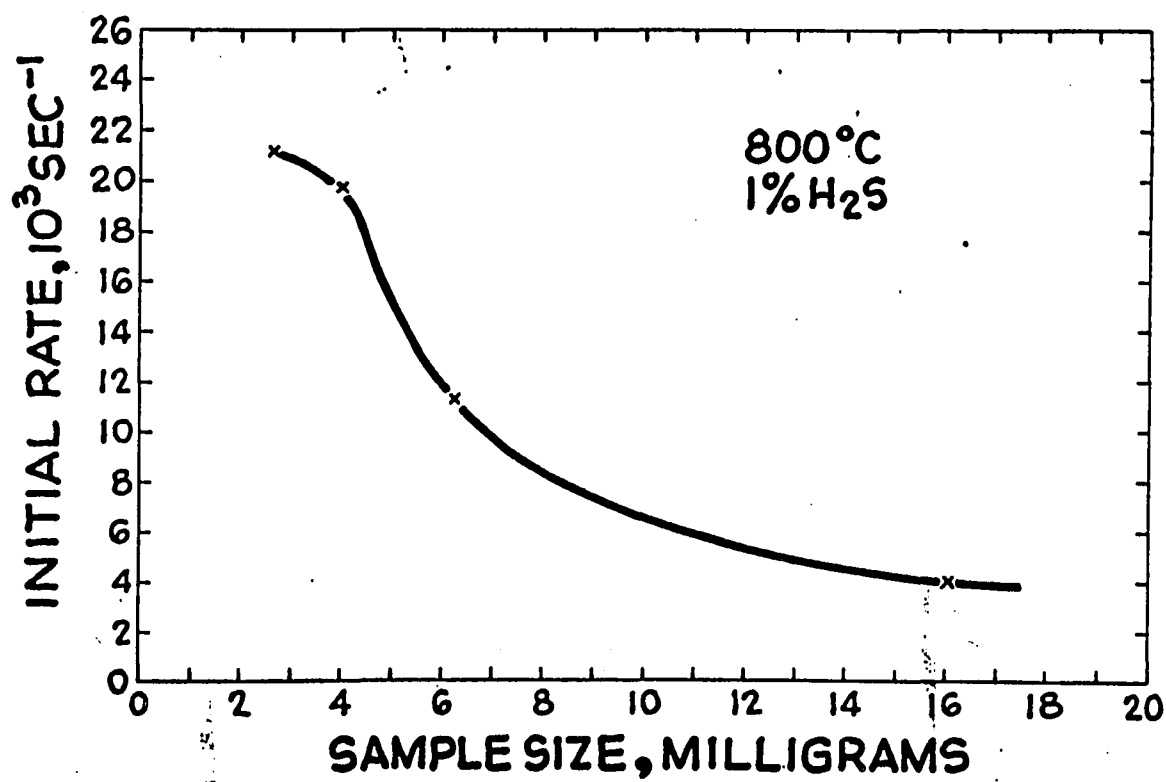


Figure 38. Initial rate versus sample size for runs made at 800° C, 1% H₂S.

diffusion effects. For other runs made at high temperatures, samples were kept small enough to minimize diffusion effects.

Figure 39 gives initial rates versus temperature for runs made with both large and small sample sizes, drawn in the manner of an Arrhenius plot. For large samples, the reaction rate is strongly modified by diffusion effects within the particle bed at higher temperatures; however, for small sample sizes, the straight-line Arrhenius behavior is obtained.

8.02 Initial Rate Behavior

When a solid reacts with a gas, it is a widely accepted principle that adsorption of the gas on the solid surface occurs prior to chemical reaction. Moreover, if the gas environment of the solid includes, in addition to the reactive species, other gases which adsorb but do not react, the reaction rate will be suppressed because of a reduction in the number of surface sites available for adsorption of the reactive gas. This situation is referred to as competitive adsorption.

For runs made at temperatures below 700°C, increasing the amount of CO₂ or H₂O in the reaction gas generally decreases the initial rate of reaction. Since it is likely that both CO₂ and H₂O can adsorb on the surface

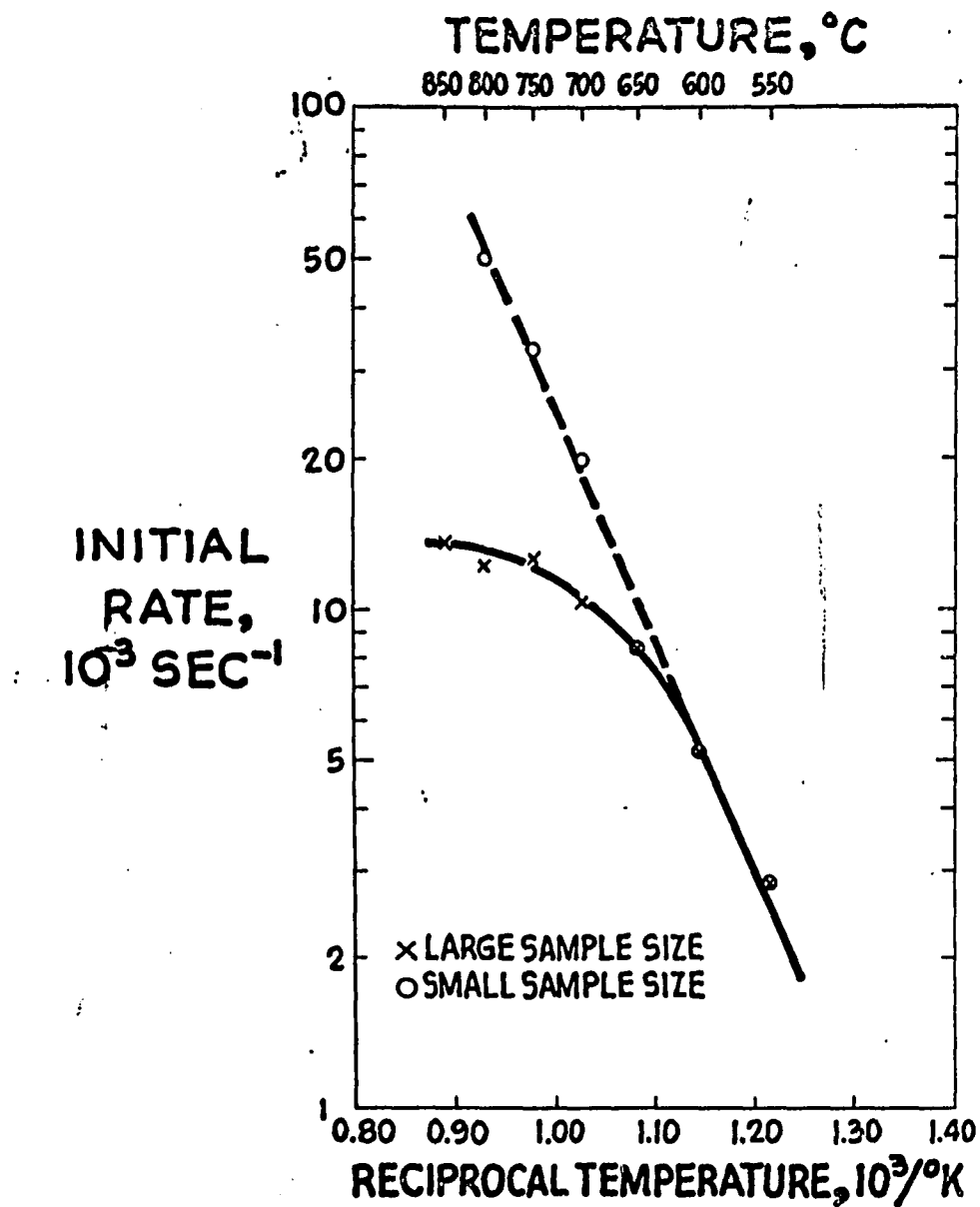


Figure 39. Arrhenius plots for runs made at 5% H_2S with both large and small sample sizes.

of a carbonate, this suggests competitive adsorption between H_2S and these other gases. Furthermore, the effect of increased CO_2 and H_2O is much greater at low temperatures; this may indicate that, relative to adsorption of H_2S , both CO_2 and H_2O adsorb more strongly as temperature is lowered.

Runs made at high and low CO_2 concentrations display different activation energies and orders of reaction (with respect to H_2S). This is not surprising in light of the probability that an adsorption mechanism is operating. There are numerous reaction mechanisms involving adsorption which predict changes in observed activation energy and order of reaction when gas composition is changed. Some simple ones are given by Laidler (32).

It is important to emphasize that the rate expressions given by equations (4) and (5) for low and high CO_2 concentrations, respectively, do not represent the actual reaction mechanism. Unlike the actual mechanism, which can be used with safety over all conditions for which the mechanism operates, these expressions are the simplest which satisfactorily fit the experimental data over the specified range of gas composition and temperature. As such, extrapolation to unexplored regions must be done carefully. Fortunately, these expressions are valid over

a wide range of temperature ($450\text{--}800^{\circ}\text{C}$ for low CO_2 and $550\text{--}750^{\circ}\text{C}$ for high CO_2) and H_2S partial pressures ($0.005\text{--}0.20$ atm) and moderate extrapolation beyond these limits is probably safe. However, each equation was derived to fit the data taken at an extreme of CO_2 concentration, i.e., low or high CO_2 . For conditions of intermediate CO_2 concentration, the expected rate will be bounded by the values given by these equations, and a satisfactory estimate of the rate can be obtained by linear interpolation. The equation for high CO_2 concentrations corresponds to 60% or 0.60 atm CO_2 .

We have not attempted to set down a rate expression derived from a postulated reaction mechanism. Such a rate expression will contain at least three constants and will depend on many factors, such as which gases adsorb, how strongly different gases adsorb, which step is rate controlling, and whether gases adsorb as molecules or as ions. There is some evidence, for example, that H_2S dissociates when it is adsorbed on calcined dolomite (33). In order to find the correct mechanism it is necessary to show that this mechanism fits the data much better than all others. This requires an extensive experimental program and generally far more precise data than is usually available.

The effect of CO_2 and H_2O displayed during the initial stages of reaction are quite small when compared to those effects which occur later on and which dramatically alter the progress of the reaction. These latter effects completely overwhelm those which occur earlier in the reaction and we believe they are caused by a phenomenon other than adsorption.

8.03 Effect of CO_2 , H_2O , and O_2 on the Progress of the Reaction

The spectacular effect of CO_2 and H_2O on the reaction of H_2S with half-calcined dolomite has been an intriguing discovery of this research. CO_2 , in some manner, prevents the reaction from quitting at low conversions of CaCO_3 ; H_2O does the same, but is more effective than CO_2 at lower temperatures. We have tried to account for these effects with simple explanations.

We first considered the possibility that an alternate, faster, reaction was occurring when the concentration of CO_2 was high. However, at either high or low CO_2 levels, both weight change and X-ray analysis indicated that the reaction product was chemically the same, CaS . An alternate reaction which occurred to us was:



Consideration of equilibrium showed us that this reaction was possible. We hypothesized that COS would be produced at high CO_2 levels via reaction (I).

If reactions (I) and (K) were indeed responsible for the effect of CO_2 , then the behavior typical of runs made at high CO_2 levels should be observed if CO_2 were increased at any time during a run. Experiment showed this not to be the case. A run was made at 600°C with 5% H_2S and 3% CO_2 . As expected, after about one minute, the reaction "died" at about 15% conversion. After 10 minutes the CO_2 was increased to 60%; no effect on the reaction was observed.

We subsequently made the discovery that if the CO_2 level was increased simultaneously with the addition of a pulse of a gas containing about 0.3% O_2 , the pulse lasting about 10 seconds, the reaction revived and continued to complete conversion at the high rate characteristic of the high CO_2 level. In repeat experiments the result was always the same: CO_2 alone had no effect on a solid that is already "dead"; CO_2 plus an oxygen pulse reactivated the solid and allowed complete conversion to be attained. It will be remembered that an O_2 pulse alone permitted only another increment of conversion.

We considered another possible explanation for the effect of CO_2 . Because high rates were obtained at the beginning of a run, followed by very slow reaction, we speculated that reaction conditions at the outset of a run might be different from those encountered later on. For example, we started each run by switching the gas flowing through the furnace tube from 100% CO_2 , used to half-calcine, to the reaction gas, which contains H_2S and lower concentrations of CO_2 . It is likely that when a run begins, the sample momentarily sees more CO_2 than is present in the reaction gas because of CO_2 lingering from calcination. We asked ourselves if this situation could be the reason for high initial rates.

To answer this question we performed two experiments. In the first we half-calcined a sample in a gas containing nitrogen and only 5% CO_2 . We then reacted the sample at 600°C with a gas containing 5% H_2S and 3% CO_2 . The result was typical of runs in which the sample was calcined in 100% CO_2 , shown for example in Figure 15.

In the second experiment, we half-calcined under 100% CO_2 , but before beginning the run, we flushed the furnace tube with a gas containing nitrogen and 3% CO_2 . Again, the result was typical of all other runs made at 600°C , 5% H_2S and 3% CO_2 .

These experiments convinced us that high initial reaction rates were not caused either by calcination procedure or the high CO_2 levels that probably occur at the start of all runs.

The effects of CO_2 and H_2O , both on initial reaction rates and on the overall progress of the reaction, are similar enough to cause us to believe that the mechanisms by which they promote reactivity are closely related. It is likely that oxygen, too, does its work in a similar way, even though only trace amounts are required.

Data at 550°C and high levels of H_2S and CO_2 , shown in Figure 29, tells us that the mechanism by which CO_2 promotes reactivity is hindered by H_2S . High H_2S levels appear to "overwhelm" the effect of increased CO_2 . At each temperature, there may be a critical ratio of CO_2 to H_2S which is necessary to ensure complete conversion of CaCO_3 .

8.04 Proposed Reaction Theory: Interfacial Blockage Model

We have observed a number of kinetic phenomena during this research that, to our knowledge, have not been reported elsewhere for non-catalytic gas-solid reactions. This may be due, in part, to the fact that a relatively small number of non-catalytic gas-solid

reaction systems have been studied as compared to, for example, simple thermal decompositions of solids.

The kinetic phenomena we refer to are the sudden break in reaction rate at temperatures of 600°C or less and low CO_2 concentrations (see Figure 15), the ability of increased CO_2 and H_2O to cause the reaction to continue to complete conversion of CaCO_3 (Figures 25 and 31), and the effect of pulses of a gas containing small amounts of oxygen (Figure 32). Of exceptional interest, too, are the behavior of runs made at 550°C with both high H_2S and CO_2 concentrations (Figure 29), and the run made at 650°C with 1% H_2S (Figure 14).

We offer a reaction model which can qualitatively explain the above effects. We suggest that temperature and gas composition affect the way in which CaS grows within the solid microstructure. It may be that the reaction "drops dead" when an impervious layer of "green" CaS forms upon a crystallite of CaCO_3 . Alternatively, in runs which do not drop dead, CaS may form a porous layer, so that the interior of the crystallite remains open to the action of H_2S . We hypothesize that high temperature, presence of CO_2 or H_2O , or an oxygen pulse, favors the latter condition and permits the reaction to continue until all of the CaCO_3 is consumed.*

*See also 13.0 Addendum, Results of Examination of Reaction Solids under Electron Microscope, p. 173ff.

In what follows, we elucidate on the above hypothesis and attempt to demonstrate that it fits well into the framework of generally accepted theory of gas-solid reactions.

Half-calcined dolomite contains 300-400 Å crystallites, oriented in the same way as in the original dolomite, and unoriented magnesium oxide crystallites. Moreover, both dolomite and calcite have a rhombohedral crystal structure, but magnesium oxide is cubic. Each particle of powder used in this research has a diameter of about 50 microns, or 5×10^5 Å, and contains on the order of 10^9 calcite crystallites. For reaction to occur, H_2S must diffuse from the mainstream of gas, through the complicated pore network of each particle, up to a crystallite of $CaCO_3$. We believe we are dealing with reaction conditions under which the observed reaction rate is not significantly affected by such diffusion processes, and we have provided evidence to support our belief (see Section 8.01).

Once H_2S has reached the surface of a $CaCO_3$ crystallite, reaction can begin. The first step in all gas-solid reactions, nucleation, is the establishment of an interface. In general, this will occur at the surface of a crystal or at points of relative disorder in the

crystal, such as dislocation networks, vacancies, interstitial clusters, or high grain angle boundaries (34). Nucleation is an activated process and will increase with temperature. Gas environment and the history of the solid also affect nucleation rates since they influence the relative disorder of various sites in the solid. Nucleation is sometimes a rate-limiting process, in which case a plot of conversion versus time often shows a sigmoid shape, characteristic of nucleation and growth phenomena. However, in many gas solid reactions, the initial nucleation step occurs rapidly over the entire surface and the interface established progresses thereafter in the direction of the center of the crystal. The reaction is deceleratory throughout, since the reaction interface progressively decreases in area. A model which has been found to hold for this situation is the "contracting cube" or "contracting sphere." The kinetic characteristics of the reaction are, of course, influenced by particle and/or crystallite size distribution.

The contracting cube model is applied most frequently to solid decompositions where there is no interfering effect of solid reaction product; the reaction rate is simply proportional to the surface of the undecomposed

kernel. In the reaction under study, however, a solid product layer is involved and its properties must exert some influence on the conversion rate. The degree to which the solid product influences the reaction depends on how effectively it blocks the access of gas to the reaction interface. If the solid product volume is considerably less than that of the original solid reactant, the product does not "cover" the reactant effectively due to cracks which are developed in the product layer, and the reaction continues unhindered. However, if the product volume is greater than the reactant volume, and no visible swelling occurs, the gas no longer has free access to the reaction interface, and the gas has to diffuse through the product layer to reach the interface. The reaction rate decreases progressively as the reaction proceeds due to difficulty in penetrating the barrier layer of progressively increasing thickness. In cases where the effective diffusivity of the solid product is low, the reaction may substantially cease when the barrier layer has been formed over all the available solid surface.

When nuclei are formed, thereby initiating reaction, there is a tendency for the product to maintain perfect registry across the interface, i.e., the natural position

of a given atom in the product is either precisely the same as in the reactant or at least one plane in the product is identical with one plane in the reactant (35). This phenomenon is called epitaxial growth, or epitaxy. There may even be a three-dimensional correspondence between the structures of the product and its host, called topotaxy (36).

A model for our reaction (B) can be hypothesized. It is reasonable to assume that, in the reaction of H_2S with half-calcined dolomite, crystallites of CaS grow epitaxially behind the moving reaction interface. However, even in epitactic or topotactic reactions, the product usually shows markedly deteriorated crystallinity compared to the starting material (36). Hence, the CaS crystallites may be extremely small and imperfectly oriented. To the reaction gas, the surface will have an "amorphous" appearance having relatively little porosity. Consequently, when a sufficient thickness of product layer is attained, H_2S can no longer reach the interface, and the reaction stops.

In our hypothesized reaction model, we propose that, simultaneous to the above, there occurs the process of annealing or crystallization, whereby the product

crystallites grow and regain their more relaxed crystal lattice structure. CaS, in its normal cubic crystal state, has a lower molar volume than CaCO_3 , so that the annealing process is accompanied by shrinkage of the CaS, causing cracks which facilitate the penetration of H_2S through the product layer to the reaction interface. The progress of the reaction will depend on the relative magnitudes of the interfacial reaction rate and the annealing rate. If the reaction rate is much faster than the annealing rate, the product CaS tends to be amorphous or microcrystalline and relatively non-porous. On the other hand, when the annealing rate is faster than the reaction rate, the CaS consists of coarse cubic crystals in a porous layer. Figure 40 illustrates schematically these two cases.

In our model, we can explain the effect of temperature and gas environment on the reaction of H_2S with half-calcined dolomite in terms of their effect on the reaction and annealing rates.

At temperatures of 600°C or below, the reaction stops at low conversions because the reaction rate is faster than the annealing rate, and a thin layer of CaS over the CaCO_3 crystallites is sufficient to block the reaction.

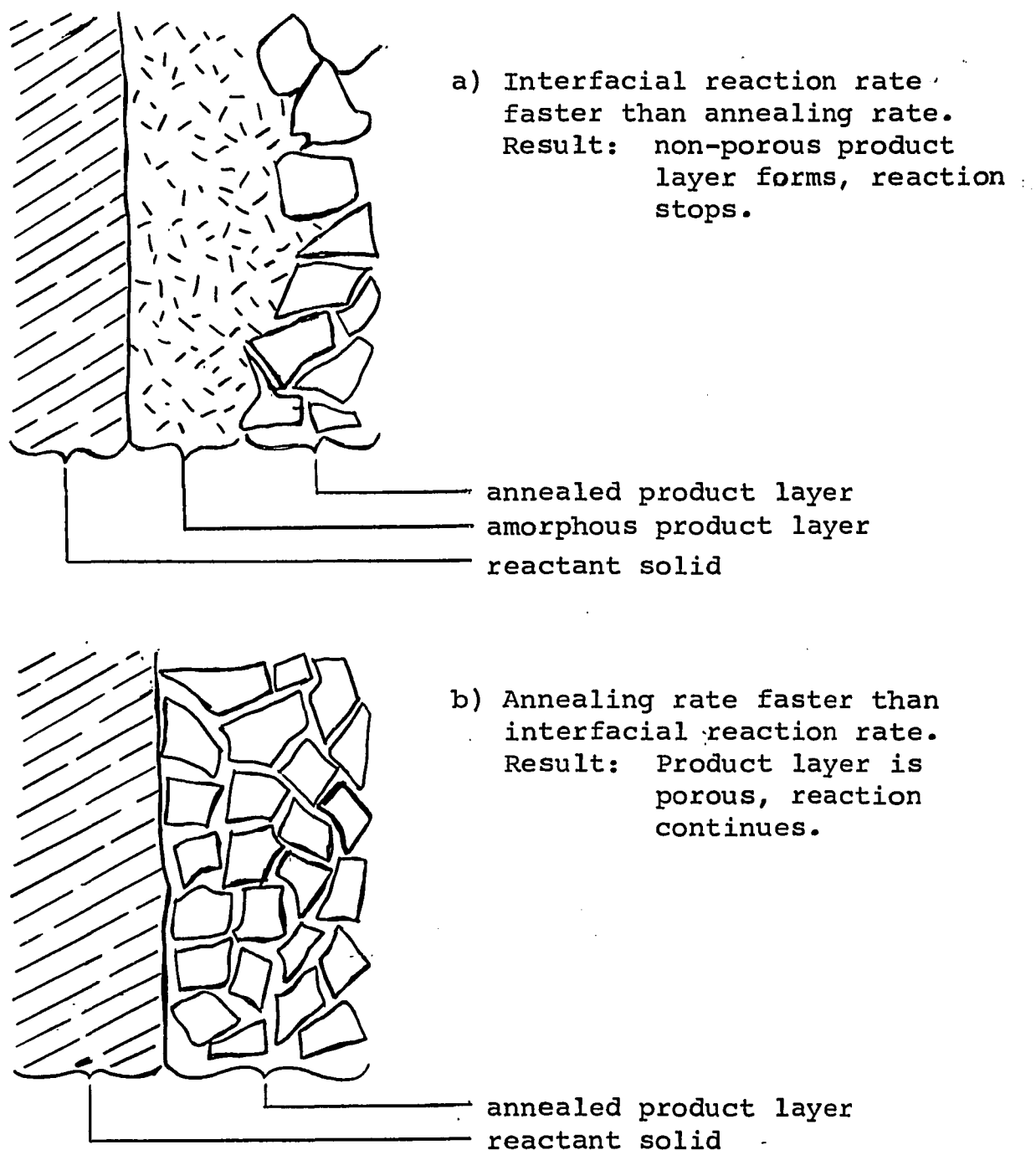


Figure 40. Schematic illustration showing that the product layer which forms on the surface of a crystallite of reactant solid can have different structures depending on the relative magnitudes of the interfacial reaction rate and the annealing rate of product.

As H_2S concentration is raised, the break in reaction rate occurs at lower conversions because the reaction rate increases relative to the annealing rate.

However, if the activation energy for the annealing process is greater than that for the interfacial reaction rate, the net result of an increase in temperature will be an increase in the coarse crystallinity of the product layer and a concomitant increase in the ultimate degree of conversion of CaCO_3 .

Hence, runs made at 650°C , particularly with 1% H_2S , proceed to higher conversions than runs made at lower temperatures. Runs made at 700°C or above proceed to substantially complete conversion and do not show any break in reaction rate.

In our model, the effect of CO_2 and H_2O on the final degree of conversion must be due to the ability of these substances to accelerate the annealing or growth of product crystallites. Thus, CO_2 and H_2O , in some as yet unknown manner, are capable of increasing the mobility of certain species in the crystal lattice of the product. At low temperatures, where the annealing rate is low, CO_2 and H_2O have a profound effect on the progress of the reaction. At high temperatures, however, the annealing rate is

already sufficiently fast to allow the reaction to proceed at a good rate, so that the effect of CO_2 and H_2O is small.

The above theory, which we will subsequently refer to as "interfacial blockage", can also explain the behavior of runs made with 5% H_2S and 20% H_2S at 550°C and high CO_2 concentrations. The run made at 5% H_2S and 57% CO_2 continues to complete conversion because the annealing rate is faster than the reaction rate, although probably not by a wide margin. Raising the H_2S concentration to 20% increases the reaction rate enough to prevent the reaction from reaching complete conversion. The reaction is quite sensitive to small changes in CO_2 concentration at 550°C and 20% H_2S , as seen from the runs at 48% CO_2 and 60% CO_2 , because at these conditions the annealing and interfacial reaction rates are presumably of the same order of magnitude.

The effect of O_2 differs from that of CO_2 or H_2O in the sense that, unlike CO_2 or H_2O , small amounts of O_2 have an effect on the reaction. Also, oxygen revives the solid after the reaction has "died", whereas CO_2 does not have this ability. Oxygen must affect the annealing rate too, but apparently in a different manner than CO_2 or H_2O .

The literature contains evidence to support the

plausibility of the interfacial blockage model. For example, in the reduction of iron ore, experimental conditions are known to effect the properties of the reaction products. Variations in physical conditions of the oxide during reduction, such as the formation of cracks and pores, affect the reduction rate. These changes depend, in turn, on chemical composition, physical condition of the sample, and experimental procedures. Consequently, the reduction rate has been presumed by different workers to be controlled by both diffusion (37) and interfacial reaction (26).

Henderson (38), in studying the reduction of hematite ore by hydrogen, found that the initial and overall reaction rates increased with temperature from 400° to 550°C , but decreased from 550°C to about 700°C . He attributed this behavior to changes in the physical properties, above 550°C , of the envelope of product iron which surrounds the unreduced oxide. Above this temperature, Henderson proposed, the iron becomes less permeable to water, which is a product of the reduction, so that the reduction rate decreases. From 700°C to 900°C , cracks formed in the iron due to the buildup of water pressure, and the initial and overall reduction rates again increased.

Another example comes from a review of the experimental

results on the decomposition of magnesite. Hüttig, et al. (39), have shown that annealing may occur at temperatures as low as 600°C and is quite rapid at temperatures near 800°C.

CO₂ has been observed to accelerate the annealing of product crystallites (40,41,42). In the decomposition of magnesite, product crystals are found to grow in increasing atmospheres of CO₂ (43). A similar effect was observed for fully calcined dolomite. This provides evidence for the hypothesis that CO₂ can increase the mobility of certain species in the crystal lattice. With regard to H₂O, many decomposition and dehydration reactions are catalyzed by the presence of water vapor (44-52). Garner (41) hypothesizes that the effects of water vapor are related to its ability to accelerate the rearrangement of disorganized material to crystalline nuclei of a new phase, a process which is accompanied by shrinkage of the new product and the formation of cracks.

8.05 Consideration of Alternative Reaction Models

We are aware that because the interfacial blockage model can qualitatively explain the observed kinetic behavior, there is no reason to assume that it is the correct model or to exclude all others. In fact, at least two other reaction models were considered, but were

later discarded because interfacial blockage was judged more acceptable.

In his earlier study of the reaction of H_2S with fully-calcined dolomite, Pell reported that some low temperature runs did not achieve complete conversion. He also reported an effect of steam, similar to that which we found for the reaction of H_2S with half-calcined dolomite. Pell correlated his data using a model based on the hypothesis that activated adsorption of H_2S by unreacted CaO hinders the reaction rate, the adsorption being in general not at equilibrium. We could have used an analogous elaboration of Pell's adsorption model to explain our kinetic results but we believe our model is much more nearly in accord with the generally accepted theory of non-catalytic gas-solid kinetics. We have also put Pell's model to experimental test and the results, although not conclusive, do not give any indication that the rate is hindered by adsorption of H_2S .

We reasoned that if adsorbed H_2S was responsible for the break in reaction rate, then allowing H_2S to desorb would permit another increment in conversion when H_2S was again turned on. In a run made at $550^{\circ}C$ and 10% H_2S with fully calcined dolomite, H_2S was turned off after the reaction rate had flagged and the sample was held in N_2

for several hours, sufficient time to allow for desorption according to Pell's estimate of the desorption rate constant at 550°C . When the sample was again exposed to 10% H_2S , we noted no significant increase in conversion, and we concluded that adsorbed H_2S was not hindering the rate. We could not make an interrupted run with half-calcined dolomite because we discovered that CO_2 has the power to regenerate CaCO_3 from CaS . Since CO_2 must always be present over CaCO_3 , regeneration would have occurred during the time the H_2S was turned off.

We considered another model, involving pore-plugging, which was more appealing than the adsorption model. Plugging of the pores in a reacting solid is known to be the reason some reactions quit before reaching complete conversion. An example is the reaction of limestone or calcined dolomite with SO_2 contained in flue gases to produce CaSO_4 . It has been shown that the reaction rate decays exponentially as sulfation proceeds until the pores are filled with reaction product; the ultimate capacity of the sample is determined by the pore volume available for product accumulation (11).

Pore-plugging is a possibility when CaS is the product; however, it is unlikely since CaS has a smaller molar volume than the CaCO_3 it replaces. Also, the effects of

temperature and gas environment are more conveniently explained by the interfacial blockage model.

We conducted two experiments designed to distinguish between the pore-plugging and interfacial blockage models. In the first, we reasoned that we could eliminate any pore plugging effects by reducing the size of our powder down to the size of crystallites. We were able to prepare a sample of powdered dolomite in which the particle size was about one micron; to further reduce the possibility of pore-plugging we diluted the sample with one micron alumina to 15 weight percent dolomite. In two runs made at 600°C , 5% H_2S , and 3% CO_2 , the reaction proceeded to an average of 20% conversion before quitting, a figure typical for runs made at these conditions with our standard dolomite powder containing 50 micron particles. Unfortunately, the one micron powder used in this experiment was still an order of magnitude larger than the crystallite size; however, if pore-plugging were responsible for the break in reaction rate, one could have reasonably expected a reduction in particle size by a factor of fifty to cause an observable increase in ultimate conversion.

In a second experiment we reacted a 0.78 cm sphere at 600°C with a gas containing 5% H_2S and 3% CO_2 . We

reasoned that if pore-plugging were occurring, then with a particle this large we should see a decrease in the ultimate degree of conversion. However, there was no significant difference in the conversion attained and, consequently, the presence of pore-plugging was not indicated.

8.06 Variability of Results

We have observed considerable variability among runs made at the same conditions. This variability is too great to be explained by differences in run temperature or gas composition, which we estimate we have reproduced to better than $\pm 5^{\circ}\text{C}$ and $\pm 5\%$, respectively. We do not suspect calcination conditions to be responsible for much variability because the calcination procedure is nearly identical for all runs.

Figure 41 shows the variability for two pairs of runs. Figure 42 gives $\log(1-x)$ plots for six runs made at 650°C , $1/2\%$ H_2S , 60% CO_2 , and 39.5% H_2 . The percentage deviation between the amounts of time needed to achieve a given conversion for runs made at identical conditions depends on the fractional conversion of CaCO_3 . For example, for the runs made at 700°C with 20% H_2S , the amounts of time needed to achieve 50% conversion differ by 69% , whereas the difference for 80% conversion is 33% .

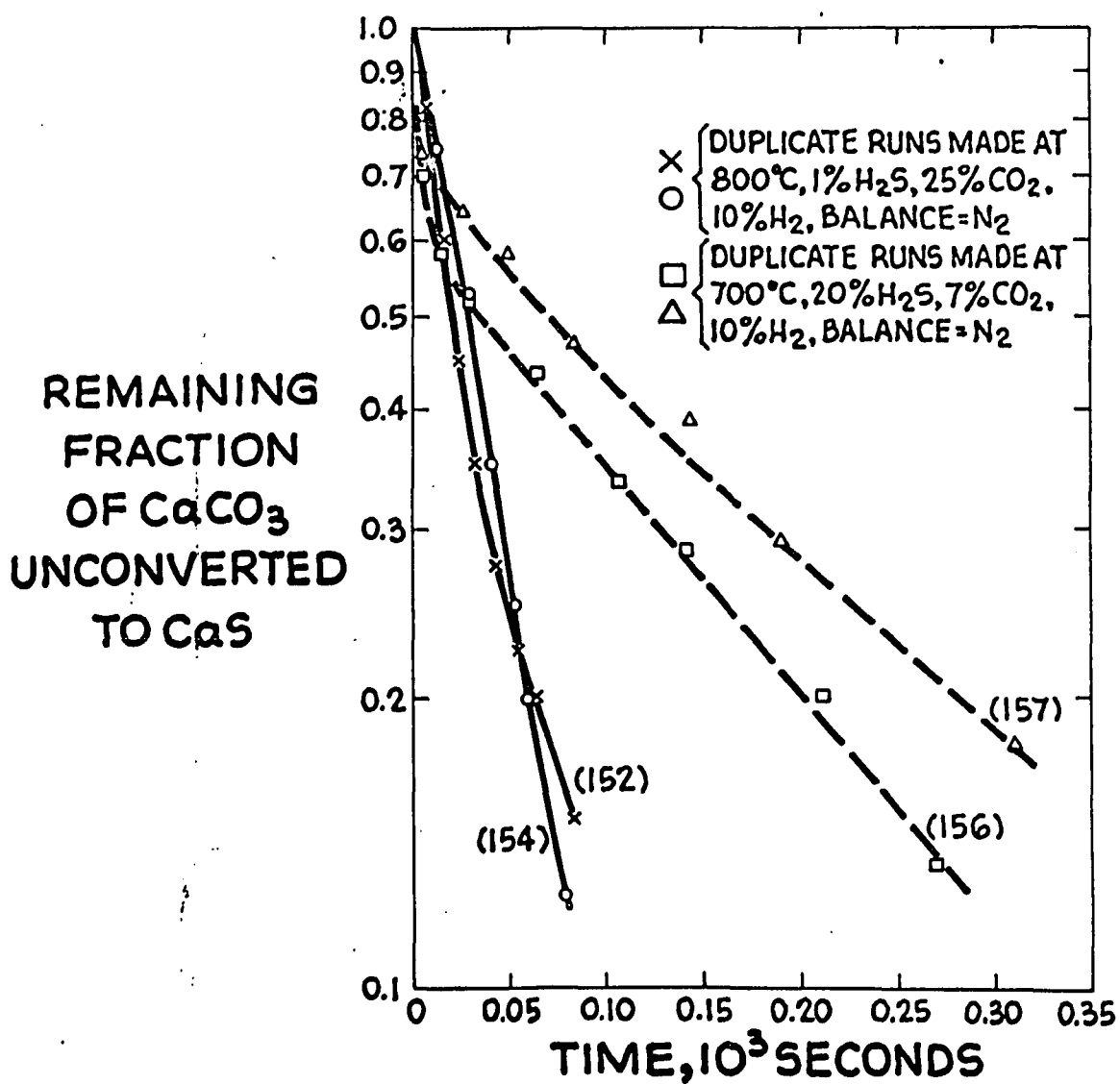


Figure 41. Log(1-x) plots for duplicate runs at 800°C, 1% H_2S , 25% CO_2 and at 700°C, 20% H_2S , 7% CO_2 .

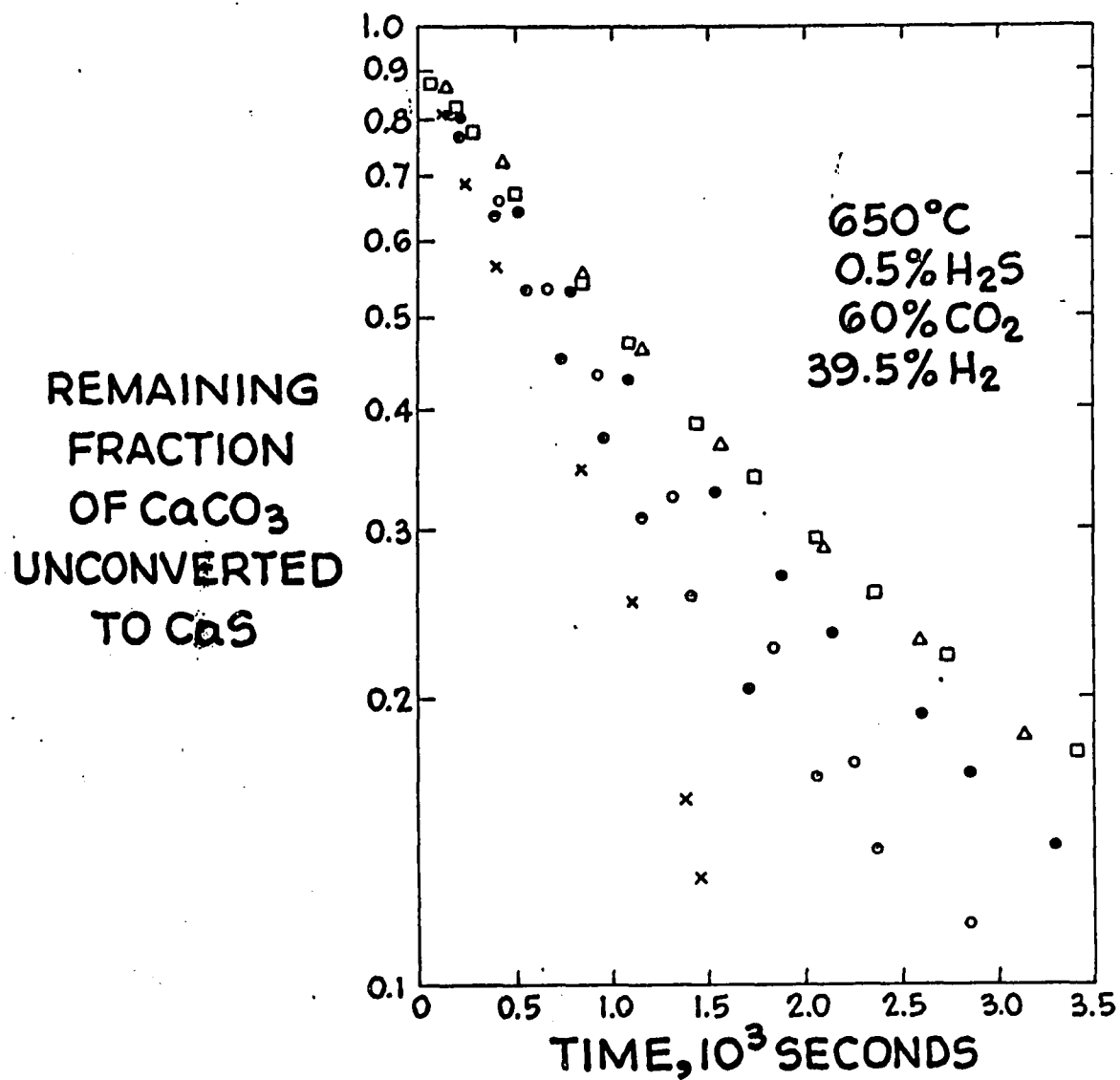


Figure 42. $\log(1-x)$ plots for six runs made at 650°C, 0.5% H_2S , and 60% CO_2 .

Part of the apparent deviation between runs may not be real, but may be the effect of errors in the capacity, or weight change corresponding to total conversion, which is needed to calculate fractional conversion. Even small errors in the capacity can cause substantial changes in the $\log (1-x)$ plot at higher conversions. For most runs, capacities were determined in the standard manner described in Section 6.04; however, occasionally this capacity was checked by raising the temperature at the end of the run. Frequently, particularly with small samples used at higher temperatures, the capacity determined by raising the temperature was smaller than the capacity determined by the standard method. It is likely that this discrepancy was caused by small amounts of impurities, such as silica or organics, present in the sample.

Initial rates show somewhat less variability than overall conversion-time data. Tables 3 and 4 give data for many duplicate runs. The average deviation of initial rates from the mean initial rate is about 8%. This is quite good agreement when one considers the conditions under which initial rates are measured. Before the run begins, the sample is kept under CO_2 . To begin a run, the CO_2 is turned off and the reaction gas mixture is

turned on. The sample, at the outset of a run, sees a changing gas atmosphere; however, because the reaction mixture is likely to be nearly in plug flow, the time interval over which the gas composition is changing is small compared to the time interval over which the initial rate is measured. To determine the initial rate, a tangent is drawn to the initial portion of the weight vs. time curve, and the slope of the tangent is measured. The procedure is slightly complicated because, due to the changing of gas flows, there is usually a bump in the curve at time equal to zero.

While changes in structure of the solid appear to be an important influence on the rate toward the latter part of a run, one would expect initial rates to be nearly free of such influence. Moreover, changes in solid structure which take place during reaction would probably be more sensitive than intrinsic kinetics to small variations in sample composition, temperature, gas composition, or time-temperature-environment history of the sample. This may explain why initial rates can be more nearly reproduced than conversion vs. time data for the entire run.

Pell's work, too, with fully calcined dolomite,

has shown much variability in reaction rate between runs conducted at identical conditions. This behavior has been particularly striking at low temperatures, 550°C for example. Unfortunately, the discrepancy between the data of Pell and Ruth, described in Section 7.08 and shown in Figure 34, cannot be explained by the variability in runs made at 550°C . The run made by Ruth with Pell's dolomite lies well outside the range of variability of Pell's runs. One explanation for the higher rates obtained by Ruth is that Pell's runs were hindered by diffusion within the bed of powder resting on the sample pan. However, this is an unlikely explanation, even though Pell used large sample sizes of typically 200-300 mg., because Pell had reacted 6 mm. spheres at 625°C without observing appreciable diffusion effects.

Variability remains one of the puzzles of both Pell's and Ruth's researches, not yet really adequately explained.

8.07 Reaction of H_2S with Limestone and Calcite

A porous solid with an appreciable internal surface area is produced when dolomite is calcined; half-calcined

dolomite is an intermingling of tiny calcite crystallites (300-400 Å) with MgO. For this reason one would expect half-calcined dolomite to react far more vigorously with H_2S than would ordinary CaCO_3 . Runs made with powdered calcite and an argillaceous limestone at 800°C and 5% H_2S confirm this expectation. Figure 43 shows that half-calcined dolomite is remarkably more reactive with H_2S than either calcite or limestone. For these materials 30% conversion to CaS was attained only after 7000 seconds, and at this conversion the rate had become extremely slow. Half-calcined dolomite achieved this conversion in less than 5 seconds.

8.08 Comparison of the Rates of Reaction of H_2S with Half-Calcined and Fully Calcined Dolomite

The present work has led to the important discovery that the reaction of half-calcined dolomite with H_2S is faster than the reaction of fully calcined dolomite, under some conditions amazingly faster. For example, at 800°C and 5% H_2S , the time for the half-calcined material to achieve 50% conversion is only 14 seconds, while it is 280 seconds for the fully calcined solid; at 700°C and 5% H_2S , the times for 50% conversion are 40 seconds and 500 seconds, respectively. It is only at conditions where

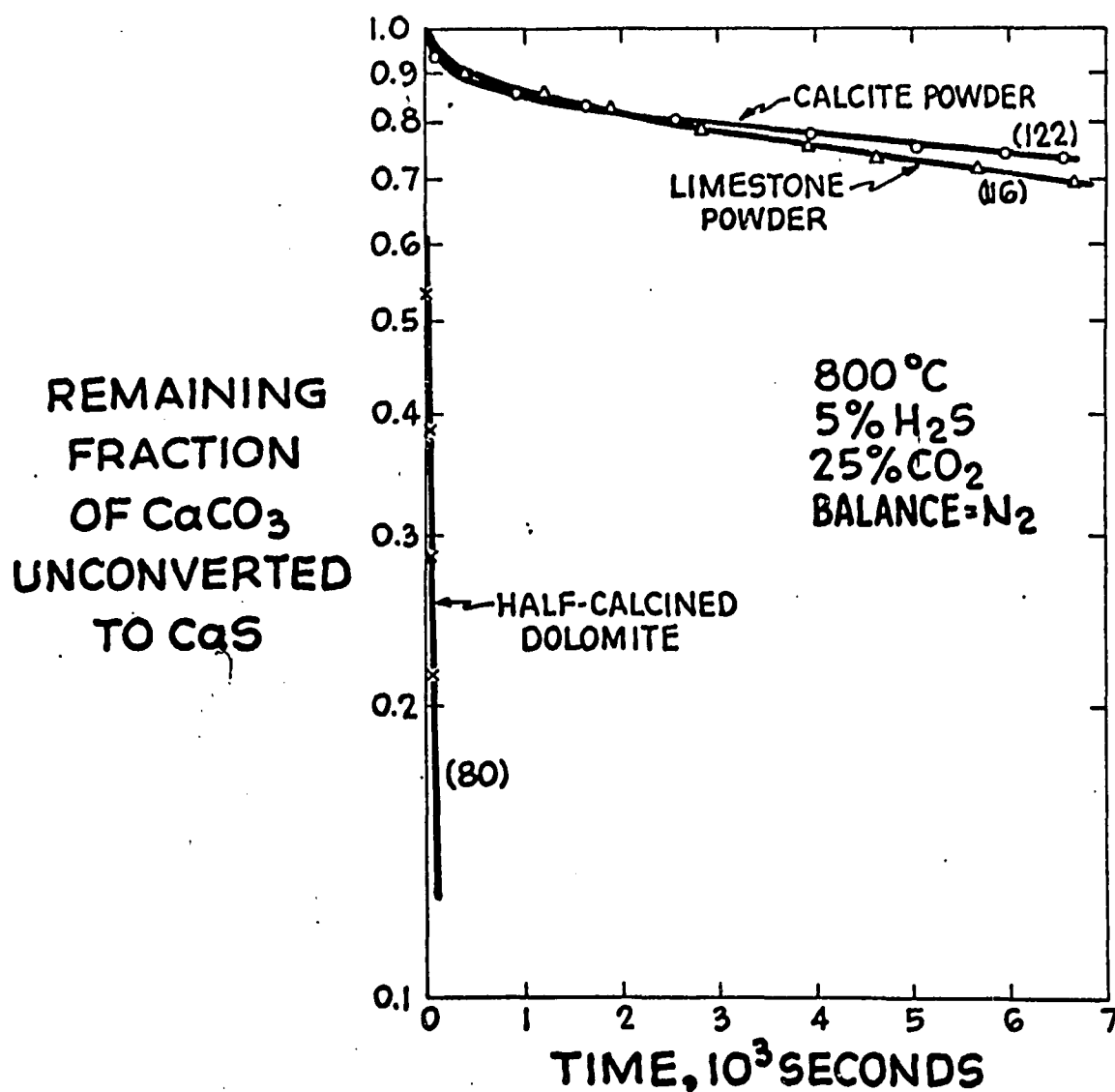


Figure 43. Comparison of $\log(1-x)$ plots for runs at 800°C, 5% H_2S , 25% CO_2 , made with half-calcined dolomite, calcite, and limestone.

the reaction of H_2S with half-calcined dolomite quits at low conversions, typically low temperatures, low CO_2 concentrations, and high H_2S concentrations, that fully calcined dolomite achieves a given conversion faster than half-calcined dolomite.

It should be remarked that in Pell's study of the reaction of H_2S with fully calcined dolomite, calcinations were conducted at 925°C , a moderate temperature from the standpoint of sintering of the calcined material. We are aware of the drastic decline in reactivity of calcined dolomite prepared at temperatures beyond about 1025°C .

It is interesting to note that the powdered Greenfield dolomite used by Pell in his work may be more reactive than the sample of Greenfield powder used by Ruth in this current study (see Figure 34 of Section 7.08).

Both Pell's work with fully calcined dolomite and Ruth's work with half-calcined dolomite have shown considerable variability among runs made at the same conditions (see Section 8.06).

8.09 Data Correlations

We have succeeded in correlating, with temperature and H_2S concentration, initial rates for runs made at

low (eqn. 4) and high (eqn. 5) CO_2 concentrations. Figures 18, 19, and 20 show that these equations fit our initial rate data well. For some runs, there is good agreement for conversions of over 50%; however, for many runs significant deviations occur for conversions over only about 10%. A limitation of our initial rate correlation is that it does not predict whether reaction (B) continues to complete conversion or "dies" at low conversions.

Clearly, it would be useful to have a correlation which gives conversion vs. time for the complete reaction. We have developed such a correlation along empirical lines. In it we have included the variety of kinetic complexities which we have observed for reaction (B), particularly the break in reaction rate at low temperatures, and the effect of H_2S and CO_2 on the progress of the reaction. Understandably, the correlation is complex and only approximates the actual data. However, it does predict whether or not the reaction goes to complete conversion and gives the approximate conversion at which the rate flags if total conversion is not attained.

Appendix 10.05 gives the empirical data correlation, along with its description and examples of its fit to the experimental data.

8.10 Process Implications

In all probability, the most important thing this research has taught us is that kinetic data on the reaction of H_2S with half-calcined dolomite has little relevance to a commercial process in which this material is used as an agent to capture sulfur. The reason for this is that H_2S reacts so vigorously with half-calcined dolomite at the temperatures of interest in a commercial process, that reaction kinetics are no longer a limiting factor in the design of equipment. For example, we have calculated that the width of a filter, of the type shown in Figure 6, to remove 99% of the H_2S from a fuel gas at 760°C , would be under one centimeter (see Appendix 10.06). Mechanical considerations alone would lead a designer to specify a width greater than this.

At this stage of our research effort, it is of the greatest importance to obtain data on material which has undergone one or more cycles of sulfur absorption and regeneration. We have determined that kinetics do not pose any problems for fresh, uncycled material, but we know nothing of the rates for material which has undergone cycling, expect that they are likely to be lower. The design of sulfur absorption equipment may well still

depend on the kinetic characteristics of recycled dolomite.

Reasons for the decline of a solid's reactivity when it is cycled have been partly given by theory. Cycling causes annealing of the solid, which has two major consequences: increase in average crystallite size of product and the removal of dislocations and other defects or surface imperfections (52, 34, 39). The former results in a decrease in the surface area of the resulting product, and the latter in the removal of potential sites for product nucleation. Consequently, with every cycle the crystals will anneal to a greater extent until a steady crystallite size is attained. The surface areas and the solid reactivity will, therefore, be lower than for the original solid. Thus, the mechanism for deactivation observed for many industrial solids is closely related to the process of annealing.

Only one type of dolomite has been used in this research, that from the Greenfield formation in Ohio. Greenfield dolomite had been reported in earlier work to be a highly reactive type (16). If dolomite is employed on a commercial scale to desulfurize fuels, many varieties of this stone will be used and the designer of such processes should keep in mind that not all dolomites are equally reactive.

The present work has shown that the reaction of H_2S with half-calcined dolomite is far more vigorous than the reaction with fully calcined dolomite. For this reason, half-calcined dolomite is likely to be the preferred solid for commercial use. Moreover, half-calcined dolomite has the advantage that a calcination step is not required in each cycle after the regeneration of $[\text{CaCO}_3 + \text{MgO}]$ from $[\text{CaS} + \text{MgO}]$. This means that the solid is not subjected to the higher temperatures required to convert CaCO_3 to CaO ; therefore, half-calcined dolomite is likely to be a better solid than fully calcined dolomite with regard to maintaining good activity with repeated cycling.

The unusual kinetics observed at lower temperatures will be of little interest in a sulfur removal step operated, for example, at 760°C . However, these phenomena may provide information useful for the forthcoming study of the regeneration reaction (C), to which desulfurization reaction (B) is the back reaction. The regeneration reaction will be carried out at lower temperatures, about 550°C .

If the process encounters unexpected difficulties, then it is possible that knowledge of the low temperature kinetics will be useful even for the desulfurization reaction, especially if the reaction is carried out in a

fluidized bed. Although we plan to use a panel-bed filter charged with half-calcined dolomite to achieve desulfurization of the raw fuel gas, Squires has proposed an alternative process wherein a unitary operation may carbonize coal and produce low-sulfur gaseous, liquid, and solid fuel products (4, 55). The fuel processing vessel would house three fluidized-solids zones; desulfurization using calcined dolomite would occur in the middle zone.

As an illustration of how one of our kinetic curiosities can conceivably influence a commercial process, consider the oxygen effect (see Section 7.05). Contact with traces of oxygen reactivates partially sulfided dolomite and permits further absorption of sulfur to occur. In a fluid bed gasifying coal, and utilizing dolomite to desulfurize the products, small amounts of oxygen are likely to be present, especially near the air inlet, due to incomplete utilization of the incoming air. It is probable that, because of the vigorous mixing characteristic of fluid-bed operation, dolomite will be periodically exposed to an atmosphere containing traces of oxygen. Hence, because of exposure to oxygen, the desulfurization performance might be found to be better than expected.

The above example is analagous to an observation made by F. J. Dent (19) concerning the gasification of carbon. Dent reported only 60% utilization of steam, when he gasified carbon with steam in a fixed bed. However, in a fluidized-bed operated at the same temperature, 99.6% steam utilization was realized. Dent explained the difference between fixed bed and fluidized-bed performance by hypothesizing that each granule of carbon in the fluidized-bed was reactivated each time the mixing of the solid in the bed brought the granule near the bottom, placing it in contact with fresh steam. In the fixed bed, on the other hand, the static carbon granules near the gas exit, where H_2 and CO left the bed along with unreacted steam, were continuously in contact with H_2 , which is known to reduce the reactivity of carbon.

8.11 Suggestions for Further Work

This research has been directed toward two goals: the first has been to provide data useful to the designer of a "clean power" system of the type proposed; the second has been to gain insight into the study of non-catalytic gas-solid reactions by acquiring detailed knowledge of a particular reaction, i.e. $[CaCO_3 + MgO] + H_2S$. The first goal has an immediate and practical value;

the second is of less immediate importance but is of considerable scientific interest, especially so because the reaction has displayed fascinating kinetic curiosities which, to our knowledge, have not been reported before for non-catalytic gas-solid reactions.

We have come closer to realizing the second goal than the first. An important reason for this is that the incredible speed of the reaction of H_2S with half-calcined dolomite makes the design of a sulfur-removal device, such as the panel-bed filter, independent of considerations of kinetics, at least for fresh dolomite. This may not be true of dolomite which has undergone a number of cycles of sulfur absorption and regeneration. Thus, it is now of the utmost importance to acquire data on the rate of absorption of H_2S by dolomite which has undergone cycling.

Our work was approached along classical lines, i.e., the reaction rate was initially studied as a function of temperature and H_2S concentration. Because of the complexity of the reaction, which was not possible to predict a priori, the classical method was somewhat inefficient with regard to obtaining data of engineering interest. For this reason, the classical approach should

be abandoned in the forthcoming study of the reaction to regenerate CaCO_3 from CaS . Work on the regeneration reaction should be concentrated on determining how regeneration conditions (e.g. temperature, gas composition) affect the reactivity of the solid toward H_2S after a number of reaction cycles. Finding the best regeneration conditions, i.e., those which give the fastest regeneration rates and the highest activity maintenance, will be of greater immediate interest than, for example, determining an activation energy for the regeneration. It will be of value also, once the optimum conditions for the regeneration are found, to determine why these conditions are the optimum ones.

Experiments to obtain data on recycled dolomite should be designed to approximate, as nearly as possible, conditions in a panel-bed filter. In light of the kinetic complexity of the reaction, it may be desirable to use a reaction gas simulating the actual power gas from an ash-agglomerating fluid-bed gasifier. This gas would contain H_2S , N_2 , a little CH_4 and CO , H_2 , CO_2 , and H_2O corresponding to equilibrium concentrations for the shift reaction at the temperature of the gasifier, about 1100°C . It would be wise also to use dolomite particles of a size that are intended to be used commercially. Following such procedures

would reduce the possibility of another kinetic "surprise" when a pilot plant is built.

Different types of dolomite should be studied in order to determine the range of reactivities and the most and least desirable stones for process use.

Our second goal emphasizes scientific, rather than engineering considerations. We have determined the behavior of the reaction of H_2S with half-calcined dolomite over a wide variety of reaction conditions, and have obtained some surprising results. We have proposed a mechanism to account for our data, but confirmatory experimental evidence is lacking. Such evidence is not likely to come from more kinetic experiments, but rather from examinations of reaction solids prepared under different conditions. For example, we ask if a solid reacted at $600^{\circ}C$, 5% H_2S , and 3% CO_2 , where the reaction ceases on its own accord at about 15% conversion, is different from a solid reacted to 15% conversion at 60% CO_2 . Our model predicts that, for solids prepared under different conditions, the CaS shells surrounding calcite crystals should display differences in structure. Future workers may perhaps be able to answer this question by applying surface area and porosity measurements, electron microscopy, and X-ray and electron diffraction to partially reacted samples, to see if differences really exist.

9.0 Conclusions and Recommendations

At the outset of this research, no kinetic data were available for the reaction of H_2S with half-calcined dolomite. We have obtained data over a wide range of temperatures and H_2S concentrations and have made some surprising discoveries which are of both engineering and scientific interest.

The speed of the reaction of H_2S with half-calcined dolomite is astonishing; for example, at 800°C and 5% H_2S , a conversion of 50% is reached within 15 seconds. It is more reactive than the fully calcined stone, which at the same conditions, requires 280 seconds. The reaction is so fast, in fact, that the design of the panel-bed filter described in Section 4.06 will not depend on kinetics, at least for fresh stone. Of crucial importance now is the question of how well the activity will hold up for a stone which has been subjected to a number of cycles of sulfur absorption and regeneration.

We have discovered some fascinating effects of temperature, CO_2 , H_2O , and O_2 , which to our knowledge, have not been reported before for non-catalytic gas-solid reactions. While runs made above temperatures of 650°C achieve complete conversion of CaCO_3 , runs made at lower

temperatures, with partial pressures of CO_2 only slightly exceeding the equilibrium decomposition pressure for CaCO_3 at the run temperature, nearly stop "dead" at conversions of typically 20%. Increasing the CO_2 level or adding steam has the effect of maintaining the high initial rate throughout the reaction and permitting complete conversion to occur. A CO_2 concentration of 60% is more effective than 60% steam at 600°C , but the reverse is true at 550°C . For runs made at 550°C with H_2S concentrations of 20%, complete conversion is not achieved even with 60% CO_2 .

A run made at 600°C , 5% H_2S , and 3% CO_2 does not progress beyond about 20% conversion. However, if a pulse of a gas containing about 0.3% oxygen and lasting only 10 seconds is then administered, the solid revives and another increment of conversion is permitted.

Figure 32 shows this effect.

We explain these effects with our interfacial blockage model. We believe that reaction conditions affect the way in which CaS grows within the solid microstructure.* When H_2S reacts on the surface of a crystallite of CaCO_3 , the product CaS first forms as an impervious layer which, if it grows to sufficient thickness, stops the reaction. However, simultaneous

*See Addendum p. 173.

with the interfacial chemical reaction, there occurs an annealing process in which "green" CaS is converted to its normal cubic crystal state. The annealing process is accompanied by shrinkage of the CaS, causing cracks to form which facilitate penetration of H_2S through the product layer to the reaction interface. The progress of the reaction will depend on the relative magnitudes of the interfacial reaction rate and the annealing rate. We propose that increased temperature and CO_2 , H_2O , or O_2 , affect the progress of the reaction because they increase the annealing rate, causing an increase in the ultimate conversion.

We have succeeded in correlating initial reaction rates with temperature and H_2S concentration. Separate correlations are given for low and high CO_2 concentrations by equations (6) and (7):

$$\text{rate} = 3040 \exp(-20,500/RT) P_{\text{H}_2\text{S}}^{0.5} \quad (6)$$

$$\text{rate} = 1.82 \times 10^8 \exp(-37,700/RT) P_{\text{H}_2\text{S}} \quad (7)$$

The rate is given as fractional conversion per second.

Also, $T = ^\circ\text{K}$, $P_{\text{H}_2\text{S}} = \text{atm.}$, and $R = 1.99 \text{ cal/gm-mole}^\circ\text{K}$.

Equation (6) is valid over the temperature range $450^\circ - 800^\circ\text{C}$. Equation (7) is valid from $550^\circ - 750^\circ\text{C}$. Both are valid over H_2S partial pressures of 0.005-0.20 atm.

Equation (6) correlates data for runs made where the CO_2 partial pressure exceeds slightly the equilibrium decomposition pressure of CaCO_3 ; equation (7) is to be used where CO_2 pressures are considerably higher, 0.60 atm. For intermediate CO_2 concentrations, a linear interpolation between the values predicted by these equations will give satisfactory results.

Increasing CO_2 or H_2O concentration decreases the initial rate of reaction, the effect diminishing with increasing temperature. We believe this is caused by competitive adsorption of CO_2 and H_2O with H_2S , which reduces the number of surface sites available for adsorption of H_2S .

Further work is needed to confirm our interfacial blockage model. Evidence to support this model is not likely to come from further kinetic experiments, but rather from physical examination of partially reacted solids to determine if solids prepared under different reaction conditions have different structures.

Half-calcined dolomite which has undergone one or more cycles of sulfur absorption and regeneration will probably be less reactive than freshly calcined stone. The study of the regeneration reaction should be aimed at finding the regeneration conditions which result in the best activity maintenance after a number of cycles.

10.0 Appendix

10.01 Determination of Capacities of Samples from

Calcination Data

In order to determine the capacity of samples to absorb H_2S , we performed experiments in which we fully calcined samples of -250+270 mesh powdered dolomite. Data for the CaCO_3 decomposition are given below:

<u>Sample Number</u>	<u>Initial Weight of Half-Calcine</u>	<u>Actual Weight Loss for $\text{CaCO}_3 \rightarrow \text{CaO}$</u>	<u>Actual Weight Loss/Initial Weight Half- Calcine</u>
1	16.24 mg	4.86 mg	0.299
2	16.48	4.82	0.292
3	16.36	4.78	0.292
4	13.26	3.94	0.297
5	16.16	4.80	<u>0.297</u>
			Avg = 0.295

From the last column, it can be seen that the weight loss per unit initial weight of half-calcine is nearly uniform from sample to sample. In fact, the small differences are likely due to the difficulty in determining where the CaCO_3 decomposition actually begins and the MgCO_3 decomposition ends.

From the average weight loss, 0.295 mg/mg initial half-calcine, plus the fact that the decomposition of one millimole of pure CaCO_3 to CaO will produce a weight loss of

44.01 mg, it is evident that 149.19 mg ($44.01/0.295$) of half-calcined dolomite contain one millimole CaCO_3 .

For the desulfurization reaction, one millimole of CaCO_3 changing to CaS produces a weight loss of 27.95 mg. Hence, the same weight loss is produced by 149.19 mg of half-calcined dolomite. The capacity for H_2S absorption is therefore 0.187 mg/mg half-calcine ($27.95/149.19$). This figure was used to determine the capacities for all runs made with -250+270 mesh powder.

A similar calculation for the reaction of H_2S with fully calcined dolomite shows that the capacity equals 0.157 mg/mg full calcine.

10.02 Calculation of Effectiveness Factor for Powder.

Application of Weisz Criterion for Diffusion

Our work on reaction (B) has been conducted under the hypothesis that this reaction takes place homogeneously, without diffusion effects, in finely powdered samples. To test this hypothesis, we calculated both the maximum rate that could occur without diffusion, according to the criterion of Weisz (31), and the effectiveness factor for our powder. In order to perform these calculations, we first determined the effective diffusivity of our solid by reacting a sphere

of half-calcined dolomite at 800°C with 1% H₂S, as described in Section 7.09. We obtained a value of 0.04 cm²/sec.

Using the above value of effective diffusivity, we estimated the effectiveness factor for a particle of the size of our experimental powder. The effectiveness factor, η , is the ratio of the observed reaction rate to the rate that would be observed in the absence of diffusion effects. For a spherical particle it is given by (56):

$$\eta = 3[mR \coth(mR) - 1]/(mR)^2 \quad (8)$$

where R = particle radius, length

$$m = k_n c^{n-1}/D$$

k_n = reaction rate constant for n^{th} order reaction,
concentration¹⁻ⁿ/time

D = effective diffusivity, area/time

For our -250+270 mesh powder reacted at 800°C with 1% H₂S, we calculated the effectiveness factor to be 0.97. For all other reaction conditions encountered in this research, it was even higher.

Weisz developed a simple criterion to indicate, on the absence of detailed a priori knowledge of reaction kinetics, whether any given operating conditions leads to appreciable diffusion effects. The criterion is based

on the fact that for negligible loss of reaction rate due to diffusion, the concentration gradient of reactant in the particle must also be negligible. The criterion can be expressed as:

$$dN/dt \cdot R_o^2 / DC_o \leq 3\beta \quad (9)$$

where $\beta = 4(1-\eta)/n$ and

dN/dt = maximum reaction rate per unit volume,
concentration/time

c_o = reactant concentration at particle boundary,
concentration

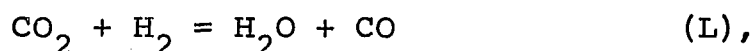
η = effectiveness factor

n = order of reaction

For a run made at 800°C with 1% H₂S, we observed an initial rate of 0.23 mg weight change/mg sample-min, or about 0.27 mmol/sec cm³. If we take the reaction as half-order with respect to H₂S, the Weisz criterion predicts that to maintain an effectiveness factor of 0.95, the highest reaction rate allowable equals 0.80 mmols/cm³-sec. For a first order reaction, the maximum rate would be 0.40 mmols/cm³-sec. Hence, the Weisz criterion and effectiveness factor are consistent in that both predict the absence of appreciable diffusion effects.

10.03 Consideration of Desulfurization Equilibrium. Runs at Shift Equilibrium.

Desulfurization reaction (B) has been assumed to be irreversible because water was omitted from most runs. For runs made with water added, however, this assumption needs to be examined to determine whether the back reaction appreciably hinders the overall rate of the forward, desulfurization, reaction. Moreover, since the reaction gas always contains CO_2 and H_2 , there is always a possibility of H_2O formation via the "shift" reaction,



especially because MgO is known to be catalytic.

Fortunately, we can easily obtain a good estimate of the effect of equilibrium on the rate of the desulfurization reaction.

The rate of reaction (B) can be written as

$$\text{Rate per unit weight CaCO}_3 = C_{\text{H}_2\text{S}} \left[k_1 - k_2 \frac{C_{\text{H}_2\text{O}} C_{\text{CO}_2}}{C_{\text{H}_2\text{S}}} \right] \quad (10)$$

where the C 's represent the indicated gas concentration and the k_1 and k_2 are kinetic constants. This expression becomes more accurate near equilibrium, where the forward and back reaction are truly first order. Equation 10 can be written as

$$\text{Rate} = k_1 C_{\text{H}_2\text{S}} \left[1 - K_c \frac{C_{\text{H}_2\text{O}} C_{\text{CO}_2}}{C_{\text{H}_2\text{S}}} \right] \quad (11)$$

where K_c is the concentration equilibrium constant for regeneration reaction (C). In terms of mole fractions, and at one atmosphere total pressure,

$$\text{Rate} = k_1 C_{H_2S} \left\{ 1 - K_p \frac{[H_2O][CO_2]}{[H_2S]} \right\} \quad (12)$$

where [...] denotes mole fraction and K_p is the partial pressure equilibrium constant for reaction (C). The quantity in { } is the factor by which the back reaction reduces the true rate of the desulfurization reaction, $k_1 C_{H_2S}$, because of proximity to equilibrium. This factor depends on temperature and gas composition.

Equation (12) tells us that small amounts of water present in the reaction gas, as might arise from water used in the manometers of the capillary flowmeters, have a negligible effect on the reaction rate. For example, at 600°C , where $K_p = 0.063$, with a reaction gas containing 1% H_2S and 60% CO_2 it would take over 2% water to reduce the forward rate by 10%. The actual H_2O concentration is probably well under 2%.

For runs made with 60% H_2O added at 600° and 550°C , the back reaction has only a small effect (Section 7.04). The rate of the desulfurization reaction is reduced by about 2% and 5% respectively, for these runs.

Water may be produced by the shift reaction. However,

even at shift equilibrium, the back reaction would have an appreciable effect only on runs made at low temperatures with high CO_2 concentrations and low H_2S concentrations.

The table below give values of $\left\{ 1 - K_p \frac{[\text{H}_2\text{O}][\text{CO}_2]}{[\text{H}_2\text{S}]} \right\}$ calculated by assuming shift equilibrium, for a gas containing 0.5% H_2S and 60% CO_2 (the highest $\text{CO}_2/\text{H}_2\text{S}$ ratio used in this research) and various temperatures:

$T^\circ\text{C}$	$\left\{ 1 - K_p \frac{[\text{H}_2\text{O}][\text{CO}_2]}{[\text{H}_2\text{S}]} \right\}$
600	0.03
650	0.53
700	0.76
750	0.86
800	0.92

Actually, we know that shift equilibrium is not approached, at least at lower temperatures, because desulfurizations were achieved at 550°C . At this temperature, the reverse reaction, rather than desulfurization, would have occurred had the shift reaction been at equilibrium.

Two runs made at 550°C and 600°C with a reaction gas containing CO_2 , H_2 , H_2O , and CO , in concentrations corresponding to shift equilibrium, displayed behavior similar to runs made at comparable conditions but with a gas which did not contain CO , and which was not at shift equilibrium.

10.04 Analysis of Greenfield Dolomite Sample

A sample of the powdered -250+270 mesh, Greenfield dolomite that was used in this research was sent to Lucius Pitkin, Inc., New York City, for analysis. The results of the analysis are given below:

<u>Component</u>	<u>Weight Percent</u>
Magnesium	13.48
Calcium	22.43
Iron	0.18
Silicon	0.X - Minor
Aluminum	0.X
Strontium	0.X low
Others (Mn, K, Cu, Pb, Sn, Ti, Na, B)	0.0X each or less

The percentages of magnesium and calcium reported are in doubt because they correspond to a total MgCO_3 and CaCO_3 greater than the original sample weight.

~~Empirical Data Correlation~~

To correlate all of our data for reaction (B), we have used what we call the "surface coverage" model. We emphasize that we have used this model because of its simplicity and its ability to fit our data reasonably well, and not because we believe that it faithfully describes the underlying

mechanism. The surface coverage model resembles the interfacial blockage model proposed in Section 8.04 only in the sense that it hypothesizes that the formation and growth of a product layer of CaS over the surface of each calcite crystallite hinders further reaction. In the interfacial blockage model, product CaS is assumed to cover all reaction surface when the reaction begins. In the surface coverage model, however, CaS may grow at comparable rates both laterally and radially into each crystallite, so that high conversions may occur before the reaction surface is completely covered with product. Furthermore, the surface coverage model does not explicitly assume the existence of intrinsic reaction and annealing rates, but does not preclude this interpretation. For correlating data, the surface coverage model has the advantage that it can be readily translated into mathematical equations. However, the interfacial blockage model is considerably more useful in explaining the effects on the reaction of temperature, H_2S , CO_2 , H_2O , and O_2 .

According to the surface coverage model, solid product can grow through both open and covered area of the crystallites of solid reactant. The growth through open area is represented by

$$\frac{dx}{dt} = k_1 (A_o - \alpha x) \quad (13)$$

and through covered area by

$$\frac{dx}{dt} = k_2 u(\alpha x) = \alpha k_2 (1-x)x \quad (14)$$

where

x = fraction converted

u = fraction unconverted

t = time, time

k_1, k_2 = kinetic constants, $\text{area}^{-1} \text{time}^{-1}$

A_0 = initial surface area, area

α = geometric factor ($=V_0/\delta$, where V_0 = volume of crystallite and δ = thickness of solid product layer), area

For $\alpha x \leq A_0$, growth occurs through both covered and uncovered area, and is equal to the sum of Equations (13) and (14):

$$\frac{dx}{dt} = k_1 (A_0 - \alpha x) + \alpha k_2 (1 - x)x, \quad \alpha x \leq A_0 \quad (15)$$

For $\alpha x > A_0$, all surface is covered with product, so that growth occurs according to:

$$\frac{dx}{dt} = k_2 A_0 (1 - x), \quad \alpha x > A_0 \quad (16)$$

Equations (15) and (16) define the model. If we integrate these equations, and let

$$K = k_2/k_1, \quad \beta = A_0/\alpha, \quad \text{and } \tau = k_1^{-1} A_0 t$$

we get:

$$\frac{\tau}{\beta} = -\int_0^x \frac{dx}{Kx^2 + (1-K)x - \beta} =$$

$$\frac{1}{\sqrt{(1-K)^2 + 4\beta K}} \ln \left(\frac{2Kx + (1-K) - \sqrt{(1-K)^2 + 4\beta K}}{2Kx + (1-K) + \sqrt{(1-K)^2 + 4\beta K}} \cdot \frac{(1-K) + \sqrt{(1-K)^2 + 4\beta K}}{(1-K) - \sqrt{(1-K)^2 + 4\beta K}} \right), \quad x \leq \beta \quad (17)$$

$$\tau - \tau' = \frac{1}{K} \ln \left(\frac{(1-\beta)}{(1-x)} \right), \quad x > \beta \quad (18)$$

where $\tau' = \tau(\beta)$

Equations (17) and (18) can be used to generate x versus time, given values of the parameters $k_1 A_0$, β , and K . It will be appreciated that $k_1 A_0$ is the initial rate, i.e., $dx/dt(x=0)$, and that β is the cutoff conversion, or the conversion at which all surface becomes covered with product. Also, it should be noted that equation (17) produces a curved line in a plot of $\log(1-x)$ versus time; however, equation (18) produces a straight line of slope $k_2 A_0$. It is clear that K is the ratio of the final rate (the slope of the $\log(1-x)$ versus time plot for $x > \beta$) to the initial rate.

To correlate our data using equations (17) and (18), we first determined the values of the three parameters, $k_1 A_0$, β , and K , which best fit the data. Next, using a strictly empirical approach, we correlated these parameters with temperature, and concentration of H_2S and CO_2 . The correlation is given below:

$k_1 A_o$

$$\log \frac{k_1 A_o}{C_{H_2S}^{0.53}} = - \frac{11764.7}{T} + 10.353, \quad T \leq 948^\circ K \quad (19)$$

$$\log \frac{k_1 A_o}{C_{H_2S}^{0.53}} = - \frac{3103.1}{T} + 1.228, \quad T \geq 948^\circ K \quad (20)$$

β

$$\beta = 0.2 \left(\frac{T}{823} \right)^{7.2} C_{H_2S} (C_{CO_2}^{-20})/100, \quad T < 973^\circ K \quad (21)$$

$$\beta = 0.6, \quad T \geq 973^\circ K \quad (22)$$

K

$$K = \left(\frac{T}{873} \right)^{8.5} \left\{ 1 - 0.77 \left[\log \frac{C_{CO_2}}{C_{H_2S}} - 1 \right]^2 \right\}, \quad T < 973^\circ K, \frac{CO_2}{H_2S} > 8 \quad (23)$$

$$K = \frac{e^{0.016T-17.62}}{C_{H_2S}^{0.37}}, \quad T < 973^\circ K, \frac{CO_2}{H_2S} < 8 \quad (24)$$

$$\log C_{H_2S}^{0.37} K = - \frac{6540}{T} + 6.060, \quad T \geq 973^\circ K \quad (25)$$

where $T = ^\circ K$, $C_{H_2S} = \%$, $C_{CO_2} = \%$.

We have assumed, for simplicity, that $k_1 A_o$ is independent of CO_2 concentration, even though our initial rate data shows this not to be the case. Also, we have used $\beta=0.6$, independent of gas composition, for temperatures equal to or above $700^\circ C$. For each parameter we have found it necessary to use separate expressions for different ranges of temperature, and in one case to use separate expressions for high and low CO_2/H_2S ratios.

For runs at 550°C and 600°C in which 60% H₂O was added, the values of $k_1 A_o$, β , and K calculated for 60% CO₂ can be used after they have been multiplied by $c_{k_1 A_o}$, c_β , and c_K , respectively. Values of these constants can be found from:

$$c_{k_1 A_o} = - 0.029T + 26.040 \quad (26)$$

$$c_\beta = - 0.0172T + 15.540 \quad (27)$$

$$c_K = - 0.0222T + 19.430 \quad (28)$$

Figures 44 through 48 give comparisons of data with curves generated by equations (17) and (18). The fit is closest for runs made at temperatures of 700°C and above. The correlation presented here is best used as a guide to the general behavior of reaction (B) under different conditions. It should be kept in mind that considerable error may result when it is used to estimate the time required to attain a particular conversion.

10.06 Design of Panel Bed Filter

The power of fresh half-calcined dolomite to absorb H₂S is so great that reaction kinetics are not a limiting factor in the design of a panel bed filter to remove H₂S from a fuel gas at high pressure; however, the reactivity of dolomite which has undergone cycling may be reduced to the extent that kinetics will play a part in such a design.

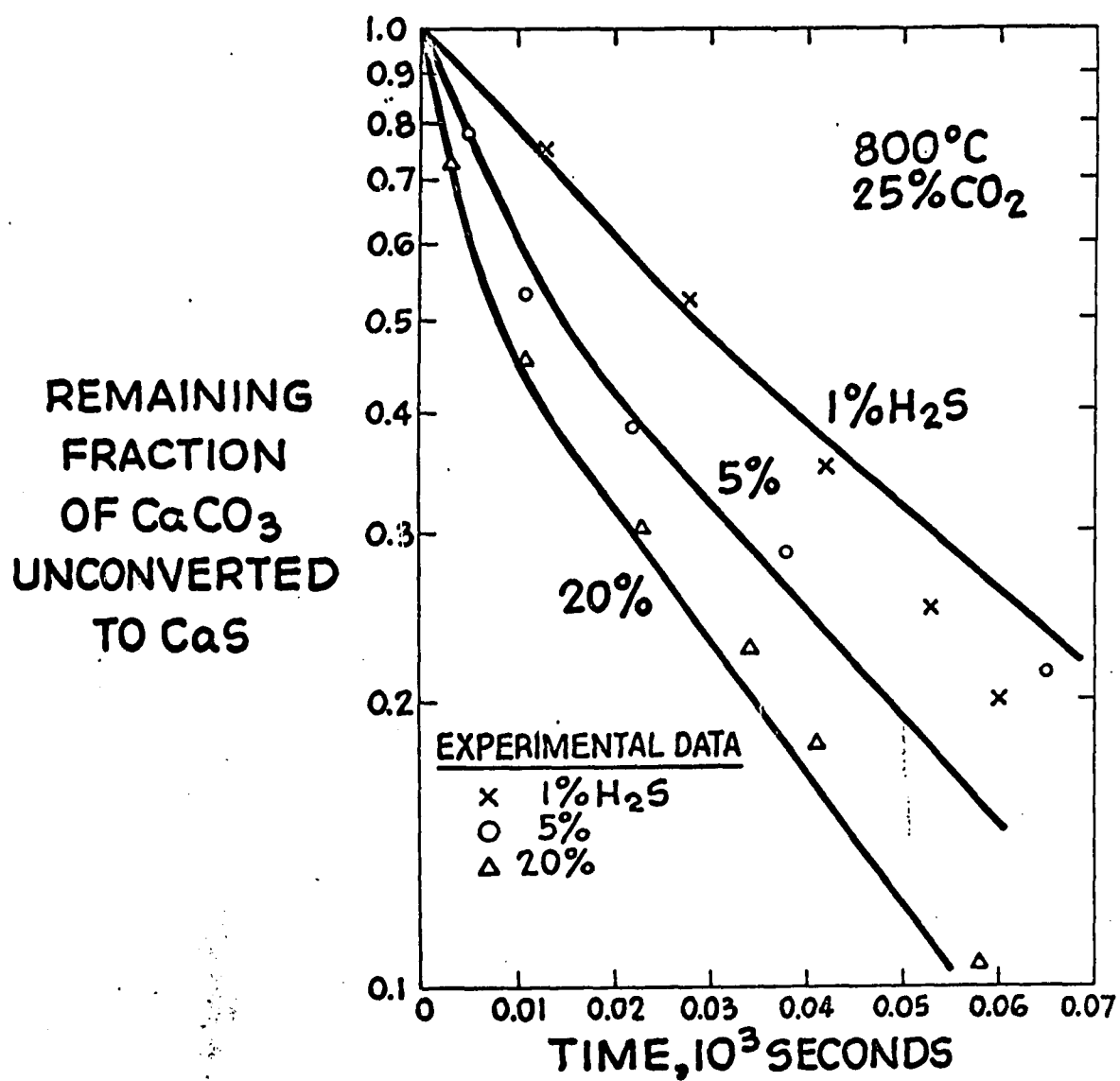


Figure 44. Comparison of curves generated by the empirical correlation of equations (17-25) with the data for runs at 800°C, 25% CO₂, and the three H₂S levels.

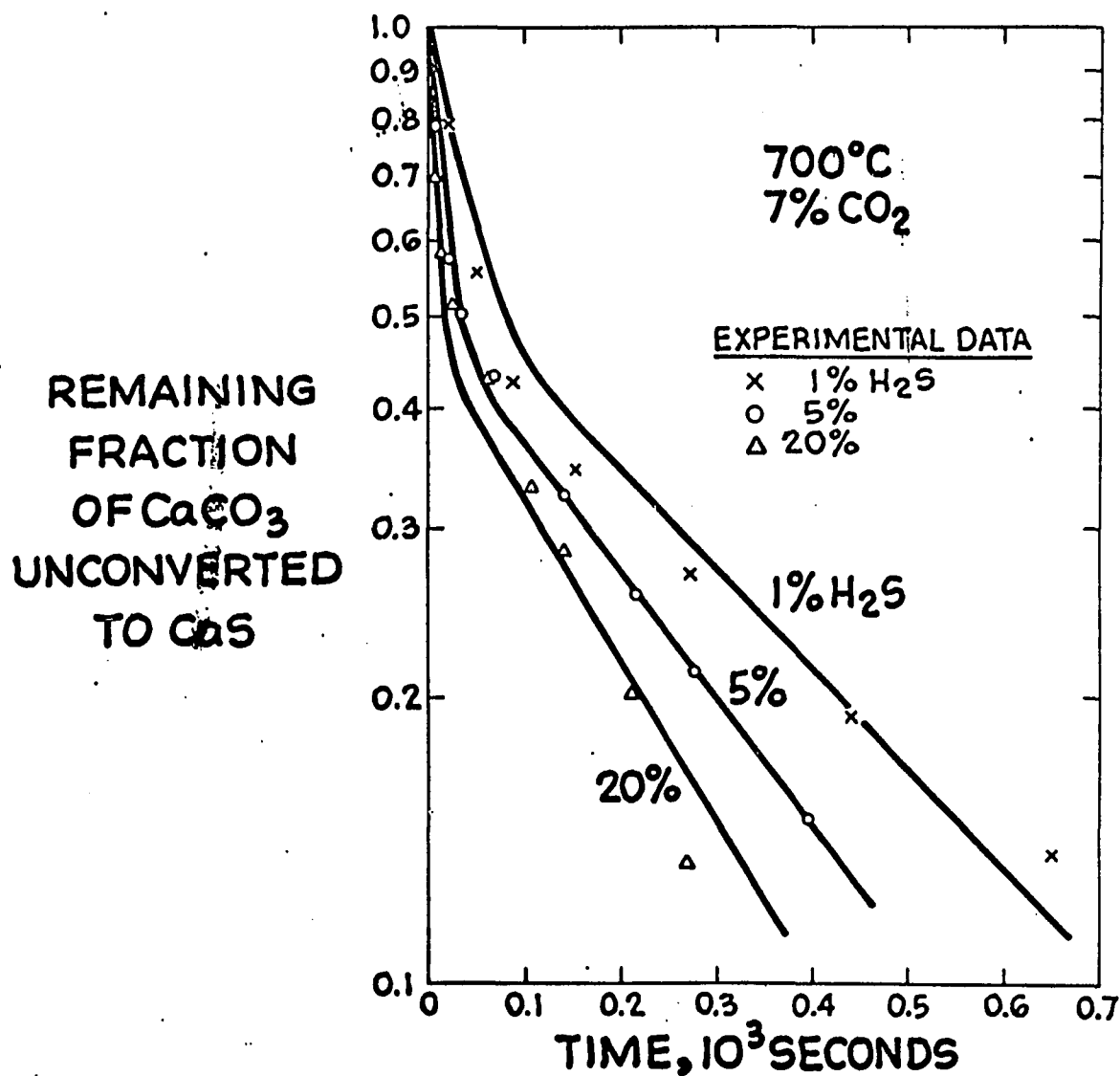


Figure 45. Comparison of curves generated by the empirical correlation of equations (17-25) with the data for runs at 700°C, 7% CO_2 , and three H_2S levels.

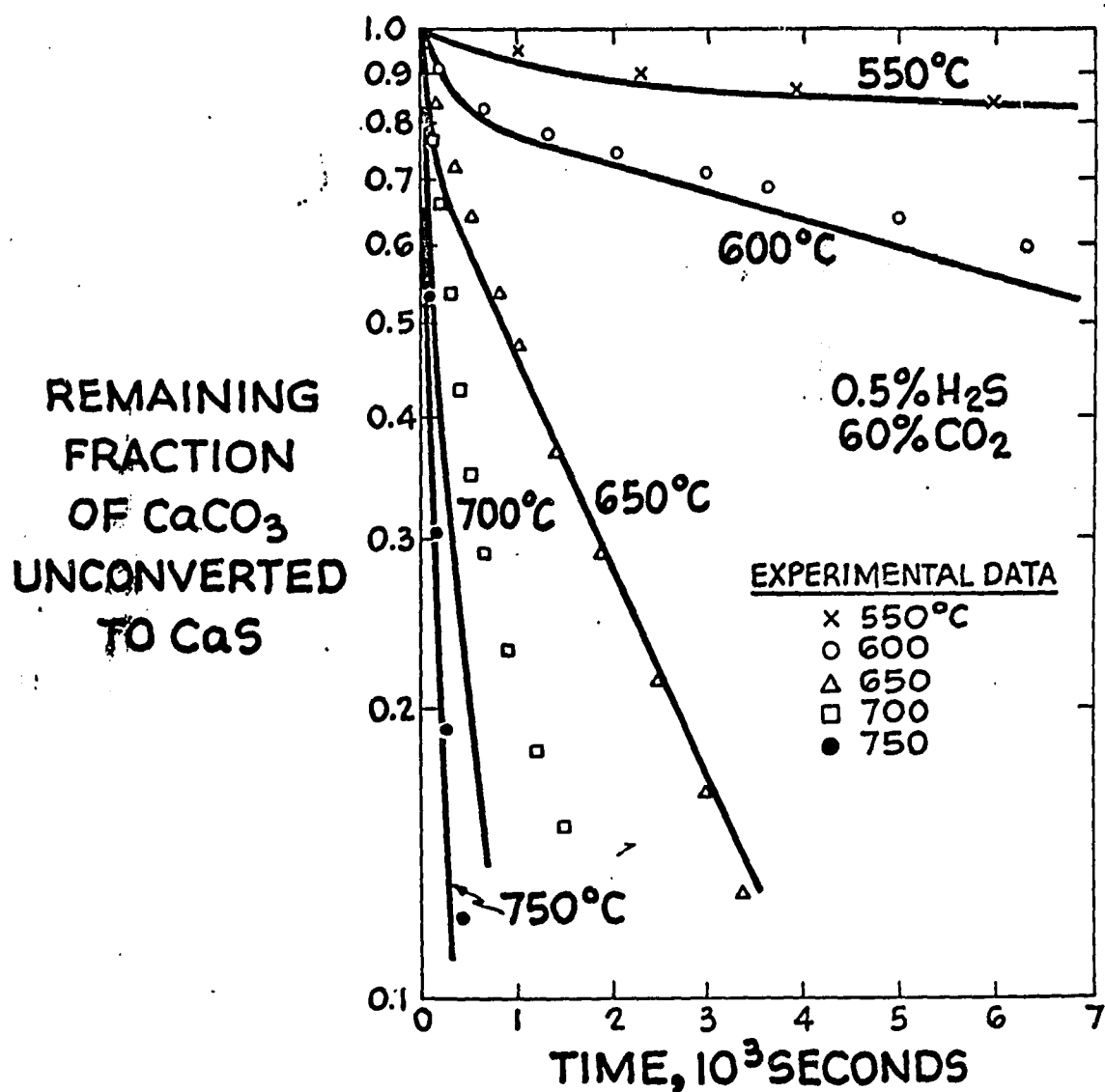


Figure 46. Comparison of curves generated by the empirical correlation of equations (17-25) with data for runs at 0.5% H_2S , 60% CO_2 , and five temperature levels.

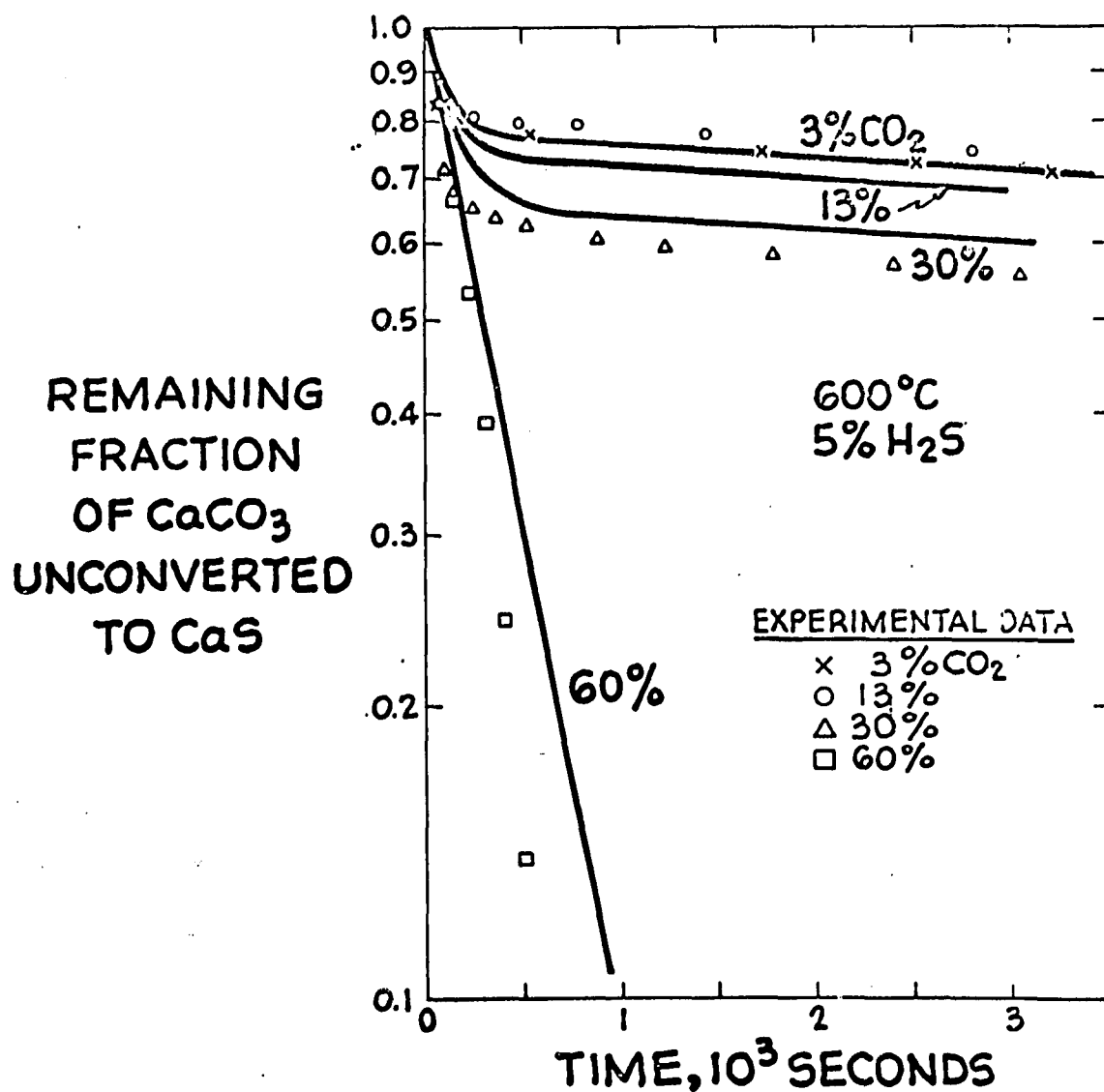


Figure 47. Comparison of curves generated by the empirical correlation of equations (17-25) with the data for runs at 600°C, 5% H_2S , and four CO_2 levels.

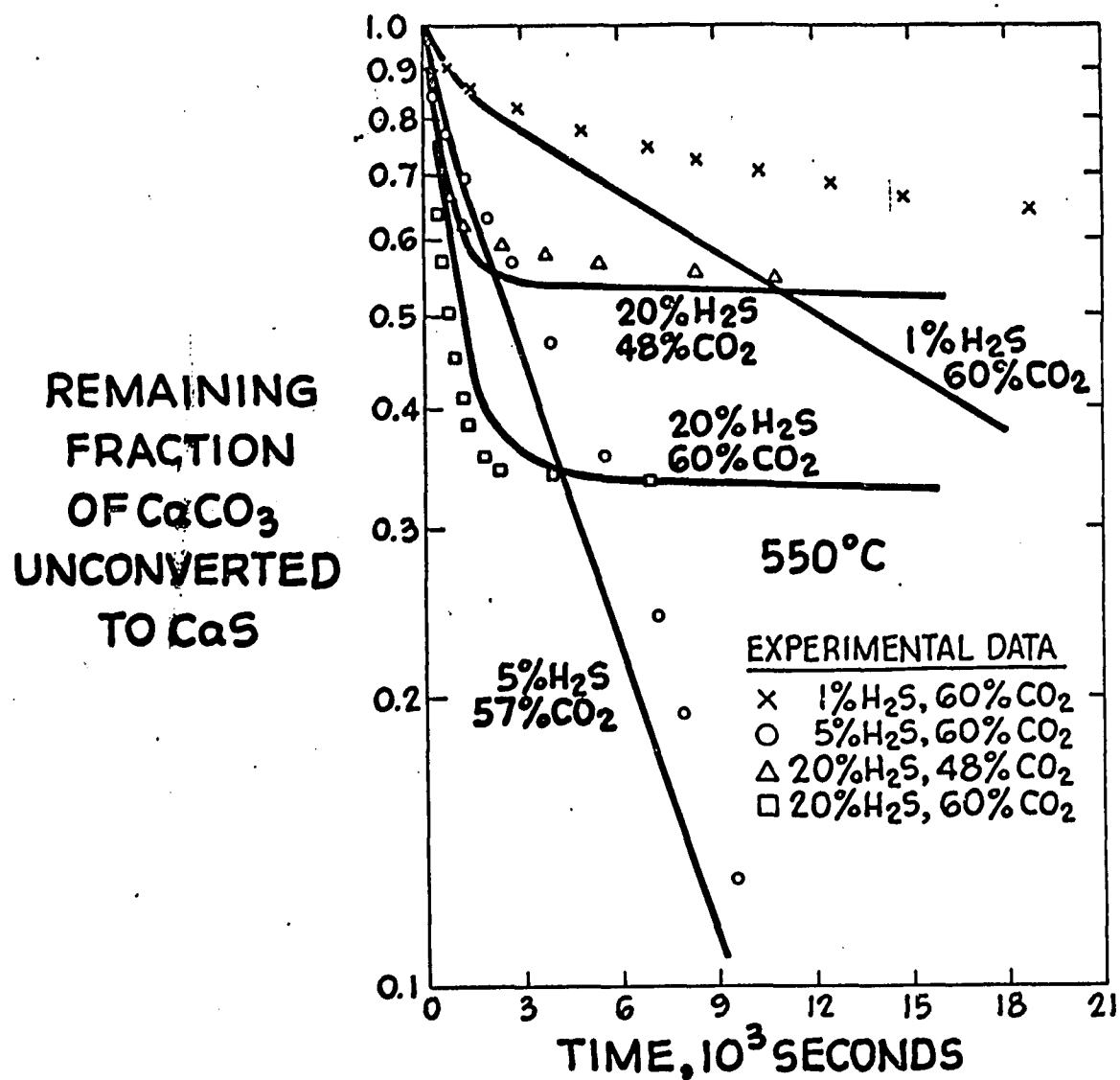


Figure 48. Comparison of curves generated by the empirical correlation of equations (17-25) with data for runs at 550°C, high CO_2 level and three H_2S levels.

In this section we outline calculations for the design of a panel bed filter. With additional information on reaction kinetics in hand, the method presented here can be used to calculate the width of filter required to produce the desired desulfurization.

In order to determine the width of filter required, the gas-solid contacting pattern in the filter must be known. For an actual filter this pattern is complex; however, limits on the design can be obtained using two simplified flow schemes: solid flowing countercurrent to gas and solid flowing cross-current to gas. These two flow schemes are treated separately below.

For countercurrent flow, with gas flowing in the +y direction, the governing differential equations are:

$$\text{for gas, } G \frac{dc}{dy} = -\rho r(c, u) \quad (29)$$

$$\text{for solids, } S \frac{du}{dy} = \rho r(c, u) \quad (30)$$

where

c = H_2S concentration, moles/volume

u = fraction $CaCO_3$, unconverted

r = reaction rate, moles H_2S reacted/mole original $CaCO_3$ -time

ρ = bed density, moles original $CaCO_3$ /volume of bed

G = gas flow rate, volume/area-time

S = solids flow rate, moles original $CaCO_3$ /area-time

From equations (29) and (30), the relationship between c and u is:

$$c - c_i = -\frac{S}{G} (u - u_e) \quad (31)$$

where

c_i = concentration of H_2S at gas inlet, moles/volume

u_e = fraction $CaCO_3$ unconverted at solids exit

To obtain the width of filter, l , we integrate equation (29) over the filter from $y = 0$ to $y = l$:

$$\int_{c=c_i}^{c=c_e} \frac{dc}{r(c,u)} = -\frac{\rho}{G} l \quad (32)$$

where c_i and c_e are the concentrations of H_2S at the gas inlet and exit, respectively. To evaluate the integral in equation (32) we must specify $r(c,u)$, e.g., $r = kuc^n$, and eliminate u using equation (31).

For a cross-flow filter, shown in Figure 49, the governing equations are:

$$\text{for gas, } G \frac{dc}{dy} = -\rho r(c,u) \quad (33)$$

$$\text{for solid, } S \frac{du}{dz} = -\rho r(c,u) \quad (34)$$

Given the reaction rate, $r(c,u)$, these equations can be solved using a digital computer, and an example program for this purpose is given in Figure 50. The filter is divided into a grid, whose height and width are equal to $M \times dz$ and $N \times dy$, respectively (statement number 2).

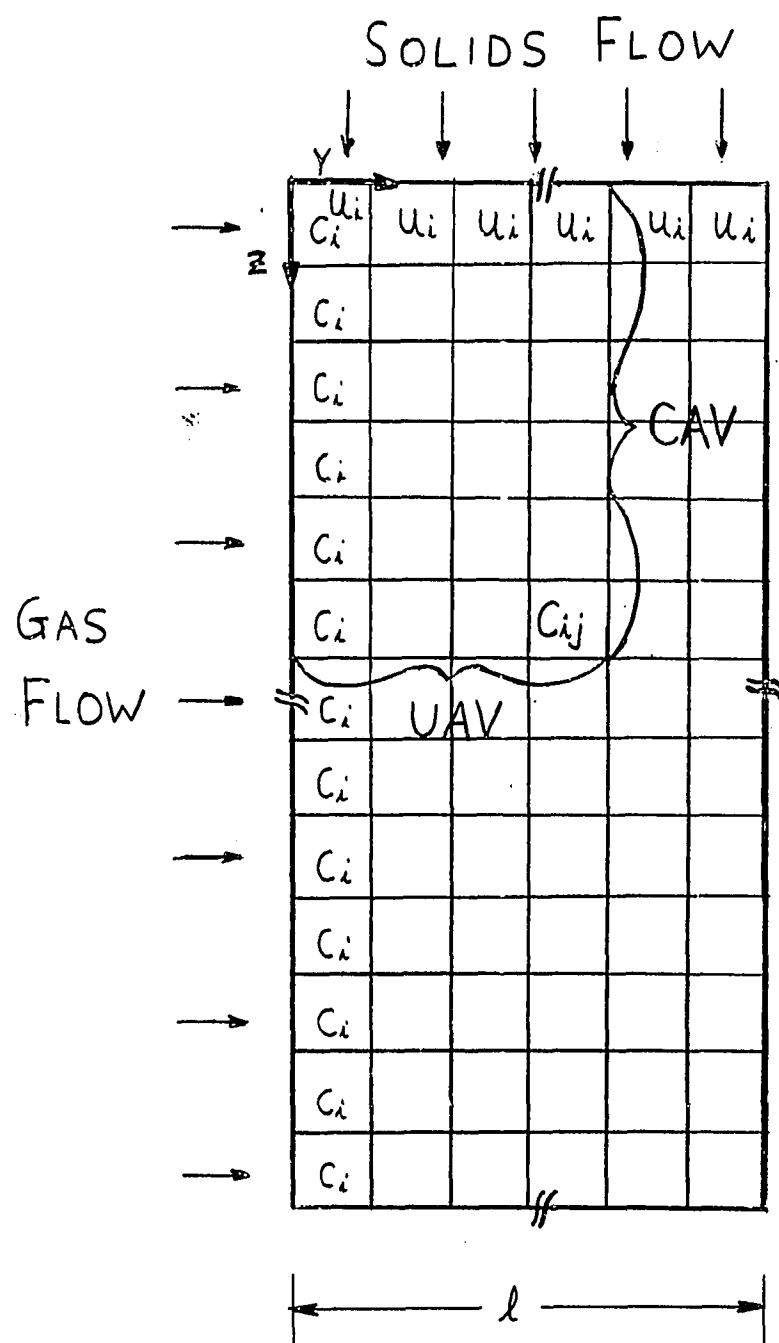


Figure 49. Cross-flow filter.

```

C  SOLUTION OF CROSSCURRENT FILTER EQUATIONS
1  REAL C(502),U(502),CAV(502),UAV(502)
2  READ(5,10)M,N,L,K,DY,DZ
3  10 FORMAT(4I4,2F5.2)
4  WRITE(6,12)M,N,DY,DZ
5  12 FORMAT('1','M=',I3,10X,'N=',I3,10X,'DY=',F5.3,10X,'DZ=',F5.3//
6  DO 1 J=1,N
7  CAV(J+1) = 0.
8  1 U(J+1) = 0.75
9  DO 2 I=1,M
10 C(2) = 14.7
11 UAV(1) = 0.
12 DO 2 J=1,N
13 IF(U(J+1).LT.0.)U(J+1)=0.
14 IF(C(J+1).LT.0.)C(J+1)=0.
15 GRAD = -U(J+1)*C(J+1)**0.43
16 C(J+2) = GRAD*DY + C(J+1)
17 UAV(J+1) = (U(J+1)+(J-1)*UAV(J))/J
18 CAV(J+1) = (C(J+1)+(I-1)*CAV(J+1))/I
19 IF((J/L*L-J).NE.0.OR.(I/K*K-I).NE.0)GO TO 2
20 WRITE(6,11)I,J,C(J+1),U(J+1),CAV(J+1),UAV(J+1)
21 2 U(J+1) = GRAD*DZ + U(J+1)
22 11 FORMAT(' ','I=',I3,' J=',I3,15X,'C=',F6.3,10X,'U=',F5.3,15X,
1'CAV=',F6.3,10X,'UAV=',F5.3)
23 STOP
24 END

```

Figure 50. Computer program to determine width of cross-current flow filter.

The unconverted fraction of CaCO_3 in the entering and exiting solid must be specified, along with the corresponding concentrations of H_2S (8, 10). (In the example program the values of these parameters are, respectively, 0.75, 0.25, 14.7% and 0.147%). The computer successively calculates c and u for each grid point. (If c or u should become negative, they are set equal to zero - 13,14.) Also, at each grid point, the computer determines the unconverted fraction of exiting CaCO_3 (UAV) and the concentration of H_2S in the exiting gas (CAV) for a filter whose size is determined by the origin and that grid point. These exit conditions are calculated by averaging the conversion and concentration at the grid points located along the lower and right hand edges of the filter, respectively -17,18 (see Figure 49). At specified intervals (given by L and K - statements 2 and 19), values of C , U , CAV, and UAV, are printed out. The size of the filter is determined when CAV and UAV fall below the desired values.

We have worked out a preliminary design for a panel bed filter using kinetic data for the reaction of H_2S with half-calcined dolomite which has not undergone cycling. We designed the filter to reduce the concentration of H_2S

in the incoming gas, 0.7 mole per cent, to 1/100th of this value (i.e., 99% sulfur removal). The operating temperature, pressure, and gas approach velocity are 760°C, 21 atm., and 10 ft./min., respectively. Half-calcined dolomite enters the filter at 25% conversion of CaCO_3 to CaS and leaves the filter, after absorbing H_2S from the fuel gas, at 75% conversion.

The width of this filter will be less than 1 cm. It should be noted that the width of filter is independent of its height.

10.07 Nomenclature

- A = surface area or pre-exponential factor, units depend on rate equation - see equations (4) and (5)
- c = gas concentration, moles/volume, or correction factor in equations (26-28), dimensionless
- D = effective diffusivity, area/time
- E = activation energy, cal/g-mole
- G = gas flow rate, volume/area-time
- k = a generalized kinetic constant
- K = ratio of final to initial reaction rate, see equation (17)
- K_c = concentration equilibrium constant
- K_p = partial pressure equilibrium constant
- l = width of panel bed filter, length

- m = kinetic parameter, see equation (8)
 n = order of reaction, dimensionless
 P = pressure, atm
 r = reaction rate in equations (29, 30), moles H_2S reacted/mole original $CaCO_3$ -time
 R = particle radius, length, or gas constant, cal/g-mole $^{\circ}K$
 S = solids flow rate, moles original $CaCO_3$ /area-time
 t = time, seconds
 T = temperature, $^{\circ}K$
 u = fraction unconverted, dimensionless
 x = fractional conversion of solid, dimensionless
 α = geometric factor, see equation (13), area
 β = $4(1-\eta)/n$ used in Weisz criterion, equation (9), or cutoff conversion in equation (17), dimensionless
 η = effectiveness factor, dimensionless
 ρ = bed density, moles original $CaCO_3$ /volume of bed.
 τ = dimensionless time, see equation (17)
 $[...]$ = mole fraction, dimensionless

Subscript e = at exit

i = at inlet

o = initial

11.0 References

1. M. Pell, "Reaction of Hydrogen Sulfide With Fully Calcined Dolomite, Ph.D., Thesis, The City University of New York (1971).
2. A.M. Squires, "Cyclic Use of Calcined Dolomite to Desulfurize Fuels Undergoing Gasification," in Advances in Chemistry Series, Number 69, "Fuel Gasification," American Chemical Society (1967) 205-229.
3. A.M. Squires, U.S. Patent 3,402,998 (1968).
4. A.M. Squires, R.A. Graff, and M. Pell, "Desulfurization of Fuels With Calcined Dolomite. I. Introduction and First Kinetic Results," Chem. Eng. Progr. Symp. Ser., 67 (1971) 23-34.
5. M. Pell, R.A. Graff, and A.M. Squires, "Desulfurization of Fuels With Calcined Dolomite. II. Reaction of CaO With H₂S," Chem. Engr. Progr. Technical Manual (1971) 151-157.
6. W.L. Bragg, The Atomic Structure of Minerals, Cornell University Press, Ithaca, New York, 1937.
7. J.R. Goldsmith, personal communication, 1962.
8. E. Cremer, Z. für anorg. Chemie, 258 (1949) 123-131.
9. E. Cremer and F. Gatt, Radex-Rundschau der Österreichischen Magnesit A.G. 1949, 149.
10. R.A.W. Haul, "Adsorptionsuntersuchungen an thermisch zersetzten Dolomitkristallen" ["Adsorption studies on calcined dolomite"], Z. anorg. allgem. Chem., 281, (1955) 199-211.
11. R.H. Borgwardt and R.D Harvey, "Properties of Carbonate Rocks Related to SO₂ Reactivity," Environ. Sci. Technol., 6(4) (1972) 350-360.
12. H.G.F. Wilsdorf and R.A.W. Haul, Nature (London) 167 (1951) 945-6.

13. R. D. Harvey, "Petrographic and Mineralogical Characteristics of Carbonate Rocks Related to Sorption of Sulfur Oxides in Flue Gases," Interim Report to the National Air Pollution Control Administration, Contract Number CPA 22-69-65, prepared at the Illinois State Geological Survey, Urbana, Illinois, June 22, 1970.
14. G. H. McClellan, "Physical Characterization of Calcined and Sulfated Limestones," paper presented at the Dry Limestone Injection Process Symposium, Gilbertsville, Kentucky, June 22-26, 1970.
15. W. E. Gluud, E. Keller, W. Klempt, and R. Bestehorn, "Entwicklung und technische Durchführung eines neuen Verfahrens zur Gewinnung von Wasserstoff and Wasserstoff-Stickstoff-Gemischen" ["Development and operation of a new process for hydrogen and hydrogen-nitrogen mixtures"], Berichte der Gesellschaft für Kohlentechnik, 3, (1930) 211-370.
16. G. P. Curran, C. E. Fink, and E. Gorin, "CO₂ Acceptor Gasification Process - Studies of Acceptor Properties," in Advances in Chemistry Series, Number 69, "Fuel Gasification," American Chemical Society (1967) 141-165.
17. A. M. Squires and R. Pfeffer, "Panel Bed Filters for Simultaneous Removal of Fly Ash and Sulfur Dioxide: I. Introduction," J. Air Poll. Control Assoc., 20 (1970) 534-538.
18. S. Dobner and B. Lewris deserve credit for working out the energy balances shown in Table 1.
19. F. J. Dent, "Steam-Oxygen Gasification of Fine Sizes of Coal in a Fluidized Bed at Elevated Pressure discussion," Trans. Inst. Chem. Engrs. 39 (1961) 22-23.
20. A. A. Godel, "Ten years of experience in the technique of burning coal in a fluidized bed," Revue Generale de Thermique, 5 (1966) 349-359.
21. F. Robson, United Aircraft Corp., personal communication.

22. T. Uno, Tetsu To Hagana, 37 (1951) 14-17.
23. T. Rosenqvist, "A Thermodynamic Study of the Reaction $\text{CaS} + \text{H}_2\text{O} = \text{CaO} + \text{H}_2\text{S}$ and the Desulfurization of Liquid Metals with Lime," J. Metals Trans. A.I.M.E., 3 (1951) 535-540.
24. K. J. Hill and E. R. S. Winter, "Thermal Dissociation Pressure of Calcium Carbonate," J. Phys. Chem., 60 (1956) 1361-1362.
25. Joint Army, Navy, and Air Force Thermochemical Tables, (JANAF Tables) prepared under direction of P. R. Stull, Thermal Research Laboratory, Dow Chemical Company, Midland, Michigan (1960-65), First Addendum, August, 1966.
26. W. M. McKewan, "Kinetics of Reduction of Iron Ores," in Physical Chemistry of Steelmaking, ed. by J. F. Elliot, M.I.T. Press (1965) 141-154.
27. O. Kubaschewski and E. L. Evans, Metallurgical Thermochemistry, Third Edition, Pergamon Press, New York (1958).
28. K. K. Kelley, "Contributions to the Data on Theoretical Metallurgy. XIII. High Temperature Heat-Content, Heat Capacity, and Entropy Data for the Elements and Inorganic Compounds," U.S. Bureau of Mines, Bulletin 584, (1960).
29. J. T. Clancey, G. P. Curran, C. E. Fink, B. Pasek, Everett Gorin, "Development of CO_2 Acceptor Process Directed Towards Low-Sulfur Boiler Fuel," Report Prepared for Division of Control Systems, Air Pollution Control Office, EPA, Durham, N.C. 22701, May 28, 1971.
30. O. Levenspiel, Chemical Reaction Engineering, John Wiley and Sons, Inc., New York (1962) 346-348.
31. P. B. Weisz, "Diffusivity of Porous Particles: I. Measurements and Significance for Internal Reaction Velocities," Zeitschrift für Physikalische Chemie, Neue Folge, 11. (1957) 1-15.

32. K. Laidler, Chemical Kinetics, 2nd ed., McGraw-Hill, New York (1965) 256-286.
33. P. L. Lee and M. J. D. Low, "Reaction of Gaseous Pollutants With Solids. IV. Infrared Study of the Reaction of H_2S With a Calcined Dolomite, CaO , and MgO ," Department of Chemistry, New York University, New York, New York, 10453 (1972).
34. A. K. Galwey, Chemistry of the Solid State, Chapman and Hall, London (1967) 163-199.
35. D. A. Young, Decomposition of Solids, Pergamon Press, New York (1966) 8-10.
36. L. S. Dent Glasser, F. P. Glasser and H. F. W. Taylor, "Topotactic Reactions in Inorganic Oxy-Compounds," Quart. Rev. (London) 16 (1962) 343-360.
37. J. O. Edström, "Solid State Diffusion in Reduction of Hematite," Jernkontorets Annaler, 140 (1957) 809-836.
38. J. B. Henderson, "A Study of the Rate and Mechanism of the Hydrogen Reduction of Fine Hematite Ores," report by The Broken Hill Proprietary Company Limited, Central Research Laboratories, Australia.
39. G. F. Hüttig, F. Kahler, and G. Meyenburg, Kolloid Zeit. 124 (1951) 160-163.
40. Reference 35, pages 64-72.
41. W. E. Garner, Chemistry of the Solid State, Academic Press, New York (1955) 213-230.
42. J. Zawadski and S. Breitznayder, Trans. Faraday Society, 34 (1938) 951-959.
43. M. Gibaud and M. Geloso, Peinture, Pigments, Vernis, 32 (1956) 306-308.
44. F. Bischoff, Z. für anorg. Chemie, 262 (1950) 288-296.
45. F. Bischoff, Radex-Rundschau (1949) 8-13.
46. F. Bischoff, Radex-Rundschau (1950) 141-147.

47. F. Bischoff, Monashefte, 81 (1950) 606-607.
48. W. D. Spencer and B. Topley, J. Chem Soc., 28 (1929) 2633-2650.
49. W. H. MacIntire and T. B. Stansel, Ind. Eng. Chem., 45 (1953) 1548-1555.
50. M.L. Smith and B. Topley, Proc. Roy. Soc., A134 (1931) 224-245.
51. B. Topley, Proc. Roy. Soc., A136 (1932) 413-428.
52. B. Topley and M. L. Smith, J. Chem. Soc. (1935) 321-325.
53. Reference 35, pages 67-72.
54. A.M. Squires, "Air Pollution: The Control of SO₂ from Power Stacks: IV. Power Generation With²Clean Fuels." Chemical Engineering, December 18, 1967, 101-109.
55. A.M. Squires, "Gasifying Oil for Clean Power," A.I.Ch.E. New York meeting, November 1967.
56. Reference 30, page 444.

12.0 Vita

Lawrence A. Ruth was born in Brooklyn, New York, on October 27, 1945. He received his elementary and secondary education in the New York City Public School System. He entered the City College of New York in September 1962 and graduated in February 1967 as a Bachelor of Engineering (Chemical).

He then entered the doctoral program in Engineering at The City College of The City University of New York and worked as part of a research team engaged in the development of systems to provide clean power from fossil fuels. He received his Master of Engineering (Chemical) in June 1968 and Ph.D. in February 1973.

Lawrence A. Ruth is a member of the American Institute of Chemical Engineers, American Chemical Society, Tau Beta Pi, Omega Chi Epsilon, and Sigma Xi.

The author is currently employed by the Esso Research and Engineering Company at their research center in Linden, New Jersey. He lives in Matawan, New Jersey, with his wife Ann and dog Fiddle.

13. Addendum

Results of Examination of Reaction Solids under Electron Microscope

After this dissertation was completed, Dr. Ernest Levine of the Department of Metallurgy of New York University was retained to examine the relevant reaction solids under the electron microscope. Results became available October 27, 1972. While these results must be considered tentative and subject to verification, we summarize them here for completeness. They suggest a modification of the reaction mechanism hypothesized in this dissertation.

In addition to pure powdered CaCO_3 , Levine examined the following samples prepared from powdered dolomite:

- A. Half-calcined dolomite prepared as described on page 40.
- B. Fully sulfided stone prepared at 600°C , 5% H_2S , 60% CO_2 (Fig. 25).
- C. Fully sulfided stone prepared at 800°C , 5% H_2S , 25% CO_2 (Fig. 11).
- D. 25% sulfided stone prepared at 600°C , 5% H_2S , 60% CO_2 (same as B but stopped at 25% conversion).
- E. 25% sulfided stone prepared at 600°C , 5% H_2S , 3% CO_2 (Fig. 25); these are conditions under which reaction "drops dead" at about 25% conversion.

In his examinations, constituent crystallites of the respective solids were identified from electron diffraction

patterns and dark field analysis.

Diffraction patterns characteristic of large single crystal CaCO_3 were obtained during the first few minutes of examination of the pure CaCO_3 sample. Under microscope conditions, the sample rapidly decomposed and diffraction patterns characteristic of small crystallites of CaO were obtained.

Examination of sample A (half-calcined dolomite) gave a diffraction pattern consistent with CaO and MgO . Apparently, patterns were not observed before the CaCO_3 had decomposed under the microscope. However, the CaO appeared in clusters having a preferred orientation indicating that they were formed from CaCO_3 crystallites $5000\text{\AA}$ or more in size. MgO crystallites were about $300\text{\AA}$ in size and had random orientation. All sulfided samples showed MgO of the same size and form.

Some sulfided samples showed large crystallites of CaS while other samples showed small crystallites, apparently according to conditions of the sulfiding reaction. In samples B and D (600°C , high CO_2), only fine particles of CaS were observed. Sample C (800°C , moderate CO_2) showed a mixture of large ($5,000\text{\AA}$) and fine crystallites. Sample E (600°C , low CO_2) showed only large crystals of CaS that appeared to be contiguous and to form a continuous layer of CaS .

An interpretation of these results that would be consistent with the kinetic data is as follows: High levels of CO_2 at 600°C may promote the formation of large numbers of fine crystallites of CaS that do not protect the underlying CaCO_3 ; perhaps CO_2 enhances nucleation of CaS crystals. On the other hand, at low levels of CO_2 a smaller number of large CaS crystals form and grow together to close off the surface, thereby protecting the remaining CaCO_3 from further reaction.

We may further speculate that both large and small CaS crystallites form at 800°C and intermediate CO_2 levels, the layer not being protective at 800°C . In an experiment conducted after electron microscope observations were available, we found that a layer of CaS formed at 800°C is protective at 600°C . The experiment was to convert a sample partially at 800°C and then to cool the sample to 600°C , whereupon the reaction promptly "dropped dead." This result suggests that the enhanced reactivity at the higher temperature may be a result of higher diffusivity of reactant in the CaS layer.

The results of electron microscope observations suggest a reaction mechanism that is similar in spirit to that hypothesized in the body of this dissertation, in the respect that the CO_2 partial pressure apparently affects the structure of the product CaS layer and the

degree to which this layer protects unreacted CaCO_3 . The hypothesis in the body of this dissertation refers to annealing as a mechanism affording porosity to the product layer. The electron microscope results suggest that the rate of nucleation of CaS crystallites may be at the root of the structural differences that arise at various CO_2 levels and temperatures.

Electron microscope results at this time are still tentative and do not rule out annealing as a contributing factor. Further work is planned.