INFORMATION TO USERS

This reproduction was made from a copy of a document sent to us for microfilming. While the most advanced technology has been used to photograph and reproduce this document, the quality of the reproduction is heavily dependent upon the quality of the material submitted.

The following explanation of techniques is provided to help clarify markings or notations 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 through an image and duplicating adjacent pages to assure complete continuity.

2. When an image on the film is obliterated with a round black mark, it is an indication of either blurred copy because of movement during exposure, duplicate copy, or copyrighted materials that should not have been filmed. For blurred pages, a good image of the page can be found in the adjacent frame. If copyrighted materials were deleted, a target note will appear listing the pages in the adjacent frame.

3. When a map, drawing or chart, etc., is part of the material being photographed, a definite method of “sectioning” the material has been followed. It is customary to begin filming at the upper left hand corner of a large sheet and to continue from left to right in equal sections with small overlaps. If necessary, sectioning is continued again—beginning below the first row and continuing on until complete.

4. For illustrations that cannot be satisfactorily reproduced by xerographic means, photographic prints can be purchased at additional cost and inserted into your xerographic copy. These prints are available upon request from the Dissertations Customer Services Department.

5. Some pages in any document may have indistinct print. In all cases the best available copy has been filmed.
Dombek, Priscilla Emily

IMPROVING THE CONVERSION OF THE SULFUR DIOXIDE • LIME REACTION BY USING ADDITIVES

The University of Arizona

M.S. 1986

University Microfilms International 300 N. Zeeb Road, Ann Arbor, MI 48106
PLEASE NOTE:

In all cases this material has been filmed in the best possible way from the available copy. Problems encountered with this document have been identified here with a check mark \( \checkmark \).

1. Glossy photographs or pages \( \checkmark \)
2. Colored illustrations, paper or print \( \checkmark \)
3. Photographs with dark background \( \checkmark \)
4. Illustrations are poor copy
5. Pages with black marks, not original copy
6. Print shows through as there is text on both sides of page
7. Indistinct, broken or small print on several pages
8. Print exceeds margin requirements
9. Tightly bound copy with print lost in spine
10. Computer printout pages with indistinct print
11. Page(s) lacking when material received, and not available from school or author.
12. Page(s) seem to be missing in numbering only as text follows.
13. Two pages numbered. Text follows.
14. Curling and wrinkled pages
15. Dissertation contains pages with print at a slant, filmed as received
16. Other

________________________________________________________________________

________________________________________________________________________

________________________________________________________________________

University
Microfilms
International
IMPROVING THE CONVERSION OF THE SO₂ - LIME

REACTION BY USING ADDITIVES

by

Priscilla Emily Dombek

A Thesis Submitted to the Faculty of the

DEPARTMENT OF CHEMICAL ENGINEERING

In Partial Fulfillment of the Requirements
For the Degree of

MASTER OF SCIENCE

In the Graduate College

THE UNIVERSITY OF ARIZONA

1986
STATEMENT BY AUTHOR

This thesis has been submitted in partial fulfillment of requirements for an advanced degree at The University of Arizona and is deposited in the University Library to be made available to borrowers under rules of the Library.

Brief quotations from this essay are allowable without special permission, provided that accurate acknowledgement of the source is made. Requests for permission for extended quotation from or reproduction of this manuscript in whole or in part may be granted by the head of the major department or the Dean of the Graduate College when in his or her judgement the proposed use of the material is in the interests of scholarship. In all other instances, however, permission must be obtained from the author.

SIGNED: Priscilla Emily Donlack

APPROVAL BY THESIS DIRECTOR

This thesis has been approved on the date shown below:

Farhang Shadman
Associate Professor of
Chemical Engineering

Date 12/11/86
I wish to thank Dr. Farhang Shadman, my research advisor, for his encouragement and valuable insights. His guidance is deeply appreciated.

I also wish to thank my parents and friends for helping to make my stay at graduate school an enjoyable experience.
**TABLE OF CONTENTS**

<table>
<thead>
<tr>
<th>Section</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>LIST OF ILLUSTRATIONS</td>
<td>vi</td>
</tr>
<tr>
<td>LIST OF TABLES</td>
<td>iii+</td>
</tr>
<tr>
<td>ABSTRACT</td>
<td>ix</td>
</tr>
<tr>
<td>1. INTRODUCTION</td>
<td>1</td>
</tr>
<tr>
<td>Acid Rain</td>
<td>1</td>
</tr>
<tr>
<td>Methods of Sulfur Dioxide Emissions Control</td>
<td>2</td>
</tr>
<tr>
<td>Method One: Flue Gas Desulfurization</td>
<td>4</td>
</tr>
<tr>
<td>Method Two: Use of an Additive</td>
<td>8</td>
</tr>
<tr>
<td>Addition of Lime to Combustors</td>
<td>8</td>
</tr>
<tr>
<td>Addition of Lime to Sulfide Ores</td>
<td>10</td>
</tr>
<tr>
<td>2. LITERATURE REVIEW OF THE SULFUR DIOXIDE/LIME REACTION</td>
<td>13</td>
</tr>
<tr>
<td>Theoretical Modeling</td>
<td>13</td>
</tr>
<tr>
<td>Pore Model</td>
<td>14</td>
</tr>
<tr>
<td>Grain Model</td>
<td>17</td>
</tr>
<tr>
<td>Structural Limitations</td>
<td>19</td>
</tr>
<tr>
<td>Objectives</td>
<td>25</td>
</tr>
<tr>
<td>3. EXPERIMENTAL APPARATUS AND PROCEDURES</td>
<td>26</td>
</tr>
<tr>
<td>Experimental Apparatus</td>
<td>26</td>
</tr>
<tr>
<td>Feed Gas Preperation</td>
<td>26</td>
</tr>
<tr>
<td>Reactor and Furnace</td>
<td>29</td>
</tr>
<tr>
<td>Gas Analysis</td>
<td>30</td>
</tr>
<tr>
<td>Material</td>
<td>31</td>
</tr>
<tr>
<td>Lime</td>
<td>31</td>
</tr>
<tr>
<td>Additives</td>
<td>33</td>
</tr>
<tr>
<td>Flake Preperation</td>
<td>35</td>
</tr>
<tr>
<td>Reaction Study</td>
<td>35</td>
</tr>
<tr>
<td>Experimental Data Analysis</td>
<td>37+</td>
</tr>
<tr>
<td>4. MATHEMATICAL MODEL</td>
<td>40</td>
</tr>
<tr>
<td>Derivation of the Slab Rate Equation</td>
<td>40</td>
</tr>
</tbody>
</table>

iv
TABLE OF CONTENTS — Continued

Derivation of the Grain Particle Rate Equation ...................... 43
Analytical Solution of the Flake Rate Equation ...................... 47
Parameter Estimation ................................................... 55
Solution Procedure ..................................................... 59

5. DISCUSSION AND RESULTS .......................................... 62

   Qualitative Observations ............................................ 62
   Comparison of the Reactivity of CaO and CaO/MgO Flakes ........ 63
   Effect of Kaolin Addition .......................................... 64
   Comparison of Additives ............................................ 67
   Effect of Temperature .............................................. 68
   Model Results ....................................................... 73

6. CONCLUSIONS ............................................................ 90

APPENDIX A: RAW DATA TABLES ......................................... 91
APPENDIX B: PROGRAM LIMEY ........................................... 103
NOMENCLATURE .......................................................... 108
REFERENCES ............................................................. 109
### LIST OF ILLUSTRATIONS

<table>
<thead>
<tr>
<th>Figure</th>
<th>Description</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>1-1</td>
<td>Estimated Distribution of Precipitation pH</td>
<td>3</td>
</tr>
<tr>
<td>1-2</td>
<td>Comparison of Base Case FGD Unit Costs</td>
<td>6</td>
</tr>
<tr>
<td>3-1</td>
<td>Schematic of Experimental Apparatus</td>
<td>27</td>
</tr>
<tr>
<td>3-2</td>
<td>Photo of Open Furnace</td>
<td>28</td>
</tr>
<tr>
<td>3-3</td>
<td>Photo of Closed Furnace</td>
<td>28</td>
</tr>
<tr>
<td>3-4</td>
<td>Schematic of Sulfur Dioxide Pulsed Fluorescent Analyzer</td>
<td>32</td>
</tr>
<tr>
<td>3-5</td>
<td>SEM Photo of Kaolin</td>
<td>34</td>
</tr>
<tr>
<td>4-1</td>
<td>SEM Photo of Unreacted CaO flake</td>
<td>57</td>
</tr>
<tr>
<td>4-2</td>
<td>SEM Photo of Reacted CaO flake</td>
<td>57</td>
</tr>
<tr>
<td>4-3</td>
<td>SEM Photo of Unreacted CaO/MgO 20% Kaolin Flake</td>
<td>58</td>
</tr>
<tr>
<td>4-4</td>
<td>SEM Photo of Reacted CaO/MgO 20% Kaolin Flake</td>
<td>58</td>
</tr>
<tr>
<td>5-1</td>
<td>Effect of Kaolin on the sulfur dioxide/dolomite Reaction; 700 °C</td>
<td>65</td>
</tr>
<tr>
<td>5-2</td>
<td>Effect of Kaolin on the sulfur dioxide/dolomite Reaction; 700 °C</td>
<td>66</td>
</tr>
<tr>
<td>5-3</td>
<td>Effect of Additives on the sulfur dioxide/dolomite Reaction</td>
<td>69</td>
</tr>
<tr>
<td>5-4</td>
<td>Effect of Temperature on the sulfur dioxide/lime Reaction</td>
<td>70</td>
</tr>
<tr>
<td>5-5</td>
<td>Effect of Temperature on the sulfur dioxide/dolomite Reaction</td>
<td>71</td>
</tr>
<tr>
<td>5-6</td>
<td>Effect of Temperature on the sulfur dioxide/dolomite Reaction 50% kaolin</td>
<td>72</td>
</tr>
<tr>
<td>Figure</td>
<td>Page</td>
<td></td>
</tr>
<tr>
<td>--------</td>
<td>------</td>
<td></td>
</tr>
<tr>
<td>5-7 Temporal Profile of Conversion; Comparison of Experimental Data with Model Results (CaO; 500°C)</td>
<td>74</td>
<td></td>
</tr>
<tr>
<td>5-8 Temporal Profile of Conversion; Comparison of Experimental Data with Model Results (CaO/MgO; 500°C)</td>
<td>75</td>
<td></td>
</tr>
<tr>
<td>5-9 Temporal Profile of Conversion; Comparison of Experimental Data with Model Results (50% kaolin; 500°C)</td>
<td>76</td>
<td></td>
</tr>
<tr>
<td>5-10 Temporal Profile of Conversion; Comparison of Experimental Data with Model Results (CaO; 700°C)</td>
<td>77</td>
<td></td>
</tr>
<tr>
<td>5-11 Temporal Profile of Conversion; Comparison of Experimental Data with Model Results (CaO/MgO; 700°C)</td>
<td>78</td>
<td></td>
</tr>
<tr>
<td>5-12 Temporal Profile of Conversion; Comparison of Experimental Data with Model Results (30% kaolin; 700°C)</td>
<td>79</td>
<td></td>
</tr>
<tr>
<td>5-13 Temporal Profile of Conversion; Comparison of Experimental Data with Model Results (50% kaolin; 700°C)</td>
<td>80</td>
<td></td>
</tr>
<tr>
<td>5-14 Effect of Flake Thickness on Temporal Profiles of Conversion</td>
<td>81</td>
<td></td>
</tr>
<tr>
<td>5-15 Effect of Macropore Diffusivity on Temporal Profiles of Conversion</td>
<td>82</td>
<td></td>
</tr>
<tr>
<td>5-16 Effect of Porosity of Temporal Profiles of Conversion</td>
<td>83</td>
<td></td>
</tr>
<tr>
<td>5-17 Effect of Initial Porosity of Final Conversion</td>
<td>84</td>
<td></td>
</tr>
<tr>
<td>5-18 Effect of Additives on Flake Porosity</td>
<td>85</td>
<td></td>
</tr>
<tr>
<td>5-19 Effect of Porosity on Macropore Diffusivity</td>
<td>87</td>
<td></td>
</tr>
<tr>
<td>5-20 Apparent Activation Energies</td>
<td>89</td>
<td></td>
</tr>
</tbody>
</table>
LIST OF TABLES

Table Page
1-1 Comparison of FGD Systems Installed on Boiler Plants.......... 5
5-1 Porosity and Macropore Diffusivity Values....................... 86
A-1 Conversion Data (CaO, 1020 ppm SO₂, 700 °C).................. 92
A-2 Conversion Data (CaO/MgO, 1020 ppm SO₂, 700 °C)............ 93
A-3 Conversion Data (CaO/MgO 30% kaolin, 1020 ppm SO₂, 700 °C)........ 94
A-4 Conversion Data (CaO/MgO 50% kaolin, 1020 ppm SO₂, 700 °C)........ 95
A-5 Conversion Data (CaO, 1020 ppm SO₂, 500 °C).................. 96
A-6 Conversion Data (CaO/MgO, 1020 ppm SO₂, 500 °C)............ 97
A-7 Conversion Data (CaO/MgO 50% kaolin, 1020 ppm SO₂, 500 °C)........ 98
A-8 Conversion Data (CaO/MgO 50% kaolin, 1940 ppm SO₂, 500 °C)........ 99
A-9 Conversion Data (CaO/MgO 50% kaolin, 4100 ppm SO₂, 700 °C)........ 100
A-10 Conversion Data (CaO/MgO 50% alumina, 1020 ppm SO₂, 700 °C).... 101
A-11 Conversion Data (CaO/MgO 50% silica, 1020 ppm SO₂, 700 °C)..... 101
A-12 Percent Weight Loss During Heating.......................... 102
ABSTRACT

The emission of sulfur dioxide into the atmosphere is a worldwide problem since these emissions are a major cause of acid rain. The capture of sulfur dioxide emissions by lime and dolomite is limited by structural changes that are caused by the chemical reaction and prevent complete lime utilization. A promising method of increasing sulfur capture is by the use of additives. The additives studied (kaolin, silica powder and alumina powder) affect the physical structure of the lime by increasing the available pore volume. Using these additives, over twice as much sulfur dioxide can be captured by the dolomite at 700 C. A mathematical model is developed that fits the experimental data and shows the effect of parameter changes on final conversion.
CHAPTER ONE

INTRODUCTION

Acid rain is one of the most devastating environmental problems today, one of its major causes is sulfur dioxide emissions. A brief introduction to acid rain and the methods being used and studied to control sulfur dioxide emissions are presented in this chapter.

Acid Rain

Since acid rain has become a major environmental problem a global network has been established to study major pollutants. This global network is needed since acid rain may fall a few hundred to a few thousand miles from the source of emission [1]. Although NOx emissions also are responsible, sulfur dioxide emissions are clearly the most common cause amounting, globally, to 200 million tons per year [2].

Vegetation is affected by extremely small sulfuric acid concentrations. In many cases the effect is indirect stemming from a deterioration of the soil's nutrients. Lichens die if exposed to acid concentrations of 0.01 to 0.03 ppm and coniferous trees at 0.07-0.08 ppm [2]. Soil acidification chiefly involves the replacement of basic cations (K, Ca, Mg, Na) by hydrogen and aluminum ions, this reduces the amount of available nutrients in the soil [3].
In the U.S.S.R. over 1.5 million tons of lime have been spread over the soil [4].

Acid rain also affects freshwater lakes by washing metals into the water and lowering the pH. Substantial leaching of Al from soils and into ground water and streams and lakes has been observed in areas of high acid rain deposition [5]. This process can drastically lower the reproduction rates of birds, fish and amphibians as their eggs are destroyed. Historical buildings, monuments, exposed metals and paint coatings show deterioration from sulfur dioxide and dilute acid rains.

The map in figure 1-1 is the result of intensive global monitoring activity [3]. Below a pH value of 5.6 precipitation can be considered acidic, a pH value of 4.6 is ten times as acidic as 5.6. Areas of low pH usually coincide with areas of low rainfall and/or calcareous soils. Dry deposition involves mechanisms not involving precipitation which transfer atmospheric constituents to the surface. Dry deposition is difficult to measure but it is as least as high as the wet deposition levels [3].

**Methods of Sulfur Dioxide Emissions Control**

In recent years, there have been a large number of studies on various aspects of sulfur dioxide emission control in combustors. These studies have been primarily focused on two important methods. The first method, flue gas desulfurization (FGD), has been used commercially for decades to capture the sulfur dioxide after it leaves the process. Although the sulfur removal efficiency is high in FGD, the application of FGD to all existing power plants would increase costs significantly.
Figure 1.1 Estimated distribution of precipitation pH
The second method which is potentially less expensive is based on the introduction of an additive, particularly limestone, directly into the combustor. This process would be best suited for older and smaller installations where it would be difficult to recover the high capital costs of a FGD system. The success of this method depends on improving the sulfur capturing ability of additives like limestone. Improving sulfur capture would considerably lower the cost of this method since it is heavily based on cost of the raw materials. Each of the above mentioned methods has given rise to various specific processes which are briefly reviewed below.

Method One: Flue Gas Desulfurization

There are now 144 known FGD systems operating on fossil-fueled combustion sources. Of these 74 are operating on power utility boilers with the remainder on industrial combustion sources, principally boiler plants but also on iron ore sinter plants and petroleum refinery plants [6]. Table 1-1 summarizes the basic technical data on the FGD systems surveyed in the study. Figure 1-2 summarizes the relative costs of the technologies. What follows is a brief summary of each technology that uses lime [6].

Limestone/Sludge; Primary Reagent:CaCO$_3$

This process was first used in 1933. The flue gases are scrubbed with a limestone slurry. The sulfur dioxide reacts to form insoluble calcium compounds, which are separated and partly dewatered for disposal. This process is used principally in the U.S. for coal and oil plants.
Table 1-1. Comparison of FGD Systems Installed on Boiler Plants

<table>
<thead>
<tr>
<th>FGD Process</th>
<th>Sulfur Dioxide Removal Efficiency, %</th>
<th>Predominant Fuel Type</th>
<th>Sulfur, %</th>
</tr>
</thead>
<tbody>
<tr>
<td>Limestone/sludge</td>
<td>57-92</td>
<td>Coal</td>
<td>0.5-5.4</td>
</tr>
<tr>
<td>Lime/sludge</td>
<td>70-92</td>
<td>Coal</td>
<td>0.8-4.7</td>
</tr>
<tr>
<td>Double alkali/sludge</td>
<td>90-99</td>
<td>Coal</td>
<td>0.9-5.0</td>
</tr>
<tr>
<td>Seawater scrubbing</td>
<td>90-97</td>
<td>Oil</td>
<td>3.0</td>
</tr>
<tr>
<td>Limestone/gypsum</td>
<td>90-96</td>
<td>Oil</td>
<td>0.6-2.2</td>
</tr>
<tr>
<td>Lime/gypsum</td>
<td>80-92</td>
<td>a</td>
<td>2.9</td>
</tr>
<tr>
<td>Double alkali/gypsum</td>
<td>90-95</td>
<td>Oil</td>
<td>2.0-2.9</td>
</tr>
<tr>
<td>Magnesium oxide</td>
<td>90-95</td>
<td>a</td>
<td>2.0-3.8</td>
</tr>
<tr>
<td>Carbon adsorption</td>
<td>70-80</td>
<td>Coal</td>
<td>0.9-5.0</td>
</tr>
<tr>
<td>Copper Oxide</td>
<td>80-90</td>
<td>Oil</td>
<td>2.5</td>
</tr>
</tbody>
</table>

* Equal number of coal and oil firing systems were surveyed

Source: NTIS PB-295 001, prepared by the flue gas desulfurization study group of the NATO committee on the challenges of modern society (NATO-CCMS Study) January 1979.
Figure 1-2. Comparison of base case FGD unit costs

Source: EPA-600/7-80-142

500 MW units; 3.5% sulfur coal (except seawater process)
90% sulfur dioxide removal
Lime/sludge; Primary Reagent: CaO

This process was first used in 1972. The flue gases are scrubbed with a slurry of hydrated lime where the sulfur dioxide reacts to form insoluble calcium compounds which are separated and partly dewatered for disposal. This process is used mainly in the U.S. for oil and coal plants.

Double Alkali/Gypsum; Primary Reagent: NaOH or Na CO and CaO or CaCO
2 3 2 3

This process was first used in 1973. The flue gases are scrubbed with a solution of alkaline sodium compounds. The used solution is then regenerated with lime or limestone in a separate reactor and the insoluble calcium-sodium compounds are oxidized to gypsum, separated and dewatered.

Double Alkali/Sludge; Primary Reagent: NaOH or Na CO and CaO or CaCO
2 3 2 3

This process was first used in 1974. The flue gases are scrubbed with alkaline sodium based compounds in solution. This solution is regenerated with lime or limestone in a separate reactor to form insoluble calcium compounds which are separated and partly dewatered for disposal. Recent commercial operation on industrial sized coal-fired boilers in the U.S.

Limestone/gypsum; Primary Reagent: CaCO
3

This process was first used in 1973. The flue gases are scrubbed with a limestone slurry. The resulting calcium-sulfur compounds are air oxidized to gypsum, separated and dried. This process is used in commercial operation (coal and oil), principally in Japan.
Lime/Gypsum; Primary Reagent: CaO

This process was first used in 1964. Flue gases scrubbed with a slurry of hydrated lime. Resulting calcium-sulfur compounds are oxidized to gypsum, separated and dewatered.

Other scrubbing methods that do not use lime include seawater, sodium sulfite (Wellman-Lord), magnesium oxide, copper oxide and carbon adsorption. The Japanese have developed two advanced processes, ammonia scrubbing [7] and exposing the flue gas to an electron beam [8].

Method Two: Use of an Additive

Instead of flue gas treatment, one can use additives to control the emission of sulfur dioxide in-situ [9]. The critical step in developing this technology is improving the lime utilization and sulfur dioxide capturing efficiency. There have been various studies on methods of improving lime efficiency.

Addition of Lime to Combustors

Currently, much work is being done by several power plants and other organizations on the addition of limestone to a coal-fired combustor. As an example, the Energy and Environmental Research Corporation (EERC) [10] is presently developing a method to increase the utilization of limestone by increasing its reactivity. The work focuses on using a hydrate of calcium hydroxide as opposed to calcium carbonate. Tests are done using either an isothermal entrained flow reactor or a non-isothermal Controlled Temperature Tower Furnace (CTT).
The studies have shown that when calcium carbonate is reacted it calcines to calcium oxide which has a molar volume 46% less than the carbonate. This gives a maximum theoretical porosity of 54%, thus resulting in a maximum conversion of 68% based on the internal structure. The calcination reaction of both carbonates and hydrates is complicated, at the high temperatures studied, by the concurrent desurfacing of the calcium oxide formed. Both carbonates and hydrates cannot develop high surface areas when calcined in thick beds because the transport of carbon dioxide or water becomes rate limiting, thus the calcination reaction is slowed and more sintering takes place.

EERC found that the hydrates were more reactive than precalcined carbonates. This might be due to their smaller particle size which may be due to the fact that hydrates calcine 35 times faster than carbonates, resulting in higher surface areas. The hydrates formed under pressure were more reactive than the commercial atmospheric hydrates. Hydrates made from finer quicklimes were also more reactive. Short hydration times and low temperatures also increased sulfur removal. This might indicate grain or crystal growth during hydration. They suppose that this may explain why the addition of low boiling point alcohols to the hydration water forms superior hydrates. EERC found that using hydrates and a Ca:S molar ratio of 2:1, up to 60% of the sulfur was captured.
Addition of Lime to Sulfide Ores

Many metals, such as copper, zinc and nickel, occur naturally as sulfide ores. When these ores are roasted in the atmosphere to convert them into an acid leachable form (either a metal sulfate or oxide), large quantities of sulfur dioxide and sulfur trioxide gases are formed. After acid leaching, the solution undergoes electrowinning and the desired metal product collects at the cathode.

This process is an ideal candidate for the in-situ addition of lime since typical roasting temperatures are from 500 to 1000 °C, significantly lower than coal combustion temperatures. Besides being favored at lower temperatures (450-1250 °C), the reaction is favored at higher sulfur dioxide concentrations (above 3000 ppm) which occur inside the roasting sulfide particles.

There have been several studies of this process in recent years. Havers and Wong [11] introduced magnesium calcium and sodium compounds during the roasting of chalcopyrite (primarily CuFeS) and found that only the calcium hydroxide met emissions standards. Bartlett and Huang [12] studied a stoichiometric mix of lime and copper in a fluidized bed. The sulfur dioxide capture by the lime was disappointingly low due to temperature escalation (both the roasting and sulfur dioxide/lime reactions are exothermic) and the short residence times in the fluidized bed. Due to the short residence times, the sulfur dioxide was being blown out of the bed before reaction with the lime.

To solve these problems, Bartlett and Huang [13] modified their reaction scheme by using pellets. This slowed down the reaction by
increasing the diffusion resistance at 450-800 °C and therefore improved temperature control and lime capture. The pellets were made of uniformly mixed lime and ore powders. These studies showed that the optimal temperature for both metal recovery and sulfur capture was 500 °C and that up to 98% of the sulfur released could be fixed. At higher temperatures the pellet porosity decreased due to sintering.

Ahmadzai, Blairs, Harris and Staffansson [14] roasted uniformly distributed lime and copper pellets at temperatures from 753-873 °C. They observed that lime increased ferrite formation. Ferrites occur when the metal oxide formed during the roasting process combines with the iron present in the ore; they are not easily acid leached and result in reduced metal recovery.

Because of the work discussed above a non-uniform lime/metal sulfide pellet seemed to be a logical extension to increase sulfur recovery and minimize ferrite formation. Morris [15] [16] investigated zinc sulfide pellets with a lime coating. It was found that a 1.3:1 calcium to sulfur ratio captured close to 100% of the emissions until 60% pellet conversion and had an overall sulfur dioxide capturing efficiency of 95%. Although the capture was best at the lowest temperature studied (700 °C), enough sulfur was captured at 800 °C to meet EPA standards. The sulfur dioxide escape was mainly attributed to crack formation in the lime coating. The cracks formed while heating the pellet to reaction temperature and increased as the reaction progressed. More cracks formed at higher reaction temperatures.
Increasing the water content in the lime coating almost eliminated crack formation and reduced the size of the cracks which formed. It is expected that these pellets would capture nearly all the sulfur dioxide generated by the roasting reaction.
CHAPTER TWO

LITERATURE REVIEW OF THE SULFUR DIOXIDE/LIME REACTION

Theoretical Modeling

Mathematical models are important because they can give some insight into the physical changes that take place in the reactive solid and therefore be used to modify the reaction. A mathematical model also minimizes the number of experiments needed by predicting the reaction outcome under various conditions.

Mathematical models require some prior knowledge of the structure of the solid. These parameters are needed in the model because they are used to relate to how fast the reactant gas is transported to the inner and outer surfaces of the solid, how much of the solid will react and how soon the reaction stops. Several of these structural parameters, such as surface area and pore size distribution can be obtained experimentally. Each model is unique in the parameters it requires, but almost always at least one structural parameter is needed.

Surface area measurements are determined using the BET method [17]. In this technique, the amount of nitrogen gas adsorbed at equilibrium at its normal boiling point (-195.8 °C) is measured at a range of nitrogen partial pressures below one atmosphere. This data is used to determine the volume of gas adsorbed at one monomolecular layer. From the projected surface area of a molecule on the surface the surface area can be calculated. There is some uncertainty as to the accuracy of
of this method; however, the method is standardized, widely used and reproducible.

There are two methods used to measure the distribution of pore volumes [17]. In the first method, mercury intrusion, mercury is forced into the pores of the solid and the pressure used is related to pore size. In the second method, nitrogen is condensed in the pores and slowly desorbed. The vapor pressure can be related to pore sizes below 200 Angstroms. Since it is difficult to measure the pores below 100 Angstroms using mercury intrusion because of the high pressures involved a combination of the above two methods is often used.

A thorough review of the wealth of literature relating to the modeling of the sulfur dioxide and lime reactions shows that two types of structural models have been used. One model represents the pores in the lime as a series of pores and the other model views the solid as a collection of individual grains. A basic summary of the two models is presented here.

**Pore Model**

Petersen [18] in 1957 developed a model for reaction in porous solids assuming a random collection of cylindrical pores of equal radius. A relationship between porosity and surface area was derived, taking into account pore intersection and overlap.

Szelky and Evans [19] considered a simplified version of both pore and grain models. In the pore model, the solid was assumed to consist of a series of uniformly spaced pores, all of the same radius extending into the semi-infinite solid. As the reaction progresses,
the gas first reacts with the pore walls but as the reaction product starts filling up the pore radial diffusion through this layer is taken into account and the rate of reaction is slowed. Between adjacent pores the product layers meet leaving 'unreacted fingers' [19]. The product layer on the wall is thickest near the pore entrance due to the concentration gradient inside the pore, this eventually causes the pore to close. Two diffusion constants are needed, one to describe how the reactant gas diffuses into the pores and one to describe its transport through the product layer on the pore walls.

Gavales [20] extended the random pore model developed by Petersen. Gavales notes that Petersen's model does not allow pore size variation and does not link the pore intersections to the geometry of the pores; therefore, Petersen's equations derived for surface area and porosity are largely empirical. Gavales derives these parameters as well as the length of the pores and the number of pore intersections from a single probability density function used to characterize the solid. The model is used to solve the gasification of char in oxygen which is chemically controlled; however, the model has been extended to cases where diffusion resistance is also present.

Bhatia and Perlmutter [21] developed a random pore model which they applied to the sulfur dioxide/lime reaction. The model is based on the initial porosity and surface area and a structural parameter related to the pore structure. They suggested that because of the product layer diffusivities found ($6.0 \times 10^{-12} \text{ m}^2/\text{s}$ at $760^\circ\text{C}$), a highly activated diffusion process might be involved.
Christman and Edgar [22] also used a distribution of pore sizes in their pore model instead of an average pore size. Although the model does not take into account pore intersections such as Bhatia and Perlmutter [21] it predicts reaction rates over two and a half hours of reaction time and the reaction does not stop suddenly because of pore plugging as with Hartman and Coughlin's [23] grain model. They point out that this is due to the gradual decrease in reaction rate as the different sizes of pores become plugged.

Dennis and Hayhurst [24] presented an analytical solution to the problem of diffusion-reaction of sulfur dioxide in porous lime. This model retains the detailed reaction parameters of previous models and gives rates and conversions explicitly as a function of time. The model was verified using data on the sulfation of limestone at temperatures of 1098 °K, 1148 °K and 1248 °K in an electrically heated bed of fluidized sand. The gas mixture contained .25 % by volume SO\textsubscript{2}, 1.0% by volume \textsubscript{2}O with a nitrogen balance. In the model the reaction was considered to take place in a slab, with its thickness being much smaller than its length and width. The slab consisted of parallel pores, each of finite length and wedge shaped. The width of the pore was taken to be much larger than the distance between the center of a pore and the center of the distance between adjacent pores. Because of this model feature the reaction occurs only between the "two major parallel surfaces". The authors also assumed that the rate of reaction was determined by diffusion through the product layer on the pore wall. Good agreement was found between this model and experimental data. The intrinsic rate
constant had little effect on the overall conversion in contrast to the diffusivity through the product layer and the BET surface area of the calcined particles. As the porosity increased the overall conversion increased. The opposite effect was observed for surface area since greater surface areas are associated with smaller pores which plug rapidly.

In a paper also published in 1986, Simons and Garman [25] analyzed previous sulfation models, including the work of Bhatia and Perlmutter (1981), Hartman and Couglin (1976 and 1978), Christman and Edgar (1983), Bardakci (1984) and Marsh and Ulrichson (1982). They develop a pore-plugging model with a tree-like description of pore branching developed by Simons [26]. In this model product systematically fills pore of all sizes and no adjustable parameters are needed. Instead of attributing deactivation through product layer diffusion in this model the rate controlling mechanism is attributed to the plugging of the smallest pores. Good agreement was found between this model and extensive sulfur dioxide and hydrogen sulfide adsorption data.

Grain Model

Szelky and Evans [19] described a simple grain model that imagines the solid as a collection of uniformly spaced spherical particles each of which is surrounded by a uniform but time dependent gas concentration. Each grain reacts according to the 'shrinking core model' with a progressively thicker layer of product formed as the reaction progresses. The spheres will also meet a decreasing concentration of gas depending on how far they lie below the solid surface. Because of
these phenomena, two diffusion coefficients are needed: one to describe the transfer of the gas through the solid and another to describe the gas transfer through the product shells of the individual grains. At some point during the reaction the time needed for the reactant gas to diffuse through the grain product shells is so slow that the reaction virtually ceases even though some unreacted solid may remain inside the grains.

Hartman and Coughlin [23] further developed this grain model and apply it to experimental data in a paper published in 1976. After solving the model equations using numerical integration, very good agreement was found. As referred to by Christman and Edgar [22] in the pore model section an adjustable residual porosity parameter was included.

In 1984, Bardakci [27] studied the sulfation of Greer limestone pellets in a high temperature diffusion cell reactor. The data from experimentally measured effective diffusivities of argon through the calcined pellets were incorporated into an expanding grain model. The grain radii were found to vary from 1.0 to $2.0 \times 10^{-6}$ cm depending on the calcination temperature. The diffusivity through the grain product shells was found to vary by the absolute temperature as:

$$D = 0.00420 \exp(-34130/RT)$$

(2-1)

Bardakci also found that as the reaction progresses, the diffusivity of the $SO_2$ through the grains and product shells decreases. This is related to the formation of a tortuous product shell during sulfation and the increase in tortuosity as the reaction progresses.
A recent grain model developed by Silcox et al [28] includes the sintering of the lime during reaction at very high temperatures.

**Structural Limitations**

The major problem of the sulfur dioxide reaction with limestone was demonstrated by Potter's [29] experiments in 1969. After reacting 86 carbonate rock samples in flue gas the limiting conversion was found to be about 45%. The low conversion was attributed to a loss in porosity as the reaction progressed. This is a direct result of the calcium sulfate product having a molar volume of 52.2 cm$^3$/mole which is over three times as large as the molar volume of calcium oxide of 16.9 cm$^3$/mole which was reported by Weast [30] in 1968. This causes a decrease in the pore volume and eventually pore plugging. Over the years this has been observed in numerous studies even with reaction times on the order of seconds or minutes (Borgwardt and Harvey 1972).

Borgwardt and Harvey [31] reacted eleven specimens of limestones and dolomites at 980°C in flue gas containing 3000 ppm SO$_2$ on a dry basis. Extensive measurements were made to determine the pore and grain characteristics and the limestone surface areas. Electron microprobe analysis was also done on the particle sulfate distribution. They found that particles smaller then .01 cm with pores larger the 1 um react throughout their internal pore structure at a rate proportional to their BET surface areas up to CaO conversions of 50% when the reaction changes from chemical reaction control to solid diffusion control. They also reported that not only surface area but pore size distribution is important. Small pores give higher initial rates but are quickly filled with
product while larger pores give lower initial rates but have higher capacities. They found that the dolomites which contain a high proportion of magnesium oxide reached 100% CaO conversion and attributed this to a higher ratio of pore volume to CaO content.

Hartman and Coughlin [23] placed their emphasis on the rapid decrease in porosity and point to the conflicting results of Pigford and Sliger [32] who assumed the reaction was diffusion controlled and Wen and Ishida [33] who showed that the reaction was chemical reaction controlled between 590-680 °C. In this study ten different limestones were reacted in 0.29% SO₂ by volume at temperatures ranging from 750-1000 °C. The particles were 0.5 to 1.25 mm in diameter. The optimum reaction temperature was found to be 900 °C. Working with precalcined particles the optimum rate occurred at 980 °C. This is because as calcination temperature increases the surface area decreases as noted by McClellan et al. in 1970, while the rate for the sulfation reaction increases until 1150 °C.

Electron microprobe analysis was used on cross sections of particles sulfated for various times. They noticed a distinct boundary that separated the inside unreacted CaO from the outer zone. At short times the sulfation took place on the outside of the particles. As the reaction time increased this zone gradually spread inward until calcium sulfate was present throughout the particles. However, even at sulfation times as long as two hours a considerable amount of CaO remained unreacted on the outer particle edge. This was confirmed by microscope examinations of the reacted particles which showed not all the pores were filled with product even after long reaction times. Therefore, a
residual porosity equal to 0.002 was added to the grain model. They suggest using limestone with large pore volume and small grain sizes such as marls (about 60% average porosity) and chalks.

In 1978, Cole et al [34] reacted limestones under the relatively high reaction temperatures associated with the EPA defined limestone injection into multi-stage burners or LIMB process. In this process the limestones are injected into the radiant section of a pulverized-coal-fired boiler. To simulate this process limestones were injected into a flat flame and samples were taken using a probe. No changes were found after five minutes in specific surface area or conversion. They found that surface area was the principle factor in reactivity. The optimum temperature was found to be 1200 °C, the lowest temperature used in the study. Even at this temperature the dolomite (CaCO$_3$MgCO$_3$) reached 50% conversion in one second of residence time. The high reactivity of the dolomite compared to the Vicron 45-3 (CaCO$_3$) and the calcium hydroxide (Ca(OH)$_2$) is attributed to the low intersolubility of the oxides which keeps the pore structure open and inhibits sintering.

Marsh and Ulrichson [35] in 1985 used thermogravimetric analysis (TGA) to elucidate the kinetics between SO$_2$ and CaO. They point out that limestone quickly calcines in a fluidized bed coal combustor according to the reaction below

$$\text{CaCO}_3 (s) \rightarrow \text{CaO}(s) + \text{CO}_2 (g) \quad (2-2)$$
By hydrating the CaO to form Ca(OH) and subsequent calcination a more highly porous form of lime can be formed by the reaction below:

\[ \text{Ca(OH)}(s) \rightarrow \text{CaO}(s) + \text{H}_2\text{O} \quad (2-3) \]

They found that the sulfation reaction is a complex one. Between 560 and 830 °C the product was a mixture of CaSO₃, CaSO₄ and CaS according to the reactions below. Above 830 °C only CaSO₄ and CaS were present and below 450 °C only CaSO₃ was present.

\[ \text{CaO} + \text{SO}_2 \rightarrow \text{CaSO}_3 \quad (2-4) \]

\[ \text{CaO} + 1/2 \text{O}_2 + \text{SO}_2 \rightarrow \text{CaSO}_4 \quad (2-5) \]

\[ 4\text{CaSO}_3 \rightarrow 3\text{CaSO}_4 + \text{CaS} \quad (2-6) \]

\[ 4\text{CaO} + 4\text{SO}_2 \rightarrow 3\text{CaSO}_4 + \text{CaS} \quad (2-7) \]

As reaction time increased the fraction of CaSO₃ decreased probably due to the disproportionation reaction (2-6) above or it could possibly be due to the oxidation reaction below

\[ \text{CaSO}_3 + 1/2 \text{O}_2 \rightarrow \text{CaSO}_4 \quad (2-8) \]
The reaction was found to be first order from 740-930 °C in sulfur dioxide. Below 450 °C the reaction was found to be zero order in sulfur dioxide. This change corresponds to the change in solid product from CaSO₃ to CaSO₄. Reacting sintered CaO on quartz plates it was found that pore closure, product layer diffusion and product sintering are all important at high conversion levels. Most of the grain micro-pores of the CaO grains obtained from calcining Ca(OH)₂ had a radius of about 22 angstroms.

Kocaefe, Karman and Steward [36] also used TGA to study the sulfation rates of calcium, magnesium and zinc oxides with SO₂ and SO₃. Particles of radius .071 to .151 mm were reacted at gas concentrations of .075-.62 moles/m³ and temperatures of 450-1100 K. They found that zinc oxide did not react with a mixture of sulfur dioxide and oxygen. Similarly, magnesium oxide did not react below 900 °K. Above 900 °K, MgO reacted but at a much lower rate than CaO. Magnesium oxide also reached a much smaller level of total conversion than the CaO.

Simons and Garman [25] refer to Borgwardt and Harvey [31] who found the intrinsic rate constant to be equal to 0.22 cm/s or 0.014 kg SO₂/s/m² of CaO internal surface per MPa sulfur dioxide pressure. This constant reflects the reaction being first order in sulfur dioxide partial pressure and in surface area. For the larger particles they concluded that CaO utilization was extremely dependent upon the porosity because of pore plugging. They noted that when two different limestones were reacted (Borgwardt and Harvey, 1972) the stone with the slightly greater porosity (0.52 to 0.45) was more reactive even though its surface area was much less.
Borgwardt and Bruce [37] focused on how grain size and temperature effect sulfur dioxide capture in reported test for the limestone injection multistage burner process (LIMB). Limestone particles of 1 um were dispersed in quartz wool substrate, calcined and sintered to reduce the specific surface area to the desired value. The particles were then exposed to 3000 ppm sulfur dioxide mixture for various times. Since diffusion within the pores was absent the data analysis was simplified and confirmed the conclusion of Pigford and Sliger that product layer diffusion control the ultimate rate. The apparent activation energy was found to be 37.6 kcal per mole. Because the effect of temperature was so great they concluded that the diffusion of a gaseous species, sulfur dioxide or sulfur trioxide, was not involved. They noted that since the activation energy corresponds to the diffusion of ions due to thermal defects (Beniere and Catlow [38]), one would expect O ions to diffuse to the product layer surface while equivalent counterdiffusion of the SO takes place. The reaction at the product layer surface would be

\[
\text{SO} + \text{O} \rightarrow \text{SO}_{3/4} \quad (2-9)
\]

The reactivity increased with the square of the BET surface area in a range of from 2 to 63 m/g. It was also determined that in the absence of pore diffusion the conversion increased with approximately the 0.62 power of the sulfur dioxide partial pressure. This also supports an ionic diffusion process.
Objectives

Based on available information, the main obstacle in the way of using lime for the capture of sulfur dioxide emissions is the structural limitations which prevent the complete utilization and conversion of the lime.

The objective of this work was to observe how the lime structure changes during reaction. Once the structural changes are understood this information can be utilized to control and improve conversion. A particular objective of this work was to modify this structure advantageously by using additives. In particular, the goal was to select additives which would reduce the effect of pore closure and enhance both the reactivity and capacity of the lime.
EXPERIMENTAL APPARATUS AND PROCEDURES

Experimental Apparatus

The experimental apparatus is shown in figure 3-1. It consists of three sections: gas preparation, reactor and gas analysis. These sections are described below. During an experimental run, a gas mixture of sulfur dioxide and air flowed through the system and into the quartz glass reactor where the sulfur dioxide reacted with a lime flake which was heated by a mini-furnace. The concentration of the gas flowing into and out of the reactor was analyzed by a sulfur dioxide pulsed fluorescent analyzer.

Feed Gas Preparation

Cylinders of ultra high purity air and nitrogen were used for preparing gas mixtures. The pulsed fluorescent analyzer was calibrated using a Matheson analyzed 2000 ppm mixture of sulfur dioxide in air. This calibration gas was also mixed with air for experiments where a concentration of 1000 ppm sulfur dioxide was needed. The pure sulfur dioxide gas was mixed with air as needed for gas concentrations above 1000 ppm. After an experiment was ended nitrogen gas flowed through the system until the reactor cooled and the flake was analyzed.
Figure 3-1. Schematic of experimental apparatus
Figure 3-2. Photo of open furnace

Figure 3-3. Photo of closed furnace
The system consisted of quarter inch copper tubing with brass swagelock fittings from the nitrogen and air tanks to the point where sulfur dioxide was encountered. Because the sulfur dioxide corrodes copper, all the fittings that came into contact with the sulfur dioxide consisted of polypropylene quarter inch tubing with swagelock fittings of polypropylene ferrules and stainless steel nuts. The nitrogen and air tanks were connected to flow meters so that their flow rates could be easily controlled. Since the gas from the pure sulfur dioxide cylinder and the 2000 ppm sulfur dioxide cylinder would corrode a flow meter, laminar flow elements were used to control the flow. The laminar flow elements consisted of narrowed pieces of stainless steel tubing and were connected to the cylinders directly after the pressure gauges. The flow rate could be regulated within a narrow range by changing the outlet pressure of the tank. On/Off valves were installed after the flow meters and laminar flow elements. A three-way valve was installed after the sulfur dioxide mixed with the air so that the gas flow could be switched to either flow through the reactor or through the sulfur dioxide analyzer.

Reactor and Furnace

The reactor consisted of a 7 mm ID, 9 mm OD quartz glass tube about twenty inches in length. The reactor was heated by an electric furnace. The furnace was a Lindberg model 55035 minifurnace. Since the furnace is only 14 inches high and a little over 13 inches long it was placed under the hood. The base has a temperature control dial, a built-in thermocouple, and a dial readout in degrees fahrenheit or centi-
grade. The furnace thermocouple readings proved to be inaccurate when compared to placing a type K thermocouple into the furnace, next to the reactor at the same distance inside the reactor as the flake. Therefore, the latter method was used with an omega brand digital temperature readout in degrees C.

Gas Analysis

A Thermo Electron series 40 sulfur dioxide pulsed fluorescent analyzer was used. The analyzer uses pulsed ultraviolet light to fluoresce the sulfur dioxide molecules. Using pulsed light permits the use of a small source of ultraviolet light with a lifetime in excess of ten thousand hours. The sulfur dioxide molecules emit fluorescent radiation in direct proportion to their concentration.

Sulfur dioxide absorbs light in three regions of different wavelengths. The region of light chosen for use in the analyzer excites the sulfur dioxide molecules to a state which is relatively free from air quenching and also has a very strong fluorescent radiation characteristic. This radiation is detected by a photomultiplier tube (PMT) with an absorption filter that removes interference from the excitation background. The signal is then processed through solid state electronics and displayed as the sulfur dioxide concentration in parts per million. The instrument has a range scale from 50 to 5,000 ppm. For this work the 5,000 ppm scale was used since the instrument was calibrated using a previously analyzed calibration gas mixture of 2,000 ppm sulfur dioxide in air.
Extended laboratory and field testing have shown that the instrument is linear, fast responding and insensitive to sample temperature or flow variations. The analyzer performed well in the current research although the pump had to be bypassed because it was sucking excess air into the gas sample. The analyzer was checked with the calibration gas before each run, this was an extra precaution because extremely little drift was observed.

The analyzer was used to determine the gas concentration flowing into the reactor and to monitor the outlet concentration during a run. If the outlet concentration changed suddenly or became higher than the inlet concentration the experiment was terminated and repeated. This occurred only rarely and was almost always due to a decrease in the air flow which was being monitored by a flowmeter. The analyzer was not used for conversion analysis because the difference between the inlet and outlet concentrations was about 75 ppm sulfur dioxide initially and much less as the reaction progressed, therefore the analysis was inaccurate when compared to the barium chloride precipitation method described in the data analysis section. A schematic of the analyzer is shown on the next page in figure 3-4.

**Material**

**Lime**

To simplify the modeling of the process two-dimensional lime flakes were used. The lime flakes were made of either CaO, a 1:1 molar ratio of CaO to MgO or a 1:1 molar ratio of CaO to MgO with up to 50% by
Figure 3-4. Schematic of sulfur dioxide pulsed fluorescent analyzer
weight of an additive. The MgO powder used was about 44 microns in particle size. The additives used were char, alumina (Al₂O₃) powder, silica (SiO₂) powder and kaolin. The individual flakes varied somewhat but averaged were about 0.05 inches in thick, 0.23 inches wide and 0.40 inches long. Each flake weighed between 0.05 and 0.07 grams. The size of the flake was a compromise between using the largest flake possible and being able to easily slide the flake into and out of the reactor tube without breakage.

Additives

Kaolin is one of a group of clays containing hydrous (water containing) aluminum silicate minerals that are among nature smallest crystals [37]. Kaolin contains from 13-14% water, 44-48% silicon as SiO₂ and 35 to 40% alumina as Al₂O₃. Kaolin may also contain about 1% of iron, calcium, sodium, potassium and titanium [9]. This varies according to where the kaolin is mined. An electron photomicrograph of a clay specimen is shown in figure 3-4 [9]. The flat crystals are the kaolin. The size of the crystals varies from about 5-15 microns as shown in figure 4-1, an SEM picture of an unreacted flake containing kaolin. Kaolin sells from $25 to $90 a ton depending on how much it needs to be processed [9].

Besides kaolin, silica and alumina were also used. The grain size of the silica powder was about 105 microns. The alumina powder used was grit #240 which has a grain size of about 50 microns.
Figure 3-4. SEM photo of kaolin
 Flake Preparation

The amount of powder in a flake batch varied from 1.0 grams for pure CaO flakes to 1.75 grams of powder for a 1:1 molar ratio of CaO/MgO with 50% kaolin added by weight. The goal was to have flakes with a thickness as close to 0.05 inches as possible since this was an important model parameter.

The first step in preparing a flake batch was to weigh out the correct amount of powder in a three inch square plastic boat with slightly sloping sides. If more than one type of powder was used they were mixed together using a spatula and then 15 ml of deionized water was added and mixed to form a slurry. The powder was almost insoluble in the water and formed a layer on the bottom covered by liquid. The slurry was placed into an oven at 150°F to dry overnight.

The next morning a thin layer of dry white material remained in the boat. The boat was turned over on a piece of weighing paper and tapped, the larger pieces were sliced into the shape of a rectangle using a single edged razor blade. Thus one dimensional flakes were produced. The flakes were weighed before and after the reaction. After the reaction they were also measured using a micrometer to determine exact width, length and thickness. The flakes were stored in a dessicator to prevent hydration with the water vapor in the air.

Reaction Study

The first step was to load each of the two reactor tubes with a flake. Two reactors were used because the furnace was large enough to
heat them both at the same time so that with a quick change in the fittings, gas flow could be switched from one reactor to the other and two runs could be made per day. A piece of quartz wool was placed near the end of each reactor using a thin and flexible piece of plastic tubing. This prevented any lime from being blown into the analyzer in case the flow rates changed too rapidly. A second plug of wool was added near the middle of the tube as a guide to position the flake in the center of the furnace. Next, the flake was carefully pushed into the reactor until an inch or so behind the second quartz wool plug. The other reactor was loaded in an identical manner.

The tubes were placed next to each other in the furnace and the thermocouple was placed on top with its tip next to the flakes. The swagelock fittings were attached to the first reactor tube carefully so that the flake did not tilt and remained perpendicular to the opening of the reactor tube. The gaps at the ends of the furnace were stuffed with insulation and the furnace turned on to the desired temperature setting.

After a few hours, air was turned on and the temperature further adjusted. This drove the excess water vapor from the flake. When this was accomplished, the flow was switched to bypass the reactor and flow directly into the analyzer. The air flow was then turned off and the calibration gas turned on to check the analyzer for the days runs. After the analyzer check, the air was turned on again and the flow rates of both gases were varied until the desired inlet concentration was achieved with a combined flowrate of about 900 cc per minute to eliminate mass transfer effects and steady state was reached as deter-
mined by the analyzer. The reaction was started by turning the valve back again to let the mixture pass through the reactor and noting the time and reaction conditions on the strip chart recorder. After the reaction time passed (from 15 to 120 minutes) the sulfur dioxide flow was turned off and the air flow was increased to eliminate all sulfur dioxide from the system in less than 20 seconds. The air was then turned off, the fittings were then changed over to the second reactor tube and the air flow was resumed. After the temperature stabilized the valve was switched back to bypass the reactor and the desired inlet concentration was established. The same procedure was then followed as with the first run.

The air cylinder and reactor were turned off. The first reactor was connected to a nitrogen line so that both reactors could be purged with nitrogen overnight as the reactor cooled to room temperature. The flakes were analyzed the following day.

**Experimental Data Analysis**

Each type of flake was run for two hours at 800 °C in air to determine the water content. This weight loss was subtracted from the initial weight of each flake before the initial moles of calcium oxide or calcium and magnesium oxide were calculated.

For each run, the flake was dissolved in a hot acid solution, barium chloride was added to precipitate the sulfate ion and the amount of barium sulfate was determined. The reaction equation and a detailed procedure follows.
After reaction each flake was weighed to check the weight change
to determine that the reaction had taken place as planned. Next, 1.3
grams of barium chloride crystals were weighed and added to 100 ml of
deononized water and heated on a hot plate located under the hood. The
crystals quickly dissolved at room temperature. Next 12 ml of 1 normal
HCL solution were added to 90 ml of deionized water in a beaker, a flake
was added and broken into particles with a stirring rod. This procedure
was duplicated for the other flake and both beakers were also placed on
the hotplate. After roughly half an hour, the temperature of the acid
solutions reached 60°C and with vigourous stirring the flakes dissolved
although the solutions were still cloudy. Quickly, 50 ml of the barium
chloride solution was measured out in a graduated cylinder and added
to one of the acid containing beakers with vigourous stirring. The
remaining solution was added in a similar manner to the other beaker.
The solutions turned an opaque white when the barium chloride was
added.

The solutions were allowed to digest on the hot plate for two
hours. During digestion, the crystals grow larger and continuously re-
crystallize forming a purer product. During digestion the solutions
were stirred only breifly. After digestion, the solutions were filtered
using ashless filter paper, and each beaker was rinsed three times with
deonized water to remove any remaining cystals. The filter paper was
then placed in a porcelain crucible and heated by a bunsen burner which
burnt away the filter paper until only barium sulfate ash remained. The ash was weighed to determine the moles of sulfate and the conversion was determined by dividing the moles of sulfate that precipitated by the original number of moles of calcium oxide and magnesium oxide in the unreacted flake. This method was tested using a known starting amount of calcium sulfate and over 99% of it was recovered.
CHAPTER FOUR

MATHEMATICAL MODEL

Derivation of the Slab Rate Equation

A mathematical model was formulated to describe the flake reactions. Since the flake is one dimensional the slab geometry shown below is assumed:

\[ \text{y} \]

The sulfation reaction between sulfur dioxide and lime is as follows:

\[ \text{SO}_2 \text{(g)} + \frac{1}{2} \text{O}_2 \text{(g)} + \text{CaO (s)} \rightarrow \text{CaSO}_4 \]  \hspace{1cm} (4-1)

In the following formulation this reaction will be represented as follows:

\[ A + \frac{1}{2} B + C \rightarrow D \]

where

- \( A \) is sulfur dioxide, the key reactant
- \( B \) is oxygen which is in excess and its concentration does not change significantly
C is the solid lime

The conservation equation for reaction and transport in the slab can be written as follows

\[
\frac{2}{Dm} \frac{d}{dy} \frac{C}{A} = R \quad (4-2)
\]

\(Dm\) = effective diffusivity of sulfur dioxide in the slab macropores (m²/s)

\(C\) = concentration of sulfur dioxide in the slab (moles/m³)

\(A\)

\(y\) = distance from the center of the slab (m)

\(R\) = rate per unit porous slab volume

The above equation can also be written as shown below

\[
R = \frac{\text{rate}}{\text{grain volume}} \cdot \frac{\text{grain volume}}{\text{porous solid volume}} \quad (4-3)
\]

where

\[
\text{rate} = \text{grain density} \frac{dx}{dt} \quad (4-4)
\]

where

\(t\) = time in seconds

\(x\) = conversion of the slab (dimensionless)
and

\[
\frac{\text{grain vol.}}{\text{vol. of solid}} = 1 - \varepsilon_m \tag{4-5}
\]

\varepsilon_m \text{ is the void between the grain particles or the macropore porosity in the slab}

\[
\rho_{\text{co}} = \frac{\text{initial moles}}{\text{grain volume}} \tag{4-6}
\]

Therefore, the rate expression becomes:

\[
R = \rho_{\text{co}} \frac{dx}{dt} (1 - \varepsilon_m) \tag{4-7}
\]

where

\[
\frac{2}{d} \frac{dC}{dt} = \rho_{\text{co}} (1 - \varepsilon_m) \frac{dx}{dt} \tag{4-7}
\]
Derivation of the Grain Particle Rate Equation

To find the rate per grain particle or $dx/dt$, the reaction scale of the particle should be analyzed. For an individual grain particle since the lime reaction with sulfur dioxide is fast, diffusion through the product shell controls the rate. Pseudo steady state is also assumed along with the reaction being first order in sulfur dioxide.

For an individual grain particle:

$$D_{p} \nabla C = 0$$  \hspace{1cm} (4-8)

or for a sphere:

$$\frac{d}{dr} \left( \frac{C}{r^2} \right) + \frac{d}{dr} \left( \frac{C}{r} \right) = 0$$  \hspace{1cm} (4-9)

$C$ = concentration of sulfur dioxide within the grain particle (moles/m$^3$)

$r$ = distance from the center of the particle (m)
The boundary conditions are

\[
\begin{align*}
\text{r} &= r_c \quad C = 0 \quad r_c = \text{unreacted core radius} \\
\text{r} &= r_A \quad C = C_A \quad r_A = \text{radius of grain at any time}
\end{align*}
\]

The solution to equation 4-9 is available in the literature [38] and is given as follows

\[
 t = \frac{\rho_g R^2}{2M D_{\mu} C_A^3} \left[ \frac{2/3}{[1-(1-z)x]} - \frac{1}{1-z} + 1 - (1-x)^{2/3} \right]^{2/3} \tag{4-10}
\]

\( x \) = conversion of the grain particle (dimensionless)

\( \rho_g \) = density of the grain particle (g/m³)

\( M \) = molecular weight of the grain particle (g/mole)

\( C_A \) = concentration around the grain particle, same as the concentration in the slab (moles/m³)

\( R \) = initial grain radius (m)

\( z \) = molar volume of the product divided by the molar volume of the reactant (dimensionless)

\( D_{\mu} \) = diffusivity of the grain micropores (m²/s)
To simplify the equation we can define two more constants as:

\[ H = \frac{\rho g R}{2 M D_\mu} \]

\[ z' = 1 - z \]

Therefore, the equation becomes

\[
t = \frac{2/3}{C} \left( \frac{1}{(1-z'x)} - 1 \right) + 1 - (1-x) \]

Differentiating the equation above by time \(t\) and simplifying gives the result:

\[
\frac{dx}{dt} = \frac{-3C}{A} \left( \frac{1}{2} \right) \left( \frac{1}{2} \right)
\]

\[
2 H \left[ (1-z'x) - (1-x) \right]
\]

If we define \( f(x) \) as the right hand side of the equation divided by \( C \) the derivative becomes

\[
\frac{dx}{dt} = \frac{C}{A} f(x)
\]
if we substitute equation 4-12 into equation 4-7 for $\frac{dx}{dt}$, we get

\[
\frac{d}{dy} \left( \frac{2}{A} \frac{C}{\rho \alpha (1-e^m)} \right) = \frac{3}{A} \frac{C}{\rho \alpha (1-e^m)}
\]  

(4-14)

or in terms of $f(x)$

\[
\frac{d}{dy} \left( \frac{2}{A} \frac{C}{\rho \alpha (1-e^m)} \right) = \frac{f(x)}{D_m}
\]  

(4-15)

If we define $\phi$ as

\[
\phi = [\frac{\rho \alpha (1-e^m)}{D_m}]^{1/2}
\]  

(4-16)

then equation 4-14 becomes

\[
\frac{d}{dy} \left( \frac{2}{A} \frac{C}{\rho \alpha (1-e^m)} \right) = \phi \frac{2}{A} f(x)
\]  

(4-17)
Analytical Solution of the Flake Rate Equation

Following Del Borghi et al [39], equation 4-17 can be solved analytically by using the following transformation:

\[ C^* = \int_{A}^{t} C \, dt \]  \hspace{1cm} (4-18)

Substituting for the right hand side in terms of \( f(x) \), \( C^* \) can be rewritten as

\[ C^* = \int_{0}^{x} \frac{dx}{f(x)} \]  \hspace{1cm} (4-19)

Differentiating equation 4-18 twice with respect to \( y \) one obtains

\[ \frac{2}{dy} \frac{d C^*}{dt} = \int_{0}^{t} \frac{2}{dy} \frac{d C}{A} \, dt \]  \hspace{1cm} (4-20)

Equation 4-17 is integrated to get
\[ \int_0^t \frac{d}{dy} C \, dt = \frac{2}{\phi} \int_0^t C \, f(x) \, dt \]  

(4-21)

The left hand side can be replaced in terms of $C^*$ by using equation 4-20. The right hand side can be simplified by the following equation:

\[ A f(x) = \frac{dx}{dt} \]  

(4-13)

The substitution will change equation 4-21 to the following form:

\[ \frac{d}{dy} C^* = \frac{2}{\phi} \int_0^t \frac{dx}{dt} \, dt \]  

(4-22)

Integrating the right hand side

\[ \frac{2}{\phi} [x(t) - x(t=0)] \]  

(4-23)
Now we will solve for C* in terms of x, if we substitute for f(x) in equation 4-19

\[ C^* = \int_0^x \frac{dx}{\frac{1}{2} - \frac{3}{2} \frac{1}{z'} \left( 1 - z'x \right) - \frac{1}{2} \left( 1 - x \right)} \]  \hspace{1cm} (4-24)

Integration and rearrangement of 4-24 gives

\[ \frac{2}{3} \frac{1}{z'} \left( 1 - z'x \right) - \left( 1 - x \right) = \frac{C^*}{H} + \frac{1}{z'} - 1 \]  \hspace{1cm} (4-25)

since we cannot solve for C* directly in terms of x and substitute this result in equation 4-14, we must modify equation 4-23 by multiplying each side by \( \left( \frac{dC^*}{dy} \right) dy \). This results in

\[ \frac{1}{2} \left( \frac{dC^*}{dy} \right)^2 = \phi \int_0^x [x(t) - x(t=0)] \, dC^* \]  \hspace{1cm} (4-26)

If we start with equation 4-19

\[ C^* = \int_0^x \frac{dx}{f(x)} \]  \hspace{1cm} (4-19)
which is rewritten as

\[ d\ C^* = \frac{dx}{f(x)} \]  

(4-27)

Equation 4-27 can be substituted into equation 4-26 to yield:

\[ \frac{1}{2} \left( \frac{dC^*}{dy} \right)^2 = \phi \frac{2}{5z'} \int_0^x \frac{[x(t) - x(t=0)]}{f(x)} \ dx \]  

(4-28)

Now we can substitute for \( f(x) \) and integrate by parts taking into account that \( x(t=0) \) is equal to zero since at the start of the reaction no conversion has taken place. This gives

\[ \frac{dC^*}{dy} = \phi \sqrt{2} \frac{H}{\sqrt{2}} \left[ \frac{3}{2} (1-z'x)^{3/5} - \frac{3}{5} (1-x)^{3/5} + \right. \]

\[ \left. \frac{x}{z'} (1-z'x)^{2/3} - \frac{x(1-x)}{5z'}^{2/3} + \frac{3}{5} \right]^{1/2} \]  

(4-29)

We now have an equation in terms of \( x \), a local conversion. Now we must derive an overall conversion for the slab
\[ S \cdot L \cdot X = \int_{0}^{y} (S \, dy) \cdot x \quad (4-30) \]

\[ L \cdot X = \int_{0}^{y} x \, dy \quad (4-31) \]

- \( S \) = surface area of the slab (m²)
- \( L \) = half of the flake thickness (m)
- \( X \) = overall slab conversion (dimensionless)
- \( y \) = distance from the slab center (m)

\( C^* \) is defined in equation 4-18 as being equal to the integral between zero and \( t \) of \( C \, dt \). If we differentiate both sides of this equation with respect to \( y \) and evaluate this derivative at the surface of the flake, we get

\[ \frac{dC^*}{dy} = \frac{dC}{dy} \int_{0}^{t} \frac{dA}{dy} \, dt \quad (4-32) \]

The integrated amount of \( A \) consumed or the initial moles of lime times the overall conversion (\( X \)) is equal to

\[ \int_{0}^{t} S \, Dm \frac{dC}{dy} \, \frac{A}{s} \, dt \quad (4-33) \]
therefore

\[ X = \frac{S}{L \text{ mole}} \left( \frac{D_m}{L} \int_0^t A \frac{dC}{dt} \right) \text{ mole L / dy s} \]  

(4-34)

Substituting in flake porosity and flake density terms into the above equation, gives

\[ X = \frac{1}{\rho_{co} (1-\epsilon_m)} \left( \frac{D_m}{L} \int_0^t \frac{A}{dy s} \right) \text{ mole L / dy s} \]  

(4-35)

Substituting equation 4-32 for the integral on the right hand side of the equation above, gives

\[ X = \frac{1}{\rho_{co} (1-\epsilon_m)} \left( \frac{D_m}{L} \frac{dC^*}{dy s} \right) \text{ mole L / dy s} \]  

(4-36)

Substituting in \( \phi \) defined in equation 4-16 previously results in the equation below. Del Borghi [39] relates \( \phi \) to the effectiveness factor.

\[ X' = \frac{1}{\phi} \left( \frac{dC^*}{dy s} \right) \text{ mole L / dy s} \]  

(4-37)
Evaluating equation 4-29 for dC*/dy at the flake surface (changing x to xs) and substituting the result into 4-37 results in

\[
X = \frac{\sqrt{2} H}{\phi L} \left[ \frac{3}{2} \left( 1 - z'xs \right)^{5/3} - \frac{3}{5} \left( 1 - xs \right)^{5/3} + \right.
\]

\[
\frac{x}{z'} \left( 1 - z'xs \right)^{2/3} - xs \left( 1 - xs \right) - \frac{3}{2} \frac{3}{5} \left( 1 - xs \right)^{1/2} \left( 1 - z'xs \right)^{2/3} \right]
\]

\[(4-38)\]

Since \( C^* \) was previously defined in equation 4-18, if we define this equation at the surface it is transformed into

\[
C^* = \int_{0}^{t} C \ dt
\]

\[(4-39)\]

At the surface, the concentration of sulfur dioxide is equal to the bulk concentration (\( C \)). Substituting \( C^* \)s into equation 4-39 and integrating over time results in

\[
C^* = C \int_{s}^{t} \frac{t}{Ab}
\]

\[(4-40)\]

Evaluating equation 4-25 at the surface and substituting in equation 4-40 for \( C^* \), we get the equation below

\[
\frac{(1 - z'xs)^{2/3}}{z'} - (1 - xs)^{2/3} = \frac{C}{H} \frac{t}{Ab} + \frac{1}{z'} - 1
\]

\[(4-41)\]
The model can be solved using equations 4-38 and 4-41. First, a value is picked for $x_s$ and equation 4-41 is solved for the time in seconds. Then $x_s$ is used to evaluate the overall conversion at this time using equation 4-38. After the overall conversion is evaluated the porosity of the slab macropores is decreased according to the equation used by Bhatia and Perlmutter [21].

\[
\frac{\varepsilon_m}{\varepsilon_{mo}} = 1 - \frac{(z-1)(1-\varepsilon_m)X}{\varepsilon_{mo}} \quad (4-42)
\]

$\varepsilon_{mo} = \text{initial porosity}$

The macropore diffusivity is the varied according to the porosity change by equation 4-43 given below also found in Bhatia and Perlmutter [21].

\[
D_m = D_{mo} \left(\frac{\varepsilon_m}{\varepsilon_{mo}}\right)^{2} \quad (4-43)
\]

$D_{mo} = \text{initial macropore diffusivity at time equal to zero}$

After the calculation of the current values of macropore diffusivity and porosity as shown above $x_s$, is incremented and the procedure is repeated until $x_s$ reaches the maximum conversion value of one. A more detailed solution procedure is given in the next section. A computer program was written to perform the above calculations. This program is found in appendix B.
The two equations used in the computer program derived in the mathematical model section are

Equation (4-38)

\[ X = \frac{\sqrt{2H}}{\phi L} \left[ \frac{3(1-z'xs)}{2} - \frac{3}{5} \frac{(1-xs)}{z'} + \frac{xs(1-z'xs)}{2/3} \right]^{1/2} \]

and

\[ \frac{2/3}{z'} - \frac{2/3}{(1-xs)} = \frac{Ct}{Ab} + \frac{1}{H} - 1 \]  

(3-41)

where

\[ H = \frac{2 \rho r}{2 M D} \]

and

\[ \phi = \frac{\rho (1-\xi m)}{Dm} \]

Most of the variables can be calculated from the experimental conditions, these variables are listed below:
$C_{Ab}$ is the concentration of sulfur dioxide in the bulk gas ($\text{moles/m}^3$). Since the inlet concentration of sulfur dioxide in ppm and the reaction temperature are known, the ideal gas law was used to calculate this parameter.

$z'$ was defined earlier as $1-z$. Since $z$ is equal to the molar volume of the calcium sulfate ($52.2 \text{ cm}^3/\text{mole}$) divided by the molar volume of the calcium oxide ($16.9 \text{ cm}^3/\text{mole}$), this parameter can be calculated. The molar volumes are from Weast [21].

$t$ is the reaction time in minutes and therefore also known.

$\rho_{co}$ is the initial density of the flake in grams per cubic meter; an average value was calculated from measurements of the weight, thickness, length and width of flakes before reaction, taking into account the weight loss due to water vapor.

$M$ is the molecular weight of the grains; depending on the type of flake either the molecular weight of the calcium oxide or the average molecular weight of the calcium and magnesium oxides was used.

$\rho_g$ is the grain density, this value was calculated by Hartman and Coughlin [23] as $2.71 \times 10^6 \text{ g/m}^3$.

$r$ is the grain radius in meters and was obtained from an SEM picture of the flake surface (figure 4-1) as $1.5 \times 10^{-6} \text{ m}$.
Figure 4-1. SEM photo of unreacted CaO flake (2.0 KX)

Figure 4-2. SEM photo of reacted CaO flake

(2.0 KX; 1020 ppm sulfur dioxide; 500 C; 2 hours)
Figure 4-3. SEM photo of unreacted CaO/MgO 20% kaolin flake (2.0 KX)

Figure 4-4. SEM photo of reacted CaO/MgO 20% kaolin flake
(2.0 KX; 1020 ppm sulfur dioxide; 500 C; 2 hours)
This leaves the following unknown model parameters:

- $D_m$, macropore diffusivity in units of meters squared per second
- $D_{\mu}$, micropore diffusivity in units of meters squared per second
- $\varepsilon_m$, flake porosity

After programming the model it became clear that for the model reaction times to be comparable to the experimental reaction times the order of magnitude was fixed at $10^{-10}$, for 500 C runs the value was fixed at $3.00 \times 10^{-10}$, and for 700 C runs the value was increased with the square root of the absolute temperature (assuming Knudsen diffusion was dominant) to $3.37 \times 10^{-10}$.

Therefore, the data was fitted to the model using the adjustable parameters of flake porosity and macropore diffusivity, an outline of the procedure follows. It should be noted that both the porosity and the diffusivity change with time. When the porosity reaches zero the conversion stops changing, unless the conversion has already reached its maximum value of one. Since both these parameters are part of $\delta$, $\delta$ is recalculated at each time step.

Solution Procedure

1. The surface conversion ($x_s$) is set to zero by the program and initial estimates for the flake porosity and macropore diffusivity are entered by the user.
2. Other parameters entered by the program user are the molecular weight of the grains, reaction temperature, flake thickness and the gas concentration of sulfur dioxide in ppm.

3. Using equation 3-41 the reaction time is calculated

4. Using the initial estimates of flake porosity and macropore diffusivity, equation 3-38 is solved for the overall conversion

5. Using the current conversion a new value of flake porosity is calculated using the equation 4-42

7. Using the change in macroporosity, a new macropore diffusivity is calculated using the equation 4-43

8. The surface concentration is incremented and the a new reaction time is calculated, in the program the surface conversion was incremented by 0.1 at each step

9. Using the new values for porosity and macropore diffusivity the coefficient outside equation 4-38 is calculated, in the program this is labeled COEF

\[
\text{COEF} = \frac{2H}{\phi L}
\]
10. Next the rest of equation 4-38 in square brackets is calculated using the updated value of the surface conversion, this value is labeled in the program BAR6, in the program the new value of the overall conversion is calculated using the equation below

\[ X = X_{BAR0} + COEF \times (BAR6 - BAR60) \]

where \(X_{BAR0}\) is the previous value of the overall conversion and \(BAR60\) is the previous value of the term in square brackets.

11. The values of macropore diffusivity, porosity, time and overall conversion are printed.

12. Using the new conversion value, the flake porosity and the macropore diffusivity values are updated and the procedure is repeated until the surface conversion reaches a value greater than one.
CHAPTER FIVE

DISCUSSION AND RESULTS

In general, the temporal conversion profiles of lime (CaO) and dolomite (CaO/MgO) and the dolomite flakes with additives exhibit a high initial reaction rate and a gradual drop in rate as conversion proceeds. The reaction rate approached zero in all cases before full conversion of the solid. This can be attributed to pore closure during the reaction. The loss in porosity is due to the fact that the molar volume of calcium sulfate is over three times larger than that of the calcium oxide. Therefore, both the porosity and macropore diffusivity decrease as the reaction progresses. Therefore, as the reaction proceeds, the sulfur dioxide gas molecules find it increasingly difficult to reach the fresh unreacted surface of the lime below.

The main idea explored in this study has been to control the pore closure process by using additives. This could improve the conversion and improve the economic feasibility of the process. The three additives tested at 700 °C, more than doubled the conversion of the dolomite flakes.

Qualitative Observations

Several qualitative observations were made during the experimental work. First, the tested additives improved mechanical integrity. This could potentially reduce the cracking of lime which is an important
limitation in certain applications. For example, in the work of Morris [15] [16] who coated zinc sulfide pellets with lime to control the emission of sulfur dioxide. The heating procedure was also important in crack formation. Slow heating with reduced gas flow reduced the effect of cracking.

Comparison of the Reactivity of CaO Flakes and CaO/MgO Flakes

This study showed the calcium oxide (lime) to be more reactive than a 1:1 molar ratio of calcium oxide and magnesium oxide (dolomite). As shown in figures 5-11 and 5-12 at 700 °C the maximum conversion of the lime is about 36% while the maximum conversion of the dolomite is only 17%. Since the conversion of the dolomite flake is based on the initial moles of calcium and magnesium oxide and it has been shown that the magnesium oxide barely reacts at all at 700 °C, it seems as though the magnesium oxide does not effect the reactivity of the calcium oxide. At 500 °C, as shown by figures 5-8 and 5-9, the maximum conversion of the calcium oxide is about 10% and the maximum conversion of the calcium and magnesium oxide flake is only 5%. Thus, similar behavior is shown at both temperatures. Based on available data, the reactivity of naturally occurring dolomite is higher than the flakes studied here. This is expected because natural dolomite has a higher porosity and includes occlusions which reduce pore closure. Also, since the flakes used were made from a liquid slurry, the flakes must have calcined differently from the natural dolomite.
Effect of Kaolin Addition

Kaolin was selected as the primary additive because it can be uniformly mixed into the dolomite slurry during flake preparation. It was more difficult to obtain a uniform slurry with silica and alumina. Also, kaolin is already available in large amounts industrially (it is heavily used by the porcelain and paper industries) and is relatively inexpensive.

Kaolin was added to the CaO/MgO mixture at weight percents of 30% and 50%. The 50% concentration was used at 500 and 700 °C. The 30% concentration was used at 700 °C and was less successful at improving the conversion. The reason for using the CaO/MgO mixture was to simulate the composition of naturally occurring dolomites and limestones.

The results show a dramatic increase in conversion with kaolin addition. Figure 5-1 shows that at 700 °C the dolomite base case has a conversion of 17% after two hours. As mentioned before since the rate slows down so quickly due to pore closure, most of the conversion takes place in the first half hour of reaction. In this case after 15 minutes the conversion was about 8%, after 30 minutes the conversion increased to 16% and after two hours of reaction the conversion increased by only a tiny amount. By contrast, the flakes with the kaolin additive reach a much higher level of conversion during the early stages of reaction. After 15 minutes the conversion of the 30% flake was about 19% and the conversion of the 50% flake was 28%. Figure 5-2 shows a similar increase in conversion during the early stages of reaction for flakes with 50% kaolin at 500 °C.
Figure 5-1. Effect of kaolin on the sulfur dioxide/dolomite reaction (700 °C; 1020 ppm sulfur dioxide; □ 50% kaolin; ▽ 30% kaolin; x no additive)
Figure 5-2. Effect of kaolin on the sulfur dioxide/dolomite reaction (500 °C; 1020 ppm sulfur dioxide; □ 50% kaolin; x no additive)
Therefore, during the initial stages of the reaction the kaolin helps to keep the calcium sulfate pores open and enhances the diffusion of sulfur dioxide into the flake. However, like the base case, the reaction also slowed down quickly; after 30 minutes the 30% flake has reached about 25% conversion while the 50% flake reached 32% conversion. The final conversion of the 30% flake increased to 29%, the final conversion of the 50% flake to 37%. This shows that even with the additive the reaction still stops well before complete conversion. Also, the 50% flake had a higher conversion than the 30% flake, indicating that the more additive in the flake the higher the conversion. This might be due to the difference in the structure of the flake, the more additive in the flake, the less the structure is initially influenced by the inherent reaction changes. Since flake thickness influences the reaction rate (figure 5-14) the above results are given for flakes as close to 0.05 inches thick as possible.

Comparison of Additives

To further investigate the effect of additives, three other additives besides kaolin were also added to the CaO/MgO flakes. The first of these was coal char, in the hope that the carbon in the char would oxidize to form carbon dioxide and create tiny pores in the flake which would enhance the reaction rate. However, even with only one weight percent of char the flakes became brittle and developed undesirable structural cracks.
The silica powder and alumina powder flakes were as strong as the kaolin flakes and had an almost identical effect on conversion as shown in figure 5-3. After 60 minutes of reaction time the three flakes, each with 50 weight percent of an additive had conversions of about 35%. After thirty minutes the conversion of the silica flake was slightly higher than the alumina and kaolin flakes. Therefore, it seems as though the tested additives had similar effects. This indicates that the primary effect of additives is physical and not chemical. This effect is primarily modification of porosity and pore closure during the reaction.

Effect of Temperature

It is generally agreed upon that the sulfur dioxide/lime reaction is first order in sulfur dioxide concentration with an Arrhenius temperature dependence. Therefore, as expected figures 5-4, 5-5 and 5-6 show that the reaction rate and overall conversion increased for the lime, dolomite and dolomite with 50% kaolin flakes when the reaction temperature was increased from 500 to 700 °C. Over a threefold increase in final conversion was observed for the flakes without the additive, however the 50% kaolin flake only increased its conversion from 23% to 37%. Because of this phenomenon the 50% kaolin flake has a final conversion over four times that of the dolomite flake without any additive (.05 to .23) at 500 °C. This is because the additive decreases the pore closure and therefore the temperature dependence of the reaction also decreases.
Figure 5-3. Effect of additives on the sulfur dioxide/dolomite reaction (700 °C; 1020 ppm sulfur dioxide; x 50% silica; ▼ 50% alumina; □ 50% kaolin; ○ no additive)
Figure 5-4. Effect of temperature on the sulfur dioxide/lime reaction (1020 ppm sulfur dioxide; □ 700 °C; × 500 °C)
Figure 5-5. Effect of temperature on the sulfur dioxide/dolomite reaction (1020 ppm sulfur dioxide; □ 700°C; x 500°C)
Figure 5-6. Effect of temperature on the sulfur dioxide/dolomite reaction (50% kaolin; 1020 ppm sulfur dioxide; □ 700 °C; x 500 °C)
Model Results

The model does a good job of fitting the data as seen in figures 5-7 to 5-13. It predicts the final conversion based strictly on the initial porosity. The model predicts the shape of the experimental curves, the fast initial rate followed by a much slower rate with little conversion change. Therefore, changes in flake thickness, macropore diffusivity and inlet sulfur dioxide concentration will all result in the same final conversion although the initial reaction rates vary.

Figure 5-13 shows that the same final conversion was reached with inlet concentrations of 1020 and 4100 ppm sulfur dioxide experimentally and as predicted by the model. The effect on the model of flake thickness, macropore diffusivity and porosity on temporal profiles of conversion is shown in figures 5-14, 5-15 and 5-16.

Figure 5-17 shows how the initial porosity effects the final conversion as predicted by the model in equation 4-41. The final conversion occurs when the porosity equals zero unless the initial porosity is higher than about 0.7 which is the critical porosity. When the initial porosity is higher than this value the model predicts total conversion. Figure 5-18 shows how the porosity changes with the additives. Table 5-1 gives the initial values of macropore diffusivity and porosity used to fit the data. Figure 5-19 shows that the macropore diffusivity increases with porosity and that this increase is parabolic as expected. It should be noted that flakes of the same composition show a greater porosity at 700 °C than at 500 °C, because the conversion increases with temperature for all the types of flakes tested. This might be due
Figure 5-7. Temporal profile of conversion; comparison of experimental data with model results (CaO; 500°C; 1020 ppm sulfur dioxide; x data; ______ theory)
Figure 5-8. Temporal profile of conversion; comparison of experimental data with model results (CaO/MgO; 500°C; 1020 ppm sulfur dioxide; x data;——theory)
Figure 5-9. Temporal profiles of conversion; comparison of experimental data with model results (500°C; 50% kaolin; 1020 ppm dioxide; x data; —— theory)
Figure 5-10. Temporal profile of conversion; comparison of experimental data with model results (CaO; 700 °C; 1020 ppm sulfur dioxide; x data; — theory)
Figure 5-11. Temporal profile of conversion; comparison of experimental data with model results (CaO/MgO; 700 °C; 1020 ppm sulfur dioxide; x data; ----- theory)
Figure 5-12. Temporal profile of conversion; comparison of experimental data with model results (30% kaolin; 700 °C; 1020 ppm sulfur dioxide; x data; --- theory)
Figure 5-13. Temporal profile of conversion; comparison of experimental data with model results (50% kaolin; 700 °C; x 4100 ppm sulfur dioxide; 1020 ppm sulfur dioxide; x data; — theory)
Figure 5-14. Effect of flake thickness on temporal profiles of conversion (700 °C; 1020 ppm sulfur dioxide)
Figure 5-15. Effect of macropore diffusivity on temporal profiles of conversion (700 °C; 1020 ppm sulfur dioxide)
Figure 5-16. Effect of porosity on temporal profiles of conversion
(700 °C; 1020 ppm sulfur dioxide)
Figure 5-17. Effect of initial porosity on final conversion
Figure 5-18. Effect of additives on flake porosity (× 700 °C; □ 500 °C)
Table 5-1. Values of Porosity and Macropore Diffusivity

<table>
<thead>
<tr>
<th>Flake Composition</th>
<th>Temperature (°C)</th>
<th>εm</th>
<th>(D_m) (m/s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>CaO/MgO</td>
<td>500</td>
<td>0.10</td>
<td>0.00025</td>
</tr>
<tr>
<td>CaO/MgO</td>
<td>700</td>
<td>0.265</td>
<td>0.00090</td>
</tr>
<tr>
<td>CaO/MgO 30% kaolin</td>
<td>700</td>
<td>0.38</td>
<td>0.0015</td>
</tr>
<tr>
<td>CaO/MgO 50% kaolin</td>
<td>500</td>
<td>0.36</td>
<td>0.0016</td>
</tr>
<tr>
<td>CaO/MgO 50% kaolin</td>
<td>700</td>
<td>0.44</td>
<td>0.0040</td>
</tr>
<tr>
<td>CaO</td>
<td>500</td>
<td>0.20</td>
<td>0.00040</td>
</tr>
<tr>
<td>CaO</td>
<td>700</td>
<td>0.43</td>
<td>0.0042</td>
</tr>
</tbody>
</table>
Figure 5-19. Effect of porosity on macropore diffusivity (1020 ppm sulfur dioxide; □ 500 °C; △ 700 °C)
to a faster rate of calcination at the higher temperature which would increase the surface area and porosity of the flakes. Figure 5-20 is a plot of the log of the initial rate versus the inverse of the absolute temperature, the slopes of the lines are related to the apparent activation energies and show that the apparent activation energy of the calcium oxide decreases when magnesium oxide is added and decreases even more when magnesium oxide and kaolin are added. The activation energies are all relatively low as would be expected for a diffusion controlled process. The activation energy of the flake with the kaolin is the lowest because the additive is influencing the pore closure.

The values of macropore and micropore diffusion are close to direct estimates based on Knudsen diffusion theory. For the macropore Knudsen diffusion the mean pore radius was estimated to be about 10 microns (see figure 4-1). At the reaction temperature of 700°C the diffusion of the sulfur dioxide gas was calculated to be $3.8 \times 10^{-3}$ m/s. This value is then multiplied by the porosity of the macropores and divided by the tortuosity factor. The best estimate of the tortuosity factor is the inverse of porosity. Using a porosity of 0.27 the macro knudsen diffusion becomes $2.8 \times 10^{-4}$ m/s. Using a porosity of 0.44 the diffusity becomes $7.4 \times 10^{-2}$ m/s. These values are lower than those used in the model but are in the same range. Using the same equation for Knudsen diffusion, but estimating the mean pore radius inside the grains to be 20 Angstroms (Marsh 1985), the micropore Knudsen diffusion was calculated to be $7.6 \times 10^{-7}$ m/s. Assuming the porosity of the micropores to be 0.05 the micropore Knudsen diffusion becomes $1.9 \times 10^{-9}$ m/s.
Figure 5-20. Apparent activation energies
(x CaO; • CaO/MgO; O CaO/MgO 50% kaolin)

x $E_a = 7,260$ cal/mol  • $E_a = 4,620$ cal/mol  O $E_a = 1,980$ cal/mol
CHAPTER SIX

CONCLUSIONS

1. Kaolin increased the conversion of the magnesium oxide and calcium oxide flakes significantly. At 700 °C, with the 50% by weight kaolin addition the conversion increased from about 17% to 35%. At 500 °C the conversion increased from about 5% to 23%.

2. The amount of additive in the flake influences the final conversion. The 50% kaolin flake had a higher conversion at 700 °C than the 30% kaolin flake. The final conversion of the 30% kaolin flake was about 29% compared to a final value of conversion of 35% for the flake with 50% kaolin.

3. The 50% silica powder and 50% alumina powder flakes reached about the same final conversion as the 50% kaolin flakes. Therefore, the effect of the additives is physical and not chemical.

4. The model fits the data well and bases the final conversion on the initial porosity. This indicates that the additives directly influence the porosity of the flake.
Table A-1. Conversion Data  
Flake Composition: calcium oxide  
Inlet Gas Composition: 1020 ppm sulfur dioxide in air  
Reaction Temperature: 700 °C

<table>
<thead>
<tr>
<th>Flake Thickness (in.)</th>
<th>gas flowrate (cc/min.)</th>
<th>reaction time (min.)</th>
<th>conversion X</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.049</td>
<td>942</td>
<td>15</td>
<td>0.255</td>
</tr>
<tr>
<td>0.047</td>
<td>923</td>
<td>30</td>
<td>0.319</td>
</tr>
<tr>
<td>0.050</td>
<td>907</td>
<td>60</td>
<td>0.364</td>
</tr>
<tr>
<td>0.053</td>
<td>880</td>
<td>90</td>
<td>0.357</td>
</tr>
<tr>
<td>0.044</td>
<td>916</td>
<td>120</td>
<td>0.387</td>
</tr>
</tbody>
</table>
Table A-2. Conversion Data
Flake Composition: 1:1 molar ratio of calcium oxide and magnesium oxide
Inlet Gas Composition: 1020 ppm sulfur dioxide in air
Reaction Temperature: 700 °C

<table>
<thead>
<tr>
<th>Flake Thickness (in.)</th>
<th>Gas Flowrate (cc/min.)</th>
<th>Reaction Time (min.)</th>
<th>Conversion X</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.048</td>
<td>925</td>
<td>15</td>
<td>0.083</td>
</tr>
<tr>
<td>0.054</td>
<td>889</td>
<td>30</td>
<td>0.160</td>
</tr>
<tr>
<td>0.055</td>
<td>896</td>
<td>60</td>
<td>0.168</td>
</tr>
<tr>
<td>0.043</td>
<td>916</td>
<td>60</td>
<td>0.139</td>
</tr>
<tr>
<td>0.048</td>
<td>927</td>
<td>90</td>
<td>0.180</td>
</tr>
<tr>
<td>0.043</td>
<td>909</td>
<td>90</td>
<td>0.138</td>
</tr>
<tr>
<td>0.050</td>
<td>913</td>
<td>120</td>
<td>0.173</td>
</tr>
</tbody>
</table>
Table A-3. Conversion Data

Flake Composition: 1:1 molar ratio of calcium oxide and magnesium oxide with 30% by weight Kaolin added
Inlet Gas Composition: 1020 ppm sulfur dioxide in air
Reaction Temperature: 700 °C

<table>
<thead>
<tr>
<th>Flake Thickness (in.)</th>
<th>Gas Flowrate (cc/min.)</th>
<th>Reaction Time (min.)</th>
<th>Conversion X</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.053</td>
<td>918</td>
<td>15</td>
<td>0.185</td>
</tr>
<tr>
<td>0.055</td>
<td>935</td>
<td>30</td>
<td>0.222</td>
</tr>
<tr>
<td>0.041</td>
<td>911</td>
<td>30</td>
<td>0.271</td>
</tr>
<tr>
<td>0.052</td>
<td>940</td>
<td>60</td>
<td>0.257</td>
</tr>
<tr>
<td>0.048</td>
<td>938</td>
<td>60</td>
<td>0.286</td>
</tr>
<tr>
<td>0.044</td>
<td>935</td>
<td>90</td>
<td>0.289</td>
</tr>
</tbody>
</table>
Table A-4. Conversion Data
Flake Composition: 1:1 molar ratio of calcium oxide and magnesium oxide with 50% by weight kaolin added
Inlet Gas Concentration: 1020 ppm sulfur dioxide in air
Reaction Temperature: 700 °C

<table>
<thead>
<tr>
<th>Flake Thickness (in.)</th>
<th>Gas Flowrate (cc/min.)</th>
<th>Reaction Time (min.)</th>
<th>Conversion X</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.053</td>
<td>911</td>
<td>15</td>
<td>0.276</td>
</tr>
<tr>
<td>0.050</td>
<td>914</td>
<td>15</td>
<td>0.290</td>
</tr>
<tr>
<td>0.050</td>
<td>896</td>
<td>30</td>
<td>0.319</td>
</tr>
<tr>
<td>0.044</td>
<td>937</td>
<td>60</td>
<td>0.409</td>
</tr>
<tr>
<td>0.041</td>
<td>902</td>
<td>60</td>
<td>0.409</td>
</tr>
<tr>
<td>0.038</td>
<td>930</td>
<td>90</td>
<td>0.413</td>
</tr>
<tr>
<td>0.050</td>
<td>930</td>
<td>90</td>
<td>0.374</td>
</tr>
<tr>
<td>0.048</td>
<td>935</td>
<td>120</td>
<td>0.370</td>
</tr>
</tbody>
</table>
Table A-5. Conversion Data
Flake Composition: calcium oxide
Inlet Gas Concentration: 1020 ppm sulfur dioxide in air
Reaction Temperature: 500°C

<table>
<thead>
<tr>
<th>Flake Thickness (in.)</th>
<th>Gas Flowrate (cc/min.)</th>
<th>Reaction Time (min.)</th>
<th>Conversion X</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.055</td>
<td>900</td>
<td>15</td>
<td>0.075</td>
</tr>
<tr>
<td>0.054</td>
<td>935</td>
<td>30</td>
<td>0.120</td>
</tr>
<tr>
<td>0.055</td>
<td>905</td>
<td>30</td>
<td>0.118</td>
</tr>
<tr>
<td>0.047</td>
<td>898</td>
<td>60</td>
<td>0.103</td>
</tr>
<tr>
<td>0.047</td>
<td>930</td>
<td>90</td>
<td>0.095</td>
</tr>
<tr>
<td>0.056</td>
<td>949</td>
<td>120</td>
<td>0.104</td>
</tr>
</tbody>
</table>
Table A-6. Conversion Data
Flake Composition: 1:1 molar ratio of calcium oxide and magnesium oxide
Inlet Gas Concentration: 1020 ppm sulfur dioxide in air
Reaction Temperature: 500 °C

<table>
<thead>
<tr>
<th>Flake Thickness (in.)</th>
<th>Gas Flowrate (cc/min.)</th>
<th>Reaction Time (min.)</th>
<th>Conversion X</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.048</td>
<td>902</td>
<td>15</td>
<td>0.051</td>
</tr>
<tr>
<td>0.055</td>
<td>907</td>
<td>30</td>
<td>0.041</td>
</tr>
<tr>
<td>0.054</td>
<td>878</td>
<td>60</td>
<td>0.046</td>
</tr>
</tbody>
</table>
Table A-7. Conversion Data
Flake Composition: 1:1 molar ratio of calcium oxide and magnesium oxide with 50% by weight of kaolin added
Inlet Gas Composition: 1020 ppm sulfur dioxide in air
Reaction Temperature: 500 °C

<table>
<thead>
<tr>
<th>Flake Thickness (in.)</th>
<th>Gas Flowrate (cc/min.)</th>
<th>Reaction Time (min.)</th>
<th>Conversion X</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.057</td>
<td>916</td>
<td>15</td>
<td>0.215</td>
</tr>
<tr>
<td>0.048</td>
<td>973</td>
<td>30</td>
<td>0.199</td>
</tr>
<tr>
<td>0.052</td>
<td>923</td>
<td>60</td>
<td>0.259</td>
</tr>
<tr>
<td>0.042</td>
<td>930</td>
<td>90</td>
<td>0.277</td>
</tr>
<tr>
<td>0.050</td>
<td>928</td>
<td>90</td>
<td>0.229</td>
</tr>
<tr>
<td>0.045</td>
<td>905</td>
<td>120</td>
<td>0.229</td>
</tr>
</tbody>
</table>
Table A-8. Conversion Data

Flake Composition: 1:1 molar ratio of calcium oxide and magnesium oxide with 50% by weight kaolin added
Inlet Gas Composition: 1940 ppm sulfur dioxide in air
Reaction Temperature: 700 °C

<table>
<thead>
<tr>
<th>Flake Thickness (in.)</th>
<th>Gas Flowrate (cc/min.)</th>
<th>Reaction Time (min.)</th>
<th>Conversion X</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.049</td>
<td>918</td>
<td>30</td>
<td>0.308</td>
</tr>
<tr>
<td>0.051</td>
<td>905</td>
<td>60</td>
<td>0.348</td>
</tr>
</tbody>
</table>
Table A-9. Conversion Data
Flake Composition: 1:1 molar ratio of calcium oxide and magnesium oxide with 50% by weight kaolin added
Inlet Gas Composition: 4100 ppm sulfur dioxide in air
Reaction Temperature: 700 °C

<table>
<thead>
<tr>
<th>Flake Thickness (in.)</th>
<th>Gas Flowrate (cc/min.)</th>
<th>Reaction Time (min.)</th>
<th>Conversion X</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.052</td>
<td>896</td>
<td>5</td>
<td>0.325</td>
</tr>
<tr>
<td>0.044</td>
<td>893</td>
<td>15</td>
<td>0.415</td>
</tr>
<tr>
<td>0.053</td>
<td>887</td>
<td>15</td>
<td>0.379</td>
</tr>
<tr>
<td>0.048</td>
<td>889</td>
<td>30</td>
<td>0.360</td>
</tr>
<tr>
<td>0.050</td>
<td>902</td>
<td>120</td>
<td>0.362</td>
</tr>
</tbody>
</table>
### Table A-10. Conversion Data

Flake Composition: 1:1 molar ratio of calcium oxide and magnesium oxide with 50% by weight alumina powder added  
Inlet Gas Composition: 1020 ppm sulfur dioxide in air  
Reaction Temperature: 700°C

<table>
<thead>
<tr>
<th>Flake Thickness (in.)</th>
<th>Gas Flowrate (cc/min.)</th>
<th>Reaction Time (min.)</th>
<th>Conversion X</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.052</td>
<td>907</td>
<td>35</td>
<td>0.282</td>
</tr>
<tr>
<td>0.055</td>
<td>905</td>
<td>60</td>
<td>0.355</td>
</tr>
</tbody>
</table>

### Table A-11. Conversion Data

Flake Composition: 1:1 molar ratio of calcium oxide and magnesium oxide with 50% by weight silica powder added  
Inlet Gas Composition: 1020 ppm sulfur dioxide in air  
Reaction Temperature: 700°C

<table>
<thead>
<tr>
<th>Flake Thickness (in.)</th>
<th>Gas Flowrate (cc/min.)</th>
<th>Reaction Time (min.)</th>
<th>Conversion X</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.052</td>
<td>887</td>
<td>30</td>
<td>0.361</td>
</tr>
<tr>
<td>0.056</td>
<td>918</td>
<td>60</td>
<td>0.359</td>
</tr>
</tbody>
</table>
Table A-12. Percent Weight Loss During Heating

<table>
<thead>
<tr>
<th>Flake Composition</th>
<th>Percent Weight Loss (heated in air two hours, 800 °C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>CaO</td>
<td>24.0</td>
</tr>
<tr>
<td>CaO/MgO</td>
<td>23.8</td>
</tr>
<tr>
<td>CaO/MgO 30% Kaolin</td>
<td>24.1</td>
</tr>
<tr>
<td>CaO/MgO 50% Kaolin</td>
<td>19.6</td>
</tr>
<tr>
<td>CaO/MgO 50% Silica Powder</td>
<td>14.6</td>
</tr>
<tr>
<td>CaO/MgO 50% Alumina Powder</td>
<td>21.9</td>
</tr>
</tbody>
</table>
APPENDIX B

PROGRAM LIMEY
ESTIMATE INITIAL VALUES FOR THE POROSITY OF THE CAO FLAKE (EPSZ) AND
THE DIFFUSIVITY OF SO2 IN THE FLAKE MACROPORES (DMAZ) THESE VALUES
CHANGE WITH OVERALL CONVERSION (XBAR)

WRITE(*,*) 'INITIAL POROSITY = ?'
READ(*,*) EPSZE
WRITE(*,*) 'INITIAL MACROPORE DIFFUSIVITY = ?'
READ(*,*) DMAZE
WRITE(5,9) EPSZE
9 FORMAT(2X, 'INITIAL POROSITY (EPSZE) = ', E16.4, /)
EPSZ = EPSZE
DMAZ = DMAZE
WRITE(6,10) DMAZE
10 FORMAT(2X, 'INITIAL MACROPORE DIFF. (DMAZE) = ', E16.4, /)

ENTER FLAKE THICKNESS = 2TL (IN.)

WRITE(*,*) 'FLAKE THICKNESS (2TL) IN INCHES = ?'
READ(*,*) TL
TL = TL * 0.5 * 2.54 * 0.01
WRITE(6,3) TL
3 FORMAT(2X, 'HALF OF FLAKE THICKNESS (M) = ', E14.6, /)

ENTER MOLECULAR WT. OF GRAIN PARTICLES = GMB (G/ MOLE)
GMB = 56.08 FOR CAO   GMB = 48.19 FOR CAO / MGO

WRITE(*,*) 'MOLECULAR WT. (GMB) = ?'
READ(*,*) GMB
A = RHOB * RO * RO / (2.0 * B * GMB * DMI)
WRITE(6,4) GMB, A
4 FORMAT(2X, 'MOLECULAR WT. (GMB) = ', E14.6, 2X, 'A = ', E14.6, /)

SET INITIAL SURFACE CONVERSION EQUAL TO ZERO
XS = 0.0
WRITE(6,12) XS
12 FORMAT(2X, 'INITIAL SURFACE CONC. (XS) = ', E16.4, /)

SET PREVIOUS OVERALL CONVERSION (XBAR0) TO ZERO
SET PREVIOUS VALUE OF CHANGE IN OVERALL CONV. (BAR60) TO ZERO
BAR60 = 0.0
XBAR0 = 0.0

CALCULATE TIME (T)
Z = VCS / VC0
ZP = 1.0 - Z
WRITE(6.13) Z, ZP
13 FORMAT(2X, 'Z = ', E14.6, 2X, 'ZP = ', E14.6, /)
AP1 = (1.0 - ZP * XS) ** (2.0 / 3.0)
AP2 = (1.0 - XS) ** (2.0 / 3.0)
AP = AP1 / ZP - AP2
T = AP - 1.0 / ZP + 1.0
T1 = AP - 1.0 / ZP + 1.0
T = T1 * A / CAB
TMIN = T / 60.0
WRITE(*,*) 'XS = ', XS, 'TMIN = ', TMIN
WRITE(6.15) T, TMIN
15 FORMAT(2X, 'T = ', E14.6, 'TMIN = ', E14.6, /)
CALCULATE THE CHANGE IN OVERALL CONVERSION (BAR6)

PHI = (RHO_F * (1.0 - EPS_Z) / DMA_Z)**.5
COEF = (2.0^A)**.5 / (PHI * TL)

IF (IXS.EQ.10) GO TO 23
BAR1 = (1.0 - ZP*XS)**(5.0/3.0)
BAR2 = (1.0 - XS)**(5.0/3.0)
BAR3 = (1.0 - ZP*XS)**(2.0/3.0)
BAR4 = (1.0 - XS)**(2.0/3.0)

BAR5 = 3.0 / (5.0*ZP*ZP) * BAR1 - 3.0 / 5.0 * BAR2 + XS / ZP * BAR3 - XS * BAR4
BAR6 = (BAR5 - 3.0 / (5.0*ZP*ZP) + 3.0 / 5.0)**.5

CALCULATE NEW VALUE FOR OVERALL CONVERSION (XBAR)

XBAR = XBAR_0 + COEF * (BAR6 - BAR6_0)
WRITE (6, 21) XBAR, XBAR_0

USING XBAR CALCULATE NEW VALUES FOR POROSITY AND MACROPORE DIFFUSIVITY

EPS1 = (Z - 1.0) * (1.0 - EPS_ZE) * XBAR
EPS = EPS_ZE * (1.0 - EPS1 / EPS_ZE)
WRITE (6, 30) EPS

DMA1 = (EPS / EPS_ZE)**2.0
DMA = DMA1 * DMA_ZE
WRITE (6, 31) DMA

 INCREMENT SURFACE CONVERSION (XS)

XS = XS + .1
WRITE (6, 27) XS

CHECK THE VALUE OF XS
IF THE VALUE OF XS IS EQUAL TO ONE
THE VALUES OF BAR1, BAR2, BAR3 AND AP2 ARE EQUAL TO ZERO AND
THE PROGRAM BYPASSES THEIR CALCULATION
IF THE VALUE OF XS IS GREATER THAN OR EQUAL TO ONE THE
PROGRAM ENDS

IXS = NINT (10.0 * XS)
IF (IXS.EQ.10.0) GO TO 51
IF (IXS.GE.11.0) GO TO 99
GO TO 50

AP1 = (1.0 - ZP*XS)**(2.0/3.0)
AP = AP1 / ZP
GO TO 19

BAR1 = (1.0 - ZP*XS)**(5.0/3.0)
BAR2 = 0.0
BAR3 = (1.0 - ZP*XS)**(2.0/3.0)
BAR4 = 0.0
PROGRAM FOR ESTIMATION OF CONVERSION DATA

OPEN(UNIT=6,FILE='CONV.OUT',STATUS='NEW')

DEFINE PROGRAM CONSTANTS

RHOB=DENSITY OF A GRAIN PARTICLE(G/M3)
RHOF=DENSITY OF FLAKE(G/M3)
RO=RADIUS OF A GRAIN PARTICLE(M)
VCS=MOLAR VOLUME OF CALCIUM SULFATE(CM3/MOLE)
VCO=MOLAR VOLUME OF CALCIUM OXIDE(CM3/MOLE)

RHOB=2.71E6
RHOF=5.76E5
RO=1.5E-6
VCS=52.2
VCO=16.9

ENTER DMI=DIFFUSIVITY OF SO2 IN GRAIN MICROPORES(M2/S)

WRITE(*,*) 'MICROPORE DIFFUSIVITY=?'
READ(*,*) DMI

WRITE CONSTANTS

WRITE(6,6) RHOB,RO,DMI
FORMAT(2X, 'RHOB',E14.6,'RO',E14.6,'DMI',E14.6,/)  
WRITE(6,7) VCS,VCO
FORMAT(2X, 'VCS',E14.6,'VCO',E14.6,/)  
WRITE(6,8) RHOF
FORMAT(2X, 'RHOF',E14.6,/)  

ENTER INLET SO2 CONCENTRATION IN PPMS(SCON)

WRITE(*,*) 'INLET CONC. IN PPMS(SCON)=?'
READ(*,*) SCON
YSO2=SCON/1000000.
WRITE(6,2) YSO2
FORMAT(2X, 'YSO2=',E14.6,/)  

ENTER REACTION TEMPERATURE IN DEGREES C AND CHANGE
THE MICROPORE DIFFUSIVITY IF NEEDED

WRITE(*,*) 'TEMP. IN DEGREES C=?'
READ(*,*) TEMP
TEMP=TEMP+273.15

CALCULATE BULK SO2 CONCENTRATION AROUND THE FLAKE (CAB IN MOLES/M3)
USING THE IDEAL GAS LAW AND THE REACTION TEMPERATURE

CAB1=1.0*YSO2/(82.05*TEMP)
CAB=CAB1*100.0**3
WRITE(6,1) TEMP,DMI,CAB
FORMAT(2X, 'TEMP',E14.6,2X,'DMI',E14.6,2X,'CAB',E14.6,/)  

C
GO TO 24
99 WRITE(*,A) 'PROGRAM FINISHED XS= ',XS
   WRITE(6,60)XS
60 FORMAT(2X,'PROGRAM FINISHED XS= ',E14.6,/) STOP
END
NOMENCLATURE

C
A
C
Ab
Dm
Dmo
Dµ
L
M
r
rc t TL
x
xs
X
z

concentration of sulfur dioxide gas (moles/m^3)
concentration of sulfur dioxide in the bulk gas (moles/m^3)
macropore diffusivity (m^2/s)
initial macropore diffusivity (m^2/s)
micropore diffusivity (m^2/s)
half of flake thickness (m)
molecular weight of grain (g/mole)
grain radius (m)
radius of unreacted core inside grain (m)
reaction time (min.)
half of flake thickness (inches)
local conversion inside the flake (dimensionless)
local conversion at the flake surface (dimensionless)
overall conversion of the flake (dimensionless)
molar volume of calcium sulfate divided by the molar volume of calcium oxide (dimensionless)

Greek

ε_m flake porosity (dimensionless)
ε_mo initial flake porosity (dimensionless)
ρ_g grain density (g/m^3)
ρ_o initial flake density (g/m^3)
LIST OF REFERENCES


10. EERC, *Meeting of the Western States Section of the Combustion Inst., Univ. of Arizona, Fall* (1986).


