DOE/mc/26366-T15

A CALCIUM OXIDE SORBENT PROCESS
FOR BULK SEPARATION OF CARBON DIOXIDE

DOE/MC/26366--T15

DE92 017671

Quarterly Progress Report 09
October - December 1991

A. Silaban
M. Narcida
D.P. Harrison

DISCLAIMER

February 1992

This report was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor any agency thereof, nor any of their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof.

Work Performed Under Contract No: DE-AC21-89MC26366

for

U.S. Department of Energy
Office of Fossil Fuels
Morgantown Energy Technology Center
Morgantown, West Virginia

by

Louisiana State University
Department of Chemical Engineering
Baton Rouge, Louisiana 70803

4/8/92
7/20/92
MASTER

DISTRIBUTION OF THIS DOCUMENT IS UNLIMITED

ABSTRACT

The expected commercialization of coal gasification technology in the U.S. and world-wide will create a need for advanced gas purification and separation processes capable of operating at higher temperatures and in more hostile environments than is common today. For example, a high-temperature, high-pressure process capable of separating CO_2 from coal-derived gas may find application in purifying synthesis gas for H_2 , NH_3 , or CH_3OH production. High temperature CO_2 removal has the potential for significantly improving the operating efficiency of integrated gasification-molten carbonate fuel cells for electric power generation.

This study proved the technical feasibility of a CO_2 -separation process based upon the regenerable noncatalytic gas-solid reaction between CaO and CO_2 to form CaCO_3 . Such a process operating at 650°C and 15 atm with 15% CO_2 in the coal gas has the potential for removing in excess of 99% of the CO_2 fed. Selection of a sorbent precursor which, upon calcination, produces high-porosity CaO is important for achieving rapid and complete reaction. The addition of magnesium to the sorbent appears to improve the multicycle durability at a cost of reduced CO_2 capacity per unit mass of sorbent. Reaction conditions, principally calcination and carbonation temperatures, are important factors in multicycle durability. Reaction pressure and CO_2 concentration are important in so far as the initial rapid reaction rate is concerned, but are relatively unimportant in terms of sorbent capacity and durability.

Indirect evidence for the simultaneous occurrence of the shift reaction and CO_2 -removal reaction creates the possibility of a direct one-step process for the production of hydrogen from coal-derived gas.

Table of Contents

	Page
Abstract	ii
List of Figures	iii
List of Tables	x
Acknowledgement	xi
Executive Summary	xii
Chapter 1: Introduction	1
Chapter 2: Task 1 - Preliminary Effort	5
2.1 Literature Review	5
2.1.1 Calcination and Carbonation of CaCO_3/CaO	5
2.1.2 The Sulfation of CaO	11
2.1.3 Shift Reaction	15
2.1.4 Discussion	18
2.2 Sorbent Selection	22
2.3 High-Temperature High-Pressure Electrobalance Reactor	24
Chapter 3: Task 2 - Reaction Screening Tests	36
3.1 Characteristics of the Calcination-Carbonation Reactions	37
3.1.1 The Effect of Temperature	37
3.1.2 The Effect of Gas Composition	40
3.2 Comparison of Test Sorbents	49
Chapter 4: Task 3 - Two-Cycle Test Series	62
4.1 Reactivity and Capacity Indices	63
4.2 Reaction Parameter Evaluation	80
4.2.1 The Effect of Calcination Temperature	80
4.2.2 The Effect of Carbonation Temperature	87
4.2.3 The Effect of Carbonation Pressure	91
4.2.4 The Effect of CO_2 Mol Fraction	96
4.3 Direct Comparison of Base Sorbents	96
4.4 Optimum Reaction Conditions	100
Chapter 5: Task 4 - Detailed Parametric Tests	102
5.1 Calcination Pressure	102
5.2 Calcination and Carbonation Temperatures	105
5.3 Discussion	112
Chapter 6: Task 5 - Five-Cycle Tests	114
6.1 Preliminary Tests	116
6.2 Reactivity and Capacity Indices	125

Table of Contents

	Page
Chapter 7: Task 6 - Structural Property Measurements . . .	129
7.1 Mercury Porosimetry	129
7.1.1 Changes in Pore Characteristics During Reaction	133
7.1.2 Sintering Studies	139
7.1.3 Changes in Pore Characteristic During the Second Cycle	140
7.2 BET Surface Area	146
7.2.1 Surface Area Changes During Reaction . . .	148
7.2.2 Sintering Studies	149
7.3 Discussion	152
7.4 Scanning Electron Microscopy	153
7.5 X-Ray Diffraction	168
Chapter 8: Conclusions and Recommendations	174
Chapter 9: References	178

List of Figures

	Page
Figure 1. Equilibrium CO ₂ Pressure as a Function of Temperature	3
Figure 2. Calcination-Carbonation Test Results from Barker (1973)	8
Figure 3. Porosity of the Calcine as a Function of the Porosity of the Precursor (Hartman et al., 1978)	12
Figure 4. The Extent of Calcium Oxide Sulfation as a Function of the Porosity of the Precursor (Hartman et al., 1978)	14
Figure 5. The Shift Process Using Two High-Temperature Reactors With Intermediate CO ₂ Removal (Kohl and Riesenfeld, 1979)	16
Figure 6. Equilibrium Fractional Conversion of CO as a Function of Temperature With and Without CaO Addition	21
Figure 7. Electrobalance Reactor Schematic	28
Figure 8. Typical Electrobalance Response: One Complete Calcination-Carbonation Cycle	31
Figure 9. Weight Loss Caused by Reactor Upsets During the Injection of Steam at High Pressure	33
Figure 10. Diagram of the Insert Added to the Hangdown Tube to Prevent Steam Condensation	35
Figure 11. The Effect of Temperature on Calcination Kinetics: Sorbent 1	38
Figure 12. The Effect of Temperature on Carbonation Kinetics: Sorbent 1	39
Figure 13. Long-Term Carbonation Results: Sorbent 1	41
Figure 14. The Effect of CO ₂ Concentration on Carbonation Kinetics: Sorbent 1	42
Figure 15. The Effect of Gas Composition on Carbonation Kinetics; The Addition of CO and H ₂ : Sorbent 1	44
Figure 16. The Effect of Gas Composition on Carbonation Kinetics; The Addition of CO, H ₂ O, and H ₂ : Sorbent 1	45

List of Figures

	Page
Figure 17. Testing for the Presence of the Shift Reaction: Sorbent 1	47
Figure 18. Carbonation Kinetics With Constant CO ₂ Concentra- tion and Varying Background Gas Composition: Sorbent 1	48
Figure 19. Carbonation With No CO ₂ in the Feed Gas: Sorbent 1	50
Figure 20. Comparison of Calcination Kinetics: Sorbents 1, 2, 4 and 5	51
Figure 21. Comparison of Calcination Kinetics: Sorbents 1, 3, and 6	52
Figure 22. Comparison of Carbonation Kinetics: Sorbents 1, 2, 4, and 5	54
Figure 23. Comparison of Carbonation Kinetics: Sorbents 1, 3, and 6	55
Figure 24. Decomposition-Carbonation Kinetics: Sorbent 7 .	57
Figure 25. Calcination-Carbonation Kinetics: Sorbent 9 .	59
Figure 26. Comparison of First Cycle Carbonation Kinetics: Sorbents 1, 7, and 9	61
Figure 27. Reaction Reproducibility: Weight-Time Results for Two Calcination-Carbonation Cycles	67
Figure 28. Evaluation of the Lag Time, t_o , During Carbonation	69
Figure 29. The Effect of Calcination Temperature on First- Cycle Reactivity, R_1	81
Figure 30. The Effect of Calcination Temperature on Second- Cycle Reactivity, R_2	82
Figure 31. The Effect of Calcination Temperature on First- Cycle Capacity, C_1	83
Figure 32. The Effect of Calcination Temperature on Second- Cycle Capacity, C_2	84
Figure 33. The Effect of Calcination Temperature on Two- Cycle Reactivity Maintenance, R_{12}	85

List of Figures

	Page
Figure 34. The Effect of Calcination Temperature on Two-Cycle Capacity Maintenance, C_{12}	86
Figure 35. The Effect of Carbonation Temperature on First-Cycle Reactivity, R_1 , at Low Carbonation Pressure	89
Figure 36. The Effect of Carbonation Temperature on First-Cycle Reactivity, R_1 , at High Carbonation Pressure	90
Figure 37. The Effect of Carbonation Temperature on Capacity Maintenance	92
Figure 38. The Effect of Carbonation Pressure on First-Cycle Reactivity, R_1	94
Figure 39. The Effect of Carbonation Pressure on Capacity Maintenance, C_{12}	95
Figure 40. The Effect of CO_2 Mol Fraction on First-Cycle Reactivity, R_1	97
Figure 41. The Effect of CO_2 Mol Fraction on First-Cycle Capacity, C_1	98
Figure 42. Comparison of Sorbent 9 Calcination Kinetics at Different Pressures	103
Figure 43. The Effect of Calcination Pressure on First-Cycle Carbonation Kinetics. Sorbent 7	104
Figure 44. Calcination Kinetics of Sorbent 7 as a Function of Temperature	106
Figure 45. The Effect of Calcination Temperature on First-Cycle Carbonation Kinetics. Sorbent 7	107
Figure 46. Sorbent 7 Capacity Maintenance as a Function of Carbonation Temperature	108
Figure 47. The Effect of Temperature on Carbonation Kinetics During the Early Phases of the Reaction	109
Figure 48. Two-Cycle Capacity Maintenance of Sorbent 9 as a Function of Carbonation Temperature	111
Figure 49. Two-Cycle Capacity Maintenance of Sorbent 7 as a Function of Carbonation Temperature	113

List of Figures

	Page
Figure 50. Calcination-Carbonation Results for Sorbent 1 Through Five Cycles	117
Figure 51. Comparison of Capacity Decrease for Sorbent 1 With Literature Results at Similar Reaction Conditions	119
Figure 52. Carbonation Results for Sorbent 7 Through Five Cycles	120
Figure 53. Carbonation Results for Sorbent 9 Through Five Cycles	121
Figure 54. Carbonation Capacity of the Three Base Sorbents as a Function of Cycle Number	122
Figure 55. CO ₂ Capacity Per Gram of Sorbent for Four Test Sorbents as a Function of Cycle Number	124
Figure 56. Cumulative Pore Volume and Pore Size Distribution for Sorbent 7 Calcined at 750°C for 1 Hour	132
Figure 57. Pore Size Distribution of Sorbent 1	134
Figure 58. Pore Size Distribution of Sorbent 7	135
Figure 59. Pore Size Distribution of Sorbent 9	136
Figure 60. The Effect of Sintering Temperature on the Pore Size Distribution of Calcined Sorbent 9. 1 Hour Sintering Time	141
Figure 61. The Effect of Sintering Time on the Pore Size Distribution of Calcined Sorbent 9. 900°C Sintering Temperature	142
Figure 62. Comparison of Pore Size Distribution Curves for Sorbent 1 Following the First and Second Calcination Cycles	143
Figure 63. Comparison of Pore Size Distribution Curves for Sorbent 9 Following One and Two Complete Cycles	145
Figure 64. The Effect of Sintering Temperature on Surface Area. 1 Hour Sintering Time	150
Figure 65. The Effect of Sintering Time on Surface Area. 900°C Sintering Temperature	151
Figure 66. Pore Size Distribution Curves for Sorbent 9 After Two Complete Cycles Comparing the Effect of Carbonation Temperature	154

List of Figures

	Page
Figure 67. SEM of As-Received Sorbent 1. a) 3500X b) 20,000X	155
Figure 68. SEM of As-Received Sorbents at 3500X. a) Sorbent 7 b) Sorbent 9	157
Figure 69. SEM of Calcined Sorbents at 20,000X. a) Sorbent 1 b) Sorbent 9	158
Figure 70. SEM of Calcined Sorbent 7. a) 750X b) 20,000X	160
Figure 71. SEM of Sorbents Calcined at 1000°C (20,000X) a) Sorbent 1 b) Sorbent 9	161
Figure 72. SEM of Sorbents After First Carbonation (20,000X) a) Sorbent 1 b) Sorbent 7	162
Figure 73. SEM of Sorbent 9 After One Complete Calcination- Carbonation Cycle. a) 750X b) 20,000X	164
Figure 74. SEM of Sorbent 7 After Five Complete Cycles. a) 750X b) 3500X	165
Figure 75. SEM of Sorbent 9 After Five Complete Cycles. a) 750X b) 3500X	166
Figure 76. High Magnification SEM of Sorbent 7 After Five Complete Cycles (20,000X)	167
Figure 77. XRD Spectrum of As-Received Sorbent 9	169
Figure 78. XRD Spectrum of Calcined Sorbent 9	170
Figure 79. XRD Spectrum of Carbonated Sorbent 9	171

List of Tables

	Page
Table I. Description of Calcium-Based Sorbent Precursors .	23
Table II. Chemical Analysis of Mallinckrodt Analytical Reagent Calcium Carbonate (Sorbent 1) . . .	25
Table III. Chemical Analysis of Mallinckrodt Analytical Reagent Calcium Acetate (Sorbent 7) . . .	26
Table IV. Chemical Analysis of National Lime Co. Dolomite (Sorbent 9)	27
Table V. Task 3 Test Matrix for Calcium Carbonate (Sorbent 1)	64
Table VI. Task 3 Test Matrix for Calcium Acetate (Sorbent 7)	65
Table VII. Task 3 Test Matrix for Dolomite (Sorbent 9) .	66
Table VIII. Summary of the Lag Time, t_o , at Various Reaction Conditions	71
Table IX. First and Second Cycle Reactivity Results for Sorbent 1	73
Table X. First and Second Cycle Reactivity Results for Sorbent 7	74
Table XI. First and Second Cycle Reactivity Results for Sorbent 9	75
Table XII. First and Second Cycle Capacity Results for Sorbent 1	77
Table XIII. First and Second Cycle Capacity Results for Sorbent 7	78
Table XIV. First and Second Cycle Capacity Results for Sorbent 9	79
Table XV. Five-Cycle Test Matrix for Task 5	115
Table XVI. Reactivity Results for Task 5 Five-Cycle Tests .	127
Table XVII. Capacity Results for Task 5 Five-Cycle Tests .	128
Table XVIII. Summary of Mercury Porosimeter Tests and Pore Volume Results	130
Table XIX. Summary of BET Surface Area Test Results . .	147
Table XX. Crystalline Phase Determinations from X-Ray Diffraction Studies	173

ACKNOWLEDGEMENT

This project was supported by the Morgantown Energy Technology Center of the U.S. Department of Energy under contract DE-AC21-89MC26366. The authors would like to thank Dr. Richard Johnson who served as Contracting Officer's Representative for most of the project, and Mr. Sam Sharp who served as Contract Officer's Representative for the last few months of the study. The general support and helpful suggestions made by both is gratefully acknowledged.

EXECUTIVE SUMMARY

This research project has investigated the feasibility of a high-temperature, high-pressure (HTHP) process for the bulk separation of CO_2 from coal-derived gases. The contract was awarded in September 1989 in response to solicitation number DE-RA21-89MC26040 entitled "Novel Concepts for Bulk Separation of Gases in Coal Gasification Systems." The contract period was originally two years, but a four-month no-cost time extension increased the total project period to 28 months.

The overall project consisted of 6 tasks and this report is organized along the task lines. Three objectives were met in Task 1. A literature search on the calcination-carbonation reactions of CO_2 with calcium-based sorbents was completed. An analysis of related reactions such as the sulfation of CaO and the water-gas shift reaction was also included in the literature search. Nine candidate calcium-based sorbents were also acquired in Task 1. These samples were subjected to reaction screening tests as part of Task 2, and on the basis of the screening results, three sorbents were selected for more detailed kinetic testing in Task 3. The third objective accomplished under Task 1 was the construction of a high-temperature, high-pressure electrobalance reactor which was used for studying the kinetics of the calcination-carbonation reactions. The reaction studies covered a temperature range of 550-900°C, pressure range of 1-15 atm, and with gas compositions varying from pure nitrogen to a simulated coal gas containing N_2 , CO , CO_2 , H_2 , H_2O and H_2S .

During the early phases of the project while the HTHP reactor was being constructed, an existing atmospheric pressure electrobalance reactor was used to become familiar with the characteristics of the calcination-carbonation reactions and to compare the kinetics of the

nine test sorbents. This effort constituted Task 2. Three of the nine candidate sorbents were selected for detailed testing in Task 3 and the range of reaction conditions to be covered in the Task 3 test matrix was defined.

The first of the test sorbents, designated sorbent 1, was obtained from a chemically pure (99.97%) calcium carbonate precursor. The precursor was a highly crystalline, low surface area material which was essentially nonporous. Complete calcination was easily achieved but the subsequent carbonation reaction effectively stopped well before completion. Sorbent 1 also experienced significant performance degradation as the number of cycles increased. Chemically pure calcium acetate hydrate, designated sorbent 7, was chosen as the second precursor for the Task 3 test sequence. Complete calcination was easily achieved, and, in addition, essentially complete calcium carbonation was possible. The improved performance of sorbent 7 relative to sorbent 1 is attributed to the more open pore structure of CaO produced by decomposition of the acetate. The third sorbent precursor chosen for detailed Task 3 testing was a commercial dolomite (sorbent 9). Dolomite calcination caused both the calcium and magnesium carbonates to decompose, producing a highly porous sorbent composed of equal molar quantities of CaO and MgO. Magnesium carbonate was not reformed at the carbonation conditions of interest, but essentially complete calcium carbonation was achieved. Although the presence of the inert MgO reduced the CO₂ capacity per gram of sorbent, sorbent 9 exhibited superior multicycle performance.

Task 2 exploratory tests established the range of calcination and carbonation reaction conditions which were examined in Task 3. It was

during the Task 2 exploratory tests that indirect evidence of the simultaneous occurrence of the water-gas shift reaction with CO_2 removal was noticed. The possibility of simultaneous reactions was examined in more detail in Task 5 and a follow-up proposal to study the feasibility of combining CO_2 -removal with the shift reaction for the direct production of hydrogen was developed.

In Task 3, the HTHP electrobalance reactor was used to study the calcination-carbonation behavior of the three chosen sorbents as a function of calcination temperature (750-900°C), carbonation temperature (550-750°C), carbonation pressure (1-15 atm), and CO_2 mol fraction (0.01 to 0.15). Each test consisted of two complete calcination-carbonation cycles to provide kinetics data and preliminary indications of sorbent performance in multicycle operation. A test matrix of 243 runs (5 variables each at 3 levels) was defined. 98 of these runs were completed with the remaining 143 runs eliminated from the experimental program based upon equilibrium considerations or upon results of previously completed tests.

These tests showed the importance of low calcination temperature (~750°C) and identified 650 to 750°C as the most desirable temperature range for the carbonation reaction. Surprisingly, lower temperature carbonation at 550°C resulted in decreased sorbent capacity and, in particular, poorer second-cycle carbonation performance. Carbonation pressure and CO_2 mol fraction had the expected effect on carbonation kinetics during the early rapid reaction phase, but had little effect on sorbent capacity.

The original Task 4 work plan called for the selection of one sorbent, based upon Task 3 results, for a more detailed examination of

the effect of reaction conditions on sorbent performance. However, both sorbents 7 and 9 were found to have unique favorable properties and both were retained in the Task 4 and Task 5 tests. In addition, expansion of the Task 3 test matrix beyond that originally planned resulted in prior coverage of some of the Task 4 test objectives. In the revised Task 4 tests, we found that high-pressure calcination could be accomplished without adverse effects, thus creating the possibility of an overall isobaric process in which calcination and carbonation cycling could be effected by either one or a combination of temperature and CO_2 partial pressure changes. Further examination of low carbonation temperatures confirmed the Task 3 conclusion that the carbonation temperature should not be lower than 650°C . High carbonation temperature tests indicated that, while temperatures greater than 750°C are, for a number of reasons, undesirable, temperature excursions to as much as 850°C do not cause serious short-term sorbent degradation.

In the Task 5 tests the number of cycles was increased from two to five, and, in limited tests to ten. More complex background gas compositions ranging from the simple CO_2/N_2 mixture to a simulated coal gas containing CO_2 , CO , H_2 , H_2O , H_2S , and N_2 were studied.

[Author's note: Experimental tests in this task are still underway at the time this draft is being written. In the final report this section will be expanded to include a overview of Task 5.]

Structural property characterization of the sorbent precursors, the sorbents following calcination, and the sorbents after carbonation comprised Task 6 activities. BET surface area, mercury porosimetry, scanning electron microscopy, and x-ray diffraction were the characterization methods used. In all cases, calcination of the sorbent precursors resulted in an increase in surface area and pore volume as

volatiles were released from the solid. Subsequent carbonation then caused the surface area and pore volume to decrease as CO_2 re-entered the solid phase. Calcination of sorbents 7 and 9 involved the release of greater quantities of volatiles and produced a more porous sorbent, which is believed to be responsible for the superior performance of sorbents 7 and 9 relative to sorbent 1. Scanning electron microscopy studies provided visual confirmation of the surface area and porosimeter results, and helped to understand portions of the kinetics results. X-ray diffraction was used to identify crystalline phase present in the as-received sorbent precursors, and in the sorbents following calcination and carbonation.

CHAPTER 1

INTRODUCTION

An important responsibility of the U.S. Department of Energy is the development of new technology to promote the use of the nation's vast reserves of coal, thereby decreasing our dependence on imported petroleum. Coal gasification technology offers the opportunity for achieving the above objective, while at the same time improving process energy efficiency and reducing the adverse environmental impact associated with present coal utilization processes. Prior DOE research has concentrated upon the development of novel gasification processes, improving existing processes, and in developing technology for the removal of trace impurities present in the coal-derived gas.

The current DOE program seeks to develop novel concepts for the bulk separation of gases from product streams which will provide further improvements in gasification process efficiency and economics. Gas stream components subject to bulk separation include carbon dioxide, carbon monoxide, hydrogen, nitrogen, and methane; separation processes should operate within a temperature range of 100 to 700°C.

This project has examined the technical feasibility of a high-temperature, high pressure (HTHP) process for the bulk separation of CO₂ based upon the reversible reaction between CO₂ and CaO

The ability to achieve HTHP bulk separation of CO₂ could have a positive effect on a number of processes in which coal-derived gas is utilized. These include heating value upgrade, hydrogen production, ammonia or

methanol synthesis gas manufacture, and the operating efficiency of molten carbonate fuel cells. In addition, CaCO_3 decomposition during regeneration can produce high-purity CO_2 which may be marketed as a refrigerant, for use in fire extinguishers, for beverage carbonation, or for improved petroleum recovery.

This research was limited to a laboratory-scale experimental effort using an electrobalance reactor to identify appropriate ranges of temperature, pressure, and gas composition for both the forward and reverse reactions. A number of CaO-based sorbents having different chemical composition and structural properties have been investigated to define those properties required to achieve high reactivity, capacity, and acceptable durability.

Justification for the HTHP CO_2 separation process is based upon a thermodynamic analysis of the reversible reaction. The equilibrium constant, expressed in terms of component activities, may be calculated from the Gibbs free energy by the well-known equation

$$K = \frac{a(\text{CaCO}_3)}{a(\text{CaO}) a(\text{CO}_2)} = \exp(-\Delta G^\circ/RT) \quad (2)$$

If one assumes that pure solid phases are present, $a(\text{CaCO}_3) = a(\text{CaO}) = 1$, and if the gas phase is ideal, $a(\text{CO}_2) = P(\text{CO}_2)$, so that

$$P(\text{CO}_2) = K_p^{-1} = \exp(\Delta G^\circ/RT). \quad (3)$$

Figure 1 shows calculated values of $P(\text{CO}_2)$ over CaO as a function of temperature using thermochemical data from Hougen et al. (1959). At 650°C , $P(\text{CO}_2) \sim 0.008$ atm. At that temperature whenever $P(\text{CO}_2) > 0.008$ atm, the reaction should proceed to the right (carbonation). When

Figure 1. Equilibrium CO_2 Pressure as a Function of Temperature.

$P(\text{CO}_2) < 0.008 \text{ atm}$, thermodynamics favors carbonate decomposition. For an entering gas at 650°C , 15 atm and containing 15% CO_2 , it is theoretically possible to achieve 99.6% CO_2 removal. With lower temperatures, higher pressures, and/or higher inlet CO_2 mol fractions, still greater CO_2 removal efficiencies are theoretically possible.

CHAPTER 2

TASK I - PRELIMINARY EFFORT

Three major subtasks were carried out in the preliminary effort. These included a literature review on the CaO , CO_2 , CaCO_3 reactions and other closely related reactions, acquisition of a number of sorbent precursors exhibiting a range of chemical compositions and structural properties, and the design and construction of a high temperature-high pressure (HTHP) electrobalance reactor. Each of these efforts are summarized in the following.

2.1 LITERATURE REVIEW

2.1.1 Calcination and Carbonation of CaCO_3/CaO

The calcination of limestone for lime production is one of the largest tonnage commercial reactions carried out world-wide. Modern lime kilns operate at atmospheric pressure with temperatures in the range of 1200 to 1300°C. These temperatures, which are well in excess of the minimum decomposition temperature, are necessary to insure that limestone lumps are completely calcined during their passage through the kiln. The calcination reaction forms the basis of the sorbent regeneration step in the proposed HTHP CO_2 -separation process. The primary CO_2 removal reaction, which is the reverse of the calcination reaction, is not carried out commercially.

The possibility of using the forward carbonation reaction for CO_2 separation was considered at least as early as the 1920's. Gluud et al.

(1931) patented a process for producing hydrogen via a water-gas shift reaction in the presence of calcined dolomite. The MgO component of the calcined dolomite was claimed to be responsible for the shift catalysis, while CaO reacted with the CO₂ product, thereby continually shifting the reaction to the right and permitting essentially complete removal of carbon oxides from the gas stream, and the production of high-purity hydrogen.

Squires (1967) revived the concept by suggesting the use of dual fluidized-bed reactors to permit steady-state operation and to overcome some of the heat transfer problems associated with Gluud's fixed-bed concept. Squires also proposed the use of calcined dolomite with MgO serving as the shift catalyst and CaO used to react with CO₂. Also in the 1960's, the CO₂-acceptor process (Curran et al., 1967) was studied as a possible means for the simultaneous removal of H₂S and CO₂ from coal-derived gases. Dolomite was used in a fluidized-bed reactor and the sorbent was subjected to numerous carbonation-calcination cycles. Each of these studies concentrated upon the process aspects and little or no fundamental kinetics data were reported. Reliable and highly efficient low temperature processes for CO₂ removal were available, and research on the high-temperature process was terminated.

On a more fundamental level, Dedman and Owen (1962) studied the reaction of CO₂ with calcined limestone over the temperature range of 100 to 600°C and the pressure range of 10 to 600 mmHg. The initial reaction was found to be very rapid followed by an abrupt transition to a much slower reaction. The slower second stage was attributed to a process controlled by diffusion of CO₂ in the pores of the solid. An activation energy of 9.5 ± 2 kcal/mol between 200 and 600°C was reported

for the diffusion-controlled second stage. It is interesting to note that this is the first instance in which the carbonation reaction was reported to occur in two stages. Such behavior has been regularly reported since.

Two studies by Barker (1973 and 1974) on the CaO-CO_2 reaction provide results which are relevant to the current study. In the initial paper, the reaction was studied in an electrobalance reactor at 866°C and 1 atm using calcium carbonate particles in the range of 2 to 20 micron diameter. Figure 2 (from Barker, 1973) shows a typical electrobalance response to multiple calcination-carbonation cycles (curve b). Calcination, which is represented by the weight loss from 100% to 56% [$M(\text{CaCO}_3) = 100$, $M(\text{CaO}) = 56$], was rapid and complete. Carbonation, represented by the weight gain, was initially rapid but the reaction rate dropped off to near zero well short of completion. Calcination was complete in each cycle but the transition from the rapid to the slow reaction rate occurred at progressively smaller sample weights with increasing cycle number. The fact that the reaction did not completely stop after the initial rapid rate is shown by curve (a) in which a single carbonation test was extended for 24 hours, at the end of which time the sample weight had increased to approximately 98%.

Such reaction behavior can be explained on the basis of the varying structural characteristics of the reacting solid as the calcination-carbonation reactions progress. Natural limestones commonly possess quite low porosity. However, the calcination reaction creates porosity as CO_2 is driven off. During carbonation the pores are refilled. The refilling process occurs preferentially at the exterior of the particle, and the end of the rapid reaction period is presumed to correspond to

Figure 2. Calcination-Carbonation Test Results from Barker (1973).

total surface pore closure. The remaining unreacted CaO within the particle is carbonated very slowly since further reaction is controlled by a solid state or ionic diffusion mechanism through the nonporous carbonate layer. Similar problems of pore closure are faced when calcium oxide is used for SO₂ removal in flue gas desulfurization applications. Key characteristics of this related reaction are discussed subsequently.

In his second paper, Barker (1974) used extremely small particles of approximately 20 nm diameter to minimize the quantity of CaO which could be isolated within the particles after pore closure. Calcination was carried out at 629°C and 1 atm in N₂, and carbonation at 577°C under 1 atm of CO₂. Approximately 93% carbonation was achieved during the rapid reaction phase and this value remained essentially constant through 30 complete cycles. While this latter study is of importance in understanding the mechanism of the carbonation reaction, the use of such small particles is not feasible in a commercial process.

Oakeson and Cutler (1979) studied the CaO-CO₂ reaction using an electrobalance over a temperature range of 853 to 1044°C under CO₂ pressures between 2.35 and 24.9 atm. The rate of reaction was reported to follow a parabolic correlation with time, while the pressure dependence was related to a Langmuir-type adsorption isotherm. The reaction was reported to be diffusion controlled with a diffusion activation energy of 29 ± 6 kcal/mol.

Bhatia and Perlmutter (1983) investigated the kinetics of the CO₂-CaO reaction using a CO₂-N₂ mixture at 1 atm over the temperature range of 400 to 725°C. Their data were analyzed using a random pore model (Bhatia and Perlmutter, 1980 and 1981) and the average value of

the rate constant during the initial rapid reaction period was found to be $0.0595 \pm 0.0018 \text{ cm}^4/\text{mol}\cdot\text{s}$. The slow second phase was reported to be diffusion controlled with an activation energy of $88.9 \pm 3.6 \text{ kJ/mol}$ below 515°C and $179.2 \pm 7 \text{ kJ/mol}$ above 515°C . 515°C was claimed to be near the Tamman temperature of CaCO_3 (about 533°C), where a change in the solid state diffusion mechanism was said to occur.

DeLucia (1985) studied the multicycle behavior of the calcination-carbonation reactions using CO_2 at atmospheric pressure over the temperature range of 50 to 800°C . The carbonation reactivity decreased by 10 to 25% per cycle, which was attributed to continued particle shrinkage during calcination.

A number of methods for minimizing or eliminating pore closure to permit more complete calcium utilization have been suggested. Dhupe and Gokarn (1987 and 1990) mixed inert solid with calcium-based sorbent pellets and studied the reaction with CO_2 . Metallurgical grade silicon powders were used as the inert. While they reported a maximum CO_2 uptake capacity at a particular inert concentration, no clear explanation of the results was presented. Beruto et al. (1988) observed that higher oxide porosity, and subsequently higher fractional carbonation, could be achieved when CaO precursors other than CaCO_3 were used. In one test using calcium acetate precursor, 90% carbonation was achieved in less than 1 1/2 hours, compared to approximately 60% carbonation at the same reaction conditions using CaO from a calcium carbonate precursor.

Finally, Mess (1989) studied the diffusion process through the CaCO_3 product layer using an electrobalance under CO_2 pressures up to 12 atm at temperatures from 550 to 1050°C . At temperatures of 600°C and

above, the product layer contained crystalline grains whose size varied from 1 to 20 microns. The CaCO_3 grains grew laterally and were temperature dependent. Above 900°C , the reaction was first-order in CO_2 pressure and the activation energy in the diffusion controlled region was 56.9 kcal/mol.

2.1.2 The Sulfation of CaO

A closely related reaction, the sulfation of CaO,

has been the subject of a great deal of research as a potential method for SO_2 control in flue gas desulfurization applications. One study in particular (Hartman et al., 1978) provides information which is directly applicable to the carbonation reaction. The effect of porosity of the calcium carbonate sorbent precursor on the sulfation reaction was examined. While the initial pore volume of most limestones is low ($\leq 0.05 \text{ cm}^3/\text{g}$), related natural carbonate products such as chalks and marls may have initial pore volumes in the range of 0.1 to $0.2 \text{ cm}^3/\text{g}$ and 0.25 to $0.9 \text{ cm}^3/\text{g}$, respectively (Boynton, 1980).

Hartman et al. (1978) showed that the porosity of the calcined product (CaO) was a strong function of the porosity of the natural rock (CaCO_3). Figure 3 shows test results which include limestones, chalks, and marls as precursors. The straight lines in the figure are from the equation

$$\epsilon_{\text{CO}} = 1 - \epsilon_{\text{CC}} \left[\gamma \left(\frac{V_{\text{CO}}}{V_{\text{CC}}} - 1 \right) + 1 \right] \quad (5)$$

Figure 3. Porosity of the Calcine as a Function of the Porosity of the Precursor (Hartman et al., 1978).

where ϵ represents porosity, V is the molar volume, and y is the fractional purity. The subscript CC represents the original calcium carbonate precursor and the subscript CO presents the calcined product, calcium oxide. Values of $V_{CO} = 16.6 \text{ cm}^3/\text{mol}$ and $V_{CC} = 36.9 \text{ cm}^3/\text{mol}$ were assigned along with values of $y = 0.8, 0.9, \text{ and } 1.0$ to obtain the straight lines. The correlation between measured precursor and product porosities and the geometric arguments represented by equation (5) is quite good. Calcines from nonporous limestones had porosities in the range of 0.5 to 0.55, while chalks and marls produced calcines having porosities as high as 0.69 and 0.85, respectively.

Subsequent sulfation results shown in Figure 4 (Hartman et al., 1978) illustrate the importance of the calcine porosity on the sulfation reaction. Using nonporous limestone precursor ($\epsilon_{LS} = 0$), the fractional sulfation was less than 0.3 after 60 minutes. The moderate porosity chalk ($\epsilon_{LS} = 0.27$) resulted in 0.6 to 0.7 fractional sulfation after 60 minutes (depending upon particle size), while the calcine from the high porosity marl ($\epsilon_{LS} = 0.71$) was completely sulfated in approximately 20 minutes.

Finally, any review of the use of calcium-based sorbents in noncatalytic gas-solid reactions would be incomplete if the work of Borgwardt was not cited. Borgwardt has studied both the carbonation and sulfation reactions of CaO. One paper (Borgwardt, 1989) will provide a point of entry which the reader can use to trace back the numerous contributions made by Borgwardt and associates.

Figure 4. The Extent of Calcium Oxide Sulfation as a Function of the Porosity of the Precursors (Hartman et al., 1978).

2.1.1.3 Shift Reaction

Experimental results obtained during the Task 2 screening studies suggested that the water-gas shift reaction was occurring simultaneously with CO₂ removal. Because of the potential commercial significance of the combined reactions, the literature search was extended to include key characteristics of the shift reaction.

The water-gas shift reaction is used for the production of H₂ from synthesis gas containing varying proportions of CO, CO₂, H₂ and H₂O. Most synthesis gas is currently obtained from the steam reforming of natural gas or naphtha, but the partial oxidation of fuel oil and the gasification of coal provide alternate sources which may become increasingly important in the future.

Synthesis gas is commonly submitted to the water-gas shift reaction

to reduce or eliminate CO and increase the yield of H₂. The reaction is exothermic and reversible, and normally requires a heterogeneous catalyst. The operating temperature is chosen to provide the proper balance between reaction rate and equilibrium CO conversion. CO₂ is removed via absorption using an amine solvent or by pressure swing adsorption.

Two reaction stages are normally required to achieve the desired level of CO conversion. A typical two-stage process using gas absorption for CO₂ removal following each reaction stage is shown in Figure 5 (Kohl and Riesenfeld, 1979). In other process options, the intermediate CO₂ removal may be avoided by the use of a low temperature shift catalyst in the second reaction stage (Rase, 1977).

Figure 5. The Shift Process Using Two High-Temperature Reactors With Intermediate CO₂ Removal (Kohl and Riesenfeld, 1979).

Two metal oxide catalysts are in common use. The high-temperature shift catalyst, which normally operates in the 350-450°C range, consists of chromia-promoted iron oxide. The low-temperature catalyst, composed of copper and zinc oxide supported on Al_2O_3 , is active in the temperature range of 200-250°C. While equilibrium yield is improved at low temperature, the low-temperature catalyst is susceptible to poisoning by sulfur compounds and is more expensive. This susceptibility to sulfur poisoning could be extremely important when the synthesis gas is derived from coal gasification.

The literature indicates that a number of materials will catalyze the shift reaction. Rofer-DePorter (1984) reports that the metals Rh, Co, Fe, Ni, Pt, Pd, and Os are active for the shift reaction, both in bulk form and dispersed on supports such as alumina or silica. Metal sulfides and metal oxides other than those used commercially will also catalyze the reaction. MgO is a known shift catalyst but no references to catalysis by CaO have been found.

Early literature indicates that the shift reaction will occur at sufficiently high temperature even in the absence of a catalyst. For example, the Chemical Abstracts summary of a paper by Gauthier (1909) states that when "CO is heated to about 1200°C in a porcelain tube with a variable excess of steam, hydrogen is set free with formation of a volume of CO_2 ..." Similarly, Chemical Abstracts reports that Kondrat'ev and Ziskin (1946) studied the shift reaction at 700 and 800°C in the absence of a catalyst. The fact that MgO is a known catalyst and the probability that the shift reaction will occur without a catalyst near 700°C is important to the current study. Potential implications are discussed in the following section.

2.1.4 Discussion

The literature provides guidance into the expected behavior of the CaO-CO_2 reaction and the possibility of coupling CO_2 removal with the shift reaction for a one-step process for the production of H_2 . In general, the carbonation reaction is characterized by a rapid initial reaction period followed by an abrupt transition to a slow reaction phase well short of complete calcium conversion. This behavior seems to be related to pore closure at the exterior surface of the particle which prevents CO_2 from reaching unreacted CaO at the particle interior. Multicycle tests generally show decreased reactivity with each carbonation cycle, a phenomenon consistent with particle shrinkage and associated reduction in porosity. At least one paper (Bhatia and Perlmutter, 1983) implies that exceeding the Tamman temperature of CaCO_3 could be responsible for the shrinkage.

The literature also suggests possible ways of avoiding or at least delaying the transition from the rapid to the slow reaction phase to obtain increased fractional calcium utilization. Decreasing the sorbent particle size appears to be an effective, but commercially impractical, method. Nanometer diameter particles used by Barker (1974) require special preparation techniques and would be impossible to confine in a commercial process. Increasing the porosity of the sorbent by using a high-porosity precursor such as described by Hartman et al. (1978) and Beruto et al. (1988) seems to be a more promising option.

Although a number of previous studies on the behavior of the CaO-CO_2 reaction have been cited, none provide the broad scope of work necessary to evaluate fully the feasibility of a CaO -based high-temperature CO_2 removal process. The process patent of Gluud et al. (1931)

contains no fundamental kinetic data. Similarly, Squires' (1967) paper presents a conceptual modification to Gluud's process but again without the necessary kinetic data. Many of the more fundamental studies have examined only a narrow range of conditions such as a single pressure, or a single sorbent, or only a single carbonation cycle. The objectives of the present study are to build upon this past work by studying a number of sorbents having a wide variation in structural properties, to determine the effects of the important reaction parameters over a range of conditions likely to be encountered in a commercial process, and to develop information on sorbent durability through multi-cycle testing. The kinetic data will be supplemented with key structural property measurements of the sorbents at various stages in the reaction cycles.

Combining high temperature CO_2 removal with the shift reaction opens the possibility of a direct process for hydrogen production. The concept was first proposed by Gluud et al. (1931) and later revived by Squires (1967). The ideas were not pursued, however, because of the availability of reliable and low-cost methods of CO_2 removal near ambient temperature. The potential of the combined process is illustrated in the following. A typical synthesis gas composition produced by methane reforming with sufficient steam added to produce 3.1 mol steam per mol of dry gas has been used for illustration:

H_2	18.9 % (mol)
CO	3.0
CO_2	2.5
H_2O	75.6

The equilibrium constant for the shift reaction (6) is

$$K_{p(\text{Shift})} = \frac{P_{\text{CO}_2} P_{\text{H}_2}}{P_{\text{CO}} P_{\text{H}_2\text{O}}} \quad (7)$$

$K_{p(\text{Shift})}$ as a function of temperature is given by Moe (1962)

$$K_{p(\text{Shift})} = [4577.8/T - 4.33] \quad (8)$$

where T is in Kelvin. The equilibrium fractional conversion of CO based on the example inlet composition as a function of temperature is shown as curve A in Figure 6. At the typical 723 K outlet temperature from a single high-temperature shift reactor, only about 93% conversion of CO is possible. However, the equilibrium CO conversion from the low-temperature shift reactor at 523 K approaches 100%.

Combining the shift reaction with CO_2 removal according to reaction (1) will reduce the CO_2 partial pressure to the value given by equation (3). The overall equilibrium for the combined reactions becomes

$$K_{\text{oa}} = K_p K_{p(\text{Shift})} = \frac{P_{\text{H}_2}}{P_{\text{CO}} P_{\text{H}_2\text{O}}} \quad (9)$$

The combined reactions are pressure dependent since CO_2 removal causes a reduction in the number of mols in the gas phase.

Equilibrium fractional conversion of CO for the combined reactions based upon the previously specified inlet gas composition is shown as curves B and C of Figure 6 for 1 atm and 22.1 atm, respectively. At 1 atm the equilibrium conversion of CO is essentially 100% for all temperature less than 800 K and is greater than 95% up to about 950 K. At 22.1 atm, essentially complete CO conversion is feasible to about 900 K. As the CaCO_3 decomposition temperature is approached, the

Figure 6. Equilibrium Fractional Conversion of CO as a Function of Temperature With and Without CaO Addition.

equilibrium CO_2 pressure increases and the equilibrium CO conversion approaches that expected from the shift reaction alone.

Therefore, direct coupling of the shift reaction and high-temperature CO_2 removal provides the potential for higher temperature operation at a specified CO conversion level or higher CO conversion at a specified temperature. Alternatively, the desired level of CO conversion at a fixed temperature could be achieved with reduced quantities of excess steam.

2.2 SORBENT SELECTION

A total of nine calcium-based sorbent precursors were acquired and subjected to preliminary screening tests (see Chapter 3). A general description of the sorbents is presented in Table I. Sorbent selection was based upon availability and also upon the desirable properties identified in the literature search. Sample 1, reagent-grade CaCO_3 from Mallinckrodt, was selected as the base sorbent against which others would be compared. Samples 2 through 6 were all commercial-grade CaCO_3 obtained from producing quarries. Limestone, chalk, and marl were included in this group in the hopes of matching the type of results obtained by Hartman et al. (1978) shown in Figure 4. Instead, as will be shown, the calcination-carbonation behavior of samples 1 through 6 was qualitatively similar.

Sorbents 7 and 8, reagent-grade calcium acetate and reagent-grade calcium sulfate, respectively, were selected in the hope that their decomposition would yield a higher porosity CaO so that the rapid reaction phase would be extended to higher fractional calcium utilization. Finally, sorbent 9, a commercial dolomite containing approxi-

Table I

Description of Calcium-Based Sorbent Precursors.

Sorbent No.	General Description	Source
1	Reagent grade calcium carbonate, CaCO_3	Mallinckrodt Chemicals
2	Marl from producing quarry	Gifford-Hill Co. Harleyville, SC
3	Chalk from producing quarry	United Cement Co. Artesia, MS
4	Chalk from producing quarry	Texas Crushed Stone Co. Georgetown, TX
5	Limestone from newly developed quarry in Yucatan, Mexico	Vulcan Materials Co. Houston, TX
6	Chalk from producing quarry	Gifford-Hill Co. Midlothian, TX
7	Reagent grade calcium acetate, $\text{Ca}(\text{C}_2\text{H}_3\text{O}_2)_2 \cdot x \text{H}_2\text{O}$	Mallinckrodt Chemicals
8	Reagent grade calcium sulfate, $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$	Mallinckrodt Chemicals
9	Dolomite, $\text{CaCO}_3 \cdot \text{MgCO}_3$	National Lime Co. Findley, OH

mately equal molar quantities of MgCO_3 and CaCO_3 , was tested to evaluate the effect of an inert on the carbonation reaction. At calcination conditions, both MgCO_3 and CaCO_3 decompose to their respective oxides; both components, therefore, are effective in creating porosity during calcination. At carbonation conditions MgO is inert so that pore closure due to CaCO_3 formation should be moderated, and open pores for CO_2 diffusion should remain.

On the basis of the screening tests to be described in Chapter 3, three sorbents - 1, 7, and 9 - were selected for more detailed testing in Task 3 (see Chapter 4). Chemical analyses of the three selected sorbents (as reported by the supplier) are presented in Tables II, III, and IV. More detailed structural property results for these samples are presented subsequently in this report.

2.3 HIGH-TEMPERATURE HIGH-PRESSURE ELECTROBALANCE REACTOR

The high-pressure electrobalance reactor system shown schematically in Figure 7 was constructed and used for all reaction tests beginning with Task 3. The key component is a Cahn Model C-100 pressure balance having 100 g capacity and 10 μg sensitivity. The housing and hang-down tube are constructed of 316 stainless steel and the unit is rated for 1500 psig at 600°C. Gases from high-pressure cylinders are fed to the reactor using high pressure mass flow controllers (Porter Instruments Model 201). Water may be added to the feed mixture using a high-pressure syringe pump (Harvard Apparatus Model 909). The feed line leading to the side-arm of the hang-down tube is heat traced to induce water vaporization. A surge volume consisting of a 300 ml high pressure sampling bomb is included in the syringe pump exit line to dampen steam

Table II Chemical Analysis of Mallinckrodt Analytical
 Reagent CaCO_3 (Sorbent 1), Chelometric Standard
 (as reported by Mallinckrodt)

CaCO_3	99.97% (after 2 hours at 285°C)
Alkalinity	Passes Test
Ammonium (NH_4)	0.002%
Barium (Ba)	0.002%
Chloride (Cl)	0.001%
Fluoride (F)	0.0009%
Heavy Metals (as Pb)	0.0005%
Insoluble in HCl and NH_4OH ppt	0.00025%
Iron (Fe)	<0.0002%
Magnesium (Mg)	0.0006%
Other Alkalis	Passes Test
Oxidizing Substances (as NO_3)	<0.005%
Potassium (K)	0.0006%
Silica (SiO_2)	<0.0006%
Silicon (Si)	0.0003%
Sodium (Na)	0.002%
Strontium (Sr)	0.006%
Sulfate (SO_4)	<0.0025%

Table III. Chemical Analysis of Mallinckrodt
Analytical Reagent Calcium Acetate (Sorbent 7)
(as reported by Mallinckrodt)

$\text{Ca}(\text{C}_2\text{H}_3\text{O}_2)_2$	> 91.47%
Barium (Ba)	< 0.005%
Chloride (Cl)	< 0.001%
Heavy Metals (as Pb)	< 0.001%
Iron (Fe)	< 0.001%
Magnesium and Alkali Salts	< 0.2%
Sulfate (SO_4)	< 0.01%
Water	8.3%

Table IV

Chemical Analysis of Dolomite (Sample 9)

(as reported by National Lime Co., Findlay, Ohio)

Component	Wt. %
CaCO_3	54.5
MgCO_3	45.0
SiO_2	0.2
Fe_2O_3	0.07
Al_2O_3	0.08
S	0.03
Other	0.12

Loss on ignition after calcination

at 1800°F - 47.4%

flow variations. Inert gas (N_2) which is fed to the balance housing joins with reactive gases (N_2 , CO, CO_2 , H_2 , H_2S , and H_2O) which enter through the side-arm and the combined gases flow downward over the solid reactant. At typical test conditions the volumetric flow rate of inert through the balance housing was $300\text{ cm}^3/\text{min}$ (STP) while the total flow of reactive gases through the reactor side-arm was $200\text{ cm}^3/\text{min}$ (STP). Exit gases pass first through a condenser immersed in an ice bath and are vented either through a three-way valve for atmospheric pressure tests or through a back-pressure regulator (Tescom Model 26-232-24-0301) for high pressure tests. A similar condenser, three-way valve, back-pressure regulator arrangement is provided in the side-arm gas feed line. Reactive gas flow rate and pressure adjustments are made while directing the gases to vent. At the start of a test the reactive gases are introduced to the reactor with minimum system upset and time delay.

Reactor temperature is maintained using a single-zone split-tube furnace (Applied Test Systems Series 3210) equipped with a single-zone temperature controller which is microprocessor programmable for up to eight ramp and soak intervals. An over-temperature controller provides protection against temperature run-away.

An IBM PS/2 Model 30/286 computer is provided to acquire, store, and process sample weight, reactor temperature, and mass flow controller readings. A data interface package and software supplied by Cahn Instruments are used for data acquisition and processing. Both a printer (Epson RX-100) and plotter (IBM 6/80/001) are provided for hard-copy data output.

A typical electrobalance response curve through one complete calcination-carbonation cycle using reagent grade $CaCO_3$ (sorbent 1) is

shown in Figure 8. 11.8 mg of CaCO_3 were heated at a rate of approximately $5^\circ\text{C}/\text{min}$ to 750°C under one atmosphere of nitrogen. The high reactor mass produced a nonlinear response during the first 50 minutes of the heating cycle. However, the heating rate approached linearity well before the active reaction temperature was reached.

The sample weight showed a small apparent increase during the early heat-up period prior to the beginning of active calcination. This apparent weight increase was due to increased aerodynamic drag exerted by the flowing nitrogen. Calcination began after 125 minutes at a temperature of approximately 650°C and was complete after 150 minutes, coinciding approximately with the time that the temperature reached the final 750°C set-point. The sample weight of 6.6 mg at the end of calcination corresponds to the theoretical weight associated with the complete decomposition of pure CaCO_3 to CaO (44% weight loss). After 160 minutes, the reactor pressure was increased to 5 atm of nitrogen. At the same time, the pressure and flow rates of N_2 and CO_2 in the side-arm were adjusted and directed to vent. No CO , H_2 , H_2S , or H_2O was present in the feed gas for this run.

As shown in Figure 8, system pressurization produced a temporary upset in the sample weight. Once the final pressure of 5 atm was reached, the sample weight stabilized. After 210 minutes, the two valves controlling gas flow in the side-arm were switched and reactive gas composed of 15% CO_2 , balance N_2 was directed over the sample. The carbonation reaction began immediately and the solid weight increased to approximately 10.3 mg within two minutes. Thereafter, the rate became quite slow and a maximum weight of 10.9 mg was reached when the run was terminated after 280 minutes. The 10.3 and 10.9 mg weights correspond

Figure 8. Typical Electrobalance Response: One Complete Calcination-Carbonation Cycle.

to fractional carbonations of 0.71 and 0.83, respectively. These typical results are, therefore, consistent with previous results reported in the literature.

The reactor system as described worked well in tests at all pressures when no H_2O was included in the carbonation gas. No experimental problems were encountered in exploratory runs at 1 atm when water was added to the carbonation gas. Severe experimental problems were encountered, however, when high pressure carbonation tests with steam in the carbonation gas were attempted.

A typical electrobalance response during the carbonation cycle of a test in which 10% steam was introduced at 5 atmospheres is shown in Figure 9. For approximately 30 minutes, carbonation proceeded in a normal manner. Rapid initial reaction was followed after approximately 5 minutes by the expected abrupt transition to the slow reaction phase. However, at about 35 minutes an abrupt solid weight loss of about 4 mg occurred. Five minutes later another 4 mg of solid was lost. Two additional weight losses occurred before the run was terminated after 60 minutes. Only about 0.5 mg of sorbent remained in the sample pan. The actual solid loss was confirmed after the reactor was cooled and opened for inspection.

Steam condensation on the inside of the reactor hang-down tube in the cool region where the hang-down tube joined the electrobalance housing was identified as the cause of the problem. Condensate drops fell periodically into the hot zone where almost instantaneous vaporization occurred. This produced a pressure wave of sufficient magnitude to dislodge sorbent from the sample pan. The problem was not encountered in atmospheric pressure tests because the volumetric flow

Figure 9. Weight Loss Caused by Reactor Upsets During the Injection of Steam at High Pressure.

rate of inert gas through the balance housing was sufficient to prevent steam from back-diffusing to the cool regions where condensation could occur. At elevated pressures the volumetric flow rate of inert gas was insufficient to prevent back diffusion of steam.

A stainless steel insert shown in Figure 10 was added to the upper section of the hang-down tube to provide a physical barrier to prevent steam from reaching the condensation surface. The insert is supported by a press fit to the flange joining the balance housing and the hangdown tube and is machined to provide a minimum gap between the insert and the hangdown tube. Near the bottom of the insert a teflon sleeve contacts the hangdown tube throughout its circumference to prevent diffusion of steam. A small hole in the side of the insert provides for pressure equalization so that the teflon sleeve does not serve as a pressure seal. The insert terminates just above the side-arm where reactive gases are added. At the position of the teflon sleeve, the temperature is high enough to prevent condensation but low enough to avoid degrading the teflon. The reduced flow area of the insert provides sufficient velocity of inert gas from the balance housing to prevent steam from back-diffusing up the insert and condensing there.

Figure 10. Diagram of the Insert Added to the Hangdown Tube to Prevent Steam Condensation.

CHAPTER 3

TASK II - REACTION SCREENING TESTS

A number of calcination-carbonation screening tests were carried out as part of Task 2 activities to determine the general characteristics of the reactions as a function of temperature, pressure, and gas composition as well as to compare the reactivity of the various sorbents (see Table I). As a result of these screening tests, three sorbents were selected for more detailed kinetic testing in Task 3, and the ranges of reaction parameters to be studied in Task 3 were defined.

Most screening tests were conducted using an existing atmospheric pressure electrobalance reactor system while the high pressure reactor was being constructed. The principle behind the two reactors is identical. Important practical differences between the two, in addition to the pressure limit, are as follows. Gas flow rates in the atmospheric pressure reactor were controlled manually using rotameters and needle valves instead of mass flow controllers. The reduced thermal mass of the atmospheric pressure reactor permitted much faster temperature response. For example, rates of temperature change of 50°C/min were easily achieved in the low pressure reactor while approximately 5°C/min was the maximum practical value in the high pressure unit. In the low pressure unit, the experimental data (sample weight and temperature as a function of time) were acquired and stored using an electronic recorder (Bascom-Turner) rather than the PS-2 computer system used in the high pressure unit. In addition, at approximately 750°C, the actual temperature in the low pressure reactor was 20 to 30°C lower than the set-point. This caused no problems in

comparing results among low pressure reactor runs, but caution must be exercised in comparing runs at "identical" conditions from the low and high pressure reactors.

3.1 CHARACTERISTICS OF THE CALCINATION-CARBONATION REACTIONS

The general characteristics of the calcination-carbonation reactions were studied using sorbent 1 (reagent calcium carbonate) in the atmospheric pressure reactor. The results were used to establish the ranges of reaction parameters to be studied in Task 3.

3.1.1 The Effect of Temperature

Figure 11 shows the effect of temperature on the calcination reaction. Calcination was carried out in N_2 at 1 atm using a heating rate of $50^\circ\text{C}/\text{min}$ to the indicated temperature, with isothermal operation thereafter. Calcination began at a very low rate at approximately 600°C , and the rate increased rapidly with temperature to 845°C . Calcination was complete within the 50 minute time frame shown in the figure at both 745 and 845°C . Longer time data (not shown) suggests that calcination would be complete at 660°C after approximately 200 minutes and after about 65 minutes at 710°C .

The effect of carbonation temperature is shown in Figure 12 following calcination at 750°C . Carbonation was carried out at 1 atm in 5.6% CO_2 , balance N_2 . Each test began with an initial rapid reaction period followed by an abrupt change to a slow reaction phase, in general agreement with previous results reported in the literature. Both the time and extent of carbonation at the end of the rapid phase are strong functions of temperature. The final values of W/W_0 , which ranged from

Figure 11. The Effect of Temperature on Calcination Kinetics:
Sorbent 1.

Figure 12. The Effect of Temperature on Carbonation Kinetics:
Sorbent 1.

approximately 0.63 at 430°C to 0.89 at 750°C, correspond to fractional carbonations of 0.16 to 0.75, respectively. The global rate during the rapid reaction phase was approximately equal in the temperature range 430 to 680°C; the decrease in the global reaction rate at 750°C occurred because the actual partial pressure of CO_2 was only slightly greater than the equilibrium partial pressure.

Although each test exhibited a similar sharp decrease in global rate, the carbonation reaction never stopped completely as shown in Figure 13. In this test, calcination at 895°C in N_2 at 1 atm was followed by carbonation at 710°C in 15% CO_2 , balance N_2 , with the carbonation cycle extended to 24 hours. The rapid reaction period, which lasted for approximately 5 minutes, appears to end instantaneously at $W/W_0 = 0.85$, corresponding to fractional carbonation of 0.66. Over the next 24 hours, W/W_0 gradually increased to 0.93, corresponding to a final fractional carbonation of 0.84.

3.1.2 The Effect of Gas Composition

The most interesting and unexpected result from the reaction screening tests concerned the effect of gas composition on carbonation kinetics. An expected strong dependence of the carbonation rate on CO_2 concentration is confirmed in Figure 14. The time scale in this figure is enlarged to emphasize the early reaction period. All calcination conditions and carbonation temperature were equal in each run. While higher CO_2 concentration produced a marked increase in rate during the rapid reaction period, there was relatively little difference in the carbonation level at the end of the test.

In all carbonation tests discussed to this point, the reactive atmosphere consisted of CO_2 and N_2 only. Other components were

Figure 13. Long-Term Carbonation Results: Sorbent 1.

Figure 14. The Effect of CO₂ Concentration on Carbonation Kinetics: Sorbent 1.

subsequently added, in a stepwise manner, to produce a simulated coal gas containing CO, CO₂, H₂, H₂O and N₂. Sorbent 1 (reagent calcium carbonate) was used in all tests. Figure 15 compares carbonation results from the CO₂/N₂ atmosphere to results obtained in an atmosphere containing CO₂/CO/H₂/N₂ (at the same CO₂ concentration). The latter atmosphere contains all of the major components present in coal-gas except steam. While the addition of CO and H₂ appears to result in a decrease in rate during the rapid reaction period, the decrease is slight and is probably the result of normal data scatter. In each case the rapid reaction period ends at essentially the same level of W/W₀.

The more complex gas composition lies in the equilibrium carbon deposition region (Lamoreaux et al., 1986), and, after the above test, carbon deposits were noted on the walls of the hang-down tube downstream of the sorbent. Carbon deposition on either the sorbent or the hang-down wire or pan would produce a weight gain, thereby confounding the carbonation kinetics. In order to check for carbon deposition, two blank runs were made in which inert Al₂O₃ was substituted for reactive CaO. Two gas compositions, that shown in Figure 15 and a similar gas with H₂O added, were tested. Addition of H₂O moved the gas composition nearer to the boundary of the carbon deposition region, thereby reducing the carbon deposition tendency. However, no weight gain was observed with either test showing that carbon deposition does not occur on the critical components to an extent sufficient to confound the carbonation results.

The addition of steam to complete the simulated coal-gas atmosphere produced a dramatic increase in the carbonation rate during the rapid reaction phase as shown in Figure 16. Once again there was no apparent

Figure 15. The Effect of Gas Composition on Carbonation Kinetics; The Addition of CO and H₂: Sorbent 1.

Figure 16. The Effect of Gas Composition on Carbonation Kinetics, The Addition of CO, H₂O, and H₂: Sorbent 1.

change in the final fractional carbonation. Two possible reasons for the rate increase were considered. All components required for the water-gas shift reaction were present; the occurrence of this reaction would increase the CO_2 concentration above that of the feed gas, and cause the rate in the rapid reaction phase to increase. It was also possible that H_2O simply served as a rate enhancer.

Results of additional tests to evaluate the importance of the shift reaction are shown in Figure 17. In one test, the "simple" gas composed of 5% CO_2 in N_2 was used. In the second, a simulated coal gas containing 5% CO_2 and the indicated amounts of CO , H_2 , H_2O and N_2 was fed. A marked increase in rate during the rapid reaction period with no change in the final value of W/W_0 was observed. The third test gas was composed of 8.9% CO_2 in N_2 , and the rate was similar to that observed in the simulated coal gas. Calculations showed that if the simulated coal gas feed was allowed to equilibrate, the CO_2 composition would be increased to approximately 9%. While the evidence is indirect, the similarity in the two curves suggests that the carbonation and water-gas shift reactions occur simultaneously when the necessary shift components are present.

Other evidence of the occurrence of the shift reaction is shown in Figure 18. In this test, the CO_2 feed concentration was held constant while the background gas composition was changed ten minutes into the run. Initially the feed gas consisted of 5% CO_2 /27% H_2 /68% N_2 , and no carbonation occurred. Reverse shift equilibrium under these feed conditions would leave approximately 1% CO_2 in the gas, which is below the equilibrium CO_2 pressure for the carbonation reaction. After 10 minutes, H_2O was substituted for H_2 to prevent the shift from occurring.

Figure 17. Testing for the Presence of the Shift Reaction:
Sorbent 1.

Figure 18. Carbonation Kinetics With Constant CO₂ Concentration and Varying Background Gas Composition: Sorbent 1.

Carbonation began immediately and proceeded to a W/W_0 value approximately equal to that observed in the simple CO_2/N_2 composition.

Results of one final test showing the importance of background gas composition are shown in Figure 19. The feed gas contained no CO_2 but did contain the shift reactants CO and H_2O . The observed weight increase proves that carbonation did occur, and the only reasonable source of CO_2 was the shift reaction. Carbonation was transitory as the W/W_0 value reached a maximum of approximately 0.68 after 10 minutes and declined thereafter. This behavior is consistent with CaO serving as a shift catalyst. Early in the test when most of the sorbent was in the oxide form, the shift reaction produced CO_2 which subsequently reacted to form $CaCO_3$. Once an appreciable quantity of $CaCO_3$ was formed, the catalytic effect diminished, less CO_2 was formed, and the $CaCO_3$ began to decompose.

The possibility of simultaneous shift reaction - CO_2 removal introduces the possibility of a one-step process for the production of hydrogen. While this option should be pursued, it is beyond the scope of the present study. The combined reactions create problems for the current study in that the CO_2 concentration in contact with the CaO sorbent is not equal to the feed gas composition whenever shift reaction components are present. For this reason, a decision was made to concentrate in the Task 3 kinetic studies on the "simple" reactive gas containing only CO_2 and N_2 .

3.2 COMPARISON OF TEST SORBENTS

Calcination results for the six calcium carbonate precursors (sorbents 1-6) are compared in Figures 20 and 21. Calcination

Figure 19. Carbonation With No CO₂ in the Feed Gas: Sorbent 1.

Figure 20. Comparison of Calcination Kinetics: Sorbents 1, 2, 4, and 5.

Figure 21. Comparison of Calcination Kinetics: Sorbents 1, 3, and 6.

conditions were equivalent in each test and results from sorbent 1 are included in both figures for reference. All calcination results were qualitatively similar. The calcination rate became appreciable after about 12 minutes with $T \sim 625^{\circ}\text{C}$. Complete calcination, as evidenced by constant W/W_0 occurred in the range of 43 to 75 minutes. We attribute the differences in time for complete calcination primarily to particle size effects. Differences in W/W_0 at complete calcination were due to differences in purity. The final weight of sorbent 1, pure CaCO_3 , was quite close to the theoretical value of 0.56. The final values of W/W_0 for the other samples, all of which were obtained from commercial quarries, ranged from 0.56 to 0.64.

Comparable carbonation curves for these sorbents are shown in Figures 22 and 23. Again, data for sorbent 1 is included for reference. In Figure 22 carbonation was carried out at 630°C while 750°C carbonation temperature was used in the Figure 23 tests. The carbonation gas in all tests consisted of 5.6% CO_2 in N_2 . Differences in the initial values of W/W_0 reflect the differences in the final W/W_0 values from the previous calcination cycle. Each of the carbonation curves are similar. In particular, the final values of W/W_0 ranged from 0.82 to 0.85 at 630°C (Figure 22), while the final W/W_0 values from the three 750°C tests (Figure 23) were all approximately 0.89. Instead of chalks and marls providing significantly increased reactivity as reported by Hartman et al. (1978) in their sulfation studies, the carbonation behavior of all samples was similar to that of the reagent grade CaCO_3 .

An alternate approach to increasing sorbent reactivity was then pursued. Sorbents 7 and 8, consisting of reagent grades of calcium

Figure 22. Comparison of Carbonation Kinetics: Sorbents 1, 2, 4, and 5.

Figure 23. Comparison of Carbonation Kinetics: Sorbents 1, 3, and 6.

acetate and calcium sulfate, respectively, were evaluated. The rationale in these selections was that decomposition of either precursor would involve driving off a significantly increased quantity of volatile material leaving CaO with increased pore volume and, presumably, greater carbonation reactivity.

Figure 24 shows decomposition-carbonation results for one complete cycle using sample 7 (calcium acetate). The precursor, $\text{Ca}(\text{C}_2\text{H}_3\text{O}_2)_2 \cdot x\text{H}_2\text{O}$ containing 8.3% H_2O , was heated in N_2 as shown. Water of hydration was driven off in two increments in the temperature range 100-300°C, leaving $\text{Ca}(\text{C}_2\text{H}_3\text{O}_2)_2$ with $W/W_0 \sim 0.92$. Acetate decomposition began at about 450°C and a constant weight plateau was reached at 600°C with $W/W_0 \sim 0.58$, corresponding to CaCO_3 formed from the original acetate. Additional weight loss to $W/W_0 = 0.314$ occurred in the vicinity of 750°C. No further weight loss occurred during 60 minutes in N_2 at 750°C, and the final weight corresponded closely to the theoretical value of $W/W_0 = 0.325$ for the production of CaO from calcium acetate containing 8.3% H_2O . When carbonation was initiated after 210 minutes, the weight gain was rapid and the final value of $W/W_0 = 0.57$ corresponded closely to the value expected for total conversion of CaO to CaCO_3 ($W/W_0 = 0.58$).

Hydrated calcium sulfate, $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ (sorbent 8) proved to be an unsatisfactory sorbent precursor. The atmosphere during CaSO_4 decomposition was 50% N_2 -50% H_2 , with the hydrogen added to promote the removal of sulfur as H_2S . Past work in this laboratory (Focht et al., 1989) showed that when ZnSO_4 was exposed to a reducing atmosphere at high temperature, ZnO was produced as the solid product. CaSO_4 , however, decomposed to CaS which had no carbonation activity. The

Figure 24. Decomposition-Carbonation Kinetics: Sorbent 7.

attempt to increase the carbonation reactivity by decomposing calcium compounds to produce CaO having greater porosity was half successful. Calcium acetate (sorbent 7) was selected as the second base sorbent to be tested in Task 3.

Sorbent 9 was a commercial dolomite containing approximately equal molar quantities of CaCO_3 and MgCO_3 obtained from National Lime Co. Dolomite was chosen to test the effect of magnesium on the reactions. Calcination of both CaCO_3 and MgCO_3 should create porosity in the product mixed oxides. Subsequent carbonation of CaO would reduce porosity as before, but, at carbonation conditions of interest, MgO does not carbonate. MgO, acting as a diluent, should to modify the pore closure experienced by pure CaO. Results for one complete calcination-carbonation cycle using the high pressure reactor are shown in Figure 25. Calcination began at approximately 450°C and was complete at about the time the sample reached the desired final temperature of 750°C . Calcination of MgCO_3 should occur at lower temperature, followed by calcination of CaCO_3 . Experimentally, although calcination began at a lower temperature compared to pure CaCO_3 , there was no clearcut distinction in the weight loss curve between MgCO_3 and CaCO_3 . The final value of W/W_0 corresponded closely to the loss on ignition value reported by National Lime, and represented complete conversion of CaCO_3 and MgCO_3 to CaO and MgO.

Carbonation was carried out at 750°C , 1 atm, in 15% CO_2 (balance N_2), conditions where CaO can be carbonated but not MgO. Carbonation behavior was qualitatively similar to that exhibited by other sorbents. A rapid initial reaction period lasting less than 5 minutes was followed by an abrupt transition to a slow reaction phase. The transition,

Figure 25. Calcination-Carbonation Kinetics: Sorbent 9.

however, occurred at $W/W_0 \sim 0.73$, which corresponds to a fractional calcium carbonation of 0.85, significantly higher than observed using pure CaCO_3 . One hour after the beginning of carbonation the value of W/W_0 was 0.75, which corresponds to 0.93 fractional calcium carbonation. Because of the favorable results, dolomite (sample 9) was chosen as the third base sorbent for Task 3 testing.

Figure 26 provides a direct comparison of first-cycle carbonation behavior of the three base sorbents at equivalent carbonation conditions. Fractional carbonation, X , is reported on the y-axis instead of W/W_0 to facilitate direct comparison between different samples. While each sorbent exhibits qualitatively similar behavior, it is clear that greater than 90% carbonation can be achieved using sorbents 7 and 9, compared to only about 80% carbonation for sorbent 1.

Figure 26. Comparison of First Cycle Carbonation Kinetics: Sorbents 1, 7, and 9.

CHAPTER 4

TASK III - TWO-CYCLE TEST SERIES

The objective of Task 3 was to test the calcination-carbonation kinetics of the three base sorbents as a function of temperature, pressure, and gas composition. Each test consisted of two complete calcination-carbonation cycles so that preliminary information on sorbent durability was also obtained. Reaction conditions were chosen on the basis of results from the Task 2 screening program. The reaction parameters tested and their values were:

- a. Calcination Temperature (3): 750, 825, 900°C
- b. Carbonation Temperature (3): 550, 650, 750°C
- c. Carbonation Pressure (3): 1, 5, 15 atm
- d. CO₂ Mol Fraction (3): 0.01, 0.05, 0.15

Calcination pressure was one atmosphere and the calcination gas was pure nitrogen. The carbonation gas consisted of the indicated CO₂ mol fraction in nitrogen. This complete matrix consists of 243 tests (3 sorbents x 3 calcination temperatures x 3 carbonation temperatures x 3 carbonation pressures x 3 CO₂ mol fractions). Only ninety eight of these tests were actually carried out; positions were eliminated from the test matrix on the basis of reaction equilibrium considerations and on the basis of results from earlier tests. This test matrix represented a substantial enlargement of the 108 test matrix originally contained in the statement of work. This enlargement, in turn, impacted the Task 4 test matrix and effectively reduced the number of tests required in that task.

The three sorbents chosen on the basis of the Task 2 screening tests were:

Sorbent 1 - Reagent Grade Calcium Carbonate

Sorbent 7 - Reagent Grade Calcium Acetate Hydrate

Sorbent 9 - Commercial Dolomite.

More detailed information on the source and chemical composition of these base sorbents was presented in Chapter 3.

The complete Task 3 test matrix is shown in Tables V, VI, and VII for sorbents 1, 7, and 9, respectively. The 98 runs which were completed are designated in these tables by the run number. Duplicate tests were made periodically as indicated to check reaction reproducibility.

4.1 REACTIVITY AND CAPACITY INDICES

The electrobalance response through two complete cycles is illustrated in Figure 27. Two tests using sorbent 9, HP057 and HP105, were carried out at the conditions illustrated, and results from both tests are plotted to show the level of reproducibility which was achieved. The ordinate in Figure 27 is W/W_0 , the normalized sample weight, while the abscissa is time. Calcination of the dolomite precursor consisting of 54.5% CaCO_3 and 45.0% MgCO_3 (mass %) produced the final value of $W/W_0 = 0.528$ which corresponds to complete calcination of CaCO_3 and MgCO_3 to CaO and MgO . Complete calcination was achieved in both cycles of both tests. Indeed, effectively complete calcination was achieved in all tests with all three of the base sorbents. 15 mol% CO_2 (in N_2) was introduced after 210 minutes to initiate the carbonation reaction. Carbonation was quite rapid initially but after about 5 minutes the rate decreased abruptly and was quite slow thereafter. After carbonation for 40 minutes, fractional

Table V

Task 3 Test Matrix for Calcium Carbonate (Sorbent 1)

CALCINATION TEMP C	CARBONATION TEMP C	CARBONATION ATM% CO ₂	CARBONATION PRESSURE 1 ATM	CARBONATION PRESSURE 5 ATM	CARBONATION PRESSURE 15 ATM
900	750	15	HP048	HP082	HP040
900	750	5			
900	750	1			
900	650	15	HP084	HP096	
900	650	5			
900	650	1			
900	550	15	HP083	HP099	
900	550	5	HP085		
900	550	1	HP086		
825	750	15	HP047	HP113	HP039
825	750	5			
825	750	1			
825	650	15	HP045	HP117	HP134
825	650	5	HP051		
825	650	1			
825	550	15	HP125	HP120	
825	550	5	HP129		
825	550	1	HP126		
750	750	15	HP066 HP095	HP063	HP032
750	750	5			HP034
750	750	1			HP033
750	650	15	HP046	HP097	HP141
750	650	5	HP043		
750	650	1			HP133, HP137
750	550	15	HP049	HP098	HP139
750	550	5	HP130		
750	550	1	(HP059)		HP138

Table VI

Task 3 Text Matrix For Calcium Acetate (Sorbent 7)

CALCINATION TEMP C	CARBONATION TEMP C	CARBONATION ATM% CO ₂	CARBONATION PRESSURE 1 ATM	CARBONATION PRESSURE 5 ATM	CARBONATION PRESSURE 15 ATM
900	750	15	HP055		HP076
900	750	5		HP109	
900	750	1			
900	650	15			HP091
900	650	5			
900	650	1			
900	550	15			HP100
900	550	5			
900	550	1			
825	750	15	HP053		HP106
825	750	5		HP108	
825	750	1			
825	650	15	HP054		HP121
825	650	5	HP052	HP118	
825	650	1			
825	550	15	HP123		HP127
825	550	5		HP131	
825	550	1			
750	750	15	HP067;068	HP064	HP036
750	750	5		HP124	HP037
750	750	1			HP038
750	650	15	HP056	HP110	HP101
750	650	5			
750	650	1		HP147	
750	550	15	HP061	HP144	HP128
750	550	5	HP093		
750	550	1	HP060	HP145	

Table VII

Task 3 Test Matrix for Dolomite (Sorbent 9)

CALCINATION TEMP C	CARBONATION TEMP C	CARBONATION ATM% CO ₂	CARBONATION PRESSURE 1 ATM	CARBONATION PRESSURE 5 ATM	CARBONATION PRESSURE 15 ATM
900	750	15	HP062		HP077
900	750	5			HP088
900	750	1			HP087
900	650	15			
900	650	5			
900	650	1			HP090
900	550	15			
900	550	5			
900	550	1			HP089
825	750	15	HP078	HP112	HP103
825	750	5			
825	750	1			HP135
825	650	15			HP115
825	650	5			HP132
825	650	1			HP116
825	550	15			
825	550	5			
825	550	1			HP122
750	750	15	HP057 HP105	HP069	HP075
750	750	5			HP092
750	750	1			HP080
750	650	15	HP071	HP111	HP136
750	650	5	HP072		
750	650	1			HP102
750	550	15	HP073	HP143	HP140
750	550	5	HP074		HP142
750	550	1	HP094		HP114

Figure 27. Reaction Reproducibility: Weight Time Results for Two Calcination-Carbonation Cycles.

carbonation for the two cycles of the two tests varied from 0.90 to 0.93. This degree of reproducibility is typical of all cases in which repeat tests were carried out.

Because of the large amount of experimental data acquired in each run, it was necessary to develop a means of reducing the data to a more manageable form to permit direct comparison of results and to evaluate the effect of the reaction parameters. Indices based upon fractional carbonation at equivalent reaction times in both the early rapid reaction phase and the final slow reaction phase were developed to provide this basis for comparison. Selection of the appropriate reaction time for the slow phase comparison presented no major problem since the slope of the weight-time curve for each run approached zero during the latter stages. Selection of the proper time for comparing results in the rapid reaction phase was complicated by two factors. The first was associated with a time lag between opening the reactive gas valve in the reactor side-arm and the sample being exposed to the full reactive gas concentration. The second complicating factor was the large slope of the weight-time curve early in the reaction. A relatively small time error would result in a large change in fractional carbonation, and a correspondingly large error in the index.

This problem was solved by evaluating the lag time, t_0 , associated with each run as described below. Figure 28 shows the general response of the weight-time curve during a carbonation cycle. This example at high pressure and low CO_2 mol fraction was chosen to accentuate the time lag. $t = 0$ corresponds to opening the side-arm reactive gas valve. There was no reaction for approximately 5 minutes thereafter. In the next couple of minutes the reaction rate gradually increased and after

Figure 28. Evaluation of the Lag Time, t_0 , During Carbonation.

about 7 minutes there was a period in which the weight-time curve was essentially linear. During the first 5 minutes the sorbent was exposed to essentially no CO_2 ; between 5 and 7 minutes the CO_2 concentration increased from zero to its steady-state value, in this case 1% (volume). The duration of the unsteady state period was found to be a strong function of pressure and a weak function of temperature and CO_2 mol fraction. The lag time t_0 shown in Figure 2 was obtained by extrapolating the linear portion of the weight-time curve to the initial weight. Constant values of $t - t_0$, therefore, were taken to represent equivalent reaction time. Table VIII summarizes the t_0 values for the first and second cycles at each of the Task 3 reaction conditions. No dependence of t_0 on either calcination temperature or solid reactant has been found except for carbonation at 750°C , 1 atm, and 15% CO_2 . Multiple table entries are included for these conditions. In other cases there are two t_0 values for each set of reaction conditions. These represent cycles 1 and 2, respectively. There is either no change or a slight increase in t_0 in the second cycle. The overall values range from 6.6 minutes at high temperature, high pressure, and low CO_2 mol fraction to 0.2 minutes at low temperature, low pressure, and high CO_2 mol fraction. Each entry represents the average value from all runs at the particular set of conditions.

Values of fractional carbonation at fixed values of $t - t_0$ were used to compare the kinetics of different runs. As a result of trial-and-error comparison, $t - t_0 = 1$ min was chosen as the most suitable time for comparing kinetics during initial reaction phase, while $t - t_0 = 40$ min was chosen to compare the slow reaction phase. In the Figure 28 example, the rapid reaction phase lasts for several minutes

Table VIII: Summary of the Lag Time, t_o at Various Reaction Conditions.

Carbonation Temp., C	%CO ₂	t_o (min.)		
		PRESSURE		
		1 atm	5 atm	15 atm
750	15	0.6/* (S-1) 1.4/* (S-7) 0.3/* (S-9)	0.9/1.0	0.9/1.0
750	5	**	2.2/2.2	2.2/2.2
750	1	**	**	6.8/6.9
650	15	0.2/0.3	0.7/0.8	1.2/1.3
650	5	0.3/0.4	0.9/1.0	1.5/1.5
650	1	**	2.0/2.5	2.7/3.0
550	15	0.2/0.3	0.7/0.7	1.1/1.1
550	5	0.3/0.3	0.7/0.7	1.5/1.3
550	1	0.2/0.3	1.3/1.3	2.0/2.1

*Calcination Temp., °C	t_o (min)		
	S-1	S-7	S-9
900	1.4	1.7	1.3
825	1.3	1.1	0.5
750	0.7	0.9	1.0
750	0.8	0.9	0.5

** no tests were made at these conditions due to reaction equilibrium considerations.

and values of $t - t_0 > 1$ min could be used. However, at a high CO_2 concentration (15%) and low pressure, the rapid reaction phase terminates much sooner and values of $t - t_0 > 1$ min would be inappropriate. The choice of $t - t_0 = 40$ min to compare the slow reaction phase is arbitrary. It is obvious from Figure 28 that the rate of increase in fractional carbonation is quite slow in the vicinity of 40 min, and approximately the same fractional carbonation values would be obtained over a range of times.

In the following discussion, the terms reactivity, reactivity maintenance, capacity, and capacity maintenance are used. These are defined as follows:

Reactivity: R_i - fractional carbonation after $t - t_0 = 1$ min in cycle i .

Capacity: C_i - fractional carbonation after $t - t_0 = 40$ min in cycle i .

Reactivity maintenance: R_{1j} - ratio of reactivity in cycle j to reactivity in cycle 1.

Capacity Maintenance: C_{1j} - ratio of capacity in cycle j to capacity in cycle 1.

Experimental reactivity results for the Task 3 test series are summarized in Tables IX, X, and XI for sorbents 1, 7, and 9, respectively. The arrangement in these tables corresponds to the Task 3 test matrix in Tables V, VI, and VII. The two entries in each position correspond to cycles 1 and 2, respectively. For example, in the first matrix position of Table IX, we see that $R_1 = 0.21$ while $R_2 = 0.11$. The reactivity maintenance in this case was $R_{12} = 0.11/21 = 0.52$, indicating a rather severe decrease at these reaction conditions. Duplicate tests

Table IX

First and Second Cycle Reactivity Results for Sorbent 1

CALCINATION TEMP C	CARBON- ATION TEMP C	CARBON- ATION ATM% CO ₂	CARBONATION PRESSURE 1 ATM	CARBONATION PRESSURE 5 ATM	CARBONATION PRESSURE 15 ATM
900	750	15	.21/.11	.56/.47	.37/.32
900	750	5			
900	750	1			
900	650	15	.65/.41	.59/.40	
900	650	5			
900	650	1			
900	550	15	.56/.14	.55/.16	
900	550	5	.43/.19		
900	550	1	.16/.06		
825	750	15	.22/.14	.56/.56	.39/.37
825	750	5			
825	750	1			
825	650	15	.68/.50	.52/.43	.38/.37
825	650	5	.30/.17		
825	650	1			
825	550	15	.60/.41	.51/.36	
825	550	5	.45/.24		
825	550	1	.11/.08		
750	750	15	.23/.22;.20/.18	.51/.52	.37/.39
750	750	5			.21/.21
750	750	1			.10/.09
750	650	15	.67/.55	.63/.53	.42/.43
750	650	5	.25/.27		
750	650	1			.15/.10;.10/.11
750	550	15	.63/.49	.57/.43	.41/.33
750	550	5	.47/.40		
750	550	1	.05/.04		.08/.08

Table X

First and Second Cycle Reactivity Results for Sorbent 7

CALCINATION TEMP C	CARBON- ATION TEMP C	CARBON- ATION ATM% CO ₂	CARBONATION PRESSURE 1 ATM	CARBONATION PRESSURE 5 ATM	CARBONATION PRESSURE 15 ATM
900	750	15	.13/.08		.59/.48
900	750	5		.30/.29	
900	750	1			
900	650	15			.61/.41
900	650	5			
900	650	1			
900	550	15			.47/.18
900	550	5			
900	550	1			
825	750	15	.13/.27		.51/.57
825	750	5		.24/.25	
825	750	1			
825	650	15	.76/.40		.47/.51
825	650	5	.42/.20	.43/.33	
825	650	1			
825	550	15	.54/.43		.44/.35
825	550	5		.48/.24	
825	550	1			
750	750	15	.13/.29; .08/.28	.72/.72	.55/.60
750	750	5		.25/.27	.32/.27
750	750	1			.07/.10
750	650	15	.75/.68	.79/.73	.55/.58
750	650	5			
750	650	1		.10/.11	
750	550	15	.62/.57	.58/.53	.48/.42
750	550	5	.54/.47		
750	550	1	.08/.07	.11/.11	

Table XI

First and Second Cycle Reactivity Results for Sorbent 9

CALCIN- ATION TEMP C	CARBON- ATION TEMP C	CARBON- ATION ATM% CO ₂	CARBONATION PRESSURE 1 ATM	CARBONATION PRESSURE 5 ATM	CARBONATION PRESSURE 15 ATM
900	750	15	.15/.13		.53/.44
900	750	5			.28/.23
900	750	1			.05/.00
900	650	15			
900	650	5			
900	650	1			.12/.15
900	550	15			
900	550	5			
900	550	1			.11/.12
825	750	15	.20/.14	.73/.61	.38/.36
825	750	5			
825	750	1			.08/.07
825	650	15			.50/.42
825	650	5			.28/.26
825	650	1			.07/.11
825	550	15			
825	550	5			
825	550	1			.09/.11
750	750	15	.23/.19; .17/.15	.69/.71	.51/.48
750	750	5			.32/.25
750	750	1			.16/.05
750	650	15	.80/.68	.72/.66	.49/.54
750	650	5	.34/.33		
750	650	1			.11/.08
750	550	15	.73/.49	.70/.44	.41/.33
750	550	5	.49/.40		.27/.19
750	550	1	.11/.10		.13/.11

using sorbent 1 were carried out using 750°C calcination and carbonation temperatures with 1 atm carbonation pressure and 15% CO₂ in the carbonation gas. From Table IX, we find that $R_1 = 0.23$ and 0.20 and $R_2 = 0.22$ and 0.18 in the two tests. These reactivities produce values of $R_{12} = 0.96$ and 0.90 , respectively. Because of the rapid initial reaction rate and the uncertainty in fixing t_o , the above numbers are felt to represent the best levels of reproducibility that can be expected. Increased second-cycle reactivity was observed in a number of instances. For example, from Table X using sorbent 7 at 750°C calcination and carbonation temperatures, 15 atm carbonation pressure, and 0.15 mol fraction CO₂ in the carbonation gas, the sorbent reactivity increased from $R_1 = 0.55$ to $R_2 = 0.60$, yielding $R_{12} = 1.09$.

Tables XII, XIII, and XIV summarize the comparable results for sorbent capacity. Again the two entries in each matrix position represent results from cycles 1 and 2. The first entry for sorbent 1 (Table XII) shows $C_1 = 0.77$ and $C_2 = 0.57$ to give $C_{12} = 0.74$. Quite good capacity reproducibility in both cycles is indicated by the duplicate test results at 750°C calcination temperature, and carbonation conditions of 750°C, 1 atm, and 15% CO₂. There is less inherent error in the capacity values because of the lower slope of the weight-time curves in the vicinity of $t - t_o = 40$ min. The capacity results in the tables show, for most test conditions, small to quite significant capacity loss in the second cycle ($C_{12} < 1.0$). In a few cases, however, a slight increase in capacity was observed. For example, for sorbent 9 (Table XIV) at a calcination temperature of 750°C, and carbonation conditions of 650°C, 5 atm, and 15% CO₂, $C_1 = 0.93$ and $C_2 = 0.94$ yielding $C_{12} = 1.01$. Of course, since the maximum value of $C_i = 1.0$,

Table XII

First and Second Cycle Capacity Results for Sorbent 1

CALCINATION TEMP C	CARBONATION TEMP C	CARBONATION ATM% CO ₂	CARBONATION PRESSURE 1 ATM	CARBONATION PRESSURE 5 ATM	CARBONATION PRESSURE 15 ATM
900	750	15	.77/.57	.76/.58	.77/.62
900	750	5			
900	750	1			
900	650	15	.70/.46	.71/.49	
900	650	5			
900	650	1			
900	550	15	.60/.35	.60/.37	
900	550	5	.63/.41		
900	550	1	.62/.45		
825	750	15	.78/.60	.76/.66	.78/.64
825	750	5			
825	750	1			
825	650	15	.74/.56	.67/.49	.64/.48
825	650	5	.74/.54		
825	650	1			
825	550	15	.63/.44	.58/.39	
825	550	5	.62/.41		
825	550	1	.65/.48		
750	750	15	.79/.68; .78/.67	.81/.70	.77/.66
750	750	5			.77/.67
750	750	1			.77/.65
750	650	15	.73/.59	.71/.57	.67/.54
750	650	5	.76/.60		
750	650	1			.75/.60; .71/.58
750	550	15	.67/.52	.62/.48	.60/.43
750	550	5	.63/.47		
750	550	1	.72/.52		.62/.48

Table XIII

First and Second Cycle Capacity Results for Sorbent 7

CALCINATION TEMP C	CARBON- ATION TEMP C	CARBON- ATION ATM% CO ₂	CARBONATION PRESSURE 1 ATM	CARBONATION PRESSURE 5 ATM	CARBONATION PRESSURE 15 ATM
900	750	15	.94/.81		.96/.94
900	750	5		.86/.89	
900	750	1			
900	650	15			.94/.76
900	650	5			
900	650	1			
900	550	15			.93/.46
900	550	5			
900	550	1			
825	750	15	.94/.87		.98/.95
825	750	5		.91/.97	
825	750	1			
825	650	15	.92/.72		.93/.88
825	650	5	.89/.86	.95/.94	
825	650	1			
825	550	15	.91/.54		.94/.51
825	550	5		.93/.59	
825	550	1			
750	750	15	.95/.94; .95/.93	1.0/.95	.98/.94
750	750	5		.97/.92	.97/.94
750	750	1			.93/.90
750	650	15	.92/.91	.92/.93	.95/.95
750	650	5			
750	650	1		.92/.90	
750	550	15	.92/.75	.94/.73	.94/.73
750	550	5	.94/.76		
750	550	1	.88/.67	.90/.69	

Table XIV

First and Second Cycle Capacity Results for Sorbent 9

CALCINATION TEMP C	CARBON- ATION TEMP C	CARBON- ATION ATM% CO ₂	CARBONATION PRESSURE 1 ATM	CARBONATION PRESSURE 5 ATM	CARBONATION PRESSURE 15 ATM
900	750	15	.92/.84		.92/.89
900	750	5			.93/.89
900	750	1			.90/.84
900	650	15			
900	650	5			
900	650	1			.87/.84
900	550	15			
900	550	5			
900	550	1			.84/.68
825	750	15	.94/.90	.92/.94	.94/.93
825	750	5			
825	750	1			.97/.92
825	650	15			.94/.91
825	650	5			.93/.87
825	650	1			.95/.91
825	550	15			
825	550	5			
825	550	1			.90/.73
750	750	15	.93/.91; .92/.90	.98/.97	.96/.96
750	750	5			.96/.95
750	750	1			.93/.90
750	650	15	.95/.96	.93/.94	.96/.93
750	650	5	.94/.94		
750	650	1			.95/.93
750	550	15	.91/.78	.93/.79	.90/.78
750	550	5	.90/.75		.92/.61
750	550	1	.86/.69		.90/.74

there is relatively little opportunity for an increase in the capacity maintenance index when complete carbonation is closely approached.

These index values permit the effect of individual reaction parameters to be evaluated and allow direct comparison of the performance of the three sorbents under equivalent reaction conditions. These evaluations are discussed in the following sections.

4.2 REACTION PARAMETER EVALUATION

4.2.1 The Effect of Calcination Temperature

Reactivity and capacity results suggest that the lowest calcination temperature, 750°C, should be used. Higher calcination temperature, in particular 900°C, has an adverse effect on both reactivity and capacity. This is illustrated for a set of runs at the following carbonation conditions:

Carbonation Temperature	750°C
Carbonation Pressure	1 atm
% CO ₂ in Carbonation Gas	15

Figures 29 and 30 plot first- and second-cycle reactivities for the three sorbents as a function of calcination temperature while Figures 31 and 32 plot first- and second-cycle capacities, also versus calcination temperature. Of the twelve curves represented in these figures, eleven exhibit a negative slope. Only the first-cycle reactivity of sorbent 7 (Figure 29) shows improved performance following high calcination temperature. The magnitudes of the negative slopes are greater in the second cycle (Figures 30 and 32) suggesting that the adverse effect of high calcination temperature increases with increased number of cycles. These second cycle results are emphasized in Figures 33 and 34 where

Figure 29. The Effect of Calcination Temperature on First-Cycle Reactivity, R_1 .

Figure 30. The Effect Calcination Temperature on Second-Cycle Reactivity, R_2 .

Figure 31. The Effect of Calcination Temperature on First-Cycle Capacity, C_1 .

Figure 32. The Effect of Calcination Temperature on Second-Cycle Capacity, C₂.

Figure 33. The Effect of Calcination Temperature on Two-Cycle Reactivity Maintenance, R_{12} .

Figure 34. The Effect of Calcination Temperature on Two-Cycle Capacity Maintenance, C_{12} .

two-cycle reactivity maintenance and capacity maintenance are plotted against calcination temperature.

There are 19 sets of data at which a complete comparison of the effect of the three calcination temperatures is possible. The advantages associated with low temperature calcination are most apparent with respect to first-cycle capacity, C_1 , and capacity maintenance, C_{12} . In 15 of the 19 data sets, the lowest calcination temperature resulted in the highest value for these indices. Conversely, in 15 of the 19 cases the highest calcination temperature resulted in the lowest indices values.

As this adverse effect of high calcination temperature became apparent, experimental effort was concentrated in the lower calcination temperature portions of the test matrix. Tables V, VI, and VII show that only 20 of the 81 tests involving 900°C calcination were completed, compared to 29 of the 81 tests with 825°C calcination, and 49 of the 81 tests involving 750°C calcination.

4.2.2 The Effect of Carbonation Temperature

Variation in the equilibrium CO_2 partial pressure with temperature must be considered when evaluating the effect of carbonation temperature on reaction characteristics. A number of the Task 3 tests were eliminated on the basis of equilibrium considerations. Even at conditions where tests were carried out, one must be aware of equilibrium when interpreting the results. At 750°C the equilibrium CO_2 pressure is about 0.08 atm. At 1 atm total pressure no reaction will occur when either 1% or 5% CO_2 is included in the carbonation gas; the effective CO_2 pressure in 15% CO_2 is reduced by about one-half. At 550°C, however, the equilibrium CO_2 pressure is sufficiently small that

even data at 1 atm total pressure and 1% CO₂ is free from equilibrium restrictions.

Figures 35 illustrates the effect of carbonation temperature on R₁ at the following conditions:

Calcination Temperature	750°C
Carbonation Pressure	1 atm
% CO ₂ in Carbonation Gas	15

The large decrease in reactivity at 750°C is due to the equilibrium CO₂ pressure, which reduces the CO₂ driving force by approximately one-half. At 550 and 650°C the equilibrium CO₂ pressure is small compared to the actual CO₂ pressure, and Figure 35 shows a small increase in reactivity with temperature. A more realistic view of the effect of temperature on reactivity is shown in Figure 36 for reaction at the following conditions:

Calcination Temperature	750°C
Carbonation Pressure	15 atm
% CO ₂ in Carbonation Gas	15

The equilibrium pressure is small compared to the actual CO₂ pressure even at 750°C. Figure 36 shows a small increase in reactivity through the entire temperature range for sorbents 7 and 9, but a small decrease in reactivity for sorbent 1 between 650 and 750°C. The overall lack of a strong temperature dependence suggests that the reactivity is influenced more by transport resistances than by the surface chemical reaction.

The most surprising effect of carbonation temperature was an apparent sharp decrease in capacity maintenance, C₁₂, at the lowest carbonation temperature of 550°C. The negative effect was more apparent

Figure 35. The Effect of Carbonation Temperature on First-Cycle Reactivity, R_1 , at Low Carbonation Pressure.

Figure 36. The Effect of Carbonation Temperature on First-Cycle Reactivity, R_1 , at High Carbonation Pressure.

for sorbents 7 and 9 and is illustrated in Figure 37 for the following reaction conditions:

Calcination Temperature	750°C
Carbonation Pressure	15 atm
% CO ₂ in Carbonation Gas	15

At 650 and 750°C, $C_{12} > 0.95$ for sorbents 7 and 9, but at 550°C, C_{12} for sorbent 7 is only 0.78. Sorbent 1 exhibits a smaller drop at 550°C, but C_{12} for sorbent 1 was lower at all temperatures. The capacity data in Tables XII through XIV shows that the lower capacity maintenance at 550°C in Figure 37 is not unique. There is a general trend to low C_{12} values at the lowest carbonation temperature. This result is unusual in that sorbent durability would normally be expected to improve at lower temperature. Structural property results to be presented subsequently are consistent with the kinetic results, but offer no explanation of the unexpected behavior.

The experimental data shows little difference in sorbent behavior at 650 and 750°C carbonation temperatures. In addition to the similar reactivity values in Figure 36, and the similar capacity maintenance values in Figure 37, there is little difference in the actual capacity. For example, five tests using sorbent 9 and 750°C calcination temperature were carried out at carbonation temperatures of both 650 and 750°C. The average value of C_1 was 0.95 at both temperatures. For sorbent 1, where C_1 is considerably less than 1.0, there appears to be a small capacity increase between 650 and 750°C.

4.2.3 The Effect of Carbonation Pressure

Like carbonation temperature, the effect of pressure on the carbonation equilibrium must be considered. The effect of carbonation

Figure 37. The Effect of Carbonation Temperature on Capacity Maintenance.

pressure on R_1 is shown in Figure 38 at the following reaction conditions:

Calcination Temperature	750°C
Carbonation Temperature	550°C
% CO_2 in Carbonation Gas	15

At these conditions equilibrium effects are negligible even at 1 atm.

The fact that R_1 decreases with increasing pressure for all three sorbents is consistent with the previous conclusion that transport resistances are important in establishing reactivity. If the surface rate was controlling, one would expect an increase in R_1 with pressure since CO_2 concentration is directly proportional to pressure. In contrast, both the mass transfer coefficient and effective diffusivity decrease with increasing pressure so that transport resistances would produce the observed effect.

Reaction pressure has little effect on sorbent capacity in either cycle, or on capacity maintenance. The capacity maintenance behavior is illustrated in Figure 39 for the following reaction conditions:

Calcination Temperature	750°C
Carbonation Temperature	650°C
% CO_2 in Carbonation Gas	15

The 650°C carbonation temperature was chosen to avoid the adverse effect of 550°C carbonation temperature on capacity maintenance. The curves are approximately horizontal for each of the three sorbents with values of C_{12} in the range of 0.97 to 1.01 for sorbents 7 and 9 compared to $C_{12} \sim 0.81$ for sorbent 1.

Figure 38. The Effect of Carbonation Pressure on First-Cycle Reactivity, R_1 .

Figure 39. The Effect of Carbonation Pressure on Capacity Maintenance, C_{12} .

4.2.4 The Effect of CO₂ Mol Fraction

At constant temperature and pressure the reactivity of each sorbent increases with increasing CO₂ mol fraction as shown in Figure 40 for the following reaction conditions:

Calcination Temperature	750°C
Carbonation Temperature	750°C
Carbonation Pressure	15 atm

The high carbonation pressure was chosen to overcome equilibrium limits and achieve reaction at all three CO₂ mol fractions. This reactivity increase is expected and is directly due to the increased CO₂ concentration. The absence of a linear dependence throughout the entire mol fraction range is also reasonable. At the lowest CO₂ mol fraction, the values of R_1 are in the range of 0.07 to 0.15. It is obviously impossible to increase R_1 by a factor of 15 at the highest CO₂ mol fraction. In other words, reactivity is not a differential but an integral function. Sorbent capacity, however, is essentially independent of CO₂ mol fraction as illustrated in Figure 41. The reaction conditions in this figure are the same as in Figure 40. The data for all three sorbents are almost horizontal, with the slightly lower values of C_1 for sorbents 7 and 9 at 0.01 mol fraction CO₂ due to the slow progress of the reaction at the low concentration. Forty minutes are not sufficient to produce a true capacity value at these conditions. Once again, the superior capacity of sorbents 7 and 9 compared to sorbent 1 is evident in Figure 41.

4.3 DIRECT COMPARISON OF BASE SORBENTS

Sorbents 7 and 9 possess a clear advantage over sorbent 1 in terms of both capacity and capacity maintenance. These advantages have been

Figure 40. The Effect of CO₂ Mol Fraction on First-Cycle Reactivity, R_1 .

Figure 41. The Effect of CO₂ Mol Fraction on First-Cycle Capacity, C_1 .

shown graphically in Figures 31, 32, 34, 37, 39, and 41 for specific reaction conditions. For both sorbents 7 and 9, the C_1 values at favorable reaction conditions (excluding 900°C calcination temperature) range from 0.86 to 1.0, while the C_1 values for sorbent 1 range from 0.52 to 0.81 at the same conditions. There are 18 sets of reaction conditions at which all three sorbents were tested, and the average values of C_{12} are 0.80, 0.92, and 0.94 for sorbents 1, 7, and 9, respectively. When the five data sets corresponding to 550°C carbonation temperature are eliminated (see previous discussion of the adverse effect of this carbonation temperature on capacity maintenance) the average values of C_{12} increase to 0.82, 0.96, and 0.98, respectively, for sorbents 1, 7, and 9.

Although sorbent 9 exhibits somewhat higher values of C_1 and C_{12} than sorbent 7, the results are somewhat misleading. C_1 is a measure of fractional calcium utilization, which provides an unambiguous basis for comparison of sorbents 1 and 7, since both are essentially pure CaO at the beginning of a carbonation cycle. Sample 9, however, at the beginning of carbonation contains more than 40% (wt) inerts (primarily MgO). Therefore, on the basis of unit mass of total sorbent, the CO_2 capacity of sorbent 9 is less than that of either sorbents 1 or 7. This subject is discussed in more detail in a later portion of this report.

In contrast to capacity and capacity maintenance, reactivity comparisons among the three sorbents do not lead to clear-cut conclusions. Each of the three sorbents exhibited the highest value of R_1 at a particular set of reaction conditions. At 825°C calcination temperature, 750°C carbonation temperature, 1 atm carbonation pressure, and 15% CO_2 in the carbonation gas, sorbent 1 produced the highest R_1

value. At 750°C calcination temperature, 650°C carbonation temperature, 5 atm carbonation pressure, and 15% CO₂ in the carbonation gas, the highest R₁ value was produced by sorbent 7. Sorbent 9 was most reactive at 750°C calcination temperature, 550°C carbonation temperature, 1 atm carbonation pressure and 1% CO₂ in the carbonation gas.

Because of these conflicting results, a statistical analysis based on the method of hypothesis testing (Box and Hunter, 1978) was carried out. This analysis showed, at the 95% confidence level, that sorbents 7 and 9 are more reactive than sorbent 1. The 18 data sets which were common to all three sorbents were used in this comparison. Direct comparison of the reactivities of sorbents 7 and 9 using hypothesis testing suggested a slightly higher reactivity for sorbent 9, but the confidence level was significantly less than 95%.

4.4 OPTIMUM REACTION CONDITIONS

As a result of the Task 3 tests, it is possible to define, with reasonable certainty, the conditions at which a CaO-based HTHP CO₂ separation process should operate:

Calcination Temperature	750°C
Carbonation Temperature	650-750°C
Carbonation Pressure	15 atm
% CO ₂ in Carbonation Gas	15

Calcination should be carried out at the lowest possible temperature, ~750°C, to minimize sorbent deterioration and to avoid the normal operational problems associated with higher temperatures. 550°C carbonation temperature should be avoided because of the negative effect on capacity maintenance, but, at this point, there are no clear kinetic

differences between 650 and 750°C carbonation temperature. From an equilibrium viewpoint, 650°C is desirable because it will permit higher fractional CO₂ removal. The lack of a narrowly defined optimum carbonation temperature may be advantageous from the standpoint of reactor design because of the exothermic nature of the carbonation reaction.

Carbonation pressure will be dictated by the gasification process which is likely to operate at 15 atmospheres or more. High pressure is favorable for high equilibrium CO₂ removal, and the experimental studies have shown no adverse effect of high pressure other than a decrease in reactivity. In a commercial process, sorbent capacity and, in particular, capacity maintenance are more important than reactivity. The inlet CO₂ mol fraction will also be determined by the gasification process. No adverse kinetic effects of high CO₂ concentration have been detected, and high inlet concentration is advantageous for high equilibrium CO₂ removal. At the most favorable carbonation conditions, namely 650°C, 15 atm, and 15% CO₂ in the inlet gas, the theoretical (equilibrium) CO₂ removal efficiency exceeds 99.5%.

CHAPTER 5

TASK 4 - DETAILED PARAMETRIC TESTS

The original work plan called for the single "best" sorbent based upon Task 3 results to be chosen for more detailed testing in Tasks 4 and 5. However, since sorbents 7 and 9 each exhibited unique favorable properties in the Task 3 tests, both were retained in Task 4. The Task 4 test matrix was originally planned to include five calcination temperatures, three calcination pressures, five carbonation temperatures, three carbonation pressures, and three CO₂ mol fractions. The previously described expansion of the Task 3 test matrix ended up covering many of the Task 4 tests. As a result, the Task 4 test sequence involved the addition of two calcination and carbonation temperatures and examining the effect of calcination at high pressure.

5.1 CALCINATION PRESSURE

All previous calcination tests were carried out in 1 atm N₂. In this sequence, the effect of higher calcination pressure was examined. Figure 42 shows, for sorbent 9, that high pressure delays the start of calcination and decreases the calcination rate by a small amount. Nevertheless, complete calcination was achieved at 15 atm in a reasonable amount of time. Figure 43 compares the subsequent first-cycle carbonation kinetics of sorbent 7 at 750°C, 15 atm, and 15% CO₂ following calcination at 1, 5, and 15 atm. There is essentially no effect of calcination pressure on carbonation reactivity, and little, if any effect on first-cycle capacity.

Figure 42. Comparison of Sorbent 9 Calcination Kinetics at Different Pressures.

Figure 43. The Effect of Calcination Pressure on First-Cycle Carbonation Kinetics, Sorbent 7.

5.2 CALCINATION AND CARBONATION TEMPERATURES

Task 3 results showed quite clearly that high calcination temperature was to be avoided. Consequently, expansion of the study of the effect of calcination temperature was in the direction of lower temperatures, 700 and 650°C. Low calcination pressure (1 atm) was required in order to achieve calcination at lower temperature. Figure 44 shows the calcination curves for sorbent 7 at the lower temperatures with the 750°C result included for comparison. Temperature was increased at a rate of approximately 5°C/min until the indicated final temperature was reached and held constant thereafter. Minor differences in the calcination behavior were observed between 700 and 750°C, but the final step in the overall calcination process at 650°C (decomposition of CaCO_3 to CaO) was quite slow. The rate of weight loss is not actually zero, as it appears to be in Figure 44, and complete calcination was achieved after approximately 8 1/2. Rates of carbonation at 650°C, 15 atm, in 15% CO_2/N_2 following calcination at the three lower temperatures are shown in Figure 45. Once again the curves are almost coincident and there is little effect of calcination temperature on either sorbent reactivity or capacity. Likewise, there was little difference in the two-cycle carbonation capacity maintenance following low temperature calcination. Figure 46 shows that values of C_{12} are effectively 1.0 at each of the three lower temperatures. The adverse effect of higher temperature calcination (825 and 900°C) which was established in the Task 3 test series is included for comparison purposes.

The additional carbonation temperatures of 600 and 700°C were studied using sorbent 9 following calcination at 750°C, 1 atm. Fractional conversion versus time results for five carbonation temperatures are compared in Figure 47. The time scale is limited to 20

Figure 44. Calcination Kinetics of Sorbent 7 as a Function of Temperature.

Figure 45. The Effect of Calcination Temperature on First-Cycle Carbonation Kinetics: Sorbent 7.

Figure 46. Sorbent 7 Capacity Maintenance as a Function of Calcination Temperature.

Figure 47. The Effect of Temperature on Carbonation Kinetics During the Early Phases of the Reaction.

minutes in this figure in order to emphasize the initial rate period. All tests show the characteristic rapid initial rate followed by the abrupt transition to the slow rate. The initial rates at 550, 600, and 650°C are quite similar. A slight decrease in initial rate is obvious at 700°C, and at 750°C the initial rate is significantly lower. This result coincides with the increasing importance of equilibrium CO_2 pressure with increasing temperature. At the three lower temperatures the equilibrium CO_2 pressure is negligible compared to the 0.15 atm actual CO_2 pressure. At 700°C the equilibrium pressure is just becoming important and 750°C the equilibrium pressure is approximately one-half the actual pressure. The transition from the rapid to the slow reaction phase occurred more gradually at 750°C. At the lowest temperature of 550°C, the transition occurred at lower conversion and the fractional carbonation remained lower throughout the early part of the reaction. However, after 40 min most of the conversion variation was removed and the capacity values for the five tests were 0.92, 0.92, 0.96, 0.93 and 0.93 for 550, 600, 650, 700, and 750°C, respectively.

One of the unexpected results from the Task 3 test series was the poor capacity maintenance observed at the lowest carbonation temperature, 550°C. As shown in Figure 48, C_{12} values for the additional runs conform to previous results. In particular, C_{12} at 600°C lies between the previously determined values at 550 and 650°C, providing further confirmation that approximately 650°C should be considered as the minimum carbonation temperature. Similarly the new C_{12} data at 700°C lies between the previously determined values at 650 and 750°C. All of the C_{12} values in the temperature range 650-750°C are equal to or greater than 0.98.

Figure 48. Two-Cycle Capacity Maintenance of Sorbent 9 as a Function of Carbonation Temperature.

Two-cycle runs using sorbent 7 were carried out at the additional carbonation temperatures of 800 and 850°C to obtain information on adverse effects of higher carbonation temperatures. Results in the form of capacity maintenance, C_{12} , versus carbonation temperature are shown in Figure 49. Essentially no decrease in C_{12} was observed at 800°C and a relatively small decrease at 850°C. The result at 850°C, where $C_{12} = 0.92$, was superior to the result at 550°C, where $C_{12} = 0.78$. These higher temperature results are encouraging in that they suggest that no major loss in performance for temperature excursions of as much as 100°C above the normal maximum of 750°C. Such a margin of safety is desirable in any exothermic reaction system.

5.3 DISCUSSION

Task 4 tests confirmed the results and trends established in Task 3. Carbonation temperatures in the 650-750°C range are desirable, although periodic excursions to 800°C or higher seem to have no major adverse effect. Calcination temperatures as low as 700°C appear feasible as long as the calcination pressure is 1 atm. However, the calcination reaction is endothermic, and lower temperature excursions must be avoided since the calcination rate becomes extremely slow at 650°C.

High-pressure calcination is feasible at a temperature of approximately 750°C. Reactivity, capacity, and capacity maintenance for the subsequent carbonation reaction show no adverse effect of high calcination pressure. This opens the possibility of operating a commercial process with equal pressures and approximately equal temperatures in the carbonation and calcination phases, with CO_2 partial pressure determining whether carbonation or calcination occurs.

Figure 49. Two-Cycle Capacity Maintenance of Sorbent 7 as a Function of Carbonation Temperature.

CHAPTER 6

Task 5 - FIVE-CYCLE TESTS

The Task 5 test matrix was modified from the original work statement to reflect continued interest in both sorbents 7 and 9, and to extend the number and scope of multicycle runs. The original work statement called for four five-cycle runs to be followed by a single ten-cycle run. The five-cycle test series was expanded to include the examination of two sorbents at two calcination pressures, two carbonation temperatures, and four gas compositions. The complete matrix consists of 32 tests shown in Table XV. [Authors comments: Experimental work in this task is continuing at the time this draft report is being written. Entries in Table XV as well as the subsequent discussion include work completed through October 1991. Appropriate additions will be included in the final report.] A number of the tests shown in Table XV were eliminated using criteria similar to those described in Task 3. However, off-matrix tests were carried out to provide preliminary results of multi-cycle behavior.

Reaction conditions for this test series were chosen on the basis of results from Tasks 3 and 4. All tests used a calcination temperature of 750°C, 15 atm carbonation pressure, and 15 mol % CO₂ in the carbonation gas. The 15 atm calcination tests were added on the basis of Task 4 results to examine the possibility of isobaric operation with sorbent regeneration to be accomplished via a change in temperature and/or CO₂ pressure. The two carbonation temperatures of 650 and 750°C were maintained since the previous tests failed to establish a significant advantage of one over the other. Increasing the number of

Table XV. Five-Cycle Test Matrix for Task 5

SAMPLE	CALCIN PRESS (ATM)	CARBON TEMP. (C)	CARBONATION GAS COMPOSITION		
			A	B	C
7	1	750	HP162	HP206	
7	1	650	HP157		
7	15	750	HP156		
7	15	650	HP155		
9	1	750	HP161	HP205	
9	1	650	HP163		
9	15	750	HP153		
9	15	650	HP154		

Carbonation Gas Composition:

- A : 15% CO₂/N₂
- B : 15% CO₂/10% H₂O/N₂
- C : 15% CO₂/10% H₂O/20% CO/10% H₂/N₂
- D : 15% CO₂/10% H₂O/20% CO/10% H₂/1% H₂S/N₂

Calcination Conditions:

- Gas Atmosphere : N₂
- Temperature : 750 C

cycles to five may generate differences between the two carbonation temperatures.

The four gas compositions reflect increasingly complex carbonation gas mixtures. With the exception of a few of the exploratory tests of Task 2, all previous carbonation testing utilized CO_2 in N_2 . In this task, Gas A, which consisted of 15% CO_2 in N_2 , continued the previous approach. 10% water was added to Gas B to check for possible direct effects of water under conditions where the shift reaction cannot occur. Gas C approximates a sulfur-free coal gas; since both CO and H_2O were present in the feed the possibility of simultaneous shift reaction and CO_2 removal must be considered. Finally, Gas D was tested to evaluate the response of the system to small amounts of H_2S .

6.1 PRELIMINARY TESTS

Four preliminary five-cycle off-matrix tests using the three base sorbents plus a special sorbent to be described were carried out before beginning the test matrix. The primary purpose was to confirm that the trends in reactivity and capacity observed for two cycles using sorbent 1 continued through five cycles. Reaction conditions were as follows:

Calcination - Temperature	750°C
Pressure	1 atm
Atmosphere	N_2
Carbonation - Temperature	750°C
Pressure	1 atm
Atmosphere	15% CO_2/N_2

Results for the sorbent 1 test in the form of the raw weight-time data are shown in Figure 50. Complete calcination was achieved in all cycles, and each carbonation cycle exhibited the previously observed

Figure 50. Calcination-Carbonation Results for Sorbent 1 Through Five Cycles.

characteristics of a rapid initial rate followed by an abrupt transition to a slow rate. The transition occurred at successively smaller sorbent weight in each cycle. This deterioration in performance through multiple cycles is similar to the results reported by others when calcium carbonate or limestone was used as the sorbent precursor. Figure 51 compares the capacity, C_1 , of each cycle of the sorbent 1 test with previous results reported by Barker (1973) and DeLucia (1985). Although the specific sorbents used and reaction conditions were somewhat different in each study, the trends are remarkably similar.

Five-cycle test results using sorbents 7 and 9 at the same reaction conditions are shown in Figures 52 and 53, respectively. In these figures the calcination data are omitted and carbonation results for each of the five cycles are overlaid for ease of comparison. Figure 52 (sorbent 7) shows two interesting results. First, there is a significant increase in reactivity between cycles 1 and 2, with the reactivity then remaining approximately constant in cycles 2 through 5. Secondly, while there is a gradual deterioration in sorbent capacity with increasing cycle number, the deterioration is less severe than with sorbent 1 (Figure 50). Sorbent 9 data in Figure 53 shows quite similar behavior through each of the five carbonation cycles. The reactivity during the initial rapid reaction phase is essentially equal in all cycles. There is a small drop in capacity between cycles 1 and 2 but the capacity in cycles 2 through 5 is essentially constant.

A direct comparison of the capacity of the three base sorbents as a function of cycle number for these tests is shown in Figure 54. During the first two cycles the capacities of sorbents 7 and 9 are essentially equal and both have significantly greater capacity than sorbent 1. In the third and subsequent cycles, however, the performance of sorbent 7

Figure 51. Comparison of Capacity Decrease for Sorbent 1 With Literature Results at Similar Reaction Conditions.

Figure 52. Carbonation Results for Sorbent 7 Through Five-Cycles.

Figure 53. Carbonation Results for Sorbent 9 Through Five-Cycles.

Figure 54. Carbonation Capacity of the Three Base Sorbents as a Function of Cycle Number.

deteriorates more rapidly and the order of capacity becomes sorbent 9 > sorbent 7 > sorbent 1.

The capacity index, C_i , is a measure of the fractional calcium conversion to carbonate. An alternate basis for capacity comparison is the mass of CO_2 sorbed per unit mass of sorbent. On this latter basis, sorbent 9 is not as attractive because of the presence of the large amount of inert MgO . Figure 55 compares sorbent capacity on this alternate basis using data from the same runs as used for Figure 54. The alternate comparison causes no change in the slope of the curves, but does produce a downward shift in the sorbent 9 curve relative to the curves for sorbents 1 and 7. On this alternate basis, sorbent 9 has the lowest capacity through the first three cycles, but the superior capacity maintenance of sorbent 9 permits its capacity to exceed that of sorbent 1 by the fourth cycle.

The fourth curve in Figure 55 represents results from a special sorbent obtained by calcining calcium magnesium acetate (CMA) precursor. This material is currently being marketed by Chevron Chemical Co. as an alternate to salt for deicing roads and bridges. The test was added because of the similarity of the composition of the CMA precursor to the composition of the precursors to both sorbents 7 and 9. CMA is represented by the formula $\text{Ca}_x\text{Mg}_y(\text{C}_2\text{H}_3\text{O}_2)_{2(x+y)}$ with $x = 3$ to 4 and $y = 6$ to 7 . It has the following composition (as reported by Chevron):

CMA	91% min
Water (free and hydration)	5% max
Water-Insoluble Material	4% max

The CO_2 capacity per unit mass of sorbent is considerably below that of the three sorbents of this study, due primarily to the large concentration of inert MgO . However, the capacity maintenance, which is

Figure 55. CO₂ Capacity Per Gram of Sorbent for Four Test Sorbents as a Function of Cycle Number.

represented by the slope of the curve in Figure 55, is comparable to that of dolomite (sorbent 9). This similarity suggests that MgO is important not only for providing excess pore volume to prevent pore plugging, but also to stabilize the structure for multicycle operation.

These exploratory five-cycle runs provided general confirmation of the two-cycle results from Task 3. Subsequent five-cycle tests followed the matrix shown in Table XV.

6.2 REACTIVITY AND CAPACITY INDICES

The five-cycle tests generated 2 1/2 times more experimental data than generated by the two-cycle tests. Consequently, reactivity and capacity indices similar to those developed for the two-cycle tests were used to analyze and compare much of the five-cycle data. The time for reactivity evaluation was shortened to $t - t_0 = 0.5$ min from the previous $t - t_0 = 1$ min. Similarly, the time for capacity comparison was shortened to $t - t_0 = 20$ min from $t - t_0 = 40$ min. In the two-cycle tests $t - t_0 = 1$ min was chosen as the best compromise for the group of tests representing wide ranges of CO₂ concentration and carbonation temperature and pressure. The range in Task 5 reaction conditions was much smaller, however, as all tests utilized 15% CO₂ at 15 atm. The shorter evaluation time of $t - t_0 = 0.5$ min was found to provide better reactivity discrimination than $t - t_0 = 1$ min. Reducing the time for capacity evaluation to $t - t_0 = 20$ min was done primarily as a time saving measure. As suggested in Figure 50, more than 8 hours were required for each five-cycle run when start-up and shut-down time were included. Reducing each carbonation cycle by 20 minutes reduced the overall run time by one hour without causing a significant change in

capacity values. In a series of comparison tests the C_i values at 20 minutes were no more than 0.02 or 0.03 less than the C_i values at 40 minutes.

Values of R_i and C_i ($i = 1, \dots, 5$) are summarized in Tables XVI and XVII, respectively. The format of these tables is the same as Table XV where run numbers are identified. Overall, the R_i values of Table XVI show a small decrease with increasing cycle number, and the magnitude of the decrease is somewhat larger for sorbent 7 than for sorbent 9. Capacity results from Table XVII also show a general decrease with cycle number, and once again the magnitude of the decrease is somewhat larger for sorbent 7 than for sorbent 9.

[Authors Note: since experimental activity in Task 5 is ongoing, none of the analysis and comparison of results is included in this draft. These sections will be included in the final report.]

Table XVI. Reactivity Results for Task 5
Five-Cycle Tests ($t - t_0 = 0.5$ min)

SAMPLE	CALCIN PRESS (ATM)	CARBON TEMP. (C)	CARBONATION GAS COMPOSITION			
			A	B	C	D
7	1	750	.35/.36/ .37/.32/ .33			
7	1	650	.28/.28/ .30/.30/ .29			
7	15	750	.30/.29/ .26/.30/ .28	.44/.44/ .44/.44/ .43		
7	15	650	.26/.25/ .24/.22/ .22			
9	1	750	.28/.29/ .28/.27/ .28			
9	1	650	.27/.24/ .23/.21/ .20			
9	15	750	.21/.23/ .24/.18/ .22	.47/.44/ .45/.44/ .44		
9	15	650	.22/.23/ .22/.22/ .20			

Table XVII. Capacity Results for Task 5
Five-Cycle Tests

SAMPLE	CALCIN PRESS (ATM)	CARBON TEMP. (C)	CARBONATION GAS COMPOSITION			
			A	B	C	D
7	1	750	.98/.96/ .94/.90/ .87			
7	1	650	.98/.96/ .94/.89/ .81			
7	15	750	.97/.96/ .95/.93/ --	.98/.97/ .96/.97/ .97		
7	15	650	.95/.93/ .93/.93/ .89			
9	1	750	.95/.94/ .94/.94/ .93			
9	1	650	.95/.94/ .93/.88/ .84			
9	15	750	.95/.94/ .94/.94/ .94	.97/.95/ .96/.95/ .94		
9	15	650	.94/.92/ .90/.90/ .90			

CHAPTER 7

TASK 6 - STRUCTURAL PROPERTY MEASUREMENTS

The importance of sorbent structural properties in determining the kinetics of gas-solid noncatalytic reactions is well established. Such structural property changes are particularly important in the carbonation of CaO since the addition of CO₂ to the solid phase inevitably results in the filling of pore volume which, in some cases, can prevent CO₂ from diffusing into the particle, thereby terminating the reaction before completion.

A number of structural property characterization techniques were used to supplement the kinetics study, including BET surface area, mercury porosimetry, x-ray diffraction, and scanning electron microscopy. Initial plans to include helium pycnometry were cancelled since extended exposure of the sample to ambient air could not be avoided in the pycnometer. It became apparent early in the test program that atmospheric exposure of calcined samples had to be minimized because of the tendency of CaO to react with moisture from the air. As a result, the transfer of all calcined samples to the sample holders of the respective instruments was carried out under glove-box conditions. The sorbents were characterized in their as-received form, after calcination at various conditions, after carbonation at various conditions, and at selected stages of multiple calcination-carbonation cycles.

7.1 MERCURY POROSIMETRY

Table XVIII identifies the conditions under which the mercury porosimetry tests were carried out and the resultant pore volumes. All pore volumes are reported in units of cm³ per gram of solid. It is important to emphasize this definition since both the pore volume and

Table XVIII. Summary of Mercury Porosimeter Tests and Pore Volume Results.

	Sorbent 1		Sorbent 7		Sorbent 9	
	PV ¹	X ²	PV	X	PV	X
As-Received						
Sample 1	0.07	1.0	0.31	----	0.33	1.0
Sample 2	0.09	1.0	0.31	----	0.31	1.0
First Calcination						
300 C/1 hr	****	****	0.75	----	****	****
550 C/1 hr	****	****	1.32	1.0	****	****
750 C/1 hr	0.42	0.01	3.08	0.01	0.92	0.01
	****	****	****	****	0.92	0.02
900 C/1 hr	0.39	0.01	3.04	0.01	0.98	0.02
1000 C/1 hr	0.40	0.00	3.11	0.00	0.97	0.00
900 C/10 min	0.40	0.00	3.20	0.03	0.97	0.03
	0.39	0.00	****	****	****	****
900 C/6 hr	0.40	0.00	3.26	0.01	1.02	0.02
First Recarbonation (15% CO ₂ ; calcination and carbonation for 2 hrs)						
750 C/550 C ³	0.10	0.71	1.51	0.81	0.43	0.91
750 C/750 C	0.07	0.81	1.38	0.96	0.38	0.96
900 C/550 C	0.09	0.63	1.83	0.79	0.58	0.77
900 C/750 C	0.05	0.72	1.37	0.86	0.63	0.83
Second Calcination (15% CO ₂ ; calcination and carbonation for 2 hrs)						
750/550/750 ⁴	0.34	0.00	2.02	0.01	0.88	0.02
750/750/750	0.35	0.00	2.31	0.02	0.92	0.02
Second Recarbonation (15% CO ₂ ; calcination and carbonation for 2 hrs)						
750/550/750/550 ⁵	0.10	0.57	1.43	0.63	0.60	0.73
750/750/750/750	0.07	0.71	1.22	0.90	0.52	0.91
900/550/900/550	0.11	0.40	2.37	0.45	0.66	0.61
900/750/900/750	0.08	0.60	1.43	0.90	0.57	0.94

¹PV = Pore volume (6.0-0.003 μm), ml/g²X = moles CaCO₃/ moles Ca³calcination temp./ carbonation temp., C⁴1st calcination/1st carbonation/2nd calcination temp., C⁵1st calcination/1st carbonation/2nd calcination/2nd carbonation temp., C

solid mass change as a result of reaction. The X values in Table XVIII represent the fraction of calcium which is present in carbonate form. For as-received sorbents 1 and 9, $X = 1.0$. For calcined samples, $X \leq 0.03$ which indicates effectively complete calcination. For sorbent 7, calcium is present as acetate in the as-received precursor and following calcination at 300°C. 300°C treatment of the hydrated calcium acetate is only sufficient to drive off the water of hydration. 550°C treatment causes the acetate group to decompose leaving essentially pure CaCO_3 with $X \sim 1.0$. Further heating to 750°C or higher causes the CaCO_3 to decompose to CaO .

As noted in the kinetics studies, recarbonation was frequently incomplete and the X values in this group represent the fraction of calcium reconverted to carbonate at the end of the run. These values are in qualitative agreement with the capacity results obtained in the kinetics tests. Values of $X \sim 0$ following the second calcination indicate complete carbonate decomposition, again in agreement with the kinetics results. Finally, the values of X following the second carbonation are often somewhat lower than the comparable values after the first carbonation, also in agreement with kinetics studies which showed reduced sorbent capacity in the second cycle.

In addition to the total pore volume results in Table XVIII, the mercury porosimeter provides information on the pore size distribution and the cumulative pore volume at any specified pore diameter. An example is shown in Figure 56 for sorbent 7 calcined at 750°C in N_2 for one hour. The pore diameter range covered is 0.003 to 6.0 microns, corresponding to the pressure range of 30 to 60,000 psia. The pore size distribution (PSD) curve shows a major concentration of pores having an average pore diameter of about 4.0 microns. Between about 0.2 and 1.0

Figure 56. Cumulative Pore Volume and Pore Size Distribution for Sorbent 7 Calcined at 750°C for 1 Hour.

microns diameter a broad band of pores exist. A second, smaller peak corresponding to pores having an average diameter of about 0.035 microns is also evident. Approximately one-half of the total pore volume of $3.08 \text{ cm}^3/\text{g}$ is associated with pores having diameters equal to or greater than 2 microns, and the total volume associated with pores having diameters equal to or greater than 0.1 microns is about $2.7 \text{ cm}^3/\text{g}$, or about 90% of the total. Although the small pores around 0.035 microns diameter are important in determining reaction characteristics, they contribute less than 10% of the total pore volume.

7.1.1 Changes in Pore Characteristics During Reaction

The pore volumes of the as-received sorbents are $0.08 \text{ cm}^3/\text{g}$ for sorbent 1 and $0.31 \text{ cm}^3/\text{g}$ for both sorbents 7 and 9 (Table XVIII). Curves A in Figures 57, 58, and 59 show the pore size distribution curves for each of the as-received sorbents. Curves B and C, which represent the pore size distributions following calcination and following recarbonation, respectively, are discussed subsequently.

As-received calcium carbonate (sorbent 1) contains few pores in the diameter range of interest (Figure 57). Most of the $0.08 \text{ cm}^3/\text{g}$ pore volume is associated with pores having diameters greater than 3 microns. As-received sorbent 7 (calcium acetate) shown as curve A in Figure 58 also contains few pores in the 0.003 to 6.0 micron range. The $0.31 \text{ cm}^3/\text{g}$ pore volume is contributed by a broad band of pore having diameters greater than 0.3 microns. Only as-received sorbent 9 (dolomite) shows a definite pore size distribution peak (curve A in Figure 59) in the diameter range of interest (at approximately 3 microns). The leading edge of this peak begins at about 0.2 microns.

Figure 57. Pore Size Distribution of Sorbent 1.

Figure 58. Pore Size Distribution of Sorbent 7.

Figure 59. Pore Size Distribution of Sorbent 9.

Note that the scales on the y-axis of Figures 57, 58, and 59 are all different, making it necessary to compare the numerical values of the peak heights as well as their apparent size.

Calcination of sorbent 1 liberates CO_2 to produce solid CaO . As shown in Table XVIII, this produces an increase in pore volume to about $0.4 \text{ cm}^3/\text{g}$, and, as shown in curve B of Figure 57, most of the resultant pores are in the diameter range of 0.02 to 0.08 microns. Small increases in the volume of pores in the large (> 4 micron) and small (< 0.006 micron) diameter range also result from the calcination process. Decomposition of as-received sorbent 7 (hydrated calcium acetate) proceeds in a stepwise fashion beginning with the loss of water of hydration by 300°C , followed by decomposition of the acetate to form CaCO_3 by 550°C , and finally carbonate decomposition to CaO by 750°C . Each step involves the evolution of volatile matter and the formation of pores. The pore size distribution after each step is shown in Figure 58. Curve B1 shows that pores generated during the loss of the water of hydration are quite large, with the peak in the 7 to 8 micron diameter range (by extrapolation). Decomposition of calcium acetate to calcium carbonate (curve B2 in Figure 35) by heating to 550°C produces a broad distribution beginning at 0.2 microns and extending past 6 microns with a peak at about 0.8 microns. The increase in total pore volume (Table XVIII) is relatively small considering that more than one-third of the original solid weight is lost during this step. This suggests that the anhydrous calcium acetate may initially sinter and lose most of the large pores formed by dehydration. The new pores at 0.8 microns diameter are then formed by acetate decomposition. Carbonate calcination at 750°C produces CaO having a pore size distribution shown

by curve B in Figure 58. Large pores having diameters of approximately 4 microns are formed along with small pores in the 0.02 to 0.05 micron diameter range. There is also a broad distribution of pores in the 0.1 to 2 micron diameter range. Dolomite calcination (sorbent 9) occurs more or less continually over the temperature range of 600 to 750°C as both MgCO_3 and CaCO_3 decompose to the respective oxides. As shown by curve B in Figure 59, this calcination produces two distinct peaks, with the larger having an average diameter of about 3 microns and the smaller having an average diameter of about 0.05 microns.

The small diameter pores in the diameter range 0.02 to 0.08 microns are similar for each of the three fully calcined sorbents. We interpret these pores as being formed by the final decomposition of CaCO_3 to CaO since this reaction is common to all three sorbents. The primary difference in pore structure between sorbent 1 and sorbents 7 and 9, is the presence of large pores having diameters greater than 1 micron in sorbents 7 and 9.

Curves C in Figures 57, 58, and 59 represent the pore size distributions of the three sorbents following one complete calcination-carbonation cycle. Carbonation was carried out at 750°C and 1 atm, for 2 hours in 15% CO_2/N_2 . Table XVIII and Figure 57 show that the total pore volume and the pore size distribution of carbonated sorbent 1 and as-received sorbent 1 are almost identical. Essentially all of the pores created by calcination are refilled during carbonation. Isolated pores presumably remain at the interior of the particles because of the presence of unreacted CaO at the interior ($X = 0.81$). Such pores, however, are equally inaccessible to the mercury during characterization and to CO_2 during carbonation. In contrast to sorbent 1, essentially complete carbonation of both sorbents 7 and 9 was achieved ($X = 0.96$).

Table XVIII shows that the pore volume of carbonated sorbent 7 is almost 5 times the pore volume of as-received sorbent 7. Similarly, the pore volume of recarbonated sorbent 9 is larger than the pore volume of the as-received dolomite. Figure 58 (sorbent 7), curve C, shows that the small pores (~ 0.03 microns diameter) were refilled but that a significant number of pores having an average diameter of about 1 micron remain open. Curve C in Figure 59 for sorbent 9 shows that a fraction of both the small and large pores remain open. The average diameter of the remaining small pores has shifted to about 0.07 microns. The remaining larger pores also have a larger average diameter which appears to be (by extrapolation) about 7 microns.

The importance of the water of hydration and acetate group in sorbent 7 and magnesium carbonate in sorbent 9 are apparent from the above discussion. In both cases, decomposition produces a sorbent having "excess" pore volume which enhances the access of CO_2 to the interior of the particle, thereby providing for more complete reaction.

7.1.2 Sintering Studies

Not only is it important to create porous sorbents by calcination, but to maintain the porosity for extended time periods and through numerous calcination-carbonation cycles. Changes in pore structure with respect to time and temperature are referred to as sintering. Mercury porosimeter tests were conducted using calcined sorbents exposed to different combinations of time and temperature. Table XVIII shows that no significant changes in total pore volume occurred over the range of sintering conditions studied. For example, at a constant sintering time of 1 hour, the pore volumes of sorbent 1 sintered at 750, 900, and

1000°C were 0.42, 0.39, and 0.40 cm³/g, respectively. Similarly, the pore volumes of sorbent 7 sintered at 900°C from 10 minutes to 6 hours varied only from 3.26 to 3.04 cm³/g.

Figures 60 and 61 show the pore size distribution curves for sorbent 9 as a function of sintering temperature (750 to 1000°C, 1 hour) and sintering time (900°C, 10 min to 6 hours), respectively. The PSD curves are similar in both figures. In Figure 60, a shift in the small diameter peak from 0.04 microns at 750°C to 0.05 microns at 900°C to 0.06 microns at 1000°C is apparent. The large diameter peak at about 3 microns is essentially unchanged. At 900°C, sintering time has little effect on either the large or small diameter peaks (Figure 61). There is an increase peak height with sintering time, but almost no change in the diameter at maximum intensity.

These limited sintering studies did not produce the level of sensitivity which was obtained from multiple cycle kinetic tests. The kinetics tests showed, for example, that 750°C calcination was preferred to calcination at higher temperature. No significant advantages associated with either time or temperature were obvious from the mercury porosimeter tests.

7.1.3 Changes in Pore Characteristics During the Second Cycle

Further structural changes occur when the sorbents are subjected to a second calcination and carbonation cycle. Table XVIII shows a decrease in pore volume for each sorbent between the first and second calcinations. The magnitude of the decrease ranged from less than 10% for sorbent 9 to about 33% for sorbent 7. Small shifts in the pore size distribution also result. This is illustrated in Figure 62 where the

Figure 60. The Effect of Sintering Temperature on the Pore Size Distribution of Calcined Sorbent 9. 1 Hour Sintering Time.

Figure 61. The Effect of Sintering Time on the Pore Size Distribution of Calcined Sorbent 9. 900°C Sintering Temperature.

Figure 62. Comparison of Pore Size Distribution Curves for Sorbent 1 Following the First and Second Calcination Cycles.

PSD curves for sorbent 1 after the first and second calcination at 750°C are compared. The total pore volume decreased by almost 20%. The small pores decreased in peak height and shifted to a slightly larger average pore diameter.

Table XVIII also permits comparison of the pore volumes following the first and second carbonation cycles. For sorbent 1, the differences in pore volumes are small. However, fractional carbonation decreased significantly in the second cycle, a result which is consistent with the previously described kinetics results. For sorbent 7, no clear trends emerge. Both larger and smaller pore volumes were measured. Interpreting the pore volume data is complicated by the second-cycle variation in X from a low of 0.45 to a high of 0.96. In three of the four comparisons involving sorbent 9 (Table XVIII), an increase in pore volume between the first and second carbonation cycles was measured. However, this data is again somewhat confounded by the variation in X. Figure 63 compares the PSD curves for sorbent 9 following one and two cycles in which both calcination and carbonation were carried out at 750°C. The decrease in X was relatively small, from 0.96 in cycle 1 to 0.91 in cycle 2, but a significant increase in pore volume, from 0.38 cm³/g to 0.52 cm³/g, occurred. Figure 63 shows that most of the increase was due to a decrease in the average diameter of the large pores, from approximately 7 to 4 microns. The peak intensity for the small pores decreased in the second cycle, and there is an apparent small shift to a larger average diameter. The general trend to higher pore volume after the second cycle may be responsible for the superior capacity maintenance of sorbent 9.

Figure 63. Comparison of Pore Size Distribution Curves for Sorbent 9 Following One and Two Complete Cycles.

7.2 BET SURFACE AREA

Table XIX summarizes the results of BET surface area tests. With a few exceptions, the test program paralleled that used for the mercury porosimeter tests. However, different samples were prepared for most tests. While it is possible to pretreat a sample, measure its surface area, and then perform the mercury porosimeter test using the same sample, many of the porosimeter tests were completed during a time in which the BET apparatus was not functioning. Pretreatment of separate samples was therefore required. Surface area data was obtained for the three base sorbents in the as-received condition, following calcination in nitrogen under a variety of temperature-time conditions, following one complete calcination-carbonation cycle, following 1 1/2 cycles (including a second calcination), and following two complete calcination-carbonation cycles. The surface areas are reported in units of square meters per gram of solid product, in the same manner as the pore volume results. The X values in Table XIX again represent the fraction of calcium which is present in carbonate form.

The BET analysis is based upon the incremental addition of small quantities of nitrogen to the sample which is maintained at liquid nitrogen temperature. A portion of the nitrogen is adsorbed while the portion which remains in the gas phase causes the pressure within the sample holder to increase. The raw pressure-time data can be used to generate an adsorption isotherm which is then analyzed according to the BET method to determine the specific surface area.

Table XIX includes the results of duplicate measurements using the same sample. For example, the two entries of $0.9 \text{ m}^2/\text{g}$ on the same line for as-received sorbent 1 indicate that the measurement was repeated

Table XIX. Summary of BET Surface Area Test Results.

	Sorbent 1		Sorbent 7		Sorbent 9	
	SA ¹	X ²	SA	X	SA	X
As-Received						
Sample 1	0.9,0.9	1.0	3.8,4.0	----	1.6,1.7	1.0
Sample 2	0.9	1.0	3.8	----	1.7	1.0
First Calcination						
300 C/1 hr	----	----	18.8	----	----	----
	----	----	17.9	----	----	----
550 C/1 hr	----	----	10.5	1.02	----	----
	----	----	11.2	1.01	----	----
750 C/1 hr	17.9,18.5	0.01	22.9,23.5	0.05	14.4,14.4	0.07
	----	----	21.1	0.03	20.6,21.3	0.01
900 C/1 hr	17.6	0.05	18.8	0.06	16.6	0.01
	16.9	0.00	18.5	0.01	----	----
1000 C/1 hr	13.3	0.00	18.3	0.09	14.6	0.00
	----	----	18.3	0.01	----	----
900 C/10 min	11.4	0.18	18.8	0.02	18.1	0.03
	17.4	0.00	----	----	----	----
900 C/6 hr	14.8	0.00	16.5	0.01	14.8	0.02
First Recarbonation (15% CO ₂ ; calcination and carbonation for 2 hrs)						
750 C/550 C ³	1.0	0.71	5.8	0.90	7.0	0.96
750 C/750 C	1.1,1.2	0.82	3.7,3.9	0.93	6.0,6.8	0.96
900 C/550 C	2.2	0.64	5.2	0.85	8.1	0.76
900 C/750 C	0.8	0.77	3.9	0.93	6.6	0.95
Second Calcination (15% CO ₂ ; calcination and carbonation for 2 hrs)						
750/550/750 ⁴	12.8	0.00	12.9	0.01	16.7	0.02
750/750/750	13.7	0.01	14.3	0.02	15.6	0.02
	13.4	0.00	----	----	----	----
Second Recarbonation (15% CO ₂ ; calcination and carbonation for 2 hrs)						
750/550/750/550 ⁵	1.3	0.57	4.7	0.63	8.1	0.73
750/750/750/750	0.8	0.71	3.0	0.90	5.7	0.91
900/550/900/550	1.3	0.39	4.2	0.52	8.4	0.61
	----	----	----	----	8.3	0.60
900/750/900/750	1.4	0.60	2.7	0.91	5.5	0.94
	----	----	----	----	5.2	0.92

¹SA = BET surface area, m²/g²X = moles CaCO₃/ moles Ca³calcination temp./ carbonation temp., C⁴1st calcination/1st carbonation/2nd calcination temp., C⁵1st calcination/1st carbonation/2nd calcination/2nd carbonation temp., C

using the same sample with the same results. The single entry on the second line, also indicating $0.9 \text{ m}^2/\text{g}$, represents the results from a third test obtained using a different sample of the same material. For sorbent 9 calcined at 750°C for 1 hour, there are four entries in Table XIX. The two entries on the top line showing $14.4 \text{ m}^2/\text{g}$ represent duplicate tests using the same sample. However, calcination was incomplete in this test with $X = 0.07$. The entire test was repeated using a new dolomite sample which, upon calcination, resulted in $X = 0.01$. Duplicate tests using this sample produced surface areas of 20.6 and $21.3 \text{ m}^2/\text{g}$.

7.2.1 Surface Area Changes During Reaction

The surface areas of as-received sorbents ranged from $0.9 \text{ m}^2/\text{g}$ for sorbent 1, to $1.7 \text{ m}^2/\text{g}$ for sorbent 9, to $3.9 \text{ m}^2/\text{g}$ for sorbent 7. The low surface area of sorbent 1 is consistent with the nonporous nature of the calcium carbonate as determined by mercury porosimetry and later confirmed by scanning electron microscopy (see following section). The larger surface area of sorbent 9 is presumably associated with those pores of approximately 3 microns diameter (see Figure 59). As will be shown in the following section, the surface of as-received sorbent 7 was quite rough which was responsible for its higher surface area.

Calcination produced a large increase in surface area of all three sorbents with individual values ranging from 11.4 to $23.5 \text{ m}^2/\text{g}$, depending upon calcination conditions. The stepwise calcination of sorbent 7 produced a large increase in surface area when the water of hydration was lost, followed by a decrease in surface area when the acetate decomposed to the carbonate, and a second increase when the

carbonate decomposed to the oxide. These results are in qualitative agreement with the mercury porosimeter results previously shown in Figure 58.

Carbonation of each sorbent caused a reduction in surface area. For sorbents 1 and 7, the surface areas returned to approximately the values of the as-received sorbent when calcination and carbonation were both carried out at 750°C. Carbonation of sorbent 9 caused a reduction in surface area but not to the value of the as-received sorbent. This "extra" surface area of carbonated sorbent 9 is attributed to the fact that MgO was not recarbonated at the reaction conditions studied.

Surface areas after the second calcination were generally lower than following the first calcination at the same conditions. The decrease ranged from about 25% for sorbents 1 and 9 to almost 40% for sorbent 7. Surface areas following the second carbonation were also smaller than after the first carbonation, but the relative decrease was not as great as the decrease after calcination.

7.2.2 Sintering Studies

Surface area appears to be a more sensitive measurement of sorbent sintering than pore volume. Figures 64 and 65 show the effect of sintering temperature (1 hour sintering time) and sintering time (900°C sintering temperature), respectively, on sorbent surface area. In Figure 64, all three sorbents show a reduction in surface area with calcination temperature, and similar results concerning the effect of calcination time on surface area are shown in Figure 65. These results are in agreement with the kinetics results which showed that high calcination temperature should be avoided.

Figure 64. The Effect of Sintering Temperature on Surface Area.
1 Hour Sintering Time.

Figure 65. The Effect of Sintering Time on Surface Area. 900°C Sintering Temperature.

7.3 DISCUSSION

The porosimeter and surface area results suggest that pore volume and pore size distribution are more important than surface area in determining reaction characteristics. In particular, the increased capacity of sorbents 7 and 9 relative to sorbent 1 may be attributed to the formation of pores in the 1 to 4 micron diameter range during calcination. A portion of these pores remain open even after carbonation. Small pores in the diameter range of 0.02 to 0.08 microns, which are produced in all sorbents during calcination become filled during carbonation. The superior capacity maintenance of sorbent 9 can be attributed to the further increase in pore volume during the second cycle as well as to the apparent stabilizing effect of MgO. If surface area was the key structural property then the performance of all sorbents would decrease along with surface area. The importance of pore volume and pore size distribution is also consistent with the kinetics results which showed that transport resistances were more important than the surface reaction in determining the global reaction rate. The transport rate is determined by the diameter and volume of the pores through which diffusion occurs.

Neither the surface area nor pore volume results help to explain the unexpected drop in second-cycle capacity maintenance associated with 550°C carbonation temperature. Tables XVIII and XIX show that final fractional carbonation values (X) were lower in 550°C tests than in 750°C, in agreement with the kinetics results. The difference is particularly striking in the second-cycle comparison. But most of the remaining surface areas and pore volumes were higher following 550°C carbonation, which suggests a greater possibility of continued reaction.

Consider in particular the structural properties of sorbent 9 following two complete cycles. The only difference in the two tests was carbonation temperature, 550°C in one test and 750°C in the other. Table XIX, shows that the fractional carbonation in the second cycle of the 750°C test was 0.91, but only 0.73 in the second cycle of the 550°C test. The final surface area of the sorbent from the low temperature run was $8.1 \text{ m}^2/\text{g}$ compared to $5.7 \text{ m}^2/\text{g}$ following 750°C carbonation. Similarly, Table XVIII shows that the sorbent pore volume following 550°C carbonation was higher than after 750°C. Figure 66 compares the sorbent pore size distribution curves following the two runs. The lower pore volume following 750°C carbonation is evident from the lower peak heights. Otherwise there is a small shift to larger average pore diameters associated with both peaks after 750°C carbonation. In summary, none of the structural characterization tests provide an explanation of the poorer sorbent performance associated with 550°C temperature.

7.4 SCANNING ELECTRON MICROSCOPY (SEM)

High magnification visual images of the size, shape, and surface characteristics of sorbent particles obtained from SEM analysis supplement the quantitative results obtained from mercury porosimetry and BET surface area tests.

Figure 67 shows photomicrographs of as-received sorbent 1 at magnifications of 3500X and 20,000X. Well-formed crystals having sharp edges and dimensions in the 1 to 10 micron range are apparent at 3500X. At 20,000X it becomes apparent that the surface of the crystals is quite smooth with no apparent pores. This lack of pores is in agreement with the low pore volume and low surface area. If one approximates the shape

Figure 66. Pore Size Distribution Curves for Sorbent 9 After Two Complete Cycles Comparing the Effect of Carbonation Temperature.

(a)

(b)

Figure 67. SEM of As-Received Sorbent 1.
a) 3500X (b) 20,000X

of the crystals as cubical, then the average size of the cube can be calculated from the measured surface area and the theoretical density of CaCO_3 (assuming no pores). The ratio of the surface area to volume of a cube is $6/\ell$, where ℓ is the cube length. Using the measured surface area of $0.9 \text{ m}^2/\text{g}$ and the density of calcite of 2.71 g/cm^3 , the surface area to volume ratio is $2.44 \times 10^4 \text{ cm}^{-1}$, which corresponds to $\ell = 2.46$ microns, a value in general agreement with the SEM photomicrographs.

Figure 68 shows photomicrographs of as-received sorbents 7 and 9, both at a magnification of 3500X. As-received sorbent 7 is composed of needle-like crystals with a rough, almost fluted surface. The diameters of the crystals are in the 1 to 10 micron range and the aspect ratio varies from about 4 to 10. The rough surface and numerous imperfections account for the larger surface area and pore volume. Unlike sorbents 1 and 7 which were used directly from the container, it was necessary to grind the commercial dolomite (sorbent 9 precursor) to obtain particles in the desired size range. The result of grinding is clearly evident in Figure 68b from the wide range of particle sizes and the absence of any regular shape. The larger surface area of sorbent 9 compared to sorbent 1 is due to the presence of submicron particles while the 3 micron pores (Figure 59) contribute both surface area and pore volume.

Calcination at 750°C and one atm in nitrogen results in complete decomposition, to CaO for sorbents 1 and 7, and to a mixture of CaO and MgO for sorbent 9. The general appearance of the calcined particles at low magnification is not altered. At 20,000X, however, there is a clear difference in the surface features as shown in Figure 69 for sorbents 1 and 9. The smooth surface of as-received sorbent 1 has been replaced by a rough wavy surface (Figure 69a), with the surface indentations in the

(a)

(b)

Figure 68. SEM of As-Received Sorbents at 3500X.
a) Sorbent 7 b) Sorbent 9

(a)

(b)

Figure 69. SEM of Calcined Sorbents at 20,000X.
a) Sorbent 1 b) Sorbent 9

size range less than 0.1 microns, which corresponds to the average pore diameter of about 0.05 microns obtained from mercury porosimetry. The high magnification view of calcined sorbent 9 (Figure 69b) shows that a larger number of submicron pores have been formed.

Two views of calcined sorbent 7 at different magnifications are shown in Figure 70. At the lower magnification, it is evident that the particles maintain their general needle-like appearance. The higher magnification view clearly shows the great amount of porosity and the wide range of pore diameters, from submicron to several microns, created by calcination.

1000°C calcination temperature changes the appearance of the surface as shown for sorbents 1 and 9 shown in Figure 71 (both at 20,000X). These photomicrographs are directly comparable to those shown in Figure 69 at a calcination temperature of 750°C. Both surfaces are significantly rougher following high temperature calcination. The wavy surface of sorbent 1 at 750°C is replaced by a crackly-looking surface following 1000°C calcination.

20,000X pictures of sorbents 1 and 7 following one complete calcination-carbonation cycle are shown in Figure 72. Both the calcination and carbonation temperatures were 750°C for these tests. Some of the surface waves created in sorbent 1 by calcination are retained following carbonation. No open pores are apparent in the surface which is consistent with the mercury porosimeter results which showed that the submicron pores formed during calcination were refilled during carbonation. The extremely rough surface of carbonated sorbent 7 is in direct contrast to the relatively smooth surface of sorbent 1. A large number of pores having diameters of approximately 1 micron remain

(a)

(b)

Figure 70. SEM of Calcined Sorbent 7
a) 750X b) 20,000X

(a)

(b)

Figure 71. SEM of Sorbents Calcined at 1000°C (20,000X)
a) Sorbent 1 b) Sorbent 9

(a)

(b)

Figure 72. SEM of Sorbents After First Carbonation
(20,000X)
a) Sorbent 1 b) Sorbent 7

unfilled which is also in qualitative agreement with the mercury porosimeter results (see Figure 58). The sorbent 7 particles had lost much of their original strength, and the needle-like crystals were subject to shattering into powder if handled roughly.

Figure 73 shows photomicrographs of sorbent 9 after one complete cycle at magnifications of 750X and 20,000X. The low magnification view shows that the original particle structure is retained, and, at high magnification, it is obvious that the surface remains quite porous. Essentially complete conversion of CaO to CaCO_3 was achieved, and the remaining pores were due to the excess porosity created by decomposition of MgCO_3 .

Interesting results after five complete calcination-carbonation cycles are shown in Figures 74 and 75 for sorbents 7 and 9, respectively. These pictures are of the actual sorbents used in runs HP153 and HP156 of the Task 5 five-cycle test series, and in both cases the final fractional calcium carbonation exceeded 0.90. Each figure shows the sorbents at magnifications of 750X and 3500X. The 750X view of sorbent 7 (Figure 74) shows that the needle-like shape of the crystals has been maintained. At higher magnification a definite change in the surface is apparent. The surface is much smoother than shown in Figure 72b, and the fluted structure has been replaced by clearly defined grains. The latter observation is reinforced by the high magnification (20,000X) view in Figure 76 of sorbent 7 which had experienced five complete calcination-carbonation cycles in Run HP162. Sorbent 9 (Figure 75), in contrast to sorbent 7, shows little apparent change in particle morphology between cycles 1 and 5. Photomicrographs of sorbents 7 and 9 following five complete cycles in runs where the

(a)

(b)

Figure 73. SEM of Sorbent 9 After One Complete
Calcination-Carbonation Cycle
a) 750X b) 20,000X

(a)

(b)

Figure 74. SEM of Sorbent 7 After Five Complete Cycles
 a) 750X b) 3500X

(a)

(b)

Figure 75. SEM of Sorbent 9 After Five Complete Cycles
a) 750X b) 3500X

ABSTRACT

The expected commercialization of coal gasification technology in the U.S. and world-wide will create a need for advanced gas purification and separation processes capable of operating at higher temperatures and in more hostile environments than is common today. For example, a high-temperature, high-pressure process capable of separating CO_2 from coal-derived gas may find application in purifying synthesis gas for H_2 , NH_3 , or CH_3OH production. High temperature CO_2 removal has the potential for significantly improving the operating efficiency of integrated — gasification-molten carbonate fuel cells for electric power generation.

This study proved the technical feasibility of a CO_2 -separation process based upon the regenerable noncatalytic gas-solid reaction between CaO and CO_2 to form CaCO_3 . Such a process operating at 650°C and 15 atm with 15% CO_2 in the coal gas has the potential for removing in excess of 99% of the CO_2 fed. Selection of a sorbent precursor which, upon calcination, produces high-porosity CaO is important for achieving rapid and complete reaction. The addition of magnesium to the sorbent appears to improve the multicycle durability at a cost of reduced CO_2 capacity per unit mass of sorbent. Reaction conditions, principally calcination and carbonation temperatures, are important factors in multicycle durability. Reaction pressure and CO_2 concentration are important in so far as the initial rapid reaction rate is concerned, but are relatively unimportant in terms of sorbent capacity and durability.

Indirect evidence for the simultaneous occurrence of the shift reaction and CO_2 removal reaction creates the possibility of a direct one-step process for the production of hydrogen from coal-derived gas.

Figure 76. High Magnification SEM of Sorbent 7 After Five Complete Cycles (20,000X).

carbonation gas contained steam did not differ significantly from those shown in Figures 74, 75, and 76.

7.5 X-RAY DIFFRACTION

X-ray diffraction (XRD) studies were carried out to identify crystalline phases present in the as-received, calcined, and recarbonated sorbents by matching experimental and library diffraction spectra. Examples of the XRD results are shown in Figures 77, 78, and 79 for sorbent 9 in the as-received, calcined, and carbonated conditions, respectively. The experimental spectrum for as-received sorbent 9 (Figure 77) provides an ideal match to the library spectrum of calcium magnesium carbonate (dolomite). The experimental spectrum of calcined sorbent 9 (Figure 78) is matched by superimposing the library spectra of calcium oxide and magnesium oxide (periclase). The most intense peak at $2\theta \sim 37$ degrees is formed by contributions from both CaO and MgO. The second and third most intense peaks at $2\theta \sim 54$ and 32 degrees are due to CaO, while the peaks at $2\theta \sim 43$ and 62 degrees are due to MgO. Although the ratio of the atomic concentrations of Ca and Mg in sorbent 9 is approximately 1, the intensity of the peaks attributable to MgO is considerably less than the intensity of the CaO peaks.

A similar difference in peak intensity is noticeable in the spectrum of recarbonated sorbent 9 (Figure 79). The most intense peak at $2\theta \sim 29$ degrees is due to calcium carbonate (calcite). The remaining experimental peaks are much less intense, but each can be attributed to one or a combination of calcite (CaCO_3) and periclase (MgO) peaks. The absence of dolomite in the recarbonated sorbent is proven by the absence

Figure 77. XRD Spectrum of As-Received Sorbent 9.

FN: SAMP9H.NI ID: 750C SCINTAG/USA
 DATE: 08/08/91 TIME: 11:30 PT: 0.360 STEP: 0.0300 WL: 1.54060

Figure 78. XRD Spectrum of Calcined Sorbent 9.

Figure 79. XRD Spectrum of Carbonated Sorbent 9.

of any peak at $2\theta \sim 31$ degrees, the position of the most intense dolomite peak.

XRD results for the three sorbents are summarized in Table XX. The experimental spectrum of as-received sorbent 1 provided an excellent match with the library spectrum for calcite (CaCO_3). After calcination, the experimental spectrum matched the library spectrum of synthetic lime (CaO). The experimental spectrum of carbonated sorbent 1 was dominated by calcite peaks with minor peaks which could be attributed to unreacted CaO .

The experimental spectrum of as-received sorbent 7 contained many peaks associated with water of hydration and the acetate group. The experimental spectrum appeared to result from a mixture of the spectra for $\text{Ca}(\text{C}_2\text{H}_3\text{O}_2)_2 \cdot 0.5 \text{ H}_2\text{O}$ and $\text{Ca}(\text{C}_2\text{H}_3\text{O}_2)_2 \cdot \text{H}_2\text{O}$. The former contains 6.8% H_2O (by mass) and the latter contains 12.6% H_2O . A mixture of the two hydrates is, therefore, consistent with the 8.3% H_2O present in the actual sample. The five major peaks in the experimental spectrum of calcined sorbent 7 matched the five major peaks in the library spectrum for synthetic lime, while all of the major peaks in carbonated sorbent 7 matched the library peaks for calcite. Some indication of trace amounts of unreacted CaO was evident in the experimental spectrum of carbonated sorbent 7.

Table XX. Crystalline Phase Determinations from X-Ray Diffraction Studies.

	Sorbent 1	Sorbent 7	Sorbent 9
As-Received	Calcite (CaCO_3)	Calcium Acetate Hydrate $\text{Ca}(\text{C}_2\text{H}_3\text{O}_2)_2 \cdot x\text{H}_2\text{O}$	Dolomite $\text{CaMg}(\text{CO}_3)_2$
Calcined at 750°C	Synthetic Lime (CaO)	Synthetic Lime (CaO)	Synthetic Lime (CaO) + Periclase (MgO)
Carbonated at 750°C	Calcite (CaCO_3) + Small Amount of CaO	Calcite (CaCO_3) + Trace CaO	Calcite (CaCO_3) + Periclase (MgO)

CHAPTER 8

CONCLUSIONS AND RECOMMENDATIONS

The research performed under contract DE-AC21-89MC26366 has proven the technical feasibility of a high temperature-high pressure process for the bulk removal of CO_2 from coal-derived gases using a calcium-based sorbent. The process is based upon the reversible noncatalytic gas-solid reaction involving CO_2 removal from the gas via the formation of CaCO_3 (carbonation) and sorbent regeneration by decomposing CaCO_3 to CaO (calcination). The kinetics of both the calcination and carbonation reactions have been studied as a function of temperature, pressure, and gas composition. Multicycle runs have shown that repeated calcination and carbonation of the sorbent is possible. Structural property characteristics of test sorbents in as-received, calcined, and carbonated conditions have been measured to supplement the kinetics data and to assist in understanding the reaction behavior.

Reaction characteristics are strongly dependent on the structural properties of the sorbent precursor. A porous sorbent, which is required for rapid and complete reaction, is created during the calcination step. Calcination of highly-crystalline, non-porous CaCO_3 produces CaO having "minimum" porosity. While in principle there should be sufficient pore volume created during calcination to permit complete recarbonation, the fact that carbonation occurs preferentially at the particle surface causes pores near the surface to close and prevent CO_2 from reaching unreacted CaO at the particle interior. CaO sorbents having "excess" pore volume, which were formed from the decomposition of hydrated calcium acetate, $\text{Ca}(\text{C}_2\text{H}_3\text{O}_2)_2 \cdot x\text{H}_2\text{O}$, or dolomite, $\text{CaMg}(\text{CO}_3)_2$, exhibited more favorable reaction properties. Decomposition of hydrated calcium acetate occurs in a series of steps with increasing temperature,

beginning with the loss of water of hydration, followed by decomposition of the acetate group to form CaCO_3 , and finally complete calcination to essentially pure CaO . In the decomposition of dolomite, both CaCO_3 and MgCO_3 are calcined to their respective oxides, CaO and MgO . The pore volumes of the latter sorbents are considerably higher than the pore volume of the sorbent formed by direct decomposition of CaCO_3 because of the increased quantities of volatile material driven off. Essentially complete carbonation of these sorbents was possible.

The capacity of the dolomite sorbent, measured as mass of CO_2 adsorbed per unit mass of sorbent, is lower than the capacity of the other sorbents because of the presence of inert MgO . While the magnesium is present in the original dolomite in the carbonate form, MgCO_3 cannot be reformed at the reaction conditions of interest in this study. In addition to magnesium producing excess pore volume during calcination, thus permitting more complete carbonation of calcium to occur, the magnesium seems to provide the sorbent with improved multicycle durability. The general ranking of the sorbents in terms of multicycle durability was dolomite greater than calcium acetate, greater than calcium carbonate.

Reaction conditions also play an important role in sorbent reactivity, capacity, and durability. Calcination should be carried out at the minimum practical temperature, approximately 750°C . At lower temperatures the calcination rate is too slow to be of practical interest and the sorbents produced at higher calcination temperatures are not as reactive or durable. Carbonation temperature in the range of $650\text{--}750^\circ\text{C}$ appears to be most promising. At higher temperatures the equilibrium CO_2 partial pressure is too large to be of commercial interest. However, limited carbonation studies at higher temperatures

did not indicate severe sorbent deterioration, indicating that the CO_2 removal process should be able to recover from temporary temperature excursions resulting from the exothermic reaction. Low carbonation temperatures, on the other hand, are to be avoided. For an unknown reason or reasons, sorbent performance at 550°C carbonation temperature was significantly poorer than in the $650\text{--}750^\circ\text{C}$ range. The structural characterization tests failed to provide an explanation of this behavior.

High pressure operation (15 atm) had no adverse effect on either the calcination or carbonation reactions other than leading to a decrease in carbonation rate during the rapid initial rate period. Such behavior is consistent with a reaction whose kinetics are controlled by transport resistances instead of surface chemistry. Both the mass transfer coefficient and effective pore diffusion coefficient decrease with increasing pressure. Otherwise, high operating pressure is favorable from the equilibrium CO_2 removal standpoint. If the carbonation reactor operates at 650°C and 15 atm with 15% CO_2 in the inlet gas, a theoretical CO_2 removal efficiency of greater than 99.5% is possible. The operating pressure of a commercial CO_2 -removal process will probably match the operating pressure of the gasifier.

CO_2 concentration was important in determining the rate during the rapid initial rate period, but had no impact on sorbent capacity. Because of equilibrium considerations, high CO_2 is desirable in terms of increasing the fractional removal of CO_2 . However, high inlet CO_2 concentration will require increased sorbent inventory and/or more frequent sorbent regeneration.

A great deal of indirect evidence was accumulated which suggested that the water-gas shift reaction occurred simultaneously with CO_2 -

removal. The evidence was indirect since no effluent gas composition measurements were included in this study. Composition measurements would be required to prove, without question, that the shift reaction does actually occur. Assuming that the shift reaction does occur, it is not clear if the reaction is catalyzed by CaO or is a straight thermal reaction. No references to CaO catalysis were found in the literature, while some references in the early literature were located which suggest that the reaction will occur thermally at the conditions of the carbonation reaction. There has been little past interest in the thermal reaction because of the adverse effect of high temperature on equilibrium in the exothermic shift reaction.

Simultaneous shift reaction-CO₂ removal creates the possibility of a one-step process for the direct production of H₂ from coal gas. Such a process would be favored by the high pressures associated with gasification. A further advantage will result from elimination of the sulfur-sensitive shift catalyst, which will always be a problem in the production of H₂ from coal gas using the traditional shift process. The one-step process for the direct production of H₂ would probably operate with dual recirculating fluidized-bed reactors in a manner similar to the fluidized-bed catalytic cracking process. Energy requirements for such a process would be relatively small with the exothermic shift and carbonation reactions providing energy for the endothermic sorbent regeneration reaction.

Because of the potential importance of such a process for the direct production of hydrogen, it is recommended that this concept be investigated by carrying out a series of tests in a small fixed-bed reactor with provision for inlet and outlet gas composition analysis.

CHAPTER 9

REFERENCES

- Barker, R., 1973, The Reversibility of the Reaction $\text{CaCO}_3 \rightleftharpoons \text{CaO} + \text{CO}_2$, J. Appl Chem. Biotechnol., 23, 733.
- Barker, R., 1974, The Reactivity of Calcium Oxide Towards Carbon Dioxide and Its Use for Energy Storage, J. Appl. Chem. Biotechnol., 24, 221.
- Beruto, D., et al., 1988, Microstructure and Reactivity of Porous and Ultrafine CaO Particles With CO_2 , High Temperature-High Pressure, 20, 25.
- Bhatia, S.K. and D.D. Perlmutter, 1980, A Random Pore Model for Fluid-Solid Reactions: I. Isothermal, Kinetic Control, AIChE J, 26, 379.
- Bhatia, S.K., and D.D. Perlmutter, 1981, A Random Pore Model for Fluid-Solid Reactions: II. Diffusion and Transport Effects, AIChE J, 27, 247.
- Bhatia, S.K., and D.D. Perlmutter, 1983, Effect of the Product Layer on the Kinetics of the CO_2 -Lime Reaction, AIChE J, 29, 79.
- Borgwardt, R.H., 1989, Sintering of Nascent Calcium Oxide, Chem. Engr. Sci., 44, 53.
- Box, G.E.P., W.G. Hunter, and J.S. Hunter, 1978, Statistics for Experimentors, Wiley, New York.
- Boynton, R.S., 1980, Chemistry and Technology of Lime and Limestone, John Wiley and Sons, New York.
- Curran, G.P., C.E. Fink, and E. Gorin, 1967, CO_2 Acceptor Gasification Process: Studies of Acceptor Properties, in Advances in Chemistry, 69, Fuel Gasification, F.C. Schora, ed., American Chemical Society, Washington, D.C., 141-165.
- Dedman, A.J., and A.J. Owen, 1962, Calcium Cyanamid Synthesis. Part 4: The Reaction $\text{CaO} + \text{CO}_2 \rightleftharpoons \text{CaCO}_3$, Trans. Farad. Soc., 58, 2027.
- DeLucia, D.E., 1985, The Cyclic Use of Limestone to Capture CO_2 , M.Sc. Thesis, Massachusetts Institute of Technology.
- Dhupe, A.P., and A.N. Gokarn, 1987, An Experimental Study of the Effect of Inert in Gas-Solid Reactions, Chem. Engr. Sci., 42, 2285
- Dhupe, A.P., and A.N. Gokarn, 1990, Use of Inert Solids in Some Industrially Important Gas-Solid Reactions, Ind. Engr. Chem. Res., 29, 784.

- Focht, G.D., P.V. Ranade, and D.P. Harrison, 1989, High Temperature Desulfurization Using Zinc Ferrite: Regeneration Kinetics and Multicycle Testing, Chem. Engr. Sci., 44, 2919.
- Gauthier, A., Bull. Soc. Chim., 35, 929, from Chemical Abstracts, 1909, 1, 274⁷.
- Glud, W., K. Keller, R. Schonfelder, and W. Klempt, 1931, Production of Hydrogen, U.S. Patent 1,816,523.
- Hartman, M., J. Pata, and R.W. Coughlin, 1978, Influence of the Porosity of Calcium Carbonates on Their Reactivity With Sulfur Dioxide, Ind. Engr. Chem. Proc. Des. Dev., 17, 411.
- Hougen, O.A., K.M. Watson, and R.A. Ragatz, 1959, Chemical Process Principles, Part II: Thermodynamics, Second Edition, John Wiley and Sons, New York.
- Kohl, A., and F. Riesenfeld, 1979, Gas Purification, Third Edition, Gulf Publishing, Houston.
- Kondrat'ev, V., and M. Ziskin, from Chemical Abstracts, 1946, 38, 5131⁵.
- Lamoreaux, R.H. et al., 1986, Determination of Solid Phase Boundaries in Coal Gas Desulfurization by Zinc Ferrite, Final Report, DE-AC21-84MC21096.
- Mess, D., 1989, Product Layer Diffusion in the Carbonation of Calcium Oxide, Ph.D. Thesis, Massachusetts Institute of Technology.
- Moe, J.M., 1962, Design of Water-Gas Shift Reactors, Chemical Engineering Progress, 58, 33.
- Oakeson, W.G., and I.B. Cutler, 1979, Effect of CO₂ Pressure on the Reaction With CaO, J. Am. Ceram. Soc., 62, 556.²
- Rase, H.F., 1977, Chemical Reactor Design for Process Plants, Vol. II, Wiley-Interscience, New York.
- Rofer-DePoorter, C., 1984, Untangling the Water Gas Shift from Fischer-Tropsch, in Catalytic Conversions of Synthesis Gas and Alcohols to Chemicals, R.G. Herman, ed., Plenum Press, New York, p. 97.
- Squires, A.M., 1967, Cyclic Use of Calcined Dolomite to Desulfurize Fuels Undergoing Gasification, in Advances in Chemistry, 69, Fuel Gasification, F.C. Schora, ed., American Chemical Society, Washington, D.C., 205-227.

END

**DATE
FILMED**

9 / 8 / 92